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Characterization of evaporated tellurium oxide films

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The evaporation of tellurium dioxide was carried out by resistive heating and electron-beam evaporation, and the resulting films were subsequently characterized using X-ray diffraction, infrared absorption spectroscopy and electron diffraction techniques. The infrared results of these films showed a marked deviation from the initial stoichiometry, indicating decomposition of the compound. From X-ray and electron diffraction data, it was found that the films had Te_2O_5 stoichiometry. Electron-beam evaporated films showed single crystal growth on a sodium chloride substrate, while those films obtained by resistive heating were wholly amorphous. Furthermore, when fabricated into capacitors, these films showed high capacitance and high dielectric strength (4.6×10^6 V cm^{-1}) suitable for passive devices.

1. Introduction

Thin insulating films are at present used for surface passivation and diffusion masking during the fabrication processes of planar devices. In general, these films can be obtained by various techniques, and at times the resulting films differ from their initial stoichiometry. Furthermore, it has been observed that evaporation of many oxides and fluorides leads to decomposition. Thus it becomes necessary to characterize the films obtained.

In the present study, tellurium dioxide was evaporated using electron-beam evaporation and resistive heating. The resulting films were subsequently characterized for structural differences and stoichiometry, and their possible application in the fabrication of passive devices such as capacitors is reported here. Some of the studies reported on tellurium dioxide films in recent years are of dielectric properties [1] and electrical conduction [2] through these films. However, none of the studies on the characterization of these films has been reported so far. The techniques used for evaluating the above parameters included the use of X-ray diffraction, infrared absorption spectroscopy and electron diffraction.

2. Experimental details

Tellurium dioxide compound of high purity (99.9%) was evaporated to obtain films by resistive heating and electron-beam evaporation using a Varian e-gun (model 922-0220) from a tantalum boat. A pressure of 3×10^{-5} torr was maintained using a liquid nitrogen trap for all depositions. Films 100 nm thick were deposited on compressed KBr and NaCl pellets. The thickness of these films was measured by a capacitance method using an RCL bridge at 1 kHz. Films deposited on KBr pellets were used for infrared (IR) measurements using a Beckman 4250 double-beam spectrophotometer. In all cases a bare KBr pellet from the same material was placed in the reference beam in order to eliminate the effect, if any, of KBr. Films deposited on NaCl pellets were floated on water, so that on dissolving, the NaCl leaves the film free and floating, which is then collected on a copper grid, dried and transferred for electron diffraction under a Philips transmission electron microscope (model EM 300) operated at an energy of 80 kV.

For X-ray diffraction, films 250 nm thick were deposited on a carefully cleaned glass substrate. A Philips X-ray diffractometer model (PW-1051) and Cu$K\alpha$ ($\lambda = 0.154\,19$ nm) radiation were used and

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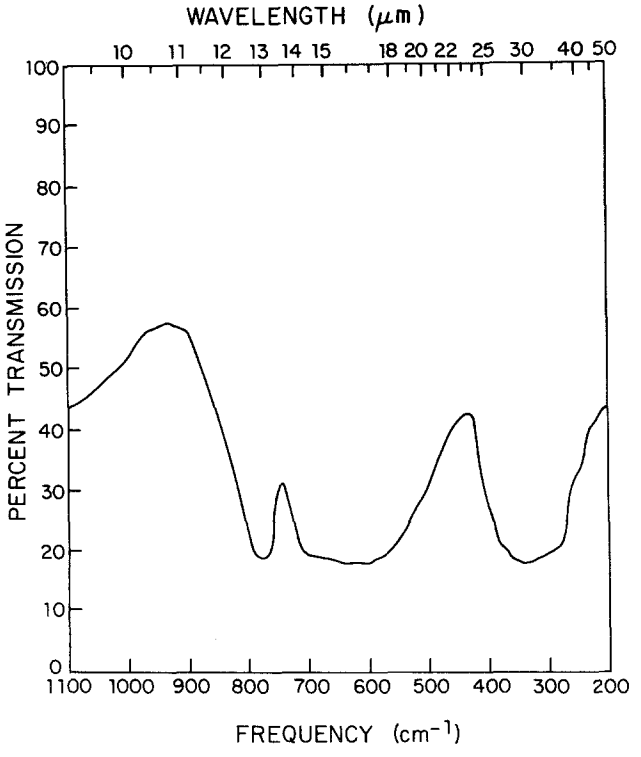

Figure 1 Infrared transmission spectrum of bulk TeO_2.

the scanning range of 2θ was restricted to the range 15° to 45° as no detectable peaks were observed beyond these values.

3. Results and discussion

To characterize the films obtained, it was necessary to obtain an IR spectrum of the TeO_2 bulk sample dispersed in KBr; this is shown in Fig. 1. Strong absorption bands were observed in the frequency range 1000 to 200 cm^{-1}. This spectrum was compared with that reported by Nyquist and Kagel [3] and was found to be identical.

To evaluate for any change in stoichiometry, a series of IR spectra was recorded, while maintaining all the deposition parameters constant. The IR spectra of films obtained by resistive heating and electron-beam evaporation are shown in Fig. 2. A decrease in the absorption level, and shift in the absorption maxima are observed. The spectrum (in Fig. 2) when compared with the bulk spectrum (Fig. 1) indicates a vast change in the position of the absorption band, which clearly indicates a change from the initial stoichiometry. This means that the films resulting from these techniques are no longer tellurium dioxide, but may be Te_xO_y. Several workers [4–6] have investigated the spectra of oxides with various intent and have observed a broad absorption band for many inorganic oxides in these frequencies.

The absorption maximum for the films obtained by electron-beam evaporation is centred at 600 cm^{-1}, with a shoulder at 720 cm^{-1}. For films obtained by resistive heating, the absorption maximum is found to be at 590 cm^{-1} indicating a shift, with a shoulder at 720 cm^{-1}. On comparing this with Fig. 1, it appears that the peak at 770 cm^{-1} (Fig. 1) now appears as a shoulder at 720 cm^{-1} in Fig. 2, whereas the band below 340 cm^{-1} in Fig. 1 just appears as a shoulder, with very weak absorption in Fig. 2, thus indicating a change from its initial stoichiometry.

The IR studies of the oxide films reveal that the mode of deposition, substrate temperature, and hence the stoichiometry of the film, greatly influence the IR absorption band. Pliskin and Lehman [7] have reported IR results on silicon oxide films. The shift towards the lower frequency is caused by the porosity and the strain in the stretching bonds. Films with greater porosity and bond strains will show an even greater shift to lower frequencies. Moreover, the increase in film density will show a shift of the band to a higher frequency together with a sharpening of the band and a decrease in its half width. Thus a decrease in

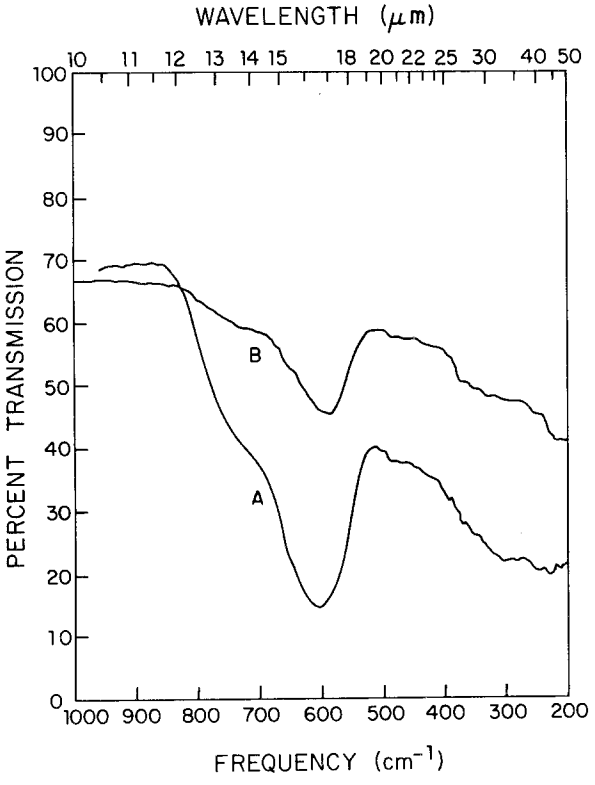

Figure 2 Infrared transmission spectra of films obtained by electron beam evaporation (curve A); resistive heating (curve B).

absorption level and a shift towards lower frequency for films prepared by thermal evaporation is an indication of greater bond strain, porosity and decrease in film density. Similar results have also been reported by other workers [8–10] for different films.

To characterize the films obtained, a series of X-ray diffraction patterns was obtained for films obtained by electron-beam evaporation, as these films exhibited single crystal growth. A reproducible X-ray diffraction pattern was obtained, and a typical X-ray diffractometer trace is shown in Fig. 3; the results obtained are summarized in Table I.

The calculated d values were compared with the ASTM diffraction data for TeO_2, Te_2O_5 and TeO_3 compounds [11]. It was found that the strongest reflection corresponded to 0.384 69 nm d value while the other reflection from the 0.2233 nm d value was weak. The interplanar d values obtained agreed well with the reported values for Te_2O_5. For TeO_3 and TeO_2 the strongest reflection corresponded to 0.347 and 0.299 nm d values, which were not observed in the X-ray diffraction of these films. Thus X-ray diffraction also provides evidence of a deviation from the initial stoichiometry of TeO_2; moreover it confirms that the resulting films have the stoichiometry of Te_2O_5.

TABLE I X-ray diffraction results of evaporated tellurium oxide films

2θ (deg)	Intensity	Interplanar spacing d (nm)	Reported values d (nm)
23.1	VS	0.2846	0.286; 0.288 (Te_2O_5); (TeO_3) [11]
40.38	W	0.2233	0.2244 (Te_2O_5) 0.2216 (TeO_3)

Transmission electron diffraction patterns were obtained for films deposited on sodium chloride substrate. Typical electron diffraction patterns obtained are shown in Fig. 4. Films obtained by electron-beam evaporation showed a single crystal spot pattern, while films obtained by resistive heating showed diffuse rings, thus suggesting they are wholly amorphous.

Spot electron diffraction patterns were analysed by carefully measuring the radii of the first two spots, and the corresponding interplanar d values were calculated. The results are shown in Table II. The strong reflection from the 0.3831 nm

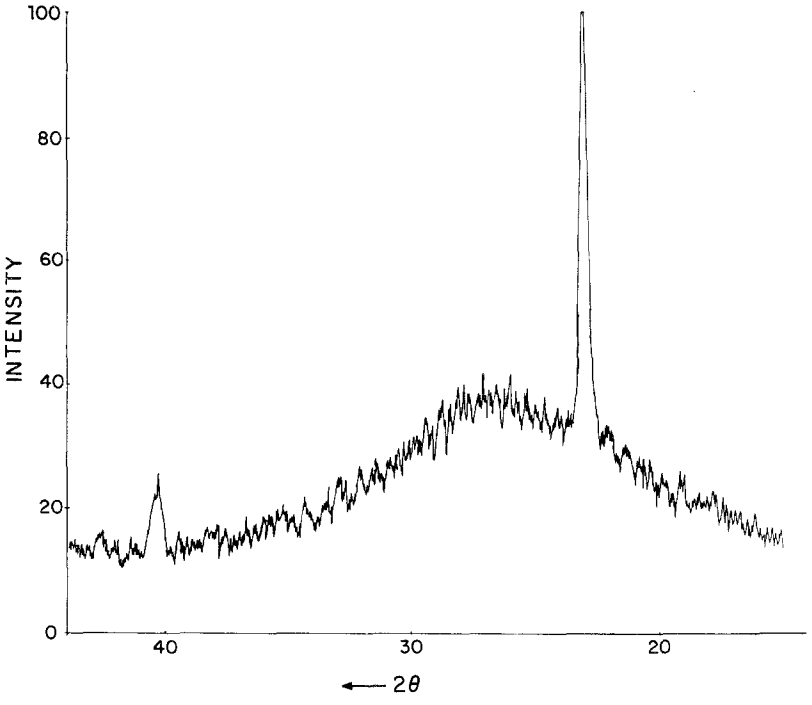

Figure 3 X-ray diffraction pattern of electron-beam evaporated oxide film of thickness 250 nm deposited on glass at room temperature. Scattering angle is 2θ.

d value agreed fairly well with the value of 0.3846 nm given by X-ray diffraction for Te_2O_5.

To evaluate their possible use in passive components, films 100 nm thick were sandwiched between two aluminium electrodes 100 nm thick. This resulted in the fabrication of many square capacitors of area 0.09 cm^2. Altogether 12 capacitors of the same thickness were tested. Individual capacitors were subjected to linearly rising a.c. voltage, and dielectric breakdown was observed on an oscilloscope screen. The electrical circuit has been described elsewhere [12]. It was observed that when a critical voltage is reached across a given capacitor, transient pulses and microsparks could be seen by the naked eye, thus indicating the onset of the breakdown. In these capacitors, breakdown was observed at 46 V at 1 kHz frequency. Furthermore, a capacitance of 8.5 nF, a dissipation factor ($\tan\delta$) as low as 0.065 and a breakdown strength of 4.6×10^6 V cm^{-1} were

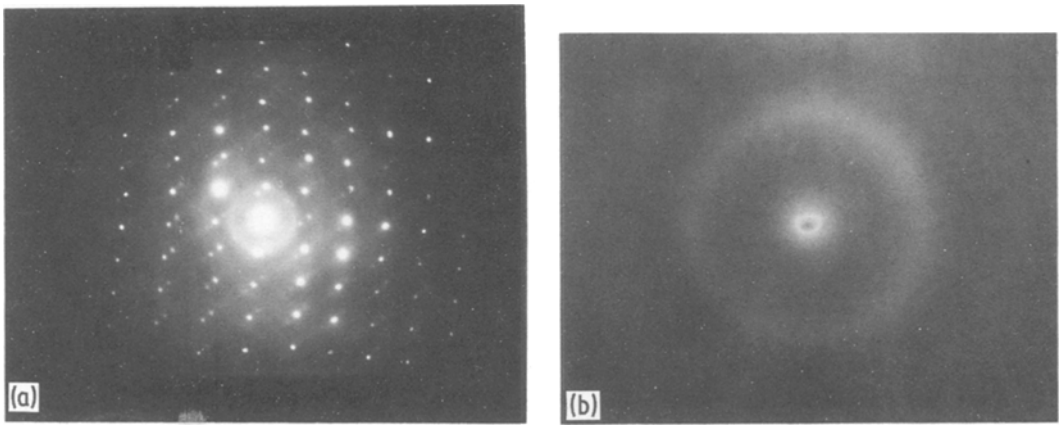

Figure 4 Electron diffraction pattern at 80 keV (a) of electron-beam evaporated film, (b) obtained by resistive heating.

TABLE II Electron diffraction results of electron-beam evaporated films

Interplanar spacing d (nm)	Reported d values (nm)
0.3831	0.386 (Te_2O_5)
0.2930	0.2976 (Te_2O_5)

obtained for 100 nm thick films. Fig. 5 illustrates the dielectric breakdown events shown by the transient pulses.

Thus from the results of X-ray and electron diffraction it can be concluded that the films obtained are very likely to have Te_2O_5 stoichiometry, because the reflection obtained for d values agrees very closely with the value of d reported for Te_2O_5. Furthermore, these films are found to have a high capacitance, a low dissipation factor and a high dielectric breakdown strength, which are important in an electronic material.

4. Conclusion

It is concluded that when tellurium dioxide is evaporated it decomposes and the resulting films show deviation from the initial stoichiometry. Films obtained by resistive heating have a greater bond strain and porosity, and their electron diffraction results show them to be amorphous, while electron-beam evaporated films show single crystal growth. Furthermore, analysis of the X-ray and electron diffraction results reveals that the evaporated films are Te_2O_5. These films have a low dielectric loss and a high breakdown field, indicating their possible application in passive components as capacitors.

Acknowledgements

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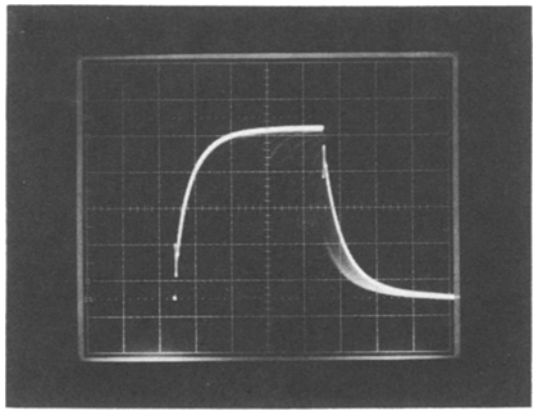

Figure 5 Micrograph of oscillogram of capacitor voltage against time illustrating pulse breakdown; vertical scale 10 V cm^{-1}. Oxide thickness = 100 nm.

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