PREPARATION AND SOME ELECTRICAL PROPERTIES OF THULIUM OXIDE FILMS

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The electron-beam method was used for preparing thulium oxide films with thicknesses in the range 70–250 nm. The analysis of d.c. I–V characteristics suggests that space charge limited current (SCLC) seems to be prevailing mechanism of conductivity in these structures. When the samples were annealed, the field-dependent conductivity (i.e. Schottky and/or Poole–Frenkel effect) was observed. The activation energy calculated from the $I = f(1/T)$ plots was about 0.90 eV. For measured samples the temperature-dependent increase of current was observed up to some critical temperature of 490–500 K and above this temperature this dependence was decreasing. This temperature was adopted as some recrystallization temperature of thulium oxide. Dielectric constant of thulium oxide films varied in the range 7–22. Resistivity of examined structures was 10^{13}–10^{14} $\Omega \cdot$ cm and breakdown voltage changed from 8×10^5 to 7×10^6 V/cm. The energy gap of thulium oxide from the optical absorption data was 5.1 eV.

1. Introduction

Rare earth oxides seem to be promising group of materials which can be used in thin-film technology [1–5, 10]. Fromhold and Foster made an experimental survey on rare earth oxides [1] and suggested that some of them showed the most promising properties as potential materials for use in thin-film capacitors.

Thulium oxide is the representative of this group which, as far as we know, was not yet investigated in thin-film devices.

The purpose of this work was to obtain an insight into fundamental conduction processes in Al-Tm_2O_3-Al thin-film sandwiches and to examine some dielectric properties of thulium oxide thin films as well.

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2. Experimental

2.1. Sample preparation

Investigated structures were deposited in vacuum of 5×10^{-6} Torr on glass substrates in sandwich configuration. As electrode material aluminium was used, which is characterised by a low temperature of evaporation, low surface mobility of atoms and is fine-grained [1, 2, 6]. The geometrical "active" area of the capacitors was approximately 1 mm^2. Thulium oxide films were deposited by electron gun method. The starting material was Johnson Matthey C. L. spectrally pure Tm_2O_3, however the exact stoichiometry of obtained films has not been tested in this work and it was referred to as thulium oxide films. During the deposition the power of the electron beam was gradually increased to avoid splashings of the thulium oxide powder due to adsorbing gases. The evaporant source-to-substrate distance was approximately 15 cm. The substrate basically was not heated. Its temperature measured by copper-constantan thermocouple increased during the evaporation up to 100–200°C due to heat radiation depending on the beam power and evaporation time. The evaporation was carried out for three different electron beam powers, i.e. 150 W, 260 W and 340 W corresponding to accelerating voltages 3 kV, 4 kV or 4.2 kV, respectively. The evaporation time ranged from 8 min. to 40 min. The described method yielded oxide films with thicknesses between 70 nm and 250 nm measured by interference method. For structural and optical investigations thulium oxide was also deposited directly onto KCl and quartz glass substrates. For structural investigations JEM-120 Jeol transmission electron microscope was used.

2.2. Measurements

All measurements were made in air. For obtaining d.c. characteristics the sample was placed in screened metal box on the brass stage which could be resistively heated.

The current intensity was measured with a 610c Solid State Keithley Instruments

TABLE I

Some average parameters of examined thulium oxide films for different deposition conditions

No of process	U[kV]	I[mA]	t[min]	$v_{av}\left[\frac{nm}{S}\right]$	ε_{av}	U_b[V]$\times 10^6$	n[%]	$\tan\delta \times 10^{-2}$
1	4	65	8	0.13	8.71	3.87	90	1.60
2	4	65	16	0.17	14.67	1.86	83.8	1.89
3	4	65	24	0.12	12.52	4.25	71.9	7.18
4	4	65	32	0.12	14.76	1.80	53.1	7.28
5	3	50	40	0.18	10.38	1.78	55.0	5.86
6	4.2	80	16	0.22	14.9	1.05	28.1	1.34

U — accelerating voltage; J — beam current; t — deposition time; v_{ev} — average deposition rate (calculated as a ratio of average film thickness and deposition time); U_b — breakdown voltage; n — figure of merits i.e. ratio of the number of good unshort-circuited structures to all structures obtained in the particular process; $\tan\delta$ — loss factor; ε_{av} — dielectric constant at $\omega = 10^4 s^{-1}$.

electrometer. For capacitance measurements Tesla BM484 semiautomatic bridge was used. Frequency-dependent characteristics were made with Schering bridge.

Calculated from the capacitance data dielectric constant of investigated films varied in the range 7–22. Average parameters of the examined samples for different deposition conditions are presented in Table I. The optical absorption data were obtained by using Acta M-4 Beckman spectrophotometer and the value of optical energy gap was estimated as 5.1 eV.

3. Results and discussion

Fig. 1 presents examples of I–V characteristics in double logarithmic scale for different temperatures. Resistivity of the investigated films calculated from d.c. characteristics was 10^{13}–10^{14} Ω · cm. Breakdown voltage of the structures changed from 8×10^5 to 7×10^6 V/cm.

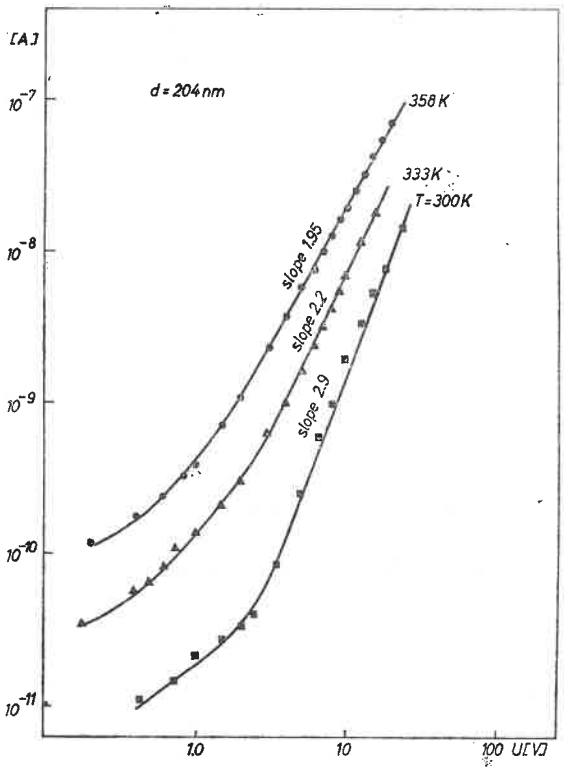


Fig. 1. I–V characteristics for Al-thulium oxide-Al structure at different temperatures

The slope of the curves gradually increased from unity for lower fields (up to about 10^4 V/cm) to approximately two for higher electric fields. The slope's value of the rectilinear parts of the plots changed from 2.9 at 300 K to 1.95 at 358 K.

Then, we can conclude that space charge limited current (SCLC) is the basic conduction mechanism in thulium oxide thin films in accordance with Mott's and Gurney's equation which predicts that SCL current is proportional to V^2 [7].

The part of the samples were annealed in air and these showed different shape of I–V characteristics. The example of this can be the sample for which such characteristic is plotted in Fig. 2 both in lg-lg scale and as lg I vs $V^{1/2}$. This sample was previously annealed

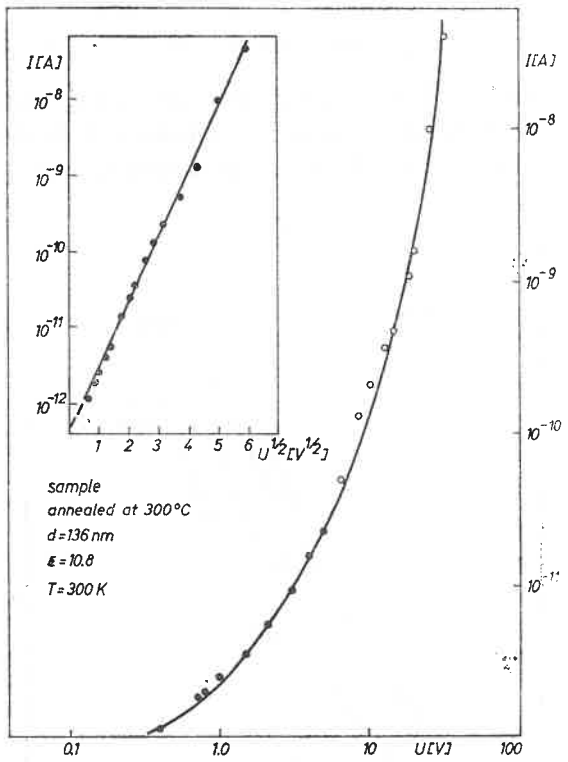


Fig. 2. I–V characteristic for annealed Al-thulium oxide-Al structure plotted in two different scales

at 300°C. Richardson–Schottky emission seems to be the prevailing conduction mechanism in this case. This type of conductivity is analytically described by the expression [8]

$$J = AT^2 \exp\left(-\frac{\varphi - \beta_{R-S}E^{1/2}}{kT}\right), \tag{1}$$

where J is current density, E — applied electric field, $\beta_{R-S} = \left[\frac{e^3}{4\pi\varepsilon\varepsilon_0}\right]^{1/2}$ — Richardson–Schottky coefficient, T — temperature, φ — the height of potential barrier at the metal-dielectric boundary, k is Boltzmann constant and ε — high frequency dielectric constant.

The plot lg I vs $V^{1/2}$ enables us to determine the height of the potential barrier at the electrode–dielectric interface as

$$\varphi = -kT\left(\frac{I_0}{SAT^2}\right), \tag{2}$$

where I_0 is cut-off current, S — sample area and A is Richardson constant. And so

$$\beta_{\mathrm{R-S,exp}} = 1.8\times10^{-5}\ \mathrm{eV}\left(\frac{\mathrm{m}}{\mathrm{V}}\right)^{1/2}, \qquad \varphi = 0.92\ \mathrm{eV}.$$

The theoretical value of $\beta_{\mathrm{R-S}}$ is

$$\beta_{\mathrm{R-S,theor}} = 1.2\times10^{-5}\ \mathrm{eV}\left(\frac{\mathrm{m}}{\mathrm{V}}\right)^{1/2}.$$

For calculations the value of $\varepsilon = 10.8$ given in Fig. 2 was assumed. The difference between the values of $\beta_{\mathrm{R-S,exp}}$ and $\beta_{\mathrm{R-S,theor}}$ can be due to Poole–Frenkel effect which can occur simultaneously to Richardson–Schottky effect.

In Fig. 3 the dependence lg I vs $1000/T$ is plotted. Up to temperature approximately 500 K the dependence is increasing. For we know that: lg $I \sim E/kT$, so from the slope of

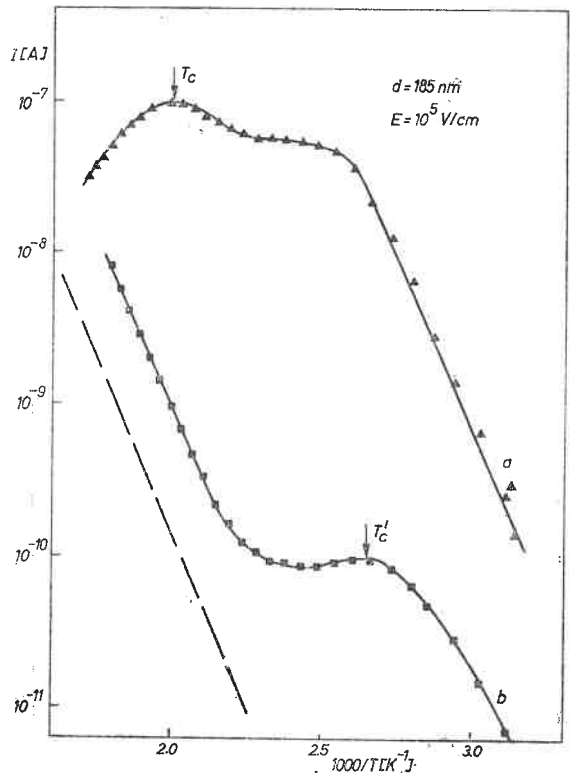
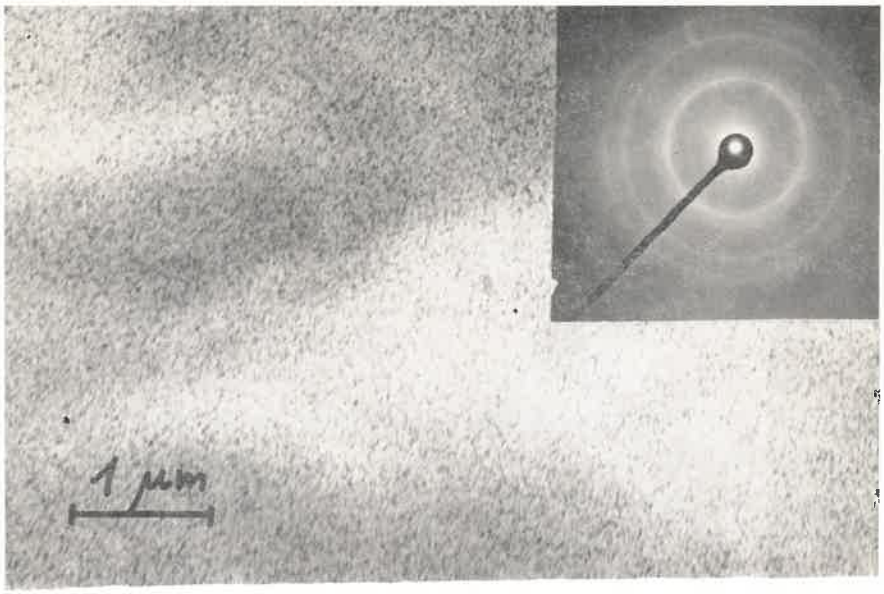
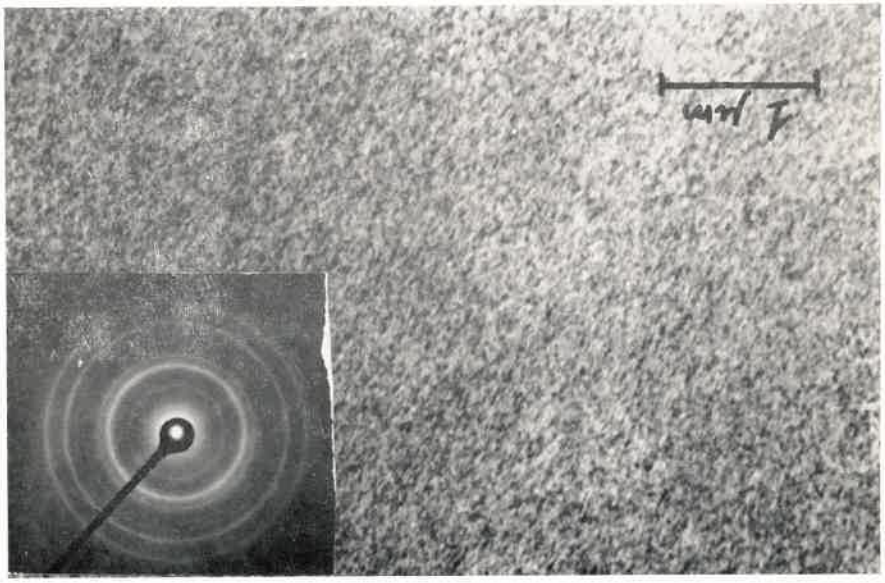


Fig. 3. Current vs $1000/T$ plot for Al-thulium oxide-Al structure; curve a — first measurement, curve b — repeated measurement



a



b

Fig. 4. Microphotographs and electron diffraction patterns of thulium oxide deposited on KCl; a — film as-deposited and annealed at 200°C, b — film annealed at 400°C

rectilinear rising part of the curve the activation energy we can calculate. The obtained values are in the range 0.40–0.95 eV and average value is 0.90 eV. The critical temperature T_c of 490–500 K, where the maximum value of current was observed, we adopted as some recrystallization temperature (Fig. 3, curve *a*). After cooling the sample the characteristic was made again. The slope of the rectilinear part of the plot did not changed but current is now much smaller and critical temperature removes to approximately 360 K (curve *b*). Such behaviour of the sample means that resistivity of the oxide film distinctly increased and its internal arrangement changed as well.

Structural changes after oxide films annealing at 200°C and at 400°C are shown on the electron diffraction patterns and microphotographs in Fig. 4. The as-deposited films as well as films annealed at 200°C have slightly polycrystalline structure (Fig. 4a) and only when annealed at 400°C they become distinctly polycrystalline (Fig. 4b).

The typical trends of capacity C and loss dielectric factor (tan δ) with the frequency are plotted in Fig. 5. Characteristics were made for the unannealed sample and for the very same sample after annealing at 200°C and then at 400°C. As it can be seen the influence of the annealing on capacity and loss is rather strong. Then, for obtaining stable capacity and low loss capacitors adequate annealing process seems to be necessary.

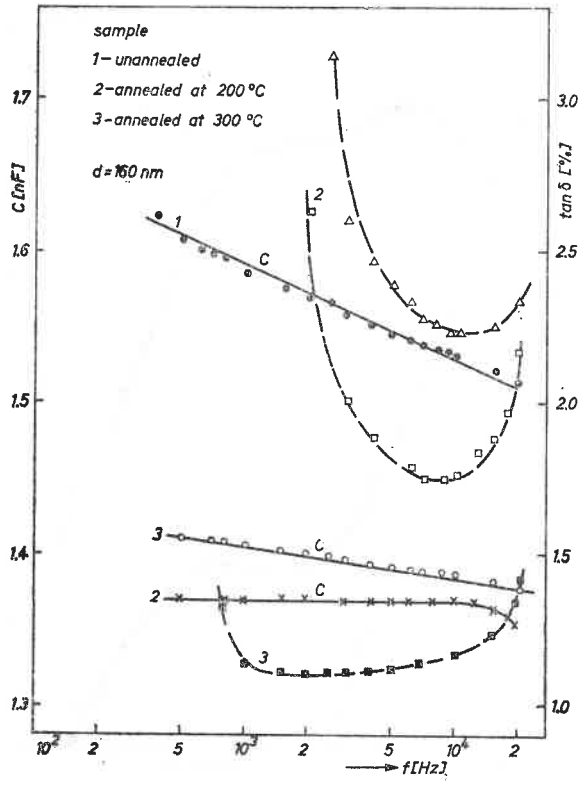


Fig. 5. The influence of the annealing on the capacity C and loss dielectric factor tan δ; continuous line — C vs f, dashed line — tan δ vs f

4. Conclusions

On the basis of presented preliminary investigations and obtained results we can make following conclusions [9]:

1. It is possible to prepare with relative ease homogeneous polycrystalline thulium oxide films by electron gun method.

2. The obtained films are characterised by high resistivity of the order $10^{13}\ \Omega \cdot \mathrm{cm}$ and after annealing even up to $10^{14}\ \Omega \cdot \mathrm{cm}$. Then thulium oxide is a typical dielectric with energy gap of about 5.1 eV.

3. The sufficient annealing of investigated thulium oxide films appreciably improves their dielectric properties.

4. Dielectric constant, loss factor and breakdown voltage of examined films depend on preparation conditions and it seems that picking them out properly we can obtain thin-film capacitors with $\varepsilon = 14$–15, $U_b \geqslant 3 \times 10^6$ V/cm and $\tan \delta \leqslant 1\%$ (see Table I), giving high capacity per unit area ($> 0.1\ \mu\mathrm{F/cm^2}$). However, to obtain the most favourable devices, properly fitted deposition and annealing conditions are indispensable.

For precise knowledge of composition of obtained films quantitative chemical analysis is also necessary.

For better examining of conduction mechanisms measurements at low temperatures and high frequencies will be performed by us.

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