Dielectric studies on tellurium oxide thin films

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Tellurium has been evaporated in an r.f. glow discharge of oxygen onto negatively-biased glass substrates at room temperature. These tellurium oxide thin films have been used as dielectrics in capacitors. The variations of capacitance, C, and dielectric loss, ϵ'', with frequency in the range of 0.5 to 30 kHz at various temperatures (300 to 443 K) have been studied. The temperature coefficient of capacitance and the dielectric constant for the material have been evaluated. The ϵ'' spectrum reveals a loss peak and a loss minimum, both shifting towards higher frequences with increasing temperatures. The maximum in the dissipation factor is explained on the basis of a dipolar relaxation phenomenon. The activation energy for the process has also been evaluated.

1. Introduction

From the time that a successful thin film transistor (TFT) had been reported by Weimer [1] much work has been carried out in the fabrication of TFTs and in the improvement of their characteristics [2–7]. Transistor action has been reported in a number of semiconductor materials [8]. Of the materials investigated tellurium has certain obvious advantages, such as the absence of non-stoichiometry problems, low melting point (725 K) and its ability to act both as the semiconductor channel in a TFT and as a resistor. The oxide of tellurium in thin-film form could find useful device applications [9] in tellurium-based thin-film circuits.

Tellurium oxide is better known for its piezoelectric properties. Not much work has been conducted on the dielectric properties of tellurium oxide thin films. Only recently Phahle has reported [9] the characteristics of tellurium oxide thin films, deposited by reactive evaporation. Also, tellurium oxide films have been prepared earlier by aqueous anodization, reactive sputtering and plasma anodization techniques [10–13]. The optical properties of the film have been reported [11, 12] and the oxide films have been tried as a protective layer [13] for the underlying semiconductor Te during annealing cycles. In the present study the dielectric properties of tellurium oxide films formed in a radio-frequency (r.f.) oxygen glow discharge are reported for the first time.

2. Experimental procedure
2.1. Sample preparation

Metal oxide films can be grown by forming metal ions and oxygen ions which combine either at the metal surface, inside the oxide, or the oxide–oxygen interface, depending on which ion migrates through the oxide. Thus, anodic oxidation in a wet electrolyte, plasma anodization and thermal oxidation have been successfully used for the growth of coherent and uniform oxide films in the thickness range of 5 to several 100 nm [14]. Oxide films could also be prepared by reactive sputtering [11, 12], evaporation of the oxide or reactive evaporation of the metal.

In the present investigation the base electrode was formed on carefully cleaned glass substrates by evaporating pure aluminium of (99.999% purity, from Balzers, Switzerland) from a tungsten filament through suitable masks at a pressure of 2.66×10^{-3} Pa. Prior to deposition the substrates had been heated to 423 K to enable good adhesion of the lower electrode.

The dielectric oxide films were deposited by a method which could be termed as plasma-activated, reactive, bias-assisted deposition (PARBAD). A schematic diagram of the deposition apparatus is
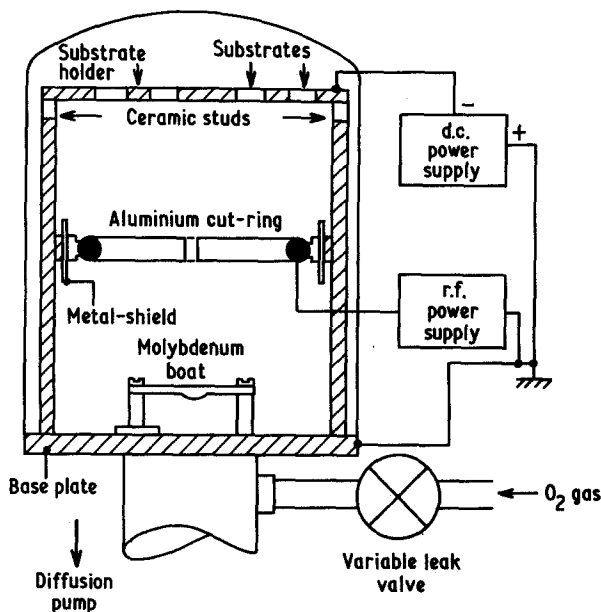
Figure 1 Schematic diagram of the deposition apparatus.

given in Fig. 1. A conventional 0.306 m vacuum coating unit (from Hind Hivac Co., Bangalore) has been used. The substrates were placed in an aluminium substrate holder isolated electrically by insulating ceramic studs. Mica masks were used for demarcating the dielectric area. The distance between the molybdenum boat, which served as the resistively heated source, and the substrates was kept at 0.21 m. The discharge electrode consisted of a pure aluminium cut-ring supported by stand-off insulators fixed to the tripod legs inside the chamber.

The glass chamber was initially evacuated to 5.32×10^{-3} Pa. Oxygen was then introduced and the pressure maintained at 2.66 Pa. The r.f. power used (120 W) was sufficient to engulf the complete chamber volume in the glow. A negative bias of 50 V was applied to the substrate holder. Tellurium (of 99.999% purity, from Special Materials Plant, Department of Atomic Energy, Hyderabad, India) was evaporated under the above conditions from the molybdenum boat. The melted Te evaporated with a characteristic bluish glow to form the oxide. Nascent dielectric oxide films that had been formed were then exposed to r.f. glow under deposition-bias conditions for 5 min after completion of the deposition.

Finally, aluminium was then evaporated in a vacuum of 2.66×10^{-3} Pa to form the upper electrodes and the metal—insulator—metal structures thus formed were investigated.

2.2. Measurements
The thickness of the dielectric layer was measured with a multiple-beam interferometer (Fizdeau fringes). A mean deposition rate of 0.78 nm sec^{-1} was calculated. The capacitance, C, and tan δ were measured at 400 mV r.m.s. *in vacuo* in the frequency range 0.5 to 30 kHz at various temperatures (301 to 443 K) using a RADART 0.1% Universal Bridge (Type 1204) coupled with an external audio oscillator (APLAB low distortion audio generator, Type TAG 3S).

3. Results and discussion
3.1. Dielectric film composition
The oxide films of tellurium deposited on plane glass substrates were visually analysed. Under transmitted daylight the transparent films appeared to have a characteristic mild grape-red tinge.

The identifying reaction for TeO_3, an oxidizing agent, is its reaction with warm concentrated HCl [15, 16]. The starch iodide test was positive testifying to the presence of TeO_3. Though the presence of TeO_2 could not be chemically established its presence was not excluded [12]. Also, no reliable information is available for the existence of TeO in solid form [17, 18]. Hence, the films would be designated $TeO_{2+x}(0 < x \leqslant 1)$, following the notation used by Lieberman [12].

3.2. Dielectric constant
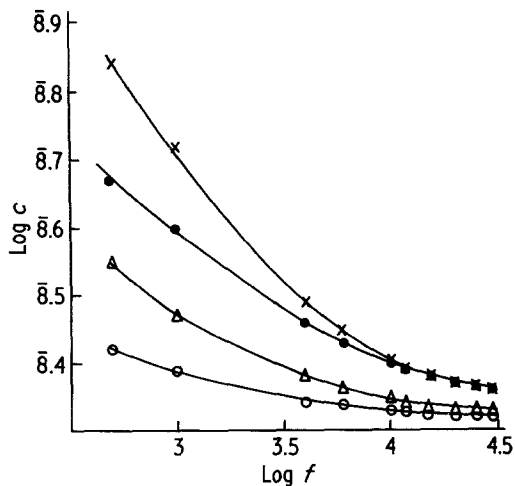The dielectric constant of the film was calculated

Figure 2 Audio frequency spectrum of C for TeO_{2+x} films (of thickness 51.5 nm) in the temperature range 301 to 443 K. o, 337 K; △, 365 K; •, 387 K; ×, 443 K.

Figure 3 Audio frequency spectrum of ϵ'' for TeO_{2+x} films (of thickness 51.5 nm) in the temperature range 301 to 443 K. o, 301.5 K; •, 319 K; △, 337 K; ▲, 365 K; □, 387 K; ×, 443 K.

with the knowledge of its thickness (51.5 nm) and area of the capacitor (4.148×10^{-6} m^2) from the determination of its capacitance at room temperature (301.5 K) at 1 kHz. The value of dielectric constant at 1 kHz (33) was found not to differ much from the value at 30 kHz (30) at room temperature and is in good agreement with the value (32) already reported by Phahle [9] for reactively evaporated films.

3.3. Dependence of C on frequence, f, at different temperatures

The dependence of log C on log f at different temperatures is shown in Fig. 2. The value of C was found to be invariant with frequency for temperatures from room temperature up to 340 K and was coincident along the frequency span in that temperature range. At higher temperatures (365 K to 443 K) the variation in the capacitance at lower frequencies was more pronounced, the rate of variation increasing with temperature. The observed trend could be caused by a sort of interfacial space-charge build up of an ionic nature which could be effective at low frequencies. This is in agreement with suggestions made by Von Hippel *et al.* [19]. Similar behaviour has been reported earlier [20–22].

The temperature coefficient of capacitance, γ_c, at 1 kHz at room temperature was calculated to be 210 ppm K^{-1} and this value is comparable in magnitude to that of any of the other dielectric films successfully used as capacitor elements.
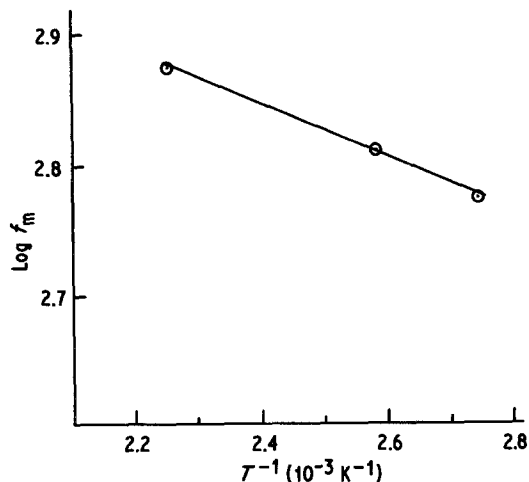
3.4. Variation of ϵ'' with frequency at different temperatures

The spectrum in the frequency, f, range 0.5 Hz to 30 kHz (Fig. 3) shows a sharp maximum. This peak on the lower side of the audio frequency response advances towards higher frequencies, f, with increasing temperature. A minimum in the value of ϵ'' is also exhibited. ϵ''_{min} is temperature dependent and becomes shifted gradually to higher frequencies with rise in temperature, as observed previously for ZnS [23] and indium oxide [24] films.

Tellurium is a Group VI element and, in proceeding from oxygen to tellurium, there is a transition in the compounds formed from those of a covalent character to those of ionic character [21]. The TeO_{2+x} film under consideration should evidently be ionic in nature with the possibility of defects in the form of anion vacancies [25] giving rise to ionic dipoles. It is hence taken that the relaxation phenomenon was due to dipole orientations. The observed shift in the loss-peak towards the high-frequency region with increasing temperature is in accordance with the Debye theory of orientation [26]. The rise in temperature causes a reduction in the mean time of stay of ionic dipoles [27] and hence leads to the observed temperature dependence as given by

$$2\pi f_{relax} = 1/T, \qquad (1)$$
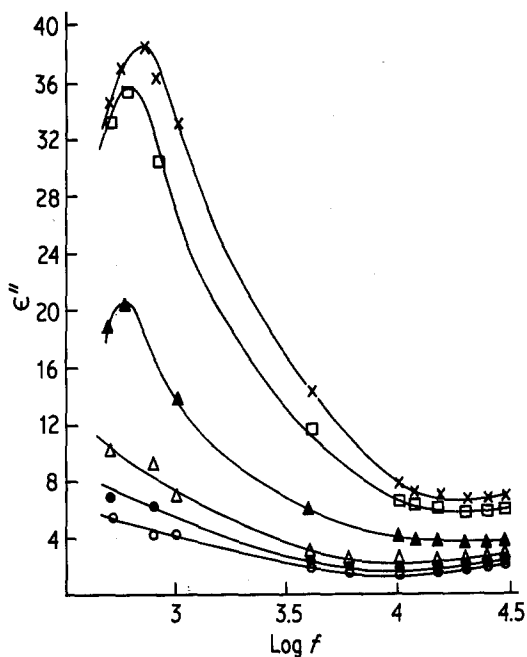
where T decreases. Similar loss peaks have been

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Figure 4 Plot of log f_m against T^{-1}.

reported earlier for cerous fluoride and molybdenum oxide films [28, 29].

The value of f_{min} increases with increasing temperature. This is in accordance with the behaviour of the model suggested by Goswami and Goswami [23]. Accordingly,

$$2\pi f_{min} = (rRC^2)^{-1/2}, \quad (2)$$

where r is the lead (electrode) resistance, R is the bulk resistance of the dielectric and C is a temperature and frequency independent capacitance taken as a theoretical assumption. As the temperature increases, R decreases considerably causing a shift of f_{min} to higher frequencies at higher temperatures and vice versa.

3.5. Activation energy

Making use of the relation [29]

$$f_m = f_0 \exp(-E/kT),$$

where E is the activation energy and k is the Boltzmann constant, a plot was made (Fig. 4 of logarithm of the frequency at which ϵ'' is a maximum, f_m, against the inverse absolute temperature. The slope of this curve yields an activation energy of 0.04 eV.

4. Conclusions

The capacitors prepared with thin (51.5 nm) dielectric films of TeO_{2+x} formed by the PARBAD

possess the following characteristics: a high capacitance density of $5.7 \times 10^3 \ \mu F \ m^{-2}$, a comparatively high dissipation factor and a low TCC (210 ppm K^{-1}). The high value of dielectric constant (33) would enable useful application of the dielectric oxide films.

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