Structured surfaces of wide band gap insulators as templates for overgrowth of adsorbates

TOPICAL REVIEW

Structured surfaces of wide band gap insulators as templates for overgrowth of adsorbates

Roland Bennewitz

Physics Department, McGill University, 3600 rue University, Montréal, Quebec H3A 2T8, Canada

E-mail: roland.bennewitz@mcgill.ca

Abstract
Surface structures on wide band gap insulators and their use as templates for
the growth of adsorbates are reviewed. Surface structures include evaporation
structures, vicinal surfaces, facetted surfaces, epitaxial structures, or structures
transferred to or induced by the growth of thin films. Most structures have been
realized so far on Al_2O_3 and on alkali halide crystals. The guided growth of
adsorbates is discussed, considering the examples of metallic clusters or wires
and ordered films of organic molecules.

Contents

1. Introduction

Surface Science comprises our knowledge of the chemical and physical properties of surfaces. Its methods cover the preparation and characterization of surfaces, and analyse the relations between geometrical and electronic structure of surfaces and adsorbates on one hand and functional properties like chemical reactivity, mechanical stability, or magnetism on the other hand. In this review we explore the extent to which the methods of Surface Science are applied to the creation and characterization of lateral structures on electrically insulating surfaces, which then can serve as templates for guided adsorbate overgrowth. Adsorbates on surfaces of wide band gap solids are decoupled from any delocalized electronic structure and can develop a local electronic structure with specific functionality. As an example, the chemical reactivity of supported metal clusters on insulators is a central topic of Surface Science [1]. Furthermore, the guided growth of isolated small structures is also a prerequisite in the emerging field of Nanoscience, which attempts to address the properties of individual nanometre-scale objects.

Here we want to mention two examples in which Surface Science methods applied to insulators have been essential to the success of important experiments in Nanoscience. The first example is the use of ultrathin insulating films for the separation of single molecules or atoms from metal substrates. Physical properties of the single molecules are probed by scanning tunnelling microscopy (STM) at low temperatures, providing the necessary stability of the atomic configuration and the reduction of thermal noise in the systems. Such studies have achieved the measurement of vibrational features in the light emission from single molecules excited by inelastic electron tunnelling [2], the addition and subtraction of single electron charges to isolated gold atoms [3], or the detection of the Zeeman effect in single atoms [4]. The other example is the use of structured surfaces of insulators to grow nanometre-scale magnetic particles in ordered arrays. One achievement is the growth of a regular array of nanometre-wide wires of Fe on a facetted NaCl(110) surface, where the wires exhibit a strong in-plane magnetic anisotropy [5].

The review starts with an overview of experimental methods for the preparation and characterization of structured surfaces of insulators. We then discuss different strategies to create surface structures like the use of stepped surfaces, faceting, homo- and heteroepitaxy, thin-film growth, and radiation-induced structuring. The last part discusses the adsorbate growth on such structured surfaces by considering two examples, metal clusters and assemblies of organic molecules.

We limit this overview to wide band gap insulators, which are particularly difficult in their surface preparation, but provide a complete electronic decoupling. We do not cover semiconductors or oxides like TiO_2 or $SrTiO_3$ which after vacuum annealing have a defect-related electric conductivity which allows, for example, for STM analysis. Only lateral structuring through some form of self-organization is considered but no lithographic methods and no vertical stacking of thin films into functional systems. For the related field of template surfaces created by polymer self-assembly we refer the reader to [6] and [7].

2. Experimental methods

2.1. Low-energy electron diffraction

Many experimental methods in Surface Science rely on charged particles for probing the structure and composition of surfaces. While there is no principal reason foreclosing their use on electrically insulating surfaces, their application is often hampered by the effects of charging and radiation damage. In low-energy electron diffraction (LEED) the surface may be

charged negatively or positively, depending on the secondary electron coefficient, which in turn depends on the primary electron energy. Below a primary energy threshold which is typically around 60–80 eV for many insulating surfaces, the sample will be charged negatively up to a potential which will deflect all incoming primary electrons. Consequently, no diffraction pattern will be observed. Above the threshold the sample charges up positively assuming a potential of the order of 10 eV, depending on the exact energy distribution of the secondary electron emission. In this case, diffraction patterns can be observed. Pesty and Garoche have argued that such positive charge does not alter the geometry of the diffraction pattern, but that it affects the intensity distribution in the diffraction spots [8]. The feasibility of quantitative LEED studies on wide band gap insulators has been confirmed in the detailed analysis of the surface structure of thick alkali halide and fluorite crystals provided by Vogt and Weiss [9–11]. Sample charging in these studies was minimized by limiting the electron beam current to only 5 nA. Primary electrons with an energy above 50 eV create electron–hole pairs even in wide band gap materials, very possibly resulting in sample damage by electron-stimulated desorption or point defect creation. Again, small beam currents can minimize such damage as well as low sample temperatures. The latter diminish damage since many electronic excitations in insulators will favour radiative decay over defect creation at lower temperatures.

Despite these experimental limitations, LEED has been used to study the complex reconstructions of the Al_2O_3 surface [12] and the terrace width on stepped oxide surfaces [13]. Including the analysis of spot profiles in LEED, it is even possible to observe lateral structures on the nanometre scale, like the mosaic grains of average size of 7 nm which are formed in the initial growth of MgO on Ag(100) [14].

2.2. Scanning electron microscopy

Another electron probe method that can be hampered by charging is secondary electron microscopy, where the resolution of features is greatly reduced by inhomogeneous charging. Like in LEED studies, negative surface charges will build up until most contrast is blurred, while positive charging comes to an equilibrium which will allow imaging of surface structures. For many insulators, there is a second threshold between 1500 and 2500 eV, below which the secondary electron coefficient is larger than one. Above the threshold strong negative charging can occur. Scanning electron microscopy of insulating surfaces is possible for relative low primary energies around this threshold [15]. These energies are a compromise between reduced charging effects for lower energies and better focusing at higher energies. An overview over the charging mechanisms in electron spectroscopies has been given by Cazaux [16]. The recent development of low-vacuum electron microscopes addresses the problem of charging by dissipating the charges through ionized residual gas [17].

Beyond direct imaging of the surface, electron microscopy has been used to study the distribution of metal clusters on insulating surfaces after transfer to a conducting film. In this method, pioneered by Bassett [18] and Bethge [19], a carbon film is evaporated onto the sample enclosing the metal clusters. The film is subsequently stripped off and imaged by electron microscopy. Not only is the structure of surface steps revealed through decoration, but also the growth mode and crystalline structure of the adsorbed metal clusters [20, 21].

2.3. Electron spectroscopies

Photoelectron emission spectra of insulating samples exhibits both shift and broadening of peaks due to surface charging. The effects of charging and various compensation schemes like sample heating, potential grids at the sample rear side, or flooding with low-energy

electrons are described in a book by Henrich and Cox [1]. While electron spectroscopy does not yield direct information on lateral structures, it is a very important tool to determine the electronic structure of thin insulating films. In particular the question of how many atomic layers are required to classify a thin film as insulating can be answered through the observation of the developing band structure. In a recently described example, Klust *et al* have grown increasingly thick films of CaF_2 on $Si(111)7 \times 7$ and observed how first the surface states of the substrate disappear, then a bulk-like band gap develops, and finally the valence band structure evolves [22].

2.4. Scanning probe microscopy

The invention of scanning tunnelling microscopy (STM) [23, 24] and atomic force microscopy (AFM) [25] has provided us with very versatile tools to study the structure of surfaces with high resolution in real space. In the following we briefly describe the basic concept of force microscopy since it is less often used in the context of Surface Science, but is most relevant for the topic of this review. A very sharp tip is scanned over the surface of the sample under study. The micro-fabricated tip is attached to a cantilever force sensor, typically with a sensitivity of better than 1 nN at a bandwidth of 10 kHz. By controlling the tip–sample distance to maintain a constant force, an image of the sample topography can be recorded. The cantilever bending is usually detected via the deflection of a light beam reflected from its back side. Beyond the static bending of the cantilever, several dynamic techniques have been developed to measure the tip–sample force [26]. In these techniques, the cantilever is excited to oscillate and the tip–sample interaction is deduced from its influence on the oscillation amplitude or frequency. The main advantage of dynamic modes is that a sliding contact between tip and sample is avoided, thereby reducing damage to the tip and the surface.

The resolution of AFM is essentially given by the aspect ratio of the tip apex. For surfaces with structures of atomic dimensions, the ultimate resolution depends on the atomic structure of the cluster forming the very tip apex and on the ability to resolve forces between single atoms. It has taken a longer time to establish atomic resolution in AFM as compared with STM. Additional difficulties in AFM arise from the long-range forces between tip and sample which often exceed the atomic-scale forces between the apex atoms the atoms of the surface structure. In contrast, the resolution in tunnelling microscopy is provided by the short-ranged characteristic of the tunnelling current which includes only the apex atoms and their counterparts on the surface. Only after the development of a frequency-modulation technique has force microscopy become a method of Surface Science with the ability to resolve atomic structures [27].

Meanwhile, a wide variety of surface structures has been studied by what is usually referred to as non-contact AFM in ultrahigh vacuum. The results are documented in the proceedings of a series of conferences [28, 29]. Examples of insulators whose atomic structure has been revealed include alkali halide crystals [30–32], fluorite [33], aluminium oxide [34], magnesium oxide [35], and nickel oxide [36–38]. Atomic-scale imaging has also been achieved in a liquid environment. Actually, one of the first AFM experiments revealing atomic interactions was performed on calcite in aqueous solution [39]. More recent studies include the mineral anhydrite [40], alumina [41], or polydiacetylene [42].

For the purpose of this review we are particularly interested in techniques for imaging structured surfaces of insulators with nanometre or atomic resolution. This has proven to be even more difficult than the imaging of atomically flat surfaces for two main reasons. First, the atomic cluster at the tip apex is rarely perfectly symmetric. Asymmetry even on an atomic scale will produce a different contrast at different edges of monatomic islands. Second, structured

surfaces by their very nature contain many edge and corner atoms. These low-coordinated sites often show a great variation in interaction with the tip, making it difficult to find experimental parameters for stable imaging. On the other hand, the enhanced interaction at low-coordinated sites is exactly what facilitates the guided growth of adsorbates, and it is one of the fascinating prospects of AFM that such enhanced interactions can be measured in real space. The special role of step edge and corner sites for force microscopy has been studied in detail for monatomic NaCl islands [43]. It is interesting to note that a high density of corners and kinks is often found in monatomic steps on cleaved surfaces. Barth and Reichling have studied the atomic structure of monatomic cleavage steps on SrF_2 and BaF_2 by means of non-contact AFM and found that these steps exhibit significant disorder on atomic scale [44]. The irregular interaction at such kinks and corners makes their high-resolution imaging particularly difficult [45].

The only insulating surfaces which can be imaged by STM are those of ultrathin films on conducting substrates. Among the first studies were films of Al_2O_3 on NiAl [46, 47], MgO on Mo [48], NaCl on Ge [49], and NiO on Ni [50]. Scanning tunnelling spectroscopy on thin insulating films can reveal the development of the band gap with film thickness, as shown for MgO on Ag [51]. As mentioned in section 1, tunnelling spectroscopy can also probe the electronic structure of adsorbates on these insulating films [2–4].

2.5. Helium scattering

Helium atom scattering is a fully non-destructive scattering technique that uses uncharged helium atoms with thermal energies to analyse the outermost surface layer. Helium scattering has been employed to study the structure of many insulating surfaces and adsorbates. Examples are the unexpected reconstruction of alkali halide surfaces [52], the cleaved MgO(100) surface [53], or the surface structure of a ferroelectric oxide [54]. Duan *et al* have used the method to investigate the homoepitaxial growth of NaCl on a NaCl(100) surface [55].

2.6. Surface preparation

Strategies for the preparation of surfaces of insulating solids always need to consider the stoichiometric constitution of the resulting surface. Insulating crystals are generally at least diatomic, and any form of preparation may shift the relation between the atomic species at the surface, resulting in new, eventually desired properties. A typical example is the annealing of surfaces. Heating an Al_2O_3 surface in ultrahigh vacuum will result in a loss of oxygen relative to aluminium in the outermost layers. Heating of the same crystal in an oxygen atmosphere, however, is believed to produce a surface more similar to the bulk terminated structure. Annealing of TiO_2 in vacuum creates oxygen vacancies which colour the crystal blue and turn it into a semiconductor [1], while the annealing of alkali halide crystals in vacuum results in molecular evaporation and a preservation of stoichiometry.

A very fast and clean method of surface preparation for insulating crystals is their cleavage. Cleavage can be performed by breaking thin platelets of material or by hitting with a knife edge parallel to a crystalline plane [56]. When this is performed in vacuum, the newly exposed surface will have the impurity content of the crystalline material and often show the bulk-terminated atomic structure. One has to keep in mind, however, that cleavage is a very energetic process on the scale of the cleavage plane. Often charges are separated across the cleavage and exciton luminescence observed during the cleavage of alkali halide crystals reveals electronic excitation across the band gap. Residual charges from the cleavage process can influence the growth of adsorbates and are very disturbing for imaging by AFM. Careful heating in vacuum can help to dissipate the charges and still preserve the stoichiometry.

Auger electron spectroscopy and ion sputtering, both well established procedures in the Surface Science of metals and semiconductors, will regularly change the stoichiometry of the surface, usually in favour of the metallic constituent [57].

Thin films of insulating materials can be grown by molecular beam epitaxy. Alkali halide molecules evaporate in significant rates from edge and corner sites at temperatures as low as two thirds of the melting temperature. Consequently, heating the powder of an alkali halide in a Knudsen cell allows one to grow stoichiometric films with comparatively simple means. The strong ionic cohesion within these films favours the formation of structurally perfect islands of large extent, often overgrowing steps of the substrate in a carpet-like manner [49, 58]. Thin regular films of CaF_2 can be grown on Si(111) if the substrate temperature is chosen such that the interface between Si and CaF_2 is constituted by one layer of CaF [59]. Films of MgO can be prepared on Ag(100) [14, 51] and Mo(100) [48] by evaporation of Mg in an oxygen atmosphere. Furthermore, growth of MgO films on Fe(001) by electron beam evaporation has been reported [60]. Finally, thin oxide films can be produced by oxidation of a clean metal surfaces, where the most prominent example in Surface Science is the formation of Al_2O_3 on NiAl [47].

3. Structured surfaces

In this section we review surface structures on insulators which have been realized experimentally. Such structures include step structures formed on vicinal surfaces, in evaporation structures, or in thin-film growth. Faceting occurs on surfaces of insulators, but is also induced on metal surfaces by thin insulating films.

Tasker has shown theoretically that surfaces of ionic crystals are unstable if repeated unit cells carry an electric dipole moment perpendicular to the surface [61]. Since then, most theoretical descriptions of surface structure have focused on monatomic steps. The relaxation of atomic positions at steps and the respective surface energies have been calculated for NaCl [62], calcite [63], or CaF_2 [64]. Beyond the geometric structure of step and corners, electronic structure calculations have been presented mainly for MgO [65–67]. The interest in MgO is motivated by the chemical activity at corners and edges [68].

3.1. Structured pure surfaces

The smallest structures on surfaces which possess sizes beyond the crystal's unit cell are reconstructions of the surface, a fundamental topic in the Surface Science of metals and semiconductors. Large-scale reconstructions certainly influence the structure of adsorbate growth, as for example in the preferred nucleation of metal clusters in parts of the Si(111)-7×7 surface reconstruction [69]. Reconstructions are rarely observed in wide band gap insulators, an important exception being the $Al_2O_3(0001)$ surface, for which various high-temperature forms are observed. Some of these reconstructions are reactive, and ring-like structures have been identified as hydroxide clusters which form even under vacuum conditions [34]. In this section, we discuss structures in stoichiometric surfaces, including regular step arrays in evaporation spirals and on vicinal surfaces, ridge–valley formation of stable crystal facets, and structures evolving in homoepitaxy. Examples of such structures are summarized in table 1.

3.1.1. Evaporation structures. Heating of alkali halide crystals in vacuum results in molecular evaporation from corner sites of steps. This process smoothes cleavage steps and evolves spirals of steps around the intersection of dislocations with the surface. Such evaporation spirals provide a regular array of monatomic or diatomic steps separating atomically flat terraces. The typical terrace width is between 50 and 150 nm [19, 21, 71]. The enhanced interaction at the steps of evaporation spirals which makes them a candidate for guided growth of adsorbates has

Table 1. Examples for structured surfaces of stoichiometrically pure insulators.

$Al_2O_3(0001)$	Regular step structure after annealing in air	[70, 71]
$Al_2O_3(\bar{1}012)$	Regular step structure after polishing	[72, 73]
$Al_2O_3(10\bar{1}0)$	Faceting into ridges upon annealing in air	[70]
$CaF_2(110)$	Ridge and valley structure in homoepitaxy	[74]
$KBr(100)$	Regular steps in evaporation spirals	[21]
$LiF(110)$	Ridge and valley structure in homoepitaxy	[74]
$MgO(110)$	Ridge and valley structure in homoepitaxy	[75]
$NaCl(100)$	Regular steps in evaporation spirals	[19, 21]
$NaCl(110)$	Faceting into ridges upon annealing in vacuum	[5]
$NaCl(110)$	Regular ridge and valley structure in homoepitaxy	[76]
$NaCl(111)$	Faceting into pyramids upon annealing in vacuum	[77]

been directly measured as increased friction at the step sites [78]. Complementary structures to evaporation spirals are the spirals found in crystal growth, one example being AgBr grown on NaCl and mica where such spirals have been imaged by means of the decoration technique and AFM [79].

3.1.2. Vicinal surfaces. Regular arrays of steps can be prepared on metal and semiconductor surfaces by polishing the crystals with a small miscut with respect to a crystallographic plane. The regular step arrays are then produced by dedicated cycles of sputtering and annealing, which minimize unwanted step bunching. Reviews of the preparation and application of vicinal surface structures have been written by Jeong and Williams [80] and Kuhnke and Kern for metal surfaces [81]. For silicon surfaces, a refined choice of the miscut angle allows the creation gratings where the terrace-step pattern is repeated with atomic accuracy [82]. A similar strategy for the preparation of regular step arrays on insulating solids is hampered by the deteriorating effect of sputtering and annealing on their stoichiometry. However, regular arrays of monatomic steps have been reported for the $Al_2O_3(\bar{1}012)$ surface after polishing with a small crystallographic miscut [72, 73]. The direction of the parallel steps was found to be given by the azimuthal orientation of the miscut which was not aligned to one of the crystallographic directions. The monatomic step structure has been revealed by AFM after polishing and acidic cleaning without further annealing. Similarly, high-precision polishing of a $CaF_2(111)$ surface has been found to create regular arrays of monolayer steps without further annealing [83].

A particularly interesting material regarding the regularity of steps is Al_2O_3 where a self-straightening faceting process takes place upon heating vicinal surfaces in air. Details of the process have been discussed for the (0001) and the $(10\bar{1}0)$ surface by Heffelfinger and Carter [70]. Vicinal (0001) surfaces with a small miscut develop into a terrace-step structure, where the terraces are atomically flat (0001) facets and the steps have heights which are multiples of $c/6$, a sixth of the lattice constant along the c-axis. Steps with a height of $c/6$ have no preferential orientation, while steps of height c or larger run along $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ planes. After nucleation of single facets, a process of facet coarsening and facet joining takes place. After three hours of annealing the lateral distance between steps saturates at 175 nm and the density of facet junctions at 0.5 μm^{-2}. A similar preparation of atomically flat terraces on $Al_2O_3(0001)$ separated by steps with a height of multiples of 0.2 nm and their observation by means of AFM have been described by various groups [84, 71].

3.1.3. Faceting of pure surfaces. Certain surfaces of crystalline solids are more stable than others. Consequently, less stable surfaces may undergo faceting to produce the more stable

ones when elevated temperatures allow for the mobility or desorption of atoms or molecules. The facetted surface eventually exhibits a very regular long-range structure. Faceting of an insulator was shown by Henrich in 1957 for the MgO(110) and MgO(111) surfaces which form (100) facets upon annealing [85].

For $Al_2O_3(10\bar{1}0)$ surfaces, the topography will take the form of parallel ridges and valleys when annealed in air, where one slope is a $(1\bar{1}02)$ facet and the other slope a complex curved surface which does not resemble any simple crystallographic plane. After ten hours of annealing the distance between ridges assumes a value of 300 nm and the number of facet junctions essentially drops to zero [70].

Similarly, the (110) surfaces of alkali halide crystals are unstable surfaces, which undergo faceting upon annealing in vacuum. Sugawara *et al* have for example produced a ridge–valley pattern with 90 nm periodicity on a NaCl(110) surface where the stable slopes were formed by (100) and (010) surfaces [5]. The surface has been prepared by short etching in water before transfer to the vacuum chamber and annealing. An array of pyramidal structures could be prepared by annealing of a NaCl(111) surface [77]. However, the control of the final ridge structure made of (100) facets has proven difficult due to a complex competition between nucleation of etch pits at dislocations, desorption of NaCl from kink sites, and desorption of contaminants. The higher quality of the resulting structure on Al_2O_3 surfaces as compared to NaCl is explained by the different processes of surface reorganization. While mass transport on the surface prevails on Al_2O_3, molecular desorption dominates in the case of alkali halide surfaces, resulting in a mixture of facets and evaporation spirals around dislocations. This problem can be addressed by employing homoepitaxial growth instead of annealing.

3.1.4. Homoepitaxy. The creation of stable (100) facets on a NaCl(110) surface through additional evaporation of NaCl has been described by Sugawara and Mae [76]. The authors evaporated NaCl layers onto a preheated NaCl(110) surface and produced a very regular ridge structure with a self-limited width of 30 nm for film thicknesses above 75 nm. The same authors have repeated the experiment for the evaporation of MgO onto a MgO(110) surface [75]. While MgO is a preferable material compared to NaCl as it is more stable at high temperatures and less hygroscopic, the formation of the ridge–valley structure seems to be more difficult to prepare. The use of electron-beam assisted evaporation which is known to produce oxygen deficient films may explain these difficulties. Ridge and valley structures have also been obtained in homoepitaxy of LiF and CaF_2 on LiF(110) and CaF_2(110) surfaces at elevated temperatures [74].

Duan *et al* have used helium scattering to investigate the homoepitaxial growth of NaCl on a NaCl(100) surface [55]. A layer-by-layer growth in a wide range of temperatures was found, where the height of one layer would correspond to half a NaCl unit cell. The rapid decay of the scattering cross-section for adsorbed NaCl above a temperature of 250 K indicates that NaCl molecules become very mobile above this threshold. Yang and Flynn described epitaxial growth in alkali halide homo- and heteroepitaxy even for temperatures as low as one tenth of the melting temperature [86]. While homoepitaxy does not allow for a controlled lateral structuring of the surface it still can produce an increased step density with its nucleation potential for adsorbate overgrowth. A general growth feature providing atomically straight steps is observed in the growth of thin films of alkali halide or oxides. While the first monolayer or double layer covers large areas of the substrate surface in single domain islands of often micrometre size, the subsequent monolayer grows in form of rectangular islands with a side length of some tens of nanometres, as observed for example for NaCl/Cu(111) [58], MgO/Ag(100) [51], NaCl/Ag(100) [87], or KBr/Ge(100) [88]. This growth mode continues to form pyramidal structures for thicker films of KBr [89].

Table 2. Examples for structured surfaces involving thin insulating films.

CaF$_2$ on Si(111)	Stripes of CaF and CaF$_2$ on a stepped substrate	[90]
CaF$_2$ on Si(111)	Sawtooth pattern upon annealing	[91]
KBr on NaCl(100)	Superstructure with 2.8 nm periodicity	[92]
KCl on NaCl(100)	Regular array of defects	[93]
MgO on Ag(100)	Mosaic formation with average size of 7 nm	[14]
MgO on Ag(100)	Mosaic formation obscures the structure of the stepped substrate	[94]
NaCl on Cu(211)	Ridge–valley faceting of substrate into Cu(111) and Cu(311)	[95]
NaCl on Cu(532)	Pyramidal faceting of substrate into Cu(111), Cu(311), and Cu(531)	[96]

3.2. Thin films of insulators

In this section we present experimental results from studies of thin films of insulators which exhibit some form of regular structure. The film may reflect the structure of the substrate, develop its structure as a mean of strain relief in heteroepitaxy, or induce a faceting of the substrate. All examples are listed in table 2.

3.2.1. Insulating films on structured substrates.
One pathway to create structured surfaces of wide band gap insulators is the growth of such material on metal or semiconductor substrates which have been structured beforehand using well-established recipes. Viernow *et al* produced striped phases of CaF and CaF$_2$ with a periodicity of about 15 nm which was defined by the stepped substrate [90]. The substrate, a 1.1° vicinal miscut of a Si(111) surface, was covered by a monolayer of CaF forming a strong chemical bond with the silicon surface. The next half monolayer of CaF$_2$ forms stripes on top of the CaF layer along the underlying steps. The difference in electronic states of the two materials, namely a lower conduction band minimum for the exposed CaF stripes, has been revealed by locally resolved tunnelling spectroscopy. Other attempts to transfer the step structure of a vicinal substrate to an insulating thin film have been less successful due to the strong cohesive energy within the films which results in a carpet-like coverage of substrate steps for NaCl on Ge(100) [97] or NaCl on Cu(111) [58]. Kramer *et al* have grown MgO films on vicinal Ag(100) substrates [94]. They find that closed films are formed at a coverage higher than five monolayers. However, it is only partly possible to transfer the step structure of the MgO film surface because of mosaic formation [14].

A different approach has been followed by Ernst *et al* who have used the 6×1 reconstruction of Ge(100) covered in small amounts of Na to produce a regular modulation in an overgrown NaCl film [98].

3.2.2. Film structures resulting from strain relief.
Insulating thin films regularly exhibit a lattice mismatch with the underlying substrate. The resulting strain produces structural defects in the film during its transition from the strained interface to a relaxed film of more than about ten monolayers. Typical examples are the mosaic formation in MgO films on Ag(100) [14] or the misfit–dislocation network in MgO on Fe(001) [60]. Furthermore, the borders between areas of different epitaxial orientation can form a network of domain boundaries, like in the case of Al$_2$O$_3$ on NiAl(110) [47].

Mauch *et al* have studied NaCl growth on Cu(100) and found a surprisingly strong interaction of NaCl with the substrate. A straightening of the substrate steps and the formation of regular stripe patterns was observed [99]. A similar expression of the film–substrate symmetry in strain relief structures was found by Heim *et al*, who observed saw-tooth pattern upon annealing of stepped structures of CaF$_2$ grown on Si(111) [91].

Table 3. Examples for radiation-induced structures in insulators.

CaF$_2$(111)	Triangular metallized patches after low-energy electron irradiation	[109]
KI(100)	Rectangular pits after UV irradiation	[103]
KBr(100)	Rectangular pits after low-energy electron irradiation	[104–107]
NaCl(100)	Rectangular structures in the course of layer-by-layer desorption under photon irradiation	[102]
MgF$_2$	Formation of ripples after sputtering under 72° angle	[111]

3.2.3. Restructuring of the substrate upon film growth. Fölsch *et al* have found that the Cu(211) surface undergoes faceting when NaCl is evaporated on top of the surface [95]. The facet surfaces are Cu(111) and Cu(311). The driving force behind the faceting is the tendency of the NaCl film to form a (100) structure and the perfect lattice match between the NaCl(100) and the Cu(311) planes. Consequently, only the Cu(311) facets are covered in NaCl, while the Cu(111) surface are bare of NaCl. For a coverage of 0.6 monolayer NaCl a periodicity of about 10 nm is obtained. The study has been extended towards a Cu(532) surface which formed a regular array of pyramids after evaporation of NaCl. The side walls of the pyramids are bare Cu(111) surfaces and NaCl(100)-covered Cu(311) and Cu(531) surfaces [96]. Chemically selective adsorption on the bare Cu(111) side walls has been demonstrated by dosing CO$_2$ molecules and analysing the resulting surface structure by STM at 80 K.

3.3. Superstructures in heteroepitaxy

The strain relief in heteroepitaxial systems can produce quite regular dislocation networks. Dislocation networks in metal heteroepitaxy have been successfully used as templates for the growth of arrays of clusters [100].

Duan *et al* have studied the growth of KBr films on NaCl(100) by means of He atom scattering [92]. They found signatures of a superstructure with a periodicity of 2.8 nm which arises from a match between six lattice constants of KBr and seven lattice constants of NaCl. Helium diffraction further revealed that for the first three monolayers KBr assumes the substrate lattice constant while building up a corrugation with the periodicity of the superstructure. Further evaporation causes a transition to the KBr lattice constant which is completed at a coverage of seven monolayers. The superstructure has been also been observed as a surface corrugation by means of non-contact AFM [101].

Henzler *et al* have suggested that the misfit in heteroepitaxy may produce regular arrays of stacking faults in certain systems [93]. One example is a 2.2 monolayer film of KCl grown on a NaCl(100) surface, which exhibits a LEED pattern that can not be explained by any strained film configuration but requires a regular defect array interpretation.

3.4. Radiation-induced structures

Radiation by photons or electrons can cause desorption induced by electronic transitions from insulating surfaces. The creation of defects quite generally changes the reactivity of the surface and consequently influences the structure of adsorbates on it. One example is the change of the morphology of Fe films grown on CaF$_2$ upon electron irradiation of the substrate [91]. In the cases discussed below (see also table 3) the structure of the radiation damage reflects the symmetry of the crystallographic surface structure.

On surfaces of alkali halide crystals, radiation-induced defect processes can produce ordered structures. Höche *et al* used He atom scattering to study a layer-by-layer desorption

Table 4. Metal clusters and wires on structured insulators.

Au on KBr(100)	Clusters on evaporation spirals	[21]
Au on NaCl(100)	Clusters on evaporation spirals	[21]
Au on NaCl(110)	Clusters and wires the facetted surface	[117, 118]
Fe on $Al_2O_3(10\bar{1}0)$	Wires and clusters on the facetted surface	[119, 120]
Fe on CaF on Si	Wires through photolysis of ferrocene on films of CaF on stepped Si surfaces	[121]
Fe on NaCl(100)	Clusters on cleavage steps and evaporation spirals	[112]
Fe on NaCl(110)	Wires on facetted surface	[77]
Fe on NaCl(111)	Clusters on facetted surface	[77]
Nb on $Al_2O_3(10\bar{1}0)$	Wires at the ridges of facetted surface	[122]
Pt on $Al_2O_3(10\bar{1}0)$	Clusters on facetted substrate	[123]
Sn on NaCl(100)	Crystalline clusters oriented along the steps of evaporation spirals	[116]
Sn on KCl(100)	Epitaxial clusters nucleated along the steps of evaporation spirals	[116]

from NaCl(100) surfaces under photon irradiation and documented the square structure of radiation-induced pits in the surface by means of the decoration technique and SEM [102]. Wilson *et al* have irradiated the surface of KI with ultraviolet light and studied the developing surface structure by means of AFM under dry atmosphere conditions [103]. They found square pits with edges oriented along the crystallographic ⟨100⟩ directions. A similar process was observed for the irradiation of KBr(100) with low-energy electrons [104, 89, 105]. High-resolution AFM reveals that the pits in KBr have a depth of one atomic layer and are bordered by atomically straight edges along crystalline directions [106, 107]. Such atomically straight steps are not obtained when the pits are produced by He^+ irradiation [108]. In the case of CaF_2, low-energy electron irradiation induces the metallization of the surface in form of triangular patches which reflect the symmetry of the $CaF_2(111)$ surface [109].

The formation of ripples on surfaces after sputtering with non-normal incidence, which is well described for metal surfaces [110], has been also found for an insulating surface, namely MgF_2 [111].

4. Adsorbate growth on structured insulators

In the second part of this overview of experimental results, we will discuss adsorbate growth on wide band gap insulators which is influenced by the surface structures introduced above. The discussion will focus on two topics, the growth of metallic clusters and wires (see table 4) and the formation of molecular assemblies (see table 5).

4.1. Metal clusters and wires

Nanometre-scale metal clusters or wires on insulating surfaces have been extensively studied for their role in catalysis. Here we are interested in how far the distribution of such metal particles can be influenced by a structured surface. The lateral distribution can be studied in some detail by means of AFM. Since steps on the surface are the elementary building block of any structure, their effectiveness as templates for guided metal cluster growth needs to be analysed. Gai *et al* have studied the decoration of NaCl steps by Fe layers [112]. By means of non-contact AFM experiments in vacuum they found that Fe clusters are nucleated at kinks in step edges and then grow in size on the upper NaCl terrace to eventually form wires along the steps. A decoration of cleavage steps was also found for Au on KBr(100) for small coverage [113].

On the other hand, some systems exhibit a nucleation of metal clusters on terraces which is largely independent of the step structure. Haas *et al* employed AFM at variable temperatures

to study the growth of Pd clusters on MgO(100). A constant island density was found for a wide temperature range, indicating heterogenous nucleation on point defects with a high trapping potential [114]. Similarly, Pd clusters were found to nucleate evenly over terraces on Al_2O_3(0001) surfaces by Tait *et al* [84]. Again for the MgO(100) surface, Hojrup *et al* studied the growth of Au clusters and concluded that heterogenous nucleation at point defects is the dominating process [115]. Without too many systems studied, one might ask if in general the number and the trapping potential of point defects on oxide surfaces are higher than those for alkali halide surfaces. The challenges in imaging oxide surfaces with atomic resolution by non-contact AFM [34, 35, 37, 45] as compared to alkali halide surfaces [30, 33, 32] point into this direction. On the other hand, the subsequent paragraphs will introduce studies which describe a complete metal dewetting of facets on the Al_2O_3 surfaces. Certainly, randomly distributed nucleation sites will always compete with ordered surface structures in their effect on adsorbate overgrowth.

4.1.1. Metal cluster on evaporation structures. For the surfaces of alkali halide crystals, the regular evaporation structure evolving around emerging dislocations can be used as a template for the growth of metal particles. The early work in this field, focusing on the step structure and the nucleation mechanisms on terraces and steps has been reviewed by Krohn [20]. Kasukabe and Osaka have compared the growth of Sn clusters at the steps of evaporation spirals on KCl and NaCl. They found that the competition between epitaxial growth, i.e., orientation of the Sn crystallites along the substrate direction, and grapho-epitaxial growth, i.e., orientation of the Sn crystallites along the step direction, favours the latter for NaCl, while epitaxial growth is found for KCl [116]. Yamamoto *et al* have studied the growth forms of small Au clusters on KBr(100) and NaCl(100) evaporation structures [21]. Epitaxial clusters grow at higher temperatures on KBr(100) surfaces, while multiply twinned particles dominate at lower temperatures. The crossover temperature is higher (200 °C) for particles attached to steps compared to particles found on flat terraces (150 °C). In the case of NaCl(100), multiply twinned particles dominate for the whole accessible temperature range. The results indicate a delicate balance between epitaxial interactions, orientation along the step, and internal crystallinity of the metal clusters.

4.1.2. Metal clusters and wires on facetted structures. The surfaces of Al_2O_3 are preferred substrates for the growth of metal clusters due to their stability in ambient environment and at high temperatures. As described above, parallel structures can arise from faceting upon annealing of the $Al_2O_3(10\bar{1}0)$ surface. The facet structure can be used to produce metallic wires through shadow evaporation under high angles of incidence. Following this approach, Huth *et al* grew Nb nanowires and demonstrated that Nb grows with the (100) planes parallel to the $Al_2O_3(1\bar{1}02)$ facet plane [122]. The striped morphology of the film is explained by a dewetting from the facets which favours wire formation at the ridges. Westphalen *et al* studied the growth of Fe on the facetted $Al_2O_3(10\bar{1}0)$ surface and analysed that dewetting from facet planes influences the growth, however yielding clusters rather than wires [119]. Oster *et al* succeeded in growing Fe nanowires, when the ridges of the facetted substrate were separated by 250 nm and had a height of 50 nm [120]. The substrate was held at 450 °C, and the resulting morphology depended strongly on the evaporation angle. For shallow deposition angles, separated Fe islands with sizes determined by the ridge distance dominated, while larger deposition angles produced continuous wires which show characteristic lacings indicating growth by coalescence. Ravishankar *et al* have produced ordered arrays of Pt nanoparticles at high temperatures using the same facetted $Al_2O_3(10\bar{1}0)$ surface as the template but without exploiting the shadowing effect of the facets [123]. The authors observe the nucleation of

particles on the crests of their facetted surface. They attribute this effect to electrostatic singularities along the crests. The uniform size distribution of particles is explained as the equilibrium state of liquid droplets subject to electrostatic and capillary forces. Scanning electron microscopy could reveal their coherent crystallographic orientation with the substrate.

For the class of alkali halide surfaces, Sugawara *et al* have grown Fe nanowires on NaCl(110) facetted surfaces through shadow evaporation [5]. Wires with a width of 30 nm and an estimated length of 10 μm are found which show a strong in-plane magnetic anisotropy. A similar template strategy for the creation of metal dot arrays has been based on the annealing of the NaCl(111) surface [77]. Kitahara *et al* have grown Au nanowires on faceted NaCl(110) surfaces. As repeatedly observed, Au grows in form of dots along the facets, and only high coverage provides a connection between dots into wires. An optical anisotropy of the wires was demonstrated by means of non-linear optical response [117, 118]. The use of alkali halide surface structures for the growth of metal clusters is limited in the accessible substrate temperatures. In many cases, the substrate structure starts to change through evaporation before a temperature is reached that would activate epitaxial orientation of the metal clusters.

4.1.3. Metal clusters on structured thin films. Structured thin films of insulators on conducting substrates can be considered a particularly interesting option for the growth of clusters. Not only can the methods of electron spectroscopy be applied for an analysis of the electronic structure, but the electronic coupling between the metal particle and the substrate can be controlled through the film thickness. The range of possibilities has been demonstrated in two recent experiments. Variations of the electronic states in a single Pd atom were shown to indicate defects in the ultrathin underlying Al_2O_3 film by Nilius *et al* [124]. Repp *et al* were able to control the charge state of a single Au atom on a monolayer NaCl film electron by electron [3].

As discussed in section 3.2, only a few examples have been reported where a regular substrate structure could be transferred to a thin film. Lin *et al* have used a vicinal Si(111) surface as stepped substrates and created a template by CaF_2 overgrowth. By choosing the appropriate coverage and evaporation conditions, they could produce nanometre-wide trenches of CaF separated by stripes of CaF_2 film. Ferrocene molecules self-assembled in the CaF trenches. Finally, the structure was developed by means of ultraviolet light which removed organic ligands and left Fe on the surface. Repeated cycles of selective adsorption, photolysis, and annealing produced Fe nanowires of 3 nm width and 0.8 nm height [121].

4.2. Molecular assemblies

The self-organization of organic molecules into ultrathin layers with high order is currently a growing field at the interface between Nanoscience and Surface Science [125]. The prospect of molecular electronics, i.e., a device physics which is based on both the rich conductance properties and the self-organization ability of organic molecules, is a strong driving force behind these activities. Most experiments reported so far deal with metal substrates, posing obvious questions regarding the separation of the envisaged molecular electronic device from the delocalized electronic structure of the substrate. Dedicated molecular designs have been proposed for such separation and tested for their function [126]. Here we are interested in ultrathin ordered layers of molecules which are guided by structures on wide band gap insulators. While insulating crystals are widely used as substrates to grow three-dimensional crystallites of organic molecules, only limited work has been done with regard to ordered molecularly thin layers. Examples are high-resolution AFM studies of C_{60} on NaCl(100) [127] or vinylidene on KCl(100) [128]. The weak interaction between wide band gap insulators

Table 5. Assemblies of organic molecules on structured insulators.

Alq$_3$ on KBr on Ag(111)	Cluster with similar appearance for one and two layers of KBr	[134]
C$_{60}$ on KBr(100)	Ordered films nucleated at cleavage steps	[135]
Cu–TBBP on Al$_2$O$_3$(0001)	Irregular assemblies at steps of annealed surface	[71]
Cu–TBBP on KBr(100)	Irregular assemblies at steps of evaporation spiral	[71]
DPP on CaF on Si	Striped pattern of assemblies following substrate steps	[136]
Ferrocene on CaF on Si	Striped pattern of assemblies following substrate steps	[121]
PTCDA on KBr(100)	Confined assemblies in radiation-induced pits	[71]
PTCDA on KBr on Ag(111)	Cluster with shape and orientation depending on film thickness	[137]
SubPc on KBr(100)	Ordered assembly within radiation-induced pits	[138]
ZnDBPc on Al$_2$O$_3$($\bar{1}$012)	Organic crystallites oriented along substrate steps, not any substrate crystallographic direction	[73]

and organic molecules as compared to intermolecular interaction favours the growth of three-dimensional crystallites even at very low coverage [129].

An analytical model for the interaction between molecules and steps on surfaces of insulators has been developed by Briquez *et al* [130]. In comparing dispersive forces and electric dipole forces, the authors suggested that the former align the molecular axis along the step, while the latter favour perpendicular configurations. Stable adsorption of small molecules like CO$_2$ on a step on the NaCl(100) surface can be expected only at temperatures below 100 K [131]. Ramseyer *et al* have calculated how the confinement of a molecular layer on a vicinal surface could influence the molecular ordering [132]. Beyond the potential of steps and corners at surfaces to trap molecules, their particular electronic structure can also be directly involved in chemical processes. Such a 'chemistry of corners and edges' has recently been studied experimentally and theoretically for the dissociation of H$_2$ at photo-excited corner sites on the MgO(100) surface [68]. Other studies include the photochemistry of acetylene at steps on the NaCl(100) surface [133]. The modelling of the interaction of larger molecules with steps on insulating surfaces is still limited by the required amount of computing power.

4.2.1. Molecular layers on structured crystal surfaces. Our first example of template growth on an insulator is a thin film of ZnDBPc on an Al$_2$O$_3$($\bar{1}$012) surface which was polished with a slight miscut, reported by Hayashi *et al*. The group found that the organic crystallites were oriented along the direction of the monatomic steps on that surface, following the azimuthal orientation of the miscut rather than any crystallographic direction of the substrate [73].

Nony *et al* have studied the adsorption structure of various organic molecules on stepped surfaces of KBr and Al$_2$O$_3$. Several molecules which form well-ordered monolayer structures on metal surfaces were found to grow in form of irregular clusters at step edges on these insulating surfaces. The only case where molecules could be confined to a flat monolayer assembly was the trapping of perylene-type (PTCDA) molecules in rectangular pits of monatomic depth, which had been produced by electron irradiation. However, only small pits with a side length of less than 30 nm would trap such a molecular assembly [71]. For larger holes Mativetsky *et al* observed that trapping of PTCDA molecules in the pits occurred when crystallites of three molecular layers height had formed. Only for clusters of four layers height did the cluster start to grow beyond the confinement of the pit [139]. On the same surface structure, a monolayer of SubPc molecules was found to arrange in small pits in an ordered fashion, and the molecular structure was resolved by high-resolution AFM [138]. A calculation of the different interactions revealed that the strong interaction between the molecular dipole and the uncompensated charge in the corner of a pit in the KBr surface nucleates the molecular layer in the pit, while intermolecular interactions determine the structure of the layer [138].

Burke *et al* have studied the growth of C_{60} molecules on cleaved KBr(100) surfaces [135]. They found that C_{60} islands start to grow from monatomic cleavage steps on the surface. High-resolution imaging of kinks in such steps by means of non-contact AFM revealed small noisy patches close to the kinks. The patches can be interpreted as loosely bound molecules which constitute the initial phase of island nucleation. Different growth was found for islands attached to steps compared with islands on terraces. The island shapes indicate a complex competition between intermolecular interaction, molecule–substrate interactions, and molecule–step interactions: the frequent appearance of a hexagon motive in the island shape shows intermolecular ordering, the adjustment of such hexagon to cleavage steps reveals the influence of steps sites, and the registry of islands found in the of middle of large terraces to the substrate lattice demonstrates the role of the molecule–substrate interaction. Furthermore, exotic branching of the islands indicates that the islands may not be in stable equilibrium after thermal evaporation of the molecules onto the substrate at room temperature.

Tanaka *et al* have prepared surfaces of $SrTiO_3$ with straight monatomic steps in order to explore their influence on the growth of CxTBPP molecules. In this case, however, a strong molecule–substrate interaction suppresses the molecule mobility necessary for an assembly process, and single molecules are found on surface terraces [140]. Similar covalent contributions to the growth process of molecules have been observed before in high-resolution AFM studies of semiconducting TiO_2 surfaces [141].

4.2.2. Molecular layers on thin insulating films. The use of ultrathin insulating films for the study of molecular layers seems particularly promising. Repp *et al* have shown by means of low-temperature STM that the electronic structure of an adsorbed molecule can be disentangled from that of the metal substrate by means of a monolayer NaCl film [142]. Similarly, Cavar *et al* have demonstrated on the example of C_{60} on NaCl/Au(111) that molecular identification through vibrational spectroscopy is possible on the single molecule scale. The detection was realized by spectroscopy of luminescence emitted from the molecules under the STM tip [143]. The ordering of molecules depends strongly on the molecule–substrate interaction and, consequently, on the thickness of the insulating films. Ramoino *et al* observed a hierarchical degree of ordering in the self-assembly of CuOPEC molecules on NaCl films of different thickness grown on an Ag(100) substrate [87]. A similar effect was found for the growth of PTCDA molecules on monolayer and double-layer films of KBr on Ag(111) [137]. The intermolecular interactions become dominant over the molecule–substrate interactions going from one to two layers of KBr as evident in the cluster size and orientation. No difference between the first and the second layer of KBr on Ag(111) is observed in the growth of Alq_3 molecules [134].

As one example for the ordering of organic molecules on structured thin films, Rauscher *et al* have used a template of CaF trenches between CaF_2 stripes to assemble 3,10-di(propyl)perylene molecules in parallel, equidistant stripes of 1–15 nm width [136]. The authors assume that the π-electron system of the molecules interacts strongly with the CaF based on a good match of the molecular HOMO–LUMO gap and the band gap of the CaF layer. The stronger electronic interaction as compared to the expected van der Waals interaction with the fully insulating CaF_2 stripes facilitates the selective adsorption of the molecules. The same thin-film template has also been employed to guide the growth of ferrocene molecules [121].

5. Concluding remarks

The experimental results collected in this review document the progress that has been achieved in the Surface Science of wide band gap insulators. An important contribution to this field

has come from the development of force microscopy into a characterization tool with atomic resolution. Further progress in the microscopic understanding of the growth of adsorbates along surface structures would profit from an improvement of the preparation of atomically straight steps. Considering the results obtained so far, molecular growth seems to be the most promising route to follow for the creation of insulating substrates. Defect-free terraces of MgO(100) bounded by straight steps have been created as thin films, not by cleavage or sputtering. Similarly, a controlled faceting of the NaCl(110) surface was obtained by homoepitaxy rather than by thermal annealing. Variation of the thickness of insulating films also gives an opportunity to tune the interaction between adsorbates and the substrate, as several recent studies have impressively demonstrated. The growth experiments on stepped surfaces indicate that steps act indeed as nucleation sites. The interaction with metal atoms or organic molecules, however, is still weak so that isolated clusters are formed rather than ordered structures along the steps. One fascinating possibility in wide band gap insulators is the selective optical excitation of step and corner sites which may increase their trapping potential through defect formation [68].

A parallel approach to the methods of Surface Science for the structuring of insulators may be looked for in working at the liquid–solid interface. Structures similar to the ones described in this review have been created using growth and dissolution processes. Examples for these structures are regular steps at the slopes of growth spirals [144], rectangular dissolution pits of monolayer depth in $CaSO_4$ surfaces [145], or the faceting of $CaCO_3$ surfaces [146]. Furthermore, polar ionic surfaces like NaCl(111) can be stabilized at the solution interface [147]. For the investigation of the interface between insulating substrates and solution, x-ray diffraction [148] and electron spectroscopy [149] have been developed in addition to force microscopy.

Acknowledgments

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