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Study of optical properties of Mo_xC_{1-x} films

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Abstract

Metallic optical mirrors are foreseen to be exploited in plasma diagnostic systems in ITER. They will suffer from deposition of impurities like carbon causing marked changes of the reflectivity. In this paper, we have focused on the co-deposition of Mo_xC_{1-x} films ($0 \leqslant x \leqslant 0.61$) and have studied the influence of the deposited thin film composition on the optical properties. Deposits were performed by magnetron co-sputtering with argon as process gas in a high vacuum system. In-situ XPS measurements, real time reflectometry, ex-situ spectrophotometry and spectroscopic ellipsometry were used to characterize the resulting layers. Carbide formation was evidenced. As expected, optical constants of the films and reflectivity were found to depend strongly on the film composition. Simulations of the impact of thin film composition on the reflectivity of a molybdenum mirror show how a thin deposited layer can drastically degrade the reflectivity.

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1. Introduction

In a fusion reactor, and especially in ITER, knowledge of the plasma parameters is of highest interest to control and understand the performances of such a device. All regions of the plasma will be investigated, and so diagnostic systems will be installed in different locations. The broad variety of the determined parameters (impurity species, density) requires the application of different spectroscopic methods [1]. Metallic mirrors are planned to be used either as plasma facing components or as light transmitter through a labyrinth. Despite the harsh ambient conditions these mirrors will have to preserve the required optical performances. First mirrors will suffer from intense UV and X-rays radiation as well as particle fluxes due to charge exchange atoms. Moreover, deposition of impurities from the erosion of the first wall protection and the divertor tiles can be expected. Several investigations of the changes of the optical features of mirrors when the dominant damage mechanism is erosion have been made [2–4]. It was found that high-Z refractory materials such as tungsten or molybdenum, particularly in the form of single crystals, can have a sufficiently long lifetime. The influence of a contamination surface layer on the reflectivity has only been studied so far for pure boron and carbon contaminants [5]. A possible diffusion into the bulk material and the possible chemical reaction between the mirror material and the diffused impurities has not been taken into account. In present devices like TEXTOR, metallic mirrors, e.g. polycrystalline Mo, are exposed in the

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sputter dominated zone to investigate the reflectivity changes in dependence on the implantation of carbon into the surface. For one of the exposed sample, local overheating up to 1000 °C was observed [6]. Impurities have been found to be deeply diffused in the Mo bulk, and the resulting layer appears to be an intermixing of Mo and impurities like carbon and boron. In the present study, we have focused on the co-deposition of molybdenum and carbon, to model somehow this intermixing effect, and have studied both the influence of the layer composition on the optical properties and the formation of molybdenum carbide. Transition metal carbide formation [7] and properties [8,9] have been widely studied because of their high interest for catalytic applications. However, to the best of our knowledge, no study about the impact of the carbide formation in a mixed Mo-C layer on the optical properties has been carried out so far.

2. Experimental

Co-deposition of molybdenum and carbon were performed in a high vacuum chamber pumped down to a base pressure of about 2×10^{-4} Pa using a conventional pumping system associated to a liquid nitrogen trap. A water cooled dual magnetron, consisting of a circular molybdenum target and a ring shaped graphite target, was used. The inner Mo target was driven by a rf power supply (13.5 kHz), the outer one by a pulsed-DC power supply. The relative concentrations of Mo and C in the film were changed by modifying the power applied to each target. During thin film deposition, the grounded substrate faces the targets at a distance of several centimetres. Argon, introduced through a mass flow controller, is used as sputter gas leading to a pressure of 5.4×10^{-1} Pa in the deposition chamber adjusted by a throttling value to the pumping system. Depositions were made at room temperature on silicon (100) substrates cleaned by Ar sputtering provided by a Kaufman-type ion source. Simultaneously to the thin film formation, reflectivity data were measured using a real time laser reflectometer (λ = 532 nm) [10]. A quantitative determination of the optical constants was made by a numerical fit of the formula for the reflectivity of a single layer on a substrate [11]. This fit yields the index of refraction n and extinction coefficient k at the laser wavelength (532 nm) as well as the growth rate of the film. Knowing the deposition time it is then possible to calculate the film thickness. Samples whose results are presented here have thickness in the range 150–250 nm.

After deposition, the samples were transferred from the high vacuum plasma chamber to the UHV XPS chamber without breaking the vacuum. The electron spectrometer is equipped with a hemispherical analyser and an X-ray source (Mg Kα excitation, $h\nu$ = 1253.6 eV) for core level spectroscopy. As reference for the electron energy calibration a gold sample with the Au $4f_{7/2}$ line at 84.0 eV is used.

Traces of oxygen as detected by XPS are probably due to the residual presence of gas in the deposition chamber. However, the concentration has been found to be less than 5 at.%, and its effect will be neglected.

Ex-situ measurements of the total reflectivity were carried out with an UV–VIS–NIR spectrophotometer (Varian Cary 5), equipped with an integrating sphere, under normal incidence in the spectral range 250–2500 nm. Moreover the ellipsometric angles (Ψ, Δ) were measured by means of a spectral ellipsometer in the range 300–850 nm for the incident angles 45,55 and 65°. The fit of these data enables the determination of the optical constants as a function of the wavelength.

3. Results and discussion

3.1. XPS measurements on Mo_xC_{1-x} films

Mo_xC_{1-x} films have been prepared in the composition range $0 \leqslant x \leqslant 0.61$. From intensities of the Mo 3d

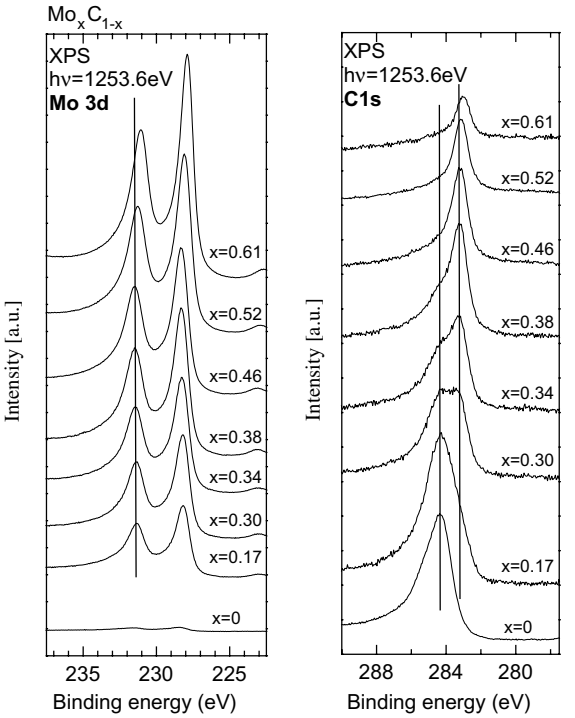

Fig. 1. Mo $3d_{3/2,5/2}$ doublet and C 1s core level spectra of Mo_xC_{1-x} films deposited at room temperature. Vertical lines are present as eye guide.

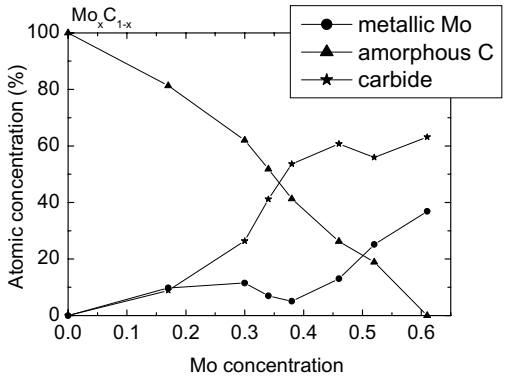

Fig. 2. Composition of the Mo_xC_{1-x} films in terms of the three phases Mo, C, and MoC as a function of x.

and the C 1s peaks and taking into account the photoionization cross sections of both elements, the atomic concentrations in Mo and C have been calculated. Fig. 1 shows the Mo 3d and C 1s lines. The graphs on the bottom correspond to a pure amorphous carbon phase deposited by operating solely the graphite target. The Mo doublet exhibits a slight shift towards lower binding energy when x increases. The most pronounced effect is noticed on the carbon line. It shows both a shift towards lower binding energies and a modification of the line shape. A deconvolution with 2 lorentzian-gaussian curves performed, after a Shirley background subtraction [12], (not shown here), reveals two components of the C 1s line at 284.3 and 283.2 eV respectively. The former line is associated to a pure amorphous carbon phase and the latter one reveals the typical chemical shift of molybdenum carbide. These positions are consistent with the ones reported by other authors [13,14]. The intensity of the amorphous carbon peak decreases and the intensity of the carbidic component increases with increasing x. The stoichiometry of the carbide formed was found to be MoC, probably in a hexagonal structure, which is a stable phase at room temperature as reported by Hugosson et al. [15]. Hence, a simultaneous deposition of Mo and C can lead, at room temperature, to the formation of carbide. Nevertheless, XPS shows that in all cases, the films are composed of a mixture of a-C, Mo and MoC, i.e. the reaction between Mo and C is not complete.

Fig. 2 shows the composition of the Mo_xC_{1-x} films in terms of the three phases Mo, C, and MoC as a function of x. As seen for x higher than 0.4, the layer is mainly composed of carbide.

3.2. Optical measurements on Mo_xC_{1-x} films

Fig. 3(a) shows the dependence of reflectivity of the deposited thin films on the composition of the layer.

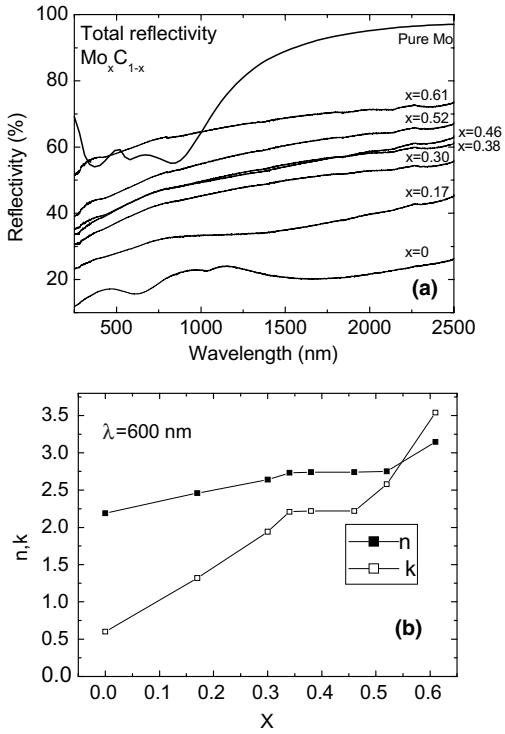

Fig. 3. (a) Evolution of total reflectivity of Mo_xC_{1-x} films as a function of wavelength. (b) Refraction and absorption index determined at 600 nm from spectroscopic ellipsometry measurements as a function of x.

Reflectivity spectra for $x = 0.34$, 0.38 and 0.46 exhibit approximately the same behaviour over the wavelength range investigated. For an easier reading, reflectivity spectrum for $x = 0.34$ has been omitted. Reflectivity of pure molybdenum has been calculated using optical constants found in the literature [16]. As seen, the more carbon the film contains, the lower the reflectivity. From the ellipsometry measurements, the optical constants n and k have been calculated in dependence of the composition (Fig. 3(b)). For this calculation, we used the model of a semi-infinite silicon substrate covered with a 2 nm thick layer of native silicon oxide and with a layer with a known thickness as determined by in-situ laser reflectometry (but with optical constants as free parameters). As can be seen in Fig. 3(b), evolution of both n and k as a function of x, at 600 nm, shows a plateau for the three values of x mentioned before. It remains unclear to know how three films with different compositions (as shown in Fig. 2) can exhibit the same optical properties. It is quite difficult to determine which phase rules the evolution of the reflectivity, and knowledge of the spatial organization of the different phases is needed to quantify it by the use of an effective medium approximation (will be published elsewhere).

3.3. Simulation of reflectivity of Mo_xC_{1-x} layer on pure Mo

Since molybdenum mirrors are foreseen to be used in the diagnostic systems of ITER, and since carbon is one of the major impurities in tokamaks, deposition of a carbon overlayer on the Mo surface is expected. To investigate how it will affect the optical features, molybdenum mirrors have been exposed in the scrape-off layer of TEXTOR and on one sample overheating up to 1000 °C was observed and so carbon was found to be deeply diffused in the bulk molybdenum [6]. In this case, possible formation of molybdenum carbide has to be taken into account. Using dedicated software and values of the optical constants found before, we have simulated the impact of a growing Mo_xC_{1-x} layer on the specular reflectivity (which is the mirror-like reflection) of a polycrystalline molybdenum mirror. This simulation should reproduce the effect of both deposition and diffusion of carbon on a Mo mirror. Indeed here we consider the case of an ideal system with a fixed composition although carbon concentration decreases from the surface to the bulk in the real case. Nevertheless the use of such an approximation is justified by the effective medium theory and has already been used to predict optical properties of inhomogeneous media [17]. Results for $\lambda = 600$ nm are shown in Fig. 4. As described before, composition of the overlayer has a strong influence on the reflectivity. Even a layer with a thickness of about 50 nm can significantly degrade the optical properties of the mirror. After deposition of 200 nm, the reflectivity is only ruled by the layer formed. Observations of the effect of carbon and boron deposition on stainless steel mirrors were made in [2,5] but with thicknesses less than 21 nm. A significant decrease of the reflectivity was observed. But in these references, only a pure depositing layer on a mirror surface was investigated without taking into account possible interactions between the deposited layer and the substrate. It is now clear that in case of diffusion of impurities into the mirror material, chemical reaction between elements may have an influence on the optical features of the mirror.

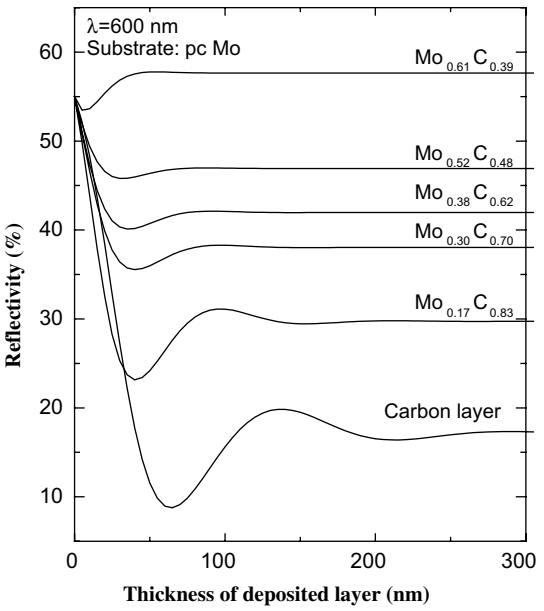

Fig. 4. Simulated impact of a mixed Mo_xC_{1-x} layer deposition on the reflectivity of a polycrystalline molybdenum mirror.

4. Conclusion

Co-deposition of Mo and C has been made by use of magnetron sputtering. Formation of molybdenum carbide was evidenced. Optical properties of the deposited layer were found to depend strongly on the film composition. Simulations of the impact of thin film composition on the reflectivity of a molybdenum mirror show how a thin deposited layer can significantly degrade the reflectivity. In case of mirrors placed in diagnostic systems in fusion device, if diffusion of impurities into the bulk occurred then impact of the chemical reaction between host material and impurities on optical properties has to be taken into account.

Acknowledgment

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