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DIELECTRIC PROPERTIES OF SPUTTERED TiO_2 FILMS

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TiO_2 films 0.27–2.8 μm thick were prepared by r.f. sputtering in an atmosphere of argon and their dielectric properties were studied. The source materials were anatase- and rutile-type TiO_2 powders. The dielectric constant and the dielectric losses of the TiO_2 films were measured at room temperature in the frequency range 30 Hz–1 MHz. There is no noticeable difference in the dielectric properties of TiO_2 films prepared from anatase and from rutile powders. The thickness dependence of the dielectric constant at 1 kHz shows a rapid rise at a thickness of about 1 μm and attains a saturation value of about 100 at larger thicknesses. This rise in dielectric constant at a thickness of about 1 μm corresponds to the appearance of X-ray diffraction lines. The dielectric losses of the films are relatively high. The electrical resistivity of the films was found to be lower than the bulk value. This is attributed to reduction of the TiO_2 during the sputter deposition in argon.

1. INTRODUCTION

In recent years the electrical properties of TiO_2 have been extensively studied. Reviews of these studies are given by Grant[1], Frederikse[2], Seitz *et al.*[3] and Jarzebski[4]. TiO_2 exists in three crystalline modifications: rutile, brookite and anatase. Many studies have been made on the conduction mechanism[5–11], photoelectronic properties[12–16] and dielectric properties[17,18] of rutile single crystals.

TiO_2 is attractive as a dielectric material in integrated electronic applications because it has a high dielectric constant. It has been reported that the dielectric constants of rutile[12] are 80 and 160 perpendicular and parallel respectively to the *c* axis and that the dielectric constant of anatase[19] is 36. Currently, several techniques are being utilized to develop thin film capacitors suitable for the microminiaturization of electronic circuits. Thin films of TiO_2 can be prepared by various methods such as vapor deposition[20,21], oxidation of the metal in air[22–25], vacuum evaporation[26], anodic oxidation[27–32] and sputtering[33–36]. Feuersanger[20] has prepared TiO_2 films by the vapor reaction of titanium tetrachloride or tetraisopropyl titanate with water vapor. His films have dielectric constants of over 80. Films of TiO_2 prepared by oxidation of the metal in air[23] have dielectric constants

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of about 60–110. Anodized dielectric films of TiO_2 have a relatively small dielectric constant (about 40)[27].

In contrast, relatively little work has been reported in the literature on the sputter deposition of TiO_2 because the deposition rate of this material is very small. Prokhorov *et al.*[37] prepared capacitors by the reactive sputtering of titanium and studied their dielectric properties such as capacitance, tan δ and breakdown voltage. Deb[34] reported the photoconductivity and photoluminescence in r.f. sputtered thin films of TiO_2.

We have studied the sputter deposition of TiO_2 in an attempt to obtain films with a high dielectric constant. Our results on the behavior of the dielectric constant of TiO_2 films at different frequencies and thicknesses are presented in this paper.

First, the experimental procedures for the preparation of the TiO_2 films and for the electrical measurements are described. Experimental results of the dielectric properties of the films are then given. Finally we discuss briefly the relation between the dielectric constant and the thickness of the sputtered films.

2. EXPERIMENTAL

2.1. Preparation of thin TiO_2 films

All the films investigated were prepared from TiO_2 powders by r.f. sputtering in an atmosphere of argon using a conventional diode-type r.f. sputtering system. Two kinds of TiO_2 powders, anatase and rutile, were used as target materials. The anatase powder was of first grade (98.5%, Wako Pure Chemical Industries Ltd.). The rutile powder was of a special grade (99.0%, Koso Chemical Co. Ltd.). The mean particle sizes of these powders were about 19 μm for the anatase type and 13 μm for the rutile type. The TiO_2 powder was packed into a quartz vessel to form the target. Brass strips 40 mm × 25 mm × 1 mm were employed as the substrates. All substrates were mechanically polished and cleaned before being placed in the vacuum chamber. The substrate holder was positioned 16 mm from the target and was water cooled. A copper–constantan thermocouple was used to measure the substrate temperature. The sputtering was carried out in an atmosphere of argon at a pressure of 2.0×10^{-1} Torr and a typical sputtering power density of 7 W cm^{-2} at a frequency of 13.56 MHz. The chamber was pumped to a pressure of 5×10^{-6} Torr before the sputtering gas was admitted. There was no noticeable dependence of the deposition rate (about 17 Å min^{-1}) on the rutile or anatase target materials. The substrates were not heated before deposition but reached about 200 °C after a few minutes. A presputtering period of 30 min was allowed before deposition. The thickness of the sputtered films was determined by the interference method. Under these conditions TiO_2 films with thicknesses in the range 0.27–2.8 μm were prepared. Generally, excellent adherence of the TiO_2 films was found.

The crystallinity of the sputtered films was examined with nickel-filtered copper radiation using a Shimazu VII diffractometer unit.

2.2. Electrical measurements

To study the dielectric properties of the sputtered films a test capacitor was fabricated by evaporating an aluminum electrode (with an area of about 3.5×10^{-3} cm^2) onto the TiO_2 layer on the brass substrate. The aluminum layer was contacted with a spring-loaded probe; silver conducting paint was used to complete the external contact to the brass strip substrate.

The measurements of the capacitance and dielectric loss from 30 Hz to 1 MHz were carried out with an Ando Electric TR-1C capacitance bridge. The electrical resistance of the sputtered films was measured with a Takedariken TR-8651 electrometer. All measurements were made in air at 20 °C.

The dielectric constant and resistivity of the sputtered films were calculated from the capacitance, resistance and geometrical dimensions of the structure (film thickness and electrode area).

3. RESULTS

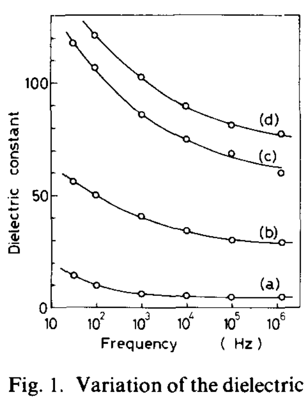
3.1. Structural properties

Anatase and rutile TiO_2 powders were both used as sputtering target materials. In both cases, however, the as-sputtered films with thicknesses less than about 1 μm did not show any X-ray diffraction peaks; these films therefore appear to be amorphous. This is consistent with the results obtained by Deb[34]. In contrast, as-sputtered films with thicknesses of about 1 μm or more showed faint diffraction peaks of both the anatase and the rutile phase, regardless of the target material. The diffraction lines became stronger with increasing thickness, indicating an enhancement of the crystallinity of the films with increasing film thickness. Generally, the diffraction lines for films grown from the rutile target were stronger than those for films grown from the anatase target.

The sputtered films were hard and adhered well to the substrates.

3.2. Dielectric constant, dielectric loss and electrical resistivity

Figures 1 and 2 show the frequency dependence of the dielectric constant of sputtered films of varying thickness prepared from anatase and rutile powders. The dielectric constants of all specimens decreased gradually with increasing frequency. A distinct dispersion region was not observed.



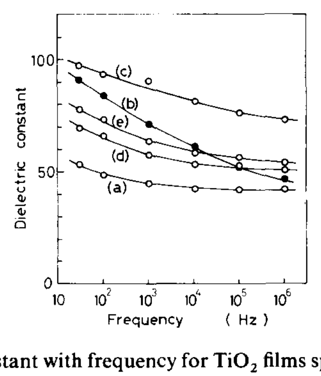
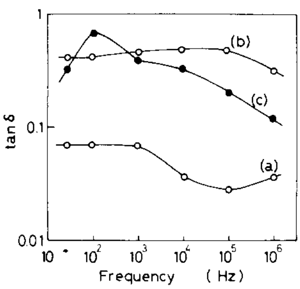


Fig. 1. Variation of the dielectric constant with frequency for TiO_2 films sputter deposited from anatase powder: (a) 0.41 μm; (b) 0.66 μm; (c) 0.82 μm; (d) 2.8 μm.

Fig. 2. Variation of the dielectric constant with frequency for TiO_2 films sputter deposited from rutile powder: (a) 0.54 μm; (b) 0.95 μm; (c) 1.6 μm; (d) 2.7 μm; (e) 2.8 μm.

The results of the dielectric loss measurements as a function of frequency are shown in Figs. 3 and 4 for the sputtered films prepared from anatase and rutile powders respectively. The dielectric loss of the sputtered films is relatively high. It was confirmed in our experiments that the dielectric losses of films sputter deposited in air were about one order of magnitude lower than those of films sputter deposited in argon. Therefore the high dielectric losses of the films prepared in argon may be attributed to the loss of oxygen during the sputter deposition of the TiO_2 films in argon.



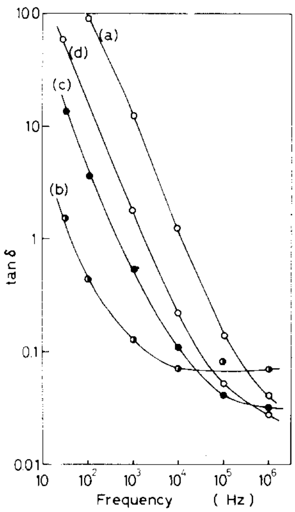


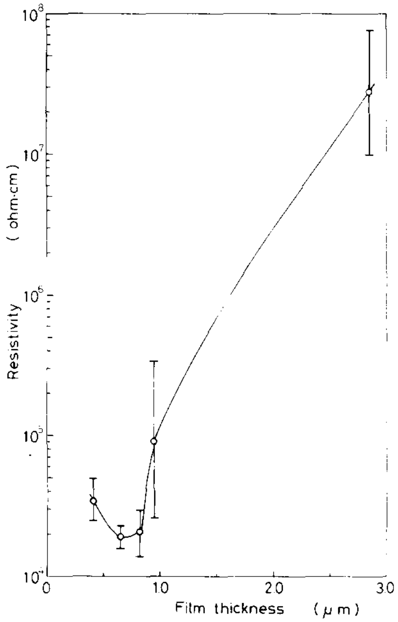
Fig. 3. Variation of the dielectric loss tan δ with frequency for TiO_2 films sputter deposited from anatase powder: (a) 0.41 μm; (b) 0.95 μm; (c) 2.8 μm.

Fig. 4. Variation of the dielectric loss tan δ with frequency for TiO_2 films sputter deposited from rutile powder: (a) 0.54 μm; (b) 0.95 μm; (c) 1.6 μm; (d) 2.8 μm.

Figures 5 and 6 show the electrical resistivities of the sputtered TiO_2 films as a function of film thickness. Generally, the resistivity of sputtered films at 20 °C increases with increasing film thickness. These values are much lower than the bulk value (about 10^{12} Ω cm for single-crystal rutile). This difference may be due to some degree of reduction of TiO_2 during the sputter deposition of TiO_2 films in argon[3,8]. It is well known that the reduction of TiO_2 results in greatly increased conductivity[5]. This interpretation of the behavior of our films is supported by our results on films sputter deposited in air; such films had resistivities that were about two orders of magnitude higher than those of the films sputter deposited in argon.

4. DISCUSSION

We give a brief discussion on the dielectric constant of the sputtered TiO_2 films relative to the film thickness. The dielectric constants at 1 kHz in Figs. 1 and 2 are plotted as a function of film thickness in Figs. 7 and 8. The variation of dielectric constant with thickness shows a sharp rise at about 1 μm and a nearly constant value



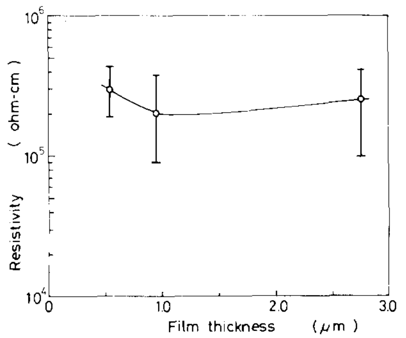
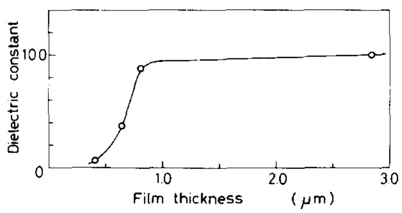


Fig. 5. Variation of the resistivity with film thickness for TiO_2 films sputter deposited from anatase powder.

Fig. 6. Variation of the resistivity with film thickness for TiO_2 films sputter deposited from rutile powder.



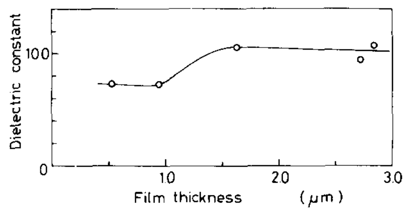


Fig. 7. Dielectric constant at 1 kHz *vs.* film thickness for TiO_2 films sputter deposited from anatase powder.

Fig. 8. Dielectric constant at 1 kHz *vs.* film thickness for TiO_2 films sputter deposited from rutile powder.

beyond 1 μm for films sputter deposited from both anatase and rutile powders. The rise in dielectric constant at this thickness corresponds to the appearance of X-ray diffraction lines. The lower values of the dielectric constant at lower thickness may be attributable to an amorphous structure at lower thickness. The saturation values of the dielectric constant are approximately 100 for both films. This value is comparable with the reported values for a rutile crystal.

5. CONCLUSION

Thin TiO_2 films were prepared by r.f. sputtering from rutile and anatase powders. As-sputtered films with thicknesses less than about 1 μm did not show any

X-ray diffraction peaks. In contrast, as-sputtered films with thicknesses of about 1 μm or more showed faint diffraction peaks of both the anatase and the rutile phase. These films have dielectric constants of about 100 when the film thickness exceeds about 1 μm. However, the dielectric losses are relatively high. The electrical resistivity of the films varies from about 10^4 to about 10^7 Ω cm depending on film thickness.

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