Influences of thickness ratio of two materials on the residual stress of multilayers

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The effect of thickness ratio of two materials on the residual stress was studied in HfO_2/SiO_2 multilayers deposited by electron beam evaporation on BK7 glass substrates. An optical interferometer was used to analyze the residual stress, and X-ray diffraction (XRD) was applied to characterize the structural properties. The results showed that the residual stress of multilayers was compressive when the optical thickness ratio of HfO_2 to SiO_2 was 1:3. Then the value of residual stress decreased with the increase of optical thickness ratio, the residual stress became tensile when the thickness ratio increased to 3:1. HfO_2 was monoclinic and SiO_2 was amorphous in all the multilayers. The microstructures of 1:3, 6:13 and 1:1 multilayers were similar. For crystal plane $m(020)$, the interplanar distance decreased and the crystallite size increased when the optical thickness ratio increased to 3:1. In addition, the evolutions of residual stress were corresponding with the variations of microstructure to some extent.

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Multilayers are widely used for a variety of technological applications that take advantage of their unique optical, magnetic, electrical, and mechanical properties[1−6]. For many of these applications, film stress is an important parameter that must be characterized and ultimately controlled, which can cause severe problems for a number of applications in advanced technology; for instance, excessive residual stress can limit the reliability and function of thin films-based structures due to peeling, cracking and curling. So the control of the residual stress is very crucial in almost all coatings. Considerable of effort has been devoted to the analysis of residual stress in multilayers, for instance, basing on the study of residual stress in single films, Ennos[7] studied the residual stress in ZnS/Cryolite, $ZnS/ThOF_2$ and PbF_2/Cryolite multilayers, and the relations were discussed between the stress of single films and multilayers. Schweitz *et al.*[8] studied the stress in Au/Ni multilayers and estimated the interfaces. The stress of W/C multilayers and strain relaxation upon annealing were analyzed by Geisz *et al.*[9]. Shao *et al.*[10] studied the stress of ZrO_2/SiO_2 deposited on different substrates with different thickness periods.

HfO_2 and SiO_2 are widely used in optical and microelectronic films[11,12]. In our previous research[13,14], experiment results had shown that the residual stress of high index and low index materials may be reverse. Therefore, the different stress properties of two materials can be applied to reduce the total residual stress of a multilayer. In this paper, the effect of thickness ratio of two materials on the residual stress was studied in HfO_2/SiO_2 multilayers, deposited by electron beam evaporation on BK7 glass substrates. The results can provide references for the preparation of multilayers with lower residual stress. An optical interferometer was used to analyze the residual stress, and X-ray diffraction (XRD) was applied to characterize the structural properties.

HfO_2/SiO_2 multilayers were deposited on BK7 glass substrates ($\phi 50 \times 5$ mm) by electron beam evaporation method. The film stacks were $(HL)^6$, $H3L(H2L)^6$, $(HL)^6$ and $(3HL)^6$, respectively. The deposition was carried out at 290 °C with a base deposition pressure of 2.0×10^{-3} Pa. The oxygen partial pressures were 2.0×10^{-2} Pa during HfO_2 deposition process, which was adjusted to 1.0×10^{-2} Pa when SiO_2 was deposited. The deposition rates of HfO_2 and SiO_2 were 0.45 and 0.75 nm/s, respectively. The films thickness was controlled by the single-wavelength turning point method with a wavelength of 550 nm.

The substrate radius of curvature was measured by TECHO(OSI-200XP) interferometer. The residual stress σ in the film is then given by Stoney's equation[15]

$$\sigma = \frac{E_s}{6(1-\nu_s)} \frac{t_s^2}{t_f} \left(\frac{1}{R} - \frac{1}{R_0} \right), \qquad (1)$$

where $\dfrac{E_s}{1-\nu_s} = E_s'$ (102 GPa) is the biaxial modulus of the substrate, R_0 and R are the radii of the substrate curvature before and after deposition, respectively. t_s and t_f are the thicknesses of the substrate and the film, respectively.

The microstructure of multilayers was characterized by XRD with 2θ angle in the range of $15° - 90°$ using Cu $K\alpha$ radiation in a step of 0.02°, the interplanar distance, d, was calculated by the equation of $2d \sin\theta = \lambda$, where θ is the Bragg diffraction angle and λ is the X-ray wavelength. The crystallite size of thin films D was calculated using the formula of $D = 0.9\lambda/(\beta \cos\theta)$ where $\lambda_{\mathrm{Cu}K\alpha} = 0.1542$ nm, β is full width of peak at half maximum intensity.

The total stress in a multilayer film is composed of the intralayer stresses and the interface stress. The interface stress tensor represents the work required to deform elastically by a unit strain and a unit area of interface. For the case of periodic multilayer films consisting of alternating layers of material A and B with thickness d_A and d_B and intralayer stresses σ_A and σ_B, respectively, the total stress σ in the multilayers can be expressed as[16]

$$\sigma = \left(\frac{d_A}{\lambda}\sigma_A + \frac{d_B}{\lambda}\sigma_B \right) + \frac{N}{d_f} f_{AB}, \qquad (2)$$

where λ is the thickness of one repeating period, N is the number of interface, d_f is the total thickness of multilayers, and f_AB is the interface stress. The first term is the average stress in individual films; the second term is the average interface stress.

Figure 1 shows the residual stress of HfO_2/SiO_2 multilayers with different optical thickness ratios of HfO_2 to SiO_2. It can be seen that the residual stress of multilayers is compressive when the optical thickness ratio of HfO_2 to SiO_2 was 1:3. Then the value of residual stress decreases with the increase of optical thickness ratio, the residual stress becomes tensile when the thickness ratio increased to 3:1.

The XRD pattern of HfO_2/SiO_2 multilayers with different optical thickness ratios of HfO_2 to SiO_2 is shown in Fig. 2. It can be found that HfO_2 was monoclinic and SiO_2 was amorphous in all the multilayers. The diffraction peaks of multilayers with the optical thickness ratio of 3:1 are stronger than that of other multilayers. In addition, the multilayers exhibit a strong (020) texture.

The interplanar distance and the crystallite size of m (020) have been calculated (shown in Table 1). Comparing Fig. 2 and Table 1 we find that the microstructures of 1:3, 6:13 and 1:1 multilayers are similar, the interplanar distance decreases and the crystallite size increases when the optical thickness ratio increases to 3:1. This may be attributed to the change of HfO_2 thickness in a single repeating period. The optical thicknesses in a single period of multilayers with the optical thickness ratios of 1:3, 6:13 and 1:1 are all H, then the optical thickness in a single period increases to 3H in the multilayers with the optical thickness ratios of 3:1. The change of film thickness may lead to difference of film microstructure, the HfO_2 films grow on the amorphous surface of SiO_2 films, at the beginning of the growth, the HfO_2 deposition particles are not easy to crystallize for the influence of amorphous surface, the influence decreases with the increase of HfO_2 film thickness. So the multilayers with the optical thickness ratios of 3:1 have larger crystallite size. In the θ-2θ mode, only crystallites with lattice planes parallel to the surface are measured. Compressive stress parallel to the surface causes vertical expansion of the film and leads to a increase of interplanar distance that is parallel to the surface. Therefore, the decrease of interplanar distance (or the increase of 2θ) indicates that compressive stress decreases with the increase of optical thickness ratio. But the sample with optical thickness ratio of 1:1 is not accorded with the changing rule, this maybe because the relations between the macroscopical stress and microcosmic strain are complex, sometimes, it is difficult to explain residual stress with strain only in one crystal plane. In our future work, the relations between macroscopical stress and microcosmic stress will be studied deeply.

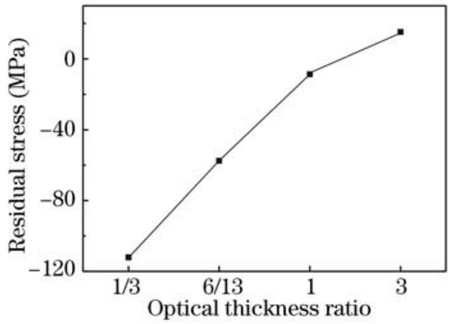

Fig. 1. Residual stress of multilayers with different optical thickness ratio of HfO_2 to SiO_2.

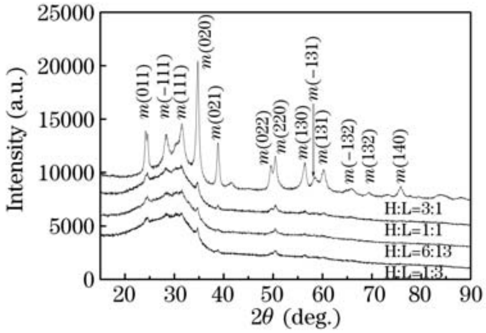

Fig. 2. XRD spectra of multilayers with different optical thickness ratios.

Table 1. Interplanar Distance and Crystallite Size Versus Optical Thickness Ratio of HfO_2 to SiO_2

Optical Thickness Ratio of HfO_2 to SiO_2	Diffraction Peak (deg.)	Interplanar Distance (nm)	Crystallite Size (nm)
1:3	34.701	0.25830	18.46
6:13	34.721	0.25816	18.46
1:1	34.695	0.25837	18.46
3:1	34.745	0.25799	19.94

In conclusion, experiments have indicated that the residual stress of HfO_2/SiO_2 multilayers was compressive when the optical thickness ratio of HfO_2 to SiO_2 was 1:3. Then the value of residual stress decreased with the increase of optical thickness ratio, the residual stress became tensile when the thickness ratio increased to 3:1. The residual stress of multilayers can be adjusted by altering the thickness ratio of two materials. This implied that we can reduce the residual stress by choosing appropriate film stacks. In the same time, the evolutions of stress accord with the variations of microstructure to some extent.

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