Enhancement of the reflectivity of Al(1%wtSi)/Zr multilayers at near normal incidence by a new concept of multilayer structure

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We report a significant increase in the reflectivity of Al(1%wtSi)/Zr multilayers at near normal incidence by using a new concept of multilayer structure. In our design model, the Al layer is divided into a number of layers along the in-plane direction, and the Si layer is inserted between each layer. The advantages of the new multilayer structure could improve the interfacial boundary between Al and Zr layers, lower the interfacial roughness, and disfavor the crystallization of Al in the theoretical fields. To verify those features of the new multilayer structure in the experiment, we have fabricated several different samples, including the traditional multilayers and the new multilayers with and without Si interlayers. Based on the results of grazing incident X–ray reflectometry and extreme ultraviolet measurements, the new multilayers (Al=2.8) with Si interlayers present lower interfacial roughness, and improve the reflectivity to 50.0% at 5° incident angle. Finally, we discuss the benefits of the new multilayers will be widely used not only in the extreme ultraviolet and soft X-ray multilayers, but also in semiconductor industry and other fields. This is also the first report of observations of enhanced reflectivity in the extreme ultraviolet and soft X-ray multilayers by using the new concept of multilayer structure.

1. Introduction

The Al(1%wtSi)/Zr multilayer system is an alternately layered structure consisting of two materials of different scattering powers at extreme ultraviolet (EUV) spectral region.[1-3, 7 and 8] The multilayer could be useful in making reflective mirrors to detect specific coronal or transition-region emission lines in the wavelength region of 17–19 nm, since few good Al-based multilayer combinations have a significant reflectivity in the EUV region.[1-6] The reflectivity of Al(1%wtSi)/Zr multilayers depends sensitively on the microstructures and thermal environment.[2, 3] The four principal features responsible for the loss of reflectivity at room temperature are the inhomogeneous crystallization of aluminum, contamination in the multilayer, surface oxidized layer and interdiffusion between Al and Zr layers.[2] During annealing,[3, 7] the interdiffusion between layers, the formation of intermetallic compounds ($ZrAl_3$ and $ZrAl_2$) and the changes in surface and interfacial roughness each also contribute to altering the reflective performance of the multilayer as a reflective mirror. In order to obtain the highest optical performance of multilayers, there are many ways to enhance the reflectivity of the multilayers, such as optimization of the multilayer structure by adding capping layer,[9] the third material [3,4,10 and 11] or buffer layer [12], and thermal treatment [13, 14,] etc. Although there are several methods to increase the reflectivity, the simplest method to enhance the reflectivity is to focus on the multilayer structure. Preferably is the multilayer structure itself could solve the impact factors responsible for the loss of reflectivity in the practical applications.

Therefore, we describe a new concept of multilayer structure in this paper, which could disfavor

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the crystallization of Al, smooth the interface, and consequently enhance the reflectivity at near normal incidence. The concept of new multilayer structure is presented in Sec.2. After a brief description of the experimental process (Sec. 3), we compare different multilayer types (traditional Al(1%wtSi)/Zr multilayers, new multilayers Al(1%wtSi)/Zr with Si interlayers and without Si interlayers) with different Al layer thicknesses (Sec .4-1) by using grazing incident X–ray reflectometry (GIXR). In Sec. 4-2, the enhancement of the reflectivity of Al(1%wtSi)/Zr with Si interlayers at near normal incidence is characterized by near–normal incident EUV reflectance. We also find the best multilayer structure to obtain the highest optical performance in the experiment. In Sec. 4-3, the widely applications of the new multilayer structure are also discussed. We conclude in Sec. 5 with comments regarding the performances of the new Al(1%wtSi)/Zr multilayers.

2. The concept of new multilayer structure

To ensure the highest optical performance of the multilayers, the new multilayer structure should contain several features to solve the impact factors on the reflectivity. Based on the previous works, the variable interfacial and surface roughnesses are mainly caused by the inhomogeneous crystallization of Al.[1-3] In order to prevent the crystallization of Al, the Al layer in our design is divided into a number of layers along the in-plane direction, and the Si layer is inserted between each layer. The Si interlayers are also added in the structure to smooth the interfaces. The model is presented in the Fig. 1.

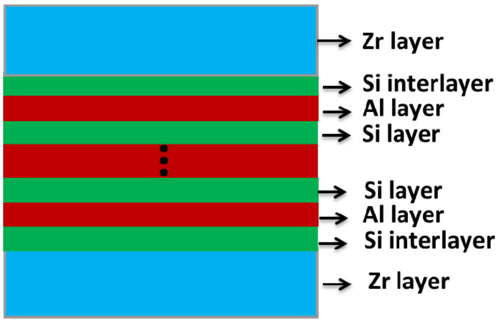

FIG. 1. The concept of new multilayer structure.

The advantages of this design over the traditional multilayer structures are:

- **Disfavor the crystallization of Al--**Using the thin Al layer means the Al layer thickness could decrease blow critical thickness of Al layer,[8] but also keep the periodic thickness of Al/Zr multilayers around 9.0 nm, designed as reflective mirrors in the region of 17-19 nm. Because of the interdiffusion between Al and Si layers, the Si could penetrate into the crystal lattice of Al and disfavor the crystallization of Al. Depending on the different practical applications, the Al layers could be divided into different numbers of layers. This flexibility will allow a greater range of applications in different fields.
- **Smooth the interfaces between Al and Zr layers--**In particular, there is large interdiffusion among Si, Al and Zr layers. We found that the Si could not only disfavor the crystallization of Al, but also enhance the crystallization of Zr, which present a smooth interface in the multilayers.[1] Therefore, the performance of Si interlayers is not to prevent the interaction between Al and Zr layers, but to smooth the interfaces between Al and Zr layers.
- **The optical contrast between the constituting materials remains the same--**The atomic number of Si is similar with that of Al. When the Si layer inserted into Al layers, it could not influence the electron standing wave field, but keep the original optimization of multilayer structure. However, with too much Si layers, the optical constant of Al will still change.
- **The improvement in lateral uniformity--**Because the multilayer could have the amorphous Al

or crystallite Al layers, the thickness must below the thickness (3.0 nm) of Al layers.[8] The Al<111> of Al fcc could not be observed in the Al layers. There is no specific orientation of Al in relation with the direction perpendicular to the layers, which could improve the lateral uniformity of Al layers in the multilayers. The surface and interfacial roughnesses are also lowered.

Generally speaking, these advantages are responsible for enhancing the reflectivity.[13] At present, we can get the new multilayer structure could increase the reflectivity in the theoretical field. In order to simplify the symbol of the complex multilayer structure in this paper, we use the thickness of Al layer to present the new multilayer structures. For example, the symbol of new Al(1%wtSi)/Zr multilayers with 40 periods, which the Al layer is divided into 8 layers and the thickness of each layer is 0.6 nm, is simplified to Al=0.6, etc. For the traditional Al(1%wtSi)/Zr multilayers with 40 periods, the symbol is Al/Zr-N40.

3. Experiment

All Al(1%wtSi)/Zr multilayers were prepared by using the direct-current magnetron sputtering system.[1-3] The sputtering targets with diameter of 100 mm were zirconium (99.5%) and silicon doped in aluminum (Al(1%wtSi)). The base pressure was 4.0×10^{-5} Pa, and the samples were deposited on Si polished wafers under a 0.16 Pa argon (99.9999% purity) pressure. In order to present the advantages of new multilayers, we fabricated different samples including the traditional Al(1%wtSi)/Zr multilayers (Al/Zr-N40), the new multilayer structure without Si interlayers (the samples Al=0.6, Al=1.4, Al=2.8 and Al=3.5) and the new multilayer structure with Si interlayers (the samples Al=0.6, Al=2.8). The thickness of each layer is shown in Table 1.

To perform the interfacial structure, the GIXR was characterized by using a Cu K_α source (λ=0.154 nm), and the fitting data were simulated by the Bede Refs software (genetic algorithm),[15] which the precision on the determination of the layer thickness and roughness are about 0.1nm and 0.01nm, respectively. The EUV reflectivity measurements were made at a 5° incident angle, using the reflectometer to detect the wavelength region from 16.5 to 20.5 nm at ELETTRA - Synchrotron Light Laboratory in Italy.

4. Results and Discussions

4.1 Grazing incident X–ray reflectometry

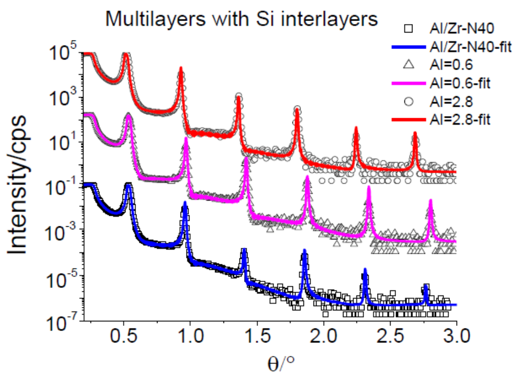

FIG. 2. Comparison between the GIXR experimental (black dots) and fitted curves (color curves) with Al(1%wtSi)/Zr for the Al/Zr-N40, Al=0.6nm, Al=2.8nm samples.

To present the advantages of the new multilayer structure, all samples were characterized by GIXR, measured over the angular range of θ=0°~3°. Because of different amount of Si penetrated into Al layers, the GIXR data is fitted by different models which are shown in the Table 1. The examples of the GIXR spectra and fitting data from the Al/Zr-N40, Al=0.6 and Al=2.8 with Si interlayers are shown in Figure 2. From the fitting data (not all fitting data are presented in Figure 2) for the multilayers without Si interlayers in Table 1-a, the Al and Si layer do not form intact layers in the sample Al=0.6. Because of large interdiffusion between Al and Si, the Si is penetrated into Al crystal lattices to form a new alloy Al(42%wtSi). The weight percent of Si is calculated from the quantity of Si materials in the whole Al layers. The roughnesses of different layers (Zr, Zr-on-Al, Al(42%wtSi) and Al-on-Zr) are 0.90, 0.32, 0.88 and 0.28 nm, respectively. With the increasing of Al layers in the samples (Al=1.4 and Al=2.8), the Al layer could form an intact layer in the multilayers. An interesting features of the GIXR measurements of Al=1.4 and Al=2.8 is that the curves of two samples are similar, which the roughnesses of different layers (Zr, Zr-on-Al, Al(1%wtSi), Si and Al-on-Zr) have few differences. After the Al layer thickness above 3.0 nm in the sample Al=3.5, the roughnesses of Si and two interlayers are similar with the samples Al=1.4 and Al=2.8. But the roughnesses of Zr and Al(1%wtSi) in Al=2.8 and Al=3.5 samples are increased from 0.70 to 0.92 nm and 0.72 to 0.95 nm, respectively. From results of the samples without Si interlayers, we can get that the roughnesses of different layers in the new multilayer are influenced by the formation of Al-fcc in the multilayer. The good Al layer thickness in the new multilayers should keep below the thickness (3.0 nm) of Al layer.[8] Lacking of the crystallization of Al-fcc, the surface and interfacial roughness are lower, and the lateral uniformity of Al layer is also improved in the new multilayers. Because of the similar GIXR curves of Al=1.4 and Al=2.8, we just add the Si interlayers in the samples Al=0.6 and Al=2.8 to further estimate the other advantages of the new multilayers.

Table 1. Parameters deduced from the GIXR measurements using the different models to fit the traditional multilayer, the new multilayers without and with Si interlayers.

Table 1-a. Fitting parameters of new multilayers without Si interlayers

New multilayers without Si interlayers									
Samples	**Layers**		**Thickness /nm**	**Roughness /nm**	**Samples**	**Layers**		**Thickness /nm**	**Roughness /nm**
Al=0.6	Zr		3.4	0.90	Al=1.4	Zr		2.7	0.68
	Zr-on-Al		0.5	0.32		Zr-on-Al		0.5	0.24
						Al(1%wtSi)	N =3	1.3	0.30
	Al(42%wtSi)		7.7	0.88		Si		0.4	0.18
						Al(1%wtSi)		1.3	0.28
	Al-on-Zr		0.3	0.28		Al-on-Zr		0.3	0.20
Al=2.8	Zr		3.0	0.72	Al=3.5	Zr		2.6	0.95
	Zr-on-Al		0.5	0.25		Zr-on-Al		0.5	0.26
	Al(1%wtSi)	N =1	2.8	0.70		Al(1%wtSi)	N =1	3.4	0.92
	Si		0.4	0.20		Si		0.4	0.17
	Al(1%wtSi)		2.9	0.72		Al(1%wtSi)		3.4	0.93
	Al-on-Zr		0.3	0.23		Al-on-Zr		0.5	0.27

Table 1-b.Fitting parameters of new multilayers with Si interlayers

New multilayers with Si interlayers							
Samples	**Layers**	**Thickness**	**Roughness**	**Samples**	**Layers**	**Thickness**	**Roughness**

		/nm	/nm				/nm	/nm
Al=0.6	Zr	3.3	0.75	Al=2.8	Zr		3.1	0.51
	Si	0.4	0.20		Si		0.4	0.22
	Al(42%wtSi)	5.4	0.73		Al(1%wtSi)	N	2.8	0.63
	Si	0.4	0.21		Si	=2	0.4	0.20

Table 1-c. Fitting parameters of traditional multilayer structure

Traditional multilayer structure			
Samples	**Layers**	**Thickness /nm**	**Roughness /nm**
Al/Zr-N=40	Zr	2.6	0.90
	Zr-on-Al	0.5	0.21
	Al(1%wtSi)	6.0	0.89
	Al-on-Zr	0.5	0.19

To identify the performance of Si interlayers, we compare Al/Zr-N40 and the samples (Al=0.6 and Al=2.8) with and without Si interlayers (Table 1). With Si interlayers (Table 1-b), the roughnesses of Zr and Al(42%wtSi) are 0.75 nm and 0.73 nm, which are lower than those (0.90 nm and 0.88 nm) in the sample Al=0.6 without Si interlayers (Table 1-a), respectively. In the sample Al=2.8, the roughnesses in the Zr and Al(1%wtSi) layers are also lowered because of Si interlayers. We can found the Si interlayers could prevent the formation of Zr-on-Al and Al-on-Zr interlayers, which can reduce the interfacial roughness in Table 1. The measurements in Figure 2 of the new multilayers (Al=0.6 and Al=2.8) show significantly enhanced reflectivity at the high-order Bragg peaks, especially for 5^{th} and 6^{th} order in the corresponding curves, compared to the reflectivity curve of the traditional multilayers Al/Zr-N40, which also present lower roughness of Al layers in Table 1-b and c. That means the Si layers could penetrate into the Al layers in the new multilayers, and disfavor the crystallization of Al, which could also influence the interfacial roughness of Al layers. From the results, we can get the Si interlayers and Si layers play a different role in the new multilayers. The Si interlayers could reduce the interaction between Al and Zr layers, and smooth the interface. While the Si layers could penetrate into Al layers, and influence the crystallization of Al, which could lower the roughness of Al layers. The performances of Al=0.6 and Al=2.8 with Si interlayers are much better than those without Si interlayers. Therefore, we decide to focus on the new multilayers with Si interlayers to characterize their EUV optical performance.

4.2 Near normal incident EUV reflectance

In order to verify the GIXR results shown in Table 1 and Fig. 2, the multilayers are measured and fitted in the wavelength region of 16.5-20.5 nm. The measurements are shown in the Fig. 3. They are best fitted by using the same parameters and models mentioned from the GIXR fitting data in Table-b and c. The reflectivities of Al/Zr-N40, Al=0.6 and Al=2.8 multilayers are 48.2 % at 18.6 nm, 48.7 % at 18.2 nm and 50.0 % at 19.0 nm, respectively. The lower reflectance of Al/Zr-N40 multilayers indicates the poor interface structure in this multilayer system, which is consistent with the conclusion of GIXR results. The Si interlayers and Si layers in the new multilayers could lower the interfacial roughness, and enhance the reflectivity, which verify that the new concept multilayer structure could not only increase the reflectivity in the theoretical field, but also in the experimental measurements. However as shown in Fig.3, although the Al layers could keep amorphous in the theoretical fields and the roughness of each layer is not too much, the reflectivity of sample Al=0.6 is still lower than that of sample Al=2.8 in the experiment. Because of too much Si layers inserted into Al layer in the sample Al=0.6, the optical constants of Al are changed, which could influence the optical performance of the multilayers. From the EUV measurements, we can get that the thickness of Al layer keep below the critical thickness is good to enhance the reflectivity in the theoretical field, but too much Si layers are penetrated into Al layers to keep the total periodic thickness around 9.0 nm. The optical constant of Al layers is changed and the reflectivity is decreased in the experiment.

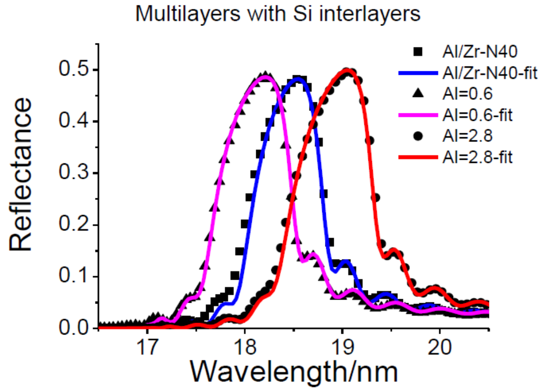

FIG. 3. (Color lines) Measured reflectivity versus wavelength of the multilayers at 5° incident angle by synchrotron radiation. The fitting lines use the models in the Table 1.

4.3 Discussions

To present the widely applications of the new concept of multilayer structure for other systems or other fields, we describe the situation of Al(1%wtSi)/Zr systems firstly. In our previous works,[1-3, 7 and 8] the crystallization of Al could influence the optical and structural performances in Al(1%wtSi)/Zr multilayers. In order to reduce the effects on the performances, the new multilayers are designed that the Al layers are divided into many layers, and the Si layer is inserted into each layer to hinder the formation of Al-fcc. Based on the measurements and fitting data of GIXR and EUV, we found the best structure is that the Al layers could not cut into too much layers, which the Si layers might influence the optical constant and lower the reflectivity. The thickness of Al layer should be below 3.0 nm, and using one Si layer in Al layer. The reflectivity is improved to 50.0% in sample Al=2.8.

Therefore, we can get that this kind of multilayer structure is suitable for the multilayers or devices which performances are influenced by the crystallization of material layers. In the other EUV and soft-x-ray multilayers, the crystallization of material layers could also influence the optical and structural performances, such as the reflectivity, stress, etc. For Al/Mo multilayers,[16, 17] the reflectivity of the multilayers is influenced by the crystallization of Al. We can use this new multilayer structure to prevent the formation of Al crystal and improve the performance of Al/Mo multilayers in the practical applications. In some multilayers, residual stresses in multilayers is the main problem to hinder the performances of the multilayers. Scientist had used many ways to reduce residual stresses in multilayers, such as using buffer layer [18] or sputtering the material layers in the different gases (the Ni/Ar [6] or Ar/air [19] mixtures and low Ar pressure [20]), etc. Although these methods could be useful, we can use the simplest way to prevent the problem, which should solve the impact factors on residual stresses. For the impact factors, we can know that the stress is influenced by the crystallites preferred orientation (texture), numbers of layer and the layer thickness. And the basic problem is the texture of the material layer.[21] For these problems, the new multilayer structure could prevent the crystallites preferred orientation in the material layers effectively. For example in Mo/Si and Mo/Be multilayers [18], the crystallization of Mo is the main problem to increase the residual stresses. Using buffer layer could solve the problem in the experiment, but also decrease the reflectivity, which is not suitable for the practical applications. While for the new multilayer structure, it could hinder the crystallization of Mo, and finally reduce residual stresses. The most important is the new structure could not influence the optical performance. The new multilayer structure could also use in the semiconductor industry. In particular, the crystallization of the hole transport layer (HTL) could decrease the lifetime of organic LED. In order to extension the lifetime of LED, the new multilayer structure could be very useful. We can insert a layer into the HTL to prevent its crystallization. The lifetime of the LED could improve from 10 000 h to 50 000 h.[22] To sum up, the new multilayer structure could effectively solve the problems caused by the crystallization of material layers. Meantime, other performances are not influenced by the new structure in the different applications.

5. Conclusion

We have demonstrated that the new multilayer structure could enhance the reflectivity of Al(1%wtSi)/Zr multilayers at near normal incidence. Based on the results of GIXR and EUV, the roughnesses of Zr and Al layers of new multilayers are lower than those of the traditional Al/Zr-N40 multilayers. With the Si interlayers, the interfacial becomes smooth, and improves the reflectivity. Although the Al layers can be divided into many layers, too much Si layer inserted into each layer could influence the optical and structural performances in the experiment. Therefore, the best multilayer structure is keeping the thickness of Al below 3.0 nm, and inserting only one Si layer into the Al layers. The new multilayer structure could not only enhance the optical performance of EUV and soft-x-ray multilayers, but also solve other problems caused by the crystallization of the material layers in other fields. With this achieved the benefits of the new multilayers will be fully realized and the new structure should be widely used in many practical applications.

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