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Multilayer Structure Analysis Using Angular Fluorescence Intensity Variation under Grazing Incidence Condition

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Glancing-angular dependence of the fluorescence intensity from a layered sample typically shows Kiessing fringe similar to an X-ray reflectivity curve, and it can be explained by a concept of the X-ray holography, because X-rays directly reaching at a layer emitting fluorescence act as reference waves in holography, and X-rays singly reflected at interfaces act as object waves. In the present work, to prove the validity and availability of this idea, we designed a Pt/Si/Ti/Ag/Si multilayer, whose top Pt layer was ultra-thin film and the holographic oscillations in angular dependence of the Pt Lα X-ray fluorescence intensity from Pt/Si/Ti/Ag/Si multilayer were evaluated theoretically and experimentally. In the theoretical study, depth positions at the three interfaces of Si/Ti, Ti/Ag and Ag/Si were successfully reconstructed in the magnitudes of Fourier transforms of the oscillations in the angular dependence of the Pt Lα X-ray fluorescence intensity, whereas magnitudes of Fourier transforms from the X-rat reflectivity showed quite different tendency. In the experimental study, peaks corresponding to the interfaces of Ti/Ag and Ag/Si appeared in the magnitude of the Fourier transform of the oscillation in the angular dependence of the Pt Lα X-ray fluorescence intensity.

Key words: grazing incidence X-ray fluorescence, X-ray holography, multilayer, Fourier transformation

1. INTRODUCTION

The phase problem of X-ray diffraction method is well known by X-ray researchers. Due to the lack of phase information in X-ray diffraction data, crystal structures cannot be reconstructed directly by Fourier transformation. Thus, the phase problem has been resolved by fitting based algorithm like maximum entropy method Rietveld (MEM/ Rietveld), anomalous X-ray diffraction technique and X-ray fluorescence holography. Analogous to the phase problem of X-ray diffraction, X-ray reflectivity method has inherently the same problem. Sakurai et al. proposed to apply the Fourier transformation to the oscillations of Kiessing fringes in X-ray reflectivities, and successfully obtained the thickness value of each layer in the measured film sample.[1] However, depth distribution of these layers can not be determined directly.

We have studied X-ray fluorescence holography which can provide three dimensional atomic images by Fourier transformation. This technique has been developed for these two decades, and recently it was applied to practical materials. There are two types of X-ray fluorescence holography methods; one is called "normal X-ray fluorescence holography" and another one is called "inverse X-ray fluorescence holography". In the inverse X-ray fluorescence holography, the fluorescing atoms serve as detectors on interference field originating from incident and scattered X-rays by neighboring atoms, which respectively act as reference and object waves in holography. To record the X-ray fluorescence hologram in inverse mode, X-ray fluorescence intensities are measured as a function of direction of a crystal sample.[2] The glancing-angular dependence of the fluorescence intensity, which was used to obtain information on composition as a function of depth,[3,4] can be explained using the holography theory. In previous report[5], one of present author modeled a Fe/Si/Ti/Ag/Au multilayer, whose top Fe layer was monatomic, and calculated the glancing-angular variation of the Fe fluorescence intensity. From the oscillation in its angular dependence, depth positions at the interface were successfully obtained using the Fourier transformation technique.

To prove the validity and availability of our idea, we fabricated Pt/Si/Ti/Ag/Si multilayer, and measured the glancing angular dependence of fluorescence intensity from Pt ultra-thin film. In the present report, the holographic phenomenon is discussed through the theoretically and experimentally obtained X-ray reflectivities and angular dependences of Pt Lα X-ray fluorescence intensity using the Pt/Si/Ti/Ag/Si multilayer.

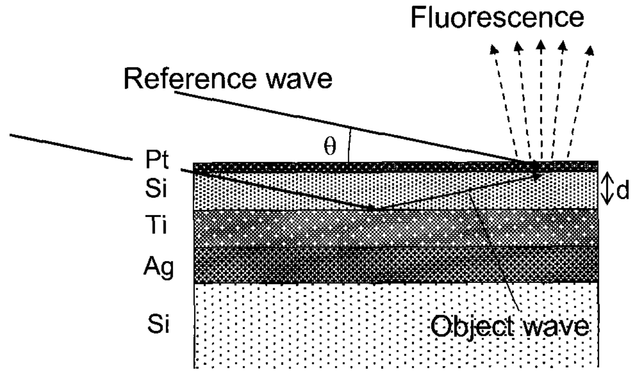

Fig. 1 Schematic drawing of multilayer sample used in the present work.

2. PRINCIPLE

In the present work, we designed the Pt/Si/Ti/Ag/Si multilayer, as shown in Fig. 1. The Pt top layer was ultra-thin film like a monatomic layer. In Fig. 1, we added the scheme of the generation of the holographic signal from the layered material under the grazing incidence condition. X-rays directly reaching at a top Pt layer (ultra-thin layer in Fig.1) emitting fluorescence are regarded as reference waves in holography, and X-rays singly reflected at interfaces act as object waves. These reference and object waves interfere each other and form X-ray standing wave. X-ray intensity at the ultra-thin Pt layer is modulated with the glancing angle of the incident X-ray beam, and the fluorescence intensity from the ultra-thin layer is proportional to it. The path difference between the reference and object wave is briefly expressed as,

$$\Delta l = 2d \cdot \sin\theta \cong 2d\theta, \qquad (1)$$

where the θ is the glancing angle of the incident X-rays above the critical angle for total reflection θ_c, and the d is the depth of the interface. Thus, the fluorescence intensity from the top layer oscillates with the phase $4\pi d\theta/\lambda$, where λ is the wavelength of the incident X-rays. Therefore, the angular dependence of fluorescence intensity is considered to be a hologram, which can reconstruct the depth of the interfaces.

3. THEORETICAL STUDY

As shown in Fig.1, we designed the Pt/Si/Ti/Ag/Si multilayer, where the thicknesses of the Si, Ti and Ag layers were 13 nm, 40 nm and 30 nm, respectively. In the present session, the X-ray reflectivity curve and the angular dependence of the fluorescence intensity of Pt Lα line were calculated using the formalism described in Refs. [6,7]. The densities of the Pt, Si, Ti and Ag layers were 21.5, 2.35, 4.50 and 10.5 g/cm^3, respectively, which were same to the bulk crystal ones. The roughness at each surface and interface was assumed to be 1.0 nm. The X-ray energy for the calculation was 13.5 keV (0.092 nm), which was just above Pt L_2 X-ray absorption edge (13.273 keV).

Figures 2 (a) and (b) show calculated reflectivity and fluorescence intensity of Pt Lα line, respectively, as a function of the glancing anle. Here, the fringes above the critical angle for total reflection at Ti/Ag interface θ_{cAg} (= 0.26°) were Fourier transformed to real spaces. The baseline in the X-ray reflectivity curve was obtained by polynomial equation fitting in the logarithmic plot, and the oscillation was obtained by subtracting the baseline from the reflectivity. Since the amplitude of the oscillation decreases logarithmically with the increase of the glancing angle, it was normalized with respect to the baseline intensity. On the other hand, the baseline of Pt X-ray fluorescence intensity was determined by the polynomial equation fitting in the linear plot. Strong oscillation is seen below the θ_{cAg} in Fig. 2 (b). When the glancing angle is lower than the critical angle for total reflection, X-ray standing waves

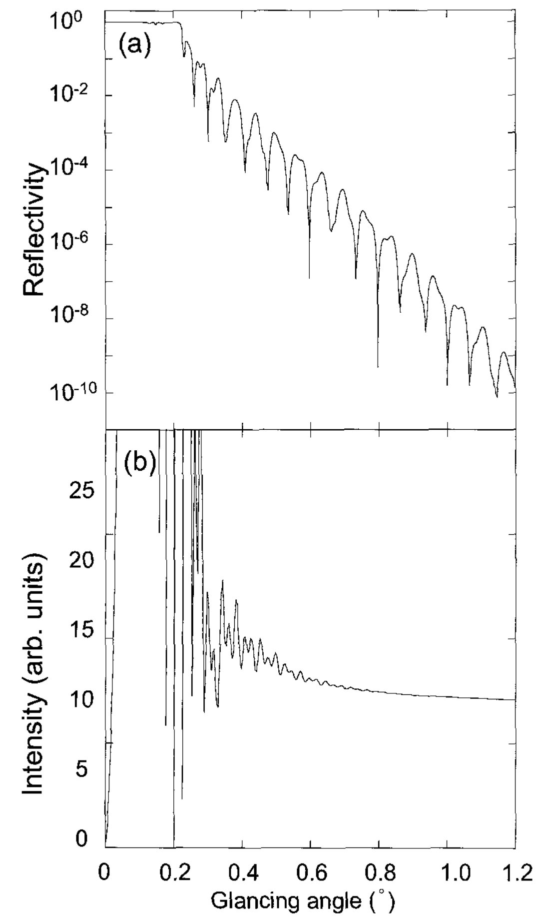

Fig. 2 Angular dependence of (b) reflectivity and (a) Pt Lα fluorescence intensity.

form in multilayer due to multiple X-ray external reflections. Maxima of the fluorescence intensity below the θ_{cAg} correspond to the appearances of the X-rays standing waves. Since the holographic oscillation was created by the interference between the incident X-ray and the reflected X-ray, the oscillation below the θ_{cAg} can not be recognized as a hologram. The holographic oscillation above θ_{cAg} was obtained by subtracting the baseline from the fluorescence intensity. The amplitude of the extracted oscillation damps with the increase of the glancing angle. To compensate the weakness of the amplitude in the higher angle region, the oscillation was multiplied by the value of the glancing angle. Here, both oscillations were expressed as a function of $\sqrt{\theta^2 - \theta_{cSi}^2}/\lambda$, and then they were Fourier transformed.

Figures 3 (a) and (b) show the magnitudes of the Fourier transforms of the oscillations extracted from the plots in Figs. 2 (a) and (b), respectively. Tendencies of both profiles are quite different. In Fig. 3 (a), strong peak appears at 39.3 nm. Since the thicknesses of the Ti and Ag layers are 40 and 30 nm, respectively, we can regard peak **a** as the combination of the Fourier transforms of the thicknesses of Ti and Ag layers. Weak peak indicated by **b** at 87.8 nm, which is considered to correspond to Ti+Ag layer (70 nm) or Si+Ti+Ag layer (83 nm). Thicknesses of both Ti+Ag and Si+Ti+Ag layers are shorter than that of peak **b**. The reason is describes in the followings. X-rays passing through a multilayer media necessarily refract at a surface and interfaces and the glancing angle changes according to the equation of $\theta = \sqrt{\theta^2 - \theta_c^2}$, where θ_c is the critical angle for total reflection at each layer. This effect elongates the path difference between X-ray reflected at top and bottom interfaces of the layer, causing elongations of the thickness values obtained from Fourier transforms. This problem was fixed by expressing the fringe as a function of $\sqrt{\theta^2 - \theta_c^2}/\lambda$. In the present analysis, we set the $\sqrt{\theta^2 - \theta_{cSi}^2}/\lambda$ as the abscissa of the oscillation function. Since the θ_{cSi} is the smallest critical angles among the layers in the multilayer, the reconstructed peak necessarily appear at the distance value slightly higher than the actual thickness. Although the position of peak **b** is close to the thickness of Si+Ti+Ag layer, it is unlikely that the peak of Si+Ti+Ag appears at the thickness lower than the actual thickness in the Fourier transform. From these considerations, it is unclear whether peak **b** corresponds to Ti+Ag or Si+Ti+Ag layer. While, the peak of a layer consisting of two mediums is strongly appears that that of three mediums in general. Therefore, peak **b** is considered to be Ti+Ag layer, although the obtained thickness is 17.8 nm longer than the actual value. Although peaks of Ti and Ag layers exist markedly, a peak corresponding to the Si layer is not seen in Fig. 3 (a). Moreover, peaks corresponding to Si+Ti layer (53 nm) and Si+Ti+Ag layer (83 nm) are not observed.

Figure 3 (b) shows three peaks attributable to the depths of the interfaces of Si/Ti, Ti/Ag and Ag/Si, which

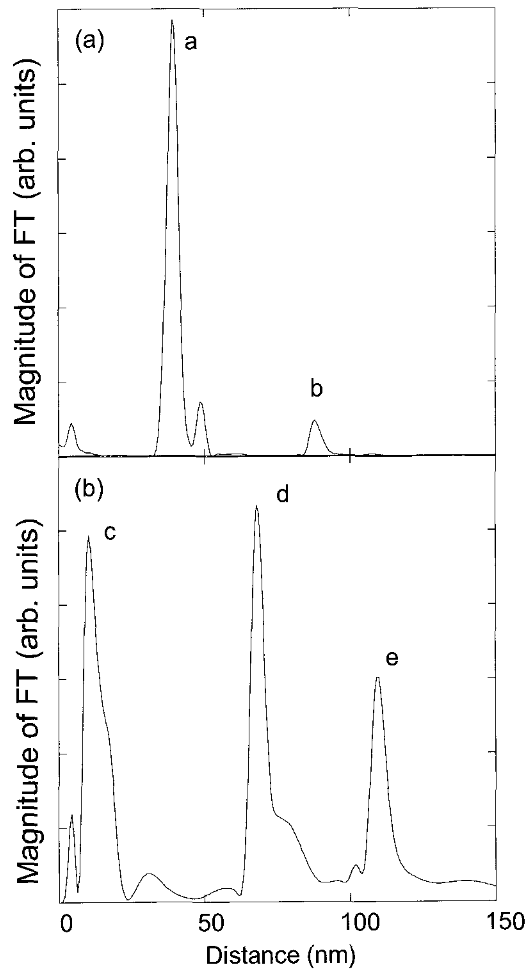

Fig. 3 Magnitudes of the Fourier transforms of the oscillation extracted from Figs 2 (a) and (b).

are indicated by **c**, **d** and **e**, respectively. The estimated positions of peaks **e**, **f** and **g** are 13.4 nm, 68.1 nm and 109.5 nm, respectively. Since the actual depths of Si/Ti, Ti/Ag and Ag/Si are 13 nm, 53 nm and 83 nm, respectively, the present three peaks also shift toward 0.3 – 26.5 nm higher distances, due to same reason of the shift in Fig. 3 (a). This result confirms that peak **b** in Fig. 3(a) corresponds to Ti+Ag layer. The tail accompanied by peak **d** might be also created by the refraction effect.

4 EXPERIMENTAL

We fabricated the Pt/Si/Ti/Ag multilayer on Si wafer by sputtering technique. The diameter of the sample was 100 mm. X-ray experiments were carried out at bending magnet beam line of BL6C in Photon Factory. Incident X-rays were monochromatized by Si (111) double monochromator. We chose X-ray energy of 13.5 keV, which is same energy used in section 3, so as to emit Pt Lα X-ray fluorescence. The beam size of the incident X-rays was limited to be 8.0 × 0.2 mm^2 by slit. Figure 4 shows the experimental setup for measuring X-ray reflectivity and Pt Lα fluorescence intensity. The intensity of the incident X-rays was monitored by an ionization chamber (IC). The

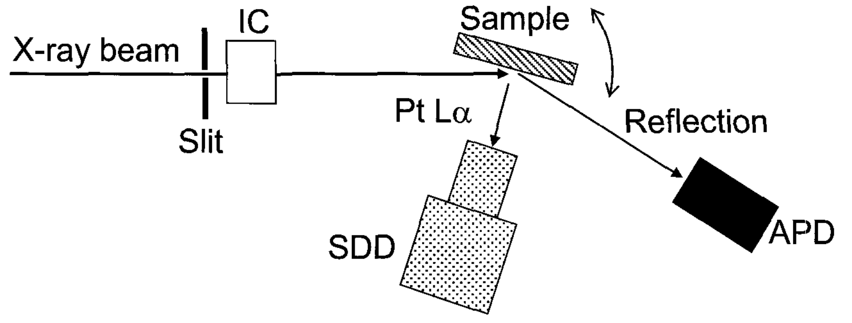

Fig. 4 Experimental setup.

reflected X-rays are detected by avalanche photo diode (APD). A 0.5 mm thick aluminum plate was set in front of the APD to reduce the intensity of the reflected X-rays. Pt Lα X-ray fluorescence was detected by a silicon drift detector (SDD). The glancing angle was changed from 0.0o to 1.2o with the step of 0.001o. Signals of Pt Lα X-rays fluorescence from an amplifier were discriminated by a single channel analyzer, and then they were counted by a scaler connected with a computer. To gain the statistical accuracy, at least 10^5 counts of Pt Lα X-ray photons were collected at each point.

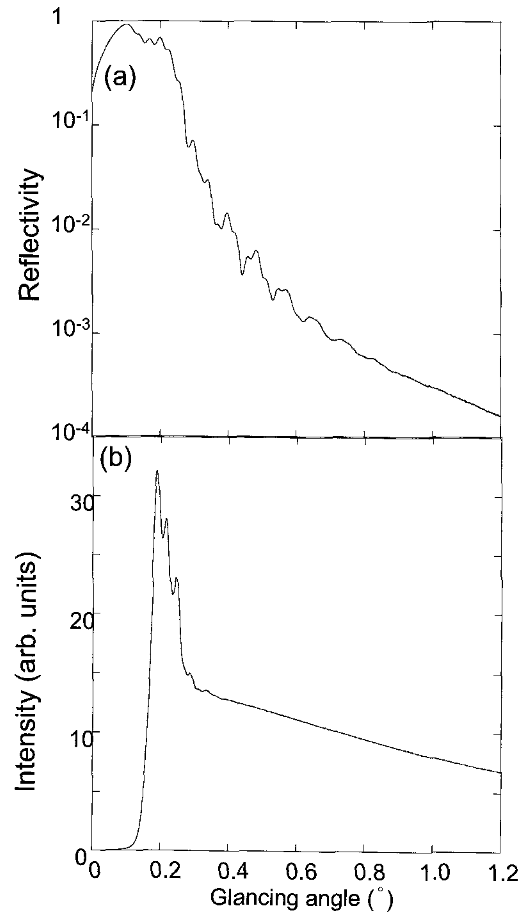

Fig. 5 (a) Reflectivity and (b) angular dependence of Pt Lα fluorescence intensity.

5 RESULTS AND DISCUSSIONS

Figures 5 (a) and (b) show the measured X-ray reflectivity and angular variation of the Pt Lα fluorescence intensity, respectively. The X-ray reflectivity in Fig. 5 (a) exhibits large damping rate of the oscillation, compared to the theoretical reflectivity in Fig. 2 (a). Moreover, amplitude of the oscillation in Fig. 5 (b) is much small compared to that in Fig. 2 (b). These behaviors were caused by large surface and/or interface roughness. The oscillation extracted from the angular dependence in Fig. 5 (b) is shown in Fig. 6, and the fringe pattern is markedly visible up to 0.45°. Using similar data processing in section 3, magnitudes of Fourier transforms of the oscillations in Figs. 5 (a) and (b) were obtained, as depicted in Figs. 7 (a) and (b), respectively.

In Fig. 7 (a), a strong peak indicated by **a** appears at 29.7 nm. Taking into account the fact that the strong peak exits at 39.3 nm in Fig. 3 (a), peak **a** can be attributed to the overlap of the Fourier transforms of Ti and Ag layers. A small peak indicated by **b** is visible at 83.2 nm. Peak **b** in Fig. 3(a) was determined to be attributed to the Ti+Ag layer. Analogously, the peak **b** in Fig. 7 can be attributed to the Ti+Ag layer. Except peaks **a** and **b**, a small peak exists at 11.0 nm, and this value is close to the thickness of Si layer that we designed. However, since the peak of Si layer cannot be observed in the Fourier transform from the theoretical reflectivity in section 3, we hardly recognize it to correspond to Si layer.

In Fig. 7 (b), many small and noisy peaks are visible differently from Fig. 7 (a). While, strong peak indicated by **c** is observed at 35.1 nm. This value is 5.4 nm larger than the distance of peak **a**. Comparing with Fig. 3 (b), peak **c** is considered to originate from the Ti/Ag interface. However, distance of peak **c** is 22.7 nm smaller than that of peak **d** in Fig. 3 (b), which also corresponds to the Ti/Ag interface in the model Pt/Si/Ti/Ag/Si multilayer. This result suggests that thickness of Si+Ti layer was about 20nm smaller than that of designed one. Among many noisy peaks in the distance region above 40 nm, a peak indicated by **d** is markedly observed at 87.0 nm. It is speculated that peak **d** corresponds to the Ag/Si interface, however, we are not sure of this assumption only from the peak intensity. Thus, the inverse Fourier transformation from peak **d** was carried out, and corresponding oscillation was obtained and was compared with the oscillation extracted from Fig. 5 (b), as shown in Fig. 6. Since it seems that the phases of the higher frequent

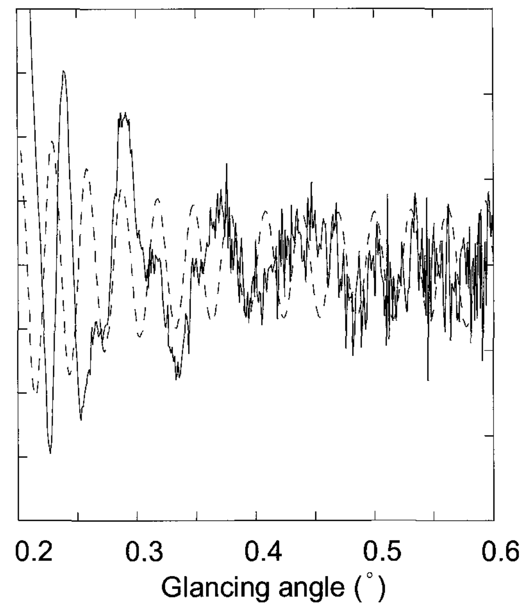

Fig. 6 Extracted oscillations from the angular dependence in Fig. 5. Broken lines indicates inverse Fourier transform of peak **d** in Fig. 7 (b).

oscillation component of the solid line in Fig. 6 coincide with the break line especially in the angle range between 0.26o and 0.4o, it is known that peak **d** originates truly from the interference effect, and that it corresponds to Ag/Si interface. In addition to peaks **c** and **d**, a strong peak appears at 12.2 nm. However, since the low frequent undulation corresponding to this is not seen in the solid line in Fig. 6, this might be caused by the edge effect of Fourier transformation.

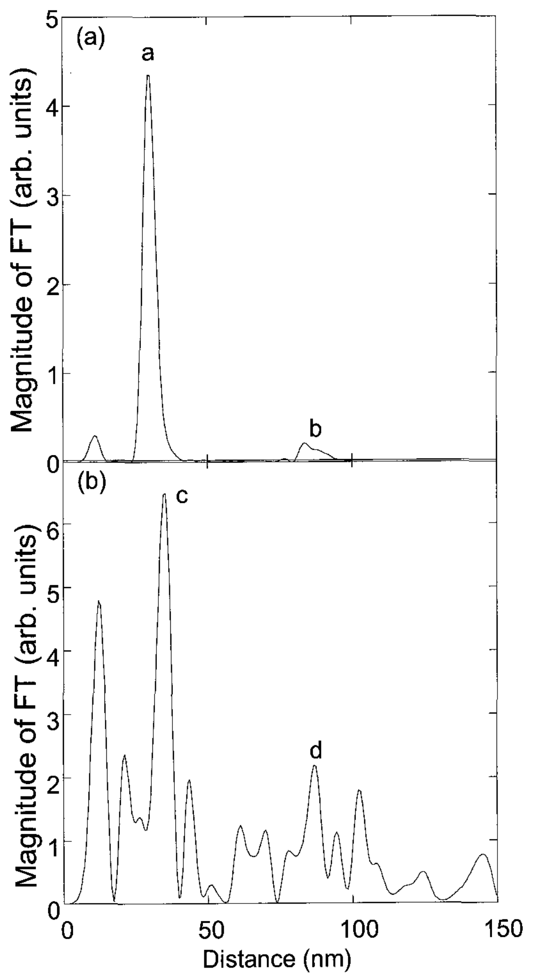

Fig. 7 Magnitudes of the Fourier transforms of the oscillation extracted from Figs 5 (a) and (b).

6 CONCLUSION

The holographic phenomenon in the grazing incidence X-ray fluorescence data has been discussed through calculations and experiments of the angular dependence of the X-ray fluorescence intensity of Pt Lα X-ray fluorescence from Pt/Si/Ti/Ag/Si multilayer. From the calculation study, magnitudes of Fourier transforms of the oscillations in the X-rat reflectivity and the angular dependence of the Pt Lα X-ray fluorescence intensity showed quite different tendencies. Especially for the latter case, depth positions at the three interfaces of Si/Ti, Ti/Ag and Ag/Si were successfully reconstructed. The reconstruction from the experimental data exhibited peaks corresponding to the interfaces of Ti/Ag and Ag/Si. Since these obtained depth values are far from those of designed multilayer, further analysis must be carried out.

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