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Short Communication

Effect of oxygen partial pressure on the optical properties of DC magnetron sputtered TiO_2 films[†]

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Abstract

Titanium oxide (TiO_2) thin films were deposited by DC magnetron sputtering of titanium target at various oxygen partial pressures in the range 1×10^{-4}– 5×10^{-3} mbar and at a constant substrate temperature of 573 K. Good-quality TiO_2 films were obtained at an oxygen partial pressure of 8×10^{-4} mbar.

Keywords: Optical properties, oxygen partial pressure, TiO_2 films, magnetron sputtering.

1. Introduction

Titanium oxide (TiO_2) is a hard material, chemically resistant and transparent in the visible and infrared regions with high refractive index. It is widely applied in thin film form as electrochromic devices, gas sensors, hard coatings and high-index optical coatings. Thin films of TiO_2 were prepared using many deposition techniques such as reactive evaporation,[1] electron beam evaporation,[2] chemical vapour deposition,[3] ion-assisted deposition,[4] DC magnetron sputtering,[5] RF magnetron sputtering[6–9] and sol–gel process.[10] Of all the techniques, DC magnetron sputtering is industrially adaptable. In this technique, metal targets are used and high deposition rates are possible. The composition of the deposited films is easily controllable. In the present investigation, we study the thin films of TiO_2 prepared using DC magnetron sputtering technique and the effect of oxygen partial pressure on the optical properties.

2. Experimental

Thin films of TiO_2 were deposited onto Corning glass substrates using the DC magnetron sputtering technique developed in our laboratory.[11] Pure metallic titanium (99.99%) was used as the sputtering target, and pure oxygen (99.99%) and argon (99.995%) were used as reactive and sputtering gases, respectively. Thin films of TiO_2 were deposited at various oxygen partial pressures in the range 1×10^{-4}–5×10^{-3} mbar, at a constant substrate temperature of 573 K and at a sputtering pressure of 5×10^{-2} mbar. The deposition conditions maintained for the preparation of TiO_2 films are given in Table I. The experimental films were characterized by studying their chemical composition and optical properties.

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Table 1
Deposition parameters for the preparation of TiO_2 films

Deposition technique	:	DC reactive magnetron sputtering
Target	:	99.99% pure metallic titanium (100 mm dia and 3 mm thick)
Substrates	:	Corning glass and silicon wafer
Target–substrate distance	:	65 mm
Ultimate pressure (p_u)	:	2 x 10^{-6} mbar
Sputtering pressure (p_w)	:	5 x 10^{-2} mbar
Oxygen partial pressure (pO_2)	:	1 x 10^{-4}–5 x 10^{-3} mbar
Cathode potential (V)	:	310–410 V
Cathode current (I)	:	300 mA
Substrate temperature (T_s)	:	573 K

3. Results and discussion

Figure 1 shows that the cathode potential increases with increase in cathode current. The variation of cathode potential with variation in oxygen partial pressure on the titanium target shows three distinct regions, i.e. an initial increase, a decrease at a critical oxygen partial pressure and another increase with the oxygen partial pressure (Fig. 1). The initial increase of cathode potential with oxygen partial pressure is due to negative oxygen ion formation, the decrease is due to enhancement of the secondary electron emission from the oxidized titanium target and further increase is due to reduction in the conductivity of the fully oxidized target surface.[12] Similar results were also observed in different sputtering targets like copper[13] and cadmium.[14] The deposition rate of the experimental films is directly influenced by the oxygen partial pressure (Fig. 2) and remains nearly constant around 1.4 nm/min up to an oxygen partial pressure of 6×10^{-4} mbar and gradually decreases to 0.5 nm/min at higher oxygen partial pressures. The decrease in the deposition rate at higher oxygen partial pressures is due to the oxidation of the target and resultant low sputtering yield.[15]

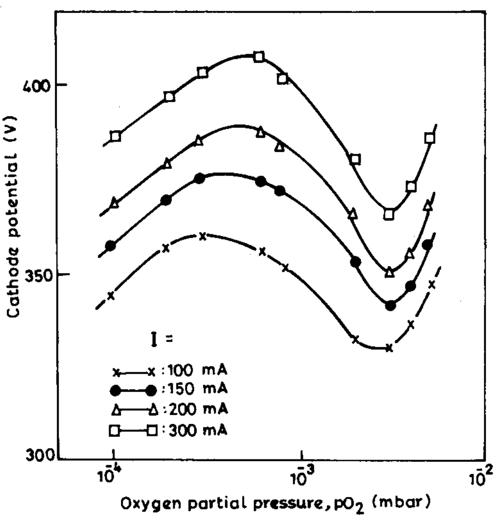

FIG. 1. Variation of cathode potential on titanium target with oxygen partial pressure.

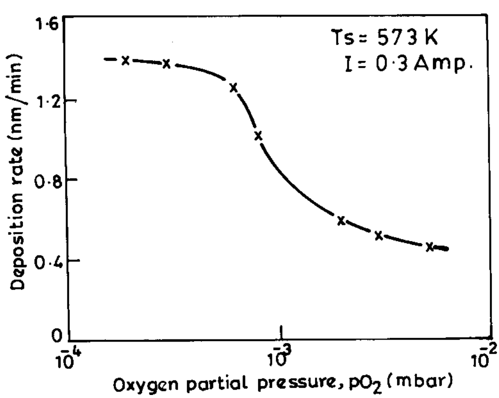

FIG. 2. Dependence of deposition rate of TiO_2 films on the oxygen partial pressure.

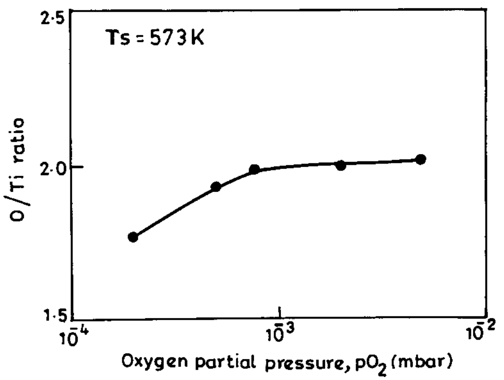

FIG. 3. Dependence of O/Ti ratio on oxygen partial pressure.

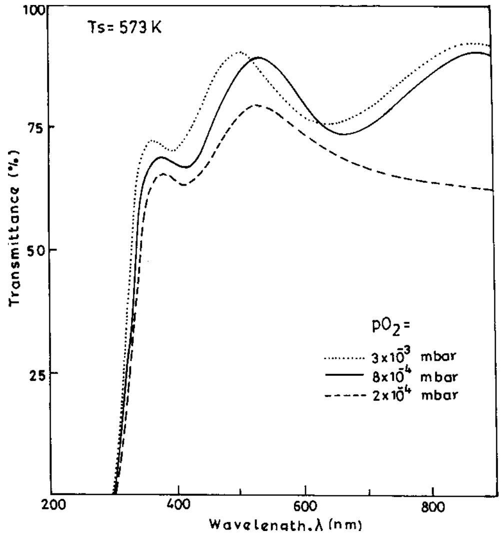

FIG. 4. Optical transmittance spectra of TiO_2 films formed at various oxygen partial pressures.

Chemical compositional analysis of experimental films formed on silicon wafers was carried out under various oxygen partial pressures during deposition using energy-dispersive analysis of X-rays (EDAX) attached to a scanning electron microscope. Figure 3 shows that the O/Ti ratio increases with oxygen partial pressure. At lower oxygen partial pressures, the compound formation is limited by the arrival rate and utilization of oxygen and thus a metal-rich film is formed. When the oxygen pressure is increased, the arrival rate of oxygen increases and the film becomes less metallic. This trend continues until the film is saturated with oxygen. The compositional analysis revealed that the films formed at an oxygen partial pressure of 8×10^{-4} mbar are stoichiometric. Such a variation of chemical composition of the films formed at different oxygen partial pressures was also observed in DC magnetron sputtered films[8] where compositional analysis was performed by X-ray photoelectron spectroscopy.

The optical transmittance and reflectance of the films were recorded as function of photon energy in the wavelength range 200–900 nm using Hitachi UV VIS NIR double-beam spectrophotometer. The optical transmittance spectra of the TiO_2 films formed at various oxygen partial pressures (Fig. 4) show that transmittance is high in the visible region and increases with increase in oxygen partial pressure. The low transmittance at low oxygen partial pressures ($<8\times10^{-4}$ mbar) is due nonstoichiometirc titanium oxide since O/Ti ratio is less than 2.0 as revealed by the EDAX analysis. It is observed that the optical transmittance in the wavelength range 500–900 nm increases from 66% to 86% with increasing oxygen partial pressure. When the oxygen partial pressure is increased, the stoichiometry of the films increases and defect centres decrease. The light loss by the scattering of defect centres decreased which results in an increase of optical transmittance.[14]

The optical absorption coefficient (α) was evaluated from the optical transmittance data where the reflection losses were taken into consideration. The optical bandgap was evaluated from the

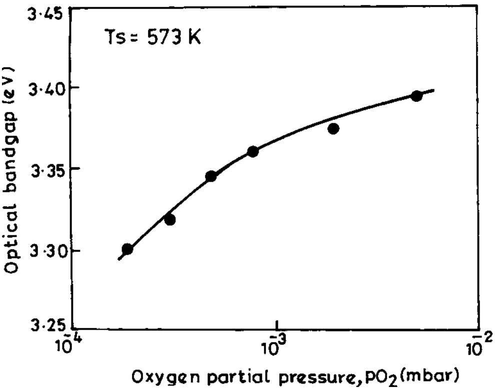

FIG. 5. Dependence of optical bandgap on the oxygen partial pressure.

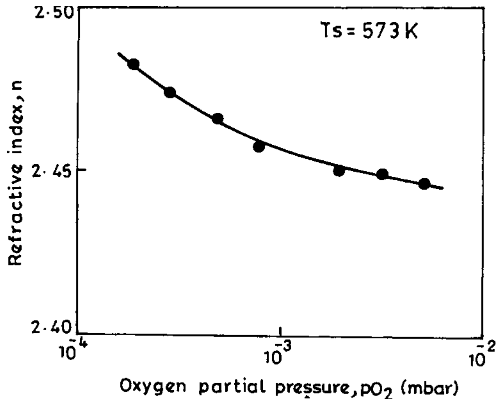

FIG. 6. Variation of refractive index with oxygen partial pressure.

plots of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$). The optical bandgap depends on the oxygen partial pressure (Fig. 5) and increases from 3.32 eV to 3.40 eV with increase in the oxygen partial pressure from 2×10^{-4} mbar to 5×10^{-3} mbar. The observed variation of the optical bandgap is in good agreement with the films deposited by magnetron sputtering,[17] electron beam evaporation[18] and ion-assisted deposition.[19]

The refractive index (n) of the films is evaluated from the transmittance data employing Swanepoel's envelope method[20](Fig. 6). It decreased from 2.48 to 2.44 with increase in oxygen partial pressure from 2×10^{-4} mbar to 5×10^{-3} mbar. The index obtained in the present investigation is in good agreement with the sputtered films reported by Suhail *et al.*[21] and electron beam evaporated films reported by Bannet *et al.*[22]

The extinction coefficient of the films at λ = 500 nm decreased from 8×10^{-3} to 3.5×10^{-3} with increase in oxygen partial pressure from 2×10^{-4} mbar to 5×10^{-3} mbar. The variation of extinction coefficient can be related to the variation of optical transmittance. As the oxygen partial pressure is increased, the transmittance is increased which leads to decrease of the extinction coefficient.

4. Conclusions

In the present investigation, titanium oxide thin films were deposited using DC reactive magnetron sputtering technique. The chemical composition of the films depends on the oxygen partial pressure. Stoichiometric titanium oxide films with O/Ti ratio of 2 were obtained at an oxygen partial pressure of 8×10^{-4}mbar. The optical transmittance of the films increased from 66% to 86% with increase in oxygen partial pressure. The optical bandgap varied from 3.32 eV to 3.40 eV with increase in the oxygen partial pressure from 2×10^{-4} mbar to 5×10^{-3} mbar. The refractive index and extinction coefficient decreased with increase in oxygen partial pressure. Stoichiometric and better optical quality titanium oxide films were obtained at an oxygen partial pressure of 8×10^{-4} mbar.

References

1. MERGEL, D., BUSCHENDORL, D., EGGERT, S., GRAMMES, R. AND SAMSET, B. *Thin Solid Films,* 2000, **371**, 218.

2. LOTTIAUX, M., BOULESTEIX, G. AND NIHOUL, G. — *Thin Solid Films*, 1989, **170**, 107.

3. YEUNG, K. S. AND LAM, Y. W. — *Thin Solid Films*, 1983, **109**, 405.

4. DEMIROUT, H. AND SITES, J. R. — *J. Vac. Sci. Technol. A*, 1984, **2**, 1457.

5. SONODA, T. *et al.* — *Thin Solid Films*, 2001, **386**, 227.

6. SZCZYRBOWSKI, J. *et al.* — *Surf. Coatings Technol.*, 1999, 261.

7. OKIMURA, K., MAEDA, N. AND SHIBATA, A. — *Thin Solid Films*, 1996, **281**–**282**, 427.

8. MENG, L., ANDRITSCHKY, M. AND SCOS SANTOS, M. P. — *Thin Solid Films*, 1993, **223**, 242 and *J. Appl. Surf. Sci.*, 1993, **68**, 319.

9. GAN, J. Y., CHANG, Y. C. AND WEK, T. B. — *Appl. Phys. Lett.*, 1998, **72**, 332.

10. XAGAS, A. P., ANDROULAKI, E., HISKIA, A. AND FALARAS, P. — *Thin Solid Films*, 1999, **357**, 173.

11. SUBRAMANYAM, T. K. — *Studies in this films–Preparation and characterization of DC magnetron sputtered Cdo and Zno films*, Ph. D. Thesis, S. V. University, Tiruapti, India, 1999.

12. MOHAN RAO, G. AND MOHAN, S. — *J. Appl. Phys.*, 1991, **69**, 52.

13. MOHAN RAO, G., PANCHAPAGESAN, T. S. AND MOHAN, S. — *Appl. Phys. A*, 1990, **51**, 423.

14. SUBRAMANYAM, T. K., UTHANNA, S. AND NAIDU, B. S. — *Mater. Lett.*, 1998, **25**, 214.

15. GURUMURAGAN, K., MANGALARAJ, D., NARAYANADAS, SA. K. AND BALASUBRAMANYAM, C. — *Phys. Stat. Sol.(a)*, 1994, **143**, 85.

16. RAVI KUMAR, A. B. — *Studies in solid state physics–Influence of oxygen partial pressure on the optical properties of* Tio_2 *films,* M. Phil. Dissertation, S. V. University, Tirupati, India, 1998.

17. MENG, L. J. AND SCOS SANTOS, M. P. — *Thin Solid Films*, 1994, **250**, 26.

18. GOFUKU, E., TOYODA, Y., UEHARA, Y., KOHARA, M. AND MUNOSHITA, M. — *Appl. Surf. Sci.*, 1991, **48**–**49**, 343.

19. KRISHNA, M. G., RAO, K. M. AND MOHAN, S. — *J. Appl. Phys.*, 1993, **73**, 434.

20. SWANEPOEL, R. — *J. Phys. E*, 1983, **16**, 1214.

21. SUHAIL, M. H., MOHAN RAO, G. AND MOHAN, S. — *J. Appl. Phys.*, 1991, **7**, 1421.

22. BANNET, J. M., PELLETIER, E. AND SAXER, A. — *Appl. Opt.*, 1989, **28**, 3303.