

# Evaporation characteristics of TeO<sub>2</sub> in the formation of tellurium oxide thin films

N. LAKSHMINARAYAN, M. RADHAKRISHNAN, C. BALASUBRAMANIAN  
*Department of Physics, Bharathiar University, Coimbatore 641 046, India*

Thin films of tellurium oxide have been formed by evaporating TeO<sub>2</sub> with different boat materials (molybdenum and tantalum) in a high vacuum and at different oxygen partial pressures. The optical and structural properties of the films have been studied. From the variations in the properties with respect to the formation conditions the evaporation characteristics of TeO<sub>2</sub> have been discussed.

## 1. Introduction

The evaporation characteristics of oxides in general have been described in the literature [1, 2]. The constituents of the oxide in the solid or liquid state during evaporation differ in their vapour pressures. Another factor is the interaction of the oxide with its support material. In general, evaporation of the oxide in a high vacuum environment is a dissociative phenomenon. The material to be vaporized should be available in a suitable form and then evaporated from a non-reacting source, which does not reduce the oxide at the source itself. In reactive evaporation, the pressure in the chamber should then be maintained appropriately with a partial pressure of oxygen (the deficient component of the oxide film) to form the required stoichiometry.

Tellurium oxide is a comparatively rare and less well-studied material. Furthermore, TeO<sub>2</sub> is a difficult crystal to grow and process [3] but is a relatively hard material with good chemical stability, while possessing a wide optical transmission range [4]. With the interest in its potential as a useful optical storage medium [5-7] and expected device applications [8, 9] tellurium oxide films may turn out to be highly useful. Plasma anodization, aqueous anodization, reactive sputtering and another plasma deposition method (PARBAD) have been tried successfully [9-13] to form tellurium oxide films. On the evaporation of the oxide, as an elementary initial procedure, there are very few reports [5, 6, 8, 14]. An understanding of the formation process is necessary in the proper utilization of any film. The optical and structural properties of the formed films have been used in this study to analyse the evaporation phenomenon.

## 2. Experimental procedure

### 2.1. Film formation details

The evaporant charge consisted of small pieces of high-purity TeO<sub>2</sub> crystal [4] and was evaporated from a resistively heated source. In this study, molybdenum and tantalum boats were used as the sources. In the formation of films for investigation, carefully cleaned glass substrates were used at room temperature. In the reactive evaporation technique adopted the chamber had been initially evacuated to a pressure of less than

0.01 Pa, and then with a carefully controlled leak of oxygen the deposition pressure was maintained. A conventional 0.306 m vacuum coating unit (Hind Hivac Co, Bangalore) was used.

### 2.2. Measurements

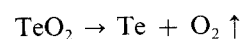
The thickness of the dielectric layer was measured with a multiple-beam interferometer. A Carl Zeiss spectrophotometer (DMR 21, West Germany) was utilized to evaluate the optical transmission quality of the formed films in the ultraviolet (UV), visible and near-infrared (NIR) regions. Unpolarized light at near-normal incidence was used. X-ray diffraction studies were performed using a Philips X-ray diffractometer (PW 1051) with  $K\alpha$  radiation of wavelength 0.15418 nm.

## 3. Results and discussion

### 3.1. Observations at the source

Tungsten, molybdenum and tantalum are the common refractory metals used for resistively heated boats. Of these, tungsten and molybdenum are known to form volatile oxides at elevated temperatures. Tungsten has been used as a de-oxidizing agent with TeO<sub>2</sub> [6] and hence its use as a boat material is definitely disallowed. Even though tantalum forms a volatile suboxide at high temperature [15], in the present instance (1006 K) it seems very much less likely and also its use with TeO<sub>2</sub> has been reported earlier [14].

In the present study it has been observed that molybdenum does react with TeO<sub>2</sub>. At the melting point of TeO<sub>2</sub> as the material changes state violent ebullition takes place. The evolution of gas, evidently oxygen, is manifested by the violent disturbances in the boat charge and ejection from even deeply recessed boats. Furthermore, if the melted charge is solidified before it has completely evaporated, the part at the bottom which had been in contact with the source displays a darkening. As the existence of TeO in the solid state is somewhat uncertain [16, 17], the TeO<sub>2</sub> could be taken to decompose into tellurium and oxygen:



The discoloration of the starting material arises

TABLE I Experimental details of the evaporation process

Sample	Pressure during deposition (Pa)	Boat material	Mean rate of formation (nm sec <sup>-1</sup> )	Thickness (nm)
f	$3 \times 10^{-3}$	Mo	1.8	200
g	2	Mo	1.0	27
h	$3 \times 10^{-3}$	Ta	3.8	146
i	2	Ta	0.7	18
a	$3 \times 10^{-3}$	Mo	2.4	270
b	2	Mo	2.5	64
c	$3 \times 10^{-3}$	Ta	4.8	180
d	$6.65 \times 10^{-3}$	Ta	1.3	65
e	2	Ta	1.3	33

from the decomposition, and the darkness is evidently due to elemental tellurium.

When tantalum is used as the boat material, calm evaporation proceeds from a clear liquid pool of the melt and the solidified remnant charge (in contact with the boat) shows no discoloration. The above observations hold true for high and low vacuum (with oxygen partial pressure) and for both molybdenum and tantalum sources.

### 3.2. Structural details

It is a familiar observation in film formation that increasing the substrate temperature improves epitaxy for a variety of film-substrate combinations and for various methods of film formation [18]. However, it has been established earlier that increasing the substrate temperature led to a decreasing oxygen content [19–22] in the case of oxide films, and the chemisorption of oxygen on to many metals needs very little or no activation energy [23]. As forming completely oxidized films was the interest of this study, substrate heating has not been resorted to.

The relevant experimental details of the samples studied (f, g, h and i) are given in Table I. In Fig. 1 the X-ray diffraction details of the various samples are shown. In the case of TeO<sub>2</sub> evaporated from a molybdenum source the films formed were highly disordered

in nature, both in the case of vacuum evaporation and with reactive evaporation. The highly disordered amorphous-like structure results from poor mobility of the adsorbed atoms such that the atoms come to rest (condense) at or near the point of impingement, before they are able to reach the most preferable energetic sites [24]. Chopra [25] lists the three mobility reducing mechanisms as

- (i) impurity stabilization,
- (ii) vapour quenching, and
- (iii) co-deposit quenching.

The same amorphous-like structure in both cases of evaporation, and the occurrence of a polycrystalline nature with reactively evaporated films formed under identical conditions with a tantalum source, rules out the first possibility. The substrate temperature involved (301 K) gives a lesser chance for the second to be the controlling factor. The substrate is basically of an amorphous nature and further, heavy dissociation of TeO<sub>2</sub> could lead to the simultaneous impingement of tellurium and TeO<sub>2</sub> on the substrate. It has been stated earlier that there is no mutual solubility in the Te-TeO<sub>2</sub> system right up to 1073 K [26]. Thus, two incompatible systems deposited on an amorphous substrate at room temperature may result in an amorphous structure, as has been reported earlier in metal and non-metal combinations [27, 28] deposited at low substrate temperatures.

The polycrystalline nature of the films deposited with a tantalum source is demonstrated by the X-ray diffractograms. The line position is unchanged but the angular width at half maximum increases in the case of films formed in a partial pressure of oxygen (reactive evaporation). This indicates a reduction in crystallite or grain size. Hence it may be due to the "impurity stabilization" of the oxidizable material. The better oxidized, and hence more transparent, films of this batch are indicative of the influence of oxygen in inhibiting mobility. This could explain the finer grain size.

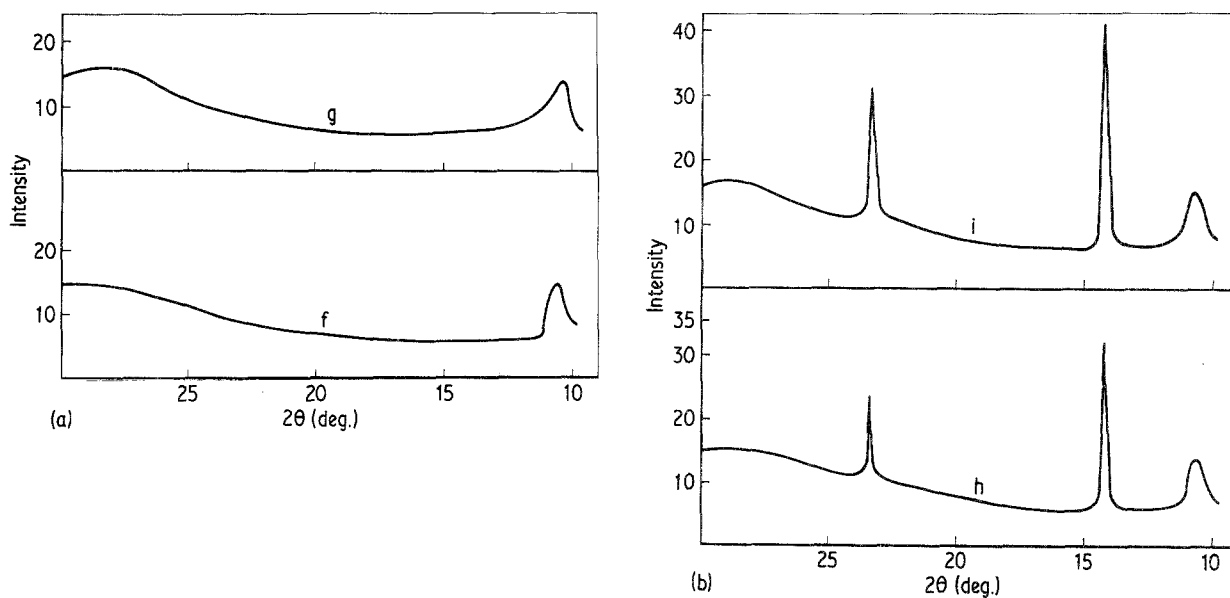


Figure 1 X-ray diffractograms for the tellurium oxide films: (a) Samples g and f, (b) Samples i and h.

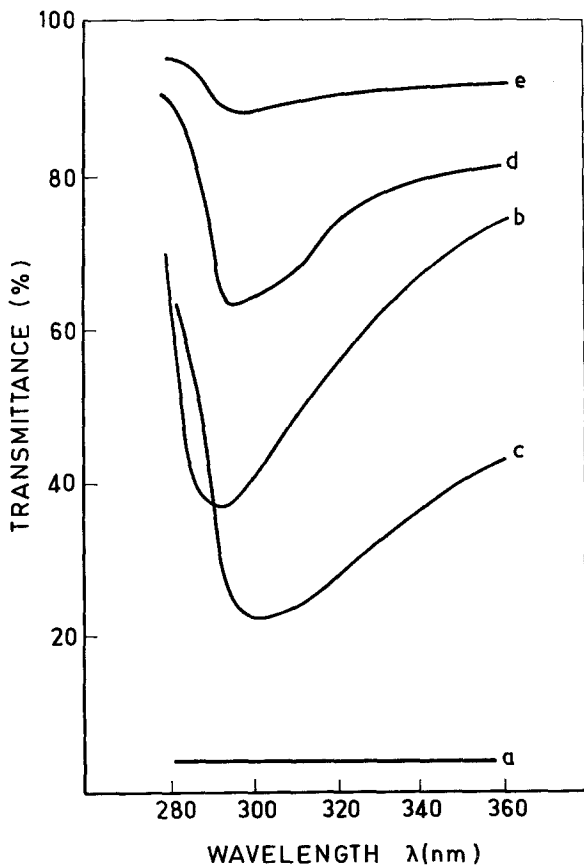


Figure 2 Transmission characteristics of the tellurium oxide films in the UV region.

### 3.3. Optical properties

The formation conditions of the samples studied (a, b, c, d, and e) are given in Table I. Fig. 2 gives the UV transmission properties of the films. It is a general phenomenon in oxide films that UV absorption decreases when the oxide molecules became well-defined [29]. From the figure it is noticed that the UV transmission increases seemingly with better oxidation of the film material. The transmission properties of the

films discussed in the visible and NIR regions are given in Fig. 3. The steep fall in the transmission for films evaporated from a molybdenum source is clearly seen near the UV end of the spectrum.

From the experimental values of  $T_0$  and  $k_f$  and a knowledge of the substrate refractive index ( $n_b = 1.509$ ) and the thickness of the films  $d$ , the values of the refractive index  $n_f$  have been evaluated at different wavelengths ( $\lambda$ ) using the equation derived by Harris *et al.* [30]:

$$T_0 = 4n_b \left[ (n_b + 1) \cos A - i \left( \frac{n_b}{B} + B \right) \sin A \right]^{-2} \quad (1)$$

where  $A = 2\kappa d(n_f + ik_f)/\lambda$  and  $B = n_f + ik_f$ , and following an iterative calculation procedure. In Figs. 4 and 5 the dispersion characteristics and the variation of extinction coefficient ( $k_f$ ) with wavelength for the tellurium oxide films have been plotted. Both  $n_f$  and  $k_f$  decrease with decrease in frequency of the incident radiation. This is the general trend. The value of  $k_f$  varies from sample to sample and decreases as the oxidation of the oxide films progressively becomes better. With oxide films, non-stoichiometry has been known to cause greater absorption due to the oxygen vacancies [31]. In the case of  $n_f$ , films formed in a high vacuum from different sources (molybdenum and tantalum) display dependence on the formation conditions. The higher refractive index, for the films formed with a molybdenum source (even though of a lower packing density), may be due to the larger content of tellurium, which may explain the comparatively high values of refractive index which lie between the values for the two materials [17, 31, 32].

The value of  $n_f$  for reactively evaporated films is less than that for films deposited in a high vacuum. The difference may be attributed to the lower packing density of the film material. This could be because of the lesser energy of the condensing atoms which suffer

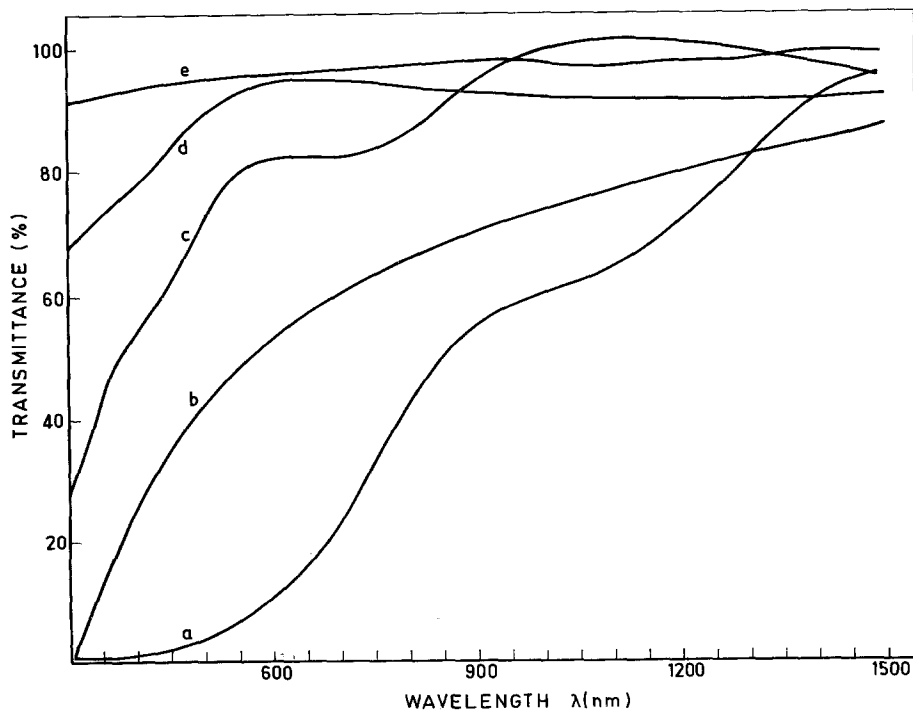


Figure 3 Transmission quality of the tellurium oxide films.

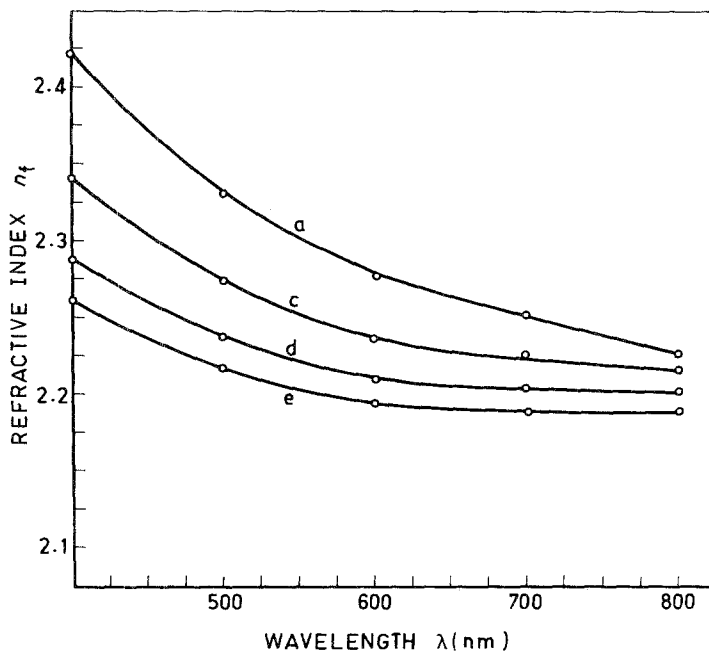


Figure 4 Dispersion characteristics of the tellurium oxide films.

a greater number of collisions in a low vacuum, in transit from source to substrate. Further, because of the better state of oxidation at higher oxygen pressures, the impurity stabilization phenomenon [25] leads to a lesser mobility of the condensing atoms and consequently to a lower packing density.

#### 4. Conclusions

It has been experimentally verified that amongst tungsten, molybdenum and tantalum, tantalum is the most suitable material to be used for  $\text{TeO}_2$ . In reactive evaporation the oxygen pressure has to be adequately maintained. From the structural and optical details of the tellurium oxide films it has been found that the pressure during evaporation has to be optimized. A high vacuum results in non-stoichiometric (oxygen-deficient) films and a lower vacuum leads to a lesser packing density.

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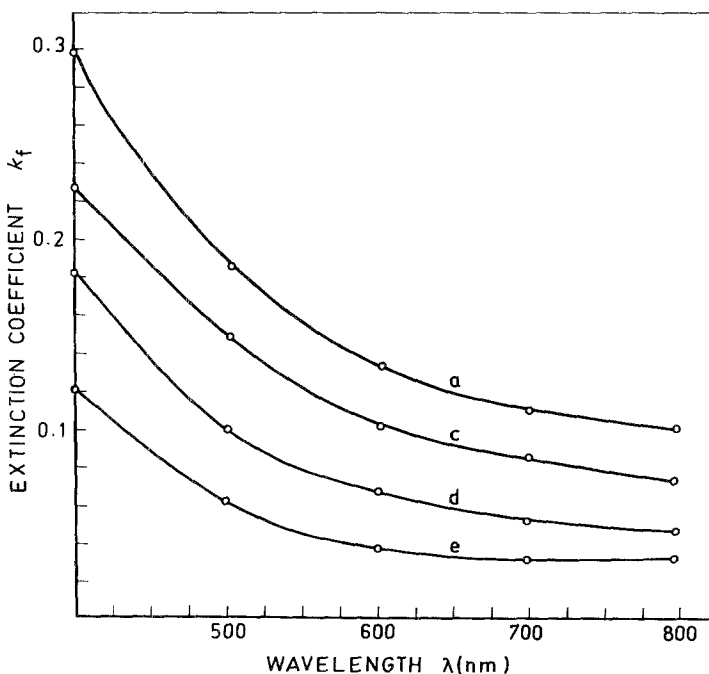


Figure 5 Variation of extinction coefficient ( $k_f$ ) with wavelength for the tellurium oxide films.

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