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# Analysis of periodic Mo/Si multilayers: Influence of the Mo thickness

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ABSTRACT

A set of Mo/Si periodic multilayers is studied by non-destructive analysis methods. The thickness of the Si layers is 5 nm while the thickness of the Mo layers changes from one multilayer to another, from 2 to 4 nm. This enables us to probe the effect of the transition between the amorphous and crystalline state of the Mo layers near the interfaces with Si on the optical performances of the multilayers. This transition results in the variation of the refractive index (density variation) of the Mo layers, as observed by X-ray reflectivity (XRR) at a wavelength of 0.154 nm. Combining X-ray emission spectroscopy (XES) and XRR, the parameters (composition, thickness and roughness) of the interfacial layers formed by the interaction between the Mo and Si layers are determined. However, these parameters do not evolve significantly as a function of the Mo thickness. It is observed by diffuse scattering at 1.33 nm that the lateral correlation length of the roughness strongly decreases when the Mo thickness goes from 2 to 3 nm. This is due to the development of Mo crystallites parallel to the multilayer surface.



## 1. Introduction

The development of efficient periodic multilayers can benefit from advanced analysis techniques that can characterize these complex structures and help in understanding the phenomena taking place at their interfaces. Indeed, it is important to obtain a relevant description of a multilayer, i.e. to know the thickness and roughness of all the various layers, the composition, thickness and roughness of the interfacial zones, if any, the correlation lengths of the roughness, etc. These informations enable the improvement of the preparation of the multilayers and lead to the choice of a strategy to adapt the multilayer for long-time operation or hot environment.

In this paper, we study a series of periodic Mo/Si multilayers by following the methodology developed in previous papers [1–6], combining non-destructive techniques, X-ray emission spectroscopy (XES), X-ray reflectivity (XRR) and diffuse scattering measurements. Using XES, we deduce the chemical composition of the interfacial zones and estimate their respective thickness. Using XRR, we determine the thicknesses, the optical indices of all the layers and the *rms* height of their roughness. Using diffuse scattering, the lateral correlation length of the roughness can be estimated. This approach is presently applied in the case of a set of multilayers having amorphous Si layers of the same thickness, but Mo layers of different thickness. Thus, the study is performed as a function of the Mo thickness to probe the amorphous–crystalline transition around 3 nm.

## 2. Experimental details

### 2.1. Sample preparation

The Mo/Si multilayers are prepared by magnetron sputtering using an apparatus described elsewhere [7]. Here, we briefly recall the main characteristics of the deposition process. Argon at a pressure of 2 mTorr (1 Torr = 133.3 Pa) was used in the deposition chamber. The plasma discharges were obtained with a RF power of 150 W for Si targets and a DC current of 0.19 A for the Mo target. Samples are deposited on Si polished wafers. The number of bilayers is 40. Three samples with different Mo layers thicknesses have been fabricated, ranging around the transition thickness from the amorphous to the crystalline state, i.e. 2, 3 and 4 nm. In all samples, the thickness of the Si layers is 5 nm. The thickness of the different layers as well as the name given to each sample is listed in Table 1.

For XES, the reference samples are a 60 nm thick amorphous Si film deposited on a GaAs substrate and high purity silicide powders: $MoSi_2$ (Aldrich, purity 99%) and $Mo_5Si_3$ (Alfa Aesar, purity 99.5%).

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**Table 1**
Name of the Mo/Si multilayers and expected thickness of the Mo layers from single layer calibration of the deposition process. All the Si layers are 5 nm thick.

| Sample name | Mo thickness (nm) |
|---|---|
| Mo-2 | 2.01 |
| Mo-3 | 2.99 |
| Mo-4 | 4.01 |

### 2.2. X-ray emission spectroscopy

The Si Kβ emission coming from the silicon atoms present in the Mo/Si multilayers has been analysed. It corresponds to the 3p-1s transition and describes the occupied valence states having the Si 3p character. This emission is very sensitive to the physico-chemical state of the silicon atoms [8,9]. The X-ray analysis was performed in a high-resolution bent-crystal soft X-ray spectrometer [10] using an InSb (1 1 1) crystal at the first diffraction order.

The Si 1s core holes are created by an electron beam coming from a Pierce gun. The energy of the incident electrons was sufficiently low so that the electrons cannot reach the silicon substrate. Then, no signal from the substrate can interfere with that of the multilayer. The current density impinging on the sample is sufficiently low (some tenths of mA/cm$^2$) so that any evolution of the samples under the electron beam is avoided. It was checked during acquisition that the shape and the intensity of the emission do not vary.

### 2.3. Grazing incidence X-ray reflectivity

The experimental reflectivity curves are obtained by means of a reflectometer working with Cu Kα radiation of 0.154 nm wavelength. The Cu Kα radiation is selected by means of a graphite monochromator in front of the detector. The reflectivity curve is obtained by varying the grazing incidence angle while tracking the reflected beam ($\theta$–$2\theta$ scan). The maximum angular amplitude is $\theta = 6°$ with an angular accuracy better than 5/1000° [11].

### 2.4. Soft X-ray reflectivity and diffuse scattering measurements

The reflectivity measurements at 0.133 nm were taken in $\theta$–$2\theta$ mode at the BEAR beamline [12] at Elettra. The reflectometer features an overall accuracy on the absolute reflectivity of ≈1%. The diffusion measurements are obtained in the transverse scan mode at 0.133 nm. The scattered intensity is measured at a fixed position of the detector while the sample is rotated [13]. The $\theta$ goniometer angular resolution was 0.01°. Impinging and reflected intensities were measured by an IRD SXUV100 solid state diode within two separate runs; incident intensities were monitored by a Au mesh inserted in the beam path whose drain current was used for normalization.

## 3. Results

### 3.1. X-ray emission spectroscopy and X-ray reflectivity measurements

In order to determine the physico-chemical state of the Si atoms in a given Mo/Si multilayer, their Si 3p spectral densities are compared to those of reference materials: a-Si, $MoSi_2$ and $Mo_5Si_3$. Such a comparison is shown in Fig. 1 for Mo-2 as an example. The spectra are normalized with respect to their maximum and a linear background has been removed. If no interaction takes place between the Si and Mo layers, the spectrum of a-Si should be observed. The presence of two silicides at the interfaces is demonstrated by the broadening of the multilayer spectrum with respect to the amorphous Si spectrum, toward both the low and high photon energies where the maxima of $MoSi_2$ and $Mo_5Si_3$ are present.

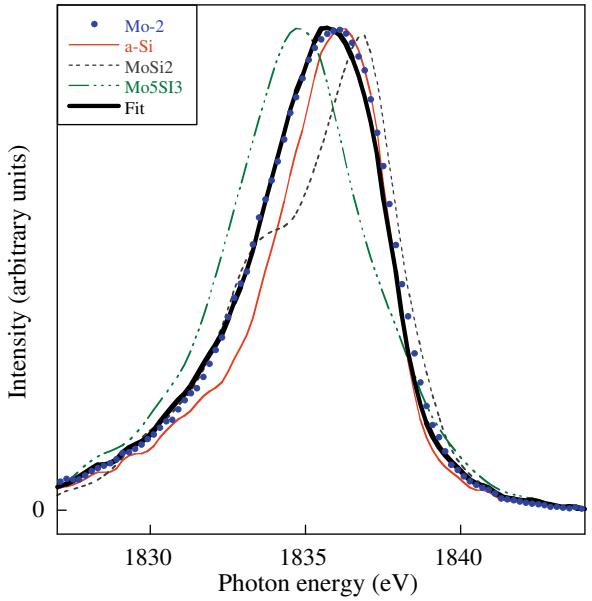


**Fig. 1.** Si Kβ soft X-ray emission spectra of the sample Mo-2 and the various references and fit of the multilayer spectrum by a weighted sum of the reference spectra.

To determine the contribution of the silicides in the spectra and then estimate the interphase thickness, the multilayer spectra are fitted as a weighted sum of the reference spectra, as now routinely done in XES for the study of buried interfaces [5]. An example of fit is presented in the Fig. 1 for the Mo-2 sample. The same operation is performed for the Mo-3 and Mo-4 samples that present Si 3p spectral densities close to that of Mo-2. The calculation of the interphase thickness is based on the model presented in Ref. [5,14] in which no distinction is made between the Mo-on-Si and Si-on-Mo interfaces. Because the multilayer spectra are quite similar, the interface (silicide) thickness is deduced to be almost the same, 0.8–0.9 nm depending on the samples (see Table 2), within the experimental uncertainty (±0.2 nm). These values are in the range of the thicknesses presented in the literature for non-annealed samples, see Ref. [15–17] for example, and determined from transmission electron microscopy (TEM) images, XRR or XES experiments. The interfacial thickness varies according to the preparation conditions, the mechanical stress within the multilayer, the considered interface (in fact the Mo-on-Si interface is wider than the Si-on-Mo one), ...

We fitted the grazing incidence reflectivity measurements by a four-layer model in a period: Mo/interlayer/Si/interlayer by taking into account the XES results (thickness of the interlayer, relative proportion of $MoSi_2$ and $Mo_5Si_3$ within the interlayer) as input parameters. The fit of the reflectivity curves is made using a trial and error method. It allows the determination of the thickness, the interfacial roughness, and at the source wavelength, the complex index $n = 1 - \delta - i\beta$ ($\delta$ is the unit decrement of the refractive index and $\beta$ is the extinction coefficient) for each of the successively deposited films on the substrate [18].

The composition of the interfaces (relative proportions of the silicides) deduced from XES is taken into account through $\delta$. Thus, the unit decrement of the interfacial layer corresponds to a weighted sum of the unit decrements of the silicides. As an example, the Fig. 2 shows the reflectivity curve of Mo-2 and its fit. The seven Bragg peaks are well reproduced as well as their relative