

dc reactive magnetron sputtering of titanium-structural and optical characterization of TiO₂ films

M. H. Suhail, G. Mohan Rao, and S. Mohan

Instrumentation and Services Unit, Indian Institute of Science, Bangalore 560012, India

(Received 13 August 1991; accepted for publication 31 October 1991)

This paper deals with the reactive sputtering of titanium in an argon and oxygen mixture. The variation in cathode potential as a function of oxygen partial pressure has been explained in terms of cathode poisoning effects. The titania films deposited during this process have been studied for their structural and optical characteristics. The effect of substrate temperature (from 25 to 400 °C) and annealing (from 250 to 700 °C) on the packing density, refractive index, extinction coefficient, and crystallinity has been investigated. The refractive index varied from 2.24 to 2.46 and extinction coefficient from 2.6×10^{-3} to 10.4×10^{-3} at 500 nm as the substrate temperature increased from 25 to 400 °C. The refractive index increased from 2.19 to 2.35 and extinction coefficient changed from 3.2×10^{-3} to 11.6×10^{-3} at 500 nm as the annealing temperature was increased from 250 to 700 °C. Anatase and rutile phases have been observed in the films deposited at 400 °C substrate temperature and annealed at 300 °C. The changes in the optical constants at higher substrate temperature have been attributed to an increase in packing density, oxygen content, and crystallinity of the films.

I. INTRODUCTION

In recent times reactive magnetron sputtering has gained significant importance for depositing a variety of hard coatings. This is due to the ease of control over the stoichiometry of the deposited film. The process of reactive sputtering has undergone considerable change in terms of the behaviour of the process parameters under the influence of the reactive gas in the system. The mechanism of reactive sputtering has been explained differently from time to time. Considering the reactive gas flow mechanism, the process has been explained^{1,2} and a review by Westwood³ considered many aspects of the technique in detail. In recent studies^{4,5} an anomalous behavior in the glow discharge characteristics as a function of reactive gas pressure has been observed. This was explained qualitatively in terms of negative ion formation and target poisoning effects. Docheva *et al.*⁴ have explained the process based on the concept of difference in electron emission coefficient of different phases of oxides formed on the target. These studies were confined to reactive sputtering of copper in oxygen and argon mixtures. In the case of refractory metals like titanium, which are good getter materials, the process should be more interesting. Moreover, titanium compounds like TiO₂ and TiN are widely used for optical and tribological applications, respectively. Titania (TiO₂) is known to exist in amorphous form and crystallizes in three distinct structures:⁶ two tetragonal phases, anatase ($a = 3.785 \text{ \AA}$, $c = 9.514 \text{ \AA}$) and rutile ($a = 4.593 \text{ \AA}$, $c = 2.959 \text{ \AA}$) and a third orthorhombic phase, brookite ($a = 5.456 \text{ \AA}$, $b = 9.182 \text{ \AA}$, $c = 5.143 \text{ \AA}$). Brookite and anatase are thermodynamically less stable than rutile. Heating the films at a temperature near 900 °C converts them to rutile phase.⁷ Normally titania films are prepared in thin-film form by a wide variety of techniques like vacuum evaporation,⁸⁻¹⁵ ion assisted deposition,¹⁶

sputtering,¹⁷⁻²⁰ etc. The study of TiO₂ films prepared by reactive magnetron sputtering should be of interest because of high deposition rates and low substrate temperature obtained in magnetron sputtering. Thus this investigation is aimed at understanding the reactive sputtering of titanium in an oxygen and argon mixture and studying the optical and structural characteristics of the titania coatings. The substrate temperature has been varied from 25 to 400 °C during deposition. The effect of the substrate temperature as well as post-deposition annealing temperature (up to 700 °C) on the properties and structure of titania films has also been investigated.

II. EXPERIMENTAL

The experiments were carried out in a home built magnetron sputtering system.²¹ High-purity argon (4 N) and oxygen (5 N) have been used as the sputtering and reactive gases respectively. The discharge characteristics have been controlled using a variable dc power supply (1 kV and 6 A). Pure titanium (99.5) of 110-mm diameter and 2-mm thickness has been used as the sputtering target. Sputtering has been carried out in a sputter up mode on to uncooled quartz substrates. The sputtering chamber was evacuated to 5×10^{-6} Torr before admitting the reactive gas into the system. Partial pressure of oxygen has been maintained and checked as per the method used by Heller²² and Mohan Rao and Mohan.⁵ In each experiment the target was presputtered in argon atmosphere until the surface oxide layers are removed from the target. The removal of oxide is characterized by the sudden change in the discharge characteristics and the change in discharge color to blue from a pale pink.

Titania films have been prepared on well cleaned quartz substrates keeping the target power at 800 W which enables a deposition rate of 2 nm/min. For all the studies,

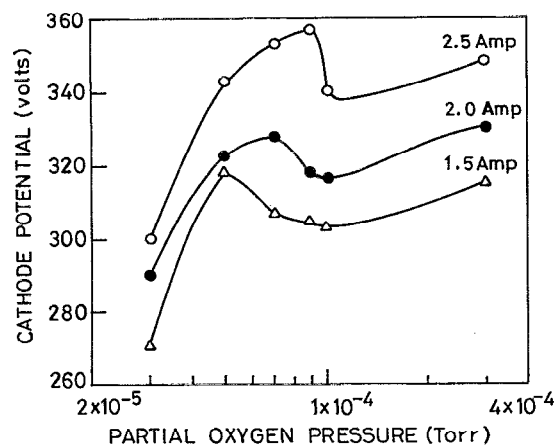


FIG. 1. Variation of cathode potential for titanium target as a function of oxygen partial pressure at different cathode current.

the substrates were maintained at a distance of 65 mm from the target as it was found to result in good uniformity.²¹ The substrate temperature (from 200 to 400 °C) was controlled by using a quartz halogen lamp whose power was controlled by varying the input voltage. Post-deposition annealing of deposited films was performed in air for half an hour in the temperature range 200–700 °C. Spectral characteristics in the wavelength range 300–850 nm were measured using an Hitachi model 330 spectrophotometer. The optical constants have been calculated using the envelope technique²³ and packing density by the Bragg and Pippard model²⁴ modified by Harris *et al.*²⁵ The crystallinity was examined by using x-ray diffraction with Co K_{α} radiation. The thickness of the films has been determined using multiple beam interferometry to an accuracy of ± 2.5 nm.

III. RESULTS AND DISCUSSION

In the first part of this section, the effect of oxygen partial pressure on the glow discharge characteristics and the deposition rate are discussed. The latter part deals with the structure and optical properties of titania films.

A. Glow discharge characteristics

The conventional explanation²⁶ that the cathode potential, to achieve a particular current decreases with the addition of oxygen into the system, was found to be incorrect in many of the earlier studies^{4,5} and a new explanation was offered for this behavior.⁵ Figure 1 shows the variation of cathode potential for the titanium target as a function of oxygen partial pressure for maintaining different cathode currents. The cathode potential initially shows a gradual increase with oxygen pressure. At a critical oxygen pressure it starts decreasing and then again starts increasing. The critical oxygen pressure, as explained by Mohan Rao and Mohan,⁵ is dependent on the cathode current density. These results are in agreement with the model proposed by them which explains this behavior on the basis of negative ion formation and target oxidation effects.

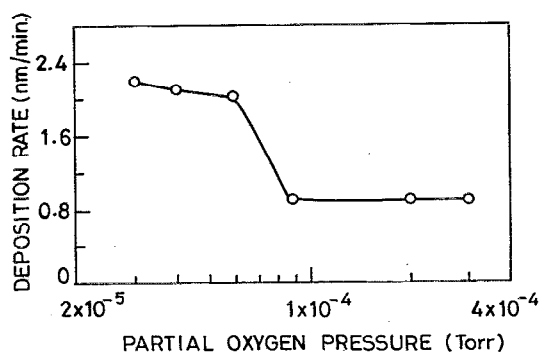


FIG. 2. Variation in deposition rate of titania films as a function of oxygen partial pressure (sputtering pressure 3×10^{-2} Torr).

One of the process parameters that is directly influenced by the oxygen pressure is the deposition rate. Figure 2 shows the variation of deposition rate corresponding to a constant current (1.5 A) as the oxygen partial pressure is varied in the system. It almost remains constant around 2.2 nm/min up to about 6×10^{-5} Torr and then gradually decreases to about 0.9 nm/min at a pressure of 9×10^{-5} Torr and at higher pressures again remains constant. The decrease in the deposition rate at 6×10^{-5} Torr is compared with to the decrease in the cathode potential at the same pressure (Fig. 1). This drop in deposition rate is the result of target oxidation and the resultant low sputtering yield of the oxide.²⁷ The drop in cathode potential is due to the high secondary electron emission of the oxide as compared to the pure metal.

Thus the variation in cathode potential and deposition rate of titanium in oxygen and argon atmosphere is in conformity with our reactive sputtering model.⁵ Similar results have been obtained using different targets like molybdenum, zirconium, and aluminum, which confirm the validity of the explanation. These results are being quantified using the Langmuir probe and will be published later.

Since the films seem to achieve stoichiometry at the critical oxygen pressure, all further studies have been carried out at an oxygen pressure of 6×10^{-5} Torr and a total pressure of 3×10^{-2} Torr.

B. Structure studies

Figure 3 shows x-ray diffraction patterns for the films deposited on quartz substrates maintained at different temperatures. The as-deposited films are amorphous to x ray and the crystallinity is seen to set in around 300 °C with a small peak of anatase (101). The diffraction pattern shows no distinguishable features but at 350 °C clear peaks are seen. The peak can be attributed to the anatase phase [at (200), (105) and (211)]. The diffraction pattern for the film deposited at 400 °C contains peaks of both the anatase [at (101), (200), and (105)] and rutile [at (101) and (210)]. However in all films, a strong amorphous background is seen. The brookite phase has not been observed in any of the films investigated. Schiller *et al.*,²⁰ by using reactive dc plasmatron sputtering, found rutile and anatase

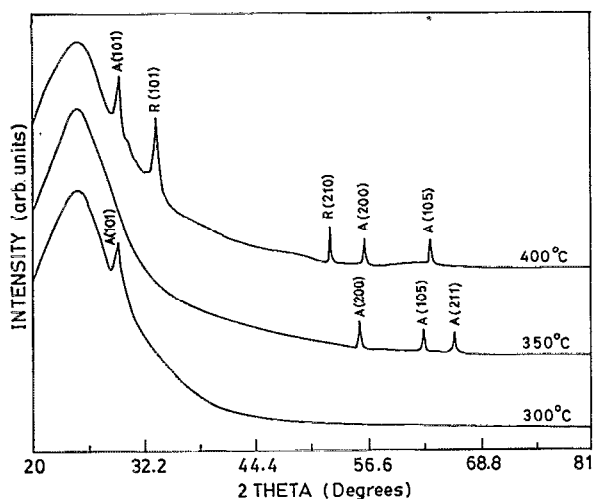


FIG. 3. X-ray diffraction patterns for titania films at different substrate temperatures.

mixture phases at substrate temperature in the range 25–500 °C at low oxygen partial pressures. At higher pressures they found rutile phase only up to 150 °C, whereas at higher temperatures they again found a mixed phase containing both rutile and anatase. Pawlewicz and Busch⁶ also observed the mixed phase of anatase and rutile for substrate temperature in the range 200–500 °C. Similar amorphous to crystalline transition around 350–400 °C was observed by Bange *et al.*²⁸ for evaporated films and by Williams and Hess²⁹ for rf sputtered films. In all the cases mixed phase is present up to around 600 °C and later only rutile structure prevailed. The brookite phase was completely absent in all the reported studies.

The film deposited at ambient temperature has been annealed at different temperatures in the range 300–700 °C and a corresponding diffraction pattern showed in Fig. 4. Crystallinity was observed around 300 °C with small peaks of anatase [(101) and (103)] and rutile {210}. Even after

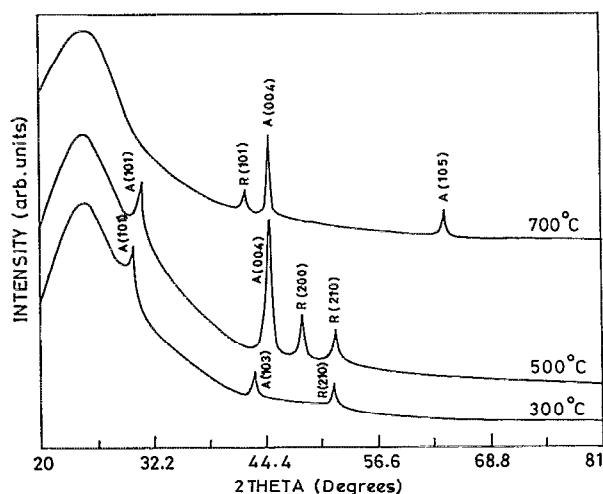


FIG. 4. X-ray diffraction patterns for titania films at different annealing temperatures.

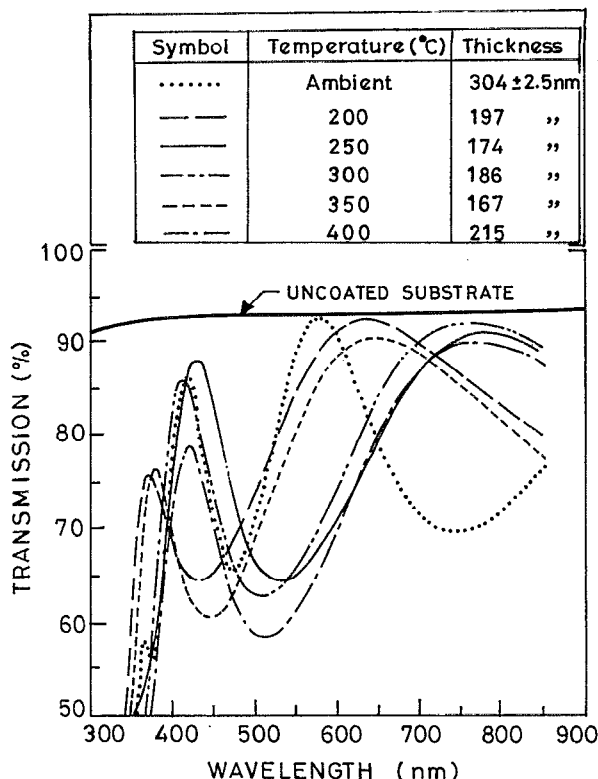


FIG. 5. Transmission spectra as a function of wavelength for titania films at different substrate temperatures.

annealing at 700 °C the anatase phase dominates with [(004) and (105)] lines along with a small peak of rutile (101). At intermediate annealing temperature of 500 °C, the diffraction pattern shows both the anatase [(101) and (004)] and rutile [(200) and (210)] phases. A significant feature of these observations is that an amorphous phase continues to exist in the film even when the film was subjected to an annealing temperature as high as 700 °C.

C. Optical properties

Figure 5 shows the spectral transmittance of the films deposited at different substrate temperatures from ambient to 400 °C. It is seen that the transmittance maxima of the films decreased as the substrate temperature is increased. In other words the films deposited at higher temperatures are more absorbing. This might be due to insufficient oxygen incorporation in the film during deposition, as the condensation of oxygen decreases at these temperatures.^{8,11} A similar observation was made by Narasimha Rao *et al.*^{13,14} for electron beam evaporated TiO₂ films.

The annealed films showed different characteristics (Fig. 6). It can be seen that the films are stable with annealing temperature up to 500 °C. On further rise in annealing temperature, to (600 & 700 °C), the interference pattern in the transmission spectrum shifted to a lower wavelength region. The transmittance maxima of the film also decreased. This might be due to the partial reduction of TiO₂ at higher temperature. As seen from the x-ray

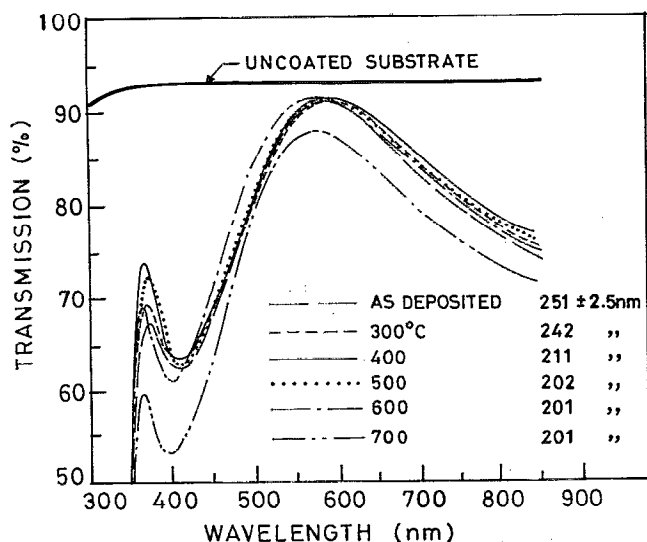


FIG. 6. Transmission spectra as a function of wavelength for as-deposited and annealed titania films.

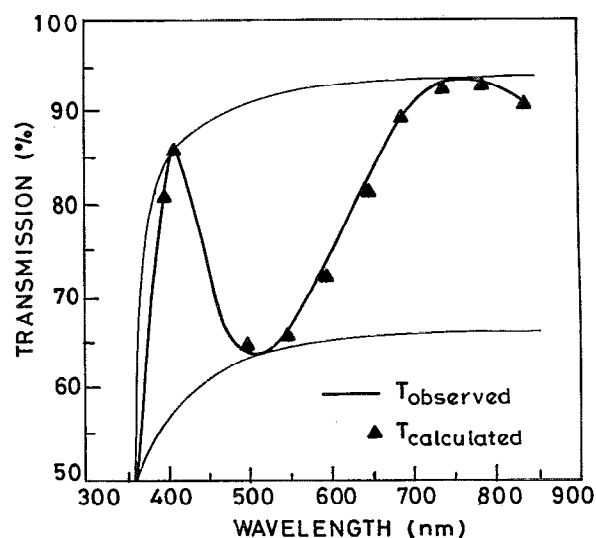


FIG. 8. Observed and calculated transmission spectra as a function of wavelength.

diffraction patterns, this may also be due to crystalline transition in the films.

The refractive index (n) and extinction coefficient (k) of the films deposited at different temperatures is plotted as a function of wavelength in Fig. 7. The films deposited at ambient temperature showed a refractive index of 2.24 (at 500 nm) which increased to 2.46 for the films deposited at 400 °C. The extinction coefficient also increased from 2.6×10^{-3} to 10.4×10^{-3} for the same films. Bennett *et al.*³⁰ used various techniques for deposition and found that the refractive index of electron beam evaporated films was the lowest (2.18) whereas it was highest for ion beam sputtered and ion plated films (2.46 and 2.61, respectively). The low values of refractive index observed in the present study may be partly due to the low deposition rates used. The increase in the refractive index and extinction coefficient of the films deposited at higher temperature may

be attributed to an increase in packing density, crystallinity of the films, and also to oxygen deficiency.

The n and k values as determined by the envelope technique have been plotted against wavelength in Fig. 7. To check the validity of this technique, the calculated n and k values at different wavelengths have been again fitted into the transmittance curve and are shown in Fig. 8. As these calculated values are in agreement with the observed transmission ($\pm 0.2\%$), this technique has been assumed to be valid. The optical constants have also been compared with those measured using an ellipsometer (Rooialph model: AUTO EL II) and found to be in good agreement. Based on all these results it was found that the error in the calculations was about ± 0.01 for refractive index, whereas it was ± 0.001 in the case of extinction coefficient.

The variation in refractive index and extinction coefficient with annealing temperature is shown in Fig. 9. The

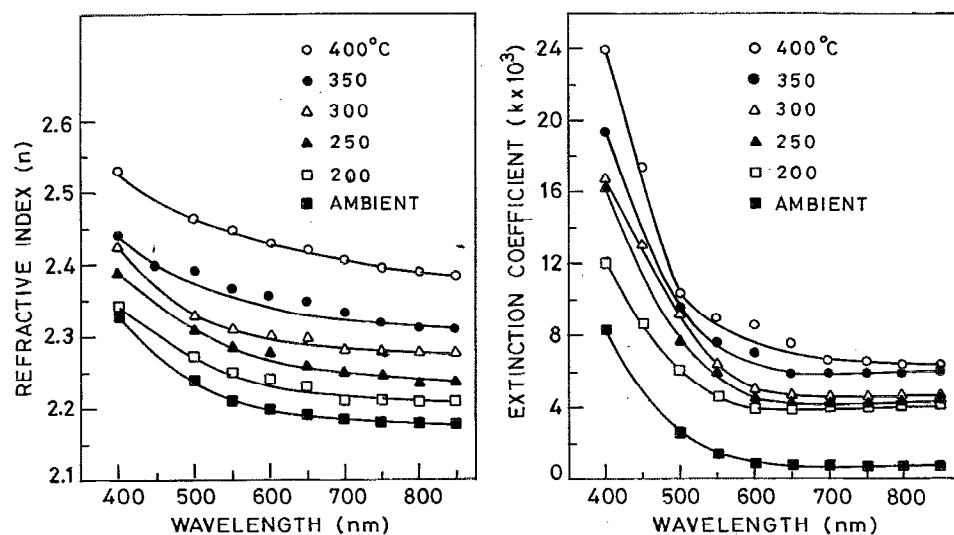


FIG. 7. Variation of refractive index and extinction coefficient as a function of wavelength for titania films at different substrate temperatures.

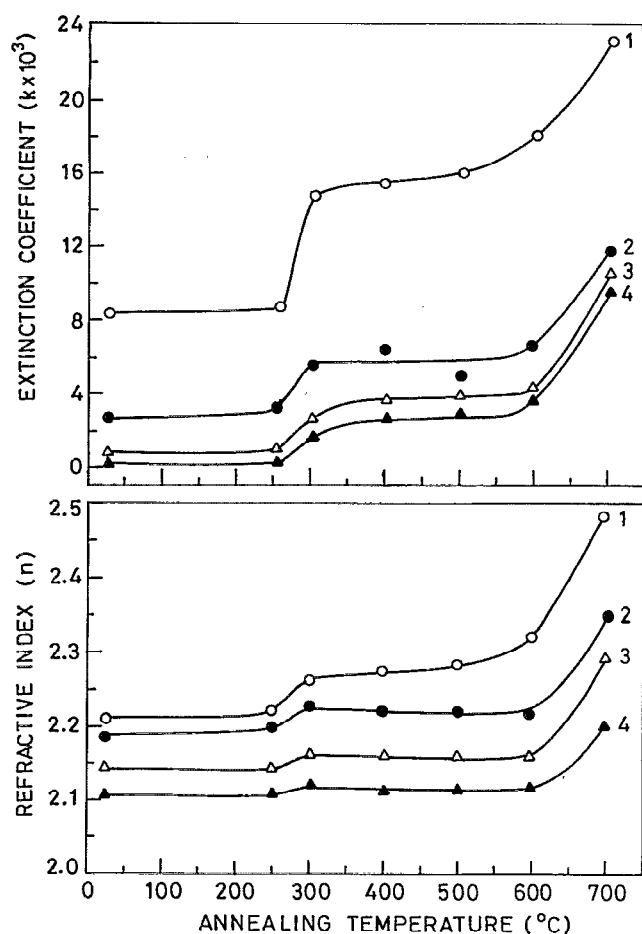


FIG. 9. Variation of refractive index and extinction coefficient of titania films as a function of annealing temperatures at different wavelength: (1) 400 nm, (2) 550 nm, (3) 650 nm, (4) 850 nm.

optical constants remain almost constant up to a temperature of around 250 °C, then show a sharp transition to a higher value at 300 °C and remain constant on further heating. It again shows a drastic rise beyond 600 °C. Significantly as shown by the x-ray diffraction studies, these temperatures also correspond to temperatures at which the crystalline transitions occur. The amorphous to crystalline transition temperature of 300 °C corresponds to the first increase in n and k and the mixed structure of anatase and rutile phases represent the curve between 300 and 600 °C. The sharp rise in the value of n and k at 600 °C is manifested in the dominance of anatase phase at higher temperatures and loss of oxygen at high temperatures. The sharp rise in the refractive index beyond 600 °C annealing temperature might also be due to reduction of TiO_2 . Rujkorakarn *et al.*³¹ have also observed a similar stepwise increase in refractive index with annealing temperature in ion beam sputtered titania films.

The inhomogeneity in the films has been determined by using the near normal reflectance of the films and the re-

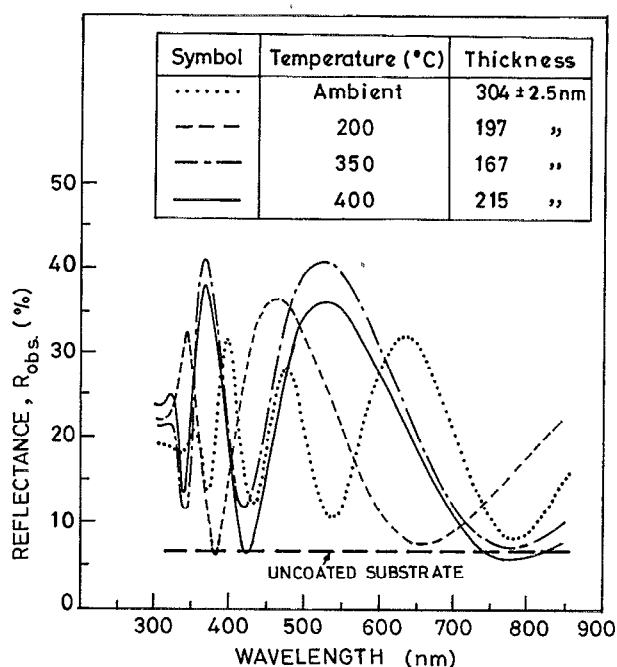


FIG. 10. Reflectance spectra as a function of wavelength for titania films at different substrate temperatures.

flectance from the bare substrate surface. Figure 10 shows the reflectance of the films formed at different temperatures (from 25 to 400 °C). The dashed curve represents the reflectance of the uncoated quartz substrate (R_s). The values of the reflectance of the films (R_f) were computed from the observed reflectance (R_{obs}), using the following expression,³² which takes into account the reflection from the back surface of the substrate

$$R_{obs} = R_f + R_s(1 - R_f)^2 / (1 - R_f R_s). \quad (1)$$

If the films are homogeneous, the minimum reflectance value would correspond to that of the substrate. The fact that it is significantly different indicates that the films are inhomogeneous. The difference ΔR between the reflectance of the film and that of the substrate is used in calculating the variation in refractive index Δn ³³

$$\Delta n = n_{av} \Delta R / 4.4 R_s, \quad (2)$$

where n_{av} is the average index of the film.

Δn will be positive or negative according to the gradation in the film. Negative value indicates that the index decreases from substrate to the top surface of the film and vice versa. The as-deposited films are slightly inhomogeneous with Δn value of 0.103 (at 770 nm) which varied from 0.072 at 200 °C to -0.093 at 400 °C. Similarly in the case of annealed films (Fig. 11) it was 0.066 at 250 °C and -0.134 at 600 °C. Thus we can conclude that the homogeneity was found to be better for (i) films deposited at a substrate temperature of 350 °C and (ii) film at ambient and annealing to 420 °C as shown in Fig. 12.

The changes in the optical constants, inhomogeneity, and crystallinity of the films at higher substrate temperatures could also be due to an increase in the packing den-

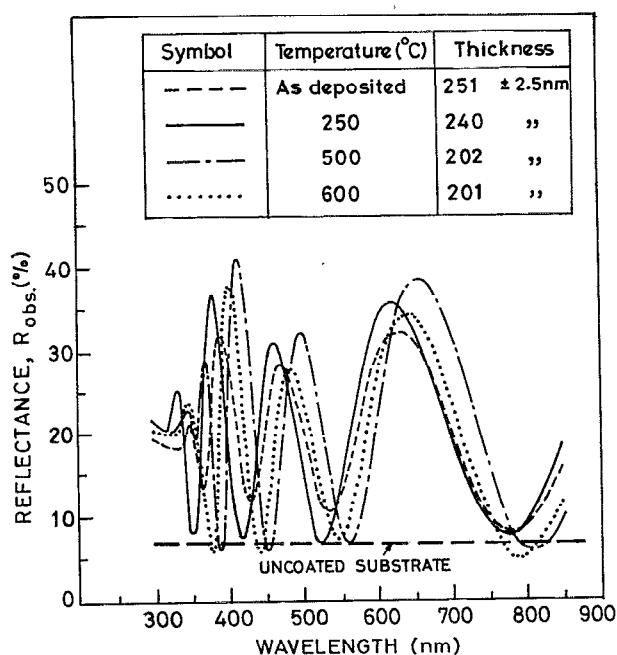


FIG. 11. Reflectance spectra as a function of wavelength for as-deposited and annealed titania films.

sity. The packing density of the films has been calculated using the refractive index data and was found to increase with the substrate temperature. This can be attributed to an increase in the adatom mobility at higher temperatures.

IV. CONCLUSIONS

In this study we established the validity of our earlier model on the reactive sputtering process. The variation in deposition rate is in conformity with the variation in cathode potential. The decrease in deposition rate has been

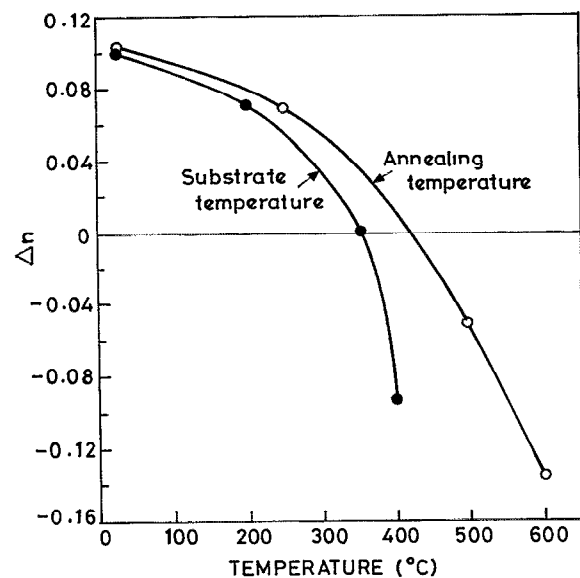


FIG. 12. Variation in refractive index as a function of temperature for titania films.

attributed to the oxidation of the target. TiO_2 films have been deposited at the critical oxygen pressure and their structure and optical properties have been studied. The films deposited at ambient temperature were found to be amorphous. Crystallinity sets in either by depositing the films above 300°C or by post-deposition annealing. The crystalline films were found to have both anatase and rutile phases coexisting up to 600°C above which anatase phase dominated. The refractive index and extinction coefficient of the films showed an increase with an increase in substrate temperature. This was attributed to insufficient oxygen incorporation in the growing film and its crystallinity. In the case of annealed films the refractive index and extinction coefficient also increased with annealing temperature. The films deposited at room temperature were found to be less dense with packing density, whereas those deposited at higher temperature (400°C) showed higher packing density. The as-deposited films were inhomogeneous and the homogeneity increased with substrate heating and post-deposition annealing.

ACKNOWLEDGMENTS

The authors are thankful to their colleagues in the thin-films laboratory, especially Ghanashyam Krishna and Dr. Narasimha Rao for many useful discussions.

- S. Berg, H.-O. Blom, T. Larsson, and C. Nender, *J. Vac. Sci. Technol. A* **5**, 202 (1987).
- T. Larsson, H.-O. Blom, C. Nender, and S. Berg, *J. Vac. Sci. Technol. A* **6**, 1832 (1988).
- W. D. Westwood, *Phys. of Thin Films* **14**, 1 (1989).
- P. I. Docheva, D. N. Popov, and M. P. Koeva, in *Optical Coatings*, edited by Tang Jinfa and Yan Yixun (International Academic, Beijing, 1989), p. 43.
- G. Mohan Rao and S. Mohan, *J. Appl. Phys.* **69**, 6652 (1991).
- W. T. Pawlewicz and R. Busch, *Thin Solid Films* **63**, 251 (1979).
- R. J. G. Clark, *The Chemistry of Titanium and Vanadium* (Elsevier, New York, 1968), p. 266.
- E. Ritter, *J. Vac. Sci. Technol.* **6**, 225 (1966).
- H. K. Pulker, G. Paesold, and E. Ritter, *Appl. Opt.* **15**, 2986 (1976).
- W. Heitman, *Appl. Opt.* **10**, 2414 (1971).
- H. Kuster and J. Ebert, *Thin Solid Films* **70**, 43 (1980).
- W. Grossklaus and R. F. Bunshah, *J. Vac. Sci. Technol.* **12**, 593 (1975).
- K. Narasimha Rao and S. Mohan, *J. Vac. Sci. Technol. A* **8**, 3260 (1990).
- K. Narasimha Rao, M. A. Murthy, and S. Mohan, *Thin Solid Films* **176**, 181 (1989).
- M. Ghanashyam Krishna, K. Narasimha Rao, and S. Mohan, *Mater. Sci. Eng. B* **5**, 427 (1990).
- J. R. Mcneil, G. A. Aljumaily, K. C. Jungling, and A. C. Barron, *Appl. Opt.* **24**, 486 (1985).
- S. Schiller, G. Beister, S. Schneider, and W. Sieber, *Thin Solid Films* **72**, 475 (1980).
- L. D. Hartsough and P. S. Mcleod, *J. Vac. Sci. Technol.* **14**, 123 (1977).
- L. F. Donaghey and K. G. Geraghty, *Thin Solid Films* **38**, 271 (1976).
- S. Schiller, G. Beister, and W. Sieber, *Thin Solid Films* **83**, 239 (1981).
- G. Mohan Rao and S. Mohan, *Vacuum* **40**, 313 (1990).
- J. Heller, *Thin Solid Films* **17**, 163 (1973).
- R. Sawnepoel, *J. Phys. E Sci. Instrum.* **16**, 1214 (1983).
- W. L. Bragg and A. B. Pippard, *Acta. Crystallogr.* **6**, 865 (1953).
- M. Harris, H. A. Macleod, S. Ogura, E. Pelletier, and B. Vidal, *Thin Solid Films* **57**, 173 (1979).

- ²⁶L. I. Maissel, in *Handbook of Thin Film Technology*, edited by L. I. Maissel and R. H. Glang, (McGraw Hill, New York, 1970), Chap. 4.
- ²⁷M. Cantagrel and M. Marchal, *J. Mater. Sci.* **8**, 1711 (1973).
- ²⁸K. Bange, C. R. Ottermann, O. Anderson, and V. Jeschkowski, *Thin Solid Films* **197**, 279 (1991).
- ²⁹L. M. Williams and D. W. Hess, *J. Vac. Sci. Technol. A* **1**, 1810 (1983).
- ³⁰J. M. Bennett, E. Pelletier, G. Albrand, J. P. Borgono, B. Lazarides, C. K. Carniglia, R. A. Schmell, T. H. Allen, T. Tuttle-Hart, K. H. Guenther, and A. Saxer, *Appl. Opt.* **28**, 3303 (1989).
- ³¹R. Rujkorakarn, L. S. Hsu, and C. Y. She, *Laser Induced Damage in Optical Materials* (NBS, Boulder, CO, 1984), No. 727, p. 253.
- ³²R. Jacobsson, *Arkiv Fys.* **24**, 17 (1963).
- ³³D. P. Arndt, R. M. Azzam, J. M. Bennett, J. P. Borgono, C. K. Carniglia, W. E. Case, J. A. Dobrowolski, U. J. Gibson, T. Tuttle-Hart, F. C. Ho, V. A. Hodgkin, W. R. Klapp, H. A. Macleod, E. Pelletier, M. K. Purvis, D. M. Quinn, D. H. Stome, R. Swenson, P. A. Temple, and T. F. Thoun, *Appl. Opt.* **23**, 3571 (1984).