Optical performance, structure and thermal stability of Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers designed for the 17–19 nm range

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We report on the optical performance, structure and thermal stability of periodic multilayer films containing Zr and Al(1wt.-%Si) or Al(pure) layers designed for the use as extreme ultraviolet (EUV) high reflective mirrors in the range of 17–19 nm. The comparison of Al/Zr (Al(1wt.-%Si)/Zr and Al(pure)/Zr) multilayers fabricated by direct–current magnetron sputtering shows that the optical and structural performances of two systems have much difference because of Si doped in Al. From the results of grazing incidence X-ray reflection (GIXR), X-ray diffraction (XRD), and EUV, the Si can disfavor the crystallization of Al and smooth the interface, consequently increase the reflectance of EUV in the Al(1wt.-%Si)/Zr systems. For the thermal stability of two systems, the first significant structural changes appear at 250 °C. The interlayers are transformed from symmetrical to asymmetrical, where the Zr-on-Al interlayers are thicker than Al-on-Zr interlayers. At 295 °C for Al(pure)/Zr and 298 °C for Al(1wt.-%Si)/Zr, the interfaces consist of amorphous Al-Zr alloy transform to polycrystalline Al-Zr alloy which can decrease the surface roughness and smooth the interfaces. Above 300 °C, the interdiffusion becomes larger, which can enlarge the differences between Zr-on-Al and Al-on-Zr interlayers. Based on the analyses, the Si doped in Al cannot only influence the optical and structural performances of Al/Zr systems, but also impact the reaction temperatures in the annealing process.

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With the research of reflective multilayer coatings in the extreme ultraviolet (EUV) spectral region in the practical application, preference is often given to the Mo/Si multilayers owing to its most advanced technological levels. This kind of multilayers have been already used in the Solar-B/EIS instrument, which could detect specific coronal or transition-region emission lines in two wavelength regions (17–21 and 25–29 nm)[1,2]. Owing to the large absorption of Si at longer wavelength region below Si L-edge, Al-based[3−5] systems have been investigated to meet the practical requirements.

Because of the low absorption below the Al L-edge near 17 nm, the Al can be a good spacer layer in the new multilayer combination. In Al-based systems, Al/Zr multilayers has the highest theoretical reflectance which makes it especially attractive for the EUV applications, such as blazed multilayer grating structure[4,6] and high reflective multilayer coatings[7]. In our previous works[7−9], the optical, structural performances and thermal stability of Al(1-%wt.Si)/Zr multilayers had been presented in details. We found four factors (the inhomogeneous crystallization of aluminum, contamination of the multilayer, surface oxidized layer, and interdiffusion between Al and Zr layers) could decreased the theoretical reflectance of Al(1.-%wt.Si)/Zr multilayer with 40 periods from 70.9% to 41.2% at 5° incident angle in the experiment. The thermal stability of six Al(1wt.-%Si)/Zr multilayers, except the room temperature (RT) samples, annealed at different temperatures (10, 200, 300, 400, and 500 °C) were characterized by a series of complementary measurements including grazing incidence X-ray reflection (GIXR), X-ray diffraction (XRD), X-ray emission spectroscopy (XES), and near-normal incident EUV reflection. Based on the simulation of GIXR and EUV, the symmetrical and asymmetrical interlayer models could be well matched with the multilayer structure blow and above 300 °C. At 200 °C, the degradation of the multilayer structure did not occure. The symmetrical interlayers still presented in the multilayers. However from 300 °C, the interface consisting of amorphous Al-Zr alloy had been transformed to the polycrystalline Al-Zr alloy, which decreased the EUV reflectance. And the Zr-on-Al interlayers become thicker than Al-on-Zr interlayers. Up to 500 °C, the multilayers structure still existed, where the reflectance contained at 17%. But the comparison of optical, structural performances, and thermal stability of the Al(1wt.-%Si)/Zr and Al(pure)/Zr systems in the wavelength region of 17–19 nm, especially for the influence of Si doped in Al, were not discussed in details[7].

In this letter, we report on the comparison of optical, structural performances and thermal stability of the Al(1wt.-%Si)/Zr and Al(Pure)/Zr systems for the purpose of investigating the difference between two systems and the performances of presence of Si in Al layers.

All samples were fabricated by direct current magnetron sputtering technology[7−9], under the base pressure of 8.0×10^{-5} Pa. The targets of Zr(99.5%) and Al(1wt.-%Si) or Al(pure, 99.999%) with diameter of 100 mm were used. The sputter gas was Ar with purity of 99.999%, and the gas pressure was held constantly at 1.35 ± 0.02 mTorr (0.180 Pa). The periodic thicknesses of Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers are 9.56 and 9.35 nm, respectively, while their gamma value (the ratio of Zr thickness to period) is 0.33. To compared the optical and structural performances between Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers, the samples were fabricated in which the period numbers of Al(1wt.-%Si)/Zr and Al(pure)/Zr are both held at 40 on FTO substrate. To evaluate the thermal stability of Al(1wt.-%Si)/Zr and Al(pure)/Zr systems, nine multilayer samples for each systems, except for RT sample, were deposited on the Si wafers, annealed at temperatures of 200, 250, 280, 285, 290, 295, 298, 300, 305, and 310 °C in a vacuum furnace for 1 h, respectively. After annealing the samples were cooled to RT naturally in the furnace with a base pressure of 4.5×10^{-4} Pa.

The GIXR and XRD measurements were carried out to test the changes in the multilayers, using an X-ray diffractometer working at the Cu Kα line (0.154 nm). The fitting calculations of GIXR curves were performed with Bede Refs software (genetic algorithm) to determine individual layer thickness and interface roughness[7,9,10].

The surface roughness was measured with a Veeco, Multi-Mode SPM scanning probe microscope, operated in atiomic force microscopy (AFM) mode. For estimating the interfacial microstructure and periodic structure of Al(1wt.-%Si)/Zr system, the scanning transmission electron microscope (TEM, FEI Tecnai G2 F20) was used on the specimen prepared by focused ion beam (FIB) etching using in the Materials Analysis Technology Ltd.

The reflectance of EUV was made at a 5° incident angle, using the reflectometer on the Spectral Radiation Standard and Metrology Beamline and Station (beamline U26) at the National Synchrotron Radiation Laboratory in Hefei, China. An Al filter was inserted into the incident light beam to remove the high order radiation.

In order to estimate the influence of Si doped in the Al layers[3], we firstly compare optical and structural performances of two systems (Al(1wt.-%Si)/Zr and Al (pure)/Zr) with 40 periods. Figure 1(a) shows the X-ray reflectance obtained by GIXR for the Al(1wt.-%Si)/Zr and Al(pure)/Zr samples. From the fitting data (not shown in the Fig. 1(a)), the calculated root-mean-square (RMS) roughness of Al(1wt.-%Si) and Zr layers are 1.0 and 0.4 nm, respectively. And the RMS of Al-on-Zr and Zr-on-Al interlayers are same, which value contains at 0.5 nm. While with the similar RMS for the Al-on-Zr, Zr-on-Al interlayers and Zr layers in the Al(1wt.-%Si)/Zr multilayers, only the RMS of Al(pure) layer was larger than that of Al(1wt.-%Si) layer in 0.2 nm. Therefore, the EUV reflectance measurements are needed to further characterize the two systems. The measured EUV reflectance curves are shown in Fig. 1(b). The peak reflectance of Al(1wt.-%Si)/Zr and Al(pure)/Zr are 41.2% at 17.8 nm and 37.9% at 17.8 nm, respectively. The higher reflectance of Al(1wt.-%Si)/Zr multilayers indicate, the better interface structure and the lower roughness in the multilayers, which consistent with the results in the GIXR analyses. Based on the measurements, we can assume that the Si doped in Al can influence the reflectance of the two systems, which Al(1wt.-%Si)/Zr multilayers have higher value than that of Al(pure)/Zr.

To identify the reason of different interfacial structures, the XRD measurements are required as shown in Fig. 2. Three phases (Fcc Al ⟨111⟩, Hcp Zr ⟨002⟩ and ⟨101⟩) are presented in both multilayers. The Al(pure) layer has an intact crystallization, but the crystallization of Al(1wt.-%Si) layer can be worse due to the material Si. Considering the scherrer formula[11], the crystal sizes of Al⟨111⟩ of Al(1wt.-%Si)/Zr (6.2 nm) is smaller than that of Al(pure)/Zr (6.3 nm). In particular, the surface and interfacial roughness are mainly influenced by the crystallization of Al[4]. Based on the results, we can conclude that a small proportion of Si in Al layers has a strong effect on the reflectance and structural performances of Al/Zr multilayers, where Al(1wt.-%Si)/Zr multilayers have higher reflectance and smoother interfacial roughness than that of Al(pure)/Zr.

To further evaluate the performances of Si doped in Al in the annealing process, the samples were deposited on the Si wafers. Based on the thermal stability of Al(1wt.-%Si)/Zr[9], the transformation from symmetrical

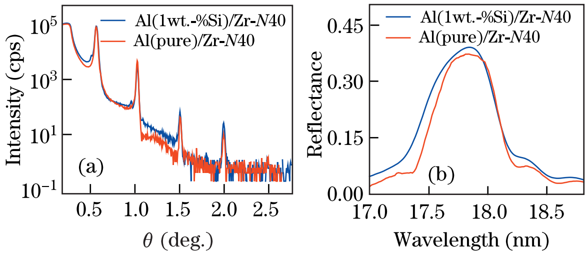

Fig. 1. (Color online) (a) Curves of fitting data with 40 periods for Al(1wt.-%Si)/Zr (blue solid line) and Al(pure)/Zr (red line) are presented; (b) measured reflectance versus wavelength of the multilayers at 5° incident angle by synchrotron radiation.

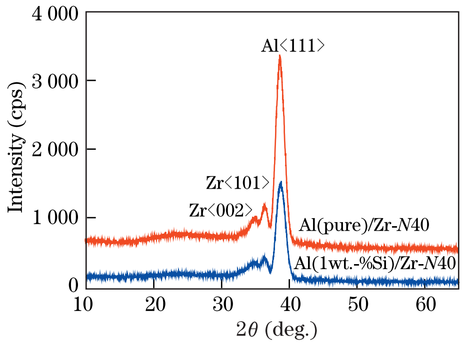

Fig. 2. (Color online) In tensity versus 2θ for XRD, the samples of Al(1wt.-%Si)/Zr (blue line) and Al(pure)/Zr (red line) with 40 periods are shown.

to asymmetrical interlayers appeared during the temperature from 200 to 300 °C. In order to verify the reaction temperatures of the transformation in two systems, eleven multilayer samples for each systems, except for RT sample, were annealed at temperatures of 200, 250, 280, 285, 290, 295, 298, 300, 305, and 310 °C in a vacuum furnace for 1 h. In Fig. 3, the periodic length of each multilayer sample is presented, where the values are normalized by those under the RT conditions. For Al(1wt.-%Si)/Zr multilayers (Fig. 3(a)), the periodic length of the multilayer first slightly decreases with the annealing temperature. At 200 °C, the relative change in the periodic length of the multilayer annealed is about 0.2%. From 250 °C, it sharply decreases to 0.5%, and from 290 to 310 °C, the changes contain at 0.8% of the initial value. For Al(pure)/Zr multilayers (Fig. 3(b)), the relative change is similar to the situation in Al(1wt.-%Si)/Zr multilayers. At 200 °C, the change is also about 0.2%, but above 250 °C, the slope of the changing trend is higher than that in the Al(1wt.-%Si)/Zr multilayers. The change is about 0.6% at 250 °C, and drops to 1.3% at 310 °C. Based on relative changes of periodic length in the GIXR measurements, the structural performances of Al(1wt.-%Si)/Zr is much better than that of Al(pure)/Zr. Because of large interdiffusion in both Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers at 250 °C, more and more amorphous Al-Zr alloy grows into Al and Zr layers, which can disturb the original balance in the interface boundary in the RT samples. That is to say, Zr diffuses and reacts more rapidly with Al than Al diffuses and reacts with Zr[12]. Therefore, the interfaces transform from symmetrical to asymmetrical in both multilayers. Thus, it is reasonable to suppose that the first reaction temperature is at 250 °C.

The surface roughnesses of the Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers prior to and following annealing are characterized with AFM, measured over a 5× 5 (μm) area. In order to eliminate the effect of the roughness before annealing, the relative surface roughnesses of different annealing samples are used. To compare the two systems in Fig. 4(a), we can find that the changing trends first slightly decrease below 250 °C. Above 250 °C, the changes become obviously, which has the lowest point at 295 and 298 °C for Al(1wt.-%Si)/Zr and Al(pure)/Zr, respectively. With the lower surface roughness and different changing trends prior to and following those temperatures, we can assume that there is a reaction between Al and Zr layers. And the crystallization of Al is the main impact factor for the surface roughness. To estimate the relations between the crystallization of Al and surface roughness, the crystal sizes of Al⟨111⟩ from XRD measurements are presented in Fig. 4(b). From the curves, the changing trends is similar to the relative changes in the AFM in both systems, which also have the lowest point at 295 and 298 °C for Al(1wt.-%Si)/Zr and Al(pure)/Zr, respectively. Therefore, we can conclude that the surface roughness in both systems is influenced by the crystallization of Al. Because of the Si doped in Al, the reaction at the lowest points in the corresponding curves are different in Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers.

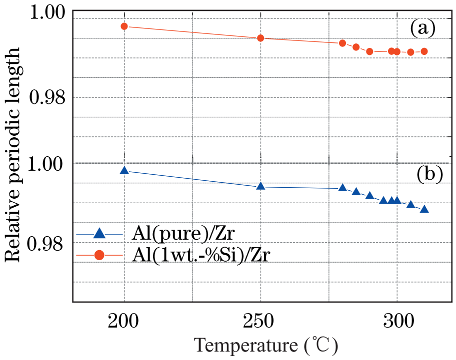

Fig. 3. (Color online) Relative periodic lengths of the Al/Zr multilayer samples (color curves) as a function of annealing temperature from RT to 310 °C. The periodic length is normalized to those of the samples before annealing.

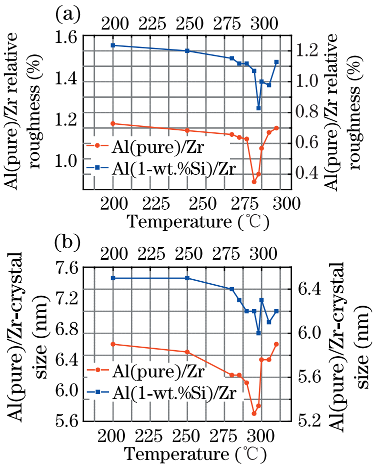

Fig. 4. (Color online) (a) Relative surface roughness of the Al(1wt.-%Si)/Zr (blue curve) and Al(pure)/Zr multilayers (red curve) as a function of annealing temperatures from 200 to 310 °C. The surface roughness is normalized by those of the samples before annealing. (b) The crystal sizes of all annealing samples in two systems are derived from the XRD measurements.

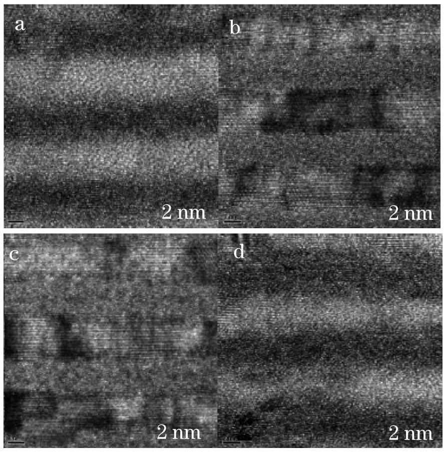

Fig. 5. (Color online) High magnification transmission electron micrographs used to observed the cross-section of five Al(1wt.-%Si)/Zr multilayers (Al layer-lighter, Zr layer-darker). The micrographs of the specimens at (a) RT, (b) 295, (c) 298, and (d) 300 °C.

To verify the results of GIXR, AFM, and XRD in the annealing process, TEM observations were carried out. Because the similar changing trends between Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers, four specimens (RT, 295, 298, and 300 °C for Al(1wt.-%Si)/Zr systems) were made and analyzed on TEM (Fig. 5). In the RT samples (Fig. 5(a)), there is clearly an amorphous Al-Zr intermixed layer at each interface. The both thicknesses of interlayers are 1.5 nm. At 295 °C (Fig. 5(b)), the Zr-on-Al interlayers are thicker than Al-on-Zr interlayers, where the thicknesses are 1.9 and 1.7 nm, respectively. When annealed at 298 °C (Fig. 5(c)), the interlayers become much obvious. The interfaces consisting of amorphous Al-Zr alloy are transformed to polycrystalline Al-Zr alloy. The thicknesses of two interlayers still contain at 1.9 and 1.7 nm, respectively. While the surface and interfacial roughness becomes much lower and consistent with the results in the XRD. Up to 300 °C (Fig. 5(d)), the interdiffusion becomes larger. The thickness of Zr-on-Al interlayer (2.4 nm) is much thicker than that (2.0 nm) of Al-on-Zr interlayer.

In conclusion, we report on two systems, Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers, designed for the EUV region. The EUV reflectance reveals significantly, while the performances of the Al(1wt.-%Si)/Zr multilayer is much better than Al (pure)/Zr. The reflectance of Al(1wt.-%Si)/Zr multilayers are 41.2% at 17.8 nm for multilayers with 40 periods, which are higher than the value (37.9% at 17.8 nm) of Al(pure)/Zr multilayers. The presence of Si can disfavor the crystallization of Al and smooth the interfacial structure. To further detect the influence of Si doped in Al during the annealing process, the thermal stability of Al(1wt.-%Si)/Zr and Al(pure)/Zr multilayers are characterized by GXIR, AFM, XRD, and TEM. At 250 °C, the width of Zr-on-Al interlayer is thicker than that of Al-on-Zr interlayer, which presents the first structural modification in the multilayers. At 295 °C for Al(pure)/Zr and 298 °C for Al(1wt.-%Si)/Zr, the crystal size of Al$\langle 111 \rangle$ has the lowest value, and the changing trend of the crystal size is consistent with the situation in AFM measurements. At those temperatures, the reactions appear between the Al and Zr layers in two systems, where the interface consists of amorphous Al-Zr alloy transforms to polycrystalline Al-Zr alloy. Therefore, in our experiment, it can be concluded that Si doped in Al, even in a small proportion, cannot only change the interfacial structure and increase the EUV reflectance, but also influence the reaction temperature in the multilayers, which is considered to be useful for further practical experimental applications.

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