

Chemical composition of electron-beam evaporated TiO₂ films

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Chemical composition and optical properties of TiO₂ films depend on deposition conditions. A detailed investigation has been made on the influence of deposition parameters, such as starting material, substrate temperature, and post deposition heating in air on the chemical composition of TiO₂ films deposited by electron-beam evaporation of Ti and TiO₂ in neutral and ionized oxygen. The chemical composition of the films has been analyzed by x-ray photoelectron spectroscopy and Auger electron spectroscopy. The composition of TiO₂ films deposited in neutral oxygen were found to contain lower oxides of titanium in addition to TiO₂, whereas films prepared in ionized oxygen were found to be stoichiometric TiO₂.

1. INTRODUCTION

Titanium dioxide has many unusual properties which make it suitable for a variety of applications. Its excellent optical transmittance, high refractive index, and durability are attractive features for optical coating applications. Optical losses, structural and chemical composition of the films depend upon preparation conditions. TiO₂ films are produced usually by evaporation and various forms of sputtering. Ion beam deposition techniques have improved the film properties such as packing density, structure, and stoichiometry. Extensive studies have been made relating the optical properties of TiO₂ films with structure and preparation condition.¹⁻⁸ But very little data exist on chemical composition of the TiO₂ films as a function of preparation conditions.

Recently, we have reported the influence of preparation conditions on the optical properties of TiO₂ film.⁹ It was observed that the oxidation was not complete when neutral oxygen was used. Low loss and durable films have been obtained by using ionized oxygen. In this study, we report on the preparation of TiO₂ films by electron-beam (e-beam) evaporation of Ti and TiO₂ in neutral and ionized oxygen atmosphere and the influence of deposition parameters such as substrate temperature and postdeposition heating in air on the chemical composition of the films using Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS).

II. EXPERIMENTAL TECHNIQUE

Titanium dioxide films were deposited by reactive electron beam evaporation in a conventional deposition plant (Edwards High Vacuum Ltd., U. K. model 19E4). The vacuum obtained was 5×10^{-6} Torr. The starting materials Ti and TiO₂ (Balzers, 99.8% purity), were evaporated from a 6 kW e-beam gun (Leybold Heraeus, Germany). The rate of deposition was about 100 Å/min and the partial pressure of O₂ (99.99% purity) was 2×10^{-4} Torr. The substrates were maintained at temperatures in

the range of 30–250 °C, during deposition. Films deposited on microscopic glass slides were used for chemical analysis. A Heitmann type discharge source was used to ionize the oxygen to enhance the reactivity between the evaporant and oxygen in order to get stoichiometric films. The schematic of the deposition plant and the other deposition conditions are described elsewhere.¹⁴⁻¹⁶ Films were postheated in air for 4 h at different temperatures (1 W 200 °C).

The x-ray photoelectron spectra of TiO₂ films were recorded using two ESCA systems (Physical Electronic Industries Inc., model Supersam 590-10 as well as V. G. Scientific Ltd., U. K., model ESCA 3 Mark-11). Al Kα x rays were employed in XPS studies with 50 eV pass energy in ESCA3 Mark II spectrometer. The full width at half-maximum (FWHM) of the Au(4f_{7/2}) was 1.35 eV. Binding energies of the core levels reported here are with reference to Au(4f_{7/2}) at 83.8 eV, and they are accurate within 0.2 eV. In most cases there were no shifts due to charging since the surface of the film was grounded. In cases where charging was observed, the binding energies were obtained taking C(1s) peak at 285 eV. In the same instrument electron beam initiated Auger spectra were recorded in the $dN(E)/dE$ mode with 1 V modulation voltage and 50 eV pass energy. The e-beam current was 5 pA. In the XPS study, the films were not etched with argon ion beam in order to avoid reduction of TiO₂ due to ion bombardment. A scanning Auger spectrometer (Phillips, model 541C) was used for depth profile analysis. Depth profiling experiments were carried out with 55 Å/min etching rate. The etching was carried out with 1 kV argon ion beam of 30 pA current.

III. RESULTS AND DISCUSSION

Initially, titanium dioxide films were deposited in neutral oxygen with Ti as the starting material. The Ti(2p) spectrum of the as-deposited film is shown in Fig. 1 [curve (a)]. Ti(2p) spectrum from bulk TiO₂ pellet is also shown [Fig. 1 curve (b)] for comparison. We see that the

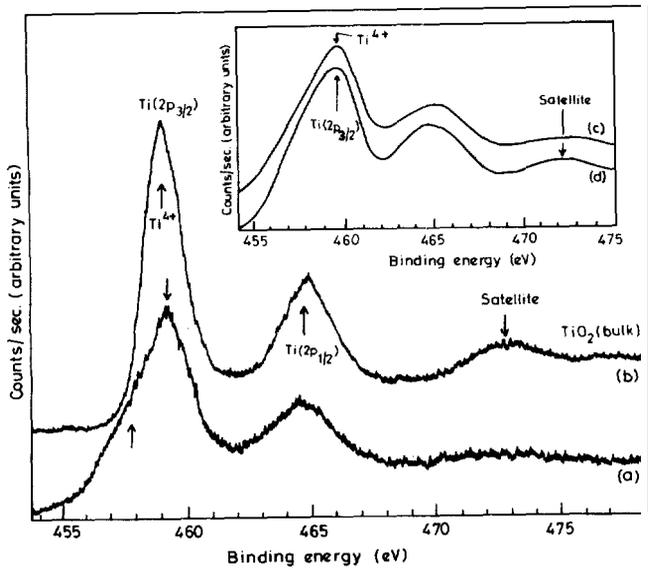


FIG. 1. XPS data Ti(2p) of TiO₂ : (a) asdeposited film in neutral oxygen, (b) bulk TiO₂, Inset for the same film heated in air at (c) 100°C and (d) 200°C.

Ti(2p_{3/2}) peak from the film [curve (a)] is having a distinct shoulder in the lower binding energy region compared to the peak at 459.4 eV due to TiO₂. Further, as-deposited film in neutral oxygen does not show a strong satellite at 14 eV from Ti(2p_{vz}) peak which is the characteristic of TiO₂.¹⁸ Therefore, as-deposited film is likely to have lower valent oxides with Ti in +2 or +3 oxidation states. Quantitative estimation of Ti:O ratio for TiO₂, [curve (b)] from the integrated intensities of Ti(2p_{3/2,1/2}) and O(1s) taking photoionization cross section from Scofield¹⁹ and mean free paths from Penn²⁰ show that it is TiO₂, for TiO₂, bulk sample and that for the as-deposited film is TiO_{1.5}. This also indicates that as-deposited film using TiO₂ as the starting material in neutral oxygen is not a fully oxidized TiO₂. Further proof that lower valent oxides present in the as-deposited film in neutral oxygen is obtained from LMV/LMM Auger intensities. E-beam initiated Auger spectrum shown in Fig. 2 shows that LMV/LMM ratio is 0.61. Under similar experimental conditions, Ti(LMV/LMM) Auger intensity ratio is shown to be 0.65 for TiO and 0.45 for TiO₂.²¹ In this experiment, the ratio is 0.61 indicating again that the films contain lower valent Ti oxides. The film was heated in air at 100 and 200 °C and on reexamination the film showed the characteristic satellite peaks (inset of Fig. 1) indicating the formation of TiO₂.

Figure 3 depicts the XPS spectra of Ti(2p_{vz}) of the TiO₂ films prepared using TiO₂ as starting material at 250 °C in neutral oxygen atmosphere. The deconvoluted spectrum which corresponds to the phases TiO₂ (459.4 eV) and TiO (457.0 eV).²² The films deposited using TiO₂ as the starting material and in the substrate temperature range of 30–250 °C are observed to be amorphous. This film also has shown considerable optical absorption. The refractive index and extinction coefficient of this film were estimated to be 2.45 and 0.004, respectively. The deviation in stoichiometry of the film deposited at higher sub-

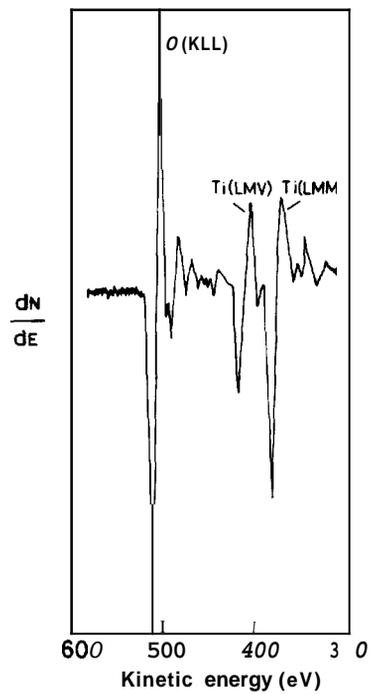


FIG. 2. Auger spectrum of the same TiO₂ film used in Fig. 1.

strate temperature might be due to insufficient incorporation of oxygen in the films at elevated substrate temperatures as the condensation of the oxygen decreases with the increase of temperature which also has been observed by Ritter.²

In order to see if a stoichiometric TiO₂ film can be obtained, the films were deposited in ionized oxygen atmosphere, Figure 4 shows the XPS spectra of as-deposited TiO₂ films prepared in an ionized oxygen medium. Curves (a) and (b) are for the films deposited using TiO₂ as the starting material, whereas curve (c) corresponds to a film deposited using TiO₂ as the starting material. Ti to oxygen ratio from the integrated intensities of Ti(2p_{3/2,1/2}) and O(1s) were found to be TiO_{1.5}, [curve (a)], TiO_{2.05} [curve (b)], and TiO_{1.8}, [curve (c)]. There has been a marked improvement in the stoichiometry of TiO₂ films deposited with TiO₂ as a starting material using ionized oxygen compared to the films formed with neutral oxygen [compare Fig. 4 with curve (a) in Fig. 11]. The lower Ti oxide component is much less in these films as is evident from Ti

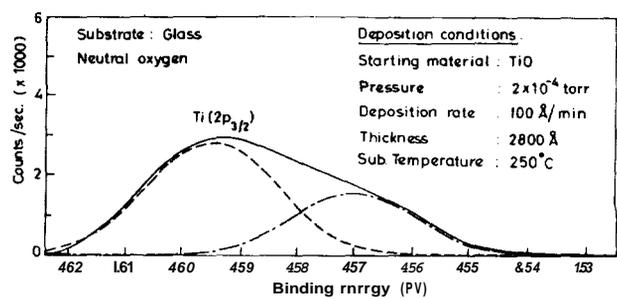


FIG. 3. XPS data Ti(2p) of TiO₂ film deposited at 250 °C in neutral oxygen medium.

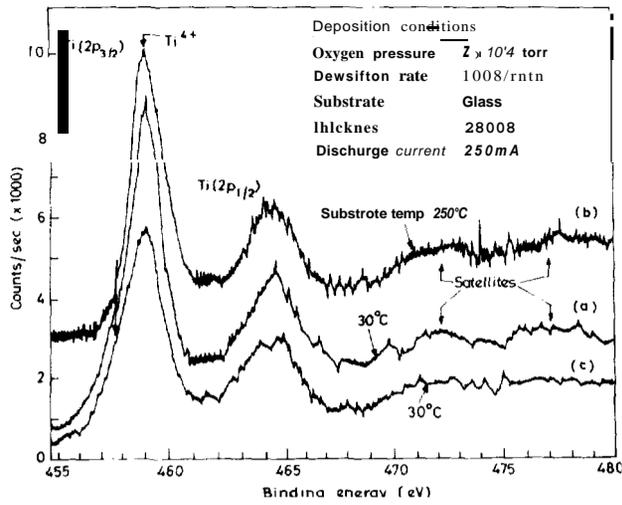


FIG. 4. Ti(2p) XPS of TiO_x films deposited in ionized oxygen with starting materials: TiO at 30 °C [curve (a)], TiO at 250 °C [curve (b)], and TiO₂ at 30 °C [curve (c)].

(2p) peaks as well as appearance of satellite peaks. The films deposited in ionized oxygen medium with substrate temperature at 250 °C showed stoichiometric TiO₂ [curve (b)]. Further, the satellite clearly seen in Fig. 4, curve (b) is an indication of TiO₂ formation. The improved stoichiometry of oxide films deposited in ionized oxygen medium is suggestive of the enhanced reactivity between the evaporant and ionized oxygen. Incidentally, only the films deposited at 225 and 250 °C and in ionized oxygen medium showed crystallinity as evidenced from x-ray diffraction shown in Fig. 5.

In order to see the composition as a function of thickness, depth profile experiments were carried out. Figure 6 shows the Auger depth profile of a typical TiO₂ film deposited in neutral oxygen at ambient temperature. From

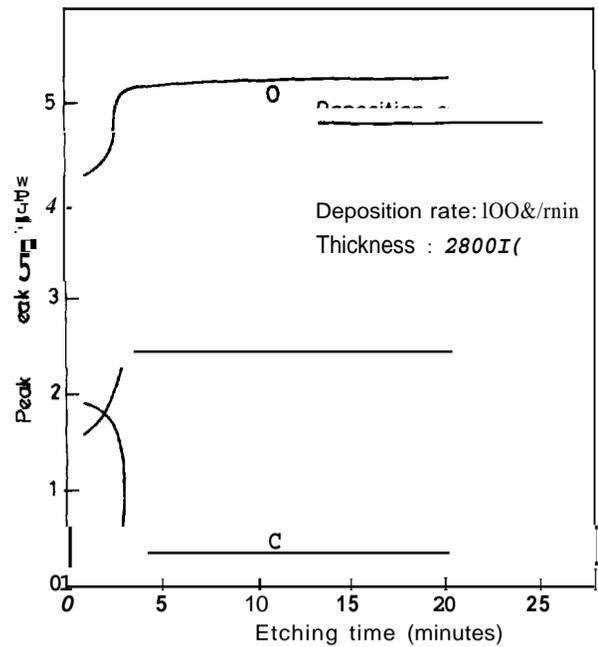


FIG. 6. Auger depth profile of TiO₂ film deposited at 30 °C

the depth profile, it can be seen that the films are homogeneous.

IV. CONCLUSIONS

Titanium oxide films deposited by conventional reactive evaporation were found to be less stoichiometric. It has been demonstrated that stoichiometric TiO₂ films can be grown by evaporating TiO in ionized oxygen medium and maintaining the substrate temperature at 250 °C. TiO was found to be a better starting material compared to TiO₂ when ionized oxygen was used.

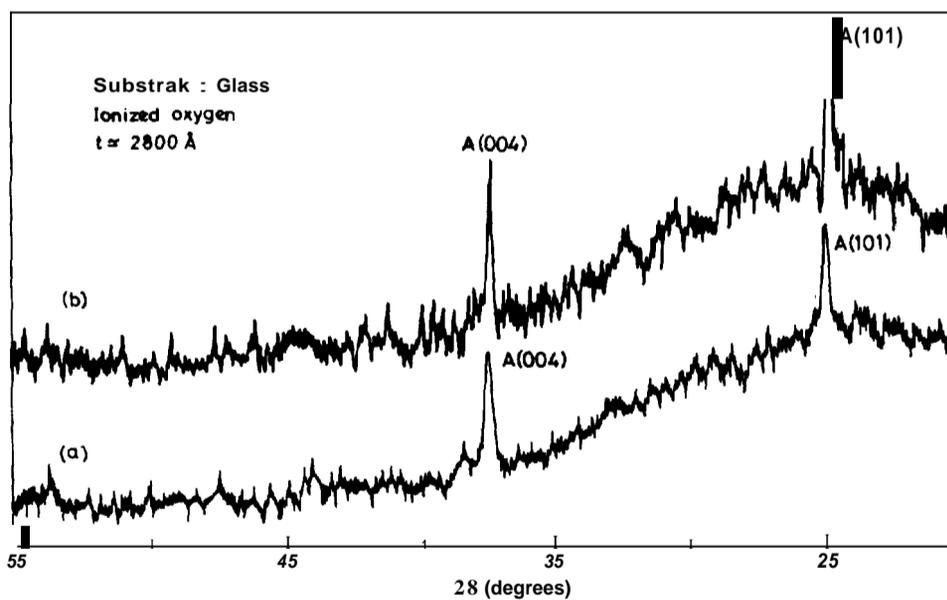


FIG. 5. Cu K α x-ray diffraction patterns of TiO₂ films deposited onto glass in ionized oxygen medium at (a) 225 °C and (b) 250 °C.

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M. A. Auwarter, **US Patent No. 2920 002 (1960).**

E. Ritter, *J. Vac. Sci. Technol.* **3**, 225 (1966).

B. Dundenhausen and G. Mollensledt, *Z. Angew. Phys.* **27**, 191 (1969).

W. Heitmann, *Appl. Opt.* **10**, 2414 (1971).

K. N. Rao, T. Radha, and M. R. Rao, *J. Ind. Inst. Sci.* **58**, 315 (1976).

H. K. Pulker, G. Paesold, and E. Ritter, *Appl. Opt.* **15**, 2986 (1976).

H. Kuster and J. Ebert, *Thin Solid Films* **70**, 43 (1980).

H. Allen, *Proc. Soc. Photo-Opti. Instrum. Eng. Opt. Thin Films* **3U**, 93 (1982).

P. J. Martin, H. A. Macleod, R. P. Netterfield, C. G. P a y , and W. G. Sainty, *Appl. Opt.* **22**, 178 (1983).

Demiryont and J. R. Sites, *J. Vac. Sci. Technol. A* **2**, 1457 (1984).

J. R. McNeil, G. A. Al-Jumaily, K. C. Jungling, and A. C. Barron, *Appl. Opt.* **24**, 486 (1985).

H. K. Pulker, M. Buhleri, and R. Hora, *Proc. Soc. Photo-Opti. Instrum. Eng. Opt. Thin Films 11—New Developments* **678**, 110 (1986).

R. P. Howson, K. Sujuki, C. A. Bishop, and M. I. Ridque, *Vacuum* **34**, 291 (1984).

K. N. Rao, M. A. Murthy, and S. Mohan, *Thin Solid Films* **176**, 181 (1989).

G. Krishna, K. N. Rao, and S. Mohan, *Mater. Sci. Eng. B* **5**, 427 (1990).

K. N. Rao and S. Mohan, *J. Vac. Sci. Technol. A* **8**, 3260 (1990).

K. N. Rao, Ph.D. thesis, Indian Institute of Science, Bangalore, India, 1988 (unpublished).

S. Hegde, *Bull. Mater. Sci.* **2**, 271 (1980).

H. Scofield, *J. Electron. Spectrosc. Relat. Phenom.* **8**, 129 (1976).

R. Penn, *J. Electron Spectrosc. Relat. Phenom.* **9**, 29 (1976).

C. N. R. Rao, D. D. Sarma, and M. S. Hegde, *Proc. R. Soc. London Ser. A* **370**, 369 (1980).

C. N. R. Rao, D. D. Sarma, S. V. Vasudevan, and M. S. Hegde, *Proc. R. Soc. London Ser. A* **367**, 239 (1979).