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Structural Evaluation of Mo/Si Multilayers based on Diffraction Theory

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Multilayered structures composed of thin layers of alternating Mo and Si have been prepared in order to evaluate the structure on an atomic scale. The interfacial mixing σ in these multilayers can be estimated from the diffraction method by comparing with the observed reflectivity at the first order Bragg peak.

KEY WORDS : /Mo/Si multilayer/X-ray diffraction theory/Optical theory/Mixing length/

I. INTRODUCTION

X-ray optical elements[1] made of synthetic multilayers have many possible applications in light element analysis, X-ray microscopy, X-ray lithography etc. and experiments with synchrotron radiation. Recent improvements in vapor deposition and sputtering techniques make it possible to produce promising Bragg reflector from multilayers. However, the ability of multilayers, which are inherently metastable, requires investigation before such applications can confidently be pursued. Even if an appropriate selection of materials is made and a sufficient number of layers of adequate thickness are deposited, the mixing in the interface and the errors in periodicity may drastically decrease the peak reflectivity and increase the inherent linewidth.

We have synthesized Mo/Si multilayers and investigated their structure to elucidate the effects of the atomic distribution at layer interfaces on the reflectivity of the multilayer.

II. EXPERIMENTAL

Mo/Si multilayers were fabricated by dual electron beam evaporation method in an UHV chamber equipped with an ion pump and a Ti sublimation pump. Initial vacuum in the deposition chamber was in the range of 10^{-8}Pa and increased to 10^{-6}Pa during evaporation. A silicon wafer (625 μm in thick) having natural oxide coating was used as a substrate. The silicon wafer was placed on a molybdenum block and initially heated to 400°C in the deposition chamber in order to desorb gas trapped on the substrate. In order to reduce the interfacial mixing,

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the substrate was cooled and kept at room temperature during the deposition. The purity of the source materials used was 99.9999% and 99.95% for Si and Mo. The thickness of each layer was monitored with two water-cooled quartz crystal oscillators. Alternative stacking was carried out with a shutter located above each crucible. Tooling factors for the crystal monitors were determined by growing thick films with the Michelson interferometer. Typical evaporation rates were 0.02 nm/sec for Si and 0.05 nm/sec for Mo. The deviation of film thickness is estimated to be within 0.1 nm. Surface condition of crystallinity was monitored by the Reflection High Energy Electron Diffraction (RHEED). The RHEED patterns, as described in detail elsewhere[2], indicate that the surface of each Si layer was amorphous and that of Mo crystalline. Three samples with nominal bilayer thicknesses ranging from 5.4 to 9.7 nm were examined. Low angle X-ray diffraction of $2\theta-\theta$ scan of the multilayer was carried out using a computer controlled double-axis diffractometer with Cu-Kα radiation in the conventional symmetric reflection geometry (Fig. 1). The incident beam was collimated with two pinholes having diameter of 100 μm and 40 μm which were 350 mm apart with each other. Beam divergence was estimated to be about 0.02° based on photographic measurement of the beam size. The intensity of the first Bragg peak and its FWHM (Full Width at Half Maximum) were measured.

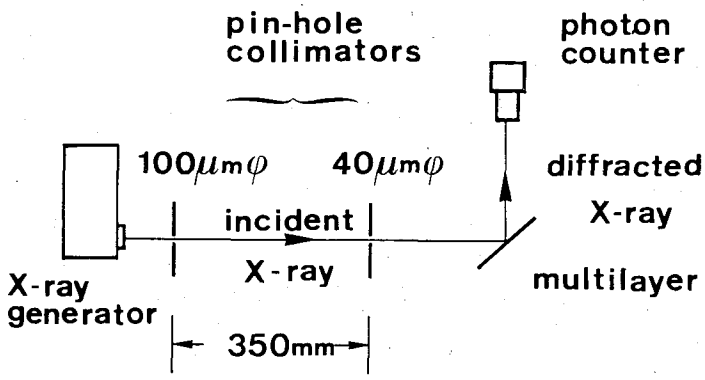

Fig. 1. Schematic diagram of the spectrometer.

III. DYNAMICAL THEORY

Dynamical effects based on the absorption as well as on the interaction between incident and scattered radiations are considered to make a significant contribution to the reflectivity. Therefore, we used two dynamical methods for extracting the structure information of the multilayer : macroscopic optical theory and diffraction theory.

A. OPTICAL THEORY

In this theory, the reflectivity of the layered structure can be calculated using Fresnel equation[3,4]. Since a good multilayer is far from being a perfect crystal because of the interfacial roughness introduced during deposition, the reflectivities are expected to be lower than those

predicted by the dynamical theory for the ideal system. If we take into account the interfacial roughness with a distribution factor similar to Debye-Waller temperature factor[5,6], the peak reflectivity, R_p, of the Bragg reflection can be expressed as a function of the *rms* interfacial roughness, σ, and the thickness of a layer pair, d;

$$R_p = R_{\text{ideal}} \exp\{-[4\pi(\sin\theta/\lambda)\sigma]^2\}, \tag{1}$$

$$\sin\theta/\lambda = n/2d \text{ (Bragg's equation)}, \tag{2}$$

where R_{ideal} is the ideal reflectivity and n is the order of reflection. In this theory, reflectivity losses are evaluated as the first order approximation by the distribution factor and the ideal reflectivity is reduced to R_p.

B. X-RAY DIFFRACTION THEORY

In this theory, Maxwell's equations are applied to crystal lattice fields which are expressed by the dielectric constant ε of the medium. When we write $\varepsilon = 1 + \chi$, χ is very small quantity, an order of 10^{-5}, for X-ray frequencies. Further we shall assume the magnetic permeability to be unity and the current density to be zero. The Maxwell's equations lead to the following differential equation for the electric flux density, D,

$$\Delta \boldsymbol{D} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\boldsymbol{D} = -\text{rot}[\text{rot}(\chi \boldsymbol{D})]. \tag{3}$$

From the periodicity of the crystal lattice, χ is expressed by a Fourier series with the reciprocal lattice vector g,

$$\chi(\boldsymbol{r}) = \sum_{\boldsymbol{g}} \chi_{\boldsymbol{g}}\, e^{2\pi i \boldsymbol{g}\cdot\boldsymbol{r}}. \tag{4}$$

The Fourier component χ_g is related to the crystal structure factor F_g as

$$\chi_{\boldsymbol{g}} = \frac{1}{V}\int_V \chi(\boldsymbol{r}) e^{-2\pi i \boldsymbol{g}\cdot\boldsymbol{r}} dv = -\frac{r_c}{\pi}\frac{\lambda^2}{V}F_{\boldsymbol{g}}. \tag{5}$$

where $r_c = 2.818 \times 10^{-13}$ cm is the classical radius of an electron and V is a volume of the crystal unit cell.

The diffraction pattern of a crystal can be obtained by solving Eq. (3) with the desired structure factor F_g and the given boundary conditions. The solution of Eq. (3) is very complicated for an absorbing crystal and described in detail by Zachariasen[7]. A diffraction pattern can be obtained for an arbitrary distribution of the dielectric constant in the crystal lattice by the dynamical theory. This is more powerful than the optical theory in which sharp boundaries of the dielectric constant are assumed. Structure models of multilayers in our calculation will be given in the following section.

IV. RESULTS AND DISCUSSION

Mo/Si multilayers, which were expected to have high reflectivity in the soft X-ray region, were fabricated with a thickness(t) of the layer pair of 5.4–9.7 nm and a number(N) of layer pairs of 10. They are listed in Table 1, together with peak reflectivities of first-order Bragg reflections for Cu-Kα. The ratio of the layer thickness of Mo atom to that of Si atom is selected to be 7 to 8. For an actual multilayer, the boundary between the layers is not expected to be discrete, because the interfacial mixing as well as the interfacial roughness take place between the layers during evaporation. The former has been confirmed by analyzing the composition of layers through high-resolution electron microscopy[8].

First, we calculated the reflectivity and FWHM of Mo/Si multilayers using optical theory (Eq. (1)). The results are shown in Table 1b. In calculating the reflectivity with this method, we used the values of the density of $\rho(\mathrm{Mo})=9.94$ g/cm^3 for Mo and $\rho(\mathrm{Si})=2.25$ g/cm^3 for Si and optical constants of $\Delta f'$ and $\Delta f''$ for Cu-Kα were taken from International Tables for X-ray Crystallography, Vol. III[9]. As seen in Table 1, from the observed reflectivity, the interfacial roughness in these multilayers can be estimated at $\sigma \sim 0.8$ nm, but with Fresnel equations, σ becomes larger as the X-ray energy decreases. It is difficult to evaluate the interfacial mixing

Table 1a. Summary of Mo/Si multilayers parameters. t is the layer thickness in nm, and N is the number of bilayers.

Sample	N	t_{bilayer}	t_{Mo}	t_{Si}
A:Mo/Si	10	5.4	2.5	2.9
B:Mo/Si	10	6.8	3.2	3.6
C:Mo/Si	10	9.7	4.5	5.2

Table 1b Measured and Calculated X-ray reflectivity and FWHM for Mo/Si multilayers ($\lambda=0.154$ nm).

	A		B		C	
	R_p	FWHM	R_p	FWHM	R_p	FWHM
Observation	13(%)	281″	31(%)	220″	59(%)	230″
optical method						
$\sigma=0$ (nm)	48	331	69	317	80	317
$\sigma=0.8$	18	310	35	295	55	295
$\sigma=1.7$	0.6	340	3.5	306	15	306
diffraction method						
Model I	40	328	53	410	59	384
Model II	21	283	40	270	55	300
x^*_1(nm)	3.4		3.4		3.4	
x_2	2.0		2.0		2.0	

* x_1: the mixing length which Mo penetrates into the preceding Si layer.
x_2: the mixing length which Si penetrates into the preceding Mo layer.

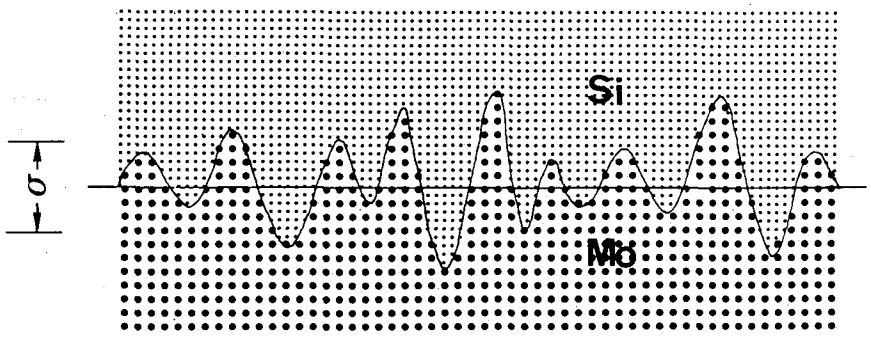

Fig. 2 The interfacial roughness, σ, presents the rms of the interfacial fluctuation between Si and Mo layers in the optical method.

with the optical method because the dielectric constant distributes discretely in this method (Fig. 2).

Second, the reflectivity and FWHM of the multilayer structure models were calculated with the diffraction method to elucidate the contribution of the interfacial mixing to the intensity. The Mo/Si multilayers show that the Mo sublayers are crystalline and the Si sublayers are considered to be amorphous because of the absence of the corresponding Bragg spots[2,8,10]. When a multilayer is periodic, we can consider the structure as an artificial crystal and calculate the diffraction profile with the formalism of the dynamical theory in X-ray crystallography. In the calculation, we used the same values for the density of each layer as in optical method. Atomic scattering factors were taken from International Tables for X-ray Crystallography, Vol. III[9]. Energies and cross sections for each orbital used in the dispersion calculations were obtained from Los Alamos Scientific Laboratory Report[11]. The results are presented in Table 1b. Structure models have been proposed for these multilayers (Fig. 3). The number of each atom is equal for models. As seen in Fig. 3, in Model I interfaces are discrete between Mo and Si sublayers and Model II has the gradient of the atomic concentration expressed by $\exp(-x/\delta)$, where x is the mixing length, and rms interfacial mixing, $\delta=1.0$ and 1.7 nm based on the rsult reported by Petford-Long et al.[8]

As shown in Table 1, the mixing length is evaluated at $x=2\delta$ by comparing the theoretical reflectivity with the observed one in the diffraction method. But, in the samples A($t=5.4$ nm) and B($t=6.8$ nm), the observed intensities are lower than the calculated ones. In such a case, it is considered that the mixing length is longer than the estimated one. The values of FWHM for Model II are fits for the observed ones in all samples. Models based on the diffraction method can correctly predict the reflected intensity and FWHM at a selected Bragg peak.

The investigation on both specularly and diffusely scattered radiation is in progress over a range of q to make inferences regarding multilayer structures including the contribution of bilayer thickness fluctuations to peak width of higher order Bragg reflections.

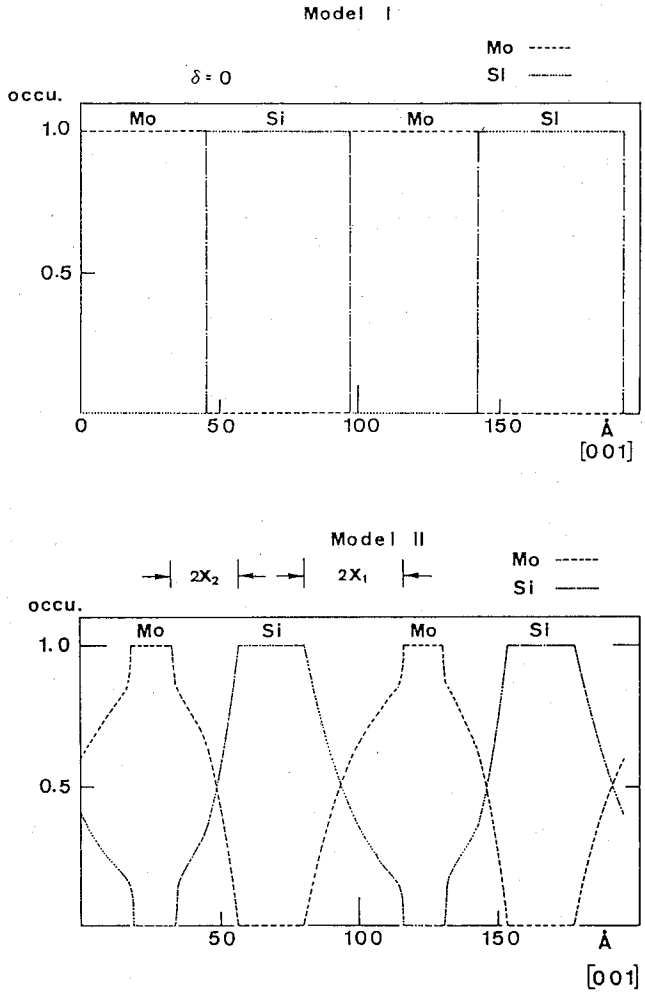

Fig. 3. Schematic representation of diffraction model for the Mo/Si multilayers. The structure in the interface between Mo and Si layers are as follows; I : discrete type ($\delta=0$), and II : a concentration gradient for each atom represented by $\exp(-x/\delta)$, where x is the mixing length and δ is the rms interfacial mixing. x_1 is the mixing length along the growth direction [001] between the preceding Si layer and Mo layer ($\delta=1.7$ nm). x_2 is the mixing length along the growth direction [001] between the preceding Mo layer and Si layer ($\delta=1.0$ nm).

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