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用 X 射线反射测量法表征双层结构中低原子序数材料的特性

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摘要：介绍了用 X 射线反射测量术表征双层薄膜中低原子序数材料特性的方法。由于低原子序数材料的光学常数与 Si 基板材料的光学常数非常接近，用 X 射线反射法确定镀制在 Si 基板上的低原子序数材料膜层结构的变化十分困难，因此，提出了在镀制低原子序数材料前，首先在基板上镀制一层非常薄的金属层的方法。实验中，选用 Cr 作为金属层材料，制备并测试了三种不同 C 膜镀制时间的 Cr/C 双层薄膜。反射率曲线拟合结果表明，C 膜密度约为 2.25 g/cm^3，沉积速率为 0.058 nm/s。

关　键　词：X 射线衍射仪；低原子序数材料；反射率测试；薄膜
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Characterization of low-Z material layer profiles in bilayer structures by X-ray reflectivity measurement

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Abstract: A convenient method, low-angle X-ray reflectivity measurement method, is presented to characterize the parameters of low-Z material layers in bilayer structures using X-ray diffractometer (XRD). Because the low-Z material optical constant is similar to the silicon (Si) substrate, the change of the low-Z material layer profiles is difficult to determine. Therefore, an ultra-thin metal layer is deposited as the Base Layer (BL) onto the substrate prior to the low-Z material layer. By choosing chromium (Cr) as the BL material, three Cr/C bilayer films with different C deposition times are fabricated and measured. After the simulation of the reflectivity curves, the density of C is approximately 2.25 g/cm^3, while the deposition rate of C layer is 0.058 nm/s under our laboratory conditions.

Key words: XRD; low-Z material; reflectivity measurement; thin films

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1 Introduction

High reflectivity multilayer films, made up of alternating layers of highly reflective and transmissive materials, have important applications in X-ray spectroscopy, X-ray microscopy, and X-ray lithography[1-2]. Because of the multilayer element special working region, the thickness of each layer is in nanometer scales[3-4]. For these films, parameters such as layer thickness, interface roughness and material density play a decisive role in achieving optimum performance. Improvement in the method to determine the profiles of materials in the multilayer structure accurately is critically important in the development of multilayer optics[5-7].

In multilayer structures low-Z materials generally are deposited as the spacer layers which do not play a leading part in the performance of multilayer elements, but they do influence the reflectivity of the multilayer. We cannot determine accurately the parameters of multilayer structures if we ignore the effect of the low-Z material layers. Consequently one could not then produce the exact specimen according to the design, so it is crucial to characterize their parameters accurately in multilayer structures.

People frequently use X-ray low-angle reflectivity measurement to investigate the structure profiles of multilayers[8-9]. However the data with such complex information can not properly characterize the parameters of the given material. Some profiles like density and roughness determine the performance of the whole multilayer structure, cannot obtain the real data concerned accurately. Both the multilayer sample preparation and the measured curve simulation would take a long time. Here we present an effectual method using low-angle X-ray reflectivity measurement to provide an accurate estimation of the low-Z material layer structure. In previous investigations, we studied Ni films and W/B_4C bilayer films using a similar method[10-11], but we cannot simply investigate the low-Z material layer using the same method. Here we present a novel method to investigate the structure of low-Z material layer through the adoption of metal BL.

2 Experimental details

For low-Z material, the optical constant is usually close to that of the substrate materials such as silicon and glass, and, consequently the oscillation of a single low-Z material layer X-ray reflectivity curve is difficult to detect. The wavelike reflectivity curve of the low-Z material single film varies only slightly, while the intensity versus grazing angle curve decreases rapidly. Hence we cannot estimate the change of the layer structure accurately. Here we deposit an ultra-thin metal layer on the substrate prior to the low-Z material layer, which makes it much easier to measure the change of layer thickness from X-ray reflectivity data. Fig. 1 shows the theoretical comparison of a C layer on a silicon substrate before and after depositing a 1 nm Cr layer as the BL.

To find the most appropriate BL material, four metal materials including tungsten, cobalt, molybdenum and chromium were considered. Fig. 2 shows the theoretical reflectivity curves of 30 nm C layer with four different metal materials as the BL where the thickness is 1 nm. We find that the reflectivity curve with Cr as the BL material fluctuates more than that the other metals, and the reflectivity intensity decreases more slowly than other materials, so that the measuring range can be increased. Accordingly Cr was chosen as the BL material in this experiment.

Three Cr/C bilayer samples with different C deposition times were fabricated by using an ultra-high vacuum dc magnetron sputtering coater, model JGP560C6, from a 10 cm diameter target of Cr (99.95% purity) and C (99.95% purity)

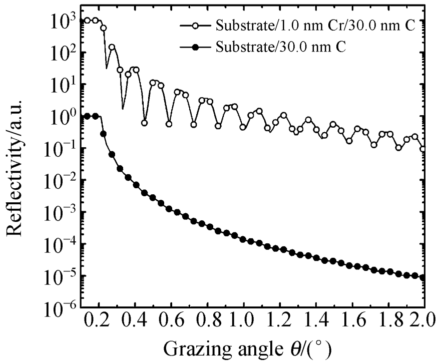

Fig. 1 Theoretical comparison of 30 nm C film with and without 1 nm Cr BL

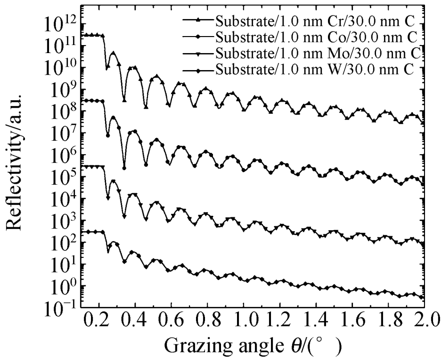

Fig. 2 Reflectivity curve of 30 nm C layer with the four different metal materials as the BL with thickness 1 nm. From top to bottom the BL materials are Cr, Co, Mo and W.

in Ar (99.999% purity). The base pressure in the deposition chamber before deposition was 5×10^{-5} Pa. The sputtering took place at a pressure of 0.106 Pa. Super-polished Si (100) wafers measuring 20 mm × 30 mm were used as deposition substrates which were placed about 8 cm above the target. The substrate temperature was not controlled during the deposition process. The time a sample stays over the target can be used to control the thickness of each layer. Alternatively, by facing the substrate toward each target for a predetermined time the films were fabricated, and using a stepping motor controlled by a computer the deposition time can also be controlled.

It is important to investigate and increase the understanding of the effects of some parameters in multilayer structures[12]. X-ray reflectivity measurement is a technique used for probing the structure of single-layer and multilayer thin film materials irrespective of their crystalline perfection[13-14]. Hence, the technique can be applied equally well to crystalline, polycrystalline and amorphous materials, and provide accurate information about the thickness, roughness and density in thin-film structures. Furthermore, a precise estimate of these parameters can be obtained through curve-fitting of the X-ray reflectivity measured data. Consequently, after fabrication, low-angle reflectivity curves of the bilayer samples with different thicknesses were measured using an X-ray diffractometer, which was the main technique used to determine the thickness of thin films for deposition-rate calibration. The instrument is the Bede D^1 system which was manufactured by the Bede Company in the UK. The voltage and current values for the copper anode were −30 kV and 20 mA, respectively. A collimated beam of X-rays from copper Kα emission at wavelength of 0.154 nm was generated and incident on a sample. For diffraction at grazing angles, the XRD reflectivity was obtained by measuring the reflected beam intensity as a function of the reflectivity angle over the angular range 2θ. The film thickness was determined by fitting the diffraction data to the Fresnel equations. The fitting parameters include the carbon

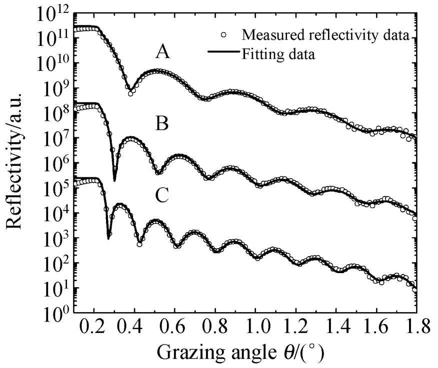

Fig. 3 XRD measured data of Cr/C bilayer structure deposited on Si substrate and the fitting data

film thickness and the roughness of both the silicon substrate and the carbon surface expressed in the form of a Debye-Waller factor. A series of bilayer X-ray reflectivity curves recorded as a function of reflectivity angle and simulation curves are shown in Fig. 3.

3 Results and discussion

In this paper we employed an evolutionary algorithm called 'Differential Evolution' to fit the experimental data[15]. Through simple mutation, recombination and selection schemes, parameter vectors with better fitting are found. The ability to explore many different areas of parameter space simultaneously is a key to their success. Assuming that there are N measured points (θ_j, I_j) in the measured data, where θ_j is the incidence angle, I_j is the intensity measured at θ_j and $j = 1, 2, ... , N$, we obtain the error function:

$$E(\boldsymbol{p}) = \frac{1}{N-1}\sum_{j=1}^{N} \mid \log I_j - \log I(\theta_j ; \boldsymbol{p}) \mid$$

The vector $\boldsymbol{p} = [p_l, p_2, . . . , p_n]$ involves n adjustable parameters which are used to construct a model that describes approximately the sample structure. The theoretical calculation of the supposed structural model is compared with the experimental data using the error functions $E(\boldsymbol{p})$. The error functions adequately describe the data at low intensities occurring at large scattering angles but they have low sensitivity to outlying data points (due mainly to statistical noise in the experimental data). They also contain information on the smallest length-scales present in the structure, which are often those at which the X-ray characterization is aimed[16].

Fig. 3 shows both measured and simulated curves of bilayer structures. Six adjustable parameters: density, layer thickness, and interface roughness of both Cr and C layers were obtained by fitting the experimental data.

Tab. **1** Structure parameters obtained from the recursive formalism.
(d is layer thickness, ρ is material density, and σ is roughness of each film interface)

Specimen	d_{Cr}(nm)	d_C(nm)	ρ_{Cr}(g/cm^3)	ρ_C(g/cm^3)	$\sigma_{Substrate}$(nm)	σ_{Cr}(nm)	σ_C(nm)
A	1.56	10.30	6.79	2.24	0.38	0.54	0.57
B	1.58	15.58	6.79	2.25	0.37	0.48	0.53
C	1.58	20.78	6.79	2.25	0.35	0.41	0.52

As can be seen in the fitting results (Tab. 1), the surface roughness and the layer interface roughness both decrease as C layer thickness increase. From the calculated results we can observe that both the thickness and the density of Cr keep nearly constant when the C thickness changes, which indicates that the fabrication is stable. This is also helpful in the research of low-Z material parameters, and it also ensured that the simulated data of the C-layer structure is realistic.

For the low-Z material parameters, it is perhaps strange that the densities are almost equal to the bulks' values. First, it is due to the deposition method using DC magnetron sputtering, which normally results in a high-quality film structure. Second, the densities can be influenced by diffusion or intermixing of Cr atoms into the C layer and vice versa. The data also indicate that with an increase of the C deposition time the interfacial roughness between Cr and C decreases which can explain the preparation difficulty of ultra-short period multilayers. Further the surface roughness of the C layer exposed in the air is almost same as the variation in the interfacial roughness between Cr and C. This represents the advantage of X-ray reflectivity analysis which can detect the embedded information while some surface analytical technologies such as AFM that only focus on the exterior information.

Then using the sputtering time of each film (Tab. 2), we can determine the deposition rate for the experimental condition accurately as $r=0.058$ nm/s (Fig. 4).

Tab. **2** Results of deposition rate calibration

Specimen	A	B	C
C thickness/nm	10.30	15.58	20.78
Depositing time/s	174	264	354

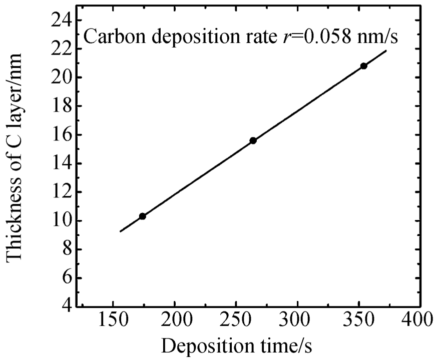

Fig. 4 Fitting curve of deposition time versus C layer thickness. The regression coefficient of the fitting line is 0.999 99, and the deposition rate r is 0.058 nm/s.

4 Conclusions

Using the low-angle X-ray reflectivity measurement we have presented an effecting method to determine the parameters of the low-Z material layer in a multilayer structure. With the employment of an ultra thin metal film we can observe the change of C film profiles especially the layer thickness, which makes the low-Z material deposition rate calibration more straight forward. We found that the interface roughness decreased slowly with the increase of the C layer thickness. Compared with simulation of the multilayer structure, it is much simpler to obtain the accurate structure profiles by fitting the measurement data of bilayer samples and time for sample preparation and measurement curve simulation is much shorter. The density and the deposition rate of the C layer are more easily to obtained by this method which is helpful in controlling the quality of the multilayer structure. In this experiment, the density of the C film is 2.25 g/cm^3 and the deposition rate is 0.058 nm/s. This convenient method is an effective improvement of multilayer studies.

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