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DIELECTRIC AND OPTICAL PROPERTIES OF EUROPIUM OXIDE FILMS

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The dielectric properties of vacuum-deposited europium oxide films have been investigated in the frequency range from 1 kHz to 1 MHz at various temperatures (300–543 K). The dielectric constant is found to depend on film thickness and it attains a constant value beyond 1000 Å. Films deposited at higher substrate temperatures (above 423 K) exhibit improved dielectric properties owing to the recovery of stoichiometry. The frequency variation of the loss factor exhibits a minimum which increases with rise in temperature. The breakdown field strength (about 10^6 V cm^{-1}) is found to be thickness dependent and it varies in accordance with the Forlani–Minnaja relation. The films exhibit ohmic conduction with an activation energy of 0.86 eV at low electric fields but at higher fields the conductivity becomes space charge limited. X-ray studies show that the films are amorphous in nature. The a.c. conductivity is proportional to ω at low frequency, whereas a square law dependence is observed at higher frequencies. The optical constants n, α and k and optical band gap are calculated from the UV–visible–near-IR spectra.

1. INTRODUCTION

Rare earth oxide films have been studied previously[1–5] with a view to their use in thin film capacitors in which the required degree of perfection varies according to the specific application. The high dielectric constant and low dielectric loss are generally desirable for low volume capacitors. The variations in these parameters with temperature, frequency, film thickness and applied field are also of such importance as to merit serious consideration in many situations. While a low dielectric constant is preferable for insulating films, dielectric constants in the range 7–30 and relatively low dissipation factors of 0.55%–2.5% are reported for oxides of lanthanum[6], cerium[7], neodymium[4], dysprosium[3] and erbium[1]. Studies on Eu_2O_3 [5], Pr_2O_3 [8], Nd_2O_3 [4] and Dy_2O_3 [3] thin films, which form useful capacitors, revealed a thickness-dependent dielectric constant. The dielectric properties of rare earth oxide films are found to change with annealing or aging and they required an annealing time of about 200 h to have stable dielectric properties[5]. In this paper we report the dielectric and optical properties of evaporated Eu_2O_3 films which exhibit improved dielectric properties when prepared with higher substrate temperatures.

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2. EXPERIMENTAL DETAILS

High purity (99.99%) Eu_2O_3 pellets were vacuum deposited from tungsten baskets onto thoroughly cleaned glass substrates maintained at a temperature of 150 °C. Vacuum-evaporated aluminium (99.99%) thick films (about 0.2 μm) form the rear and front electrodes in a metal–insulator–metal structure. The effective area of a capacitor thus fabricated was 0.36 cm^2. The dielectric and electrical measurements were carried out under vacuum (10^{-2} Torr) conditions. The film thickness was measured by Tolansky's interference method with an accuracy of ± 10 Å.

The capacitance and loss factor were measured over a range of frequencies (1 kHz–1 MHz) and temperatures (300–543 K) for various film thicknesses (500–2500 Å) using a 0.1% Universal Bridge and LCZ Bridge (Hewlett–Packard model 4277A). The temperature was monitored using a chromel–alumel thermocouple with an accuracy of ±1 °C. The dielectric constant was evaluated from the capacitance measurement data using the area and thickness of the film. The current–voltage characteristics and breakdown voltage were measured using an electrometer and a $4\frac{1}{2}$ digit autoranging multimeter. The optical constants were calculated from the transmittance spectra in the UV–visible–near-IR region obtained using a Hitachi spectrophotometer (model 330).

3. RESULTS

3.1. X-ray diffraction

X-ray diffraction studies show that the films obtained are essentially amorphous in nature. No indications of crystallinity were observed for films deposited at substrate temperatures of 150–170 °C.

3.2. Dielectric properties

Figure 1 shows the variation in dielectric constant ε and loss factor $\tan\delta$ as a function of Eu_2O_3 film thickness. The dielectric constant evaluated from the measured capacitance and dimensions of the film increases with increase in film

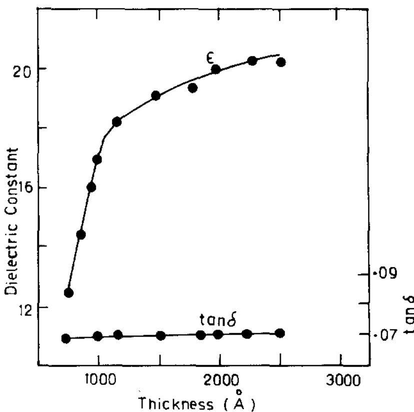

Fig. 1. Variation in dielectric constant ε and loss factor $\tan\delta$ with dielectric film thickness.

thickness and attains a steady value of 20.4 for insulator thicknesses greater than 1000 Å. The loss factor of 0.07 evidently is independent of film thickness. A similar thickness dependence of ε has been observed for thin films of other rare earth oxides[3–5].

Figure 2(a) shows the variation in dielectric constant ε with frequency at different temperatures for a film thickness of 1200 Å. At higher temperatures ε increases drastically with decrease in frequency. The variation in ε with frequency is small at room temperature. From the plot of capacitance *vs.* temperature at different

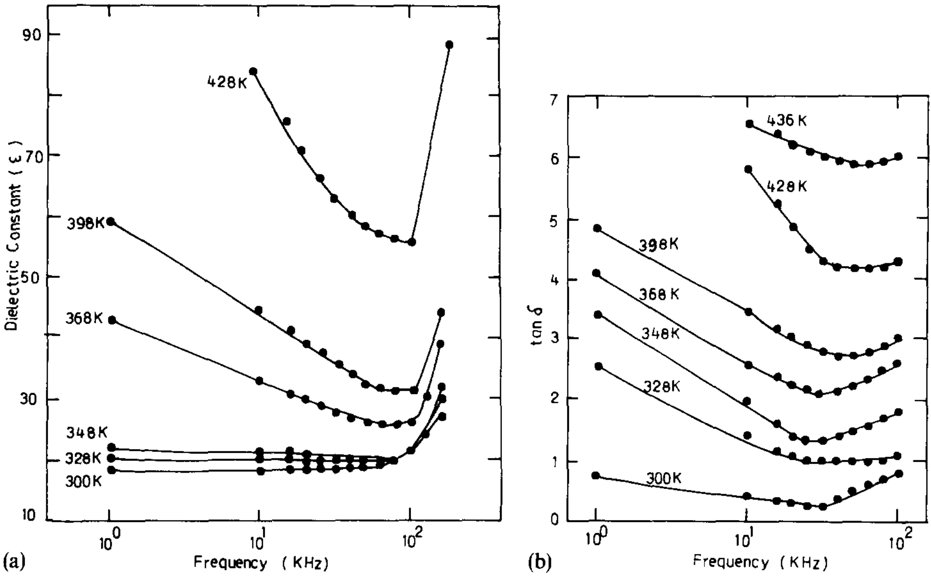

Fig. 2. (a) Variation in dielectric constant ε with frequency at different temperatures (film thickness, 1200 Å); (b) variation in tan δ with frequency at different temperatures (film thickness, 1200 Å).

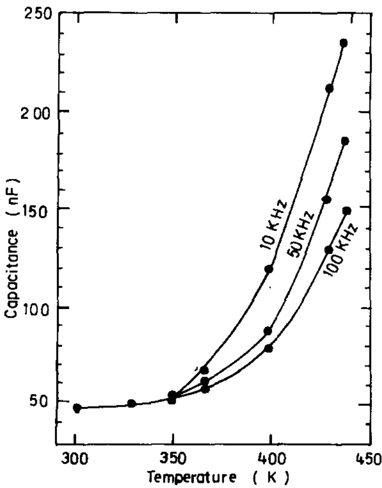

Fig. 3. Capacitance *vs.* temperature at different fixed frequencies (film thickness, 1200 Å).

frequencies (Fig. 3) it is observed that below room temperature the plots merge to a single curve and the capacitance varies only slightly when the temperature is low. On extrapolating we obtain the value of static dielectric constant $\varepsilon_s = 16.4$. The temperature coefficient of capacitance $\gamma_c = (1/C)\mathrm{d}C/\mathrm{d}t$ was also obtained from the graph, and this has a value of 234 ± 10 ppm K^{-1} at room temperature (evaluated at 1 kHz). This value compares favourably with those reported in the literature[3,9,10] for other well-known dielectric materials. The variation in $\tan\delta$ with frequency at different temperatures is shown in Fig. 2(b). The $\tan\delta$ value decreases with increase in frequency and attains a minimum value which itself decreases at higher temperatures. At low temperatures the decrease in $\tan\delta$ with frequency is less marked.

3.3. *Electrical properties*

From the current–voltage I–V measurements carried out it can be seen that the films exhibit ohmic conduction at low electric fields but at higher fields the conduction becomes space charge limited so that $I \propto V^2$. From the conductivity plot ($10^3/T$ *vs.* $\ln\sigma$; Fig. 4) the activation energy is found to be 0.86 ± 0.03 eV. The space-charge-limited current and low activation energy suggest the presence of shallow traps in the films. Consequently the observed activation energy is less than the expected band gap.

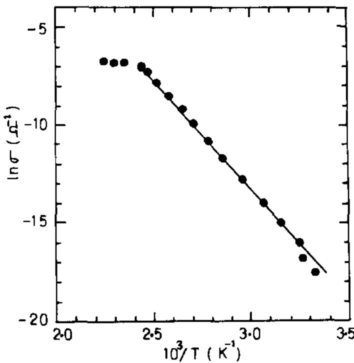

Fig. 4. $\ln\sigma$ *vs.* $10^3/T$.

The dielectric breakdown field strength F_b is of the order of 10^6 V cm^{-1}. The breakdown strength F_b is found to decrease with increase in film thickness. A log–log plot of the dielectric breakdown strength *vs.* film thickness yields a straight line (Fig. 5) with a negative slope of 0.518 from which it can be found that the breakdown field strength follows the Forlani–Minnaja [11] relation: $F_b \propto d^{-1/2}$.

The variation in a.c. conductivity at various temperatures with frequency is shown in Fig. 6. Here the conductivity exhibits two distinct dispersive regions, one below 100 kHz and the other above it. The a.c. conductivity is porportional to ω in the first region and becomes proportional to $\omega^{1.9}$ in the second region at room temperature. The same trend is also observed at higher temperatures. The second region of the conductivity thus exhibits a square law dependence on frequency.

From the plot of ln σ *vs* $10^3/T$ the activation energy is calculated to be 0.13 ± 0.03 eV in the temperature range 300–365 K at 10 kHz (Fig. 6).

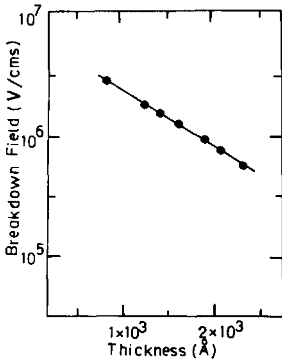

Fig. 5. Breakdown field strength *vs.* dielectric film thickness.

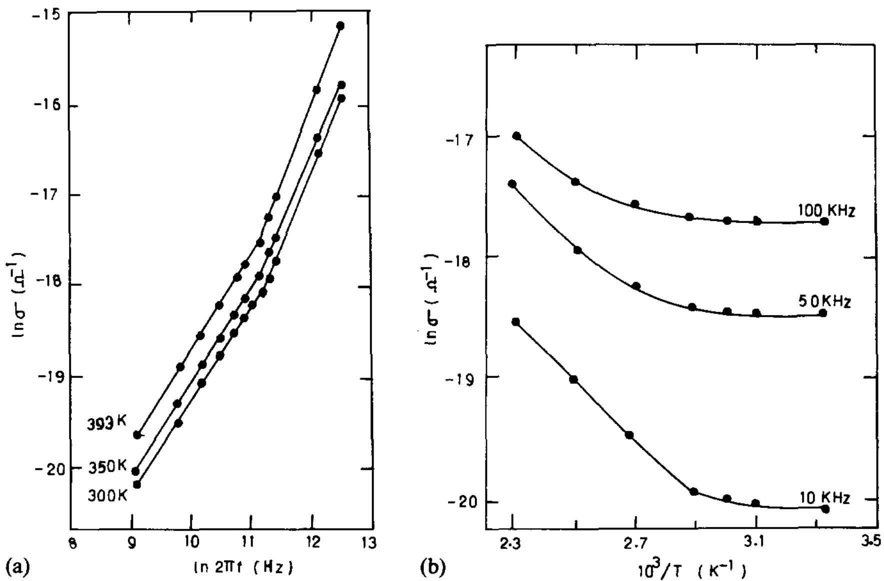

Fig. 6. (a) A.c. conductivity *vs.* frequency at different temperatures (film thickness, 1200 Å); (b) ln σ *vs.* $10^3/T$ at different fixed frequencies (film thickness, 1200 Å).

4. OPTICAL PROPERTIES

To evaluate the optical constants we used the method proposed by Manifacier *et al.*[12] which makes use of the fringe pattern of the transmission spectrum of a thin transparent dielectric film surrounded by non-absorbing media. The film can be considered to be bounded by two transparent media with refractive indices n_0 and n_1. If we consider a unit amplitude for the incident light (in this case normal

incidence) and the case of weak absorption where $k^2 \ll (n-n_0)^2$ and $k^2 \ll (n-n_1)^2$, the transmission T is given by

$$T = \frac{16 n_0 n_1 n^2 \alpha_1}{c_1{}^2 + c_2{}^2 \alpha_1{}^2 + 2 c_1 c_2 \alpha_1 \cos(4\pi n t/\lambda)} \tag{1}$$

where

$$\begin{aligned} c_1 &= (n+n_0)(n+n_1) \text{ and } c_2 = (n-n_0)(n_1-n) \\ \alpha_1 &= \exp(-4\pi k t/\lambda) = \exp(-\alpha t) \end{aligned} \tag{2}$$

Here α is the absorption coefficient of the thin film and t is its thickness; k and λ are the extinction coefficient and the wavelength of the light respectively.

The extreme values of the transmission are given by

$$T_{max} = 16 n_0 n_1 n^2 \alpha_1/(c_1 + c_2 \alpha_1)^2 \tag{3}$$

$$T_{min} = 16 n_0 n_1 n^2 \alpha_1/(c_1 - c_2 \alpha_1)^2 \tag{4}$$

Thereby

$$n = \{N + (N^2 - n_0{}^2 n_1{}^2)^{1/2}\}^{1/2} \tag{5}$$

where

$$N = \frac{n_0{}^2 + n_1{}^2}{2} + 2 n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}}$$

Thus n can be determined from knowledge of T_{max}, T_{min}, n_1 and n_0 at the same wavelength. The accuracy in n is a critical function of the errors in the measured values of T_{max} and T_{min}. In the best case the precision possible in these measurements is of the order of 1% giving an overall accuracy of 2% for the value of n. Using eqns. (3) and (4) we can find α_1 and then eqn. (2) gives the absorption coefficient α and extinction coefficient k. Figure 7 shows the variation in n and k with wavelength. The value of the refractive index is found to remain constant (about 1.64) in the visible and IR regions. Outside the region of fundamental absorption, the dispersions of n and k are not very large. The absorption coefficient α and extinction coefficient k evaluated from the transmission data were found to be almost zero for longer wavelengths, *i.e.* below the fundamental absorption frequency. Figure 8 shows the dependence of absorption coefficient on photon energy. The optical absorption data of Eu_2O_3 films were examined for evidence of either indirect or direct transitions in accordance with the theory of Bardeen *et al.*[13] For such transitions

$$\alpha = \frac{A(h\nu - E_g' \pm E_p)^r}{h\nu}$$

where $r = 3$ for forbidden indirect transitions, $r = 2$ for allowed indirect transitions and E_g' is the indirect band gap, E_p being absorbed or emitted phonon energy. The plot of $(\alpha h\nu)^2$ *vs.* photon energy $h\nu$ gives a straight line portion and on extrapolation the intercept gives a band gap of 3.38 ± 0.1 eV. Thus the conclusion may be drawn that the transition leading to fundamental absorption takes place at 3.38 ± 0.1 eV and the transition is indirect.

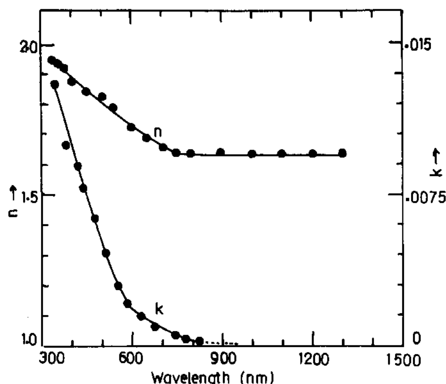

Fig. 7. Variation in refractive index and extinction coefficient of the dielectric film with wavelength.

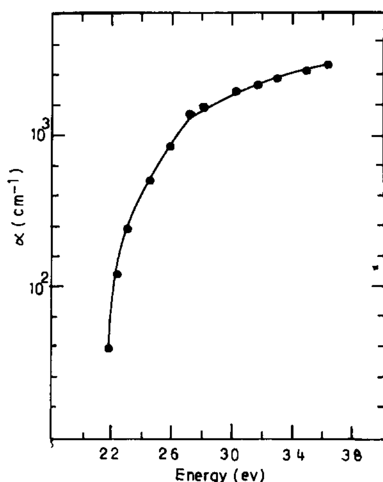

Fig. 8. Absorption coefficient α *vs.* photon energy $h\nu$.

5. DISCUSSION

The results outlined above give clear indications of the physical behaviour of Eu_2O_3 films prepared in the laboratory. The films are essentially amorphous in nature and the X-ray studies reveal no crystallinity for films prepared at higher substrate temperatures. This is fully in accordance with the observation that vacuum-evaporated rare earth oxide films are generally amorphous in nature[3–5]. The observed thickness dependence of the dielectric constant for films of thickness less than 1000 Å is apparently due to defects such as voids, stress and inhomogeneity which are normally present in vacuum-deposited films rather than being due to non-stoichiometry of the deposits caused by excess of oxygen or metal ions. As films become thicker, the density of voids decreases[14], resulting in higher values of the dielectric constant, which eventually becomes thickness independent. A theoretical

analysis by Kornyshev *et al.*[15] suggests that the observed effect was too large to be ascribed to the non-local nature of the dielectric response alone and the presence of voids and other inhomogeneities contributes to the observed anomaly in rare earth oxide films. The observed dependence of ε and $\tan\delta$ on frequency and temperature may be accounted for by considering the equivalent circuit proposed by Goswami and Goswami[16]. This comprises an inherent capacitive element C_i unaffected by frequency and temperature, a discrete resistance element R which is assumed to be temperature dependent and in parallel with C_i and a series resistance r due to lead resistance. The effective capacitance with series resistance increases with decreasing frequency when R is small[16]. The decrease in $\tan\delta$ with frequency seen at high temperatures may be similar to the effect of the shunt resistance R. In contrast, when the temperature is low the shunt resistance R can be neglected and the rise in $\tan\delta$ at high frequencies is probably due to the electrode resistance[16].

The d.c. current–voltage measurements show that the specimens exhibit ohmic conduction at low electric fields but at higher fields $I \propto V^2$. The activation energy of 0.86 eV and the fact that the d.c. conduction in the films is space charge limited at higher fields suggest the presence of shallow traps. A.c. conductivity is proportional to ω at low frequencies and has a square law dependence at higher frequencies. The low activation energy coupled with the square law dependence of the conductivity on frequency suggest the prevalence of an electronic hopping conduction mechanism[17,18].

The optical constants calculated from the fringe pattern of transmission spectra show that the absorption coefficient is almost zero above the fundamental absorption wavelength. Also, the refractive index is almost constant at 1.64 above 4500 Å. The optical band gap is found to be 3.38 ± 0.1 eV, which is comparable with that of other kinds of insulators[19].

6. CONCLUSION

The dielectric and optical properties of Eu_2O_3 films obtained by the vacuum evaporation of bulk material have been presented. The films possess high dielectric constant, good stability, low dissipation factor and low temperature coefficient of capacitance. The characteristics of the films are suitable for device applications. The Eu_2O_3 film described here has been successfully made use of for low voltage operation of a.c. thin film electroluminescent devices[20] in metal–insulator–semiconductor–metal structures.

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