한국표면공학회지
Journal of Korean Institute of Engineering
Vol. 30, No. 1, Feb. 1997
<연구논문>

스퍼터링 TiO_2막의 구조 및 광학적 성질에 미치는 열처리 효과

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Thermal Annealing Effects on the Structural and Optical Properties of Sputtered TiO_2 Films

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Abstract

The effects of the post-deposition annealing on the structural and optical properties of sputtered TiO_2 thin films were studied; annealing was carried out in air up to 1000℃ for different duration. The results of the X-ray diffraction and the Raman spectroscopy showed the annealing-condition dependent structural transformation of TiO_2 films from the as-deposited amorphous phase to the anatase and rutile phases. The spectroscopic ellipsometry was used to investigate the deposition-condition dependence of the as-deposited film optical constants and also the evolution of the optical constants correlated with the annealing-induced structural transformation.

I. INTRODUCTION

It is very well known that the properties of the thin films are different from those of the bulk materials, and exhibit a strong dependence on the deposition conditions. Hence, the characterization of the thin films has been the indispensible prerequisite for the various applications. In case of optical coatings, the investigation of the deposition condition dependence of the spectral refractive indices and the optical absorption which are the two major intrinsic properties that govern the performance of the optical coatings has been widely carried out. Titanium dioxide is one of the most extensively used optical coating materials due to its desirable optical properties and good stability in adverse environment[1]. In spite of its excellent properties, the use of the TiO_2films in the applications with stringent constraints requires cautious approach due to the diverse phases in that TiO_2 films can appear. Titanium dioxide can exist in the three different crystalline phases; rutile, anatase, and brookite[2], and generally TiO_2 films are deposited in either amorphous, anatase or rutile phases according to the deposition conditions[3]. Hence when the the TiO_2 films are used for the applications that make the TiO_2 films to be exposed to the high temperature or high power laser light, the structural transformations are always a concern.

In this paper we deposited TiO_2 films by the RF magnetron sputtering, and the Raman spectroscopy and the X-ray diffraction were used to investigate the annealing condition dependent crystallization. We also investigated the deposition condition dependent optical constants of the as-deposited TiO_2 films and the evolution of the optical constants due to thermal annealing.

II. EXPERIMENTAL

TiO_2 thin films were deposited at room temperature by the RF magnetron sputtering on silicon substrates which were either thermally oxidized, HF-etched, or only chemically cleaned, while the sputtering power was increased from 100 W to 250 W at the interval of 50 W. Sputtering chamber has the base pressure of 2.0×10^{-6} torr and the Ar working pressure was maintained at 5×10^{-3} torr. The as-deposited films were annealed in air up to 1000℃ for different durations.

Raman spectroscopy, X-ray diffraction, and spectroscopic ellipsometry (SE) were used for the structural and optical characterization of the as-deposited and thermally annealed TiO_2 films. Raman spectroscopy was perfor-med using an 5145 Å laser line up to an effective frequency shift of 1000 cm^{-1}, X-ray diffraction was performed using a Cu target with 0.02° resolution, and photon-energy-dependent eillpsometeric constant Δ-and Ψ-spectra were measured by a Rudolph model S2000 spectroscopic ellipsometer.

III. RESULT AND DISCUSSION

For all the as-deposited films regardless of the deposition conditions, both the Raman spectroscopy and the X-ray diffraction produced only features related to the silicon substrates, which is the strong evidence for the amorphous nature of these films. Not surprisingly, our attempts to fit the measured SE spectra of the as-deposited films based on either rutile and anatase optical constants were failed. However, we were able to fit the measured SE spectra of the as-deposited films by representing the optical constants with the dispersion equations in our multilayer modeling. In multilayer modeling, the films were assumed to be composed of multilayers with different thickness and void fraction, and the effective optical constants of each layer were calculated using the Bruggeman effective medium theory[4]. In Fig. 1, we show the measu-red SE spectra of the as-deposited amorphous TiO_2 film which is deposited with RF power of 100 W together with the best

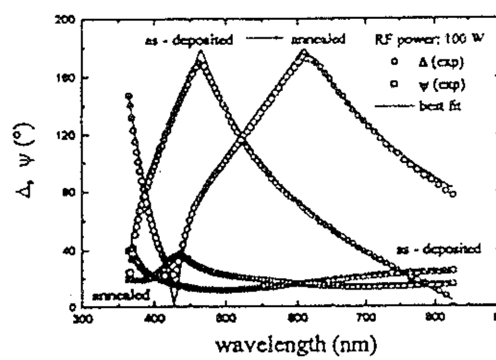

Fig. 1 The comparison of the SE spectra of the as-deposited and thermally annealed TiO_2 films. The film is deposited with the sputtering power of 100 W and annealed at 900℃ for 3 hours. The best fit curves are also shown in solid lines.

fit curves. We also present the refractive indices of the as-deposited TiO_2 films determined from the multilayer modeling in Fig. 2. The refractive indices of the rutile and the anatase phases are added for comparison. In Fig. 2, it can be seen that the refractive indices of all the as-deposited TiO_2 films are smaller than those of the crystalline phases except the film deposited with RF power of 150 W. The exceptionally large refractive indices of the film deposited with 150 W RF power suggests that unlike the other as-deposited films which seem less dense then the crystalline phases, this film has some rutile seeds which are undetectable by the Raman spectroscopy or the X-ray diffraction, but can contribute to the observed large refractive indices. In Fig.1, we also show the SE spectra which is measured after the film deposited with RF power of 100 W is thermally annealed at 900 ℃ for 3 hours, together with the best fit curves. The observed large difference between the spectra of the as-deposited film and thespectra of the annealed film is the sign of the optical property change caused by the thermal annealing. Especially, the magnitude of the spectral difference indicates that the film underwent a significant evolution which is far more than the mere densification of the amorphous film. The quantitative change of the refractive indices induced by the thermal annealing is shown in Fig. 3. In this figure, we find that the annealed film exhibit the refractive indices which are very close to those of the anatase phase TiO_2, which lead us to conclude that the thermal annealing induced the transformation of TiO_2 film from the amorphous phase to the anatase phase.

The above discussions based on the optical characterizations can be directly confirmed by the structural investigation of the annealed films using the Raman spectroscopy and the X-ray diffraction. We present the results of the Raman spectroscopy and the X-ray diffraction of the TiO_2 films annealed at 900℃ for 3 hours in Fig. 4.

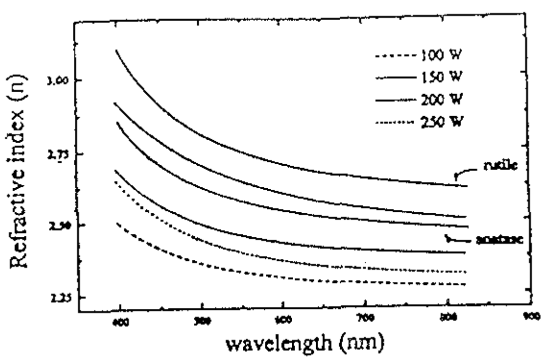

Fig. 2 The refractive indices of the as-deposited amorphous TiO_2 films. These films were deposited at room temperature with the RF power of 100, 150, 200, and 250 W. The refractive indices of the rutile and the anatase phases are also shown.

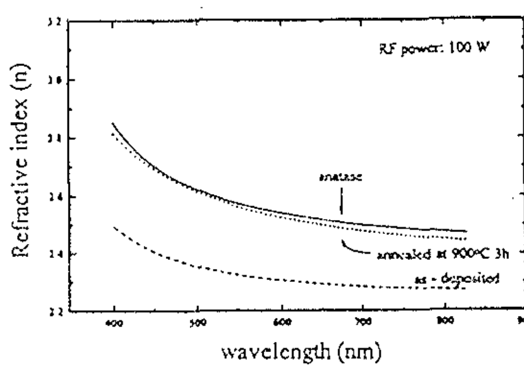

Fig. 3 The variation of the refractive indices of the TiO_2 film due to the thermal annealing. The film is deposited with the sputtering power of 100 W and annealed at 900 ℃ for 3 hours.

First, the Raman spectra presented in Fig. 4 (a) shows the typical features of the anatase for all the an-nealed films. These are the Raman bands at about 144, 400, and 640 cm^{-1} [5], and are labeled accordingly in addition to the band from the silicon substrate. Also, the closer examination of the Raman bands shows the difference in the intensities and the values of the FWHM among the films deposited with different RF sputtering power, which indicates the dependence of the degrees of crystallization on film deposition conditions. Second, the X-ray diffraction pattern presented in Fig. 4 (b) shows mainly the anatase peaks which were individually indexed[6]. The differences in the peak areas and the peak widths of the anatase peaks shown in this figure also indicate that each film has the different preferential orientation and also the different degrees of crystallization. Very interestingly we find small rutile (110) peaks at about 27° from the films deposited with RF power of 150 or 200 W in addition to the anatase peaks. We propose that these stem from the rutile crystalline seed that were embedded in the amorphous phase, as we already discus-sed above. Currently, we do not

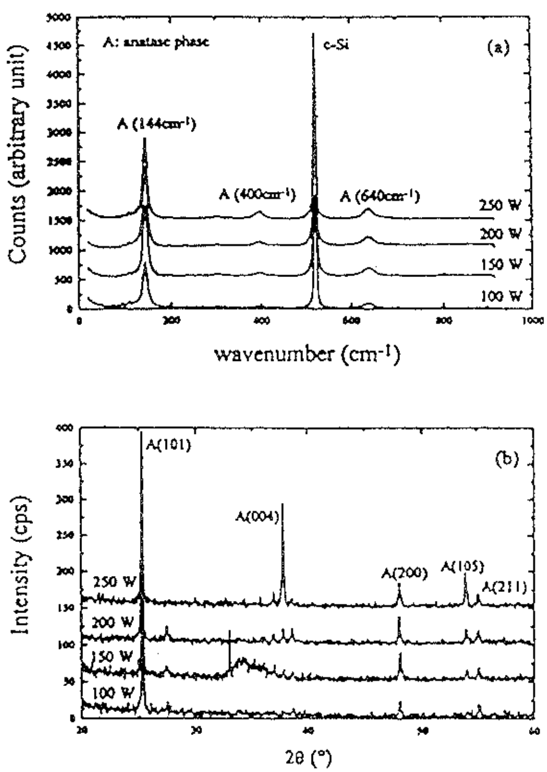

Fig. 4 The results of the Raman spectroscopy and the X-ray diffraction of the annealed TiO_2 films: (a) Raman spectra, (b) X-ray diffraction patterns. The TiO_2 films were deposited at 100, 150, 200, and 250 W and annealed at 900 ℃ for 3 hours.

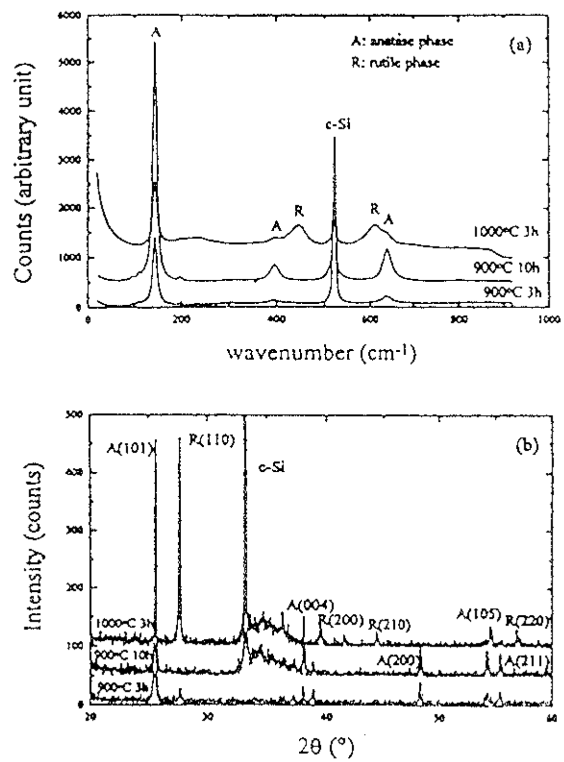

Fig. 5 The effects of the annealing temperature and the annealing time on the structural transformation of TiO_2 films: (a) Raman spectra, (b) X-ray diffraction patterns. The TiO_2 films were deposited at 200 W and annealed at 900℃ for 3 hours, then annealed 6 more hours (total 9 hours), and finally another 3 hours at 1000℃.

understand why the rutile seed were formed in the first place, and why they do not grow into the large grains as we anneal the films. However, the disappearance of the small rutile (110) peak due to the additional annealing at 900℃ as shown in Fig. 5, strongly suggest that at this temperature either the anatase phase is more stable than the rutile phase or the amorphous-rutile transformation is energetically unfavorable compared to the amorphous-anatase-rutile transformation. The transformation from the anatase phase to the rutile phase is observed from the sample that was annealed at 1000℃ for 3 hours. From the Raman spectra shown in Fig. 5 (a), we find that the rutile Raman bands appear, while the anatase bands become weaker. The growth of the rutile phase at the expense of the anat-ase phase is more clearly seen from the X-ray diffraction patterns shown in Fig. 5 (b). In this figure, it can be seen that as we raise the annealing temperature to 1000℃ and anneal for three hours, the well defined anatase peaks which were observed when the film was annealed for 10 hours at 900℃ weaken significantly, and simultaneously the strong rutile peaks appear. Based on the above disc-ussions, it has to be emphasized that the TiO_2 films can undergo very complicated structural transformations, and consequently the TiO_2 films can exhibit diverse optical constants. For example, the increase of the refractive indices can originate not only from the improved packing density but also from the onset of crystallization. On the other hand, the increase of the crystallinity can induce larger extinction coefficients due to the enhanced scattering loss. Hence, it is a very interesting and also very challenging problem to study the structural transformation and the optical constant evolution simultaneously, and to correlate them. Currently, such studies are in progress and the results will be reported in another paper.

Ⅳ. CONCLUSIONS

In this paper, we investigated both the structural transformation and the optical constant variation of the sputtered TiO_2 films. We find that the refractive indices of the as-deposited films are smaller than those of the crystalline phases, and also that thermal annealing increases the refractive indices. The similarity of the refractive indices between the annealed film and the anatase phase is found due to the structural transformation from the amorphous to anatase. We also extended our investigation to the structural transformation from the anatase phase to rutile phase. Our study shows that the X-ray diffraction and Raman spectroscopy are the complementary techniques to investigate the structural transformation of TiO_2 films. Our study also shows that the simultaneous studies of the structural transformation and optical constant evolution are indispensible to understand the diverse and complex variation of the TiO_2 film properties.

ACKNOWLEDGMENTS

This paper was supported by '95 SPECIAL FUND for UNIVERSITY RESEARCH INSTITUTE, Korea Research Foundation.

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