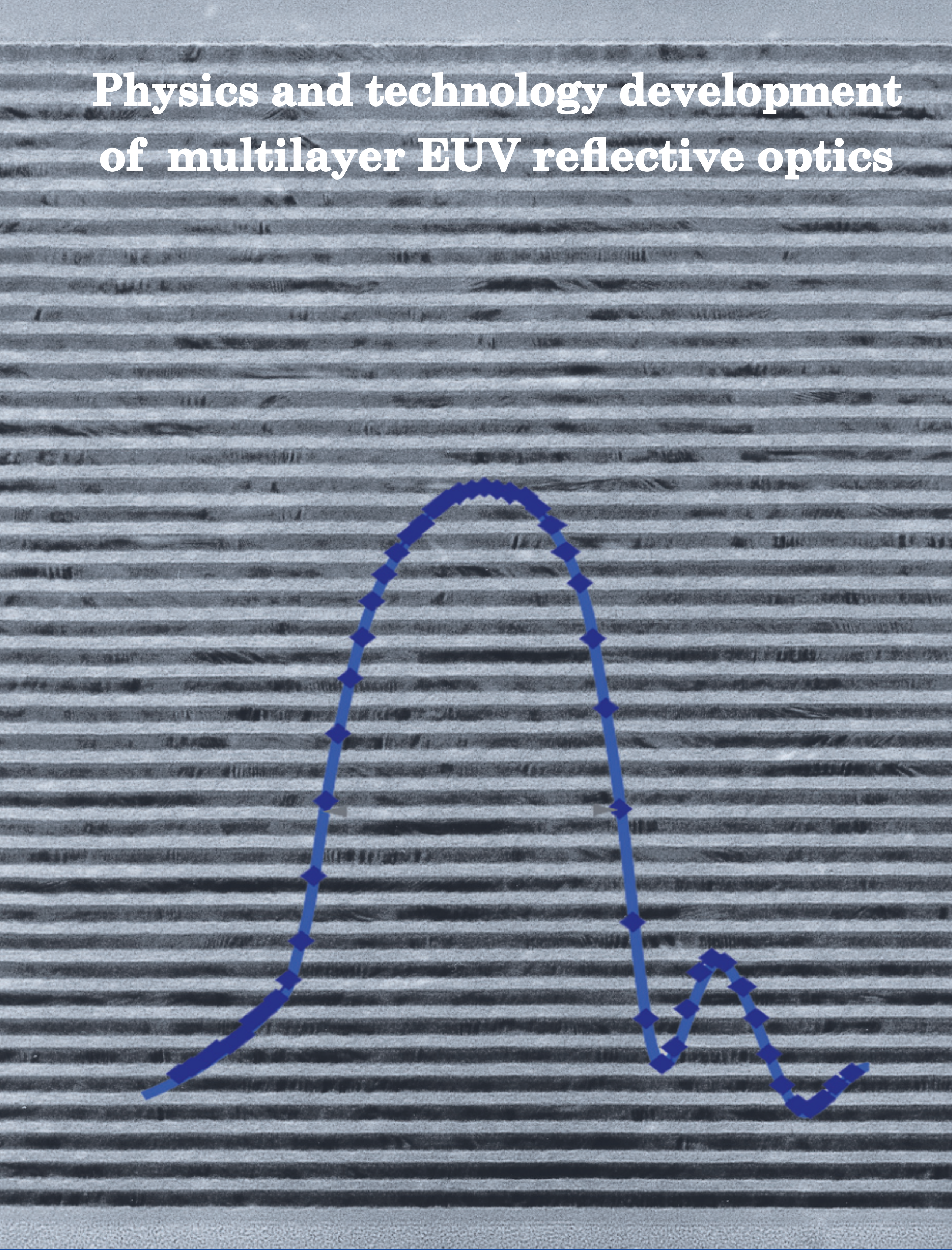
Physics and technology development of multilayer EUV reflective optics



Eric Louis

Physics and technology development of multilayer EUV reflective optics

Eric Louis

PhD committee

Chairman:
Prof.dr. G. van der Steenhoven — University of Twente

Secretary:
Prof.dr. G. van der Steenhoven — University of Twente

Promotor:
Prof.dr. F. Bijkerk — University of Twente, FOM Institute DIFFER

Members:

Prof.dr.ing. D.H.A. Blank	University of Twente
Prof.dr. K.J. Boller	University of Twente
Prof.dr.ir. B. Poelsema	University of Twente
Prof.dr.ir. J.P.H. Benschop	University of Twente
Prof.dr. A.W. Kleijn	University of Amsterdam FOM Institute DIFFER
Prof.dr.ir. M.C.M. van de Sanden	Eindhoven University of Technology FOM Institute DIFFER
Dr. S. Müllender	Carl Zeiss SMT GmbH
Dr.ir. E.M.C.M. Reuvekamp	PANalytical BV

Cover:
Cross-section transmission electron microscopy image of a Mo/Si multilayer, clearly showing the polycrystalline nature of the Mo layers and the formation of interlayers. The image is produced by F. Tichelaar (Delft University of Technology). The blue curve represents the wavelength dependence of the reflectance of the multilayer around $\lambda = 13.5$ nm (figure 2.11)

Printed by Ipskamp Drukkers (2012)

PHYSICS AND TECHNOLOGY DEVELOPMENT OF MULTILAYER EUV REFLECTIVE OPTICS

PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
op gezag van de rector magnificus,
prof.dr. H. Brinksma
volgens het besluit van het College voor Promoties
in het openbaar te verdedigen
op vrijdag 23 november 2012 om 12.45 uur

door

Eric Louis

geboren op 20 mei 1954

te Amsterdam

Dit proefschrift is goedgekeurd door de promotor:
Prof.dr. F. Bijkerk

ISBN: 978-90-9027163-7

The work described in this thesis is part of the FOM Industrial Partnership Programme I10 ('XMO') and I23 ('CP3E') which have been, respectively still are carried out under contract with Carl Zeiss SMT GmbH, Oberkochen, and ASML, Veldhoven, and the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', the latter being financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)'. Also the Technology Foundation (STW) is acknowledged for funding the early projects Solv'X and EX2, as well as Carl Zeiss SMT for several research assignments, and the AgentschapNL, for the ACHieVE and EXEPT programmes in the frame of the 'Internationale Samenwerkingsprogramma's'.

Table of contents

Physics and technology development of multilayer EUV reflective optics

Preface - Scientific accountability

At the time of publication of this PhD thesis, the development of reflective coatings for photolithography at Extreme UV wavelength has taken over twenty years, or, alternatively expressed, five consecutive periods of PhD physics research. So far, at FOM-Rijnhuizen, now the FOM Institute for Fundamental Energy Research, eleven PhD theses have been devoted to this theme, while in The Netherlands alone at least 18 PhD projects are still running or scheduled, of which twelve are at FOM. The first exploration of reflective coatings for 13.5 nanometer light date from 1992. These have gradually evolved from basic thin film growth and design studies to a broad palette of topics including, for example, photochemical investigations, and designs for diffractive optical elements. The use of reflective coatings for lithography at even shorter wavelengths, i.e. for 6.7 nanometer, is currently still in its infancy, but will most likely result in a considerable number of PhD theses in its own right.

The series of these PhD theses, produced to date, forms a part of the science basis of a major industrial development in photolithography. A multiple of the PhD manpower effort is currently being spent on further development of know-how towards the level of industrial products. The total R&D effort at ASML alone is estimated to reach around 5000 man-years [1] by the time EUVL enters the high volume manufacturing stage in the commercial semiconductor or chip market.

The special context of a prolonged and focused research activity at academia and industry has provided the breeding ground of the current PhD thesis. It is a condensation of a sustained line of research, spanning over two decades. This thesis might, therefore, have been composed of several tens of refereed journal papers, when following the standard criterion for inclusion of papers in a PhD thesis [2]. Some 52 journal publications, published in the past twenty years contain essential contributions by the author of this PhD thesis. These vary from suggestions for key experiments to interpretations of experimental data, and from signalling important data sets to the development of clarifying models. Overall, they are of a basic, thin film and solid-state physics nature, with excursions to short wavelength optics. Undoubtedly, 'der roter Faden' of these works is the gradual development of multilayer structures into robust optical elements for advanced photolithography and other high tech applications of practical interest.

Only a small selection of these papers has been included in this thesis. Obviously, a first criterion was that they were not used in any existing PhD or Masters thesis, while the underlying subject, the development of EUVL multilayer optics was considered as a central theme, and formed a second criterion. A paper dealing with an aside into specific reflectivity effects has been included: specifically, the suppression of undesired wavelength bands. The assessment of the potential for a new application, namely optics for so-called Free Electron Lasers, is another aside, putting the results in a broader perspective.

It is noted that the type of the motivation, either 'physics driven' or 'application driven' in this and many other cases of research, was not found to be a relevant factor in practice. Both types have served as stimulus in executing the research and have contributed in equal weight to the end result: the basic understanding of atomic scale processes in the layered materials structure. The valorisation nature of this research has simply enabled many studies that would otherwise not be possible. Many nanoscopic thin film aspects could be explored through sometimes costly nanotechnology or instrumentation specially developed for the purpose of EUVL mirrors. As such, thin film physics owes lithography as much as lithography owes physics.

The figure of merit of this thesis works is the sustained, continuous development of these physics processes so that they collectively enabled the production of real prototype optics of direct relevance for a demanding industrial process. Such optics have been produced by the candidate in several stages, from simple imaging elements, based on first principles, to more complex systems with high temperature, contamination and radiation resistivity. At first sight such a step may seem to be of a pure technological kind, but in reality it contains the understanding and control of numerous basic physics processes. One particular example of such a partial process is film material induced stress: the application of multilayer films to optics substrates with finite stiffness but extreme requirements on their figure necessitates the reduction of film stress to values in the order of magnitude below 100 MPa. Fulfilling this demand required a study for the origins of film stresses down to nano crystalline structures. The roots of film stress were found in the material, the material ratio and the deposition conditions. Only on the basis of these findings could a practical solution for real EUV optics, which fulfil optical requirements, be developed.
The nature of the candidate's work, his extended pursuit of thin film research, and the numerous proofs of scientific results in the form of published journal articles, in itself fully justifies a physics dissertation. In this particular case, the nomination is supported by the presence of the many processes of producing multilayered Extreme UV optical coatings developed by the candidate. These all have greatly helped in progressing the state-of-the-art of multilayer optics and the development of short wavelength photolithography. This thesis, which has resulted in

18 patents, contains numerous examples of such processes, both of a physics and engineering kind, including instrumentation development. All are described in this thesis in detail and substantiated to being proofs of independent pursuit of science. The many science papers, mentioned above, but not included here support the candidate's thesis. The scope, the profoundness, and the quality of the work by the candidate justify his ambition for obtaining the academic degree of doctor in science, to be publicly defended on 23 November 2012.

Fred Bijkerk, supervisor

References:

[1] Private communication.

[2] Promotiereglement Universiteit Twente, version Oct 2011.

1 Introduction

1.1 Motivation

Bragg reflection of radiation by the lattice planes of crystalline structures is a well known phenomenon that is educated in all solid state physics classes. It can serve as a technique to analyse crystalline materials, it can be used to monochromatize radiation and to design X-ray optics. However, the wavelength range is largely determined by the lattice spacing of the available natural crystals, which can be too small to reflect soft X-rays or even Extreme UV radiation, particularly at non grazing angles of incidence. This limitation can be overcome by the use of synthetically produced layered structures of alternating materials with a high optical contrast. The interfaces between the materials have the same functionality as the lattice planes in a crystal, thus forming a multilayer mirror to be used for hard X-rays at grazing incidence and soft X-rays or even EUV radiation at more normal angles of incidence. In such schemes the possible angle and wavelength ranges are determined on the one hand by a balance between reflection and absorption [1-3] and on the other hand by the manufacturability of the 'synthetic crystal'. The latter is the field of the experimental thin film physicist.

With this approach, multilayer science has so far had a pragmatic and phenomenological nature, and very useful results have been achieved. For a physicist, it is amazing that multilayer reflectors can show close to theoretical performance. For the normal incidence case and a wavelength ranging from the water window up to several tens of nanometers, the individual layers can have thicknesses as small as a few nanometers or 10 to 20 atomic layers. Materials of very different mechanical properties are deposited on each other. How is it possible that these layers still show their standard, bulk optical properties and that we can still consider them as solid state material? How can they best be grown? Are they thermodynamically stable and if not, what can we do about it? All these issues can be studied from the physics and material science point of view. And, if we are successful in that, application in imaging systems and other optical elements becomes feasible.

It is this combination of curiosity in atomic scale growth and the possibility to apply this research to technological and eventually societal relevant optics that forms the perfect breeding ground for a thin film physicist to study the physics and the applications of EUV and soft X-ray multilayer structures.

1.2 Theme of this work

The work described in this thesis is the result of 20 years of multilayer research. In this period the lead motivation has been the development of reflective multilayers for optics to be used in imaging systems for Soft X-ray projection lithography, as it was initially called, or Extreme UV lithography or EUVL, its current name. The lithographic process transfers a mask pattern onto a resist coated wafer, the key component of a chip. The need for the semiconductor industry to eventually make use of reflective instead of transmissive optics originates from the resolution driven requirement to use shorter and shorter wavelength radiation in the lithographic imaging process, thus entering the wavelength range where materials are highly absorbing.

In 1992 the Dutch Technology Foundation STW granted our group at FOM the funds for the first research project in Europe on Soft X-ray Projection lithography. This was carried out at the FOM Institute for Plasma Physics Rijnhuizen in collaboration with the FOM Institute for Atomic and Molecular Physics AMOLF and the Delft Institute for Micro-Electronics and Submicron Technology, DIMES, part of the Delft University of Technology. Ambitiously, the goal within this project was the development of a lithographic system based on a laser produced plasma as light source, one collector mirror, a curved reflection mask and a tenfold demagnifying Schwarzschild system [4] to image the mask on a wafer. Fig. 1.1 shows a photograph of the lithographic system. Initially we aimed at an operating wavelength of 10.6 nm, generated through an aluminium plasma [5] and reflected by Ru/C multilayer mirrors. However, this was not considered to become sufficiently efficient and we moved to a wavelength at the transmissive side of the Si-absorption edge and focused on Mo/Si multilayers for λ= 13.5 nm (see Chapter 2). The work, described in [6-11] resulted in the first structures imaged in photoresist as shown in Fig. 1.2, at sub-half micron resolution. Topics like EUV plasma generation, optics design and contamination could already be addressed at a fundamental level. Especially much knowledge was acquired about the Mo/Si multilayer systems: the growth models, the mechanism of smoothening Si-layers, or the conditions to avoid inclusion of light absorbing oxygen in the silicon layers. These are described in detail in Chapter 2. During this project we also faced the challenge of lateral uniformity of the multilayer deposition. This project, together with a follow-up project also made possible by the Technology Foundation STW, has set the basis for the groups and the author's understanding and awareness of many lithographic processes and the accompanying challenges.
After this early success, a side step into multilayers for space research was under-

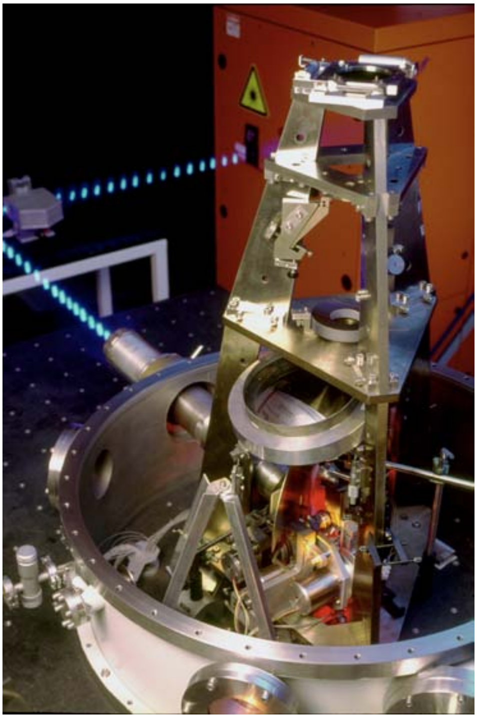


Figure 1.1: The 10x Schwarzschild system developed at FOM Rijnhuizen. On the background the driving laser and beam for the laser plasma light source.

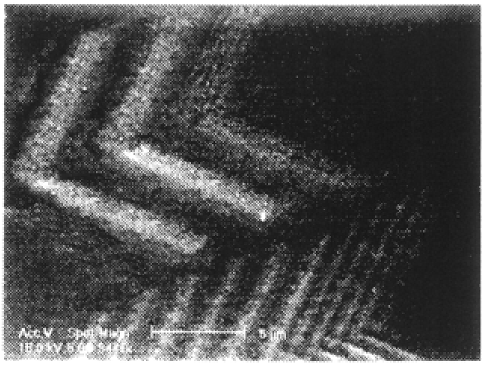


Figure 1.2: The first elbow structures imaged in photoresist using a 10x Schwarzschild Mo/Si coated optical system shown.

taken in collaboration with the Danish Space Research Institute (DSRI) and Dr. Eberhard Spiller. This work is described in more detail as an example of the use of multilayers for space research in the Outlook section. It formed a fruitful experience in the field of even thinner layers and other materials such as Ni, Co and C,

but also in issues as uniformity and run to run reproducibility of the deposition process.
In the second half of the 1990's the European lithographic industry, headed by ASML (Veldhoven, the Netherlands) and optics supplier Carl Zeiss SMT (Oberkochen, Germany) entered the field of EUV lithography. This has led to some technological programmes in the form of contract research and at a later stage to more fundamental research programs, among which two Industrial Partnership Programs (IPP). The first IPP was between FOM and Carl Zeiss, the second one, still running, is through a combined programme with FOM, Carl Zeiss and ASML. Initially the prime goal was to achieve the highest possible reflectance, and this had to be demonstrated over large curved surfaces, in combination with lateral control of the multilayer periodicity. The task was to assure high reflectance of a fixed wavelength at every spot of the mirror, at the designed angle of incidence. Also, the process reproducibility had to be demonstrated and the first work on radiation induced damage and contamination of the multilayers was carried out in close collaboration with Carl Zeiss, ASML, Philips Research and the Netherlands Organisation for Applied Scientific Research TNO.
The effect of radiation or secondary electron induced damage in the form of oxidation of the top Si layer of the mirror was initially of a severe kind, reducing the mirror lifetime to hours. Oxidation resistant capping layers had to be developed under the boundary condition that the reflectance should not, or only marginally be reduced. These capping layers should also be resistant to cleaning processes to remove radiation induced carbon contamination on the mirrors.
Another topic was the multilayer induced stress. The stress, initially in the GPa range, leads to intolerable deformation of the optics, and had to be reduced or compensated.
An important aspect of the work was knowledge transfer to the multilayer team at the industrial partner Carl Zeiss by means of reports, quarterly meetings and numerous telephone conferences. A very important aspect of this knowledge transfer was the development of a very large e-beam based multilayer coating facility; the 1605. The know-how of the FOM team was used to develop this machine, installed in the laboratories of Carl Zeiss. This machine also served as a prototype for a new facility at FOM, developed in collaboration with Leybold Optics. This FOM facility, the Advanced Development Coater (ADC), shown in Fig. 1.3, is based on the same vacuum concept as the 1605, but equipped with six e-beam evaporators and additionally with four modified magnetron sputter sources, a Kaufman ion gun and an RF-discharge plasma source. The unique capabilities to combine the two multilayer deposition techniques with ion treatment of the layers enabled us to study the fundamental processes during the multilayer deposition. For this pur-

pose X-ray Photoelectron Spectroscopy equipment (XPS) was installed at the ADC and connected to the facility with a vacuum sample transfer system. This possibility proved its usefulness in the process of creation of compounded materials such as nitrides and carbides as described in Chapter 2. The in-vacuum analysis capabilities were extended with a Scanning Tunnelling Microscope (STM) to study the morphology of the layers, in close collaboration with Leiden University [12,13].

Figure 1.3: The Advanced Development Coater at FOM developed based on thin film process data described in this thesis.

Meanwhile, it was required to make sure that all processes could be applied on large curved substrates, meeting the ever more stringent requirements for lithography. To demonstrate this, real mirrors for the Micro-Exposure Tool (MET), the first American lithographic system, were multilayer coated [14]. Other MET mirror sets were coated in the US by Soufli et al. [15].

In a later stage, in 2004, the optics for the first two full field lithography machines, the so-called Alpha Demo Tools (ADT), had to be coated. The larger part of all reflecting elements in each of these machines were coated in one of the FOM facilities (Fig. 1.4). The two ADT machines are in operation at IMEC (Leuven, Belgium) and at the NanoTech Complex of the College of Nanoscale Science and Engineering (Albany, New York). After the successful ADT's, further improvement of the multilayers and the protective capping layers together with improved surface quality of the multilayer substrates by Carl Zeiss has resulted in a considerable improvement of the multilayer reflectance, leading to 50% more transmission of

Figure 1.4: The multilayer coating facility MUCO.

the optical system in the first so-called pre-production tools, the ASML NXE:3100 series [54], installed at semiconductor manufacturer plants in 2011. For these machines, several elements in the demagnifying optics were deposited at FOM. The multilayers for the ADT's and the pre-production tools are described in detail in section 2.4 to this thesis.

Besides enabling the deposition of real optics within tight specifications, research on the growth of materials, and particularly on compounded materials, and knowledge of their optical properties also made it possible to develop mulitlayer based solutions for very specific problems. An example of this is the need for a multilayer with a high reflectance in the EUV wavelength range while having suppressing or even anti-reflective properties for longer wavelength such as UV radiation, thus reducing the transmission of the optical system for parasitic UV radiation from the plasma source. A thus developed layer of silicon-nitride on top of the EUV reflecting coating, as described in Chapter 3, strongly reduces the reflectance of the multilayer for light in the wavelength range of 100 – 200 nm while reducing the EUV reflectance by only 6.6%.

A most challenging issue is the lifetime and stability of the Mo/Si multilayers when used under high intensity exposure with radiation. The reflectance for 13.5 nm light is typically around 70%, the remaining 30% being absorbed in the multilayer. Annealing experiments have shown the diffusion driven formation of molybdenumsilicide interlayers [16], thus a purely thermal process. But what happens during pulsed exposure with high peak power density? To answer this question and to examine the possibility to use multilayer optics in the beam lines or user stations at X-ray Free Electron facilities and to develop even more stable multilayers for lithography, we exposed our mirrors to extreme high peak power densities at the X-ray Free Electron Laser FLASH [17] in Hamburg, Germany. Surprisingly, above a certain damage threshold the femtosecond exposures by the free electron laser beam induced the same silicide formation as observed in the long term classical annealing experiments. However, the permanent damage of the multilayer occurs on a much longer timescale than the pulse duration and the reflection process. The investigations of the damage mechanism and the timescale are described in detail in Chapter 4.

1.3 Valorisation processes

The concept of valorisation is described by Karl Marx in his 'Critique of political economy', published in 1859 [18]. The German original term is 'Verwertung', meaning to make things useful, productive or even 'making money out of something'. A similar process can be found in physics and originates from a much earlier date. Van Leeuwenhoek applied his knowledge of optics already to practically use it for his microscope studies. Many more examples can be found, though physics research with the aim to make or improve commercial products is traditionally the field of companies. At universities, as well as at FOM, the common thinking was along the lines of fundamental science, or curiosity driven research, although many scientists had intensive relations with industrial laboratories such as Philips Research, Hoogovens, NXP and many others.*
However, during the last decade a gradual change of culture took place. Because of the increasing awareness of the need for societal relevance of physics research, an increasing number of physicists has widened their field during the last decade. At FOM for instance, there has been a change of balance towards equal importance for 'Physics for Science' and 'Physics for Society', as for instance stated in the 'Beleidsnota Fundamenteel Onderzoek voor de Maatschappij, Valorisatie bij FOM' [19]. This is made very specific in the FOM Industrial Partnership Programmes (IPP), a platform enabling fundamental research on areas of physics relevant for industrial applications.

* *It should be noted that the freeform basic science that many of these labs enabled, has been gradually diminished in favour of more applied, technology-driven science, Philips Research being the prime example.*

The work described in this thesis is a good example of 'Physics for Society' because it is an attempt to be relevant for a demanding imaging process used in the chip manufacturing industry. After all, we can hardly imagine our present society without progressing abilities of automated systems, data storage, computers or smart phones. This thesis work is the outcome of the STW projects 'Excimer-laser induced plasma as X-ray source for X-ray projection lithography' (EX2) and 'Soft X-ray projection lithography: solutions to possible show-stoppers' (Solv'X), both dealing with research on EUV Lithography. These projects were the basis for several bi-lateral research contracts with Carl Zeiss SMT GmbH and ASML, the world's leading providers of respectively optics and lithography systems for the semiconductor industry. The close collaboration with Carl Zeiss continued in the IPP programme 'eXtreme UV Multilayer Optics' (XMO), followed by a currently running programme 'Controlling photon and plasma induced processes at EUV optical surfaces' (CP3E) carried out with ASML and Carl Zeiss SMT.

The moment the work described in this thesis started, many multilayers were already developed for space research and other applications, although the specifications for these mirrors were not yet very tight. The extremely demanding application in optics for lithography has given an enormous boost to the research, worldwide, but certainly in the Netherlands. At FOM, the fundamental study of the layer growth and smoothing mechanisms in thin layer deposition has led to a fine tuned deposition process and a reflectance value of 69.5%, a world record for Mo/Si mirrors (see Chapter 2). Meanwhile, methods to control the multilayer periodicity as well as the lateral profile have been developed and the technology has been transferred to industry, enabling the coating of optics for the world's first industrial full field EUVL systems. Furthermore, the dependence of the multilayer performance on the substrate quality has been determined, resulting in tight specifications of the roughness of the surface to be coated, giving a boost to substrate and multilayer polishing processes. This, in combination with the development of stability enhancing techniques that simultaneously reduce the interlayer formation and enhance the reflectance, has brought the multilayer performance on real optics to close to 70%, the same level as obtained on small super polished laboratory samples. In parallel, improvement of the protective capping layer has resulted in a significant increase in reflectance of the mirrors for the HVM tools (Fig. 1.5). Since there are at least 10 reflecting surfaces, a reflectance improvement of several percent results in an overall enhancement of the transmission of the Carl Zeiss optical system in ASML's EUV scanners with 50%. This constitutes a major step in the optics for high volume manufacturing systems.

Other typical examples of valorisation are the thin film growth studies leading to the development of substrate smoothening or buffer layers [21] and the understanding of the stress inducing mechanisms in the multilayer deposition process.

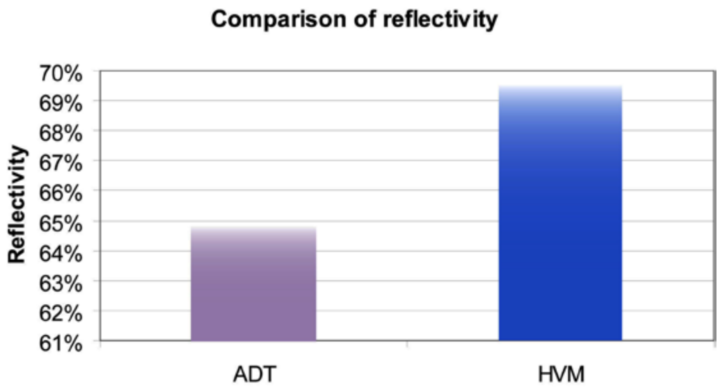


Figure 1.5: Gain in normal incidence reflectance by enhanced multilayer deposition and substrate polishing techniques from the Alpha Demo Tools (ADT) to the first series of high volume manufacturing machines (HVM) (reproduced as presented by Carl Zeiss SMT [20]).

The latter enabled the development of stress compensation layers which serve to keep mirror distortions to acceptably low levels (Chapter 2).
The presence of a core activity in valorisation environments such as IPP programmes allows responsive, relatively fast replies to ad-hoc research requests. An example is the unforeseen and very undesired high fraction of longer wavelength light in the spectrum of most EUV sources. For short wavelength, or Deep UV light, a special anti reflection layer was already developed (Chapter 3), but also a much longer wavelength happened to form a problem. This infrared light from the driver laser could be suppressed by means of diffraction by a multilayer coated grating or a multilayer grating deposited with our deposition technology. Since the grating period was large with respect to the EUV wavelength, the infrared light could be diffracted out of the optical path while the EUV light was reflected specularly by the multilayer grating. Knowledge of the multilayer growth mechanisms was found to be mandatory to assure layer growth up to the edges of the facets of the grating [22-24]. Suppression of infrared was also achieved using antireflective techniques integrated in the multilayer [25, 26].

Thin layer research also led to spin off activities that directly valorise the knowledge, as for instance in the case of a project with ASML and the Materials Research Institute M2i to investigate the possibilities to monitor carbon contamination on the multilayer optics. This has resulted in an advanced contamination

analysis method by means of spectroscopic ellipsometry, not only to detect the contamination layers, but also to analyse their nature and monitor the subsequently applied cleaning process [27, 28].
The above mentioned examples, all from the past period of research from the author of this thesis, illustrate that the multilayer physics at FOM has gone hand in hand with the process of valorisation for the last two decades. What made this possible?

Firstly, the research topic should be suitable to define possible applications, as was, and still is, the case for thin layer physics for multilayers. Knowledge of possibly interesting topics for industrial application is thereby indispensable. The topics encountered in the research have to be translated in a physics question, rather than approaching them as technical problems. The latter could induce the risk to only work on quick solutions. Furthermore, the research topics must be truly scientifically challenging, which also warrants the continuity of the basic research line involved.
Secondly, the research environment should at least allow, but preferably stimulate to work on phenomena that could possibly be valorised. FOM Rijnhuizen has been such an environment. Applying for STW or Industrial Partnership projects has always been encouraged and both form platforms that are pre-eminently suited for this type of research.
Thirdly, the individual researchers should have the 'entrepreneurial' willingness to undertake the additional steps to show the industrial importance of their research. This can imply additional technical work to demonstrate proofs of principle of application of research results, as in our case the deposition of genuine, large area lithography optics.

Obviously, valorisation of research is best served when the research laboratories and universities collaborate directly with the industrial parties. As ASML's SVP Technology and University of Twente's professor of Industrial Physics Jos Benschop stated in his inaugural lecture: 'Human intelligence and capital are most efficiently used when academia and industry work together from the beginning on a possible application they have in mind.' [29].

1.4 Outlook and other valorisation opportunities

The chances for utilization of multilayer systems in science and society, other than photolithography, are numerous. Although lithography is one of the most demanding applications, each of the other and sometimes newer ones still have their own particular challenges. The general state of the physics research to date is one of assessment of these opportunities and a state of translating the lithography mirror knowledge into systems specifically tailored for such new applications. First examples already exist. Multilayer designs developed for lithography have been used to produce test mirrors for femtosecond light pulses with extreme peak power levels. Clearly, such synergies do not exist for all new applications and substantial development needs to be expected. Yet, the availability of the basic expertise and staff, and many new methods and instrumentation, will make the optics effort for these new applications considerably more realistic and the outcome of such work more predictable.

1.4.1 Short wavelength Free Electron Laser optics

Along such lines, the application of multilayer optics for the so-called fourth generation light sources, or Free Electron Lasers (FEL), is expected to come within reach in the next few years. A major goal on this roadmap is the development of optics for the X-ray Free Electron Lasers, aimed for at several locations world-wide [30-35] . Multilayer optics is expected to play an important role in these X-ray FELs as it would allow a variety of user experiments, like beam focusing to arrive at the highest photon density levels, wavelength selection and spectral filtering, and optical beam splitters to multiply the available beam lines or to enable in-situ beam diagnostics. FELs are essentially operated as single beam devices, which hinders the possibility to simultaneously serve multiple user-stations. Therefore, devices such as multilayer-based beam splitters are generally considered most desirable.

The main optics goal for FEL consists of the development and supply of single- and multilayer-based optics, aiming for systems which are capable of handling the extreme irradiation loads of these light sources. Complementary to the more conventional scheme of grazing incidence optics, for which basically a single optical layer is used, or the use of natural Bragg crystals, multilayer optics are most promising for a number of optical schemes at FELs. These optics can fulfil requirements in terms of optical figure and roughness, wave front and coherence preservation, and materials stability. The advantages of multilayer optics over natural Bragg crystals are: the possibility of obtaining diffraction limited imaging and beam focusing for different angles by choosing the multilayer periodicity, the use of a bandwidth that covers the full bandwidth of the

FEL beam, and the option to filter out higher orders and/or spontaneous emission. The advantage of the use of multilayers over grazing incidence, single layer mirrors is the possibility to use large beam acceptance angles with limited size optics, by circumventing the limitation of the materials critical angle. Of special interest for the FEL case are micro-focusing optics to achieve the ultimate peak power densities required for some experimental programmes at FELs, X-ray beam splitters to allow X-ray pump-probe experiments or to generate interference patterns, foreseen in many experiments to study fs and ps dynamical processes currently being defined, and novel multilayer optics with high damage thresholds.

Our approach is to directly take part in these experiments in order to efficiently develop the most desirable types of optics. The development of multilayer based optics for FELs contains many challenging issues at the forefront of technology, but insuperable barriers have not yet been encountered.

1.4.2 Wavelength dispersive optics for X-ray elemental analysis

Multilayer structures can also play a role in the elemental analysis of materials. Such analysis exploits the phenomenon that the X-ray emission lines of most elements are generally well separated and spectroscopic analysis of their fluorescent intensity, observed upon electronic excitation, can be used for quantitative elemental analysis with great precision. Especially for light elements, multilayer mirrors are used to spectrally isolate these emission lines. The technique is generally known as X-Ray Fluorescence analysis (XRF).

However, emission lines of particularly light elements can sometimes almost overlap and new methods to increase the spectral selectivity of multilayer elements are very appealing, like for instance for the XRF analytical equipment as produced and marketed by the Dutch company PANalytical (Almelo). Such methods may consist of the principle to increase the penetration depth in the multilayer by removing a part of the multilayer by etching a grating structure in the multilayer, resulting in a so-called Lamellar Multilayer Grating (LMG) [36, 37] . In such a structure an increasing number of bi-layers effectively contributes to Bragg reflection, thus reducing the width of the reflection peak. By tuning the dimensions properly, such an LMG can be used in single order mode and higher order losses become negligible. The usage of LMG structures in applications has been severely hindered by the unavailability of a precise and relatively economical grating reproduction method. Such a method has now been identified in the form of Nano Imprint Lithography [38], and a first demonstration of successful fabrication, namely an enhancement of the spectral resolution by a factor of 3.8, has been given [39].

In more general terms, the addition of a grating structure to the multilayer structure, so that a combined reflection-refraction effect occurs, is known as Bragg-Fresnel optics [40]. This type of optics has been known for many years [41], and the latest lithography methods, such as Nano Imprint lithography, open up a practical route for further usage. The use of Bragg-Fresnel optics can be very wide and spectacular such as 2D and 3D focusing by flat optical elements. Essential is the availability of a multilayer structure with a stability that is adequate for the required chemical etching procedure needed upon patterning. Work described in this thesis has provided a basis for these systems: the chemical stability of multilayer structures, for instance, allows reactive chemical treatments needed for patterning [see Chapter 2]. Such nano-scale fabrication methods therefore offers many advantages, which are likely to be further 'materialized' in the form of new optical elements in the coming years.

1.4.3 Multilayer optics for XUV space telescopes

For the past 20-25 years, X-ray emission spectroscopy has played a role of increasing importance in astrophysics. Traditionally crystals and gratings were used for reflection and monochromatisation of X-ray radiation. Multilayer mirrors were first used in X-ray space research in 1985 [42] when a W/C coated telescope was used to produce a soft X-ray image of a solar active region. Since then series of multilayer coated telescopes have been used for space research up to the recent NASA NuSTAR telescope array that will fly with depth graded Pt/SiC and W/Si multilayers to reflect X-rays up to 79 keV photon energy [43, 44].

A particular example from the past experience of the thesis author on multilayers for astronomy is work for the Objective Crystal Spectrometer for the Spectrum Röntgen Gamma satellite [45]. In this application Co/C multilayer coatings were deposited on Si(111) crystals. Reflection of low energy X-ray radiation (from Mg X and Fe XVI lines) takes place in the multilayer stack while the high energy radiation (He-like S-emission line complex around 0.51 nm) penetrates the multilayer with little absorption and is reflected in the crystal (Fig. 1.6). All 40 Si crystals were uniformly coated showing more than 8% reflection over the wavelength range of interest [46].

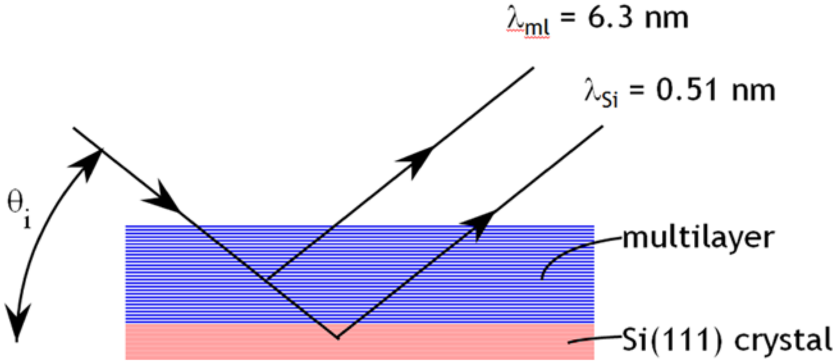


Figure 1.6. Principle of simultaneous spectroscopy in two energy bands. The multilayer coating reflects the soft x-rays while the high energy radiation is reflected in the Si crystal [46].

It is expected that the know how to uniformly deposit multilayers over very large surfaces together with the trend to use smaller multilayer periods will lead to many more new applications for astronomy.

1.4.4 Multilayers for X-ray microscopy

A particular wavelength region of interest for live sciences is the water window, the soft x-ray range between the oxygen K-absorption edge at 2.34 nm and the carbon K edge at 4.4 nm. Water is transparent in this range while nitrogen and other elements found in biological specimens are absorbing. This band is used in an X-ray microscope for viewing living specimens.
The first X-ray microscopy experiments have been performed using grazing incidence Kirkpatrick-Baez optics to focus the X-rays, followed by transmission zone plates. Because of the very low efficiency, both systems preferably make use of high intensity light sources like a synchrotron or possibly an X-ray free electron laser. X-ray microscopy has been demonstrated using a laser produced plasma source [47] and a large multilayer coated collector would be an advantage to capture more of the light from such a 4π sr emitting source [48]. Furthermore, when a sufficiently high normal incidence reflectance can be obtained from a multilayer, a full normal incidence reflective optical microscope system can be within reach [49-51]. Achieving a high reflectance however is a real challenge since the thickness of individual layers is in the order of a nm and the effects of layer roughness and interlayer formation become dominant.

1.4.5 Multilayers for lithography beyond the EUV wavelength

Reducing the operating wavelength in advanced photolithography while maintaining the lithography machine's productivity is a traditional way to enable improved imaging. However, reducing the wavelength to the water window regime would, even without multilayer imperfections, result in an unacceptable low reflectance and thus a low productivity of the machine. However, a transition from 13.5 nm to 6.5-6.9 nm optical lithography may offer a possibility to combine high imaging capabilities with high optical transmission of the imaging system. Around 6.6 nm wavelength the highest reflectance can be obtained with multilayer mirrors based on lanthanum as a reflector and boron as a spacer material [52]. Theoretically, the reflectance can be around 80%, even higher than for 13.5 nm, but the bandwidth will be smaller. Lithography in this wavelength range is very challenging in many aspects. To date the highest reported normal incidence reflectance is 53.6% [53] and the major challenge will be to increase this value to 70% or higher, possibly by applying thermodynamically more stable compounds or barrier layers. Furthermore, since the number of periods required per mirror is four times higher than in the 13.5 nm case, control of the periodicity, both laterally and from mirror to mirror, becomes critical as well. Other topics, like lifetime, thermal stability and radiation hardness, as well as multilayer induced stress have to be investigated.

1.4.6 Future developments

One of the seeds planted in the soil of this thesis work, is the establishment of a focused research group at the MESA+ Institute for Nanotechnology at the University of Twente. This 'Industrial Focus Group XUV Optics' is greatly facilitated by the industrial appreciation for the 'bottom-up' initiative from science. The Focus Group will be addressing the fundamental thin film aspects of four main groups of applications:

- photolithography at shorter EUV wavelengths,
- the use of optics for the next generation of short wavelength Free Electron Lasers,
- the use of multilayer systems as dispersive and wavelength selective elements for materials and elemental analysis
- the use of multilayer elements in space telescopes through space research programmes.

A key element in this type of research is the direct connection of academic science and technology with the industrial activities. This type of arrangement is aiming for an increased efficiency of process development, but also greatly accelerates curiosity-driven science, albeit in pre-determined directions.

In many ways, the specific application of multilayer reflective systems to photolithography has caused a tremendous boost of the general know how and technology on multilayers and thin films. Industrial appreciation for this research and the change of culture at many organizations have created a considerable research effort that has accelerated basic research. In the near future it will form the basis for many new valorisation opportunities.

References Chapter 1

[1] E. Spiller, Soft X-ray optics, SPIE - The International Society for Optical Engineering, Bellingham, USA, 1994.

[2] www-cxro.lbl.gov.

[3] D.L. Windt, IMD - Software for modelling the optical properties of multilayer films, Computers in Physics, 12 (1998) 360-370.

[4] H.J. Voorma, F. Bijkerk, Design of an extended image field soft x-ray projection system, Microelectronic Engineering, 17 (1992) 145-148.

[5] G.E. van Dorssen, E. Louis, F. Bijkerk, Optimization of x-ray emission from a laser produced plasma in a narrow wavelength band, Laser and Particle Beams, 10 (1992) 759-765.

[6] H.-J. Voorma, Mo/Si multilayer optics for micro-lithography, PhD thesis, Technische Universiteit Delft, (1997).

[7] E. Louis, F. Bijkerk, L. Shmaenok, H.J. Voorma, M.J. Vanderwiel, R. Schlatmann, J. Verhoeven, E. Vanderdrift, J. Romijn, B.A.C. Rousseeuw, F. Voss, R. Desor, B. Nikolaus, Soft X-ray Projection Lithography using a high-repetition-rate laser-induced X-ray source for sub-100 nanometer lithographic processes, Microelectronic Engineering, 21 (1993) 67-70.

[8] E. Louis, H.J. Voorma, N.B. Koster, L. Shmaenok, F. Bijkerk, R. Schlatmann, J. Verhoeven,

Y.Y. Platonov, G.E. van Dorssen, H.A. Padmore, Enhancement of reflectivity of multilayer mirrors for soft x-ray projection lithography by temperature optimization and ion bombardment, in: Microelectronic Engineering, 1994, pp. 215-218.

[9] F. Bijkerk, L.A. Shmaenok, A.P. Shevelko, R.K.F.J. Bastiaensen, C. Bruineman, A.G.J.R.v. Honk, A high-power, low-contamination laser plasma source for Extreme UV lithography, in: F. Bijkerk (Ed.) Microelectronic Engineering, Elsevier, Davos, Switzerland, 1995, pp. pp 299-301.

[10] F. Bijkerk, L.A. Shmaenok, E. Louis, H.J. Voorma, N.B. Koster, C. Bruineman, R.K.F.J. Bastiaensen, E.W.J.M.v.d. Drift, j. Romijn, L.E.M.d. Groot, B.A.C. Rousseeuw, T. Zijlstra, Y.Y. Platonov, N.N. Salashchenko, Extreme UV lithography: a new laser plasma target concept and fabrication of multilayer reflection masks, in: F. Bijkerk (Ed.) Microelectronic Engineering, Elsevier Science, Amsterdam, 1996, pp. pp. 183-186.

[11] E. Louis, H.J. Voorma, N.B. Koster, F. Bijkerk, Y.Y. Platonov, S.Y. Zuev, S.S. Andreev, E.A. Shamov, N.N. Salashchenko, Multilayer coated reflective optics for extreme UV lithography, Microelectronic Engineering, 27 (1995) 235-238.

[12] V. Fokkema, Real-time Scanning Tunneling Microscopy Studies of Thin Film Deposition and Ion Erosion, PhD thesis, Leiden University, (2011).

[13] E. Zoethout, E. Louis, F. Bijkerk, Real-space insight in the nanometer scale roughness development during growth and ion beam polishing of molybdenum silicon multilayer films submitted to Thin Solid Films, (2012).

[14] E. Zoethout, G. Sipos, R.W.E. van de Kruijs, A.E. Yakshin, E. Louis, S. Muellender, F. Bijkerk, Stress Mitigation in Mo/Si Multilayers for EUV Lithography, in: SPIE 5037, 2003, pp. 872-877.

[15] R. Soufli, R.M. Hudyma, E. Spiller, E.M. Gullikson, M.A. Schmidt, J.C. Robinson, S.L. Baker, C.C. Walton, J.S. Taylor, Sub-diffraction-limited multilayer coatings for the 0.3 numerical aperture micro-exposure tool for extreme ultraviolet lithography, Appl. Optics, 46 (2007) 3736-3746.

[16] I. Nedelcu, R.W.E. van de Kruijs, A. Yakshin, F. Bijkerk, Thermally enhanced interdiffusion in Mo/Si multilayers, Journal of Applied Physics, 103 (2008) 0835491-0835496.

[17] http://flash.desy.de/.

[18] http://en.wikipedia.org/wiki/Valorisation.

[19] www.fom.nl.

[20] P. Kürz, in: International Symposium on Extreme Ultraviolet Lithography, Lake Tahoe, USA, 2008.

[21] A.J.R. van den Boogaard, E. Louis, E. Zoethout, S. Muellender, F. Bijkerk, Surface morphology of Kr(+)-polished amorphous Si layers, Journal of Vacuum Science and Technology A, 28 (2010) 552-558.

[22] A.J.R. van den Boogaard, E. Louis, F. van Goor, F. Bijkerk, Optical Element for full spectral purity from IR-generated EUV light sources, in: SPIE 7271, 2009.

[23] A.J.R. van den Boogaard, E. Louis, E. Zoethout, K.A. Goldberg, F. Bijkerk, Characterization of Mo/Si multilayer growth on stepped topographies, Journal of Vacuum Science & Technology B, 29 (2011).

[24] A.J.R. van den Boogaard, F.A. van Goor, E. Louis, F. Bijkerk, Wavelength separation from extreme ultraviolet mirrors using phaseshift reflection, Optics Letters, 37 (2012) 160-162.
[25] V.V. Medvedev, A.E. Yakshin, R.W.E. van de Kruijs, V.M. Krivtsun, A.M. Yakunin, K.N. Koshelev, F. Bijkerk, Infrared suppression by hybrid EUV multilayer-IR etalon structures, Optics Letters, 36 (2011) 3344-3346.
[26] V.V. Medvedev, A.E. Yakshin, R.W.E. van de Kruijs, V.M. Krivtsun, A.M. Yakunin, K.N. Koshelev, F. Bijkerk, Infrared antireflective filtering for extreme ultraviolet multilayer Bragg reflectors, Optics Letters, 37 (2012) 1169-1171.
[27] J.Q. Chen, E. Louis, H. Wormeester, R. Harmsen, R. van de Kruijs, C.J. Lee, W. van Schaik, F. Bijkerk, Carbon-induced extreme ultraviolet reflectance loss characterized using visible-light ellipsometry, Measurement Science & Technology, 22 (2011).
[28] J.Q. Chen, E. Louis, R. Harmsen, T. Tsarfati, H. Wormeester, M. van Kampen, W. van Schaik, R. van de Kruijs, F. Bijkerk, In situ ellipsometry study of atomic hydrogen etching of extreme ultraviolet induced carbon layers, Applied Surface Science, 258 (2011) 7-12.
[29] J. Benschop, http://doc.utwente.nl/79862/1/oratieboekje_J_Benschop.pdf, (2011).
[30] B. Sonntag, VUV and X-ray free-electron lasers, Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment, 467 (2001) 8-15.
[31] K. Tiedtke, A. Azima, N. von Bargen, et al., The soft x-ray free-electron laser FLASH at DESY: beamlines, diagnostics and end-stations, New Journal of Physics, 11 (2009).
[32] P. Emma, R. Akre, J. Arthur, et al., First lasing and operation of an angstrom-wavelength free-electron laser, Nature Photonics, 4 (2010) 641-647.
[33] H. Tanaka, M. Yabashi, et al, A compact X-ray free-electron laser emitting in the sub-angstrom region, Nature Photonics, doi:10.1038/nphoton.2012.141 (2012).
[34] W. Ackermann, G. Asova, V. Ayvazyan, et al., Operation of a free-electron laser from the extreme ultraviolet to the water window, Nature Photonics, 1 (2007) 336-342.
[35] http://www.elettra.trieste.it/FERMI/index.php?n=Main.CDRdocument.
[36] I.V. Kozhevnikov, R. van der Meer, H.M.J. Bastiaens, K.J. Boller, F. Bijkerk, High-resolution, high-reflectivity operation of lamellar multilayer amplitude gratings: identification of the single-order regime, Optics Express, 18 (2010) 16234-16242.
[37] I.V. Kozhevnikov, R. van der Meer, H.M.J. Bastiaens, K.J. Boller, F. Bijkerk, Analytic theory of soft x-ray diffraction by lamellar multilayer gratings, Optics Express, 19 (2011) 9172-9184.
[38] R. van der Meer, B. Krishnan, I.V. Kozhevnikov, M.J. de Boer, B. Vratzov, H.M.J. Bastiaens, J. Huskens, W.G. van der Wiel, P.E. Hegeman, G.C.S. Brons, K.-J. Boller, F. Bijkerk, Proc. of SPIE 8139, (2011).
[39] R. van der Meer, B. Krishnan, I.V. Kozhevnikov, M.J. de Boer, B. Vratzov, H.M.J. Bastiaens, J. Huskens, W.G. van der Wiel, P.E. Hegeman, G.C.S. Brons, K.-J. Boller, F. Bijkerk, Single-order operation of lamellar multilayer gratings in the soft X-ray spectral range, submitted to Apl. Phys. Lett., (2012).

[40] E. Hecht, Optics, Addison Wesley, 2002.

[41] V.V. Aristov, A.I. Erko, V.V. Martynov, Principles of Bragg-Fresnel Multilayer Optics, Revue De Physique Appliquee, 23 (1988) 1623-1630.

[42] J.H. Underwood, M.E. Bruner, B.M. Haisch, W.A. Brown, L.W. Acton, X-ray photographs of a solar active region with a multilayer telescope at normal incidence, Science, 238 (1987) 61-64.

[43] C.J. Hailey, et al., Proc. SPIE 7732, 77320T, (2010).

[44] F.A. Harrison, et al., Proc. SPIE 7732, 77320S, (2010).

[45] F.E. Christensen, S. Abdali, P.K. Frederiksen, A. Hornstrup, I. Rasmussen, N.J. Westergaard, H.W. Schnopper, E. Louis, H.J. Voorma, N. Koster, H. Wiebicke, I. Halm, U. Geppert, E. Silver, M. Legros, K. Borozdin, K.D. Joensen, P. Gorenstein, J. Wood, G. Gutman, Some applications of nanometer-scale structures for current and future X-ray space research, Journal De Physique Iii, 4 (1994) 1599-1612.

[46] E. Louis, E. Spiller, S. Abdali, F.E. Christensen, H.-J. Voorma, N.B. Koster, P.K. Frederiksen, C. Tarrio, E.M. Gullikson, F. Bijkerk, Multilayer X-ray Mirrors for the Objective Crystal Spectrometer on the Spectrum Röntgen Gamma satellite, Proc. SPIE 2515, (1995) 194-205.

[47] P.A.C. Takman, H. Stollberg, G.A. Johansson, A. Holmberg, M. Lindblom, H.M. Hertz, High-resolution compact X-ray microscopy, Journal of Microscopy-Oxford, 226 (2007) 175-181.

[48] H. Stollberg, S. Yulin, P.A.C. Takman, H.M. Hertz, High-reflectivity Cr/Sc multilayer condenser for compact soft x-ray microscopy, Review of Scientific Instruments, 77 (2006).

[49] F. Schafers, Multilayers for the EUV/soft X-ray range, Physica B, 283 (2000) 119-124.

[50] F. Eriksson, G.A. Johansson, H.M. Hertz, E.M. Gullikson, U. Kreissig, J. Birch, 14.5% near-normal incidence reflectance of Cr/Sc x-ray multilayer mirrors for the water window, Optics Letters, 28 (2003) 2494-2496.

[51] J. Kirz, C. Jacobsen, M. Howells, Soft X-ray microscopes and their biological applications, Quarterly Reviews of Biophysics, 28 (1995) 33-130.

[52] I.A. Makhotkin, E. Zoethout, E. Louis, A.M. Yakunin, S. Mullender, F. Bijkerk, Spectral properties of La/B - based multilayer mirrors near the boron K absorption edge, Optics Express, 20 (2012) 11778-11786.

[53] I.A. Makhotkin, E. Louis, R.W.E. van de Kruijs, E. Zoethout, A. Yakunin, S. Müllender, F. Bijkerk, Multilayer coatings for the lithography generation beyond EUVL, in: International Symposium on Extreme Ultraviolet Lithography, Brussels, Belgium, (2012).

[54] C. Wagner, P. Kuerz, et al., EUV lithography at chipmakers has started: performance validation of ASML's NXE:3100, in: SPIE 7969, 2011, pp. 79691F.

2 Nanometer interface and materials control for multilayer EUV-optical applications

ABSTRACT

An overview is given of the progress in thin film and surface physics involved in multilayered systems with nanometer scale periodicity. When properly engineered, these enable the synthesis of reflective optics for the Extreme UV wavelength range. Design, deposition, and analysis of these structures have been driven by the demanding application of Extreme UV photolithography. This review addresses the selection of the wavelength in relation to the optical constants of materials, the layer growth mechanisms and ways to reduce layer roughness and interlayer formation. Special attention is given to the development of thin diffusion barrier layers between the materials in the multilayers to enhance the optical contrast and to reduce the interdiffusion. Practical issues like reduction of multilayer induced stress and enlargement of the reflectance bandwidth are also discussed, as well as the development of capping layers to control surface physics processes occurring under EUV irradiation. A description of the multilayer deposition techniques is given and the deposition of multilayers on large, heavily curved optics for real lithography systems is discussed.

2.1 Introduction

The continuously ongoing trend towards ever-faster computer chips requires a correspondingly improved resolution of the chip manufacturing equipment. This imaging process, usually referred to as photolithography, takes place in lithography equipment, or wafer scanners, that to date operate at a wavelength of 248 and 193 nm, the so-called Deep UV range. In the next generation lithography equipment, the resolution will be enhanced by reducing the wavelength to 13.5 nm, known as Extreme Ultra Violet (EUV) radiation. This wavelength has been selected as the first shorter wavelength to still enable a high transmission optical imaging system. The choice for 13.5 nm is explained in detail in Section 2.3.1. Because of the extremely high absorption of 13.5 nm radiation in any material, advanced reflective multilayer optics will need to be used. These basically consist of artificial Bragg crystals with a periodicity of a the half of the 13.5 nm wavelength, and practical layer control down to around two orders of magnitude smaller values.

Fig. 2.1 shows an example of an optical system as can be applied in an EUV wafer scanner. It consists of a collector mirror, a set of four mirrors to enable uniform illumination of the mask containing the pattern to be imaged and a six mirror demagnifying projection system. The relatively large number of mirrors in the projection part is required to obtain the high resolution in combination with a sufficiently large image field.

In proof-of-principle set-ups, such types of reflective multilayer optics have enabled the sensational development of the high-resolution lithographic technology: Extreme Ultraviolet Lithography (EUVL) which is now scheduled to succeed Deep UV imaging schemes in the manufacture of integrated circuits [1-3]. A major milestone accomplished consisted of the successful operation of two demonstration wafer scanners, so called Alpha-Demo Tools, yielding printed features with sizes down to 35 nm [4-7]. A world-wide consortium, led by ASML and its optics partner Carl Zeiss SMT GmbH, is now carrying out an industrial development programme to introduce the technology for high volume chip manufacture, and the first versions of such production equipment have already been shipped to pilot chip-production plants [8]. This has set a new standard in integrated-circuit manufacturing [3, 9].

The use of radiation of such extreme short wavelength has implied an extensive research programme, which by now is well mastering all new physics and technological aspects. FOM, the Foundation for Fundamental Research on Matter, plays

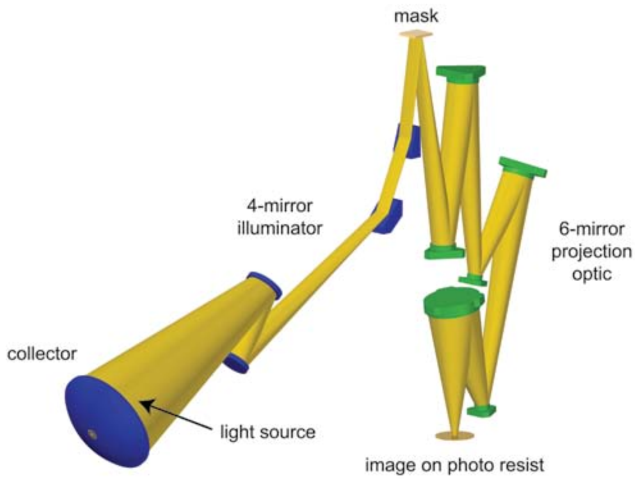


Figure 2.1: Design example of an all-reflective, i.e. multilayer coated, optical system as applied in an EUV wafer scanner.

a major role in the research and development of the multilayer reflective coatings, and demonstrations of world record reflectivities have been given [10, 11]. This chapter provides an overview of the path from fundamental research towards a fully developed process to deposit optics for new generations of lithography machines. Topics addressed include the physics and technological aspects of the optimization of multilayer designs for the application in EUVL, the surface and interface physics and chemical phenomena occurring in these few hundred layer thick stacks, the development of multilayer deposition processes which meet the layer design requirements, the multilayer characterization at sub-nanometer scale, and the photochemical aspects on the final application of these optics under high radiation loads, the latter includes the photon and electron induced surface chemistry leading to degradation of the optics when used in a scanner environment. Furthermore, multilayer development required for high volume manufacturing will be discussed.

2.2 Principle of multilayer reflection

Traditionally, natural crystals are frequently used for the reflection or diffraction of X-ray radiation. The principle of operation is constructive interference of the waves reflected from the individual lattice plains of the crystal, a process known as Bragg reflection [12]. For the wavelength range between several tenths and several tens of nanometers, generally indicated as the XUV range, the spacing between the lattice plains of most practically usable crystals is too small to obey the criterion of constructive interference, namely $2d \sin \theta = n \lambda$, known as the Bragg relation [12, 13].

This limitation can be overcome by building a stack of thin layers of alternating materials with layer thicknesses such that the periodicity (or d-spacing) of the stack equals the parameter d in Bragg's formula. The reflected waves from all interfaces add up constructively and a high reflectance can be obtained. To achieve this, combinations of high-Z and low-Z materials with maximum contrast of the two materials optical indices should be used. The thus obtained multilayer can be considered as an artificial crystal that will reflect radiation similar to natural crystals (see Fig. 2.2). The huge advantage of these 'synthetic' multilayer systems is that the layer thicknesses and thus the periodicity can be freely tuned to the wavelength to be reflected at a particular angle [14, 15].
In the case of Extreme UV Lithography, near-normal incidence large-image-field optics is used at a wavelength of 13.5 nm, implying a multilayer periodicity of approximately 7 nm. The individual layers need to have a thickness which is a

fraction of this, typically several tens of monolayers only. For this type of optics and wavelength, the highest practical value for the reflection, around 70%, is achieved for the material combination of Mo and Si. Absorption limits the full stack to 50-70 Mo/Si bi-layers. In practice, phenomena like interlayer formation, layer and initial substrate roughness, lateral incoherence, nano-crystallite formation, etc. have to be taken into account. The practical task therefore involves the 'atomic engineering' of atomically flat interfaces between the Mo and the Si layers with a step like profile of the refractive index. This task requires detailed knowledge of the surface physics phenomena involved.

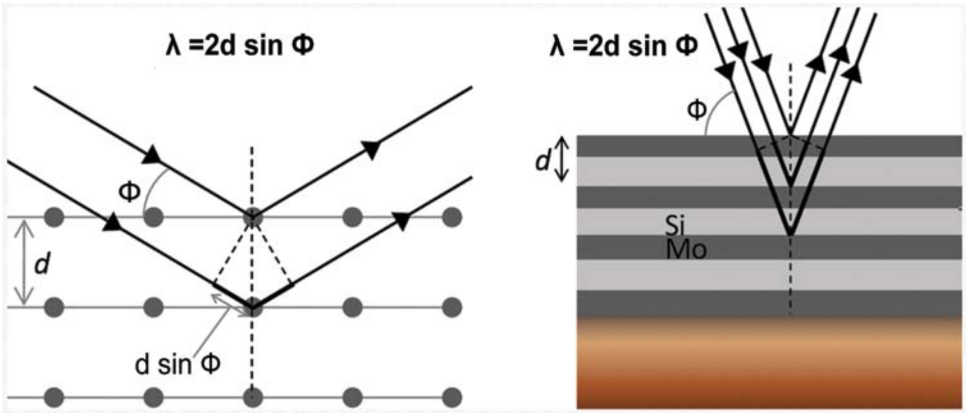


Figure 2.2: Schematic view of constructive interference from interfaces of a crystal (left picture) and a multilayer (right picture).

2.3 Development of the multilayer deposition process: from layer growth control to interface engineering

2.3.1 Multilayer design for EUVL

A critical issue for lithographic exposure tools is the transmission of the optical system, or the number of exposed wafers per hour. Only if a considerable fraction of the available light can be used to image the chip pattern on the wafer, the technique can be commercially viable. Considering that the EUV wafer scanners are typically equipped with 10-11 near-normal incidence multilayer mirrors plus a multilayer coated reflective mask, and the fact that high brightness EUV sources are not yet readily available, it is obvious that the reflectance per mirror should be as high as possible. Another factor is the bandwidth of the optical system: a multilayer Bragg reflector has a limited bandpass. The convolution of 11 reflectance curves results in a narrow-band throughput curve that imposes strict requirements on the emission characteristics of the light source. The bandwidth of the optical system and the spectral distribution of the light emitted by the source should strictly correspond.

There are several factors that determine the reflectance of multilayers, being the material choice, the ratio of the thickness of the layers in one period, the interface roughness, the composition and morphology of the layers and the thickness of the compounded interlayers, inevitably formed in the layer growth process [16, 17]. Another factor is the roughness of the substrates on which the multilayers are deposited as well as the possible roughness evolution with increasing layer number in the multilayer stack.

The material choice is determined by two important factors, being the optical constants that determine the reflectance and the thermodynamics of the materials. The optical properties are determined by the refractive index n of each material, which is defined as $n = 1 - \delta + i\beta$, where δ is the real part and β the imaginary part [14]. The index is close to unity for the X-ray and EUV regime for which multilayers are applied. This means that the reflectance per single interface is limited to a few percent at best. To still achieve a high total reflectance, two alternating materials should be selected that have a high δ (typically a high Z material) and a low δ (low Z material) with the largest possible difference. The factor β is representative for absorption of the light, and should therefore have a low value. The δ and β of several materials for a wavelength of 13.5 nm are plotted in Fig. 2.3.

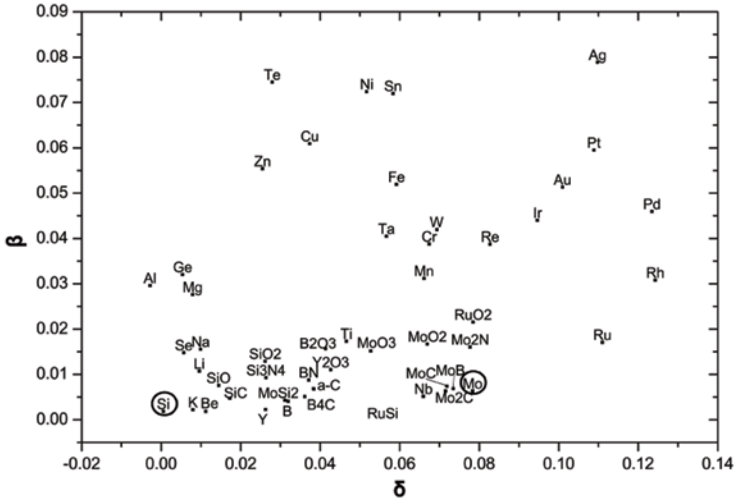


Figure 2.3: Real (δ) and imaginary (β) parts of the refractive index of several elements at the wavelength of 13.5 nm [18].

From this figure it can be seen that Be or Si are the best candidates as low δ materials and that they are best combined with high δ materials like Mo or Ru. Other high δ materials like Rh or Pd can be excluded because of the too high β value. This is, to some extent, also valid for Ru. Furthermore, from the thermodynamics point of view Ru is less favourable because of its tendency to intermix with Si [19, 20] which leaves us with the material combinations Mo/Si and Mo/Be. Since the absorption of EUV radiation in Be is lower than in Si, Mo/Be multilayers, when designed to reflect light with a wavelength just above the Be absorption edge at 11.2 nm, can have a higher reflectance than Mo/Si for a wavelength above the Si absorption edge at 12.4 nm, but Mo/Be requires more periods.

The width of the reflection peak scales inversely with the number of layers contributing to the reflection, analogous to Scherrer's formula that relates the width of the diffraction peaks in a X-Ray diffraction pattern to the size of the crystal, e.g. the number of lattice planes involved [21]. A large number of layers thus results in a reduced bandwidth of the mirror. Analysis of the calculated bandpass-integrated throughput of a 10-mirror optical system shows that the effect of the reduced bandwidth is dominant over the enhanced reflectance. As a result, the throughput of a Mo/Be coated optical system will be considerable lower than a Mo/Si system. This result is illustrated in Fig. 2.4, showing the peak and band-pass integrated reflectance of a 10 mirror system for both material combinations.

From this figure it can be seen that the highest 10-mirror throughput can be achieved when Mo/Si multilayers are optimized for 14.4 nm radiation.

The reason that the optimum occurs at 14.4 nm, rather than close to the absorption edge of Si, is that the optical contrast between Mo and Si is higher at that wavelength. This allows a lower number of layers to be used and, thus, a larger 10-mirror bandwidth. This is described in detail in [22]. Because of the throughput issue, plus the fact that beryllium is a hazardous material requiring expensive safety precautions in the deposition laboratories, Mo/Si has been selected for EUV development studies. However, the operating lithography wavelength has, mainly for historical reasons, been set to the non-optimal value of 13.5 nm.
The second result from this design study concerns the molybdenum fraction in

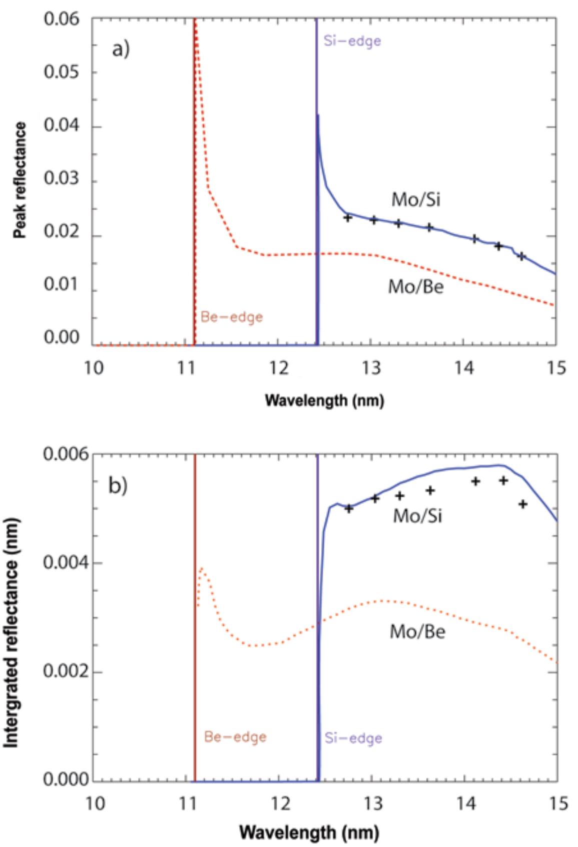


Figure 2.4: Comparison of calculated peak (a) and integrated (b) reflectivity of a 10 mirror multilayer system for Mo/Si versus Mo/Be. Crosses are experimental data of Mo/Si mirrors deposited at FOM [22]

the bi-layer. It was calculated [23][24] that the thickness ratio of molybdenum to the multilayer period, usually referred to as the Γ-factor, should be around 0.4 to achieve the highest normal-incidence reflectance. This results in an optimal quarter-wavelength stack, corrected for the optical path lengths in the constituent materials.

2.3.2 Multilayer deposition

The deposition of XUV reflecting periodical stacks of more than a hundred extremely thin and atomically flat layers requires a dedicated deposition technique. To successfully grow such layers, detailed knowledge is required on the surface science processes involved. Ideally, one would like to have layer by layer growth, as described by the Frank-van der Merwe model [25]. This would result in sharp interfaces, but this is only possible for a limited number of material combinations under very strict conditions. However, normally each of the bi-layer materials has a different structure, generally polycrystalline for metals and polycrystalline or amorphous for materials like carbon and silicon. In such systems, metal-metal or metal-semiconductor, layer growth in the Stranski-Krastanov mode [26] is fairly common. This results in a combination of layers with islands [27]. In this growth mode several factors that are basically determined by the energy of the deposited atom (a so-called ad-atom), have to be taken into account. If these atoms arriving at a surface have a very low kinetic energy, they can stick and stay at their positions without transferring energy to the layer beneath and without sufficient thermal energy to enable surface mobility. This leads to stochastical roughness in the layer grown. Adding thermal or kinetic energy to the ad-atoms, for instance by bulk heating, laser annealing or by ion bombardment, can enhance the surface mobility and clustering can take place, resulting in the island formation. When these islands grow laterally, a closed layer can be formed leading to a smooth surface. However, in the mean time new atoms are deposited on top of these earlier formed islands forming new islands in turn. This phenomenon can eventually lead to columnar growth. To prevent this, ad-atoms that are deposited on top of the islands should be able to step down one level. Even if the ad-atom has sufficient thermal energy to diffuse over the surface to approach the border of the island, it still needs energy to overcome the potential barrier that stops the atom from stepping down to the lower layer. This potential barrier is known as the Schwoebel barrier [28]. Thus, adding energy to the island ad-atom is required

to enable stepping down and form a smoother surface layer.
So, in general, the ad-atoms need energy to form smooth, dense and closed layers, but on the other hand, a too high ad-atom energy can activate a chemical reaction of the particle with the previous layer leading to compound formation at the interface, or cause penetration of the particle into the previous layer, resulting in enhanced interface intermixing. Ideally, one should be able to tune the particle energy to the different growth stages that are encountered: low in the initial growth part of the layer while increasing when the layer thickness increases. This will further be discussed in Section 2.3.3. A compromise solution consists of deposition with low, i.e. thermal particle energy and add energy only when required at the particular stage of layer growth, e.g. by means of ion or laser beams.

2.3.3 Layer deposition techniques

Thus, the energy of the ad-atom is a critical parameter in the deposition of smooth layers and this can result in conflicting requirements for the different materials in the multilayer. The challenge is to select a deposition technique that fulfils the requirements best for all constituent materials. Traditionally there are four methods to deposit reflecting multilayers for the XUV wavelength range, each having specific advantages and disadvantages. These methods are electron beam evaporation [29], magnetron sputtering [30], ion beam sputtering [31] and pulsed laser deposition [32]. An overview of these techniques is given in [14], [33] and [34].

In the particular case of multilayer coatings for EUV lithography where the material combination Mo/Si has been selected [22], the first three methods have proven to achieve a near normal incidence reflectance close to 70%.
Although pulsed laser deposition has been very appropriate for material combinations like Ni/C and W/C, the results for the Mo/Si combination have been limited. Braun et al. [35] achieved 57% reflectance, although with smoother interfaces than in their Mo/Si multilayers produced by magnetron sputtering. The EUV reflectance could have been limited by the somewhat thicker interlayers and the inclusion of droplets in the layers. The latter happens because of the low melting temperature of silicon. In other materials schemes, i.e. when containing oxygen, pulsed laser deposition has been developed with performance values that are unmatched by any of the other deposition techniques

[36, 37].
Of all technologies discussed here, ion beam sputtering has proven to result in a minimum number of defect inclusions in the multilayer [38-40]. This is of relevance for the production of reticles or mask blanks, since any defect in the multilayer structure of a mask would result in a defect in the chip pattern [41]. The technique is presently being utilized for the deposition of mask blanks. Hiruma et al. [42] claim a reflectance of 64% for a 40 bi-layers stack while Spiller et al. [31] achieved 68.8 % by applying additional ion polishing, similar to the technique described in Section 2.3.8. Furthermore, since substrate pits and scratches can lead to multilayer defects or phase imperfections that will be imaged on the wafer, this deposition technique is also used to smoothen such defects by means of a silicon buffer layer [43, 44].

For the coating of large, heavily curved optics, electron beam evaporation in combination with ion beam smoothening and magnetron sputtering are the most appropriate deposition methods to achieve high reflectance and well defined lateral thickness profiles. This has been demonstrated in several results: magnetron sputtering has been used to coat the optics of the so-called Engineering Test Stand (ETS) [45], and some copies of the Micro Exposure Tool [46], while electron beam evaporation in combination with ion beam smoothing has been used for other copies of the Micro Exposure Tool [47], the first full field scanning system, or Alpha-Demo Exposure Tool [48] and for the first commercial machines built by ASML and Carl Zeiss, the NXE:3100 systems [49]. The last two are described in more detail in Section 2.4. of this Chapter. Furthermore, multilayers produced by both techniques on super polished substrates have shown very high normal incidence reflectivity, the highest reported value being 69.5% [10]. Selection of the most appropriate technique for the deposition of EUVL optics depends not only on the physics of the deposition process, but also on economical aspects like reliability, costs of the equipment, running costs and clean room floor space required.

The configuration of the coating geometry of magnetron and e-beam deposition essentially differs: classical magnetron sputtering makes use of targets that have, at least in one dimension, a size considerably larger than the surface to be coated, whereas e-beam evaporation uses a small evaporation target, irrespective of the size of the optics. Both techniques enable a fully automated coating process.
The major fundamental difference between the two techniques concerns the energy of the deposited particles. In the case of magnetron sputtering, this

can be as high as 100 eV or more. In general, higher particle energies lead to an enhanced film density, but may also enhance the risk of interface damage during the deposition of the first part of every layer. Furthermore, high energy sputter gas ions may reach the film surface which can result in smoother films but can also result in enhanced interface layer formation and inclusion of the sputter gas in the layer, affecting the optical constants. Attempts to bias the substrate during this phase of the deposition [50] have not been very successful, possibly because the method does not affect the reflected neutral gas particles.

A special case of deposition consists of a magnetron sputter method in which the particle energy can be adjusted. The basis is a technique called "thermalized particle magnetron deposition" (TPM), which has been developed at FOM in close cooperation with Leybold Optics (Dresden, Germany). It combines advantages of magnetron sputtering and e-beam deposition and allows tuning of the particle energy to different growth stages, e.g. by adjusting the background gas pressure and thus influencing the gas phase collision processes [11].

This technique also enables stoichiometric deposition of compounds and has the stability to provide the required periodicity throughout the full layer stack. Essential in this process is the control of the energy of the particles that arrive at the layer being grown. Basically, the first atomic layer can be grown at low energy to avoid materials intermixing at the layer interfaces, while further atoms are preferentially deposited at higher energy to cause e.g. layer densification or improved stoichiometry. In the experiments using this method to deposit Mo/Si multilayers, a record reflectivity of 70.15% at the EUV wavelength of 13.5 nm was demonstrated [11].

In the case of electron beam evaporation the normal kinetic energy of the particles is already in the thermal range, typically below 1 eV, which does not cause any damage in the film. On the other hand, as described in Section 2.3.2., for many materials the particles need a considerable energy to have sufficient surface mobility and to overcome potential barriers to form smooth layers. In these cases a low energy noble gas ion treatment of the layer during or immediately after deposition can be applied. Although this additional step inevitably makes the process more complicated and more time consuming, it provides the ability to independently optimize the growth and the smoothing process. For research purposes this can be an advantage. A schematic overview of the possible deposition techniques is given in Fig. 2.5.

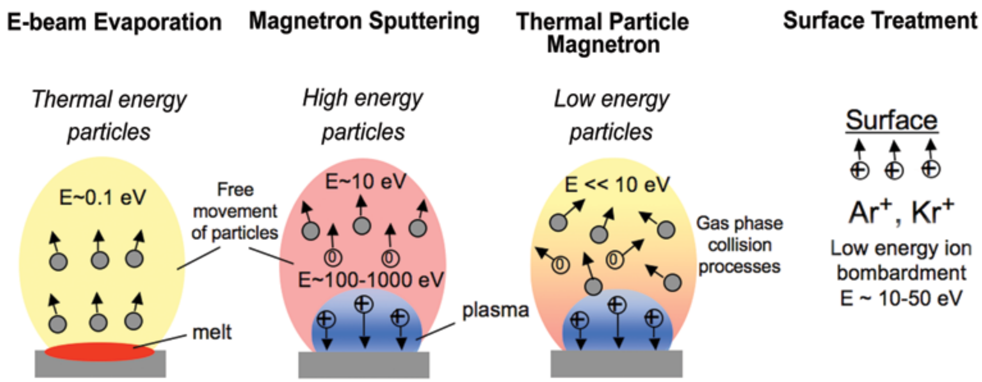


Figure 2.5: From left to right: principle of e-beam evaporation, magnetron sputtering, thermalized particle magnetron sputtering (TPM), and surface treatment by ions.

2.3.4 Electron beam evaporation deposition facility

The role of particle energy is also evident from the layout and configuration of one of the deposition facilities we have been using at FOM, both for the multilayer optimization process as well as for the coating of a considerable number of the mirrors for the first EUVL scanners. It consists of two coupled high vacuum systems with a base pressure in the 10^{-9} mbar range, separated by a large diaphragm. Fig. 2.6 shows a schematic diagram of the facility. The lower vacuum system contains the e-beam evaporator and a water cooled movable multi-target holder to position the materials in the focus of the e-beam. The separation of lower and upper chamber by a diaphragm prevents most contamination from reaching the upper system that contains the substrate to be coated. A fast shutter just under the diaphragm controls the deposition onto the substrate. The substrate is rotated during the entire coating process for enhanced uniformity of the coating. To locally transfer energy to the deposited layer, a Kaufman ion source is used. Ion energies from 50 to 2000 eV are available and the angle of incidence of the ions can be varied from grazing up to 50° with respect to the substrate surface. All noble gases can be used, as well as gases like N_2. The ion treatment of the layers is discussed in detail in Section 2.3.8.

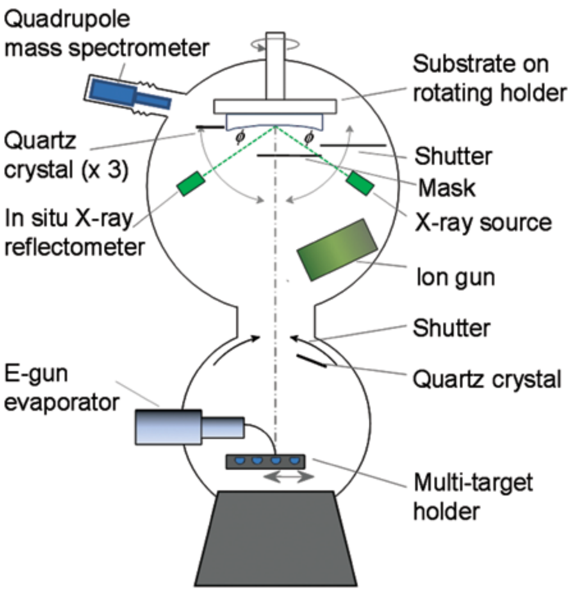


Figure 2.6: Schematic picture of a FOM e-beam evaporation coating facility.

The layer thickness is controlled by an in situ soft X-ray reflectometer [14, 51] using N, C or B-K radiation at a grazing angle between 10 and 30º, the photons being detected by a channeltron electron multiplier. The wavelength and angle are chosen such that the modulation of the reflected intensity is sufficient (see Fig. 2.7) to control the layer thickness up to the level of 0.1% or better, enabling matching of the period of the mirrors to the operating wavelength of the multi-component optical system. Special care is taken to analyze the reflected signal with dedicated fitting routines to enable fully automated deposition of the multilayers. This, in combination with quartz crystal microbalances, assures a stabilized deposition process. Several masking configurations are used to control the later profile of the coating on real optics. A residual gas analyzer is installed for vacuum control.

2.3.5 Multilayer Characterization

One of the most difficult issues in multilayer research is the analysis, since the physics to be studied is a complex combination of surface science phenomena in combination with thermodynamics of buried interfaces. The latter, because of the very thin layers, is somewhere in between the atomic level and the solid state physics of bulk materials. Actually no analysis technique that probes all these phenomena exists. Many measurement techniques that will be discussed in this section have to be combined, making the analysis not only very challenging, but the results sometimes not even unambiguous.

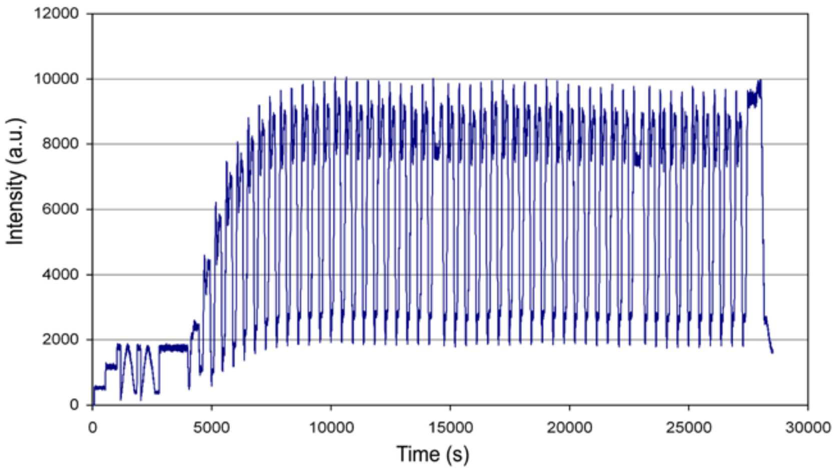


Figure 2.7: Example of the raw data of the in situ reflectometry signal during deposition.

Three stages of multilayer analysis can be distinguished: fundamental research during multilayer development, analysis during production and product assurance, and analysis while the multilayer optics is being used in lithographic equipment.

Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) can be used to determine the elemental composition of a thin layer and, in many cases, also the chemical state of the atoms. The depth resolution of both techniques however, is in the order of a few nanometer which is comparable to the thickness of the layer under study, causing the interface beneath the layer to be probed as well. Applying the technique in an angular resolved mode can, to some extent, overcome this problem. AES and XPS can also be used to study interfaces between the layers by taking the spectra while Ar sputtering is used to remove material, thus resulting in depth profiles of composition and chemical state of the layers, albeit with the same limited depth resolution. An additional complexity is that exposing a layer to atmospheric pressure e.g. for transport to the analysis facility, modifies the composition. Therefore the XPS equipment should be connected to the deposition facility. At FOM a fast

UHV sample transfer system was constructed to transport a freshly deposited sample to the XPS facility in a few minutes [11, 52]. The same vacuum transfer system also gives access to a Scanning Tunneling Microscope (STM) enabling nanometer resolution studies of the morphology of surfaces, or at least those surfaces that are conducting. Very thin isolating layers can also be probed, but with less resolution.

The technique that has the ultimate surface sensitivity is Low Energy Ion Scattering (LEIS), disclosing the elemental composition of the top few monolayers, though it does not disclose their chemical state [94]. LEIS should preferably be connected under vacuum to a deposition set up as well. In depth information to study interfaces and diffusion processes can also be obtained by depth profiling, but again with limited depth resolution [53]. Another technique that can be used is Rutherford Back Scattering (RBS).

If the roughness of the top layer must be studied, Atomic Force Microscopy (AFM) can be used, ideally also in the vacuum of the deposition equipment. AFM is also best suited to obtain insight in the lateral correlation length of the surface roughness, usually represented as the Power Spectral Density which is the Fourier transform of the surface height profile [14].

Insight in the flatness of the interfaces and in the formation of interlayers can also be obtained by High Resolution Cross Sectional Transmission Electron Microscopy (HRTEM) where a very thin slice of several tens to a hundred nanometer is imaged in transmission, also disclosing the amorphous/crystalline state of the layers. The disadvantage is that information is obtained from the full thickness of the sample, which makes quantitative analysis difficult. Nevertheless, in some cases, HRTEM analysis, in combination with hard X-ray reflectometry (discussed hereafter) can result in an in-depth density profile of the multilayer, as has been shown by Kessels et al. [54].

A completely different approach, but very well possible to be combined with the materials analysis techniques discussed so far, is to study the multilayers with photons: hard X-rays, usually Cu-Kα_1 radiation (λ = 0.15406 nm), can be used to measure the specular reflectance over many Bragg orders by varying the incident angle. The position of the Bragg maxima is a direct measure for the periodicity of the multilayer, albeit that this periodicity cannot be directly translated into the EUV wavelength where the multilayer will have the maximum normal incidence reflectance without detailed knowledge of the multi-

layer composition. Fitting of the reflectance curve [16] can be used to determine the density of the materials, interface roughness, interlayer thickness, and ratio
Γ of the constituent materials. Another approach is followed by Voorma et al. [55] who uses Fourier analysis of the Bragg peaks to determine the average interface roughness. This method is based on theory described in [56]. An additional option is to use the Cu-Kα_1 radiation to create an X-ray standing wave in the multilayer. By changing the angle of incidence the position of the antinodes of the standing wave can be tuned to specific layers, from which the X-ray fluoresence yield can be measured [57].

A Cu-Kα_1 based diffractometer can also be used in an off-specular mode to measure the diffused scattered light and gain more insight in the spatial frequency of the roughness i.e. the lateral characteristics of the interfaces. Finally, Cu-Kα radiation can be used to measure diffraction from crystallites in the layers as will be discussed in Section 2.3.10.
Eventually, the multilayers should be characterized at the wavelength and angle they are supposed to be used, which is usually 13.5 nm at angles close to normal incidence in the case of EUV Lithography. This so called 'at wavelength reflectometry' gives the final performance of the reflectors which is extremely important from the application point of view. Although it is very difficult to extract properties like roughness, interlayer thickness or density from this type of measurements only, it yields indispensable information to be combined with the Cu-Kα_1 data and the materials analysis.

In the production phase of reflecting multilayers in situ reflectometry with soft X-rays, e.g. C-K radiation (λ = 4.48 nm), can be extremely useful or even indispensable to control the multilayer periodicity in electron beam evaporation and ion beam sputtering equipment. However, in all cases post deposition characterization by at wavelength reflectometry is required to determine the mirrors performance. This should be carried out on a regular grid on the mirror to determine the deposited lateral profile as well. The requirements on reflectometry are almost as strict as on the multilayers. For example, in the alignment of heavily curved optics, a lateral misalignment of a few tenth of a millimeter already corresponds to the full error budget for the multilayer periodicity. Also a slight mismatch of the angle of incidence during the measurement can easily lead to unacceptable measurement errors. The required accuracy is strongly dependent on the shape and specifications of each mirror, but as a rule of thumb the reflectometer should be able to measure with accu-

racies of the lateral position better than 200 µm, the angle of incidence better than 0.05° and the wavelength better than 0.01%. Worldwide, only a very few facilities [58-62] are able to meet these requirements.
Metrology to check the reflectance of the multilayers when the optics is mounted in the lithography equipment, can be only very limited, because of the complexity, the available space in the machine, as well as the costs. The imaging quality of the optics will be monitored from the exposed wafers which will also give some indication of the throughput of the optics, but the state of contamination of the top surface of the multilayers can best be measured by spectroscopic ellipsometry [63] which also enables to estimate the resulting EUV reflectance loss [64].

2.3.6 Optimization of EUV reflectance

The efficiency of an EUVL wafer scanner is determined by the design, the intensity of the light source within the band pass of the optical system, the sensitivity of the photo resist and the multilayer reflectance. In Section 2.3.1. it was explained that for the first generation EUV mirrors Mo/Si has been selected as the material combination of the multilayer mirrors on the optics. For this material, a theoretical reflectance of 75 % can be calculated if perfectly sharp interfaces are assumed. However, in practice intensity is lost in scattered light from rough interfaces and the loss becomes huge if the roughness of the interfaces is a considerable fraction of the layer thickness [14]. Several models exist to calculate the reflectance loss from the rms roughness [14, 65], but can never be very accurate because of the difficulty to determine the absolute value of the roughness. The roughness of an interface depends also on the layer on top of it and can therefore not be measured directly by for instance Atomic Force Microscopy (AFM) and must be derived from XUV and X-ray reflectivity and scattering experiments, but still AFM characterization of the top layer of a multilayer gives a good indication.
Other factors that can reduce the reflectance are intermixing and the formation of compounded interlayers, both leading to a less sharp contrast in optical constants and the morphology of the layers.

The optimization of multilayers with respect to these phenomena requires an extensive research program that was carried out using the electron beam evaporation facility described in the previous section with the first goal to reduce the roughness of the interfaces to an rms value significantly below 0.2 nm.

The Mo and Si particles generated by electron beam evaporation have thermal energy during deposition, which in this case is insufficient to form smooth layers. A 50 period Mo/Si multilayer deposited on a super polished substrate with an AFM determined rms roughness σ of < 0.1 nm results, if no additional smoothing treatment in the form of added energy has been applied in a near normal incidence reflectance of less than 40 %, corresponding to an interface roughness of almost 1 nm. This clearly indicates the necessity to add energy, which can be done in two ways: by deposition at an enhanced temperature and by applying ion treatment to the layers.

2.3.7 Deposition at elevated substrate temperature.

The first and easiest way to add energy to the particles that are deposited is to enhance the substrate temperature during deposition of the layers. As a first assessment, we carried out depositions at several enhanced substrate temperatures up to 265 ° C, monitoring the deposition with the in situ soft X-ray reflectometer [51]. The best reflected intensity and the largest modulation of the amplitude were measured at a substrate temperature of 215 °C. This also resulted in a constant modulation of the in situ signal during the deposition indicating a constant level of interface roughness. This phenomenon has also been observed by Kloidt et al. [66]. A more quantitative investigation of the interface roughness as a function of temperature is obtained from the analysis of small-angle reflectivity measurements using Cu-Kα_1 radiation of 0.15406 nm. The results, shown in Fig. 2.8, show a sharp minimum in interface roughness of 0.33 nm for

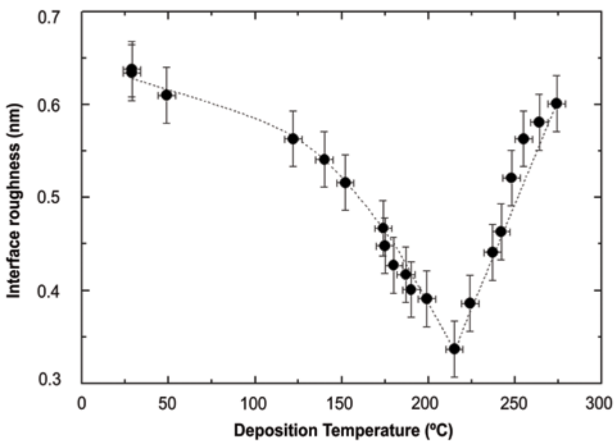


Figure 2.8: Measured interface roughness as a function of the substrate temperature during deposition [67]

a multilayer deposited at 215 °C. This minimum can be explained by two competing processes. With increasing substrate temperature surface diffusion induced smoothening takes place, leading to reduction of the interface roughness. The second process, temperature enhanced intermixing, causes roughening and dominates for temperatures above 215 °C [67], resulting in a relatively low normal incidence reflectance of this 32 period multilayer of 42%, which is a too low value for a multilayer with this interface roughness. However, the reflectivity is not only dependent on the interface roughness, but also on the structure, the density, or contamination of the layers. In other work [68] we have reported a five atomic percent content of oxygen in the Si layer for multilayers produced at elevated substrate temperatures, while the oxygen content was negligible in multilayers produced with ion beam smoothing. This oxygen content is likely to be responsible for the low reflectance of the samples produced at elevated temperature.
Another disadvantage of this method to improve the multilayer quality is the fact that the multilayer is at an elevated temperature during the entire coating process, leading to enhanced interdiffusion of the layers already deposited and buried in the stack [69].

Summarizing, deposition at elevated substrate temperatures is an easy way to improve the quality of individual layers in a Mo/Si multilayer structure, but it does not result in the highest possible reflectance. This is due to the insufficient overall interface roughness reduction, the enhanced absorption due to the residual oxygen content in the Si layers, and by the enhanced layer interdiffusion of buried interfaces in the layer stack.

2.3.8 Ion polishing

A more direct way to add energy to the particles deposited consists of a surface treatment with ions after or even during the growth of a layer. This enables transferring energy only where it is required, namely to the layer surface to be smoothened. Significant smoothing of surfaces leading to sharper interfaces was first shown by Spiller on a RhRu/C multilayer [70] and by Puik on W/C multilayers [71]. Shortly after these first publications, successful application of ion beam smoothing of Mo/Si multilayers was reported by Kloidt [72] for short period multilayers and by Louis et al. [51] for coatings in the EUV range.
Initially, most smoothing experiments have been carried out using Ar^+ ions. However, due to its small dimensions Ar^+ penetrates deeply into the layers and

can therefore damage the interface underneath the layer. To reduce this effect, the use of a larger ion, such as Kr^+ might be favourable. At FOM the use of both Ar^+ and Kr^+ was investigated by Schlatmann [73] to smoothen Mo as well as Si-layers. The best result was obtained when polishing the Si-layers only with relatively low energy, e.g. 300 eV, Kr^+ ions. However, this work was carried out on multilayers with a periodicity of 6 nm only and the results obtained are likely to be influenced by interface modification under the layers being ion treated. Furthermore, all experiments were carried out with a fixed angle of incidence of 45° of the ions on the surface.

Therefore, using the coating facility described above in Section 2.3.4., Voorma et al. [74] studied the angular as well as the energy dependence of the smoothening of the Si-layers using a Kr^+-ion beam over a wide range: from grazing angles of 10° to a more normal angle of 50°, while varying the ion energy from 300 up to 2000 eV. Using these parameters, 16-period Mo/Si coatings were produced reflecting at $\lambda = 14$ nm at near normal incidence, the relevant circumstances for EUV lithography. All samples were characterized by Cu-$K\alpha_1$ reflectivity measurements and the interface roughness was determined by analysis of the reverse Fourier transforms of the Bragg peaks [55]. The near normal incidence reflectance was measured using a laser plasma based reflectometer at the Center for X-ray Optics in Berkeley, California [75].

The most striking result, shown in Fig. 2.9, was the clear reduction of the rms interface roughness from above 1 nm to below 0.3 nm when the angle of incidence of the ions was varied from grazing to more normal incidence. This is not in agreement with the more intuitive picture that displacing atoms from upper to lower positions in the surface would be the dominant mechanism of ion smoothing. Most likely, the ion beam smoothing is not only a top surface effect, but also generates a redistribution of positions of the Si-atoms within the layer. The dependence of the smoothing effect on the ion energy was less clear. At small incident angles the smoothing was not very effective, but the use of higher energies was found to partly compensate the incomplete smoothing. At an incident angle of 50° however, there seemed to be only a marginal gain when using an energy of 2000 eV.

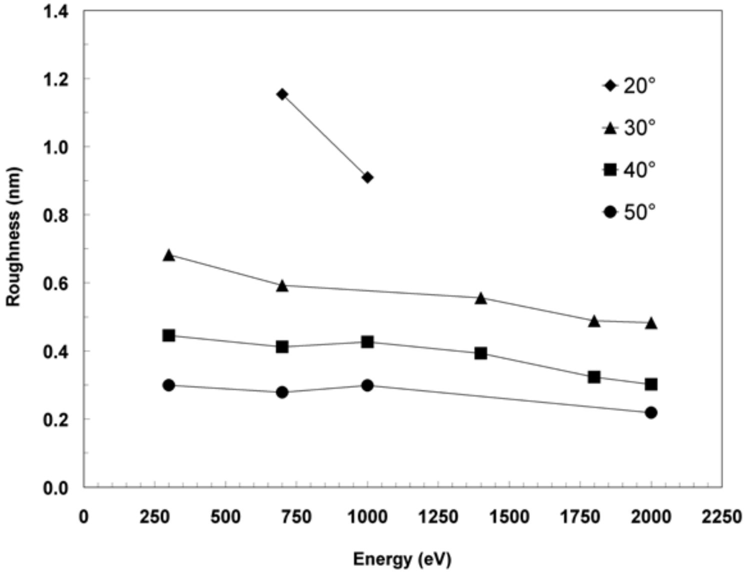


Figure 2.9: Angular and energy dependence of the interface roughness in Mo/Si multilayers when each Si-layer is polished with Kr^+-ions [74].

The effect of the reduced interface roughness is plotted in Fig. 2.10: the reflectance increases for steeper angles of incidence, while the effect is much less pronounced for increased ion energy, particularly at 50º. A more detailed analysis of the roughening and smoothening phenomena can be found in Voorma et al. [74]. The major conclusion of that work is that the dominant smoothing mechanism is proportional to the spatial frequency or lateral length scale of the roughness. This implies smoothening by ion enhanced bulk viscous flow, based on classical studies on surface perturbations for a viscous continuum [76, 77]. However, the bulk nature of such a mechanism does not explain the surface effect of the ion-polishing. In answer to this, van den Boogaard et al. [41] suggested that the strict surface confinement of the ion-enhanced viscosity should be discarded due to the annihilation of sub-surface free volume. This is the same effect as mass transport perpendicular to the surface, giving rise to a similar dispersion in smoothening kinetics. Furthermore, Voorma claims that ion polishing at an incidence angle as steep as 50º results in the lowest interface roughness (see Fig. 2.9) and consequently in the highest reflectance (Fig. 2.10) [74]. Steeper angles might even be more favourable though ion polishing at normal incidence is reported to lead to the formation of dots on the surface of silicon [78, 79].

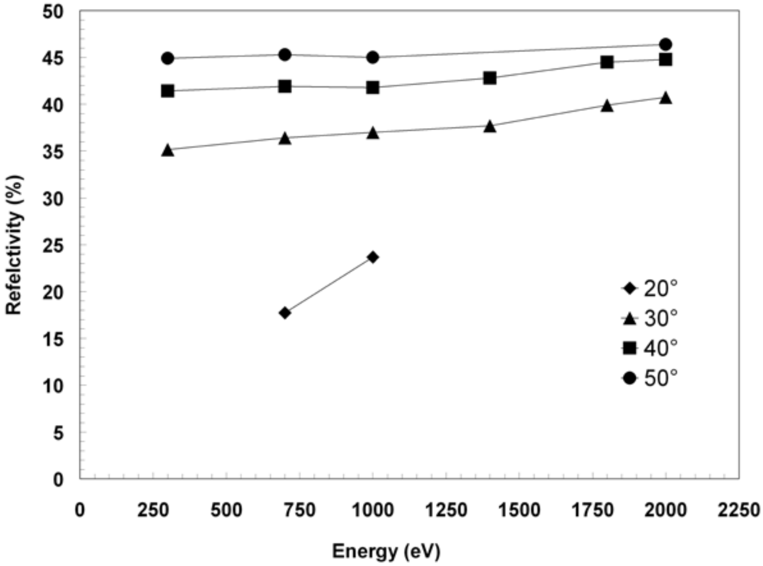


Figure 2.10: Angular and energy dependence of the near normal reflectance in Mo/Si multilayers when each Si-layer is polished with Kr^+-ions [74].

The rather weak ion energy dependence in Voorma's work at 50° might be explained by two counteracting effects. On the one hand, this is the improved surface smoothing with higher energy, while on the other hand deeper interfaces might become intermixed due to the high penetration depth of the ions. Two cases, namely the use of 300 and 2000 eV Kr^+-ions at 50° angle of incidence on Si layers, were further investigated by Yakshin [16]. Another parameter was included, namely the amount of the Si-thickness removed by the polishing. Two sets of samples were made, one where 1 nm of each Si layer and one where 3 nm of Si was removed [16]. All samples were measured using Cu-$K\alpha_1$ grazing incidence X-ray reflectivity (GIXR) and fitting of the well known modulation of the Bragg peak intensities of the 0.154 nm X-rays was then used to determine the thickness as well as the composition of the silicide layers formed at the boundaries. In all multilayers the formation of silicide layers is observed. In the 300 eV case, Yakshin found identical interlayers with a thickness of 0.8 nm when Mo was deposited on Si and when Si was deposited on Mo, leading to the conclusion that the 300 eV polishing did not heavily affect the interface under the Si. Furthermore, the composition of the interlayers was determined to be a mixture of Mo_5Si_3 and $MoSi_2$. In the 2000 eV case Yakshin found two different interlayer thicknesses at both interfaces: 1.1 and 1.3 nm, both consisting of $MoSi_2$. Clearly, the use of more energetic ions leads to more interlayer formation. Furthermore, the high Kr^+ energy leads to the transition of the interlayer composition from a mixture of Mo_5Si_3 and $MoSi_2$ into pure $MoSi_2$. This type of phase transition is also observed when these multilayers undergo thermal annealing where an abrupt phase transition into $MoSi_2$ has been reported [17, 80]. The thickness of the interlayers did not depend on the amount of Si removed, nor did the interface roughness: an rms value of 0.3 nm, obtained by fitting Cu-Kα_1 reflectance curves, was observed in all cases.

Summarizing, no difference was found in interface roughness for the different polishing conditions, but a clear effect on the thickness and composition of the interlayers was observed, explaining the lower reflectance of multilayers polished with 2000 eV Kr^+-ions, as compared to the 300 eV case.

A more detailed analysis of the formation of silicides at the interfaces is given by Nedelcu et al. in ref [80] where X-ray diffraction measurements on annealed Mo/Si multilayers with different ratios of the Mo layer thickness to the multilayer period (Γ) were used to determine the silicide formation and composition. Nedelcu et al. found that at temperatures above 350-400 °C the type of silicide formed is based on the minimization of the total free energy of the system. In general the Gibbs free energy is increasing with increasing amount of Si in the silicide, in the sequence Mo_3Si, Mo_5Si_3, $MoSi_2$. However in the multilayer structures the availability of different materials starts to play a significant role, with Γ being the determining factor. At lower temperatures formation of the silicides is limited by kinetics and therefore determined by the local availability of material at the interfaces and the activation energy of silicide formation. Unfortunately the latter is strongly dependent on the morphology of the layers and is not readily available in literature.

Finally, ion treatment of both the silicon and the molybdenum layers was tested in Ref. [16], resulting in a normal incidence reflectance of 66%. The lower value compared to the case where only Si was polished is caused by an increase of the interface roughness when Mo is treated with ions. This is caused by the polycrystalline nature of Mo [81] resulting in preferential sputtering.

Based on the parameters determined in the research mentioned above, Mo/Si multilayers are now routinely produced by electron beam evaporation and low energy ion smoothing. The reflectivity of 69.5% for λ = 13.5 nm, measured at 1.5° off normal is shown in Fig. 2.11 and has been measured at the radiometry laboratory of the Physikalisch Technische Bundesanstalt using synchrotron radiation of the BESSY storage ring in Berlin, Germany [58, 83]. The roughness of the top layer of such a multilayer has been determined by Atomic Force Microscopy (AFM) to be 0.1 nm rms.

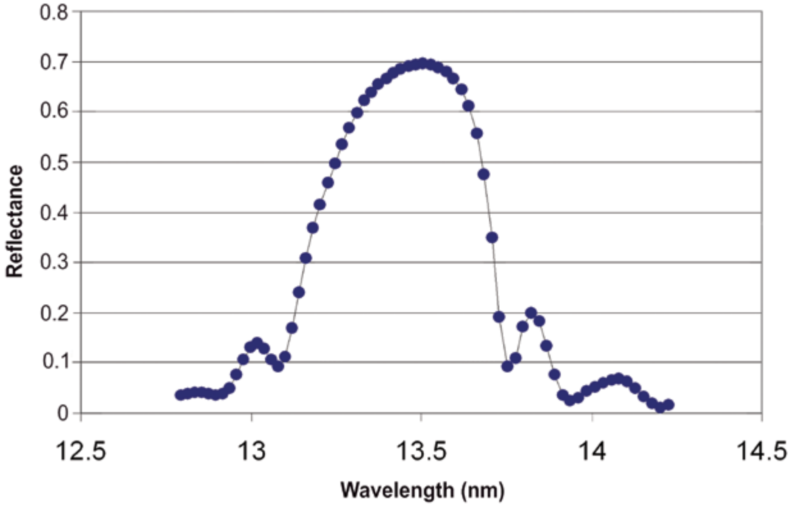


Figure 2.11: Reflectance of a Mo/Si multilayer measured at near normal incidence (1.5° off normal) [82].

This high reflectance value is obtained when the coating is applied on flat 1" diameter superpolished fused silica, Si substrates, or Si wafers. These substrates usually have an rms roughness of 0.1 nm, determined by AFM. It is noted that roughness determination by AFM can result in a different and often lower rms value than fitting Cu-Kα_1 grazing incidence reflection. This is because AFM probes only one interface, namely the surface while Cu-Kα_1 grazing incidence reflection analysis gives an average interface roughness throughout the entire multilayer stack. Furthermore, the lateral resolution of AFM is, depending on the tip used, limited to a few nm while Cu-Kα_1 measurements are also sensitive to roughness on a smaller lateral scale.

2.3.9 Deposition at cryogenic substrate temperature

An alternative way to affect roughness and interlayer formation in Mo/Si multilayer structures is to deposit films at a reduced substrate temperature. Cryogenic deposition of Mo/Si multilayer structures has been performed by different authors. Ogura [84] and Niibe [85] investigated the temperature dependence of the roughness and reflectivity of Mo/Si multilayer mirrors deposited by e-beam evaporation in the 155 to 600° C range. The mirrors were found to have a lower roughness, determined by Transmission Electron Microscopy

(TEM) and grazing incidence reflectivity for λ = 0.15406 nm radiation (GIXR) upon deposition at –155°C, as compared to room temperature deposition. This result can be explained by the fact that at a lower substrate temperature the nucleation rate is higher in the early stage of the film growth. It causes the number of nucleation centers to increase and therefore the average diameter of the islands to decrease for films of a few nm only, resulting in smoother interfaces. This mechanism is in agreement with the smoothening effect observed at significantly higher temperatures or energies of deposited particles. When the energy of the particles is high enough, the diffusion length of atoms becomes significantly larger than the interatomic distances causing the average diameter of islands to become significantly larger, but the particles also have a higher chance to descend from an existing island, thus forming a uniform flat layer.

In recent studies De Rooij-Lohmann [86] focused specifically on the effect of the cryogenic deposition on the formation of interlayer compounds. To minimize the influence of the energy of the deposition flux, electron beam evaporation was selected as the deposition method. It was determined by GIXR that the total interlayer thickness at both interfaces was reduced by approximately 60% compared to the deposition at room temperature. This effect was confirmed by annealing experiments showing larger compaction of the structures deposited at cryogenic temperature due to the initially thinner interfaces. The reduced interlayer formation obtained with cryogenic deposition was still observed after the structure was warmed up to room temperature. This can be explained by considering the interplay of kinetics and thermodynamics. Lowering the temperature during the deposition reduces the chance of atoms to overcome the activation energy barrier for displacement needed to reach a more favourable state. Diffusion of both the atoms into the layer below and the atoms of the underlying layer into the growing film is reduced, mitigating the process of interlayer formation. Once the deposition of the multilayer structure is completed, the displacement energy of the atoms located at interfaces increases significantly. Therefore, warming up to room temperature was argued to be not anymore sufficient to initiate the interdiffusion process like it occurs during film growth at room temperature. According to simulations, the observed interlayer reduction would increase the EUV reflectance of a typical state-of-the-art 50-period multilayer mirror from 69% to 71%.

2.3.10 Layer morphology

As discussed earlier, the layers of EUV and soft X-ray reflecting multilayers should ideally have an amorphous structure. This would lead to the smoothest interfaces without any risk of crystallites growing larger than the thickness of the layers. It would also result in a minimum amount of stress in the multilayers. However, it is well known that Si can grow amorphous, but metals have a general tendency to crystallize.

To study the structural and crystalline properties of the Mo/Si multilayers, Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD) using Cu-Kα_1 radiation of 0.15406 nm were performed [81]. TEM and XRD analysis both showed that Si indeed grows amorphous, while Mo clearly crystallizes. Fig. 2.12 shows a wide angle X-ray diffraction spectrum of a standard high reflection Mo/Si multilayer. The Miller indices for Mo diffracting planes are indicated and the diffraction peaks can easily be identified to originate from Mo. Also shown are the calculated diffracted intensities for randomly oriented Mo crystallites [87]. Good agreement is found, suggesting that there is no preferred crystallite orientation, which was confirmed by electron diffraction. The absence of a preferred crystallite orientation can be explained by the low kinetic energy of the deposited particles and, to some extent, rotation of the substrate during the deposition and the ion polishing. The shifts in the diffraction peak positions observed in Fig. 2.12 indicate the presence of bi-axial internal

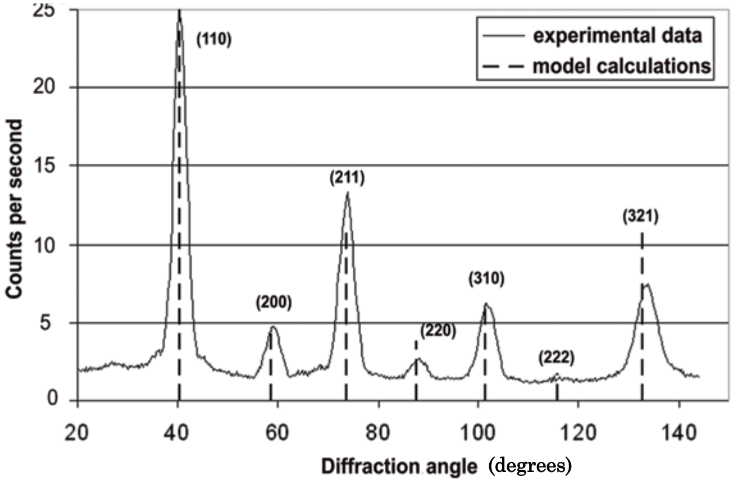


Figure 2.12: Wide angle X-ray diffraction pattern from a high reflection Mo/Si multilayer. Dashed lines show calculated integrated diffracted intensities for randomly oriented polycrystalline Mo [81].

film strains [88]. By comparing the Mo lattice strains derived from XRD with changes in substrate curvatures, as determined by interferometry, it can be shown that compressive and tensile substrate deformations are predominantly caused by the internal crystallite strains since these were found to be directly related to the macroscopic multilayer stress [81].

Extensive XRD analysis of a series of multilayers with increasing Mo layer thickness has shown that the crystallite size in the layer growth direction is limited to the as-deposited Mo layer thickness and does therefore not contribute to interface roughness. However, if ion polishing is applied to the Mo layers, the presence of these crystallites can, because of differences in sputter yield for various orientations, lead to enhanced interface roughness and this might be one of the reasons why ion polishing of Mo does not lead to better multilayer performance [73]. A more detailed description of the XRD analysis can be found in van de Kruijs et al. [81].

2.3.11 Multilayer induced stress

When a layer is deposited on another material, being a substrate or another constituent layer of a multilayer system, the first part of that layer is forced to grow with the atoms on another average interatomic distance than in bulk material. This misfit inevitably leads to shear strain in the layer. Since the layers in EUV reflective coatings have a thickness of a few nanometers, corresponding to only a few tens of atomic layers, they are too thin to relax to the bulk stress level and a huge stress, usually in the GPa range, can easily be built up in the thin layers. This can be dramatic for the optics performance. Even stress levels of an order of magnitude smaller value can already lead to a deformation of the mirror surface of a few nanometers, which is intolerable in the short-wavelength imaging process. The challenge is therefore to significantly reduce the film stress or to apply ways to compensate for it.

The development of stress in a thin film or a multilayer can be measured for instance by monitoring the change of curvature of a thin substrate or the displacement of a spring-cantilever substrate system. Both can be used in situ to monitor the stress development during layer growth. Stoney's equation [89-91] then allows calculating the film stress from the measured change of curvature of a monitor substrate. The equation contains the thickness of the film and the substrate as well as the elastic properties of the substrate. Assuming the film

to be thin with respect to the total film-substrate thickness, this thus allows to calculate the film stress without knowing the elastic properties of this film itself. In multilayered films two types of stress can occur: compressive stress, which corresponds to the situation where the reflecting surface becomes more concave, and tensile stress, which results in a more convex reflecting surface.
In standard Mo/Si multilayer systems, the stress in a full stack multilayer remains below the GPa range. The reason for this is that the stress in the two materials usually have opposite signs and partly cancel. These effects are described by Freitag et al. [92] who measured the stress development during deposition of a multilayer by magnetron sputtering. For this deposition technique stress values between –350 and –450 MPa for full stack Mo/Si multilayers have been reported by several authors [92-96]. The stress in Mo/Si multilayers deposited by electron beam evaporation and low energy ion smoothing is less than –200 MPa [97]. Although e-beam deposition apparently halves the typical stress values of sputter deposited multilayers, it is still above the allowable limit for EUV lithographic systems.
In order to reduce Mo/Si multilayer film stress to an acceptable level, several schemes can be applied. First of all the parameters in the deposition process can be optimized for minimum film stress. Deposition techniques however, do not have enough process latitude to obtain a sufficiently different layer composition to expect stress optimization, at least not under the boundary condition of minimal loss of reflectance. The additional use of ions during or after the deposition allows more freedom: different layers can be treated (e.g. Mo, Si, or both) with separate polishing conditions, resulting in different layer smoothening and densification, and therefore in a different stress value.

Another option to tune the film stress is a change of the Mo fraction (Γ) in the coating. Freitag [92] found that the stress development in the Mo and Si layers is partly counterbalanced. By selecting Γ the net stress value can be tuned. One can also introduce new materials in thin layers in between the Mo and Si layers. For instance, Shiraishi et al. [98] replaced each Mo layer by a sandwich of Mo/Ru/Mo to reduce the stress, but at the expense of reduced EUV reflectance. Other multilayer properties may change as well.

Another method to reduce the overall stress is to introduce a single or multilayer film with opposite stress underneath the high reflectance multilayer. The challenge in this method, first proposed by Mirkarimi et al. [94, 95], is to achieve the same low surface roughness on top of the stress compensation layer as on the initial superpolished substrate. Based on this, Zoethout et al.

[97] further developed a stress compensated multilayer system without any reduction of the normal incidence reflectance. Fig. 2.13 gives an overview of the stress values in Mo/Si multilayers with different Mo-fractions for e-beam deposition and magnetron sputter deposition. The black circles represent e-beam deposited multilayers consisting of 50 periods Mo/Si with a d-spacing of 7 nm and ion treatment of the Si layers only. Stress values were found to increase nearly linear with increasing Γ. The zero stress cross-over occurs for a Γ of about 0.5. This value divides the Γ range into two parts: the lower values result in compressive stress while the higher values show tensile stress. Also shown in Fig. 2.13 are the results reported for magnetron sputtering [93-95]: the crossover is now at a Γ between 0.65 and 0.7. The most notable difference between e-beam and magnetron sputter deposition is the constant off-set of the overall linear dependency of stress with Γ.

A possible explanation for the observed shift between e-beam and magnetron sputter deposited multilayers can be found in results from a separate experiment. When in the e-beam deposition case, not only the Si, but also the Mo layers are treated with ions, the overall stress increases to –550 MPa for Γ = 0.32, a value which fits remarkable well on the curve for magnetron sputtered depositions. Apparently, conditions can be found where the ion treatment of the Mo and Si mimics the growth of magnetron sputtering. The polishing seems to provide the Mo layer with sufficient energy to reconstruct to a similar com-

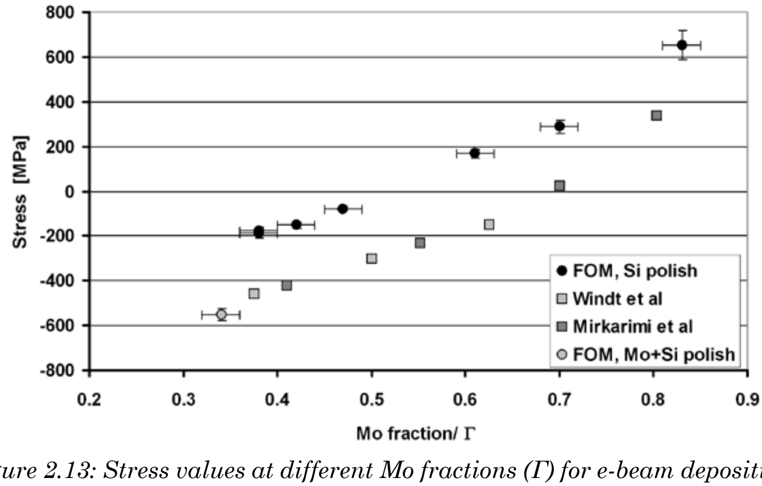


Figure 2.13: Stress values at different Mo fractions (Γ) for e-beam deposition by FOM [97] and magnetron sputtering by Windt et al. [93] and by Mirkarimi et al.[94, 95]. The black circles have been produced with e-beam and ion treatment of the Si layers, the squares have been produced by magnetron sputter deposition.

position (e.g. smoothness, density, crystal sizes, interlayer composition) as in magnetron-sputtering. This is evident from the fact that in magnetron sputter deposition the layers under growth are always exposed to ions and fast neutrals.

The easiest way to obtain stress free Mo/Si coatings is to use a Mo-fraction of 0.5 or 0.7 for the e-beam and magnetron sputtered coatings respectively, but in both cases this results in an intolerable drop in multilayer reflectance. In the work of Zoethout [97], a stress compensation multilayer of only 30 periods of $\Gamma = 0.7$ and 7 nm d-spacing was selected. Zoethout obtained a reflectance of 69% of 13.5 nm light at near normal incidence on a standard Mo/Si multilayer that has a stress value of –180 MPa. The stress mitigated multilayer has the same high reflectance (69%), but shows a dramatically reduced stress value of –33 MPa. The high reflectance of the stress mitigated multilayer can be achieved in spite of a slight increase of interface roughness resulting from the thicker, polycrystalline, Mo layers [17] in the 30 periods of the $\Gamma = 0.7$ part of the stack. This additional roughness is smoothened by the ion polishing in the first periods of the high reflectance top coating.
Stress compensation multilayers under the Mo/Si high reflectance coating have also been tested by other groups but resulted in a considerable loss of reflectance [99]. Applying a stress compensation multilayer with the same materials as used for the reflectance part has the practical advantage that no separate optimization of the material growth is needed. Others [98] sub-multilayered the Mo layers into a tri-layer Mo-Ru-Mo combination which resulted in a very low stress value (+15 MPa), but at the reflectance of 58% versus 59% for the Mo/Si multilayer deposited by this deposition technique: ion beam sputtering without additional ion polishing.

2.3.12 Wavelength matching

Due to its Bragg-nature, a multilayer reflector has a limited bandpass with maximum reflectance at a specific wavelength. This means that the periodicity of all multilayers used in an optical system should match that wavelength, selected from the emission spectrum of the source, along the full optical path along each of the mirrors, taking into account the angle of incidence in each mirror position. Two different cases of wavelength matching can be identified, namely lateral profile matching across the mirror surface, i.e. matching of the period of the multilayer to the angle of incidence at each position on that mirror, and matching of the multilayer periodicity of every mirror to the wavelength the system is designed for.

The lateral thickness profile obtained on a substrate is a function of the angular distribution of the particles emitted from the deposition source in relation to the distance to the substrate, the deposition process, the angular profile of the ion polishing (if applied), the deposition geometry and the curvature of the surface to be deposited. Once the profile of the coating process is stable and reproducible, different masking techniques can be applied to obtain the required profile. Demonstration of the ability to obtain a flat deposition profile has been given in Louis et al. [100] where uniform coatings are reported on 150 mm diameter substrates, both flat and concave with a radius of curvature representative for real EUV optics. For both geometries, a uniformity of the wavelength of maximum reflectance and therefore of the multilayer period was measured within ±0.05% of uniformity which means that the coating periodicity is uniform within ±4 pm. More recent work on the deposition of uniform coatings is given in Zoethout et al. [47] and in Section 2.4. of this chapter where we discuss the deposition of real optics for lithographic wafer scanners [101].
Once the appropriate thickness profile on a substrate can be obtained, care should be taken that the absolute periodicity of the coating is such that the effectively reflected wavelength matches the operational wavelength of the optical system, which is 13.5 nm in the case of EUVL. To achieve this with the same accuracy as the profile matching, in situ monitoring using soft X-rays is found to be essential, not only because it warrants the proper multilayer period, but it also provides the option to correct individual layer thickness errors by adjusting the thickness of subsequently deposited layers. In practice this is done automatically in the FOM e-beam deposition process.

2.3.13 Broadband reflecting multilayers

A way to adjust the standard Bragg multilayer bandwidth is being considered for future optical designs for lithography optics with higher numerical apertures [8, 102] and a larger variation of the angle of incidence of the light. Furthermore, the variation of the angle of incidence in each mirror point may increase beyond the angular bandwidth acceptance of a standard multilayer system. To overcome this problem, broadband reflecting multilayers might be required in future lithography optics. One promising solution is the use of non-periodic multilayer stacks to widen the reflectivity bandpass: a gradual variation of the period with the depth of the multilayer structure will provide an extended bandpass of the reflected wavelength [103].

Note that broadband mirrors are not only a solution to a wider angular variation but can also increase the integrated reflectance due to a wider spectral range. This approach was followed by van Loevezijn et al. [104] who studied the effects of layer thickness disorder. He optimised the extrema of sub-stacks to make a broadband multilayer, and gained 42% in integrated reflectance for radiation from 13 to 19 nm. Michette et al. [105] used a systematic method which allowed tuning of the optimum thickness of each layer in a depth-graded multilayer coating. Yakshin et al. [106] considered the minimization of the merit function, i.e. the root-mean-square deviation of the calculated angular reflectivity profile R(φ) from the intended broad-band reflectivity profile. The thicknesses of the deposited layers are used as a set of independent variables, and the solution of this so-called inverse problem was a set of layer thicknesses that provided a distinct minimum of the merit function. The calculated as well as the measured reflectivity profile was close to the one aimed for, since essentially also the interfacial roughness, natural interlayers, and thickness errors were taken into account (Fig. 2.14).

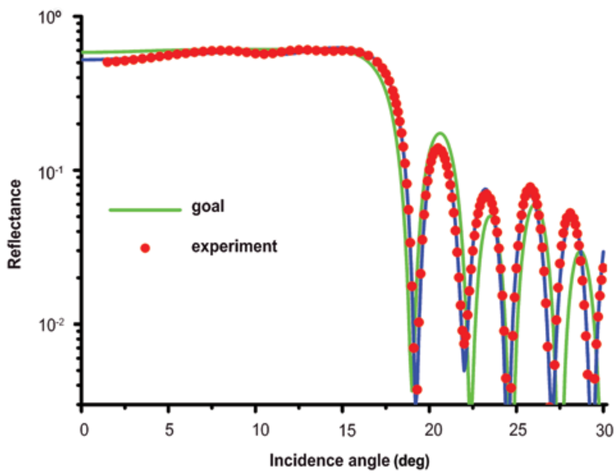


Figure 2.14: The target (green curve) and the measured (red circles) reflectivity curve versus the angle of incidence (at λ = 13.5 nm) of a Mo/Si multilayer mirror aimed to have constant reflectivity in the [0, 16°] range of incident angles. The blue curve is the result of fitting, allowing thickness fluctuations during deposition [106].

2.3.14 Interface engineering

As discussed in the previous sections, molybdenum silicide layers are formed at the interfaces in Mo/Si multilayers, reducing the optical contrast and therefore the reflectance [16]. Furthermore, diffusion results in growth of the interlayers and, since the compounded materials usually take less volume, in compaction of the multilayer. This causes the multilayer to have its maximum reflectance at slightly shorter wavelength, which in practice implies a throughput loss of the total optical system [69]. The solution for these problems can be found in modifying the naturally formed interlayer materials or their composition, a technique called interface engineering. The challenge here is to develop a diffusion barrier layer that not only creates an equal or higher optical contrast to enhance the reflectance, but also mitigates the inter-diffusion to improve the multilayer stability. As a general rule, the selection criterion for such barrier materials is a high density and high thermodynamic stability. However, critical is the combination of such properties with optimal optical properties. For instance, nitrides and oxides have a relatively high thermodynamic stability but strongly absorb EUV radiation. Carbides are generally favourable in terms of their optical properties but are inferior to nitrides and oxides for their thermodynamic stability. Pure elements can also be used, e.g. carbon, but interaction or inter-diffusion with one or both of the adjacent layers will inevitably increase the transition zone. In practice, it is also necessary to make sure that the material is able to form a continuous, smooth film with a low level of defects and, in the case of compounds, a proper stoichiometry.

Many multilayer scientists have been working on interface engineering, mostly using carbon or B_4C as diffusion barriers. If deposited as very thin films, in the order of a few tenth of a nm, both materials can enhance the reflectance of standard Mo/Si multilayers. A reflectance above 70% has been achieved by several groups: Yakshin et al. [11] achieved a value of 70.15% at 13.5 nm and Bajt et al. [108] obtained 70% at 13.5 nm, both by applying B_4C barrier layers. Braun et al. [109] used carbon as diffusion barrier and measured a reflectance of 70.1%, albeit at a shorter wavelength of 13.3 nm which naturally enhances the reflectance by 0.2%. The current reflectivity record achieved by interface engineering is 70.3% at 13.5 nm, a value obtained by Bosgra et al. by applying Y at one of the two interfaces [107] (Fig. 2.15).

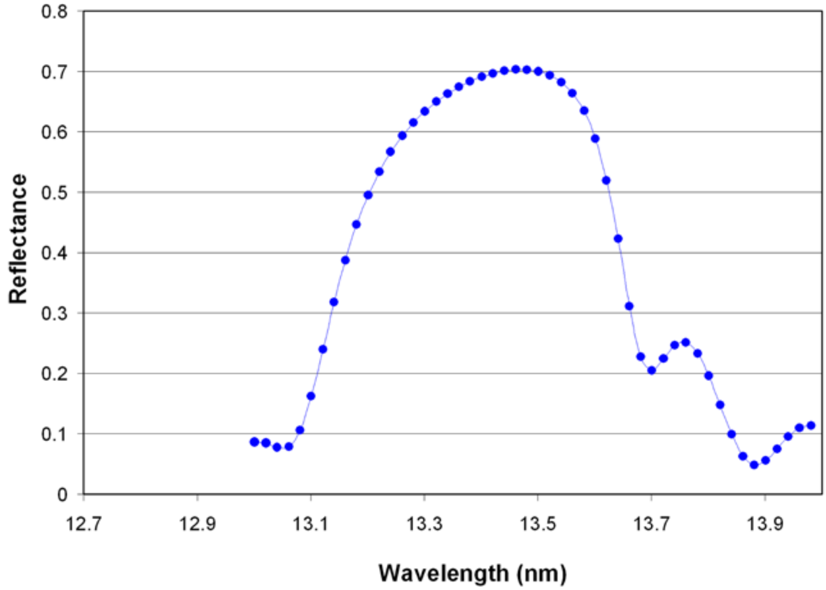


Figure 2.15: Reflectance of a Mo/Si multilayer with diffusion barriers and an Y reflectance enhancing layer. The mirror shows the current record reflectivity value of 70.3% at normal incidence of 13.5 nm [107].

Although B_4C proved to be one of the successful materials to reduce interdiffusion between Mo and Si, Yakshin et al. [11] found a different composition of the B_4C layers at the different interfaces, i.e. Mo-on-Si and Si-on-Mo. The study, based on XPS depth profiling, showed that the constituting elements, particularly carbon, diffuse out of the thin B_4C film when deposited at the Mo-on-Si interface. This asymmetrical behaviour of B_4C was observed both for e-beam evaporation and magnetron sputter deposition. The composition of the B_4C layers was also studied as a function of thickness. It is noticeable that the stoichiometry of B_4C was changing from about 6:1 for 0.5 nm films, to about 4:1 for 2 nm and thicker films when deposited at the Mo-on-Si interface. Conversely, at the Si-on-Mo interface the B:C ratio remained about 4:1 in the entire explored thicknesses range from 0.5 to 2.5 nm. To explain this asymmetry we refer to [110-112] where it was observed that the crystalline state of Mo stabilizes the interfaces of standard Mo/Si multilayer structures. In those studies, the Mo-on-Si interlayer was found to be thicker than the Si-on-Mo interlayer, provided that the Mo layer was crystalline. This was the case when the layer thickness exceeded the critical thickness for crystallization (approximately 2-3 nm) [113-115]. Therefore it is suggested here that the asymmetrical behaviour of B_4C is connected to the state of crystallization of the surface being deposited: either

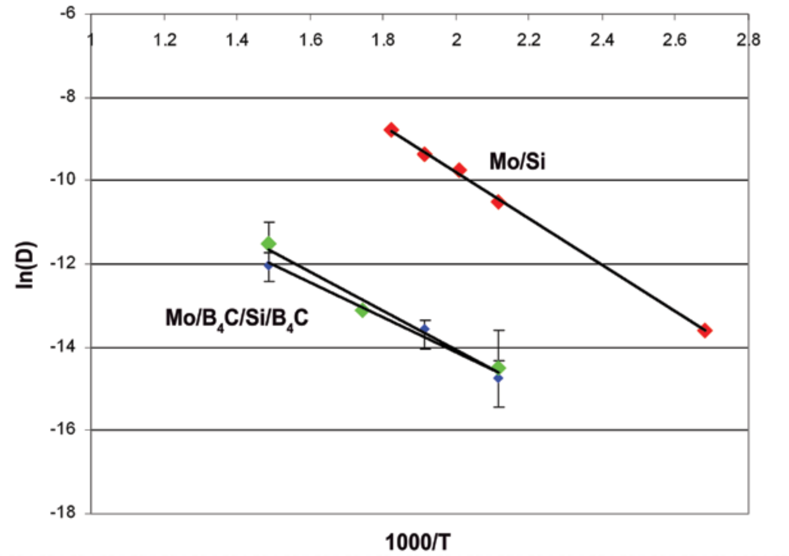


Figure 2.16: Arrhenius plot of a conventional Mo/Si multilayer and Mo/B_4C multilayer designed for higher thermal stability [83].

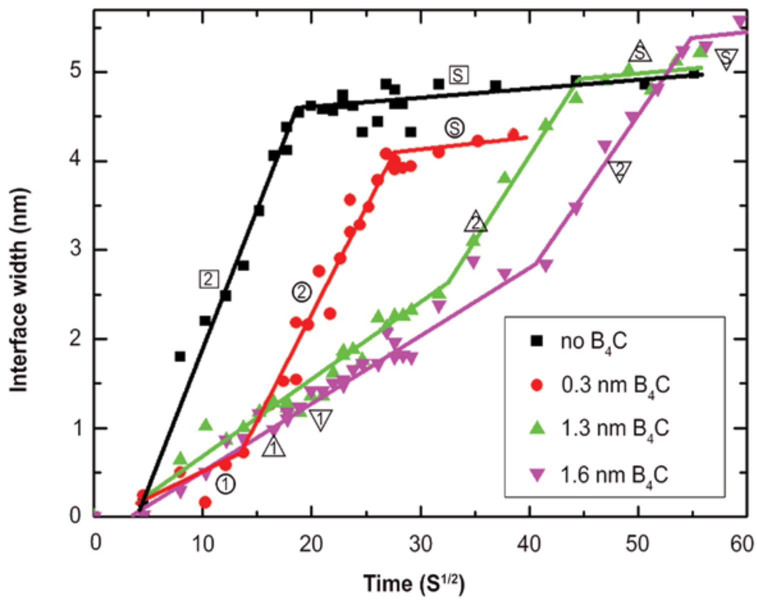


Figure 2.17: The interface width growth upon annealing at 500°C plotted as a function of time for the Mo/B_4C/Si structures having diffusion barrier layers of B_4C with 3 different thicknesses. The slope of the lines represents the diffusion coefficient, clearly showing a two stage diffusion process (indicated by the encapsulated numbers [116].

the initially amorphous Mo-on-Si interface layer or the Si-on-crystalline Mo interface after the Mo layer has undergone crystallization.
To achieve a substantial improvement of the thermal stability of the multilayers, the same barrier materials can be used as well, but the thickness has to be increased to 0.5-1 nm which will be at the expense of some reflectance. Fig. 2.16 shows an Arrhenius plot obtained for a conventional Mo/Si multilayer and a Mo/B_4C/Si/B_4C multilayer with in situ grazing incidence hard X-ray (Cu-Kα_1) reflectivity measurements during annealing. This demonstrates a significant reduction of the diffusion coefficient for the Mo/B_4C/Si/B_4C compared to the Mo/Si multilayer, which would translate to a factor of about 100 higher life time. This multilayer showed 66.7% near-normal-incidence reflectance at 13.6 nm.-

Bottger et al. [117] achieved thermal stability up to 300 ºC using B_4C but it is not clear if the very tight EUVL requirements have been used as a criterion. Nedelcu et al. [118] observed that the phase transition of the silicide interlayers into $MoSi_2$, that has been observed at 300 ºC for Mo/Si, is postponed to at least 325º due to the presence of B_4C at the interfaces. Note that De Rooij-Lohmann et al. [116] observed an enhancement of the diffusion across the B_4C interface layer in the Mo/B_4C/Si thin film structures by an order of magnitude upon annealing at 500 ºC: Fig. 2.17 shows that diffusion at that temperature occurs in two distinct stages, with the moment of transition between the stages being dependent on the B_4C interlayer thickness. The effect of the diffusion enhancement was explained by the amorphous-to-nanocrystalline phase transition inducing the atomic-scale onset of grain boundary diffusion.
Yulin et al. [119] used combinations of SiC and C barriers at the different interfaces. Their reflectivity results for thin barriers are comparable to those achieved by Louis et al. without barriers [10]. For thicker barrier layers, like 0.8 nm C at each interface, a thermal stability up to 500 ºC has been achieved while the EUV reflectance was still 60%. Another approach to stabilize the multilayers by SiC was followed by Alink et al. [120] who used implantation of low energy CH_x^+ ions, as a route to produce the SiC layers. Other very stable compounds that can be formed are nitrides that can for instance be made by low energy N^+ ion treatment of the layers after deposition. This technique has been used by Nedelcu et al. [69] and Bruijn et al. [121] who used Si_3N_4 barriers in their experiments to block the diffusion through the interfaces.

2.3.15 Multilayer stability and lifetime

Lithographic wafer scanners are expected to be in operation for many years and the lifetime target of the optics is set to 30.000 hours of operation. The throughput of the optical system should stay constant within narrow margins during this period. The required specification for the coatings is that the reflectance of a mirror should not reduce by more than 1-1.6 % during the lifetime of the optics [101, 122]. The specified period however is too long to allow real tests, calling for accelerated lifetime assessments. There are three major issues to be investigated: the temporal stability of the multilayer, its stability under exposure of radiation, and its top surface degradation and contamination due to photon-induced surface chemistry.

2.3.15.1 Temporal stability

The first requirement is that the Mo/Si multilayer stack is stable in time, without being exposed to EUV light. The Mo-silicide interlayers need to be sufficiently stable to prevent further diffusion of the Mo and Si, which would eventually lead to degradation of the multilayer structure. This was studied by Louis et al. [10] where the near-normal incidence reflectance of standard 50 bi-layer Mo/Si multilayers, that were stored at room temperature under atmospheric pressure, was monitored during 40 months. Only a minor reduction of the reflectance was observed that seems to stabilize after 6 months, which is a clear indication that the Mo-silicide interlayers are stable in time at room temperature and do not grow thicker due to diffusion. The result is shown in Fig. 2.18.

2.3.15.2 Stability under EUV exposure

The second issue is the behaviour of the coatings under exposure with EUV light. Since Mo/Si multilayers reflect close to 70% of the incidence radiation, the remaining 30% is lost in non-specular scattered light and absorption. The scattered intensity is only a minor fraction of this loss, absorption being the larger part. This indicates that the operating temperature of the Mo/Si coatings may increase during exposure. When used at temperatures below 25 ºC, the diffusion processes in standard high reflectance Mo/Si multilayers are sufficiently slow to enable long term use in optical systems, but at higher temperatures diffusion causes growing of the molybdenum-silicide interlayers at the expense of the Mo and Si layers.

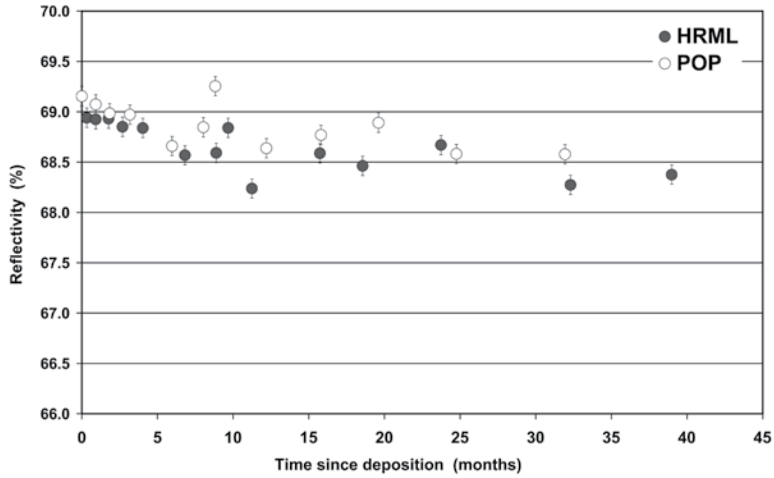


Figure 2.18: Temporal stability of the normal incidence reflectivity for λ = 13.5 nm during storage at room conditions of a standard Mo/Si system (HRML, closed circles) and a stress compensated Mo/Si multilayer (POP, open circles) [10, 82]

This has major consequences: the physical thickness of a period reduces (compaction) and the optical constants change. As a result, both the wavelength of maximum reflectance of the multilayer and the reflectance reduce. An irreversible reduction of the effective multilayer period of more than 0.5% has been observed when standard Mo/Si has been annealed at 90 °C [80, 123-125]. At higher temperatures, above 300 °C, even a phase transition of the interlayers into $MoSi_2$ occurs [69].

Another factor that affects the operating temperature is the substrate material. On substrates with high thermal conductivity, such as for instance super polished Si, the temperature will remain significantly lower than on substrates with a low thermal conductivity such as Zerodur or ULE, when exposed to the same radiation intensity.

Another phenomenon of relevance is the possible effect of an EUV standing wave in the multilayer stack: such a standing wave is the result of interference between the incoming EUV beam and the reflected one [126]. Particularly the high electric field in the antinodes of this standing wave could be harmful to the multilayer. However, experiments using extremely intense EUV radiation from the XUV Free Electron Laser FLASH (Hamburg, Germany) show that the damage, occurring above 45 mJ/cm^2, can be fully ascribed to thermal effects as described in chapter 4 [127]. It is therefore not likely that the X-ray standing wave will damage the multilayers.

2.3.15.3. *Photon-induced surface chemistry*

The most critical and also most challenging threats to the lifetime of an EUV optical system are the photon-induced phenomena happening at the multilayer-vacuum interface. In synchrotron applications, the deposition of a carbon layer [128] at the exposed spot of the optics is a well known example of radiation induced contamination.

Residual water and hydrocarbon molecules present in the vacuum can be physisorbed at the multilayer top surface. These molecules might be ionized, either by direct photo-ionization by the energetic EUV photons (92 eV), or by the photoelectrons generated in the top layer(s) of the coating. This may lead to chemisorption of carbon or oxidation of the top layer, depending on the particular local environment, like the partial hydrocarbon and water pressures, the type and nature of the molecules and their average residence time at the surface, the EUV repetition rates and the EUV flux [129-131]. The occurrence of chemical events can be enhanced if a node of the EUV standing wave coincides with the top surface of the mirror, because the large electric field will give rise to an increased amount of secondary electrons.
Carbon growth leads to a loss of reflectance, but is generally found to be reversible. Experiments using atomic hydrogen as cleaning agent have demonstrated a complete recovery of the reflectance of contaminated mirrors [132]. Furthermore, carbon growth has been observed to mitigate oxidation [133]. Oxidation of the top layer is a much more difficult process to reverse considering the extremely small thickness of the layers. Experiments have demonstrated that both effects can occur, depending on the surface and vacuum conditions [126, 134]. For instance, under oxidizing conditions at a partial water pressure of $1x10^{-6}$ mbar, 8 hours of exposure with EUV light at an intensity of 5 mW/mm^2 resulted in a drop of the normal incidence reflectance of 4%, being ascribed to oxidation [101] while other experiments show an even larger reflectance loss of 18% [135]. Such a dramatic and irreversible loss of multilayer performance would be a showstopper for the technology, justifying further systematic studies on the different mechanisms taking place at these surfaces.

2.3.15.4. *Protective capping layers*

In all cases, Si terminated Mo/Si multilayers are very vulnerable to damage of the top surface and a long lasting solution should be found in the development of a protective “capping” layer. It should not only be resistant to oxidation, but also to the cleaning method to remove carbon contamination [136, 137]. It would be even better if carbon is unlikely to grow on the capping layer material at all. Furthermore, the capping layer should be stable and should not intermix with the layer underneath, or form a very thin stable compound. Preferably, the protective capping layer should not reduce the EUV reflectance. In this respect it should be noted that a thin layer of carbon contamination on a low-Z top layer material like SiO_2, hardly affects the reflectance while on a high-Z top layer it does.

One of the first protective surfaces investigated was a C-based capping layer that had undergone a special stabilization procedure [138]. Fig. 2.19 shows the reduction of reflectance for multilayers terminated with Si, C, and the form of stabilized carbon, obtained by ion-polishing an evaporated C-film. All samples were exposed at 5-10 mW/mm^2 of EUV radiation in a vacuum dominated by a partial water pressure in the 10^{-6} mbar range. Both the Si and C terminated mirrors show a dramatic reflectance loss that is linear with exposure time whereas the stabilized C shows only a small initial reduction of reflectance in the first two hours, after which the reflectance remains constant. From Auger depth profiling a minor amount of oxidation can be observed indicating that the cap might possibly be not fully stable at the long term.

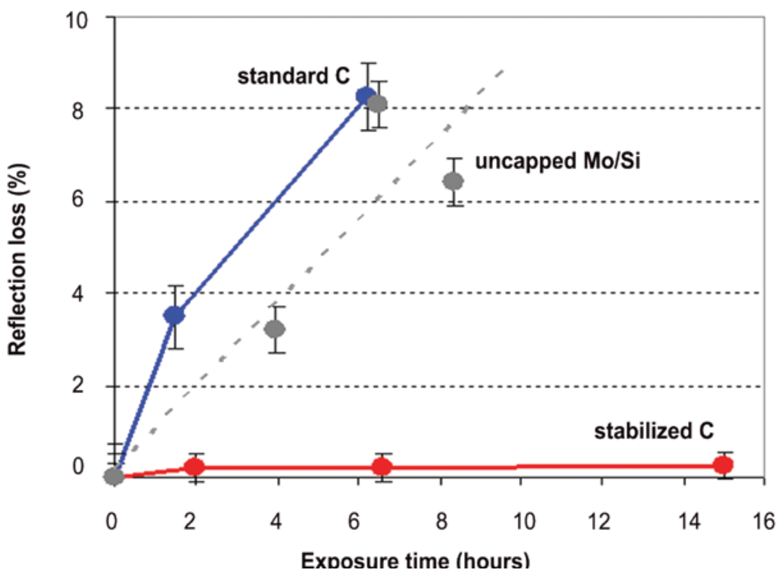


Figure 2.19: Reflection loss as function of exposure time for Si, C and stabilized C terminated multilayers [138]

Worldwide, several multilayer research groups have focused their attention on the development of oxidation resistant capping layers. An overview of the properties of capping layers that protect the top surface of the multilayers when exposed to high energy photons has been given earlier by Bajt et al. [139]. A range of studies has been performed on Ru, Rh, TiO_2 and ZrO_2 capping layers at the multilayer surface [139, 140]. Ru has been widely used by way of standard for optics lifetime studies in several development programs, since it combines a relatively high optical transparency with an adequate oxidation resistance upon exposure in a H_2O rich environment [108, 141]. The microstructure, morphology, and stability of Ru and RuO_2 under oxidizing and reducing environments have been extensively reviewed by Over et al. [142]. In essence, RuO_2 was favoured over Ru if H and O diffusion through the Ru layer would prove to be problematic for EUVL conditions. Ru, $Ru(OH)_x$ or Rh, possibly in combination with a subsurface diffusion barrier were suggested to be an alternative [143]. However, a diffusion barrier is likely to reduce the reflectance significantly, again jeopardizing the throughput of the optical system. For the case of TiO_2 and RuO_2, recent work has shown that interface-engineering limits the oxide intermixture with the Si layer underneath [140].

Capping layer catalytic properties that promote the dissociation of adsorbed background H_2O and C_xH_y are undesirable, as these result in respectively oxidation and carbon contamination of the surface. The relevance and possibly the suppression of these undesirable properties for well known catalysts like Ru or TiO_2, when used in the form of ultra-thin capping layers, remain to be demonstrated for the EUVL application [129, 144, 145]. The same holds for the surface chemistry mitigation by adjusting the partial pressures of the active background gas components [146, 147].

Application of a capping layer has implications for the theoretical reflectivity maximum. Considering the optical contrast and the standing wave generated in the multilayer stack, a Ru cap on top of a silicon terminated Mo/Si multilayer would be favourable. However, the Ru/Si interface layer is generally much thicker than the Mo/Si interface layers in the multilayer stack [17]. This reduces the reflectance as well as the protective properties. To prevent broad interface formation, a diffusion barrier layer, for instance consisting of B_4C, could be applied between the Ru and Si layer. These structures have been investigated under accelerated electron-beam as well as EUV exposure [108], suggesting lifetime improvements of up to a factor 40. This is still insufficient for EUVL and in need of further improvement. Tsarfati et al. [148]

performed in-depth analysis of thin Ru capping layers on the upper Si or Mo layer. The presence of Si and $MoSi_2$ appeared to be of more influence on Ru diffusion through the Mo layer than the effect of Mo crystallization, reported by Bajt et al. [113] and Nedelcu et al. [80]. Tsarfati reported vacancy mediated diffusion and Ru_2Si_3 formation as the main mechanisms. For the application of a B_4C layer in a range of thicknesses between the Ru and Si layers, similar observations were made [149]. The results confirm that the Si-on-Mo interface can act as a precursor for Ru silicide formation, accommodating Ru migration to minimize the energy. A way to substantially reduce interlayer formation could be nitridation of the interfaces. It proved to be successful in Mo/Si [69, 121] and La/B_4C [52, 150] multilayers. Application of Si_3N_4 in Mo/Si multilayers has also been proposed for filtering out undesired VUV spectral components from EUV light sources [151, 152].

Both the growth process, the surface oxidation, and sensitivity to carbon contamination in ambient conditions have been investigated for a range of d-metal capping layers. The noblest were indeed observed to oxidize least, but failed to limit the oxidation of Mo that was underneath the capping layer [153]. These caps were actually observed to promote the Mo oxidation in ambient conditions, compared to the case of uncapped Mo. It was argued in that work that subsurface Mo appeared to act as a sacrificial metal by means of an electron donation process to support surface oxides. Capping layers of Co and Ni were found to be completely oxidized, but these oxides appeared to be so stable and impenetrable that even single monolayers managed to largely prevent Mo oxidation. If these capping layers can indeed be very thin, this might reduce the reflectance loss to an acceptable level. Therefore, Co and Ni, although optically not very favourable, can be considered as candidate capping materials for further investigation.

Due to the high optical contrast and the presence of a standing wave, carbon contamination on d-metal based capping layers was found to dramatically affect the reflectivity. A range of dry (oxygen plasma and UV ozone) and wet (sulphuric acid with hydrogen peroxide, ozonated water, and ozonated hydrogen peroxide) carbon removal techniques have been compared for Ru. Studies show that dry cleaning does remove organic contamination, but significantly increases the oxygen concentration and surface roughness [154]. For wet cleaning, the oxygen concentration is less, but only the sulphuric acid with hydrogen peroxide technique has no noticeable effect on the surface roughness [155]. Atomic oxygen exposure (AOE) and atomic hydrogen exposure (AHE) of various caps at surface temperatures below 360 K have been investigated [156]. Based on the experiments, an AOE and subsequent AHE treatment was determined to result in clean, oxide free metal surfaces [157-159] without increasing the roughness [160].

Methods to monitor and characterize carbon growth as well as the cleaning process have been investigated by Chen et al. [63]. It was found that the type of carbon produced by EUV radiation is heavily hydrogenated, apparently including a noticeable amount of residual H-bonds from the physisorbed hydrocarbons usually present in lithography vacuum systems [161].

2.3.16 EUV reflection mask

In the all-reflective EUV imaging process, the mask, or reticle, that contains the pattern to be replicated on the resist coated wafer is multilayer-based as well. For the fabrication of reflection masks in principle two approaches could be applied. Firstly, a mask pattern could be made by local removal of the multilayer structure. However, in this case repair of opaque defects would be impossible, because of the inability to locally deposit a multilayer. The second option consists of deposition of an absorber layer on top of the multilayer structure, which is then locally removed using lithographic techniques. This last option is to be preferred because it enables repair of both clear and opaque pattern defects. The absorbing part of the mask usually consists of two layers, the actual absorber and a buffer layer in between the absorber and the multilayer. The function of this layer is to act as an etch stop for the reactive ion etching process used to etch the pattern in the absorber. Critical is that the absorber layer coating and patterning process steps should not affect the multilayer reflectance nor the periodicity. The basics of this approach, which is now standard technology, including preservation of the multilayer properties, are first described by Voorma et al. [164]. It should be noted that the lithographic printing process requires faultless and defect free multilayer structures since these multilayer defects are in the object plane of the optical system and will thus be imaged on the wafer. The fabrication of such masks imposes many additional requirements on the control and mitigation of particle production during the layer growth process, as particle inclusions are virtually beyond any repair option.

2.4 Multilayer deposition of first EUVL photolithography optics

In the previous section we described basic research on Mo/Si multilayer deposition targeting at the development of an industrially applicable process to coat large and complicated optical elements for EUVL wafer scanners. However, moving from small, near perfect laboratory samples to real, large and complex shaped optics, is a step requiring absolute control of all processes. In this section we describe some typical results on reflectance, and profile and wavelength matching of the deposition of the optical elements for two proof-of-principle EUVL exposure set-ups, the so-called Alpha Demo Tools [4] as shown in Fig. 2.20, that are operational at the College of Nanoscale Science and Engineering of the University of Albany, USA and at the Interuniversitair Micro-Elektronica Centrum (IMEC) in Leuven, Belgium. Four elements, among which two very large ones, have been coated in the new facility at Carl Zeiss SMT GmbH, the remaining six, from illuminator and projection optics, in the coating facility at FOM Rijnhuizen described in Section 2.3.4. The operating wavelength of these Alpha Demo Tools is 13.5 nm and Mo/Si was used for all multilayers that were deposited by the deposition method described in sections 2.3.4. and 2.3.8., i.e. e-beam evaporation in combination with low energy ion smoothing. Furthermore we comment on improvements obtained since the construction of the Alpha Demo Tools [48], and now implemented in the optics of the ASML NXE:3100 systems that are under construction [49].

Figure 2.20: One of the proof-of-principle EUVL-exposure set-ups: Alpha Demo Tool (courtesy ASML).

2.4.1 Reflectance

The record reflectivity for Mo/Si multilayers deposited on super polished laboratory substrates with an rms roughness better than 0.1 nm, amounts to 69.5% [10]. However, large real substrates for EUVL systems usually consist of other materials, like for instance Zerodur, and are often much more difficult to polish for two major reasons: the material is less suitable to be polished and low roughness must be achieved for all three spatial frequency domains [14]:

- The high spatial frequency roughness (HSFR), which is roughness with a typical lateral correlation length of 1 nm to 1 µm, resulting in diffuse scattered light over a large angle and therefore reducing the specular reflectance.
- The medium frequency roughness (MSFR) with correlation lengths of 1 µm up to several mm that induces near specular diffuse scatter, which reduces the image quality of the optical system. This phenomenon is usually referred to as flare and can cause blurring of the image. Depending on the reflectometer geometry, this near specular scattered light can still contribute to the measured reflectance [14, 165].
- The low frequency roughness (LSFR) or figure (shape) of the optics that determines the imaging capabilities of the system.

It is extremely difficult to fulfil the tight specifications in all three ranges of roughness. Therefore the reflectance obtained on this type of complicated substrates can be somewhat lower.

Typical lithography substrates used for the Alpha Demo Tools, have HSFR roughness values of up to ~0.3 nm. This, in combination with the use of a capping layer, results in an average reflectance of the mirrors in these optics of 65%, measured at 1.5° off normal incidence [48]. In the optical system operational angles can be considerable more off normal, which will result in an even lower reflectance, at least for unpolarised light. Taking this into account, the average reflectance in the Alpha Demo Tools is 64 % which is higher than the 63 % of the system specifications. It should be mentioned that substrate manufacturers are making significant progress in obtaining low roughness in all frequency ranges. The best values reported by Lowisch et al. [102] on real EUVL mirror substrates are well below 0.1 nm rms for all three spatial frequency ranges. Meanwhile, we improved the capping layer system resulting in a reflectance value identical to what is achievable on uncapped Mo/Si multilayers. These achievements of substrate roughness and capping layer systems have resulted in a significant increase of reflectance of the real optics for the NXE:3100 lithographic wafer scanners [49, 102], leading to a 50% improved transmission of the optical system in the newest scanners. Fig. 2.21 shows the reflectance curves of one of the first generation EUV mirrors in the Alpha Demo Tool and the strongly improved reflectance on the same type of mirror of the NXE:3100 system [48,49].

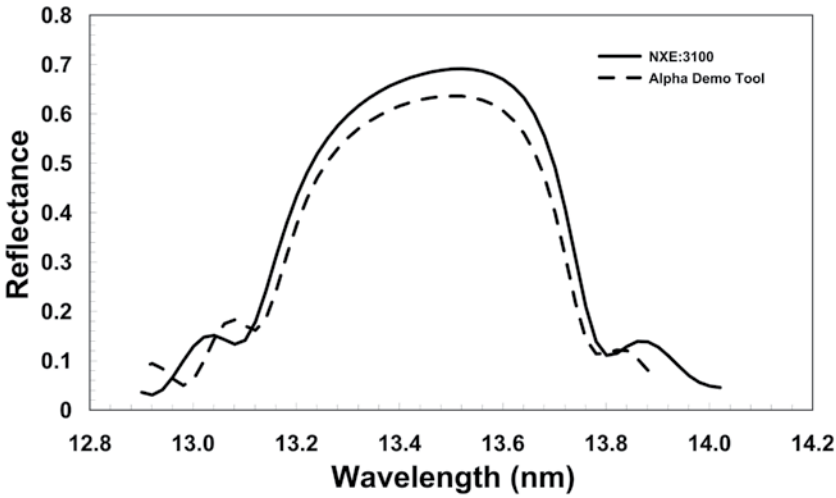


Figure 2.21: The reflectance at λ = 13.5 nm of a projection optics element of the NXE:3100 exposure or pre-production machine (black curve [49]), measured at the local angle of incidence; the dotted curve represents the reflectance of the same optic in the Alpha Demo Tool [48, 49].

2.4.2 Wavelength and profile matching

Another, actually even more crucial specification that determines the transmission as well as the imaging performance of an EUV optical system is the matching of the multilayer periodicity to the wavelength the system is designed for in every point of every mirror. This has been discussed in detail in section 2.3.12. In this section I explain how this can be realized in practise. When an optical element has to be coated, the optical design, that is the variation of the angle of incidence over the surface, is translated into a lateral profile of the required multilayer periodicity of the specific mirror. Then, test coatings on dummy substrates are carried out to deposit this profile. Once this periodicity profile can be deposited within specification, the total amount of material deposited per layer is tuned such that the wavelength that is reflected by this mirror matches the design wavelength of the optical system. To get insight in the required accuracy of the wavelength matching, let us consider a typical reflectance curve as shown in Fig. 2.21. It has a FWHM bandwidth of 0.5 nm, but this reduces to approximately 0.2 nm for a ten mirror system. For such a system it can easily be calculated that a mismatch of only 0.1 nm of the wavelength of one of the mirrors leads to a transmission loss of the optical system of 5 to 8% depending on the sign of the mismatch. If a second mirror would have a mismatch of the same magnitude, but opposite sign, the transmission loss would increase to 14%. To limit the transmission loss to an acceptable level, the tolerable mismatch of the periodicity at each point of each mirror has been set to ± 0.1 % or ± 7 pm. This periodicity is determined by EUV reflectometry at the appropriate angle of incidence. On the Alpha Demo Tool optics as well on the NXE:3100 optics this specification has been met using the in situ soft X-ray deposition monitor described in Section 2.3.4.

2.4.2.1 Illuminator optics

In the illuminator case the specification is set by the requirement that the reflectance for 13.5 nm light at each point of each mirror should not differ more than 1% in absolute units from the designed value, which can be translated into a tolerance on the periodicity profile. The tolerance depends strongly on the designed angle of incidence and its variation in each point. As an example we discuss the multilayer on a highly convex element where the local angle of incidence varies from 9° to 13.5° from the surface normal: the bandwidth of this angle in each point of the mirror is a considerable part of this. Fig. 2.22 shows the reflectance profile in the centre of this illuminator element. The points represent the measured reflectance profile for λ = 13.5 nm. The thick line is the design profile scaled to the real reflectance value. The angular dependence of the reflectance as well as the position of the maximum value is almost identical to the design profile and the coating period matches the specification within ± 0.1%. The 1% reflectance requirement on the entire optical surface of this mirror (represented by the upper and lower thin grey lines in Fig. 2.22) dictates the multilayer period to be within ± 0.1% of the design value. In ref [48] we demonstrate that the deviation of the multilayer period, calculated from normal incidence reflectance data, is within ± 0.05% of the designed profile, which is twice better than specified. A second example of an element of the illuminator is the mirror shown in Fig. 2.23. With a length of 480 mm it's one of the largest normal incidence EUV mirrors to date. It has been coated successfully in the large area EUV coating facility located in the factory of Carl Zeiss

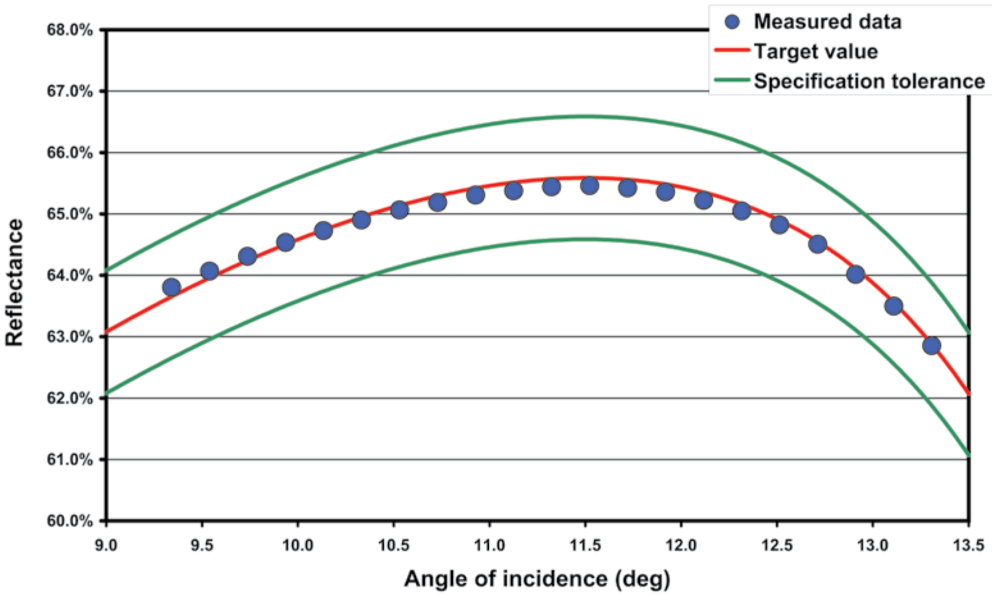


Figure 2.22: Reflectance at λ = 13.5 nm as function of the incidence angle in the centre of an illumination optic. Indicated are the measured points (dots) and the optical design values (solid line) [48].

SMT GmbH (Oberkochen, Germany) that has been designed and built based on the principles of electron beam evaporation in combination with ion beam smoothing. The multilayer periodicity on this large illuminator element has a lateral uniformity that is better than 0.2% over the entire surface, well within specification of this mirror.

2.4.2.2 Projection Optics

The task of the projection optics is to produce a demagnified image of the mask pattern on the resist coated wafer. The exposure of the resist should be uniform, which determines, like in the illuminator case, the tolerances on the lateral periodicity profile of the multilayers as well as the uniformity of the reflectance over the mirrors. In addition, the required resolution can only be achieved by using high quality reflective surfaces. This means that the accura

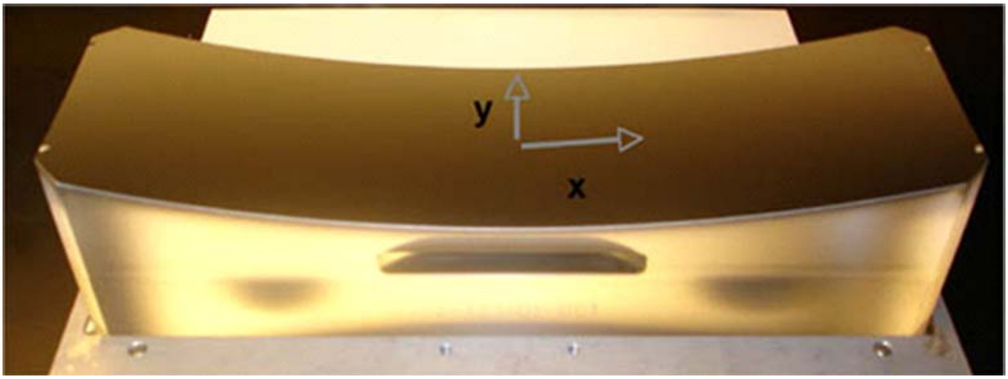


Figure 2.23: Largest element in the illuminator in the Alpha Demo Tool: 480 mm in x-direction (Photo Carl Zeiss SMT GmbH) [166].

racy of the shape or figure of the multilayer-coated optics should be in the sub nanometer regime. The surfaces that serve as substrates for the multilayers can be polished with an accuracy of this figure better than 50 pm [102] and the deposition of the multilayer should preserve this. In other words, the coating induced added figure error has to be minimized to that dimensional range, requiring an unprecedented level of accuracy in deposition technology.

There are two major effects that the coating can have on the surface figure. The first effect is the coating induced stress, which will result in an unacceptable mirror deformation if it exceeds a tensile or a compressive value of 100 MPa. However, the value of multilayer induced stress can be reduced to typically –30 MPa by using stress mitigation techniques of the kind as described in Section 2.3.11. The second effect is the figure error that the coating itself might add to the substrate. The coating has a total thickness of almost 0.5 µm, which by itself will change the radius of curvature, thus the surface figure. This change in figure can be accounted for when polishing the substrate, but in practise the coating profile is not perfect and there will be a low frequency or a long range as well as a high frequency or short-range deviation of the ideal coating thickness. The low frequency variations can, to a certain extent, be compensated by alignment of the mirror, like relative height and tilt of the mirror plane, through the lower order Zernike polynomial corrections. The remaining short-range deviations of the ideal profile add up in the residue and form the so-called non-correctable added figure error, which should be below 100 pm.

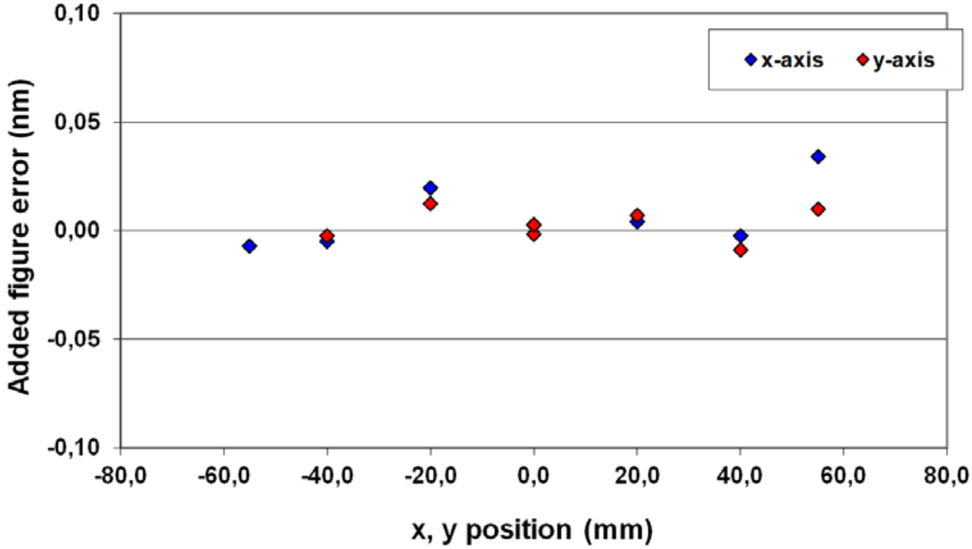


Figure 2.24: Non correctable added figure error determined in two perpendicular directions. The rms value amounts to 15 pm [48].

The change in figure due to the multilayer is difficult to measure. Ideally one would use interferometry before and after coating, but this is very laborious and thus unpractical in a process of successive depositions to optimize the coating thickness. A very reliable alternative is to calculate the total film thickness from the multilayer periodicity obtained from the EUV reflectance data, measured at various positions of the surface. The total film thickness can be compared to designed profile, taking into account the possible corrections by alignment of the mirror. From the difference the non-correctable added figure error can be calculated. An example of the distribution of this figure error is shown in Figure 2.24 and amounts to an rms value of 15 picometer only, which is seven times better than specified [48]. This result has been reproduced on multilayers for the NXE:3100 tools presently being manufactured [49].

2.5 Spin off to other applications

Apart from the direct application for EUV lithography, basically all areas of XUV and X-ray science and technology that need reflectors, spectral filters, phase retarders, beam splitters, beam shaping elements, or other optical elements, can benefit from the know-how obtained in recent research on multilayer optics.
The observed smoothing of Si-layers, for instance, can also be used to smoothen optical surfaces of mirror or lens substrates. Van den Boogaard [165] studied the ion-smoothing mechanism in more detail and applied repetitive deposition and ion polishing of silicon on substrates, demonstrating significant reduction of the roughness. When using this method for polishing mirror substrates he found EUV reflectivity gains of typically 8%.

Another spin-off example is the use of multilayers in diagnostic equipment, such as analyzers that select specific X-ray Fluorescence (XRF) radiation from X-ray excited samples, thereby allowing to identify and quantify the elements contained in the samples. Multilayers as investigated by Shimizu et al. [167], for instance, can be used in those cases where the wavelength is too long to use natural crystals as analyzers. Another direct spin-off from EUV multilayer research is the use of multilayer based detectors to measure and calibrate the yield of EUV plasma sources, a development developed by Stuik et al. [163, 168]. He used a focusing Mo/Si mirror and a calibrated semiconductor detector to compare and quantify the EUV yield of various EUV light sources developed worldwide [169-171]. In the years following that work, the usage of this diagnostic concept was continued by several groups [169].

A possible next step to enhance the resolution in lithographic systems is to apply an even shorter wavelength than the 13.5 nm used in current EUVL schemes. This requires a change of the materials in the multilayers, since silicon is highly absorbing below the L-absorption edge at 12.4 nm. The next spacer material to be used is boron, having an absorption edge at $\lambda = 6.6$ nm, or a boron-rich material like B_4C, suitable for lithography at 6.7 nm wavelength. For other applications than lithography, André et al. [172] and Ricardo et al. [173] worked on La/B_4C multilayer optics with a periodicity of ~10 nm for $\lambda = 6.7$ nm at relatively grazing (~24.5°) angle of incidence. Because of the relative thick layers, intermixing and interlayer formation at the reactive La/B_4C interfaces is not of significant influence in this case and reflectivities of 53% have been reported [174]. Going towards optics with a periodicity of ~3.4 nm, required when used at more normal angles (~25°), Andreev et al. [175] proposed the use of Cr, Mo, or Sn barrier layers and reflectivities of 44% at 74.4° or 40% at 80.5° were obtained, using interface engineering procedures. Currently, optics for applications such as photolithography, or X-ray free electron lasers that operate at shorter wavelengths then 13 nm, still suffer from the interface imperfections in the layered systems. Such optics require improvement of the reflectivity maximum and bandwidth, much along the research lines as described in this publication, albeit with new materials and new approaches. For instance Tsarfati et al. have investigated the kinetic and optical properties of related compounds, and have demonstrated that interfaces can be chemically passivated by using surface nitridation. This made them inactive to LaB_6 and LaC_2 interlayer formation and simultaneously resulted in an increased optical contrast [52, 150]. In effect, the reflectivity maximum and bandwidth in experimental multilayer optics has been considerably enhanced, with a current maximum value of 41.5% at 88.5° incidence, but there is still much room for further improvement.

Another field that has applied multilayer mirrors is the research on X-ray lasers. For instance, Ellwi et al. [176] were able to demonstrate X-ray lasing in a capillary discharge at a wavelength of 18.22 nm by using a Mo/Si multilayer mirror to isolate the lasing radiation from incoherent background. Others have used multilayers in their experiments at X-ray free electron lasers, such as in micro-focusing [177, 178] or holographic imaging [179]. Lately, there is a growing interest in the X-ray free electron laser community to make use of multilayers as beam line optics or in experimental user set ups. In many cases such experiments have taken, and will continue to take advantage of the multilayer know-how developed for Extreme UV lithography.

SUMMARY

The fabrication of multilayer reflective coatings for the demanding technique of Extreme UV photolithography has constituted a particular challenge for thin film deposition technologies, justifying new fundamental physics research. This research has well responded to the lithography demand, with verified solutions becoming available, according to a schedule which is synchronized with the industrial lithography roadmap. Examples of multilayer reflectors on illuminator and projection optics for first generations of EUVL systems clearly show that the tight specifications for EUV multilayer coatings can be well met, bringing commercial high volume manufacturing (HVM) equipment well within reach. In return, the concerted EUV lithography effort has significantly increased the general understanding of multilayer thin film physics, leading to the unravelling of a number of elementary processes involved. Many thin film deposition technologies were refined to deliver multilayered systems with atomic scale growth control over large, up to 0.5 m diameter, surface areas. The use of sub-nanometer thick diffusion barriers and contrast enhancing layers has resulted in high thermal and temporal stability and reflectivities that have exceeded 70%, less then few percent from the theoretical maximum values. These results have opened up new applications in science, as for instance the use of such optics in the newest generation of XUV light sources, like free electron lasers and high-brightness synchrotron sources for a collection of XUV optical applications.

ACKNOWLEDGEMENTS

The work described in this chapter is part of the programs EX2 and Solv'X made possible by the Technology Foundation (STW), and of the FOM Industrial Partnership Programmes I10 ('XMO') and I23 ('CP3E') which are carried out under contract with Carl Zeiss SMT GmbH, Oberkochen, ASML, Veldhoven, and the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', the latter being financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)'. Furthermore, part of the work is carried out in the EXEPT research programme by AgentschapNL, and the Thin Film Nanomanufacturing (TFN) programme of the Dutch Technology Foundation STW. Results are obtained in the frame of a collaboration programme with ASML (Veldhoven), Carl Zeiss SMT GmbH (Oberkochen), Philips Research (Eindhoven), the Physikalisch Technische Bundesanstalt PTB (Berlin), and TNO-TPD (Delft).

REFERENCES CHAPTER 2

[1] P.J. Silverman, Extreme ultraviolet lithography: overview and development status, Journal of Microlithography Microfabrication and Microsystems, 4 (2005).

[2] V. Bakshi, EUV Lithography, SPIE Press Book, 2008.

[3] J. Benschop, V. Banine, S. Lok, E. Loopstra, Extreme ultraviolet lithography: Status and prospects, Journal of Vacuum Science & Technology B, 26 (2008) 2204-2207.

[4] H. Meiling, H. Meijer, V.Y. Banine, R. Moors, R. Groeneveld, H.J. Voorma, U. Mickan, B. Wolschrijn, B. Mertens, G. van Baars, P. Kurz, N. Harned, First performance results of the ASML alpha demo tool, in: SPIE 6151, 2006, pp. 615108.

[5] N. Harned, M. Goethals, R. Groeneveld, P. Kuerz, M. Lowisch, H. Meijer, H. Meiling, K. Ronse, J. Ryan, M. Tittnich, H.J. Voorma, J. Zimmerman, U. Mickan, S. Lok, EUV lithography with the Alpha Demo Tools: status and challenges, in: SPIE 6517, 2007, pp. 651706.

[6] J.V. Hermans, E. Hendrickx, D. Laidler, C. Jehoul, D. van den Heuvel, A.-M. Goethals, Performance of the ASML EUV Alpha Demo Tool in: SPIE 7636, 2010, pp. 76361L.

[7] O. Wood, C. Koay, K. Petrillo, H. Mizuno, S. Raghunathan, J. Arnold, D. Horak, M. Burkhardt, G. McIntyre, Y. Deng, B. La Fontaine, U. Okoroanyanwu, T. Wallow, G. Landie, T. Standaert, S. Burns, C. Waskiewicz, H. Kawasaki, J. Chen, M. Colburn, B. Haran, S. Fan, Y. Yin, C. Holfeld, J. Techel, J. Peters, S. Bouten, B. Lee, B. Pierson, B. Kessels, R. Routh, K. Cummings, EUV Lithography at the 22-nm technology node, in: SPIE 7636, 2010, pp. 76361M.

[8] C. Wagner, J. Bacelar, N. Harned, E. Loopstra, S. Hendriks, I. de Jong, P. Kuerz, L. Levasier, M. van de Kerkhof, M. Lowisch, H. Meiling, D. Ockwell, R. Peeters, E. van Setten, J. Stoeldraijer, S. Young, J. Zimmerman, R. Kool, EUV lithography at chipmakers has started: performance validation of ASML's NXE:3100, in: SPIE 7969, 2011, pp. 79691F.

[9] C. Wagner, N. Harned, P. Kuerz, M. Lowisch, H. Meiling, D. Ockwell, R. Peeters, K. van Ingen-Schenau, E. van Setten, J. Stoeldraijer, B. Theuring, EUV into production with ASML's NXE platform, in: SPIE 7636, 2010, pp. 76361H.

[10] E. Louis, A.E. Yakshin, P.C. Görts, S. Oestreich, R. Stuik, M.J.H. Kessels, E.L.G. Maas, F. Bijkerk, M. Haidl, S. Muellender, M. Mertin, D. Schmitz, F. Scholze, G. Ulm, Progress in Mo/Si multilayer coating technology for EUVL optics, in: SPIE 3997, 2000, pp. 406-411.

[11] A.E. Yakshin, R.W.E. van de Kruijs, I. Nedelcu, E. Zoethout, E. Louis, F. Bijkerk, H. Enkisch, S. Muellender, Enhanced reflectance of interface engineered Mo/Si multilayers produced by thermal particle deposition, in: SPIE 6517, 2007, pp. 65170I.

[12] C. Kittel, Introduction to Solid State Physics, John Wiley & Sons, 1971.

[13] E. Hecht, Optics, Addison Wesley, 2002.

[14] E. Spiller, Soft X-ray optics, SPIE - The International Society for Optical Engineering, Bellingham, USA, 1994.

[15] D. Attwood, Soft X-Rays and Extreme Ultraviolet Radiation, Cambridge University Press, 2000.

[16] A.E. Yakshin, E. Louis, P.C. Görts, E.L.G. Maas, F. Bijkerk, Determination of the layered structure in Mo/Si multilayers by grazing incidence x-ray reflectivity, Physica B - Condensed Matter, 283 (2000) 143-148.

[17] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin, F.D. Tichelaar, E. Zoethout, E. Louis, H. Enkisch, S. Muellender, F. Bijkerk, Interface roughness in Mo/Si multilayers, Thin Solid Films, 515 (2006) 434-438.

[18] www-cxro.lbl.gov.

[19] D.G. Stearns, R.S. Rosen, S.P. Vernon, High-performance multilayer mirrors for soft x-ray projection lithography, in: SPIE 1547, 1991, pp. 2-13.

[20] P.Y. Yan, E. Spiller, P. Mirkarimi, Characterization of ruthenium thin films as capping layer for extreme ultraviolet lithography mask blanks, Journal of Vacuum Science & Technology B, 25 (2007) 1859-1866.

[21] P. Scherrer, Nachricht Gottinger Gesell, 98 (1918).

[22] R. Stuik, E. Louis, A.E. Yakshin, P.C. Gorts, E.L.G. Maas, F. Bijkerk, D. Schmitz, F. Scholze, G. Ulm, M. Haidl, Peak and Integrated reflectivity, wavelength and gamma optimization of Mo/Si, and Mo/Be multilayer, multielement optics for extreme ultraviolet lithography, Journal of Vacuum Science & Technology B, 17 (1999) 2998-3002.

[23] D.L. Windt, IMD - Software for modelling the optical properties of multilayer films, Computers in Physics, 12 (1998) 360-370.

[24] http://henke.lbl.gov/optical_constants/multi2.html

[25] F.C. Frank, J.H. van der Merwe, Proc. R. Soc. Lond. Ser. A, 198 (1949).

[26] I.N. Stranski, L. Krastanov, Sitzungsber. Akad. Wiss. Wien, 146 (1938) 797-810.

[27] M. Ohring, Material Science of Thin Films, Deposition and Structure, 2nd ed., Academic Press, 2002.

[28] R.L. Schwoebel, E.J. Shipsey, Step motion on crystal Surfaces, Journal of Applied Physics, 37 (1966).

[29] E. Spiller, A. Segmüller, J. Rife, R.P. Haelbich, Controlled fabrication of multilayer soft x-ray mirrors, Applied Physics Letters, 37 (1980) 1048.

[30] T.W. Barbee, Multilayers for X-ray Optics, Opt. Eng. , 25 (1986) 893-915.

[31] E. Spiller, S.L. Baker, P.B. Mirkarimi, V. Sperry, E.M. Gullikson, D.G. Stearns, High-performance Mo-Si multilayer coatings for extreme-ultraviolet lithography by ion-beam deposition, Appl. Optics, 42 (2003) 4049-4058.

[32] S.V. Gaponov, F.V. Garin, S.L. Gusev, A.V. Kochemasov, Y.Y. Platonov, N.N. Salashchenko, Multilayer mirrors for soft x-ray and VUV radiation, Nuclear Instruments & Methods in Physics Research, B., 208 (1983) 227-231.

[33] M.P. Bruijn, J. Verhoeven, E.J. Puik, M.J. van der Wiel, Multilayer x-ray mirrors: the state of the art, in: SPIE 984, 1988, pp. 54-63.

[34] J. George, Preparation of thin films, Marcel Dekker Inc., 1992.

[35] S. Braun, R. Dietsch, M. Haidl, T. Holz, H. Mai, S. Muellender, R. Scholz, Mo/Si-multilayers for EUV applications prepared by Pulsed Laser Deposition (PLD), Microelectronic Engineering,

57-8 (2001) 9-15.

[36] L.M. Doeswijk, G. Rijnders, D.H.A. Blank, Pulsed laser deposition: metal versus oxide ablation, Appl. Phys. A-Mater. Sci. Process., 78 (2004) 263-268.

[37] G. Rijnders, D.H.A. Blank, Materials science - Build your own superlattice, Nature, 433 (2005) 369-370.

[38] R.V. Randive, A. Ma, P.A. Kearney, D. Krick, I. Reiss, P.B. Mirkarimi, E. Spiller, Progress in the fabrication of low-defect density mask blanks for extreme ultraviolet lithography, Journal of Microlithography Microfabrication and Microsystems, 5 (2006) doi:10.1117/1111.2198853.

[39] P.B. Mirkarimi, E. Spiller, S.L. Baker, V. Sperry, D.G. Stearns, E.M. Gullikson, Developing a viable multilayer coating process for extreme ultraviolet lithography reticles, Journal of Microlithography Microfabrication and Microsystems, 3 (2004) 139-145.

[40] P.A. Kearney, C.E. Moore, S.I. Tan, S.P. Vernon, R.A. Levesque, Mask blanks for extreme ultraviolet lithography: Ion beam sputter deposition of low defect density Mo/Si multilayers, Journal of Vacuum Science & Technology B, 15 (1997) 2452-2454.

[41] T. Liang, E. Ultanir, G. Zhang, S.J. Park, E. Anderson, E. Gullikson, P. Naulleau, F. Salmassi, P. Mirkarimi, E. Spiller, S. Baker, Growth and printability of multilayer phase defects on extreme ultraviolet mask blanks, Journal of Vacuum Science & Technology B, 25 (2007) 2098-2103.

[42] K. Hiruma, S. Miyagaki, H. Yanianashi, Y. Tanaka, I. Nishiyama, Performance and quality analysis of Mo-Si multilayers formed by ion-beam and magnetron sputtering for extreme ultraviolet lithography, Thin Solid Films, 516 (2008) 2050-2057.

[43] P.B. Mirkarimi, E. Spiller, S.L. Baker, D.G. Stearns, J.C. Robinson, D.L. Olynick, F. Salmassi, J.A. Liddle, T. Liang, A.R. Stivers, A silicon-based, sequential coat-and-etch process to fabricate nearly perfect substrate surfaces, Journal of Nanoscience and Nanotechnology, 6 (2006) 28-35.

[44] P.B. Mirkarimi, E.A. Spiller, D.G. Stearns, V. Sperry, S.L. Baker, An ion-assisted Mo-Si deposition process for planarizing reticle substrates for extreme ultraviolet lithography, IEEE Journal of Quantum Electronics, 37 (2001) 1514-1516.

[45] R. Soufli, E.A. Spiller, M.A. Schmidt, C. Davidson, R.F. Grabner, E.M. Gullikson, B.B. Kaufmann, S. Mrowka, S.L. Baker, H.N. Chapman, R.M. Hudyma, J.S. Taylor, C.C. Walton, C. Montcalm, J.A. Folta, Multilayer optics for an extreme-ultraviolet lithography tool with 70-nm resolution, in: SPIE 4343, 2001, pp. 51-59.

[46] R. Soufli, R.M. Hudyma, E. Spiller, E.M. Gullikson, M.A. Schmidt, J.C. Robinson, S.L. Baker, C.C. Walton, J.S. Taylor, Sub-diffraction-limited multilayer coatings for the 0.3 numerical aperture micro-exposure tool for extreme ultraviolet lithography, Appl. Optics, 46 (2007) 3736-3746.

[47] E. Zoethout, P. Suter, R.W.E. van de Kruijs, A.E. Yakshin, E. Louis, F. Bijkerk, H. Enkisch, S. Muellender, Subatomic Accuracy in EUVL Multilayer Coatings, in: SPIE 5374, 2004, pp. 892-896.

[48] E. Louis, E. Zoethout, R.W.E. van de Kruijs, I. Nedelcu, A.E. Yakshin, S. Alonso van der Westen, T. Tsarfati, F. Bijkerk, H. Enkisch, S. Muellender, Multilayer coatings for the EUVL process

development tool, in: SPIE 5751, 2005, pp. 1170-1177.

[49] E. Louis, E.D. Van Hattum, S. Alonso van der Westen, P. Sallé, K.T. Grootkarzijn, E. Zoethout, F. Bijkerk, G. von Blanckenhagen, S. Muellender, High reflectance multilayers for EUVL HVM-projection optics, in: SPIE 7636, 2010, pp. 76362T.

[50] F. Eriksson, D.L. Windt, Growth, structure, and performance of new x-ray multilayers, in: SPIE 5900, 2005.

[51] E. Louis, H.J. Voorma, N.B. Koster, L. Shmaenok, F. Bijkerk, R. Schlatmann, J. Verhoeven, Y.Y. Platonov, G.E. van Dorssen, H.A. Padmore, Enhancement of reflectivity of multilayer mirrors for soft x-ray projection lithography by temperature optimization and ion bombardment, in: Microelectronic Engineering, 1994, pp. 215-218.

[52] T. Tsarfati, E. Zoethout, R.W.E. van de Kruijs, F. Bijkerk, Nitridation and contrast of B_4C/La interfaces and multilayers, Thin Solid Films, 518 (2010) 7249-7252.

[53] V.I.T.A. de Rooij-Lohmann, A.W. Kleyn, F. Bijkerk, H.H. Brongersma, A.E. Yakshin, Diffusion and interaction studied nondestructively and in real-time with depth-resolved low energy ion spectroscopy, Applied Physics Letters, 94 (2009) 3.

[54] M.J.H. Kessels, F. Bijkerk, F.D. Tichelaar, J. Verhoeven, Determination of in-depth density profiles of multilayer structures, Journal of Applied Physics, 97 (2005) 093513.

[55] H.-J. Voorma, E. Louis, N.B. Koster, F. Bijkerk, E. Spiller, Characterization of multilayers by Fourier analysis of x-ray reflectivity, Journal of Applied Physics, 81 (1997) 6112-6118.

[56] A.D. Akhsakhalyan, A.A. Fraerman, N.I. Polushkin, Y.Y. Platonov, N.N. Salashchenko, Determination of layered synthetic microstructure parameters, Thin Solid Films, 203 (1991) 317-326.

[57] I. Makhotkin, E. Louis, R.W.E. van de Kruijs, A.E. Yakshin, A.Y. Seregin, M.Y. Lubomirskii, S.N. Yakunin, E.Y. Tereschenko, M.V. Kovalchuk, F. Bijkerk, Determination of the density of ultrathin films using x-ray standing waves, accepted for publication in Physica Status Solidi (a), (2011).

[58] C. Laubis, C. Buchholz, A. Fischer, S. Plöger, F. Scholz, H. Wagner, F. Scholze, G. Ulm, H. Enkisch, S. Muellender, M. Wedowski, E. Louis, E. Zoethout, Characterization of large off-axis EUV mirrors with high accuracy reflectometry at PTB, in: SPIE 6151, San José, 2006, pp. 615101.

[59] F. Scholze, T. Bottger, H. Enkisch, C. Laubis, L. van Loyen, F. Macco, S. Schadlich, Characterization of the measurement uncertainty of a laboratory EUV reflectometer for large optics, Measurement Science & Technology, 18 (2007) 126-130.

[60] R. Klein, C. Laubis, R. Muller, F. Scholze, G. Ulm, The EUV metrology program of PTB, Microelectronic Engineering, 83 (2006) 707-709.

[61] L. van Loyen, T. Boettger, S. Braun, H. Mai, A. Leson, F. Scholze, J. Tuemmler, G. Ulm, H. Legall, P.V. Nickles, W. Sandner, H. Stiel, C.E. Rempel, M. Schulze, J. Brutscher, F. Macco, S. Muellender, New laboratory EUV reflectometer for large optics using a laser plasma source, in: SPIE 5038, 2003, pp. 12-21.

[62] E.M. Gullikson, S. Mrowka, B.B. Kaufmann, Recent Developments in EUV Reflectometry at the

Advanced Light Source, in: SPIE 4343, 2001, pp. 363-373.

[63] J. Chen, E. Louis, F. Bijkerk, C. Lee, H. Wormeester, R. Kunze, H. Schmidt, D. Schneider, R. Moors, Detection and characterization of carbon contamination on EUV multilayer mirror, Optics Express, 17 (2009) 16969-16979

[64] J. Chen, E. Louis, H. Wormeester, R. Harmsen, R.W.E. van de Kruijs, C.J. Lee, W. van Schaik, F. Bijkerk, Predicting EUV reflectance loss due to carbon deposition using visible-light ellipsometry, Accepted for publication in Measurement Science and Technology, (2011).

[65] D.G. Stearns, D.P. Gaines, D.W. Sweeney, E.M. Gullikson, Nonspecular x-ray scattering in a multilayer-coated imaging system, Journal of Applied Physics, 84 (1998) 1003-1028.

[66] A. Kloidt, K. Nolting, U. Kleineberg, B. Schmiedeskamp, U. Heinzmann, P. Müller, M. Kühne, Enhancement of the reflectivity of Mo/Si multilayer x-ray mirrors by the thermal treatment, Applied Physics Letters, 58 (1991) 2601.

[67] H.-J. Voorma, E. Louis, N.B. Koster, F. Bijkerk, Temperature induced diffusion in Mo/Si multilayer mirrors, Journal of Applied Physics, 83 (1998) 4700-4708.

[68] H.J. Voorma, G.E. van Dorssen, E. Louis, N.B. Koster, A.D. Smith, M.D. Roper, F. Bijkerk, EXAFS measurements on the structure of Mo/Si multilayers produced using ion bombardment and increased deposition temperature, Applied Surface Science, 93 (1996) 221-230.

[69] I. Nedelcu, R.W.E. van de Kruijs, A. Yakshin, F. Bijkerk, Thermally enhanced interdiffusion in Mo/Si multilayers, Journal of Applied Physics, 103 (2008) 0835491-0835496.

[70] E. Spiller, Smoothing of multilayer x-ray mirrors by ion polishing, Applied Physics Letters, 54 (1989) 2293-2295.

[71] E.J. Puik, M.J. van der Wiel, H. Zeijlemaker, J. Verhoeven, Ion-beam-assisted deposition of Ni/C multilayer x-ray mirrors, Thin Solid Films, 193/194 (1990) 782-787.

[72] A. Kloidt, H.J. Stock, U. Kleineberg, T. Dohring, M. Propper, B. Schmiedeskamp, U. Heinzmann, Smoothing of interfaces in ultrathin Mo/Si multilayers by ion bombardment, Thin Solid Films, 228 (1993) 154-157.

[73] R. Schlatmann, C. Lu, J. Verhoeven, E.J. Puik, M.J. van der Wiel, Modification by Ar and Kr ion bombardment of Mo/Si X-ray multilayers, Applied Surface Science, 78 (1994) 147-157.

[74] H.J. Voorma, E. Louis, F. Bijkerk, S. Abdali, Angular and energy dependence of ion bombardment of Mo/Si multilayers, Journal of Applied Physics, 82 (1997) 1876-1881.

[75] E.M. Gullikson, J.H. Underwood, P.J. Batson, V. Nikitin, A Soft X-Ray/EUV Reflectometer Based on a Laser Produced Plasma Source, Journal of X-Ray Science and Technology, 3 (1992) 283-299.

[76] C. Herring, J. Appl. Phys., 21 (1950).

[77] W.W. Mullins, J. Appl. Phys. , 30 (1959).

[78] F. Frost, B. Ziberi, A. Schindler, B. Rauschenbach, Surface engineering with ion beams: from self-organized nanostructures to ultra-smooth surfaces, Appl. Phys. A-Mater. Sci. Process., 91 (2008) 551-559.

[79] C.S. Madi, B. Davidovitch, H.B. George, S.A. Norris, M.P. Brenner, M.J. Aziz, Multiple Bifurca-

tion Types and the Linear Dynamics of Ion Sputtered Surfaces, Physical Review Letters, 101 (2008) 246102.

[80] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk, Temperature dependent nanocrystal formation in Mo/Si multilayers, Physical Review B, 76 (2007) art.no. 245404.

[81] R.W.E. van de Kruijs, E. Zoethout, A.E. Yakshin, I. Nedelcu, E. Louis, H. Enkisch, G. Sipos, S. Muellender, F. Bijkerk, Nano-size crystallites in Mo/Si multilayer optics, Thin Solid Films, 515 (2006) 430-433.

[82] E. Louis, Unpublished data.

[83] F. Scholze, C. Laubis, C. Buchholz, A. Fischer, S. Plöger, F. Scholz, H. Wagner, G. Ulm, Status of EUV reflectometry at PTB in: SPIE 5751, 2005, pp. 749-758.

[84] S. Ogura, M. Niibe, Y. Watanabe, M. Hayashida, T. Iizuka, Comparison among multilayer soft X-ray mirrors fabricated by electron beam, DC-, RF-magnetron sputtering and ion beam sputtering deposition, in: SPIE 984, 1988, pp. 140-148.

[85] M. Niibe, M. Hayashida, T. Iizuka, A. Miyake, Y. Watanabe, R. Takahashi, Y. Fukuda, Suppression of Columnar-Structure Formation in Mo-Si Layered Synthetic Microstructures, in: SPIE 1343, 1990, pp. 2-13.

[86] V.I.T.A. de Rooij-Lohmann, A.E. Yakshin, E. Zoethout, J. Verhoeven, F. Bijkerk, Reduction of interlayer thickness by low-temperature deposition of Mo/Si multilayer mirrors for X-ray reflection, Applied Surface Science, 257 (2011) 6251-6255.

[87] International Tables for Crystallography, Kluwer Acedemic Pub. for International Union of Crystallography, 1995.

[88] I.C. Noyan, J.B. Cohen, Residual Stress; Measurement by Diffraction and Interpretation, Springer, New York, 1987.

[89] G.G. Stoney, Proc. R. Soc. Lond., 172 (1909).

[90] M. Ohring, The material science of thin films, Academic Press Inc, 1992.

[91] G. Janssen, M.M. Abdalla, F. van Keulen, B.R. Pujada, B. van Venrooy, Celebrating the 100th anniversary of the Stoney equation for film stress: Developments from polycrystalline steel strips to single crystal silicon wafers, Thin Solid Films, 517 (2009) 1858-1867.

[92] J.M. Freitag, B.M. Clemens, Stress evolution in Mo/Si multilayers for high-reflectivity extreme ultraviolet mirrors, Applied Physics Letters, 73 (1998) 43.

[93] D.L. Windt, W.L. Brown, C.A. Volkert, W.K. Waskiewicz, Variation in stress with background pressure in sputtered Mo/Si mulitlayer films, Journal of Applied Physics, 78 (1995) 2423-2430.

[94] P.B. Mirkarimi, C. Montcalm, Advances in the reduction and compensation of film stress in high-reflectance multilayer coatings for extreme-ultraviolet lithography, in: SPIE 3331, 1998, pp. 133.

[95] P.B. Mirkarimi, Stress, reflectance, and temporal stability of sputter-deposited Mo/Si and Mo/Be multilayer films for extreme ultraviolet lithography, Opt. Eng., 38, 1246 (1999) 1246-1259.

[96] R.R. Kola, D.L. Windt, W.K. Waskiewicz, B.E. Weir, R. Hull, G.K. Celler, C.A. Volkert, Stress relaxation in Mo/Si multilayer structures, Applied Physics Letters, 60 (1992) 3120-3122.

[97] E. Zoethout, G. Sipos, R.W.E. van de Kruijs, A.E. Yakshin, E. Louis, S. Muellender, F. Bijkerk, Stress Mitigation in Mo/Si Multilayers for EUV Lithography, in: SPIE 5037, 2003, pp. 872-877.

[98] M. Shiraishi, W. Ishiyama, T. Ohsino, K. Murakami, Low-stress molybdenum/silicon multilayer coatings for extreme ultraviolet lithography, Japanese Journal of Applied Physics Part 1-Regular Papers Short Notes & Review Papers, 39 (2000) 6810-6814.

[99] M. Shiraishi, N. Kandaka, K. Murakami, Low-stress and high-reflective molybdenum/silicon multilayers deposited by low-pressure rotary magnet cathode sputtering for EUV lithography, in: SPIE 5374, 2004, pp. 104-111.

[100] E. Louis, A.E. Yakshin, P.C. Görts, S. Oestreich, E.L.G. Maas, M.J.H. Kessels, D. Schmitz, F. Scholze, G. Ulm, S. Muellender, M. Haidl, F. Bijkerk, in: SPIE 4146, 2000, pp. 60-63.

[101] B. Mertens, M. Weiss, H. Meiling, R. Klein, E. Louis, R. Kurt, M. Wedowski, H. Trenkler, B. Wolschrijn, R. Jansen, A. van de Runstraat, R. Moors, K. Spee, S. Ploger, R.W.E. van de Kruijs, Progress in EUV optics lifetime expectations, Microelectronic Engineering, 73-4 (2004) 16-22.

[102] M. Lowisch, P. Kuerz, H.-J. Mann, O. Natt, B. Thuering, Optics for EUV production, in: SPIE 7636, 2010, pp. 763603.

[103] P. Lee, Uniform and graded multilayers as x-ray optical elements, Appl. Opt., 22 (1983) 1241–1246.

[104] P. van Loevezijn, R. Schlatmann, J. Verhoeven, B.A. van Tiggelen, E.M. Gullikson, Numerical and experimental study of disordered multilayers for broadband x-ray reflection, Appl. Optics, 35 (1996) 3614-3619.

[105] A.G. Michette, Z.S. Wang, Optimisation of depth-graded multilayer coatings for broadband reflectivity in the soft X-ray and EUV regions, Optics Communications, 177 (2000) 47-55.

[106] A.E. Yakshin, I. Kozhevnikov, E. Zoethout, E. Louis, F. Bijkerk, Properties of broadband depth-graded multilayer mirrors for EUV optical systems, Optics Express, 18 (2010) 6957-6971.

[107] J. Bosgra, E. Zoethout, A.M.J. van der Eerden, F. Boekhout, J. Verhoeven, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk, Structural properties of sub nanometer thick Y layers in EUV multilayer mirrors, submitted to Applied Optics, (2012).

[108] S. Bajt, J.B. Alameda, T.W. Barbee, W.M. Clift, J.A. Folta, B. Kaufmann, E.A. Spiller, Improved reflectance and stability of Mo-Si multilayers, Optical Engineering, 41 (2002) 1797-1804.

[109] S. Braun, T. Foltyn, L. van Loyen, M. Moss, A. Leson, Multi component EUV multilayer mirrors, in: SPIE 5037, 2003, pp. 274-285.

[110] A.K. Petfordlong, M.B. Stearns, C.H. Chang, S.R. Nutt, D.G. Stearns, N.M. Ceglio, A.M. Hawryluk, High-resolution electron microscopy study of X-ray multilayer structures, Journal of Applied Physics, 61 (1987) 1422-1428.

[111] M.B. Stearns, C.H. Chang, D.G. Stearns, Optimization of growth-conditions of vapour deposited Mo/Si multilayers, Journal of Applied Physics, 71 (1992) 187-195.

[112] A. Ulyanenkov, R. Matsuo, K. Omote, K. Inaba, J. Harada, M. Ishino, M. Nishii, O. Yoda, X-ray scattering study of interfacial roughness correlation in Mo/Si multilayers fabricated by ion beam sputtering, Journal of Applied Physics, 87 (2000) 7255-7260.

[113] S. Bajt, D.G. Stearns, P.A. Kearney, Investigation of the amorphous-to-crystalline transition in Mo/Si multilayers, Journal of Applied Physics, 90 (2001) 1017-1025.

[114] E. Schubert, S. Mandl, H. Neumann, B. Rauschenbach, Real-time in situ spectroscopic ellipsometry investigation of the amorphous to crystalline phase transition in Mo single layers, Appl. Phys. A-Mater. Sci. Process., 80 (2005) 47-50.

[115] S. Abdali, L. Gerward, A.E. Yakshin, E. Louis, F. Bijkerk, Determination of crystallization as a function of Mo layer thickness in Mo/Si multilayers, Materials Research Bulletin, 37 (2002) 279-289.

[116] V.I.T.A. de Rooij-Lohmann, A.E. Yakshin, R.W.E. van de Kruijs, E. Zoethout, A.W. Kleyn, E.G. Keim, M. Gorgoi, F. Schaefers, H.H. Brongersma, F. Bijkerk, Enhanced diffusion upon amorphous-to-nanocrystalline phase transition in Mo/B_4C/Si layered systems, Journal of Applied Physics, 108 (2010).

[117] T. Bottger, D.C. Meyer, P. Paufler, S. Braun, M. Moss, H. Mai, E. Beyer, Thermal stability of Mo/Si multilayers with boron carbide interlayers, Thin Solid Films, 444 (2003) 165-173.

[118] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk, Microstructure of Mo/Si multilayers with B_4C diffusion barrier layers, Appl. Optics, 48 (2009) 155-160.

[119] S. Yulin, N. Benoit, T. Feigl, N. Kaiser, Interface-engineered EUV multilayer mirrors, Microelectronic Engineering, 83 (2006) 692-694.

[120] L.G.A.M. Alink, R.W.E. van de Kruijs, E. Louis, F. Bijkerk, J. Verhoeven, Improved temperature stability of Mo/Si multilayers by carbide based diffusion barriers through implantation of low energy CH^{+} ions, Thin Solid Films, 510 (2006) 26-31.

[121] S. Bruijn, R.W.E. van de Kruijs, A.E. Yakshin, F. Bijkerk, The Effect of Mo Crystallinity on Diffusion through the Si-on-Mo Interface in EUV Multilayer Systems, Defect and Diffusion Forum, 283 - 286 (2009) 657-661.

[122] J. Hollenshead, L. Klebanoff, Modeling radiation-induced carbon contamination of extreme ultraviolet optics, Journal of Vacuum Science & Technology B, 24 (2006) 64-82.

[123] T. Feigl, S. Yulin, N. Kaiser, R. Thielsch, Magnetron sputtered EUV mirrors with high-thermal stability, in: SPIE 3997, 2000, pp. 420-430.

[124] Z. Jiang, X. Jiang, W. Liu, Z. Wu, Thermal stability of multilayer films Pt/Si, W/Si, Mo/Si, and W/C, J. Appl. Phys. 65, 65 (1989) 196-200.

[125] H. Nakajima, H. Fujimori, M. Koiwa, Interdiffusion and structural relaxation in Mo/Si multilayer films, J. Appl. Phys., 63 (1988) 1046-1051.

[126] S. Oestreich, R. Klein, F. Scholze, J. Jonkers, E. Louis, A.E. Yakshin, P.C. Görts, G. Ulm, M. Haidl, F. Bijkerk, Multilayer reflectance during exposure to EUV radiation, in: SPIE 4146, 2000, pp. 64-71.

[127] A.R. Khorsand, R. Sobierajski, E. Louis, S. Bruijn, E.D. van Hattum, R.W.E. van de Kruijs, M. Jurek, D. Klinger, J.B. Pelka, L. Juha, T. Burian, J. Chalupsky, J. Cihelka, V. Hajkova, L. Vysin, U. Jastrow, N. Stojanovic, S. Toleikis, H. Wabnitz, K. Tiedtke, K. Sokolowski-Tinten, U. Shymanovich, J. Krzywinski, S. Hau-Riege, R. London, A.J. Gleeson, E.M. Gullikson, F.

Bijkerk, Single shot damage mechanism of Mo/Si multilayer optics under intense pulsed XUV-exposures, Optics Express, 18 (2010) 700-712.
[128] K. Boller, R.P. Haelbich, H. Hogrefe, W. Jark, C. Kunz, Investigation of carbon contamination of mirror surfaces exposed to synchrotron radiation, Nuclear Instruments and Methods in Physics Research, 208 (1983) 273-279.
[129] T.E. Madey, N.S. Faradzhev, B.V. Yakshinskiy, N.V. Edwards, Surface phenomena related to mirror degradation in extreme ultraviolet (EUV) lithography, Applied Surface Science, 253 (2006) 1691-1708.
[130] B.V. Yakshinskiy, R. Wasielewski, E. Loginova, M.N. Hedhili, T.E. Madey, DIET processes on ruthenium surfaces related to extreme ultraviolet lithography (EUVL), Surface Science, 602 (2008) 3220-3224.
[131] K.R. Dean, G. Denbeaux, A. Wuest, R. Garg, EUV resist outgassing: How much is too much?, Journal of Photopolymer Science and Technology, 20 (2007) 393-402.
[132] S. Graham, C. Steinhaus, M. Clift, L. Klebanoff, S. Bajt, Atomic hydrogen cleaning of EUV multilayer optics, in: SPIE 5037, 2003, pp. 460-469.
[133] L.E. Klebanoff, W.M. Clift, M.E. Malinowski, C. Steinhaus, P. Grunow, S. Bajt, Radiation-induced protective carbon coating for extreme ultraviolet optics, Journal of Vacuum Science & Technology B, 20 (2002) 696-703.
[134] N. Koster, B. Mertens, R. Jansen, A. van de Runstraat, F. Stietz, M. Wedowski, H. Meiling, R. Klein, A. Gottwald, F. Scholze, M. Visser, R. Kurt, P. Zalm, E. Louis, A. Yakshin, Molecular contamination mitigation in EUVL by environmental control, Microelectronic Engineering, 61-2 (2002) 65-76.
[135] N. Benoit, S. Schroder, S. Yulin, T. Feigl, A. Duparre, N. Kaiser, A. Tunnermann, Extreme-ultraviolet-induced oxidation of Mo/Si multilayers, Appl. Optics, 47 (2008) 3455-3462.
[136] S. Graham, C. Steinhaus, M. Clift, L. Klebanoff, Radio-frequency discharge cleaning of silicon-capped Mo/Si multilayer extreme ultraviolet optics, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures, 20 (2002) 2393-2400.
[137] H. Oizumi, H. Yamanashi, I. Nishiyama, K. Hashimoto, S. Ohsono, A. Masuda, A. Izumi, H. Matsumura, Contamination removal from EUV multilayer using atomic hydrogen generated by heated catalyzer, in: SPIE 5751, 2005, pp. 1147-1154.
[138] A.E. Yakshin, E. Louis, E.L.G. Maas, F. Bijkerk, R. Klein, F. Scholze, P. Zalm, F. Stietz, M. Wedowski, S. Muellender, B. Mertens, H. Meiling, Protection of Mo/Si multilayers with a carbon capping layer, in: Gomei (Ed.) ASET/SEMATECH Workshop on Extreme UV Lithography, Matsue, 2001, pp. P6-6.
[139] S. Bajt, N.V. Edwards, T.E. Madey, Properties of ultrathin films appropriate for optics capping layers exposed to high energy photon irradiation, Surface Science Reports, 63 (2008) 73-99.
[140] S. Yulin, N. Benoit, T. Feigl, N. Kaiser, M. Fang, M. Chandhok, Mo/Si multilayers with enhanced TiO_2- and RuO_2-capping layers, in: SPIE 6921, 2008, pp. 692118.
[141] S. Bajt, H.N. Chapman, N. Nguyena, J. Alameda, J.C. Robinson, M. Malinowski, E. Gullikson,

A. Aquila, C. Tarrio, S. Grantham, Design and performance of capping layers for EUV multilayer mirrors, in: SPIE 5037, 2003, pp. 236-248.

[142] H. Over, M. Muhler, Catalytic CO oxidation over ruthenium - bridging the pressure gap, Progress in Surface Science, 72 (2003) 3-17.

[143] H. Over, Y.B. He, A. Farkas, G. Mellau, C. Korte, M. Knapp, M. Chandhok, M. Fang, Long-term stability of Ru-based protection layers in extreme ultraviolet lithography: A surface science approach, Journal of Vacuum Science & Technology B, 25 (2007) 1123-1138.

[144] S. Zalkind, B.V. Yakshinskiy, T.E. Madey, Interaction of benzene with TiO2 surfaces: Relevance to contamination of extreme ultraviolet lithography mirror capping layers, Journal of Vacuum Science & Technology B, 26 (2008) 2241-2246.

[145] N.S. Faradzhev, S.B. Hill, T.B. Lucatorto, B.V. Yakshinskii, T.E. Madey, EUV Lithography Optics Contamination and Lifetime Studies, Bulletin of the Russian Academy of Sciences: Physics, 74 (2010).

[146] M. Niibe, K. Koida, Y. Kakutani, Protection and reduction of surface oxidation of Mo/Si multilayers for extreme ultraviolet lithography projection optics by control of hydrocarbon gas atmosphere, Journal of Vacuum Science & Technology B, 26 (2008) 2230-2235.

[147] B.V. Yakshinskiy, S. Zalkind, R.A. Bartynski, R. Caudillo, Electron-induced interaction of selected hydrocarbons with TiO_2 surfaces: the relevance to extreme ultraviolet lithography, Journal of Physics-Condensed Matter, 22 (2010).

[148] T. Tsarfati, E. Zoethout, R.W.E. van de Kruijs, F. Bijkerk, In-depth agglomeration of d-metals at Si-on-Mo interfaces, Journal of Applied Physics, 105 (2009) 064314.

[149] T. Tsarfati, E. Zoethout, R.W.E. van de Kruijs, F. Bijkerk, Chemically mediated diffusion of d-metals and B through Si and agglomeration at Si-on-Mo interfaces, Journal of Applied Physics, 105 (2009).

[150] T. Tsarfati, R.W.E. van de Kruijs, E. Zoethout, E. Louis, F. Bijkerk, Reflective multilayer optics for 6.7 nm wavelength radiation sources and next generation lithography, Thin Solid Films, 518 (2009) 1365-1368.

[151] M.M.J.W. van Herpen, R.W.E. van de Kruijs, D.J.W. Klunder, E. Louis, A.E. Yakshin, S. Alonso van der Westen, F. Bijkerk, V. Banine, Spectral-purity-enhancing layer for multilayer mirrors, Optics Letters, 33 (2008) 560-562.

[152] E. Louis, R.W.E. van de Kruijs, A.E. Yakshin, M.M.J.W. van Herpen, D.J.W. Klunder, S. Alonso van der Westen, H. Enkisch, S. Muellender, L. Bakker, V. Banine, M. Richter, F. Bijkerk, Multilayer optics with spectral purity enhancing layers for the EUV wavelength range, in: SPIE 6151, 2006, pp. 615139.

[153] T. Tsarfati, E. Zoethout, R.W.E. van de Kruijs, F. Bijkerk, Growth and sacrificial oxidation of transition metal nanolayers, Surface Science, 603 (2009) 1041-1045.

[154] L. Belau, J.Y. Park, T. Liang, G.A. Somorjai, The effects of oxygen plasma on the chemical composition and morphology of the Ru capping layer of the extreme ultraviolet mask blanks, Journal of Vacuum Science & Technology B, 26 (2008) 2225-2229.

[155] L. Belau, J.Y. Park, T. Liang, H. Seo, G.A. Somorjai, Chemical effect of dry and wet cleaning of the Ru protective layer of the extreme ultraviolet lithography reflector, Journal of Vacuum Science & Technology B, 27 (2009) 1919-1925.

[156] Y.B. He, A. Goriachko, C. Korte, A. Farkas, G. Mellau, P. Dudin, L. Gregoratti, A. Barinov, M. Kiskinova, A. Stierle, N. Kasper, S. Bajt, H. Over, Oxidation and reduction of ultrathin nanocrystalline Ru films on silicon: Model system for Ru-capped extreme ultraviolet lithography optics, Journal of Physical Chemistry C, 111 (2007) 10988-10992.

[157] Y. Iwasaki, A. Izumi, H. Tsurumaki, A. Namiki, H. Oizumi, I. Nishiyama, Oxidation and reduction of thin Ru films by gas plasma, Applied Surface Science, 253 (2007) 8699-8704.

[158] T. Tsarfati, E. Zoethout, R.W.E. v.d. Kruijs, F. Bijkerk, Atomic O and H exposure of C-covered and oxidized d-metal surfaces, Surface Science, 603 (2009) 2594-2599.

[159] H. Oizumi, A. Izumi, K. Motai, I. Nishiyama, A. Namiki, Atomic hydrogen cleaning of surface ru oxide formed by extreme ultraviolet irradiation of Ru-capped multilayer mirrors in H_2O ambience, Japanese Journal of Applied Physics Part 2-Letters & Express Letters, 46 (2007) L633-L635.

[160] I. Nishiyama, H. Oizumi, K. Motai, A. Izumi, T. Ueno, H. Akiyama, A. Namiki, Reduction of oxide layer on Ru surface by atomic-hydrogen treatment, in: AVS 23, 2005, pp. 3129-3131.

[161] J. Chen, E. Louis, R. Harmsen, T. Tsarfati, H. Wormeester, M. van Kampen, W. van Schaik, R.W.E. van de Kruijs, F. Bijkerk, In situ ellipsometry study of atomic hydrogen etching of EUV-induced carbon layers, Applied Surface Science, doi: 10.1016/j.apsusc.2011.07.121 (2011).

[162] V.Y. Banine, K.N. Koshelev, G. Swinkels, Physical processes in EUV sources for microlithography, J. Phys. D-Appl. Phys., 44 (2011) 18.

[163] V. Bakshi, EUV Sources for Lithography, in, SPIE Press Book, 2006.

[164] H.-J. Voorma, E. Louis, N.B. Koster, F. Bijkerk, T. Zijlstra, L.E.M. de Groot, B.A.C. Rousseeuw, J. Romijn, E.W.J.M. van der Drift, J. Friedrich, Fabrication and analysis of Extreme Ultraviolet reflection masks with patterned W/C absorber bi-layers, Journal of Vacuum Science & Technology B, 15 (1997) 293-298.

[165] A.J.R. van den Boogaard, E. Louis, E. Zoethout, S. Muellender, F. Bijkerk, Surface morphology of $Kr(^{+})$-polished amorphous Si layers, Journal of Vacuum Science and Technology A, 28 (2010) 552-558.

[166] E. Louis, E. Zoethout, R.W.E. van de Kruijs, I. Nedelcu, A.E. Yakshin, F. Bijkerk, H. Enkisch, S. Muellender, G. Sipos, D. Ehm, P. Kürz EUVL multilayer coating development, in: 3rd International EUVL Conference, Miyazaki, Japan, 2004.

[167] K. Shimizu, M. Kuraoka, Y. Yamada, T. Yamada, T.D. Casteel, Y. Platonov, Multilayer analyzers for XRF analysis of light elements, American Laboratory, 38 (2006) 10.

[168] R. Stuik, F. Scholze, J. Tümmler, F. Bijkerk, Absolute calibration of a multilayer-based XUV diagnostic, Nuclear Instruments & Methods in Physics Research, Section A, 492 (2002) 305-316.

[169] S. Alonso van der Westen, R. de Bruijn, F. Bijkerk, V. Bakshi, M. Schuermann, T. Missalla, U. Stamm, G. Schriever, K. Gabel, G. Hergenhan, Cross-Calibration of Extreme Ultraviolet (EUV)

Energy Sensors (http://www.sematech.org/docubase/document/4498atr.pdf), in, International SEMATECH, 2004.

[170] R. Stuik, R. Constantinescu, P. Hegeman, J. Jonkers, H. Fledderus, V. Banine, F. Bijkerk, Portable diagnostics for EUV light sources, in: SPIE 4146, 2000, pp. 121-127.

[171] R. Stuik, H. Fledderus, P. Hegeman, J. Jonkers, M. Visser, V. Banine, F. Bijkerk, Flying Circus EUV source comparison, absolute yield, absolute yield fluctuations and contamination, in: Second SEMATECH Workshop on Extreme UV Lithography, International Sematech, San Francisco, 2000.

[172] J.M. Andre, P. Jonnard, C. Michaelsen, J. Wiesmann, F. Bridou, M.F. Ravet, A. Jerome, F. Delmotte, E.O. Filatova, La/B_4C small period multilayer interferential mirror for the analysis of boron, X-Ray Spectrometry, 34 (2005) 203-206.

[173] P. Ricardo, J. Wiesmann, C. Nowak, C. Michaelsen, R. Bormann, Improved analyzer multilayers for aluminium and boron detection with x-ray fluorescence, Appl. Optics, 40 (2001) 2747-2754.

[174] C. Michaelsen, J. Wiesmann, R. Bormann, C. Nowak, C. Dieker, S. Hollensteiner, W. Jager, Multilayer mirror for x rays below 190 eV, Optics Letters, 26 (2001) 792-794.

[175] S.S. Andreev, M.M. Barysheva, N.I. Chkhalo, S.A. Gusev, A.E. Pestov, V.N. Polkovnikov, N.N. Salashchenko, L.A. Shmaenok, Y.A. Vainer, S.Y. Zuev, Multilayered mirrors based on La/B_4C(B_9C) for X-ray range near anomalous dispersion of boron (lambda approximate to 6.7 nm), Nuclear Instruments & Methods in Physics Research Section a-Accelerators Spectrometers Detectors and Associated Equipment, 603 (2009) 80-82.

[176] S.S. Ellwi, L. Juschkin, S. Ferri, H.J. Kunze, K.N. Koshelev, E. Louis, X-ray lasing as a result of an induced instability in an ablative capillary discharge, J. Phys. D-Appl. Phys., 34 (2001) 336-339.

[177] A.J. Nelson, S. Toleikis, H. Chapman, S. Bajt, J. Krzywinski, J. Chalupsky, L. Juha, J. Cihelka, V. Hajkova, L. Vysin, T. Burian, M. Kozlova, R.R. Faustlin, B. Nagler, S.M. Vinko, T. Whitcher, T. Dzelzainis, O. Renner, K. Saksl, A.R. Khorsand, P.A. Heimann, R. Sobierajski, D. Klinger, M. Jurek, J. Pelka, B. Iwan, J. Andreasson, N. Timneanu, M. Fajardo, J.S. Wark, D. Riley, T. Tschentscher, J. Hajdu, R.W. Lee, Soft x-ray free electron laser microfocus for exploring matter under extreme conditions, Optics Express, 17 (2009) 18271-18278.

[178] B. Nagler, U. Zastrau, R.R. Faustlin, S.M. Vinko, T. Whitcher, A.J. Nelson, R. Sobierajski, J. Krzywinski, J. Chalupsky, E. Abreu, S. Bajt, T. Bornath, T. Burian, H. Chapman, J. Cihelka, T. Doppner, S. Duesterer, T. Dzelzainis, M. Fajardo, E. Forster, C. Fortmann, E. Galtier, S.H. Glenzer, S. Gode, G. Gregori, V. Hajkova, P. Heimann, L. Juha, M. Jurek, F.Y. Khattak, A.R. Khorsand, D. Klinger, M. Kozlova, T. Laarmann, H.J. Lee, R.W. Lee, K.H. Meiwes-Broer, P. Mercere, W.J. Murphy, A. Przystawik, R. Redmer, H. Reinholz, D. Riley, G. Ropke, F. Rosmej, K. Saksl, R. Schott, R. Thiele, J. Tiggesbaumker, S. Toleikis, T. Tschentscher, I. Uschmann, H.J. Vollmer, J.S. Wark, Turning solid aluminium transparent by intense soft X-ray photoionization, Nature Physics, 5 (2009) 693-696.

[179] H.N. Chapman, S.P. Hau-Riege, M.J. Bogan, S. Bajt, A. Barty, S. Boutet, S. Marchesini, M. Frank, B.W. Woods, W.H. Benner, R.A. London, U. Rohner, A. Szoke, E. Spiller, T. Moller, C. Bostedt, D.A. Shapiro, M. Kuhlmann, R. Treusch, E. Plonjes, F. Burmeister, M. Bergh, C. Caleman, G. Huldt, M.M. Seibert, J. Hajdu, Femtosecond time-delay X-ray holography, Nature, 448 (2007) 676-679.

3 Suppression of the UV reflectance of multilayer EUV Bragg mirrors

ABSTRACT

Reported are calculations and experimental results of EUV normal incidence Bragg-reflective multilayer mirrors that show suppressed reflectance in the ultraviolet (UV) wavelength range. This effect is achieved by applying an UV anti-reflection (AR) layer on top of the multilayer. Design criteria are given on the required optical constants of such an AR layer for λ = 150 nm. Experimental data in the 100-200 nm wavelength band show a significant reduction of the reflectance, up to a factor of 10 around 165 nm. The reflectance loss at 13.5 nm was limited to 6.6 % (absolute), as compared to standard multilayer systems. The design and optical response of these spectrally selective coatings is reviewed.

3.1 Introduction

Multilayer reflective optics for the short wavelength band, i.e. wavelengths from a few tens to a few tenths of nanometers, generally contain Bragg-reflective stacks of bi-layers. Such film stacks are well proven reflectors for a selected wavelength [1]. They can also show substantial reflectance for longer wavelengths, which may jeopardize their use for applications that require monochromaticity. An example is from Extreme UV photolithography machines for which all multilayer optics are optimized for the highest performance at 13.5 nm wavelength. However, the most likely radiation sources [2] for EUVL machines also emit a considerable amount of light at longer wavelengths. This radiation is usually referred to as out-of-band radiation and can lead to extra heat load on the optics, parasitic resist exposure and blurring of the EUV image. This and other applications may therefore require a method to suppress such out-of-band radiation.

Mo/Si multilayers can have up to around 70% reflectance for 13.5 nm radiation [3] under the specific Bragg conditions, but the reflectance for UV radiation can be equally high [4]. Furthermore, this UV reflectance is broadband and the total amount of non-EUV light that is reflected by an EUV optical system is the integral over the entire wavelength range from the EUV up to the visible region. To what extent such parasitic reflection is critical for the final lithography application also depends on the resist spectral sensitivity, the EUV source characteristics, and the mask reflectivity. The convolution of these factors, as far as they are known, shows that especially the band from about 100 to 240 nm is most critical [5]. Detailed information on particularly the light source may shift this wavelength band or call for specific reflectance characteristics.

To achieve selective out-of-band suppression, a so-called spectral purity filter (SPF) can be used. In the past these spectral purity filters were either based on transmission through a thin filter [6, 7], or selective reflection from blazed gratings [8, 9]. Practically useful transmission filters typically have an EUV transmission that does not exceed 50%, although the best reported result is a transmission of 75% from a Zr-Si filter with a UV transmission of 0.1% [6]. The efficiency of blazed gratings depends on their output diffraction efficiency, the grating reflectivity and the slit transmission [8]. Typically, the efficiency of these gratings is below 50%, although practical values up to 63% have been reported [9]. A higher efficiency can be obtained when the grating is used in combination with a multilayer [10]. In all cases, the use of diffractive structures changes the optical path which may require adjustment of the optics design or additional EUV mirrors.

An alternative method for out of band suppression is to incorporate an UV anti-reflection (AR) layer into the multilayer design [11]. Such a system is mechanically stable and eliminates the need for additional optics components. In this chapter, we discuss the design considerations for the AR-layer and show the results obtained using a spectral purity enhancing multilayer, designed to suppress the reflectance in the 100-200 nm wavelength band while preserving most of the EUV reflectance. The principle of operation is illustrated in Figure 3.1.

3.2 Design

The most straightforward way to suppress reflection of UV light from a Mo/Si multilayer is to apply an additional layer on top of the EUV reflector, using a material that is highly absorbing for UV light but is relatively transparent in the EUV range. However, such a system would still reflect a significant part of the incident UV light from its surface-to-vacuum interface. If this additional layer would act as a UV anti-reflection coating, in principle zero reflectance can be achieved, albeit for a particular wavelength.

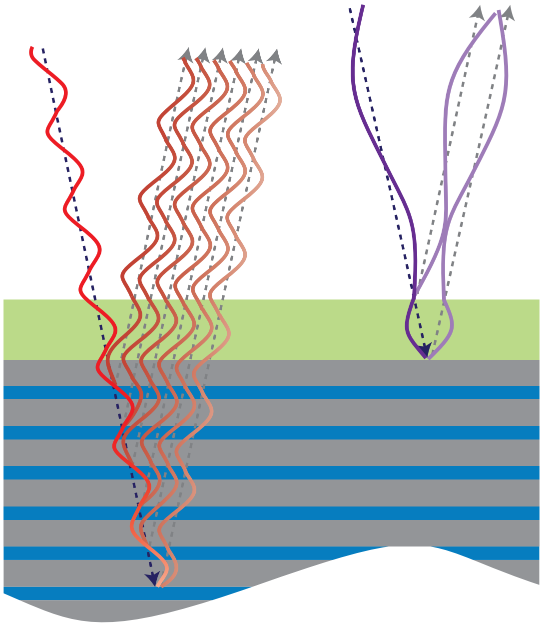


Figure 3.1: Schematic picture of an EUV multilayer system including an anti-reflection layer (green) for longer wavelengths. The reflected EUV light (red waves) interferes constructively while a suppressed reflection for the longer wavelength (blue waves)

A classical anti-reflection layer is based on destructive interference and requires equal amplitudes and opposite phase of the reflected waves, thus a thickness of $\lambda/4$ n (in the UV and EUV range the complex index of refraction $\tilde{n} = n + i\,k$ needs to be used). The required 180° phase shift between the waves reflected from the top and bottom interfaces of the AR layer is the result of the phase shift from the double pass of the wave through the AR layer, the phase jump resulting from the reflection at the bottom interface and the phase jump at the top interface. To limit the absorption of EUV light in the AR layer, this layer should be as thin as possible. This can be achieved in two ways. First, the phase shift per unit path length through the AR layer should be large for UV light, which means that a material with a large real part n of the refractive index should be selected. Secondly, also the phase jump at the bottom interface should be as large as possible, a requirement for the selection of the combination of the material of the AR layer and the top layer of the multilayer [11]. The other requirement, equal amplitudes of the waves, depends not only on the absorption in the AR layer, but also on the reflectivities at both interfaces. It is therefore not possible to make a general statement about the required extinction coefficient k of the AR-layer material and calculations are needed. It should also be noted that in reality a considerable number of the EUV mirror interfaces contribute to the reflection of UV light as well and thus to the phase and intensity of the reflected wave. To accelerate our calculations, we took this effect into account for the top 3 periods of the multilayer only. This results in a relative deviation of the UV reflectance of less than 3%.

In order to select suitable materials for the AR layer it is necessary to determine which optical constants n,k such a layer should have. Therefore, for λ=150 nm, a value in the middle of the targeted interval, we calculated the normal incidence UV reflectance for an AR layer of an imaginary material on a 3 period Mo/Si EUV multilayer. In these calculations we varied n ranging from 0 to 4.0, and k from 0 to 2.5, the boundaries being given by the possible values for existing materials. Furthermore, we varied the thickness of the AR layer. From the thus obtained matrix we selected those n,k combinations that showed an UV reflectance below a given value. The results are given in Figure 3.2. For any n,k combination within the green area in the figure a UV reflectance between 0.5 and 5% can be obtained, for the grey area this range is 0.5 – 0.05% and for the orange area in the middle the reflectance can be below 0.05%.

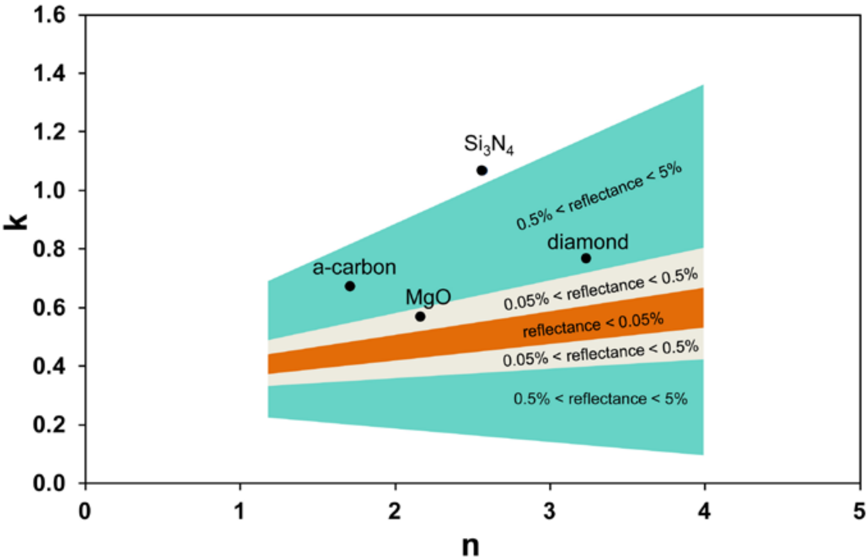


Figure 3.2: Overview of n,k combinations for which an AR layer on an EUV mirror would result in a reflectance of 0.5-5% (green area), 0.5-0.05% (gray area) or less than 0.05% (orange area) for 150 nm light. The thickness of the AR layer was limited to 20 nm. The n,k values for 4 promising materials are indicated.

These values are to be compared to the 50% reflectance at λ =150 nm for a standard Si terminated Mo/Si multilayer. The required AR layer thickness to obtain the low UV reflectance values increases with decreasing n. For practical reasons, we limited the thickness to 20 nm, since thicker layers would result in a too large absorption of 13.5 nm radiation. This limitation excludes all materials with n < 1.15. Summarizing this exploration of possible combinations of n and k, an EUV multilayer with an AR layer thinner than 20 nm can only have a UV reflectance below 5% for n,k within the coloured area of figure 3.2. This figure provides us with zones in which the anti-reflection layer material should be found. For a selected material, the EUV loss for the layer thickness needed to obtain the required AR functionality should be calculated.

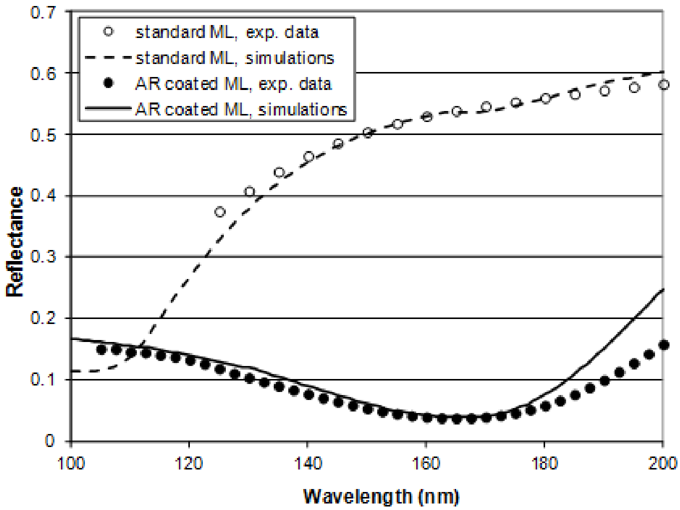
By way of example, and because of the limited EUV absorption, we selected the four materials indicated in figure 3.2 for further investigation with the goal to choose one for an experimental proof of principle. The optical constants as well as the calculated EUV and UV reflectance of AR layers of these materials on a standard Mo/Si multilayer are given in Table 3.1.

ML	AR layer	n λ=150 nm	k λ=150 nm	Reflectance λ=13.5 nm (%)	Reflectance λ=150 nm (%)
Mo/Si	none			74.2	50.0
Mo/Si	8.1 nm MgO	2.169	0.554	40.0	0.3
Mo/Si	3.6 nm cubic-C (diamond)	3.232	0.768	72.2	0.9
Mo/Si	12.8 nm a-C	1.707	0.672	63.0	2.3
Mo/Si	8.9 nm a-C	1.707	0.672	68.0	6.0
Mo/Si	5.2 nm Si_3N_4	2.564	1.070	67.5	6.1

Table 3.1. Calculated EUV and UV reflectance for five different AR layers. The refractive indices are obtained from [12, 13]

In all cases we assumed perfect layer interfaces without roughness or interlayer formation. None of the materials have optical constants within the < 0.05% reflectance region in Figure 3.2. MgO is close with an AR reflectance of 0.3%, but its EUV loss is huge. Diamond would have an EUV reflectance loss of only 2.0%, but will be difficult to make in this thickness at room temperature. Amorphous carbon has the potential to suppress the AR reflectance to 2.3% (in the green area in Fig. 3.2), but this requires a thickness of 12.8 nm resulting in an EUV loss of more than 11%. Amorphous carbon with a thinner layer of 8.9 nm would have the same performance as 5.2 nm Si_3N_4 in terms of UV and EUV reflectance. Both materials can be deposited.

For our proof of principle we selected Si_3N_4 because simulations show that its wavelength dependence is less pronounced than for a-carbon for the long wavelength part of the targeted interval (see Figure 3.3).



Figuur 3.3: Measured and calculated near normal incidence reflectance for a standard Mo/Si multilayer (open circles) and an AR coated multilayer (closed circles). The dotted and solid lines represent the respective IMD calculations. The AR coating consisted of 7 nm silicon nitride.

3.3 Multilayer Deposition

The Mo/Si multilayer films were made by means of e-beam evaporation and additional ion beam polishing in an ultra high vacuum system (base pressure during deposition typically $5x10^{-8}$ mbar). Growth and polishing of the Mo and Si layers was controlled by in-situ reflectometry using a small, built-in soft X-ray source [3]. To deposit the Si_3N_4 layer on the Mo/Si multilayer, N^+ ion assisted Si deposition by means of electron beam evaporation has been used, enabling deposition at room temperature in the same coating facility as used for the multilayer deposition. The composition of the silicon nitride layer has been optimized by tuning the N^+ ion energy as well as the ion flux to the silicon deposition rate. The Si to N ratio in the layer has been determined by in vacuo angle resolved X-ray Photoelectron Spectroscopy (XPS). In the thus optimized silicon nitride a Si to N ratio of 1:1 has been observed rather than the stoichiometric ratio of 3:4. The composition of the AR layer was found to be uniform through the entire layer. In order to compensate for a lower density of the deposited Si-nitride than the bulk value used in the design, the deposited layer had a larger thickness of 7 nm, as determined using a quartz crystal microbalance.

The multilayer reflectance at near-normal incidence around 13.5 nm and in the 100-200 nm range has been measured at the Physikalisch Technische Bundesanstalt (PTB) [14, 15] at the BESSY storage ring in Berlin.

3.4 Optical characterization

The measured near normal incidence UV reflectance of the standard Mo/Si multilayer as well as of an identical one covered with a 7 nm silicon nitride layer is presented in figure 3.3. The reflectance of the standard multilayer ranges from 38% at λ = 125 nm up to almost 60% at λ = 200 nm. The curve coincides well with calculated values obtained using IMD [16] as depicted by the dashed curve. The reflectance for the multilayer with the AR layer is much lower over the entire wavelength range and shows a suppression of a factor of 10 at λ = 165 nm with respect to the standard mirrors.

The solid line in Figure 3.3 represents IMD simulations for a 5 nm Si_3N_4 AR layer covered multilayer and coincides up to 180 nm with the measured curve of the deposited 7 nm silicon nitride AR layer. Also the minima of both curves coincide at 165 nm. However, a 7 nm Si_3N_4 AR layer with bulk density should result in a minimum reflectance around λ = 180 nm, but the position of the minimum depends on the density of the layer, as is shown in figure 3.4. This figure indicates that the shift of the minimum in the reflectance curve from 180 to 165 nm is due to the reduced density of our 7 nm deposited SiN layer, as opposed to the bulk value used for the design. From this figure we can conclude that the density of the deposited silicon nitride is 80% of the bulk value. Obviously, the additional 2 nm deposited silicon nitride compensates for the reduced density of the deposited AR layer, as well as for the observed non-stoichiometric composition. The fact that for $\lambda > 180$ nm the measured spectral dependence is flatter than the simulated one is most likely the result of uncertainty in the optical constants of our silicon nitride layer.

Figure 3.5 shows the EUV reflectance of a Mo/Si multilayer coated with a 7 nm silicon nitride AR layer, compared to the reflectance of a standard Mo/Si multilayer. It shows that there is only a minor drop in EUV reflectance from 68.4% for the standard multilayer to 61.8% for the AR coated one, which would give rise to only a small loss of transmission in an optical system compared to for instance filtering. The loss of 6.6% coincides with the predicted 6.7% loss for a 5 nm bulk density Si_3N_4 layer (see table 3.1) and is 2% less than can be calculated for 7 nm. Assuming stoichiometric Si_3N_4 this would indicate that our silicon nitride layer has a density of 85% of the bulk value, approximately the same density as concluded from the UV measurements.

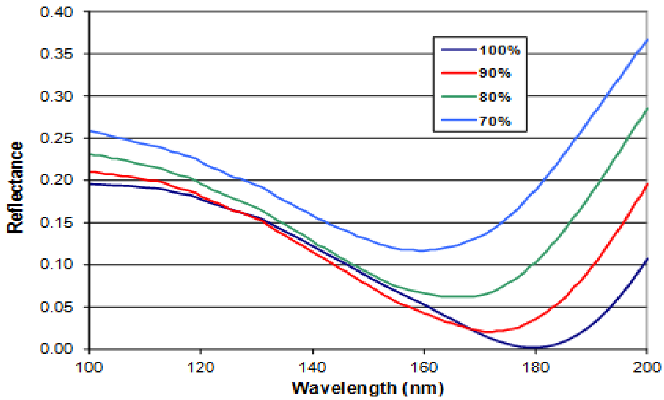


Figure 3.4: Calculated near normal incidence UV reflectance for a Mo/Si multilayer with a 7 nm Si_3N_4 *AR layer for various percentages of the bulk density.*

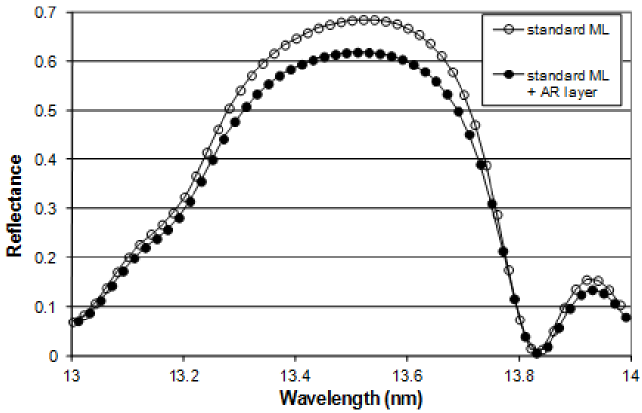


Figure 3.5: Measured near normal incidence EUV reflectance for a standard Mo/Si multilayer (open circles) and an AR coated multilayer (closed circles). The AR coating consisted of 7 nm silicon nitride.

The question if the observed reduction of out-of-band radiation results in a sufficient suppression can only be answered when the spectral characteristics of the source and the resist sensitivity are fully known. The ability of applying the AR layers without any change in the optical configuration of collector and projection optics enables adaptation of the suppression to the required level simply by selecting the number of optical elements equipped with an AR layer.

3.5 Conclusions

We have shown that the UV reflectance of EUV multilayer mirrors can substantially be suppressed when the multilayer is covered with an anti-reflection layer. Generic calculations of the UV reflectance indicate the range of optical constants of possible anti-reflection layer materials, enabling us to select these materials from the tables of UV optical constants. The use of 7 nm silicon nitride on a standard Mo/Si multilayer showed a reduction of the UV reflectance by a factor of 10 around 165 nm, while the reflectance at λ =13.5 nm was only 6.6% (absolute) less than for a standard multilayer. Both the UV and the EUV reflectance measurements indicate that a reduced density of the deposited AR layer can be compensated by the layer thickness.

ACKNOWLEDGEMENTS

This work is part of the FOM Industrial Partnership Programmes ‘eXtreme UV Multilayer Optics (‘XMO’)’ and ‘Controlling photon and plasma induced processes at EUV optical surfaces (CP3E)’ of the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’ which is carried out under contract with Carl Zeiss SMT GmbH (Oberkochen, Germany), ASML (Veldhoven, the Netherlands) and the ‘Stichting voor Fundamenteel Onderzoek der Materie (FOM)’, the latter being financially supported by the ‘Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)’. All near normal reflectance measurements have been performed at the Radiometer Laboratory of the Physikalisch Technische Bundesanstalt (PTB) (Berlin, Germany).

REFERENCES CHAPTER 3

[1] E. Spiller, Soft X-ray optics, SPIE - The International Society for Optical Engineering, Bellingham, USA, 1994.

[2] V.Y. Banine, K.N. Koshelev, G. Swinkels, Physical processes in EUV sources for microlithography, J. Phys. D-Appl. Phys., 44 (2011) 18.

[3] E. Louis, A.E. Yakshin, T. Tsarfati, F. Bijkerk, Nanometer interface and materials control for multilayer EUV-optical applications, Progress in Surface Science, 86 (2011) 255-294.

[4] R. Stuik, F. Scholze, J. Tümmler, F. Bijkerk, Absolute calibration of a multilayer-based XUV diagnostic, Nuclear Instruments & Methods in Physics Research, Section A, 492 (2002) 305-316.

[5] J.M. Roberts, R.L. Bristol, T.R. Younkin, T.H. Fedynyshyn, D.K. Astolfi, A. Cabral, Sensitivity of EUV resists to out-of-band radiation, SPIE 72731W-13, (2009).

[6] L. Shmaenok, N.N. Salashchenko, V.I. Luchin, A.Y. Lopatin, N.N. Zybin, Sematech EUV source workshop, Barcelona, Spain, (2006).

[7] I.A. Artyukov, A.I. Fedorenko, V.V. Kondratenko, S.A. Yulin, A.V. Vinogradov, Soft X-ray submicron imaging experiments with nanosecond exposure, Optics Communications, 102 (1993) 401-406.

[8] P.P. Naulleau, W.C. Sweatt, D.A. Tichenor, Theoretical efficiency analysis of a condenser-embedded grating-based spectral purity filter for EUV lithography, Optics Communications, 214 (2002) 31-38.

[9] J.A. Liddle, F. Salmassi, P.P. Naulleau, E.M. Gullikson, Nanoscale topography control for the fabrication of advanced diffractive optics, Journal of Vacuum Science & Technology B, 21 (2003) 2980-2984.

[10] A.J.R. van den Boogaard, F.A. van Goor, E. Louis, F. Bijkerk, Wavelength separation from extreme ultraviolet mirrors using phaseshift reflection, Optics Letters, 37 (2012) 160-162.

[11] M.M.J.W. van Herpen, R.W.E. van de Kruijs, D.J.W. Klunder, E. Louis, A.E. Yakshin, S. Alonso van der Westen, F. Bijkerk, V. Banine, Spectral-purity-enhancing layer for multilayer mirrors, Optics Letters, 33 (2008) 560-562.

[12] E.D. Palik, ed., Handbook of Optical Constants of Solids, Academic Press, 1985.

[13] E.D. Palik, ed., Handbook of Optical Constants of Solids II, Academic Press, 1991.

[14] J. Tümmler, H. Blume, G. Brandt, J. Eden, B. Meyer, H. Scherr, F. Scholze, G. Ulm, Proc. SPIE 5037, (2003) 265.

[15] A. Gottwald, U. Kroth, M. Letz, H. Schoeppe, M. Richter, Proc. SPIE 5538, (2004) 157-164.

[16] D.L. Windt, IMD - Software for modelling the optical properties of multilayer films, Computers in Physics, 12 (1998) 360-370.

4 Mo/Si multilayers exposed to extreme photon fluxes

(Single shot damage mechanism of Mo/Si multilayer optics under intense pulsed XUV-exposure)

ABSTRACT

We investigated single shot damage of Mo/Si multilayer coatings exposed to the intense fs XUV radiation at the Free-electron LASer facility in Hamburg - FLASH. The interaction process was studied in-situ by XUV reflectometry, time resolved optical microscopy, and "post-mortem" by interference-polarizing optical microscopy (with Nomarski contrast), atomic force microscopy, and scanning transmission electron microcopy. An ultrafast molybdenum silicide formation due to enhanced atomic diffusion in melted silicon has been determined to be the key process in the damage mechanism. The influence of the energy diffusion on the damage process was estimated. The results are of significance for the design of multilayer optics for a new generation of pulsed (from atto- to nanosecond) XUV sources.

4.1 Introduction

The rapid development of a new generation of extreme ultraviolet (XUV) radiation sources providing ultrashort (from atto- to nanoseconds) pulses creates new challenges for optics. Instruments, like free-electron lasers (FELs) [1-4], higher harmonic generating sources (HHG) [5,6], high-energy coherent sources based on laser plasmas [7] and capillary discharge lasers [8] produce pulses of very high intensity which may induce radiation damage in optical coatings. This may be a limiting factor for many scientific and industrial applications. Therefore, for a proper design of optics for current and future XUV light sources, it is crucial to understand the physical mechanisms leading to radiation damage. It is especially important for multilayer coated mirrors where the absorbed energy density is the highest when used at the resonant angle.

Multilayer coated optics are promising candidates for optical schemes at next generation XUV light sources. They were used in "front-line" experiments like XUV time resolved holography as a part of the imaging system [9], as diffraction limited XUV beam focusing optics for warm dense matter creation [10] and as a part of the delay line for one color pump and probe studies on XUV transmission of solids [11]. Moreover, this kind of optics is nowadays a standard for control of XUV and soft X-ray radiation in many fields of science and technology [12-14]. They can fulfill the extreme requirements in terms of figure errors and roughness, wavefront preservation, and stability in the XUV and soft x-ray regime. They have experienced a considerable technology boost due to the application in advanced photolithography. As a result, very stable, high reflectance coatings were developed [15]. FOM Rijnhuizen achieved the world record of reflectivity of over 70% for 13.5 nm at normal incidence [16]. Currently the know-how is used for the development of robust high reflectance multilayer optics that are stable even at enhanced temperatures and under high XUV flux irradiation [17, 18].

The photon flux from new generation XUV light sources is extremely high. In the case of the Free-electron LASer in Hamburg, FLASH, operating in the EUV and XUV regime (primary wavelength range from 40 to 6.7 nm), the ~10 - 25 fs long pulses have an energy of up to 100 μJ [1]. For a 4 mm beam spot diameter on the optics this corresponds to a radiation intensity of almost 10^{11} W/cm^2. This is at least 6 orders of magnitude higher than in a typical lithography application. Damage or even destruction of the optics can be expected. Moreover, for some applications the mirrors have to be placed in the focused beam [9,11] and the intensity on the optics can reach a value of 10^{14} W/cm^2. Under such conditions the optical properties of the reflecting elements could be changed already during the pulse and the mirror would fail to work [19, 20]. These two effects, permanent damage of the coatings and change of the optical properties of materials under high intensity XUV irradiation, can limit the performance of the multilayer optics.

Due to limited access to new sources the permanent damage mechanisms were only selectively studied until now. Basic inorganic and organic solids [21-24], single layer coatings [24, 25] and Si/C multilayer systems [19] were examined. In a simple model the radiation is absorbed by the electron gas in the surface layer of the sample. The electron system thermalizes very quickly (< 100 fs) at high temperatures, at which its optical properties may be changed compared to a cold material. At a picosecond time scale the electron gas cools down by heat transfer to the lattice and by energy diffusion. If the temperature of the lattice reaches the phase transition point, damage should occur. The depth of the damaged volume may depend on the thermal diffusion in the lattice, which occurs on a nanosecond time scale. In most cases the estimated energy density at the observed phase

transition point corresponded to melting. In case of PMMA and amorphous carbon, damage thresholds below the melting point were observed, explained as non-thermal desorption [23] and graphitization [25], respectively.
On the other hand, sub-melting threshold damage was reported for Mo/Si multilayer systems during thermal annealing. Already above 325°C enhanced interlayer atomic diffusion and formation of molybdenum silicide occurs [26-29]. The time constant for this process in annealing experiments is hours at the threshold temperature. With increasing temperature the atom mobility increases and the diffusion process speeds up (at ~600°C it takes less than 1 minute to almost completely intermix the Mo and Si atoms). Apart from the temperature, the duration of the damage process is strongly dependent on the heat rate and thickness of the layers [30]. According to our best knowledge it has never been studied on the time scale shorter than milliseconds for temperatures above the melting point of amorphous silicon [30] and minutes at temperatures below the melting point of amorphous silicon [26-29]. Thus no existing experimental results can help in predicting the damage threshold for multilayer optics at new generation XUV light sources.
The goal of this chapter is to define the mechanisms responsible for the radiation damage in Mo/Si multilayer systems exposed to an intense ultrashort pulse and to estimate the influence of the energy diffusion. The motivation for these studies is optics design for new generation of XUV light sources as well as fundamental understanding of the ultrafast processes that occur in the layers and at the interfaces at intense photon loads.

4.2 Experimental

We investigated a Mo/Si multilayer coating, deposited on superpolished Si substrate, a typical mirror as used for XUV lithography. The multilayer was deposited by e-beam evaporation in a UHV background of 1×10^{-8} mbar, with post-deposition smoothing using low energy ion treatment [31-35]. The sample was pre-characterized by means of X-ray and XUV reflectometry. The first technique provided information on the layered structure, including layer thicknesses, multilayer period, and roughness, and the latter technique determined the multilayer performance, i.e. angular resolved reflectivity of the multilayer for s-polarized light at 13.5 nm for low (non-destructive) irradiation intensities. From these measurements, the performance of the multilayer for any polarization and angle can then be predicted by means of simulations with the software package IMD [36]. The multilayer consisted of 50 bilayers of Mo and Si, with a periodicity of 7.96 nm and Mo layer thickness of 40%, optimized for maximum reflectance. The resonant angle and maximum reflectance for p-polarized light were determined to be 29.0 degrees off-normal incidence and 45%, respectively.

The sample was irradiated at the FLASH facility in Hamburg, Germany [1, 37]. The radiation wavelength was 13.5 ± 0.1 nm and the XUV pulse duration was ~10 fs (FWHM). The experimental setup, shown in Figure 4.1, was similar to the one used in ref. [38] at the first short wavelength free electron laser, TTF FEL. The sample was at resonant angle with respect to the incident photon beam which was p-polarized. The energy fluctuated from pulse to pulse in the range of 0.01 – 1 µJ and was measured with a gas monitor detector [39]. The radiation was focused with a grazing incidence carbon-coated ellipsoidal mirror to a spot size of 66 ± 3 µm^2 at the focal length of 2 m. To obtain a regular beam shape, a 3 mm diameter circular aperture in front of the focusing mirror was used. Most of the experiments were performed in "high intensity" mode, with the sample in the focus of the beam. For the given energy fluctuation, this mode corresponds to a beam fluence range of ~10 – 1000 mJ/cm^2. In addition, for the purpose of reflectance studies, lower intensity measurements were performed with the sample placed ~70 mm out of focus, corresponding to a ~15000 µm^2 spot area and a fluence range of 0.05 – 5 mJ/cm^2 for the same energy range. The sample was irradiated with ~70 pulses in single shot mode, i.e., after each irradiation the sample was moved and was irradiated at an unperturbed position. The reflected radiation intensity was measured with a photodiode placed at ~140 mm distance from the sample. To avoid diode saturation, it was coated with 350 nm molybdenum and 500 nm silicon layers and in addition it was preceded by a 0.28 µm thick aluminum foil attenuator. To determine the absolute reflectance the filter/diode combination was characterized using the direct beam.

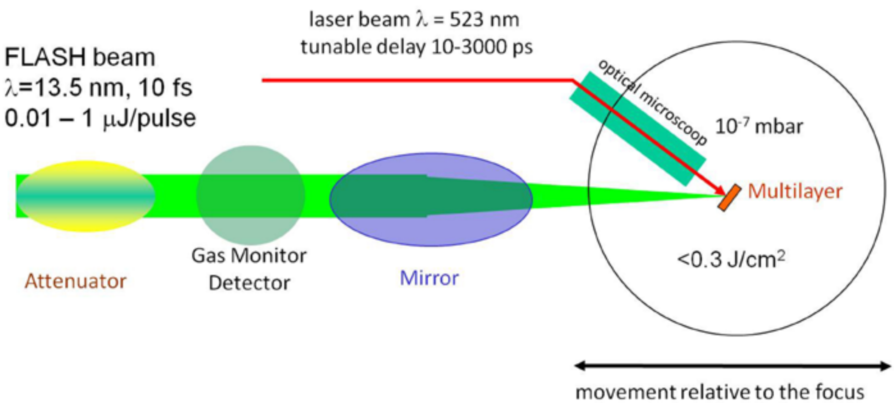


Figure 4.1: Scheme of the experimental set up for exposing the multilayers at FLASH as described in [38] and [40].

The irradiation spots were investigated "post-mortem" with different techniques: interference-polarizing optical microscopy (with Nomarski contrast) - sensitive to changes of morphology and/or material's optical properties, atomic force microscopy (AFM) – creating a 2D map of the crater depths and scanning transmission electron microscopy (STEM) – to analyze the structural changes below the crater surface.

An additional experiment was performed to study the dynamics of the irradiated system. Time resolved microscopy was used in the XUV pump – optical probe mode. The experimental setup, the optical microscope extension in Figure 4.1, is similar to the one described in [40]. The XUV pulse excited the surface of the multilayer coated sample. A time-delayed optical probe pulse of 800 nm wavelength and 100 fs duration, synchronized to the FEL with accuracy better than 2 ps, served as illumination for an optical microscope. This setup allows to measure the evolution of the optical pulse reflectivity of the XUV irradiated surfaces with temporal and spatial resolution.

4.3 Results

4.3.1 Reflectivity

XUV reflectivity measurements of the Mo/Si multilayer were carried out using 13.5 nm radiation in three different intensity regimes. The reflectivity at low-intensity was measured at the Center for X-Ray Optics, Berkeley, USA (CXRO), using s-polarized radiation from the Advance Light Source (ALS), for angles ranging from 10° - 50° from normal and transformed to p-polarized by means of IMD simulations. The reflectivity measurements at middle and high intensities were performed at FLASH at 28.2 ± 0.3° from normal. The reflectivity of p-polarized radiation at this angle is shown in Table 4.1 for all three intensity regimes.

Facility	Intensity range [W/cm^2]	Reflectivity [%]
ALS at CXRO	1×10^{2}	42.0 ± 2.0
FLASH (low-intensity regime)	1×10^{11}	43.8 ± 0.8
FLASH (high-intensity regime)	5×10^{13}	42.7 ± 0.7

Table 4.1: Reflectivity of a Mo/Si multilayer, measured at 28.2 ± 0.2° off-normal incidence using 13.5 nm radiation.

It is constant within the error-bars over the entire intensity-range investigated, from 100 W/cm^2 to approx. 5×10^{13} W/cm^2 corresponding to a fluence of 500 mJ/cm^2 in the 10 fs pulses. This is in agreement with theoretical models, where significant change of the reflectivity of femtosecond duration pulses is predicted only for fluences above 20 J/cm^2 [20].

4.3.2 Interference-polarizing microscopy

From each irradiated spot an image was made with an interference-polarizing microscope. Initially the damage was defined as radiation induced surface changes observable in the image, corresponding to changes in surface morphology and/or material's optical properties. In Fig. 4.2 the damaged area is plotted against the logarithm of the pulse energy. A threshold behaviour can be observed. The single shot damage threshold, determined [22, 41] from the intersection of the line fitted to the experimental data points with positive damage area with the x-axis is 45 ± 7 mJ/cm^2.

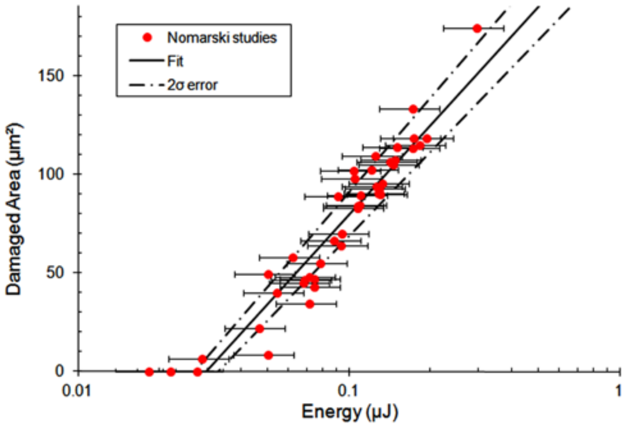


Figure 4.2: Damaged area of the Mo/Si multilayer plotted against the pulse energy. The red dots are the experimental results, the solid line is the best fit of the experimental data points with positive damage area and the dashed lines represent the 2σ error of the fit.

4.3.3 Atomic force microscopy

The morphology of the Mo/Si multilayer surface after irradiation was further investigated with atomic force microscopy. Two types of damage are observed for fluences between 45 and 125 mJ/cm^2, further named as stage 1 and stage 2 of the damage (Fig. 4.3). In the first stage, a smooth crater is formed and its area matches the area of the damage observed with the interference-polarizing optical microscope. The crater depth ranges from a few nanometers for fluences just above damage threshold to more than 30 nm at 65 mJ/cm^2. At fluences above 65 mJ/cm^2 a hill is formed in the middle of the crater (stage 2). The depth of the crater increases for fluences up to ~ 125 mJ/cm^2, when the maximum crater depth of 68 nm is obtained (the influence of the hill formation on the crater profile is considered).

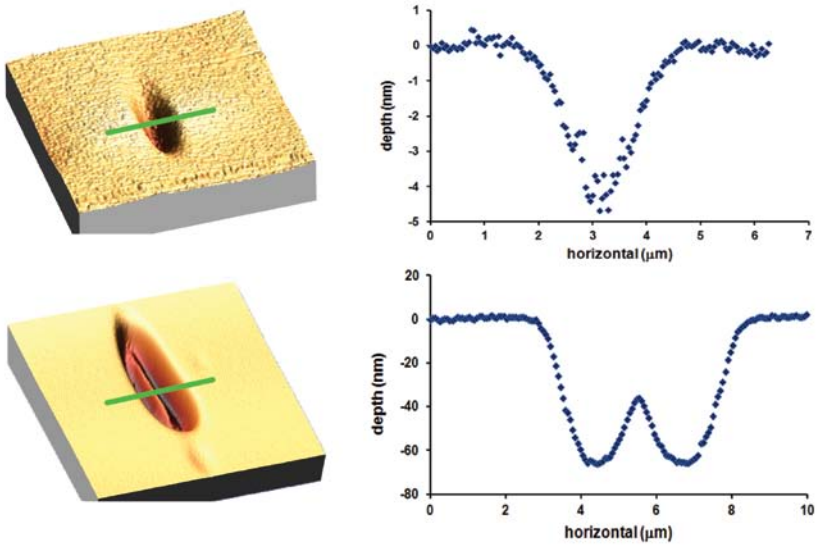


Figure 4.3: Examples of the damage at stage 1 (top) and stage 2 (bottom). On the left an AFM depth map of the surface is shown and on the right, the depth-profiles along the green lines.

4.3.4 Scanning transmission electron microscopy

Scanning transmission electron microscopy (STEM) was used to analyze the structural changes below the crater surface. A 60 nm thin slab along the green line marked in the AFM map (Fig. 4.3) was cut from the multilayer by means of a focused ion beam and subsequent argon beam polishing. STEM images at different positions with respect to the crater borders were created with variable magnifications. The results are shown in Fig. 4.4 (a-e).

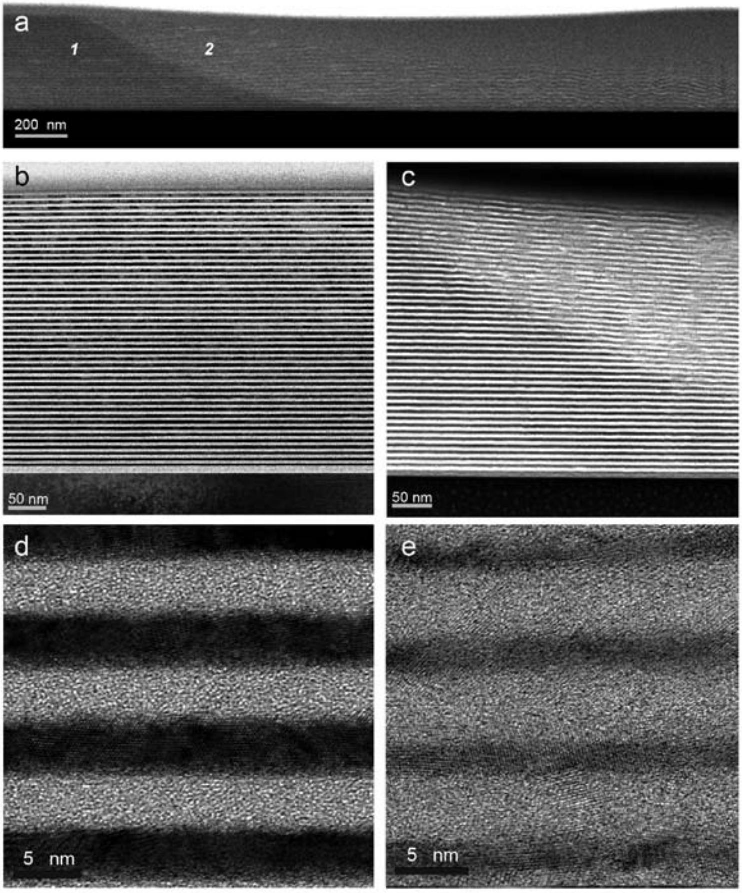


Figure 4.4. STEM images of different spots along the crater cross-section made with different magnifications. Half of the damaged cross section is shown in (a). The undamaged region (1) is magnified in (b) and (d), the damaged region (2) in (c) and (e). Images (a), (b), and (c) were taken in dark field mode (the darker the image, the lower the density) and images (d) and (e) in bright field mode.

The analysis of the STEM together with its extension, EDX mass spectroscopy, shows that, similar to the AFM analysis, three regions can be distinguished: undamaged multilayer (region 1 in Fig. 4.4(a)), a fully polycrystalline region where the Mo layers are considerably thinner than the initial ones (region 2), and a region where Mo and Si atoms have fully interdiffused (below the crater-center, the right end of Fig. 4.4(a)). In Fig. 4.4(b) and 4.4(d) the undamaged region is magnified. A clear layer structure can be seen with sharp interfaces between the polycrystalline Mo and amorphous Si layers. In Fig. 4.4(c) an apparent border, similar to the one observed in AFM and optical microscopy pictures, separating the undamaged (1) and the damaged region (2) is shown. The magnified image of the damaged region is presented in Fig. 4.4(e). The polycrystalline / amorphous layer-structure of region 1 is abruptly changed into the fully polycrystalline layered structure of region 2, with the thickness of Mo being just a fraction of its thickness in the undamaged region, clearly indicating large layer interdiffusion and subsequent (polycrystalline) silicide formation. For even higher fluences, below the hill in the crater center, a fully intermixed amorphous structure can be observed. But, since the main interest of authors is the damage mechanism at the lowest threshold, detailed analysis of this fluence range is beyond the scope of this paper.

4.3.5 Time resolved microscopy

Time resolved microscopy was performed to study the dynamics of the Mo/Si multilayer system excited just above the damage threshold. The optical pulse (probe) delay was fixed at 10 ps, appropriate to examine the initial lattice temperature after relaxation of most of the energy absorbed by the electron gas to the atoms. Increase of the visible light reflectance in the exited region was observed (see Fig. 4.5). The rise of reflectivity has sharp edges which overlap with the crater border measured a long time after the XUV pulse (after full development of the damage process) using the same microscope. It saturates in the crater center at the maximum value 35% ± 5% larger than the reference outside the irradiation spot. The threshold behavior of the reflectance indicates that its rise is caused by an abrupt change of the optical properties of at least one of the materials. Molybdenum has a much higher phase transition temperature than amorphous silicon and as a metal it is characterized by only small changes of the optical properties when heated. On the other hand, melting of amorphous silicon changes its conductivity from 1.5 W/m-K (insulating) to 62 W/m-K (metalic), and consequently the imaginary part of the refractive index, k, increases abruptly [42]. IMD simulations of the probe beam reflectivity were performed and the best fit to the experimental data at saturation in the center of the crater was obtained for k = 1.85 ± 0.2, which is a typical value for metals [43]. This implies melting of the amorphous silicon layers at a time scale shorter than 10 ps.

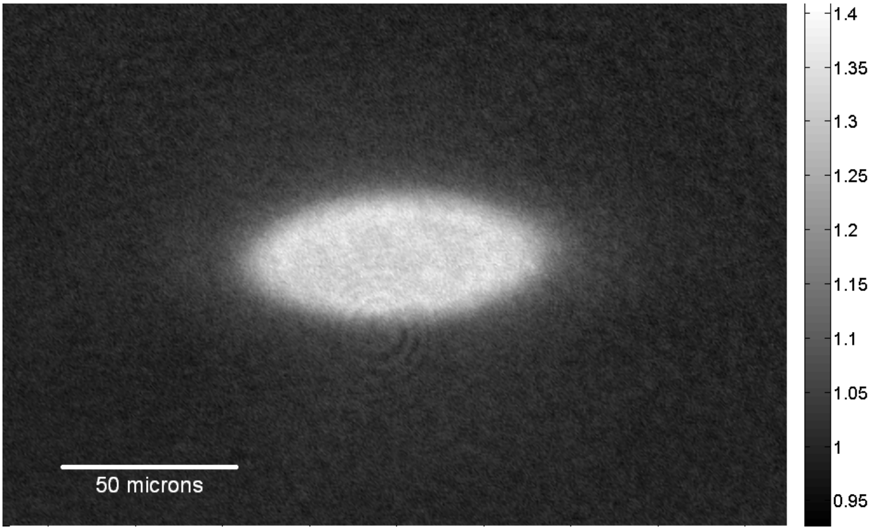


Fig. 4.5: 2-D map of the reflectance of the probe pulse (10 ps delay) after excitation with a femtosecond XUV pulse (pump) of maximum fluence just above the damage threshold. The reflectance of the probe pulse is normalized to the reflectance of the unexcited region. The intensity color scale of the normalized reflectance is shown on the right.

4.4 Discussion

All the experimental data indicate that the leading damage mechanism for Mo/Si multilayer coating, irradiated with intense femtosecond XUV radiation, is molybdenum silicide formation at the interfaces. This process has been observed previously in dedicated thermal annealing experiments. In such experiments, if the sample is heated to 325°C, the timescale of the diffusion process leading to almost complete intermixing of the layers is typically several hours [26-29], while at ~ 600°C it is measured to be shorter than a minute. Now let us consider the timescale of diffusion in our femtosecond experiments. Silicide formation can only take place if molybdenum or silicon atoms diffuse through the interface. The atomic interdiffusivity through the interfaces of a Mo/Si multilayer (D) is $(4 \pm 2) \times 10^{-4}\ nm^2/s$ at 530°C, and from Arrhenius's law, approximately $1.5 \times 10^{-3}\ nm^2/s$ just below the melting temperature of silicon [44]. One can estimate the effect of atomic diffusion in case the sample is heated up to a temperature slightly below the melting point of amorphous silicon for a very short time. Assuming that the heat conductance to the Si substrate cools the sample down to room temperature in a time shorter than 1 μs, the diffusion length can be calculated to be $(4D \times t)^{1/2} = 5 \times 10^{-5}$ nm, which is significantly smaller than the size of atoms. Hence, atomic diffusion and therefore silicide-formation can be neglected below the melting temperature of amorphous silicon at this relatively short time scale.

However, the pump and probe data show that the surface of our sample is melted in a time shorter than 10 ps after the excitation with the XUV pulse, and at an intensity above the damage threshold. In liquid silicon, the atomic diffusion coefficient is in the order of 10^{10} nm^2/s [45] which is ~15 orders of magnitude higher than in the amorphous phase. In this case the molybdenum atoms can penetrate the entire Si layer from both sides on the time scale of sub nanoseconds (much shorter than silicon resolidification time) and form a molybdenum silicide. The dependency of silicide-formation on melting implies the threshold behavior of the damage which can be observed in all experimental data, apart from reflectivity measurements that are, obviously, not sensitive to processes occurring on a time scale longer than the pulse duration.

There are various known stoichiometries of molybdenum silicide. The density of all of them is larger than the averaged density of Mo and Si atoms, resulting in a compaction of the multilayer structure upon silicide formation. The AFM data together with the STEM profile show that in case of the FLASH irradiated sample the compaction was ~17% (68 nm maximum depth of a crater for 50 bilayers, 7.96 nm thick each). This corresponds to the expected compaction if all silicon atoms are consumed for the formation of a $MoSi_2$ compound [26], which is the most thermodynamically stable state of all molybdenum silicides [46]. It has a formation enthalpy of -132 kJ/mol and has also been observed to be the final state of silicide-formation in the thermal annealing experiments for similar Mo/Si multilayers.

After the silicides are formed, energy is released due to the negative formation enthalpy of $MoSi_2$: the heat of formation of $MoSi_2$ is high enough to increase the mean temperature in the reaction volume (Mo/Si bilayer) from 350°C to just above the melting temperature of amorphous silicon. It serves as an energy reservoir for melting deeper layers and consequently their transformation into silicides. The number of the melted amorphous silicon layers (and consequently the total compaction of the multilayer) is dependent on (a) the initial temperature profile, defined by electric field intensity distribution in the multilayer and the optical constants, and (b) the energy dissipation process, which is mainly defined by the materials thermodynamic properties.
The XUV absorption profile in the multilayer can be calculated with the use of the optical parameters of Mo and Si. These parameters can, in general, be temperature-dependent. However, as described before, the optical parameters don't

change significantly during the pulse and room-temperature values [47] can be used. Subsequently, the temperature profile in the multilayer can be calculated from the heat capacities of Mo and amorphous silicon [48,49], the melting temperature (1250 K [49,50]) and the latent heat (33.7 kJ/mol [51,52]) of amorphous silicon in a thin film.

Because of the heat of formation, silicide-formation would be an almost self-sustained reaction already at the threshold fluence if one neglects heat dissipation (transport) to the substrate. But this assumption is not valid in the studied system. Using the heat-capacities of thin film molybdenum, amorphous and liquid silicon [53-59], one can calculate the ratio of the heat conductivities in two regions: conducting (where temperature is higher than the melting temperature of amorphous silicon) and insulating (solid silicon). The dissipated fraction of the energy is directly related to the heat conductivity ratio in both regions. No heat dissipation corresponds to a ratio of 0, while no heat confinement at all corresponds to a ratio of 1. In the studied case it is in the range of 0.05 - 0.15. Consequently, most but not all excess energy is confined in the conducting region and is therefore used primarily to melt adjacent silicon layers at the conducting-insulating interface.

One can calculate how much energy is needed to create silicides in a given number of bilayers. For that purpose the energy balance was calculated taking into account the absorbed energy profile, the energy released due to silicides formation, the energy needed to heat the silicon and molybdenum to a-Si melting temperature (including the latent heat of a-Si) and the energy loss due to heat dissipation into the substrate. It was assumed that each melted silicon layer is fully transformed into silicides. Since the deposited energy is defined by the incident radiation fluence, and the absolute compaction by the volume of the silicides formed, the fluence dependent compaction of the irradiated multilayer can be calculated. In Fig. 4.6 results of the calculations for different fractions of dissipated energy (0%, 10%, 15% and 20%) are shown. The damage threshold obtained from the calculations for each of the dissipation percentages is the same and is close (within error bars) to the experimentally obtained value (lines in Fig. 4.6 cross the x axis in the same point). On the other hand the predicted crater depth for fluences above the damage threshold varies significantly for different energy losses and the experimental data coincide very well with a narrow range of dissipation percentage from 10% to 20%. To calculate more precisely the heat dissipation for this multilayer, one has to solve the heat and atomic diffusion equation set. Due to the many boundary conditions, and the time-dependent heat release due to silicides-formation, advanced computer simulations are required. This goes beyond the scope of this article and will be described in the future work.

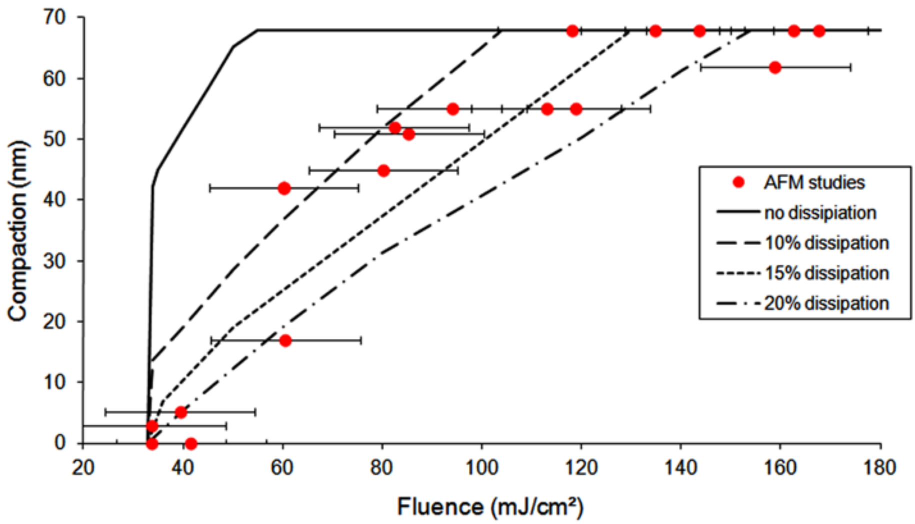


Fig. 4.6: Compaction as function of fluence. The dots are experimental values obtained from AFM studies. The lines are obtained from thermal dynamic calculations by assuming different dissipation percentages of the excess energy from conducting to insulating region (see detailed description in text).

4.5 Conclusions

We exposed standard Mo/Si multilayers to intense femtosecond pulses at the FLASH (XUV free-electron laser) facility in Hamburg, Germany. We investigated both the change of optical properties during the pulse and the single shot damage threshold of the multilayer.

Up to a fluence of 500 mJ/cm^2 no measurable effect on the multilayer reflectance is observed, indicating no significant change of the optical properties during the pulse. This is in agreement with theoretical predictions.

Permanent damage of the multilayer occurs on a much longer timescale than pulse duration and, consequently, reflection process. The single-shot damage threshold of the multilayer is determined to be 45 ± 7 mJ/cm^2. Silicide-formation was found as the leading mechanism for irreversible structural changes for fluences at and just above the damage threshold. It shows great similarity with the damage mechanism during thermal annealing experiments where silicide formation is caused by atomic diffusion in solids. However, in case of energy deposition by an intense ultrashort XUV pulse, the multilayer is hot for just a short time (typically few ns). In this timescale, atomic diffusion in amorphous silicon or solid molybdenum is negligible. Atomic diffusion occurs only when silicon is melted, in which case the atomic diffusivity is enhanced by 15 orders of magnitude. Molybdenum atoms diffuse from both sides into the melted silicon layer and form the energetically stable $MoSi_2$. Therefore, when irradiated with a femtosecond XUV pulse the critical temperature at which damage of the multilayer occurs is increased from 325°C in annealing experiments to 980°C - the melting temperature of a thin amorphous silicon film. In parallel, the timescale of the damage process is decreased from hours (at the threshold temperature) to nanoseconds in the present study. Furthermore, the energy diffusion is not significant for the single shot damage threshold, although, its effect on the crater profile for fluences above the damage threshold is observable.

The results show that standard Mo/Si multilayer optics can be used at the femtosecond XUV light sources for fluences up to 45 ± 7 mJ/cm^2 under the condition that the repetition rate of the source allows the deposited heat to dissipate between subsequent pulses (approx. 100 kHz or less). The nature of the damage mechanism (atomic diffusion in melted silicon) allows one to extrapolate the results for other 4th generation light sources with pulses longer than FLASH, up to at least a few hundred picoseconds which is the time scale of atomic diffusion in a single silicon layer.

ACKNOWLEDGEMENTS

Irradiation with FLASH has been performed within the framework of the Peak-Brightness-Collaboration [project II-20022049 EC]. Support from the PBC and the operators of the FLASH facility are gratefully acknowledged. This work has been partially supported by the Foundation for Fundamental Research on Matter (Stichting voor Fundamenteel Onderzoek der Materie, FOM) and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO), the Ministry of Science and Higher Education of Poland, SPB nr. DESY/68/2007, the Czech Ministry of Education from the National Research Centers program (Projects LC510 and LC528) and program INGO (Grant LA08024), Czech Science Foundation (Grant 202/08/H057), by Academy of Sciences of the Czech Republic (Grants Z10100523, IAA400100701, and KAN300100702), by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 and by the German Federal Ministry of Education and Research within the FSP 301 FLASH: Interaction of intense XUV-pulses with condensed matter (grant 05 KS7PG1).

REFERENCES AND LINKS CHAPTER 4

[1] W. Ackermann, G. Asova, V. Ayvazyan, et al., “Operation of a free-electron laser from the extreme ultraviolet to the water window,” Nature Photonics 1, 336-342 (2007).

[2] http://flash.desy.de/

[3] http://www-xfel.spring8.or.jp/

[4] http://www.elettra.trieste.it/FERMI/

[5] P. Balcou, R. Haroutunian, S. Sebban, G. Grillon, A. Rousse, G. Mullot, J. P. Chambaret, G. Rey, A. Antonetti, D. Hulin, L. Roos, D. Descamps, M. B. Gaarde, A. L'Huillier, E. Constant, E. Mevel, D. von der Linde, A. Orisch, A. Tarasevitch, U. Teubner , D. Klopfel, and W. Theobald, “High-order-harmonic generation: towards laser-induced phase-matching control and relativistic effects,” Appl. Phys. 74, 509-515 (2002).

[6] S. Kazamias, D. Douillet, F.Weihe, C. Valentin, A. Rousse, S. Sebban, G. Grillon, F. Auge´, D. Hulin, and Ph. Balcou., ”Global optimization of high harmonic generation”, Phys. Rev. Lett. 90, 193901 (2003).

[7] B. Rus, T. Mocek, A. R. Präg, M. Kozlová, G. Jamelot, A. Carillon, D. Ros, D. Joyeux, and D. Phalippou, “Multi-millijoule, highly coherent X-ray laser at 21 nm operating in deep saturation through double-pass amplification,” Phys. Rev. A 66, 063806 (2002).

[8] S. Heinbuch, M. Grisham, D. Martz, and J. J. Rocca,., “Demonstration of a desk-top size high repetition rate soft x-ray laser,” Opt. Express 13, 4050-4055 (2005).

[9] H.N. Chapman, S.P. Hau-Riege, M. J. Bogan, S. Bajt, A. Barty, S. Boutet, S. Marchesini, M. Frank, B.W. Woods, W.H. Benner, R.A. London, U. Rohner, A. Szöke, E. Spiller, T. Möller, Ch. Bostedt, D. A. Shapiro, M. Kuhlmann, R. Treusch, E. Plönjes, F. Burmeister, M. Bergh, C. Caleman, G. Huldt, M.M. Seibert & J. Hajdu, "Femtosecond time-delay X-ray holography," Nature 448 676-679 (2007)

[10] B. Nagler, U. Zastrau, R. Fäustlin, S. M. Vinko, T. Whitcher, A. J. Nelson, R. Sobierajski, J. Chalupsky, E. Abreu, S. Bajt, T. Bornath, T. Burian, H. Chapman, J. Cihelka, T. Döppner, S. Düsterer, T. Dzelzainis, M. Fajardo, E. Förster, C. Fortmann, E. J. Galtier, S. H. Glenzer, S. Göde, G. Gregori, V. Hajkova, P. Heimann, L. Juha, M. Jurek, F. Y. Khattak, A. R. Khorsand, D. Klinger, M. Kozlova, J. Krzywinski, T. Laarmann, H. J. Lee, R. Lee, K.-H. Meiwes-Broer, P. Mercere, W. J. Murphy, A. Przystawik, R. Redmer, H. Reinholz, D. Riley, G. Röpke, F. Rosmej, K. Saks, R.Schott, R. Thiele, J. Tiggesbäumker, S. Toleikis, T. Tschentscher, I. Uschmann, H. J. Vollmer, and J. Wark "Transparency induced in solid density aluminum by ultra-intense XUV Radiation" , Nature Physics 5, 693 (2009)

[11] R. Sobierajski, M. Jurek, D.Klinger, J. Krzywinski, R., J.B. Pelka, H. Chapman, S.P. Hau-Riege, R. London, L. Juha, J. Chalupsky, J. Cihelka, K. Tiedtke, S.Toleikis, H. Wabnitz, U. Jastrow, K.Sokolowski-Tinten, N. Stojanovic, "Evolution of optical properties of surfaces under influence of ultra short pulses of intense EUV radiation," HASYLAB Annual Report 2006, 395-396 (2006)

[12] D. Attwood, Soft x-rays and extreme ultraviolet radiation: Principles and Applications (Cambridge University Press, 2000).

[13] E. Spiller, Soft X-ray optics (SPIE, Bellingham, 1994).

[14] F. Bijkerk, S. A. van der Westen, C. Bruineman, R. Huiting, R. de Bruijn R. Stuik, „Flying Circus EUV Source Metrology and Source Development Assessment" in EUV sources for lithography V. Bakshi, ed (ISMT, Austin, TX, 2006).

[15] E. Louis, E. Zoethout, R. W. E. van de Kruijs, I. Nedelcu, A. E. Yakshin, S. A. van der Westen, T. Tsarfati, F. Bijkerk, H. Enkisch, S.Muellender, "Multilayer coatings for the EUVL process development tool," Proc. SPIE 5751, 1170-1177 (2005).

[16] A.E. Yakshin, R.W.E. van de Kruijs, I. Nedelcu, E. Zoethout, E. Louis, F. Bijkerk, H. Enkisch and S. Müllender, "Enhanced reflectance of interface engineered Mo/Si multilayers produced by thermal particle deposition," SPIE 6517 (2007)

[17] S.A. Bajt and D. G. Stearns, „High-temperature stability multilayers for extreme-ultraviolet condenser optics," Applied Optics 44, 7735-7743 (2005)

[18] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin and F. Bijkerk, "Microstructure of Mo/Si multilayers with B4C diffusion barrier layers," Appl. Opt. 48, 155-160 (2009)

[19] S. P. Hau-Riege, H. N. Chapman, J. Krzywinski, R. Sobierajski, S. Bajt, R. A. London, M. Bergh, C. Caleman, R. Nietubyc, L. Juha, J. Kuba, E. Spiller, S. Baker, R. Bionta, K. Sokolowski-Tinten. N. Stojanovic, B. Kjornrattanawanich, E. Gullikson, E. Plönjes, S. Toleikis, and T. Tschentscher, "Sub-nanometer scale measurements of the interaction of ultrafast soft x-ray

free-electron-laser pulses with matter," Phys. Rev. Lett. 98, 145502 (2007).

[20] S.P. Hau-Riege, R.A. London, H.N. Chapman, M. Bergh, "Soft-x-ray free-electron-laser interaction with material", Phys. Rev. E 76, 046403 (2007)

[21] S. P. Hau-Riege, R. A. London, R. M. Bionta, M. A. McKernan, S. L. Baker, J. Krzywinski, R. Sobierajski, R. Nietubyc, J. B. Pelka, M. Jurek, L. Juha, J. Chalupsky, J. Cihelka, V. Hajkova, A. Velyhan, J. Krasa, J. Kuba, K. Tiedtke, S. Toleikis, T. Tschentscher, H. Wabnitz, M. Bergh, C. Caleman, K. Sokolowski-Tinten, N. Stojanovic, U. Zastrau, "Damage threshold of inorganic solids under free-electron-laser irradiation at 32.5 nm wavelength," Appl. Phys. Lett. 90, 173128 (2007).

[22] J. Chalupský, L. Juha, J. Kuba, J. Cihelka, V. Hájková, S. Koptyaev, J. Krása, A. Velyhan, M. Bergh, C. Caleman, J. Hajdu, R. M. Bionta, H. Chapman, S. P. Hau-Riege, R. A. London, M. Jurek, J. Krzywinski, R. Nietubyc, J. B. Pelka, R. Sobierajski, J. Meyer-ter-Vehn, A. Tronnier, K. Sokolowski-Tinten, N. Stojanovic, K. Tiedtke, S. Toleikis, T. Tschentscher, H. Wabnitz, U. Zastrau, "Characteristics of focused soft X-ray free-electron laser beam determined by ablation of organic molecular solids," Opt. Exp. 15, 6036-6043 (2007).

[23] J. Chalupsky, L. Juha, V. Hájková, J. Cihelka, L. Vysín, J. Gautier, J. Hajdu, S. P. Hau-Riege, M. Jurek, J. Krzywinski, R. A. London, E. Papalazarou, J. B. Pelka, G. Rey, S. Sebban, R. Sobierajski, N. Stojanovic, K. Tiedtke, S. Toleikis, T. Tschentscher, C. Valentin, H. Wabnitz, and P. Zeitoun, "Non-thermal desorption/ablation of molecular solids induced by ultra-short soft x-ray pulses," Optics Express 17, 208-217 (2009).

[24] S. P. Hau-Riege, R. A. London, R. M. Bionta, D. Ryutov, R. Soufli, S. Bajt, M. A. McKernan, S. L. Baker, J. Krzywinski, R. Sobierajski, R. Nietubyc, D. Klinger, J. B. Pelka, M. Jurek, L. Juha, J. Chalupský, J. Cihelka, V. Hájková, A. Velyhan, J. Krása, K. Tiedtke, S. Toleikis, H. Wabnitz, M. Bergh, C. Caleman, and N. Timneanu, "Wavelength dependence of the damage threshold of inorganic materials under extreme-ultraviolet free-electron-laser irradiation", Appl. Phys. Lett. 95, 111104 (2009)

[25] J. Chalupský, V. Hájková, V. Altapova, T. Burian, A. J. Gleeson, L. Juha, M. Jurek, H. Sinn, M. Störmer, R. Sobierajski, K. Tiedtke, S. Toleikis, Th. Tschentscher, L. Vyšín, H. Wabnitz, and J. Gaudin "Damage of amorphous carbon induced by soft x-ray femtosecond pulses above and below the critical angle", Appl. Phys. Lett. 95, 031111 (2009)

[26] I. Nedelcu, R.W.E. van de Kruijs, A.E. Yakshin, and F. Bijkerk, "Thermally enhanced interdiffusion in Mo/Si multilayers," J. of Appl. Phys. 103, 083549 (2008).

[27] V. V. Kondratenko et al, "Thermal stability of soft x-ray Mo–Si and MoSi2-Si multilayer mirrors," Appl. Opt. 32, 1811-1816 (1993).

[28] J. M. Liang and L. J. Chen, „Interfacial reactions and thermal stability of ultrahigh vacuum deposited multilayered Mo/Si structures," J. Appl. Phys. 79, 4072 (1996).

[29] I. Nedelcu, R. W. E. van de Kruijs, A. E. Yakshin, and F. Bijkerk, "Temperature-dependent nanocrystal formation in Mo/Si multilayers," Phys. Rev. B 76, 245404 (2007).

[30] S.L. Kharatyan, H.A. Chatilyan, A.S. Mukasyan, D.A. Simonetti, and A. Varma ,"Effect of heat-

ing rate on kinetics of high-temperature reactions: Mo-Si system", AIChE J. 51, 261-270 (2005).

[31] H.J.Voorma, E. Louis, F. Bijkerk, and S. Abdali, "Angular and energy dependence of ion bombardment of Mo/Si multilayers," J. Appl. Phys. 82, 1876 (1997).

[32] E. Louis, A.E. Yakshin, P.C. Görts, S. Oestreich, R. Stuik, E.L.G. Maas, M.J.H. Kessels, F. Bijkerk, M. Haidl, S. Müllender, M. Mertin, D Schmitz, F. Scholze and G. Ulm, "Progress in Mo/Si multilayer coating technology for EUVL optics," SPIE 3997, 406 (2000).

[33] E. Louis, H.-J. Voorma, N.B. Koster, L.A. Shmaenok, F. Bijkerk, Yu.Ya. Platonov, S.Yu. Zuev, S.S. Andreev, E.A. Shamov and N.N. Salashenko, "Multilayer coated reflective optics for Extreme UV lithography," Microelectronic Engineering 27, 235-238 (1995)

[34] E. Louis, H.J. Voorma, N.B. Koster, L. Shmaenok, F. Bijkerk, R. Schlatmann, J. Verhoeven, Y.Y. Platonov, G.E. Vandorssen, H.A. Padmore, "Enhancement of reflectivity of multilayer mirrors for soft-x-ray projection lithography by temperature optimization and ion-bombardment" Microelectronic Engineering 23, 215-218 (1994)

[35] E. Louis , H.-J. Voorma, N.B. Koster, F. Bijkerk, Yu. Ya. Platonov, S.Yu. Zuev, S.S. Andreev, E.A. Shamov and N.N. Salashchenko "Multilayer coated reflective optics for Extreme UV lithography" Microelectronic Engineering 27, 235-238 (1995)

[36] D. L. Windt, "IMD—Software for modeling the optical properties of multilayer films," Comput. Phys. 12, 360-370 (1998).

[37] K. Tiedtke, A. Azima, N. von Bargen, L. Bittner, S. Bonfigt, S. Düsterer, B. Faatz, U. Frühling, M. Gensch, Ch. Gerth, N. Guerassimova, U. Hahn, T. Hans, M. Hesse, K. Honkavaar, U. Jastrow, P. Juranic, S. Kapitzki, B. Keitel, T. Kracht, M. Kuhlmann, W. B. Li, M. Martins, T. Nuñez, E. Plönjes, H. Redlin, E. L. Saldin, E. A. Schneidmiller, J. R. Schneider, S. Schreiber, N. Stojanovic, F. Tavella, S. Toleikis, R. Treusch, H. Weigelt, M. Wellhöfer, H. Wabnitz, M. V. Yurkov, and J. Feldhaus, „The soft x-ray free-electron laser FLASH at DESY: beamlines, diagnostics and end stations", New Journal of Physics 11, 023029 (2009).

[38] R. Sobierajski et al,, „Experimental station to study the interaction of intense femtosecond vacuum ultraviolet pulses with matter at TTF1 free electron laser," Rev. Sci. Instrum. 76, 013909 (2005).

[39] K. Tiedtke, J. Feldhaus, U. Hahn, U. Jastrow, T. Nunez, T. Tschentscher, S.V. Bobashev, A.A. Sorokin, J.B. Hastings, S. Möller, L. Cibik, A. Gottwald, A. Hoehl, U. Kroth, M. Krumrey, H. Schöppe, G. Ulm, and M. Richter, "Gas detectors for x-ray lasers", J. Appl. Phys. 103, 094511 (2008)

[40] N. Stojanovic, D. von der Linde, K. Sokolowski-Tinten, U. Zastrau, F. Perner, E. Foerster, R. Sobierajski, R. Nietubyc, M. Jurek, D. Klinger, J. Pelka, J. Krzywinski, L. Juha, J. Cihelka, A. Velyhan, S. Koptyaev, V. Hajkova, J. Chalupsky, J. Kuba, T. Tschentscher, S. Toleikis, S. Duesterer, H. Redlin., Ablation of solids using a femtosecond extreme ultraviolet free electron laser", Appl. Phys. Lett. 89, 241909, (2006)

[41] J.M. Liu, "Simple technique for measurements of pulsed Gaussian-beam spot sizes," Opt. Lett 7, 196-198 (1982).

[42] K. Sokolowski-Tinten, J. Bialkowski and D. von der Linde, "Ultrafast laser-induced order-disorder transitions in semiconductors." Physical Review B 51 14186 (1995).

[43] Handbook of optical constants of solids, E.D. Palik ed., (San Diego 1998)

[44] P. Jonnard et al, “Physico-chemical and X-ray optical characterizations of a Mo/Si multilayer interferential mirror upon annealing,” Surface Science 589 164-172 (2005).

[45] J.R. Chelikowsky, N. Troullier, and N. Binggeli, “First-principles simulation of liquid silicon using Langevin dynamics with quantum interatomic forces,” Phys. Rev. B 49, 114-119 (1994).

[46] F.R. de Boer, R. Boom, W.C.M. Mattens, A.R. Miedema, and A.K. Niessen, Cohesion in metals (North Holland, 1988).

[47] B.L. Henke, E.M. Gullikson, and J.C. Davis, “X-ray interactions: Photoabsorption, scattering, transmission, and reflection at E = 50-30,000 eV, Z = 1-92,” Atomic Data and Nuclear Data Tables 54, 181-342 (1993).

[48] D.R. Lide, CRC Handbook of Chemistry and Physics, 89th ed. (CRC, 2008).

[49] K.H. Tsang, H.W. Kui, K.P. Chik, “Calorimetric studies of the heat capacity and relaxation of amorphous Si prepared by electron beam evaporation,” J. Appl. Phys. 74, 4932 (1993).

[50] P. Grimaldi, P. Baeri, M. A. Malvezzi and C. Sirtori, “Thermodynamic properties of amorphous silicon investigated by pulsed laser heating,” Int J of Thermophys. 13, 141-151 (1992).

[51] S. Roorda, S. Doorn, W.C. Sinke, P.M.L.O. Scholte, and E. van Loenen , Phys Rev Lett. 62, 1880 1883 (1989).

[53] E.P. Donovan, F. Spaepen, D.Turnbull, J.M. Poate, and D.C. Jacobson, “Heat of crystallization and melting point of amorphous silicon,” Appl. Phys. Lett. 42, 698 (1983)

[53] The heat conductivity of thin film amorphous silicon was measured independently by different groups [0-0] to be equal to 1.5W/m-K and almost independent of temperature, while the conductivity in liquid Si is significantly higher: 62 W/m K [0]. Assuming similar behavior of the heat conductivity of thin film Mo compared to other thin metallic films [0,0] we used in our calculations 25 ± 15 W/m-K as the heat conductivity of the Mo layers.

[54] S.Volz, X. Feng, C. Fuentes, P. Guérin and M. Jaouen, „Thermal Conductivity Measurements of Thin Amorphous Silicon Films by Scanning Thermal Microscopy,” Int. J. Thermophys. 23 1645-1652 (2002).

[55] S.Moon, M.Hatano, M.Lee and C.P. Grigoropoulos, “Thermal conductivity of amorphous silicon thin films,” Int. J. Heat Mass Transfer 45, 2439-2447 (2002).

[56] P.B. Allen and J.L. Feldman, “Thermal Conductivity of Glasses: Theory and Application to Amorphous Si,” Phys. Rev. Lett. 62, 645-648 (1989).

[57] H. Kobatake, H. Fukuyama, I. Minato, T. Tsukada, and S. Awaji, “Noncontact measurement of thermal conductivity of liquid silicon in a static magnetic field,” Appl. Phys. Lett. 90, 094102 (2007).

[58] T. Yamane, Y. Mori, S. Katayama, and M. Todoki, ”Measurement of thermal diffusivities of thin metallic films using the ac calorimetric method,” J. Appl. Phys. 82, 1153 (1997).

[59] B. Feng, Z. Li and X. Zhang, “Prediction of size effect on thermal conductivity on nanoscale metallic films,” Thin Solid Films (2008), doi:10.1016/j.tsf.2008.10.116

Summary

This thesis describes the development of molybdenum/silicon based multilayer reflective elements for the Extreme UV wavelength range, as motivated by their application in photolithography for semiconductor manufacturing. The thesis reflects the basic thin film physics, technological developments, and valorisation activities of the last two decades of research, a period in which the author was involved in more than 20 research projects, carried out at FOM with numerous academic and industrial partners.

This thesis contains three major aspects: basic thin film growth and analysis studies, the development of deposition processes and associated instrumentation, and the demonstration of the knowledge by producing prototype industrial optics coatings for lithography.

The thin film studies described contribute to answers to basic questions such as: what are the leading film growth processes for layers with nanoscale thicknesses, which mechanisms determine layer smoothening and interlayer formation, what determines the amorphous, crystalline or chemical state, how can one control atomic diffusion and arrive at temporally and thermally more stable multilayer structures? Also described are answers to the more applied aspects, like: how can multilayer induced stress be controlled, and what optical response can result from non-periodic or laterally structured multilayer systems?

Dedicated process and instrumentation development has made many of these detailed studies possible. The various generations of deposition facilities that we designed, developed, and continuously improved during the last two decades have been based on e-beam evaporation, magnetron sputtering, as well as plasma and ion-beam surface treatments. Two new research facilities are being designed and built: the Atomic Growth and Analysis facility (AG/A) for fundamental thin film research and a large and versatile deposition system for multilayer development.

The third aspect of the thesis work, its valorisation, concerns the production of proof-of-principle prototype multilayer depositions on industrial lithography optics. This includes the successful coating of optical components for ASML and Zeiss' first two generations of EUV lithography machines. Demonstrations are described on achieving the lateral control of the deposition process over large area surfaces to meet all aspects of the optics design specifications.

In short, in the thesis the author attempts to summarize his knowledge on state-of-the-art multilayer EUV deposition know-how and technology, in order to support the EUV activities and to form a basis for further, industrially-inspired thin film physics and development programmes.

Samenvatting

Dit proefschrift beschrijft de ontwikkeling van kennis van multilaags-spiegels, gebaseerd op de materiaalcombinatie molybdeen-silicium, voor reflectie van straling in het Extreem Ultraviolette golflengtegebied. De motivatie bestaat uit de toepassing in reflecterende optische systemen voor fotolithografische processen in de halfgeleiderindustrie. Het proefschrift geeft een overzicht van het multilagenonderzoek over een periode van 20 jaar, waarin de auteur direct betrokken is geweest bij meer dan 20 onderzoeksprojecten uitgevoerd bij FOM in samenwerking met talloze academische en industriële partners.
De drie belangrijkste aspecten van dit proefschrift zijn: een fundamentele studie naar de aangroei van dunne lagen en de analyse daarvan, de ontwikkeling van de depositieprocessen en de bijbehorende instrumentatie, en het aantonen van de toepasbaarheid van deze processen door middel van het aanbrengen van multilagen op grote spiegels voor lithografische machines voor de halfgeleiderindustrie.

De fundamentele studie in dit proefschrift beschreven, probeert antwoorden te geven op basisvragen als: wat zijn de belangrijkste processen bij de aangroei van de nanolagen, welke mechanismen zorgen ervoor dat een laag minder ruw wordt, welke mechanismen bepalen of er een tussenlaag wordt gevormd, welke factoren bepalen of een laag amorf is of kristallijn, wat bepaalt de chemische bindingstoestand, hoe kunnen we de diffusie onder controle houden en multilagen maken die stabiel zijn, ook wanneer ze bij verhoogde temperatuur worden gebruikt? Daarnaast wordt ook ingegaan op aspecten die voor de toepassingen van belang zijn zoals: hoe kunnen we de stress in de multilaag beheersen en hoe zijn de reflectie-eigenschappen van multilagen die een niet-periodieke samenstelling hebben, of van multilagen waarbij over het oppervlak structuren zijn aangebracht?

Een gerichte ontwikkeling van processen en de daarvoor benodigde instrumentatie hebben veel van de genoemde studies mogelijk gemaakt. De diverse opdampfaciliteiten, in de loop der jaren ontwikkeld, gebouwd en voortdurend verbeterd, zijn gebaseerd op electronenstraalverdampen en magnetron-sputterdepositie, in combinatie met plasma- en ionenbundel-behandeling van de oppervlakken. Twee nieuwe onderzoeksopstellingen worden op dit moment ontworpen en gebouwd: één waarin de atomaire processen kunnen worden bestudeerd en een grotere multifunctionele faciliteit voor het ontwikkelen van complete multilaagsystemen.

Het derde aspect in dit proefontwerp is de valorisatie van het werk: het opdampen van multilagen op grote, industriële spiegelsubstraten ofwel het leveren van

het 'proof of principle'. Dit heeft geresulteerd in het succesvol aanbrengen van multilaagsystemen op een aantal spiegels voor de eerste twee generaties EUV-lithografiemachines die door Carl Zeiss SMT en ASML zijn gebouwd. In het proefschrift worden voorbeelden beschreven van het bereiken van voldoende beheersing van de laagdikte over het gehele spiegeloppervlak op een zodanige manier dat aan alle eisen van de optische ontwerpers is voldaan.
Daarnaast behandelt dit proefschrift nog twee aspecten, namelijk het ontwikkelen van speciale lagen op de multilaag om de reflectie van licht met een langere golflengte te onderdrukken en een studie naar mogelijke schade in de multilagen wanneer deze aan zeer hoge intensiteit EUV-straling worden blootgesteld.

Kort gezegd, met dit proefschrift probeert de auteur de nieuwste stand van zaken met betrekking tot multilaagdepositie en -technologie weer te geven met het oogmerk EUV lithografie te ondersteunen en een basis te vormen voor toekomstige onderzoeks- en ontwikkelingsprogramma's op het gebied van dunne films voor de reflectie en het manipuleren van licht met een golflengte in het nanometer en subnanometergebied.

Acknowledgements

Twenty years of multilayer research is unthinkable without the help of all the people I worked with for longer or shorter periods.
At first, I want to thank Fred, my friend, colleague, department head and supervisor. His continuous dedication to our work, his stimulating drive and his inimitable ability to generate new ideas and projects enabled the development of a large and very successful multilayer team that started with only one physicist with hardly any knowledge of thin layer physics. In this respect I also acknowledge FOM and the Institute directors throughout the years for accommodating science within an industrial perspective. Particularly Marnix van der Wiel, who initiated the multilayer work at Rijnhuizen by having the MUCO facility built, but certainly also his successors Chris, Gerard, Aart and Richard: many, many thanks!
Mentioning names of people in acknowledgements induces the risk of forgetting someone, but because I am really grateful to so many, I take that risk.
First, Jan Verhoeven, who not only taught me the first principles of multilayer deposition, together with Eric Puik, but also has been and still is, five years after his retirement, a very good partner for all kind of discussions. He was also very pleasant company on many trips to the PXRMS and other conferences.
My colleagues Leonid, Andrey, Robbert, Mike, Chris and Erwin (fabulous memory for all samples ever made): your help, discussions, ideas and company throughout many years is really extremely valuable and makes it a joy to work with you.
The post doc researchers Peter and Sebastian: I really appreciate your efforts on EUVL multilayers! Also Ryszard and Rolf: thanks a lot for all your work on Flash and other X-ray free electron lasers, together with Sam, master student in our group. Furthermore Eddie, also post doc researcher, for your work on coating the NXE:3100 mirrors.
The research engineers: I really appreciate all your technical work and indispensable help with the experiments, often late, very late or during weekends. Arend-Jan, Caspar, Edward, Fabian, Frenk, Gideon, Han, Henk, Henri, Jasper, Kees, Michel, Machiel, Norbert, Peter, Rob, Robert, Ronald, and Santi: I could always count on you to make the impossible happen!
I also want to thank all PhD students of the last 20 years. Eric and Gert in the early years, followed by Harm-Jan (always cheerful and laughing, even at 4 o'clock in the morning at the Daresbury synchrotron), Remko, René, Marc, Mark, Ileana, Tim, Veronique, Hirokazu, Saskia, Juequan, Toine, Jeroen, Igor, Steven, Slava and Dima. With many of you I worked very directly, some as daily supervisor, and I learned from all of you and appreciated the discussions on work and many other

topics as well as your company at many events and on many trips! The same holds for a large number of bachelor- and master students: thanks a lot for all your work and your sometimes difficult questions!

Furthermore, I greatly appreciate the technical support of the people from the mechanical workshop, sometimes even outside office hours and during public holidays, the design office, ICT, the administration, the librarian and the more general supportive staff. I also should mention Frits, safety first, but always understanding and supporting our scientific needs.

A very special word of thanks to Melanie for improving many of the pictures in this thesis and for taking care of the lay out, a major achievement since the combination of Microsoft Word and Endnote is not always perfect.

All of you make FOM Rijnhuizen, now DIFFER, a great place to work. It is like a family where you can get help, support, and where you can have a chat about everything that bothers you, work related or not. Also the OVR activities, the Rijnhuizen Café, the cabaret and the swimming team have contributed enormously to the quality of life in the Institute. I appreciate that very much!

Also outside the Institute I experienced a lot of collaboration for which I am very grateful. At first, the multilayer team at Carl Zeiss SMT. The long collaboration, the often very close contact in numerous telco's, during the quarterly reviews and other visits were of great importance to me and I appreciate the ample opportunities we are given to do fundamental research on the route to find solutions for problems.

Secondly the PTB staff in Berlin for the innumerable number of measurements, the direct feedback when required and the help to develop special measurement procedures. In this respect I also thank Eric Gullikson (CXRO, Berkeley) for always helping us out when there was no possibility to measure at PTB.

Furthermore I acknowledge the colleagues at ASML, TNO and Philips Research for the fruitful collaboration in the field of contamination issues and various other lithography topics, as well as the co-workers at the Delft University and the MESA+ Institute for Nanotechnology of the University of Twente for the beautiful high resolution TEM images that give such a good insight in our multilayers.

Last, but certainly not least, I thank Wim for always supporting me, helping me, being there when needed and never complaining when again, I was working late, holidays were shortened or cancelled and weekends were spent in the lab. When needed, you even joined me to help. Without you I would never have succeeded.

Thanks to all of you!

Eric

Curriculum Vitae

Eric Louis was born in 1954 in Amsterdam and studied Experimental Physics at the University of Amsterdam, where he received his education as experimental physicist in low-temperature solid-state physics in the group of Prof. Jaap Franse under supervision of Dr. Anne de Visser.

In 1988 he joined the FOM Institute for Plasma Physics Rijnhuizen, where he worked with Prof. Fred Bijkerk on the optimization of the radiation characteristics of laser produced plasmas and the characterization and reduction of atomic, ionic, and cluster particulates emmitted by these plasmas.
In 1992 Louis changed topic and became responsible for the further development of a newly engineered multilayer coating facility at Rijnhuizen, now DIFFER, and the thin film and multilayer research in the framework of an STW pilot project on lithography. This first European EUV litho project was done in collaboration with DIMES, the Delft Institute of Microsystems and Nanoelectronics, and FOM Amolf.
In the period 1994-1995 Louis developed multilayers for Space Research in collaboration with Dr. Eberhard Spiller and Dr. Finn Christensen of the Danish Space Research Institute. After that, he returned to lithography-related multilayers to further improve their optical properties, now in collaboration with Carl Zeiss SMT in Oberkochen, Germany. Meanwhile he developed several multilayer designs and processes, improved the deposition technology to levels suitable for real optical elements applied in prototype litho scanners and took part in the development of new coating facilities in the teams.

To characterize the multilayers, Louis carried out numerous measurement campaigns in the radiometry laboratory of the Physikalisch Technische Bundesanstalt in Berlin and at the Daresbury, DESY and ESRF synchrotron facilities.
From 2003 onwards, Louis has led the coating activities of many optics for the Micro Exposure Tool, a pilot EUVL test system, and for the first two series of full field exposure systems: the Alpha Demo Tools and the NXE:3100 systems.
Parallel to the coating activities, Louis was involved in design and demonstration of layers with new functionalities, like layer smoothening, modification of the

spectral response, and mitigation of contamination and damage phenomena.
Furthermore, Louis carried out the FOM part of the STW project "Engineering rules for X-ray and EUV optics: Atomic-scale controlled deposition" with Leiden University.
As a first step for lithography at an even shorter wavelength, Louis is responsible for the STW project "Multilayer Optics for Lithography Beyond the Extreme Ultraviolet Wavelength Range". Together with renewed interest from fluorescence spectroscopy, this work evolved in the establishment of a focused research effort on short wavelength multilayer optics: the Industrial Focus Group XUV Optics, to be founded at the MESA+ Institute for Nanotechnology at the University of Twente.

List of publications

This thesis is based on the following journal publications and conference proceedings:

[1] Louis, E., van de Kruijs, R.W.E., Zoethout, E., van Herpen, M.M.J.W., Alonso van der Westen, S., Muellender, S., Banine, V., Richter, M. and Bijkerk, F. "Suppression of the UV reflectance of multilayer EUV Bragg mirrors." Submitted to Applied Optics.

[2] Louis, E., Yakshin, A.E., Tsarfati, T. and Bijkerk, F. "Nanometer interface and materials control for multilayer EUV-optical applications." Progress in Surface Science 86 (11-12) (2011) 255–294.

[3] Khorsand, A.R., Sobierajski, R., Louis, E., Bruijn, S., Van Hattum, E.D., van de Kruijs, R.W.E., Jurek, M., Klinger, D., Pelka, J.B., Juha, L., Burian, T., Chalupsky, J., Cihelka, J., Hajkova, V., Vysin, L., Jastrow, U., Stojanovic, N., Toleikis, S., Wabnitz, H., Tiedtke, K., Sokolowski-Tinten, K., Shymanovich, U., Krzywinski, J., Hau-Riege, S., London, R., Gleeson, A.J., Gullikson, E.M. and Bijkerk, F. "Single shot damage mechanism of Mo/Si multilayer optics under intense pulsed XUV-exposures." Optics Express 18 (2) (2010) 700-712

[4] Louis, E., Van Hattum, E.D., Alonso van der Westen, S., Sallé, P., Zoethout, E., Von Blanckenhagen, G., Enkish, H., Müllender, S. and Bijkerk, F. "High reflectance multilayers for EUVL HVM-projection optics". Proc. SPIE Advanced Lithography, Vol. 7636, 2010

[5] Louis, E., Khorsand, A.R., Sobierajski, R., Van Hattum, E.D., Jurek, M., Pelka, J.B., Klinger, D., Juha, L., Chalupsky, J., Cihelka, J., Hajkova, V., Jastrow, U., Toleikis, S., Wabnitz, H., Tiedtke, K., Gaudin, J., Gullikson, E.M. and Bijkerk, F. "Damage studies of multilayer optics for XUV free electron lasers". Proc. SPIE Damage to VUV, EUV, and X-Ray Optics II 7361, 2009

[6] Van Herpen, M.M.J.W., van de Kruijs, R.W.E., Klunder, D.J.W., Louis, E., Yakshin, A.E., Alonso van der Westen, S., Bijkerk, F. and Banine, V. "Spectral-purity-enhancing layer for multilayer mirrors." Optics Letters 33 (6) (2008) 560 - 562

[7] Louis, E., van de Kruijs, R.W.E., Yakshin, A.E., van Herpen, M.M.J.W., Klunder, D.J.W., Alonso van der Westen, S., Enkisch, H., Muellender, S., Bakker, L., Banine, V., Richter, M. and Bijkerk, F. "Multilayer optics with spectral purity enhancing layers for the EUV wavelength range". Proc. SPIE Emerging Lithographic Technologies 6151, 2006

[8] Louis, E., Yakshin, A.E., Zoethout, E., van de Kruijs, R.W.E., Nedelcu, I., Alonso van der Westen, S., Tsarfati, T., Bijkerk, F., Enkisch, H., Muellender, S., Wolschrijn, B. and Mertens, B. "Enhanced performance of EUV multilayer coatings". Proc. SPIE Optics & Photonics 5900, 2005

[9] Louis, E., Zoethout, E., van de Kruijs, R.W.E., Nedelcu, I., Yakshin, A.E., Alonso van der Westen, S., Tsarfati, T., Bijkerk, F., Enkisch, H. and Müllender, S. "Multilayer coatings for the EUVL process development tool". Proc. SPIE Emerging Lithographic Technologies 5751, 2005

[10] Zoethout, E., Sipos, G., van de Kruijs, R.W.E., Yakshin, A.E., Louis, E., Muellender, S. and Bijkerk, F. "Stress Mitigation in Mo/Si Multilayers for EUV Lithography". Proc. SPIE Emerging Lithographic Technologies 5037, 2003

[11] Louis, E., Yakshin, A.E., Görts, P.C., Oestreich, S., Stuik, R., Kessels, M.J.H., Maas, E.L.G., Bijkerk, F., Haidl, M., Müllender, S., Mertin, M., Schmitz, D., Scholze, F. and Ulm, G. "Progress in Mo/Si multilayer coating technology for EUVL optics". Proc. SPIE Emerging Lithographic Technologies 3997, 2000

[12] Louis, E., Yakshin, A.E., Görts, P.C., Abdali, S.A., Maas, E.L.G., Stuik, R., Bijkerk, F., Schmitz, D., Scholze, F., Ulm, G. and Haidl, M. "Reflectivity of Mo/Si multilayer systems for EUVL". Proc. SPIE Emerging Lithographic Technologies 3676, 1999

[13] Louis, E., Voorma, H.J., Koster, N.B., Shmaenok, L. and Bijkerk F. "Multilayer coated reflective optics for Extreme UV lithography." Microelectronic Engineering 27 (1995) 235-238

[14] Louis, E., Spiller, E., Abdali, S., Christensen, F.E., Voorma, H.-J., Koster, N.B., Frederiksen, P.K., Tarrio, C., Gullikson, E.M., Bijkerk F., "Multilayer X-ray Mirrors for the Objective Crystal Spectrometer on the Spectrum Röntgen Gamma satellite", Proc. SPIE 2515, (1995) 194-205.

[15] Louis, E., Voorma, H.J., Koster, N.B., Shmaenok, L., Bijkerk, F., Schlatmann, R., Verhoeven, J., Platonov, Y.Y., van Dorssen, G.E. and Padmore, H.A. "Enhancement of reflectivity of multilayer mirrors for soft x-ray projection lithography by temperature optimization and ion bombardment." Microelectronic Engineering 23 (1994) 215-218

[16] Louis, E., Bijkerk, F., Shmaenok, L., Voorma, H.J., van der Wiel, M.J., Schlatmann, R., Verhoeven, J., van der Drift, E.W.J.M., Romijn, J., Rousseeuw, B.A.C., Voß, F., Désor, R. and Nikolaus, B. "Soft x-ray projection lithography using a high repetition rate laser-induced x-ray source for sub-100 nanometer lithography processes." Microelectronic Engineering 21 (1993) 67-70

The author contributed significantly to the following journal publications and conference proceedings:

[1] Van den Boogaard, A.J.R., van Goor, F., Louis, E. and Bijkerk, F. "Wavelength separation from extreme ultraviolet mirrors using phaseshift reflection." Optics Letters 37 (2) (2012) 160-162

[2] Makhotkin, I., Zoethout, E., Louis, E., Yakunin, A.M., Müllender, S. and Bijkerk, F. "Spectral properties of La/B-based multilayer mirrors near the boron K absorption edge." Optics Express 20 (2012) (11)

[3] Makhotkin, I., Zoethout, E., Louis, E., Yakunin, S.N., Muellender, S. and Bijkerk, F. "Wavelength selection for multilayer coatings for the lithography generation beyond EUVL." Proc. SPIE Advanced Lithography SPIE 8322, (2012)

[4] Liu, F., Lee, C.J., Chen, J., Louis, E., van der Slot, P.J.M., Boller, K.J. and Bijkerk, F. "Ellipsometry with randomly varying polarization states." Optics Express 20 (2) (2012) 870-878

[5] Van den Boogaard, A.J.R., Louis, E., Zoethout, E., Goldberg, K.A. and Bijkerk, F. "Characterization of Mo/Si multilayer growth on stepped topographies." Journal of Vacuum Science and Technology B 29 (5) (2011)

[6] Sobierajski, R., Bruijn, S., Khorsand, A.R., Louis, E., van de Kruijs, R.W.E., Burian, T., Cha-

lupsky, J., Cihelka, J., Gleeson, A.J., Grzonka, J., Gullikson, E.M., Hajkova, V., Hau-Riege, S., Juha, L., Jurek, M., Klinger, D., Krzywinski, J., London, R., Pelka, J.B., Plocinski, T., Rasinski, M., Tiedtke, K., Toleikis, S., Vysin, L., Wabnitz, H. and Bijkerk, F. "Damage mechanisms of MoN/SiN multilayer optics for next-generation pulsed XUV light sources." Optics Express 19 (1) (2011)

[7] Makhotkin, I., Louis, E., Van de Kruijs, R.W.E., Yakshin, A., Zoethout, E., Seregin, A.Y., Tereschenko, E.Y., Yakunin, S.N. and Bijkerk, F. "Determination of the density of ultrathin La films in La/B4C layered structures using X-ray standing waves." Physics Status Solidi A 1-4 (2011)

[8] Chen, J., Louis, E., Wormeester, H., Harmsen, R., van de Kruijs, R.W.E., Lee, C.J., Van Schaik, W. and Bijkerk, F. "Carbon induced extreme ultraviolet (EUV) reflectance loss characterized using visible-light ellipsometry." Measurement Science and Technology 22 (10) (2011) 8

[9] Chen, J., Louis, E., Harmsen, R., Tsarfati, T., Wormeester, H., van Kampen, M., van Schaik, W., van de Kruijs, R.W.E. and Bijkerk, F. "In situ ellipsometry study of atomic hydrogen etching of extreme ultraviolet induced carbon layers." Applied Surface Science 258 (2011) 7-12

[10] Loch, R.A., Dubrouil, A., Sobierajski, R., Descamps, D., Fabre, B., Lidon, P., Van de Kruijs, R.W.E., Boekhout, F., Gullikson, E.M., Gaudin, J., Louis, E., Bijkerk, F., Mével, E., Petit, S., Constant, E. and Mairesse, Y. "Phase characterization of the reflection on an extreme UV multilayer: comparison between attosecond metrology and standing wave measurements." Optics Letters 36 (17) (2011)

[11] Yakshin, A.E., Kozhevnikov, I., Zoethout, E., Louis, E. and Bijkerk, F. "Properties of broadband depth-graded multilayer mirrors for EUV optical systems." Optics Express 18 (7) (2010) 6957-6971

[12] Van den Boogaard, A.J.R., Louis, E., Zoethout, E., Müllender, S. and Bijkerk, F. "Surface morphology of Kr+-polished amorphous Si layers." Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films 28 (4) (2010) 552-558

[13] Tsarfati, T., van de Kruijs, R.W.E., Zoethout, E., Louis, E. and Bijkerk, F. "Nitridation and contrast of B4C/La interfaces and multilayer optics." Thin Solid Films 518 (2010) (24) 7249–7252

[14] Dobrovolskiy, S., Yakshin, A.E., Tichelaar, F.D., Verhoeven, J., Louis, E. and Bijkerk, F. (2010) "Formation of Si/SiC multilayers by low-energy ion implantation and thermal annealing." Nuclear Instruments & Methods in Physics Research, B. 268 (6) (2010) 560-567

[15] Chen, J., Louis, E., Verhoeven, J., Harmsen, R., Lee, C.J., Lubomska, M., Van Kampen, M., Van Schaik, W. and Bijkerk, F. "Secondary electron yield measurements of carbon covered multilayer optics." Applied Surface Science 257 (2) (2010) 354-361

[16] Van den Boogaard, A.J.R., Louis, E., Goldberg, K.A., Mochi, I. and Bijkerk, F. "EUV-multilayers on grating-like topographies." Proc. SPIE Advanced Lithography, 7636 (2010)

[17] Tsarfati, T., van de Kruijs, R.W.E., Zoethout, E., Louis, E. and Bijkerk, F. "Reflective multilayer optics for 6.7 nm wavelength radiation sources and next generation lithography." Thin Solid Films 518 (5) (2009) 1365-1368

[18] Chen, J., Louis, E., Lee, C.J., Wormeester, H., Kunze, R., Schmidt, H., Schneider, D., Moors, R., van Schaik, W., Lubomska, M. and Bijkerk, F. "Detection and characterization of carbon contamination on EUV multilayer mirror." Optics Express 17 (19) (2009) 16969-16979

[19] Van den Boogaard, A.J.R., Louis, E., van Goor, F. and Bijkerk, F. "Optical Element for full spectral purity from IR-generated EUV light sources." Proc. SPIE Advanced Lithography 7271 (2009)

[20] Tsarfati, T., Zoethout, E., Louis, E., van de Kruijs, R.W.E., Yakshin, A., Muellender, S. and Bijkerk, F. "Improved contrast and reflectivity of multilayer reflective optics for wavelengths beyond the Extreme UV." Proc. SPIE Advanced Lithography 7271 (2009)

[21] Chen, J., Louis, E., Bijkerk, F., Lee, C.J., Wormeester, H., Kunze, R., Schmidt, H., Schneider, D. and Moors, R. "Ellipsometric and surface acoustic wave sensing of carbon contamination of EUV optics." Proc. SPIE Advanced Lithography 7271 (2009)

[22] Van den Boogaard, A.J.R., Louis, E., Zoethout, E., Alonso van der Westen, S. and Bijkerk, F. "Smoothing Properties of Single- and multilayer coatings, a method to smoothen substrates." Proc. SPIE Emerging Lithograpic Technologies 6921, (2008)

[23] Nedelcu, I., van de Kruijs, R.W.E., Yakshin, A., Louis, E., Muellender, S. and Bijkerk, F. "Substrate recovery layers for EUVL optics: effects on multilayer reflectivity and surface roughness." Proc. SPIE EUV Optics 6517 (2007)

[24] Van de Kruijs, R.W.E., Zoethout, E., Yakshin, A.E., Nedelcu, I., Louis, E., Enkisch, H., Sipos, G., Müllender, S. and Bijkerk, F. "Nano-size crystallites in Mo/Si multilayer optics." Thin Solid Films 515 (2) (2006) 430-433

[25] Nedelcu, I., van de Kruijs, R.W.E., Yakshin, A.E., Tichelaar, F.D., Zoethout, E., Louis, E., Enkisch, H., Mullender, S. and Bijkerk, F. "Interface roughness in Mo/Si multilayers." Thin Solid Films 515 (2) (2006) 434-438

[26] Alink, L.G.A.M., van de Kruijs, R.W.E., Louis, E., Bijkerk, F. and Verhoeven, J. "Improved temperature stability of Mo/Si multilayers by carbide based diffusion barriers through implantation of low energy CH(x+) ions." Thin Solid Films 510 (1-2) (2006) 26-31

[27] Mertens, B., Weiss, M., Meiling, H., Klein, R., Louis, E., Kurt, R., Wedowski, M., Trenkler, H., Wolschrijn, B., Jansen, R., van de Runstraat, A., Moors, R., Spee, K., Ploeger, S. and van de Kruijs, R.W.E. "Progress in EUV optics lifetime expectations." Microelectronic Engineering 73-74 (2004) 16-22

[28] Zoethout, E., Suter, P., van de Kruijs, R.W.E., Yakshin, A.E., Louis, E., Bijkerk, F., Enkisch, H. and Muellender, S. "Subatomic Accuracy in EUVL Multilayer Coatings." Proc. SPIE Emerging Lithographic Technologies 5374 (2004)

[29] Koster, N., Mertens, B., Jansen, R., van de Runstraat, A., Stietz, F., Wedowski, M., Meiling, H., Klein, R., Gottwald, A., Scholze, F., Visser, M., Kurt, R., Zalm, P., Louis, E. and Yakshin, A.E. "Molecular contamination mitigation in EUVL by environmental control." Microelectronic Engineering 61-62 (2002) pp. 65-76

[30] Abdali, S., Gerward, L., Yakshin, A.E., Louis, E. and Bijkerk, F. "Determination of Crystalliza-

tion as a Function of Mo layer thickness in Mo/Si multilayers." Materials Research Bulletin 37 (2002) 279-289

[31] Yakshin, A.E., Louis, E., Görts, P.C., Maas, E.L.G. and Bijkerk, F. "Determination of the layered structure in Mo/Si multilayers by grazing incidence x-ray reflectivity." Physica B - Condensed Matter 283 (1-3) (2000) 143-148

[32] Oestreich, S., Klein, R., Scholze, F., Jonkers, J., Louis, E., Yakshin, A.E., Görts, P.C., Ulm, G., Haidl, M. and Bijkerk, F. "Multilayer reflectance during exposure to EUV radiation." Proc SPIE 4146 (2000)

[33] Visser, M., Constantinescu, R., Hegeman, P., Jonkers, J., Dekker, M., Louis, E. and Hambach, D. "A shearing interferometer to characterize EUVL optics with a laser plasma source." Proc SPIE Emerging Lithographic Technologies 3997 (2000)

[34] Stuik, R., Louis, E., Yakshin, A.E., Gorts, P.C., Maas, E.L.G., Bijkerk, F., Schmitz, D., Scholze, F., Ulm, G. and Haidl, M. "Peak and Integrated reflectivity, wavelength and gamma optimization of Mo/Si, and Mo/Be multilayer, multielement optics for extreme ultraviolet lithography." Journal of Vacuum Science & Technology B 17 (6) (1999) 2998-3002

[35] Voorma, H.-J., Louis, E., Koster, N.B. and Bijkerk, F. "Temperature induced diffusion in Mo/Si multilayer mirrors." Journal of Applied Physics 83 (9) (1998) 4700-4708

[36] Voorma, H.-J., Louis, E., Koster, N.B., Bijkerk, F., Zijlstra, T., de Groot, L.E.M., Rousseeuw, B.A.C., Romijn, J., van der Drift, E.W.J.M. and Friedrich, J. "Fabrication and analysis of Extreme Ultra-violet reflection masks with patterned W/C absorber bi-layers." Journal of Vacuum Science & Technology B 15 (2) (1997) 293-298

[37] Voorma, H.J., Louis, E., Bijkerk, F. and Abdali, S. "Angular and energy dependence of ion bombardment of Mo/Si multilayers." Journal of Applied Physics 82 (4) (1997) 1876-1881

[38] Voorma, H.-J., Louis, E., Koster, N.B., Bijkerk, F. and Spiller, E. "Characterization of multilayers by Fourier analysis of x-ray reflectivity." Journal of Applied Physics 81 (9) (1997)

[39] Voorma, H.J., van Dorssen, G.E., Louis, E., Koster, N.B., Smith, A.D., Roper, M.D. and Bijkerk, F. "EXAFS measurements on the structure of Mo/Si multilayers produced using ion bombardment and increased deposition temperature." Applied Surface Science 93 (3) (1996) 221-230

[40] Shmaenok, L.A., Yu.Ya. Platonov, Salashchenko, N.N., Sorokin, A.A., Simanovskii, D.M., Golubev, A.V., Belik, V.P., Bobashev, S.V., Bijkerk, F., Louis, E., Meijer, F.G., Etlicher, B. and Grudsky, A.Y. "Multilayer EUV/x-ray polychromators for plasma diagnostics." Journal of Electron Spectroscopy and Related Phenomena 80 (1996) 259-262

[41] Bijkerk, F., Shmaenok, L.A., Louis, E., Voorma, H.-J., Koster, N.B., Bruineman, C., Bastiaensen, R.K.F.J., van der Drift, E.W.J.M., Romijn, J., de Groot, L.E.M., Rousseeuw, B.A.C., Zijlstra, T., Yu.Ya. Platonov and Salashchenko, N.N. (1996) "Extreme UV lithography: a new laser plasma target concept and fabrication of multilayer reflection masks." Microelectronic Engineering 30 (1-4) pp. 183-186

[42] Hussain, A.M., Joensen, K.D., Hoghoj, P., Christensen, F.E., Louis, E., Voorma, H.J., Soong, Y., White, N., Serlemitsos, P.J. and Anderson, I. "The deposition and characterization of

multilayers on thin foil x-ray mirrors for high throoughput x-ray telescopes." Proc. SPIE Multilayer and Grazing Incidence X-ray / EUV optics III 2805 (1996)

[43] Shmaenok, L., Bijkerk, F., Louis, E., van Honk, A., van der Wiel, M.J., Yu.Ya. Platonov, Shevelko, A.P., Mitrofanov, A., Frowein, H., Voß, F., Désor, R. and Nikolaus, B. "Issues of laser plasma sources for soft x-ray projection lithography." Microelectronic Engineering 23 (1994) 211-214

[44] Christensen, F.E., Abdali, S., Frederiksen, P.K., Hornstrup, A., Rasmussen, I., Westergaard, N.J., Schnopper, H.W., Louis, E., Voorma, H.J., Koster, N.B., Wiebicke, H., Halm, I., Geppert, U., Silver, E., Legros, M., Borozdin, K., Joensen, K.D., Gorenstein, P., Wood, J. and Gutman, G. "Some applications of nanometer scale structures for current and future x-ray space research." Journal de Physique III 4 (9) (1994) pp. 1599-1612

[45] Bijkerk, F., Louis, E., van Dorssen, G.E., Shevelko, A.P. and Vasilyev, A.A. "Absolute brightness of laser plasmas in the soft x-ray emission band." Applied Optics 33 (1) (1994) 82-88

[46] Bijkerk, F., Shmaenok, L., Louis, E., van Honk, A., van der Wiel, M.J., Platonova, Y.Y., Shevelko, A.P., Mitrofanov, A., Voß, F., Désor, H., Frowein, H. and Nikolaus, B. "Optimization of excimer laser induced x-ray sources for soft x-ray projection lithography." Proc. Symposium on Opt. Science and Engineering: Applications of laser plasma radiation 2015 (1993)

[47] Bijkerk, F., Louis, E., Shmaenok, L., Voorma, H.J., van der Wiel, M.J., Turcu, I.C.E. and Tallents, G.J. "Control of debris production of laser plasma sources with high average XUV power." Proc. 24th Symposium on Optical Materials for High Power Lasers 1848 (1993)

[48] Van Dorssen, G.E., Louis, E. and Bijkerk, F. "Optimization of x-ray emission from a laser produced plasma in a narrow wavelength band." Laser and Particle Beams 10 (4) 7 (1992) 59-765

[49] Bijkerk, F., Louis, E., van der Wiel, M.J., I.C.E.Turcu, Tallents, G.J. and Batani, D. "Performance optimization of a high repetition rate KrF laser plasma x-ray source for microlithography." Journal of X-Ray Science and Technology 3 (1992) 133-151

[50] Bijkerk, F., Louis, E., Turcu, I.C.E. and Tallents, G.J. "High repetition rate KrF laser plasma x-ray source for microlithography." Microelectronic Engineering (17) (1992) 219-222

[51] Turcu, I.C.E., Gower, M.C., Reason, C.J., Huntingdon, P., Schulz, M., Michette, A.G., Bijkerk, F., Louis, E., Tallents, G.J., Al-Hadithi, Y. and Batani, D. "100 Hz KrF laser-plasma x-ray source." Proc. ECO-4 Int. Conf. on Optical Science and Engineering 1503 (1991)