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Formation, structural and optical properties of tellurium oxide films deposited by a plasma process (PARBAD)

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Tellurium oxide films have been formed by reactively evaporating tellurium in an r.f. discharge plasma of oxygen. Bias variation has been found to reveal interesting structural changes and different optical properties for the films formed. Qualitative observations regarding the physical and chemical reactions at the substrate have been reported.

1. Introduction

With the progress of technology towards fabrication of micrometre or submicrometre structures the evolution of a low-temperature process is inevitable. Oxide films have been an important part of device technology and with the development of thin-film technology they have tended to occupy a very important place with a lot of applications. These films have been formed successfully in oxygen discharges.

Since the early work of forming oxide films in an oxygen discharge [1], investigations have been carried out into the method and techniques of film formation in an oxygen plasma. Oxide films on the cathode [2, 3], on the anode [4–6] (plasma anodization), and on floating or biased electrodes [7–9] have been reported. More recently a lot of work on films grown in r.f. discharges has been reported [10–12]. Even higher frequencies (Microwaves) have generated plasmas useful [13, 14] in forming oxide films.

Plasma processes are gaining importance, as they are low-temperature, activated processes with manageable parameters. Of the plasmas reported, high-frequency plasmas have a higher concentration of electrons. This increased electron density leads to greater ionization of the gas and higher gas temperatures, leading to better oxidation. They are also found to give higher growth rates, owing presumably to a higher density of some active oxygen species [15]. So far, a fair amount of success has been achieved in growing oxides and nitrides by a semi-empirical approach. In the literature, the reaction kinetics in a glow discharge and the qualities of the discharge itself have been dealt with [12, 16–18] and a somewhat better understanding is unfolding. Tellurium oxide films, formed by PARBAD (plasma-activated, reactive, bias-assisted deposition), and their dielectric properties have been reported earlier [11]. In the present study the bias condition has been varied, keeping the other parameters constant, and the formation and formed films have been analysed to gain some insight into the formation process.

2. Experimental

2.1. Sample preparation

In the present work the oxide thin films were formed by PARBAD. The bias was varied from 0 to −270 V. The frequency of the r.f. power consumed in the oxygen discharge was 21.45 MHz. Details of the deposition set up have been given earlier [11]. The distance between the source and substrate for the inner ring in the substrate holder was 0.19 m and that for the outer ring 0.21 m. The pressure during deposition was 2.66 to 5.32 Pa. Table I gives the complete details of the experimental conditions. Metal–insulator–metal (MIM) structures were formed, with aluminium and silver as base-electrodes and aluminium as counter-electrodes, to observe the possible physical and chemical changes. The substrates were carefully cleaned glass substrates maintained at room temperature in all depositions.

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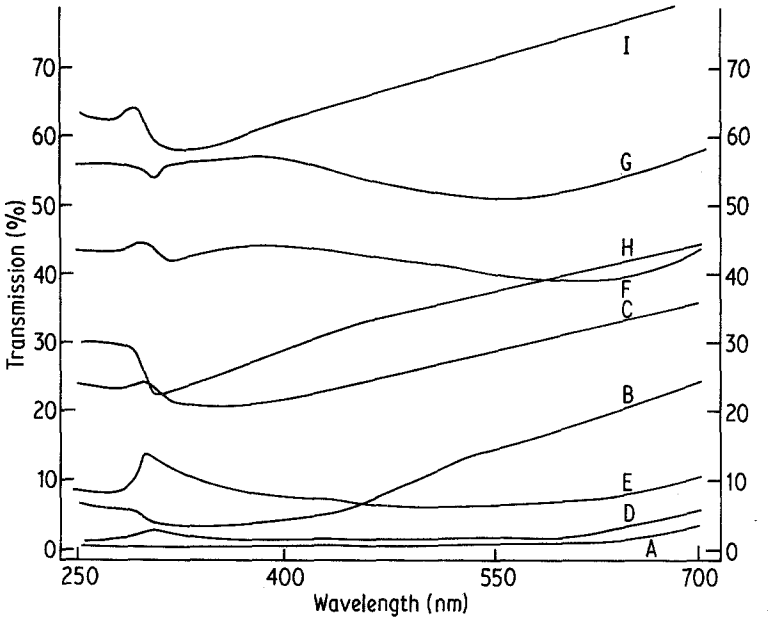

Figure 1 Transmission spectrum for the tellurium oxide films in the UV and visible range.

2.2. Measurements

The thickness of the films was measured using a multiple-beam interferometer. The structure details of the formed films were examined using a Philips X-ray generator (PW 1730) and a Philips X-ray diffractometer (PW 1051). $K\alpha$ radiation (nickel β-filter) of 0.154 18 nm wavelength was utilized. A Shimadzu double-beam spectrophotometer and recorder have been used to analyse the films optically in the UV and visible regions, in a normal incidence transmission mode.

3. Results and discussion

3.1. Optical properties

The transmission spectrum for the tellurium oxide films is given in Fig. 1. A plot of absorption coefficient (α) against photon energy is given in Fig. 2. It has been noted that with increasing bias (negative) the transmission quality of the films improves. Also, the dip (absorption minimum) is observed to be at a higher level of transmission with the dip itself being quite minimal. The absorp-

TABLE I Experimental conditions

Sample index	Bias during deposition (V)	Thickness (nm)	Mean rate of formation (nm sec^{-1})
A	0	84.6	1.52
B	−50	70.3	0.61
C	−50	45.2	0.40
D	−90	58.6	0.53
E	−90	35.3	0.32
F	−180	45.4	0.28
G	−180	39.5	0.25
H	−270	47.6	0.42
I	−270	28.2	0.25

Weight of tellurium charge = 220 ± 10 mg.
r.f. power = 100 W.

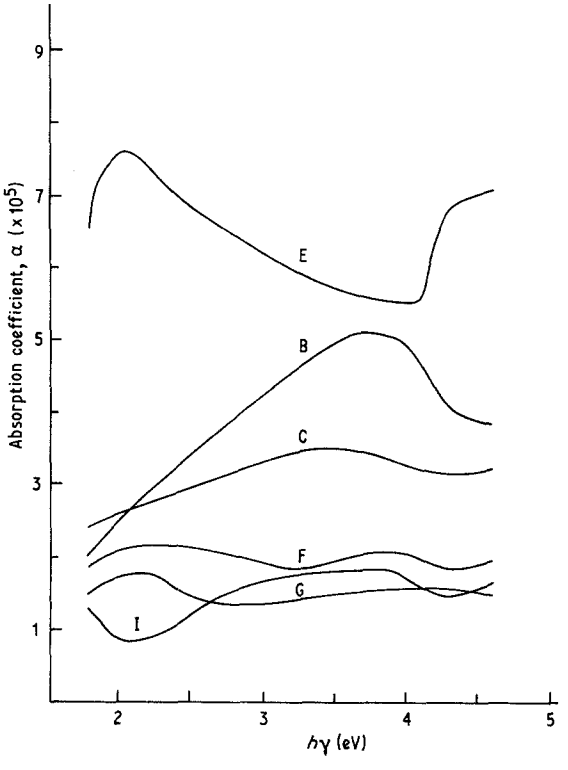

Figure 2 Plot of absorption coefficient against photon energy.

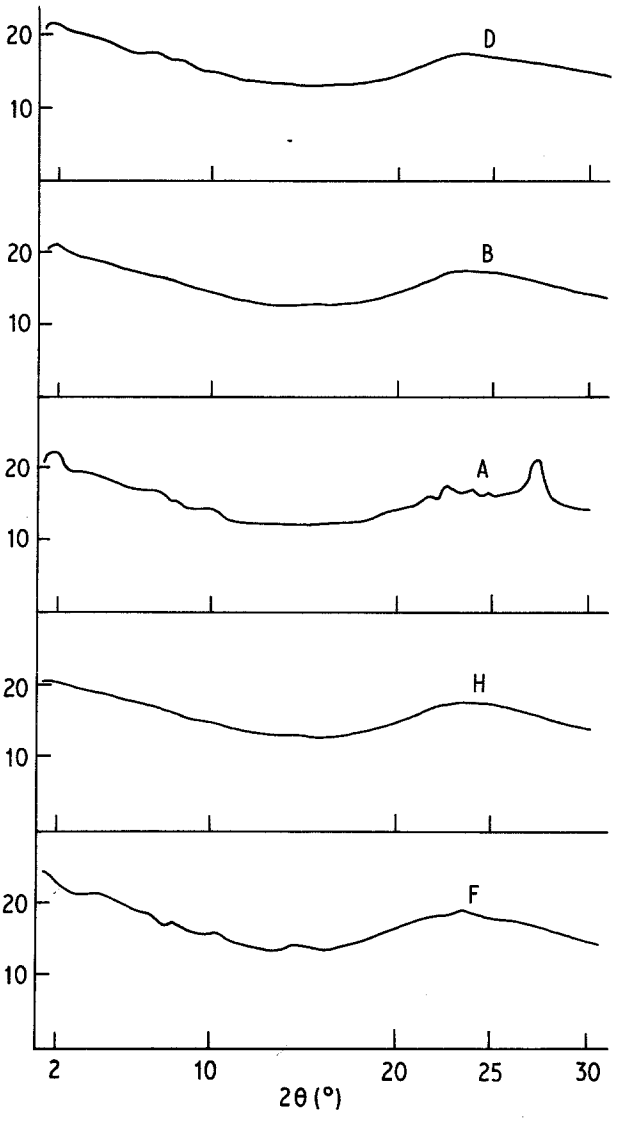

Figure 3 X-ray diffractograms for tellurium oxide films formed at different bias conditions.

tion could be due to the bound electrons [19] by $n \rightarrow \sigma^*$ or $n \rightarrow \pi^*$ transitions.

3.2. Structural studies

The two peaks in the X-ray spectrum (Fig. 3) happen to disappear for specimens formed at a negative bias. The structure analysis presented seems to indicate a microcrystalline or amorphous structure (especially for the bias-assisted films).

3.3. Physical and chemical qualitative observations

The chemical analysis of the tellurium oxide films has already been reported [11]. In the present study it has been observed that the samples deposited at the highest negative bias had a dull-yellow tinge under visible light. The colour strongly seems to indicate the presence of TeO_3 [20]. Also, when heated to around 200° C the films were found to change colour to a brown hue. This seems to confirm the presence of TeO_3 [20] and is further argumented by the results reported in Section 3.2. From the data available [21] it is evident that the films formed were tellurium oxide films with a mixture of Te(IV) and Te(VI) oxides.

The oxide films on the aluminium and silver electrodes have been found to react, as visible verification shows. The colour of the complex formed on aluminium is dark brown and that on silver is greyish black.

The counter-electrode deposited on the oxide

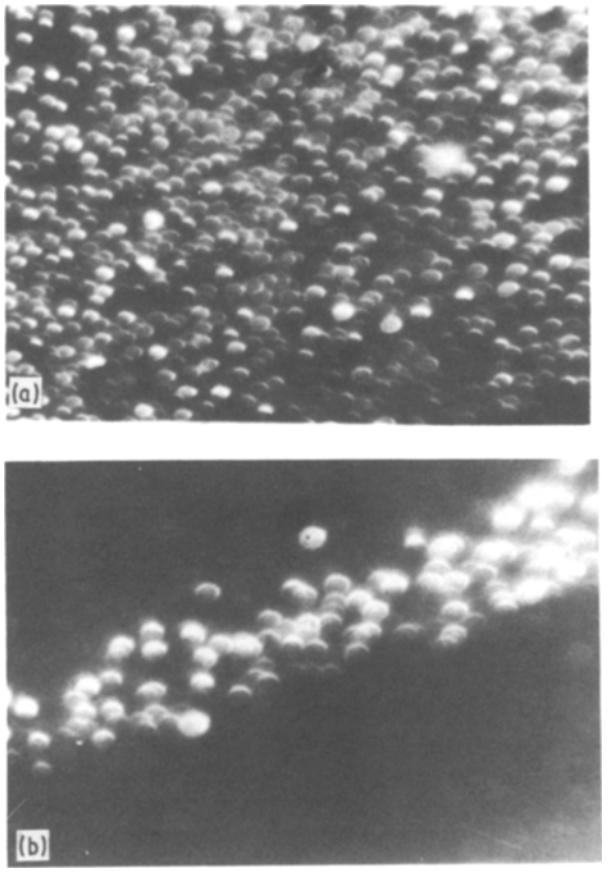

Figure 4 Photomicrographs of blisters in (a) sample B and (b) sample F.

films is found to exhibit an interesting phenomenon. At the periphery of the oxide film area, in the nonoverlapping space of the electrodes, the top electrode exhibits a speckled appearance. A photomicrograph (Fig. 4) of that spot shows an example of speckles, evidently due to evolution of some adsorbed gas. This sort of manifestation of desorption has been reported earlier [22]. The blister area is found to diminish with progressively increasing negative bias and disappears at the higher value of bias. The oxygen ions (and maybe neutrals) in the plasma bombard the exposed area (mask demarcation) during oxide formation and get adsorbed. The disappearance of the speckles at higher negative bias seems very much to indicate that the impinging ions could be negative oxygen ions, of either atomic or molecular status.

3.4. Formation status

As the negative bias increases, the dark-space region formed on the plasma side of the substrate holder extends further into the plasma. (Increase in r.f. (plasma) power results in reduced dark space (ion sheath).) This fact is clear from experimental observation and indicates greater space charge to maintain the higher potential. As the dark space increases, only highly energetic plasma species travelling the least distance in the space-charge field (along the direction of the field) hit the substrate. This may well explain the phenomenon of diminishing speckle-width observed in Fig. 4 (Section 3.3).

The constraint in the plasma volume by the ion sheath (dark space), due to bias, seems to increase the electron temperature. In a discharge, electrons, ions (positive or negative), neutral atoms or molecules, and metastables (excited molecules) exist. Excitation on electron impact could result in the production of active neutral species [23]. So, the increasing bias could lead to a higher excitation and a greater chance of Te(VI) being formed. This could happen by promotion of electrons between subshells and an occurrence of apt configuration. This encourages the formation of tellurium(VI) oxide, as has been experimentally found and earlier demonstrated [1] in the case of selenium oxide.

4. Summary

Tellurium oxide films have been formed by a plasma-activated process (PARBAD). An understanding of the reaction kinetic in the plasma has been attempted on the basis of the optical and structural analysis. It has been realised that a higher activation of the evaporating species (tellurium) leads to the formation of the higher-valence oxides.

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