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Post-annealing effects on the structural properties and residual stress of Ta_2O_5 thin films deposited by ion beam sputtering

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We studied the structural properties and residual stress of Ta_2O_5 thin films deposited by single ion beam sputtering (SIBS) and dual ion beam sputtering (DIBS) as a function of the annealing temperatures (200 ~ 800 °C). With the increase of the annealing temperatures, the refractive indexes of the Ta_2O_5 films deposited by both SIBS and DIBS processes continuously decreased. The residual stress of the post-annealed film could be minimized at an annealing temperature of 400 °C. - According to the XRD analysis, the crystallization temperature of Ta_2O_5 is found around 600 °C. As the annealing temperature was increased to 600 °C, the oxygen-concentration in the film continuously increased, but it started to saturate in the temperature range 600 °C - 800 °C.

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1. Introduction

Residual mechanical stress in thin films is composed of the intrinsic and thermal stresses acting on the plane parallel to the interface between the film and the substrate. The intrinsic stress is usually built during the growth process primarily depending on the deposition parameters, whereas the thermal stress originates from the mismatch of thermal expansion coefficients between the film and the substrate. Especially in optoelectronic devices, the mechanical stress can have a significant effect on device properties, such as refractive index and waveguide loss [1-4]. In fabricating high quality optical coatings, obtaining a proper level of residual stress in thin film is an important requirement especially for the application of DWDM (Dense Wavelength Division Multiplexing) filters, because these devices consist of multiple Ta_2O_5/SiO_2 layers (more than 150 layers) having alternating high refractive index and low refractive index materials.

The single ion beam sputtering (SIBS) deposition technique has been shown to be an excellent method in synthesizing low scattering coatings [5-7], because it involves an atom-by-atom (or molecule-by-molecule) transport process of highly energetic materials in relatively low pressure and temperature conditions. However, SIBS is a very slow deposition process compared to other deposition techniques and also it may produce a non-stoichiometric oxide films. In this study, we improved the film stoichiometry by mixing oxygen gas with the working ambient gas (Ar) in the assist ion source [8], which is referred to as a dual ion beam sputtering (DIBS). The major benefits of the DIBS process are the increased packing density of the deposited films which makes them more bulk-like, the improved adhesion resulting from the mixing of the materials at the interfaces between each layers, and the reduction of the high tensile stress in the layers [9].

In this paper, the relationship between the annealing temperature and the residual stress of Ta_2O_5 films are also discussed, and the changes in the surface morphology and refractive index during the phase transformation process of the Ta_2O_5 thin film grown by both SIBS and DIBS processes were investigated as a function of the annealing temperatures.

2. Experimental

Ta_2O_5 thin films were deposited both by SIBS and by DIBS on Si (111) wafers using a Veeco Ion Tech SPECTOR system. Kaufman-type ion sources were used for the DIBS process. The beam voltage and current were 1250 V and 600 mA for the first sputtering ion source, and 550 V and 150 mA for the assist ion source, respectively[10]. Argon gas was used as a process gas and oxygen gas was fed from the region near the sputtering target. The base pressure and the process pressure were approximately 4.0×10^{-5} and 2.7×10^{-2} Pa, respectively. A mixture of oxygen and argon was fed into the assisted ion source. Because the optical properties of thin films strongly depend on the deposition conditions, the influence of the main deposition parameters on the qualities of these films was systematically studied as a function of the annealing temperatures (200 ~ 800 ℃) for both SIBS- and DIBS-grown Ta_2O_5 thin films. For both cases, the post-deposition annealing was performed for 10 hrs in air and the heating/cooling rate was controlled at 4℃/min.

In converting the measured wafer curvature to mechanical stress, the most frequently used stress (σ)-

curvature (1/R) relationship is the Stoney equation [11], which can be written as:

$$\sigma = \frac{1}{6E(1-\nu)} \frac{t_s^{\ 2}}{t_f} \frac{1}{R} \tag{1}$$

where, 1/E(1- ν) is the biaxial modulus of the substrate, t_s is the thickness of the substrate and t_f is the thickness of the film. In this study, we mainly concentrated on investigating the influence of the annealing temperatures on the mechanical stress of Ta_2O_5 films.

In order to characterize the crystallized microstructure, the chemical binding state, and the surface morphology of Ta_2O_5 films, X-ray diffraction (HRXRD : D8 DISCOVER, BRUKER), X-ray photoelectron spectroscopy (XPS, HP 5950B ESCA spectrometer), and atomic force microscopy (AFM) were used, respectively. The optical parameter (n) and the film thickness were calculated from the ellipsometery measurements, which are based on the analysis of the transmittance spectrum measured at a wavelength of 1550 nm.

3. Results and discussion

Fig. 1 shows the variations of the thickness and the refractive index of Ta_2O_5 films deposited by SIBS and DIBS processes as a function of the annealing temperatures. The initial thicknesses of the as-deposited Ta_2O_5 films grown by SIBS and DIBS methods were about 1.20 μm and 1.03 μm, respectively. As the annealing temperature was increased from 200 to 400 ℃, the thicknesses of Ta_2O_5 films grown by SIBS and DIBS methods increased to 1.27 μm and 1.05 μm, respectively. However, in both cases, after high temperature annealing (600 ~ 800 ℃), the thicknesses of the annealed Ta_2O_5 films were lowered than those of as-deposited films. To understand this phenomenon, the following factors need to be considered. At low annealing temperature (~ 400 ℃), the increase in volume of as-deposited film with the increase of the annealing temperature is the dominant mechanism in changing the film thickness. In this temperature range, accordingly, the refractive index as-deposited film was decreased because of the decrease of density as-deposited film according to the increase in volume of as-deposited film. At higher annealing temperatures (600 ~ 800 ℃), the Ta_2O_5 film is crystallized and densified, resulting in the decrease of the film thickness. The initial refractive indices were 2.110 and 2.105 for the SIBS- and DIBS-grown samples, respectively. With the increase of the annealing temperature, the refractive indices of the annealed films decreased continuously down to 2.028 and 2.016 for the SIBS- and DIBS-grown films after 800 ℃ annealing, respectively. We believe that the decrease of the refractive index with the increase of the annealing temperature is caused by the possible increase of the oxygen concentration in Ta_2O_5 films.

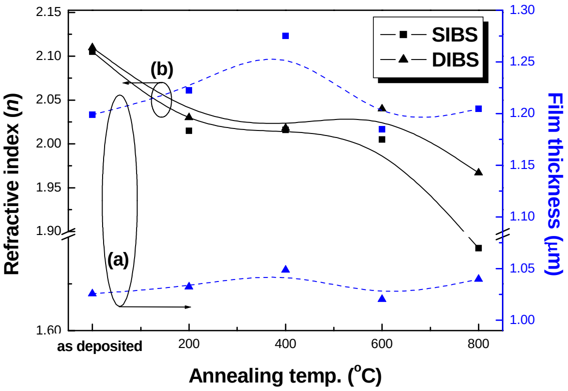

Fig. 1. (a) The film thickness and (b) the refractive index of as-deposited and post-annealed Ta_2O_5 films deposited by SIBS and DIBS as a function of the annealing temperatures.

Fig. 2 shows the residual stress and the rms (root-mean-square) surface roughness of the as-deposited and post-annealed Ta_2O_5 films deposited by SIBS and DIBS methods as a function of the annealing temperatures. The initial residual stresses of the as-deposited Ta_2O_5 films grown by SIBS and DIBS were about 1.3 and 1.0 GPa, respectively. When the annealing temperature is lower than 400 ℃, the residual stress decreased with the increase of the annealing temperature. On the other hand, when the annealing temperature is over 400 ℃, the residual stress increased with the increase of the annealing temperature. It is believed that the volumetric shrinkage of Ta_2O_5 films due to the crystallization process caused the increase of the mechanical stress after high temperature annealing. The annealed films which were deposited by SIBS and DIBS methods and subsequently annealed at high temperature showed a similar trend. However, the residual stress of the film deposited by DIBS was always lower than that of the film deposited by SIBS. The rms surface roughness of the as-deposited Ta_2O_5 films deposited by the SIBS and DIBS were about 0.18 and 0.15 nm, respectively. Below 400 ℃, the rms roughness slowly increased with increasing the annealing temperature. However, because of the transformation from amorphous to crystalline for annealing temperatures in the range of 400 ~ 800 ℃, the rms roughness of the films sharply increased to 1.43 and 1.26 nm for SIBS- and DIBS-grown samples, respectively.

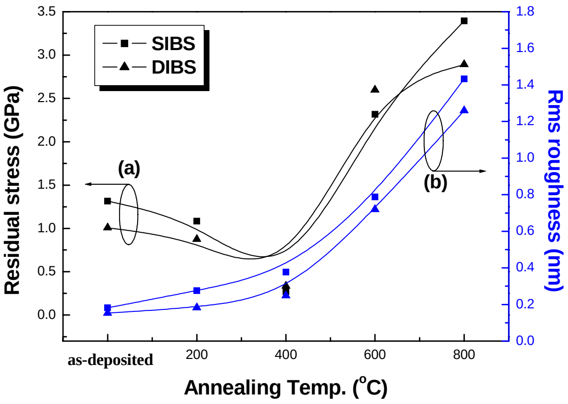

Fig. 2. (a) The residual stress and (b) rms surface roughness of as-deposited and post-annealed Ta_2O_5 films deposited by SIBS and DIBS as a function of the annealing temperatures.

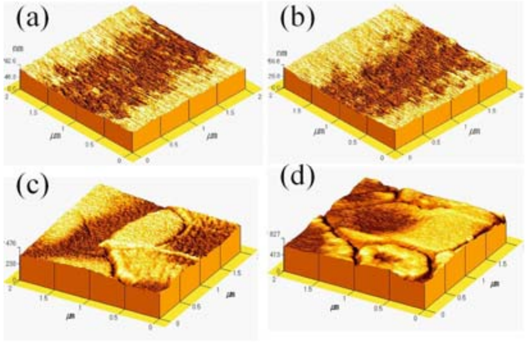

Fig. 3. AFM images of (a) as-deposited SIBS film, (b) as-deposited DIBS film, (c) post-annealed SIBS film at 800 ℃ and (d) post-annealed DIBS film at 800 ℃.

AFM images of SIBS- and DIBS-grown samples with and without thermal annealing at 800 ℃ are shown in Fig. 3. The surface morphologies of the as-deposited SIBS and DIBS films were excellent having minimum rms values. The measured grain size was about 1 ~ 2㎛ and the distinct grain boundaries could be observed for both films after annealing at 800 ℃ as shown Fig. 3 (c) and (d).

Fig. 4 shows the XRD spectra of the as-deposited and post-annealed Ta_2O_5 films deposited by DIBS process. For the films annealed below 400 ℃, no crystallized state is observed and the crystallization of Ta_2O_5 starts at around 600 ℃. After the crystallization of Ta_2O_5 film, its thickness is reduced as shown in Fig. 1 because the film is densified during the phase transformation from amorphous to crystalline.

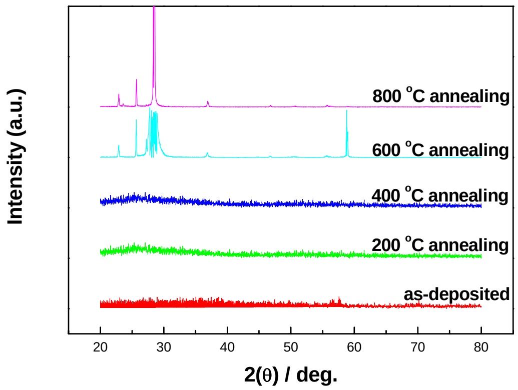

Fig. 4. The X-ray spectra of as-deposited and post-annealed Ta_2O_5 films deposited by DIBS.

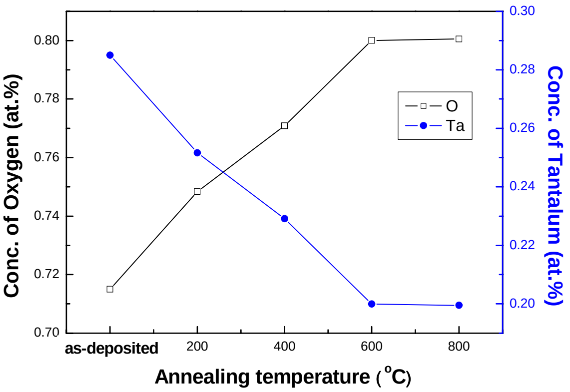

Fig. 5. The change of oxygen and tantalum-concentration of as-deposited and post-annealed Ta_2O_5 films grown by DIBS process.

Fig. 5 shows the change of chemical compositions of DIBS-grown Ta_2O_5 films measured by XPS as a function of the annealing temperatures. The relative oxygen-concentration of the film increased with the increase of the annealing temperature and remained constant after 600 ℃. When a metal oxide system having a lot of oxygen vacancies is deposited on Si substrates, it is well known that interfacial oxide is usually formed due to the fast oxygen diffusion from the surrounding annealing ambient and the strong thermodynamic driving force for forming Ta_2O_5 during high temperature annealing. Therefore, it is believed that the oxygen atoms can diffuse into the Ta_2O_5 film due to this thermodynamic driving force. During that process, these oxygen atoms may combine with crystalline defects, such as oxygen vacancies, which is confirmed by the previous our thickness measurement results as a function of annealing temperatures.

4. Conclusions

Ta_2O_5 thin films were deposited by SIBS and DIBS technique, and their physical properties were evaluated as a function of the annealing temperatures. The residual stress decreased with increasing the annealing temperature to 400 ℃. However, when the annealing temperature was over 400 ℃, the residual stress increased with the increase of the annealing temperature. The refractive indices of the SIBS and DIBS films continuously decreased as the annealing temperature was increased. Those films annealed at temperatures above 600 ℃ showed a crystallized state according to the XRD measurement. As the annealing temperature was increased to 600 ℃, the oxygen-concentration of the film increased. However, the oxygen-concentration of the film saturated when the annealing temperature was increased from 600 to 800 ℃.

References

[1] F. M. d'Heurle, Int. Mater. Rev. **A 34**, 53 (1989).
[2] M. F. Doerner, W. D. Nix, CRC Critical Rev. Solid State Master. Sci. **14**, 225 (1988).
[3] H. Windischmann, CRC Critical Rev. Solid State Master. Sci. **17**, 547 (1992).
[4] King-Ning Tu, James W. Mayer, Leonard C. Feldman, Electronic Thin film Science, ch. 4, 77 (1992).
[5] J. R. Sites, P. Gilstrap, R. Rujkorakarn, Optical Engineering **22**, 447 (1983).
[6] M. Varasi, C. Misiano, L. Lasaponara, Thin Solid Films **117**, 163 (1984).
[7] D. T. Wei, H. R. Kafuman and C. C. Lee, in F. R. Flory (ed.), Thin Films for Optical Systems, Marcel Dekker, New York, p. 133 (1995).
[8] C. C. Lee, J. C. Hsu, D. T. Wei, J. H. Lin, Thin Solid Films **308-309**, 74 (1997).
[9] H. Angus Macleod, Thin Film Optical Filters third edition (Institute of Physics Publishing, (2001) ch.3, p.87.
[10] S. G. Yoon, H. M. Kim, M. J. Kim, H. M. Lee and D. H. Yoon, Thin Solid Films **475**, 239 (2005).
[11] G. G. Stoney. Proc. R. Soc. London Ser. **A 82**, 1729 (1909).

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