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A. C. behaviour and dielectric relaxation in indium oxide films

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Abstract. Vacuum deposited blackish indium oxide films (In–O) as well as the oxidised films (In_2O_3) were studied for their a.c. behaviour at different temperatures and at various film thicknesses in the audio frequency region. ϵ of In–O films was thickness dependent and also showed dielectric relaxation at lower frequencies due to the dipolar orientation arising from their non-stoichiometric nature. However at liquid nitrogen temperature region ϵ was thickness independent similar to the oxidised films which neither showed any relaxation effect nor any thickness dependent ϵ. The results have been discussed from the classical theory of dielectric polarisation.

Keywords. Dielectric relaxation; a.c. properties; indium oxide films.

List of symbols

α — Absorption coefficient
$\tan\delta$ — Loss factor
ϵ — Dielectric constant
ϵ'' — $\epsilon \tan\delta$
π — Constant
ρ — Resistivity
τ — Relaxation time
ω — Angular frequency
a — Lattice constant
d — Film thickness
f — Frequency
k — Absorption index: Boltzmann constant
n — Refractive index
r — Lead resistance
C — Capacitance
Q — Dipole thermal activation energy
R — Film resistance
T — Absolute temperature

1. Introduction

Recent studies on several dielectric films (McLean 1961, Gaffee 1962, Maddocks and Thun 1962, Hirose and Wade 1964, Goswami and Goswami 1973, 1974 *a*,

1975 *a*, *b*) have shown that these films had thickness independent dielectric constants (ϵ), a loss minima ($\tan \delta_{min}$) in the audio frequency range, negligible absorption indices (k) and absorption coefficients (α), etc., in the visible region. Vacuum deposits of a few oxide films, *viz.*, molybdenum oxide (Nadkarni and Simmons 1970), niobium oxide (Nb-O) (Goswami and Goswami 1974 *b*), on the other hand, showed thickness dependent ϵ, loss peaks, and comparatively large k and α. During our preliminary studies of vacuum deposits of indium oxide which was blackish in nature, it was observed that these had thickness dependent ϵ (Goswami and Goswami 1974 *c*) similar to those of Nb–O film (Goswami and Goswami 1974 *b*) whilst for the thermally oxidised films (In_2O_3) ϵ was thickness independent. A comparative study has therefore been made on the a.c. behaviour of two types of indium oxide films and is presented below.

2. Experimental

The oxide films prepared by the thermal evaporation in vacuo ($\sim 10^{-5}$ torr) of the bulk indium oxide powder (99·999% purity, supplied by Fluka AG) from a preflashed Mo-boat were blackish in colour (hereafter In–O). These were then deposited on precleaned glass substrates already having a thick layer of Al film to be used as a base electrode. Capacitors of the type Al/In–O/Al of different oxide film thicknesses (200–4400 Å) were then fabricated, aged at room temperature and finally annealed by repeated heating and cooling cycles in vacuo between 27–110°C in the manner described already (Goswami and Goswami 1973). These post fabrication treatments were essential for the reproducibility of the results. In some cases a long ageing say for about a year was also carried out.

For the fabrication of the oxidised film capacitors, the blackish (In–O) films were first deposited on Al coated glass substrates. These films were then oxidised in air for about 2 hr at about 320°C. The oxidised dielectric layers thus formed (hereafter In_2O_3) were transparent showing an interference colour. The resistance of these films increased enormously whilst that of the base electrode did not change significantly. The counter electrode also of Al was then vacuum deposited to form Al/In_2O_3/Al types of capacitors. These were then given post treatments similar to those of Al/In–O/Al capacitors.

Capacitance (C), loss factor ($\tan \delta$), etc., were measured in the a.f. range (10^2–10^5 Hz) between 88–360°K in a set-up consisting of cryostat, microvoltmeter, Marconi Universal Bridge (Model TF 2700), frequency generator, etc., in the manner already described (Goswami and Goswami 1973) and ϵ and ϵ'' ($\epsilon \tan \delta$) evaluated. Film thickness (d) of the oxide layers was estimated by the multiple beam interferometry technique. The details of capacitor fabrication, measurements, precautions, etc., had been described in our previous papers. X-ray and electron diffraction methods were used respectively for the phase structures of the bulk and the deposited films.

3. Results

A. *In–O films*

The bulk indium oxide powder was crystalline and had the normal b.c.c. structure ($a = 10 \cdot 12$ Å) conforming to In_2O_3. The blackish In–O films as found by

electron diffraction method were either amorphous or had a fine grained structure. These films also had a high k (0·7–1·2) depending on the film thickness and the wavelength of the light.

(i) Thickness and temperature effects on C and ϵ.

The variations of C and ϵ with $1/d$ at 88° K and 300° K are shown in figure 1. It is seen that whilst C remained practically constant for all film thicknesses at 300° K, ϵ however increased considerably from about 10 to 320 with increasing d. A similar change of ϵ was also observed at other temperatures ranging between 260–360° K. But at a very low temperature ($\sim$ 88° K), the variations of C and ϵ were different, ϵ being constant ($\sim$ 53) for all film thicknesses $>$ 1000 Å (figure 1) as observed for ZnS, Sb_2O_3, Dy_2O_3 and praseodymium oxide films reported by us earlier. A slight thickness dependence of dielectric constant for thinner films was no doubt associated with the presence of voids, discontinuities, etc., as explained previously for ZnS and other films. The temperature dependence of ϵ and C of In–O films will be discussed later.

(ii) Effects of frequency (f) and temperature on C, tan δ, etc.

Capacitance generally decreased with the increase of frequency ($f = \omega/2\pi$) and the decrease of temperature, but never attained a constant value even at the highest frequency ($\sim 10^5$ Hz) unlike ZnS and other films. Figure 2 shows typical tan δ vs. f graphs at different temperatures for $d \sim$ 2350 Å. It is seen that tan δ_{min} occurred at a characteristic frequency (denoted by f_{min}) depending on the temperature and the variation of tan δ_{min} was not regular with either the rise or fall of temperatures unlike ZnS films. This irregularity in tan δ or f_{min} with temperatures around 297° K was similar to those of Nb–O films observed by us earlier. When the graph was replotted with tan δ against f at the same temperature region a prominent loss peak could be seen (figure 3) and this showed a shift towards

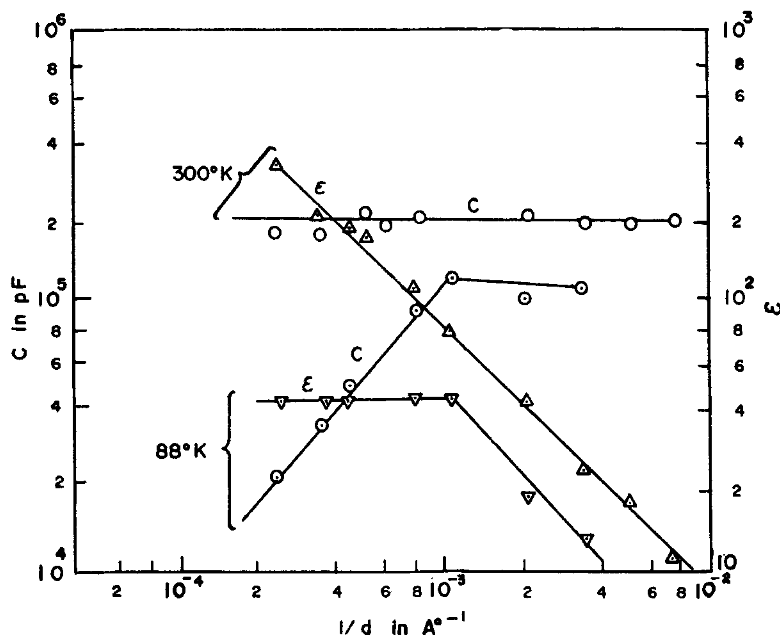

Figure 1. Variation of C and ϵ with $1/d$ at 300° and 88°K.

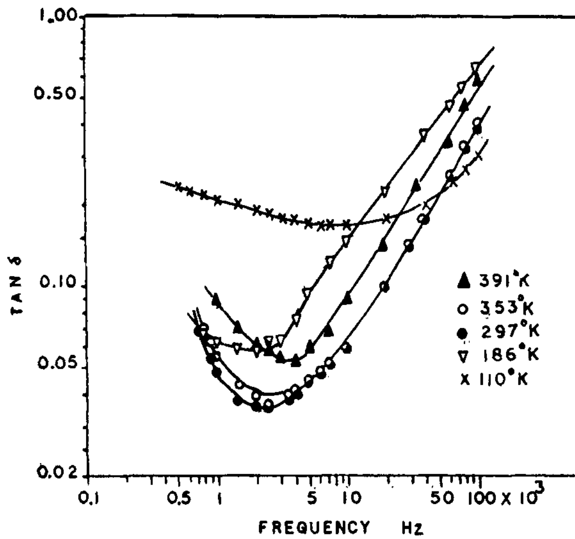

Figure 2. Variation of tan δ with f at different temperatures.

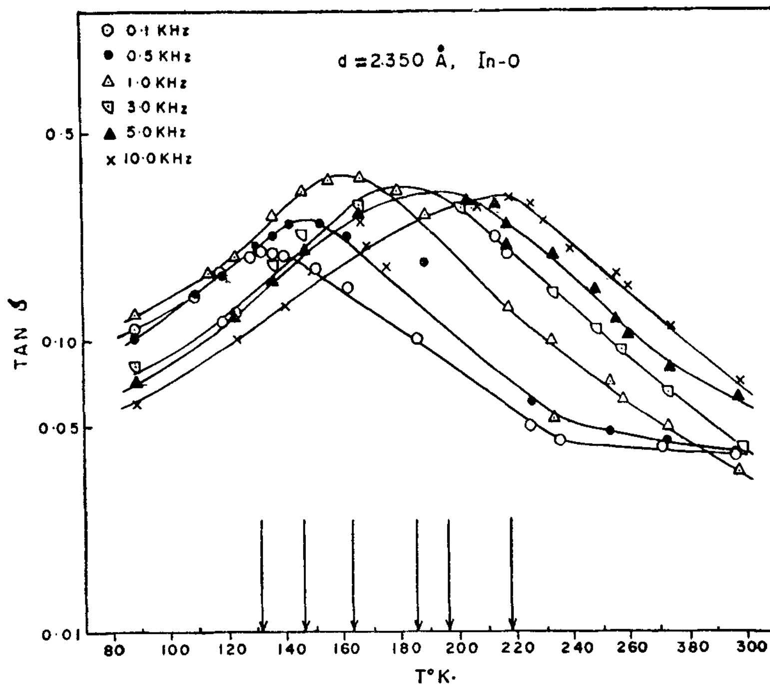

Figure 3. Variation of tan δ with temperature at different frequencies, $d = 2350$ Å

the higher temperature region with the rise of f. Similar peaks reported previously (Harrop and Wynklyn 1964, Barkhardt 1966, Goswami and Goswami 1974 *b*) had been ascribed to the dielectric relaxation phenomenon arising from the dipolar orientations. However, peaks observed in the vacuum deposited molybdenum oxide films were attributed to the presence of barrier layers between the electrodes and the dielectric oxide layers by Simmons and co-workers (Nadkarni and Simmons 1970, Simmons *et al* 1970).

The relaxation observed in the present case was also confirmed by plotting both ϵ and ϵ'' against f at different temperatures (figure 4). ϵ decreased slowly with the rise of temperature, but ϵ'' despite its slow rise at the initial stage increased rapidly, attained a maximum and decreased further with increasing f. It is interesting to note that the peak shifted towards the low frequency region with the lowering of temperature, but at a very low temperature region (say $\sim$88 °K or less) no peak in ϵ'' could be observed at the lowest frequency of our measurements. This clearly indicated the absence of any dielectric relaxation phenomena. Similar features were also observed for other film thicknesses. A Cole–Cole plot of ϵ'' vs. ϵ over the a.f. range for different temperatures is shown in figure 5. All the points lie on an arc of a circle which finally tends to become a semicircle with the increase of temperature. This deviation from an ideal semicircle at lower temperature region can be attributed to the spread in the relaxation time.

(iii) Dipole thermal activation energy (Q).

An average value of Q was calculated using the relation f(relaxation frequency) $= f_0 \exp(-Q/kT)$ (Nadkarni *et al*, Simmons *et al*, *loc. cit*) and by plotting the frequency where f_{max} occurred (figure 3) against $1/T$ (figure 6). Table 1 shows Q obtained from slopes for different values of d. It is seen that Q decreased with increasing d and had a tendency to become constant at higher film thicknesses.

B. *Oxidised films* (In_2O_3)

These films as mentioned earlier were transparent and showed interference colour. Electron diffraction studies of films formed on glass or NaCl substrates

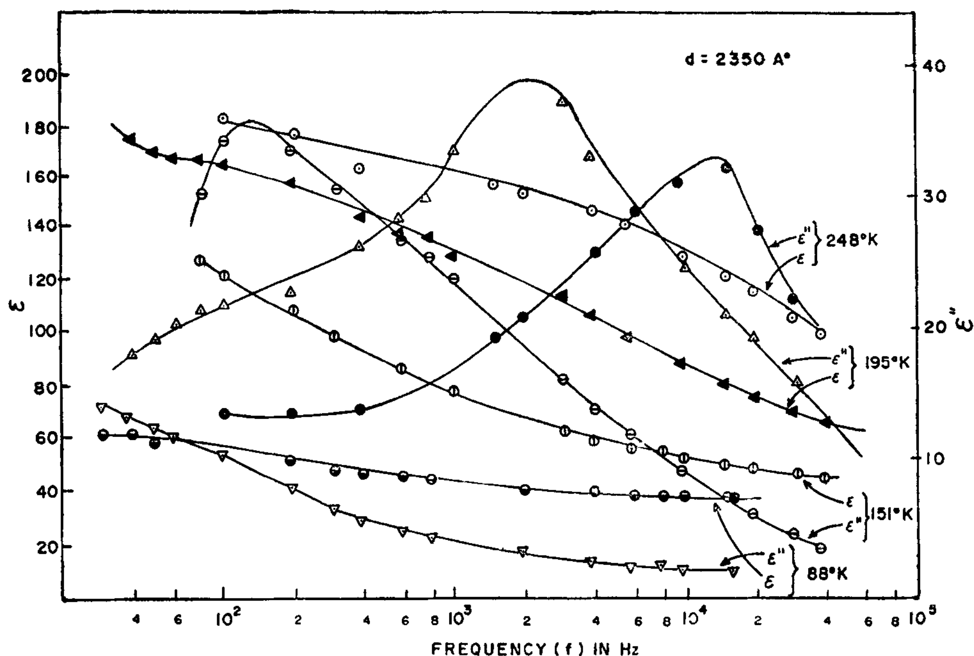

Figure 4. Variation of ϵ and ϵ'' with f at different temperatures, $d = 2350$ Å.

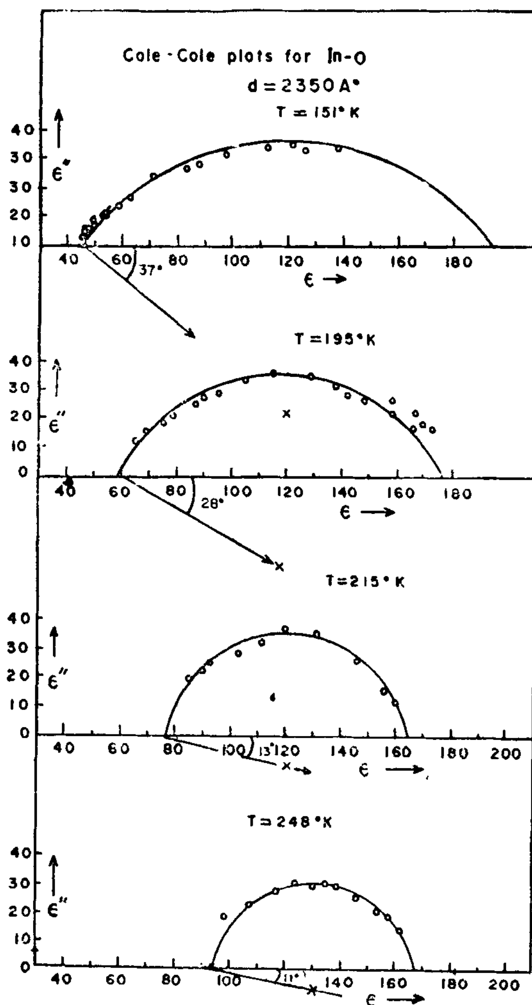

Figure 5. Variation of ϵ'' with ϵ at different temperatures, $d = 2350$ Å.

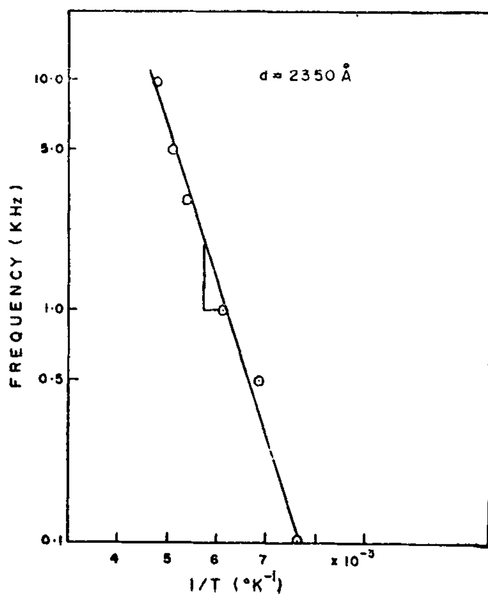

Figure 6. Variation of f_{max} with $1/T$, $d = 2350$ Å.

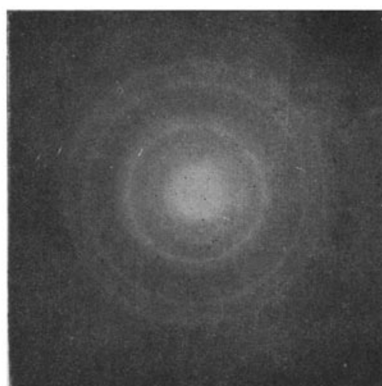

Figure 7. Electron diffraction patterns of polycrystalline In_2O_3 films.

Table 1. Variation of Q with film thickness (d)

d (in Å)	136	300	495	1120	1665	2350	3900
Q (in eV)	0·406	0·39	0·39	0·385	0·375	0·35	0·347

both by reflection and transmission techniques revealed that the deposits were crystalline and had a b.c.c. structure ($a \sim 10 \cdot 12$ Å) (figure 7) conforming to the bulk In_2O_3.

(i) Effect of d on C and ϵ.

The variation of C and ϵ with $1/d$ is shown in figure 8. Whilst C continually decreased with increasing d, except for very thin films, ϵ was constant (~ 60) similar to those of ZnS deposits. These features are no doubt in contrast to those of In–O films where ϵ continually increased with d at most temperature except for very low ones. Tan δ in the case of In_2O_3 film capacitors was very low ($\sim 0 \cdot 05$–$0 \cdot 07$) and more or less independent of film thicknesses.

(ii) Frequency and temperature effect on C, tan δ, etc.

A typical variation of C with f for $d \sim 1880$ Å at different temperatures is shown in figure 9. Capacitance decreased not only with the lowering of temperature but also with the rise of frequency and became invariant nearly at the liquid nitrogen temperature unlike In–O films. Figure 10 shows the variation of f and temperature on tan δ, where tan δ_{min} occurred at a frequency f_{min} depending on temperature. Further f_{min} shifted gradually to the higher frequency with the rise of temperature as observed previously for ZnS, Sb_2O_3, praseodymium oxide and Dy_2O_3 films (*loc. cit.*) in contrast to In–O and Nb–O films where the variation was irregular and overlapping of tan δ_{min} occurred. In_2O_3 did not show any tan δ peak at all even at lower frequencies and temperatures.

4. Discussion

The above studies clearly demonstrated the marked differences in the structural and a.c. behaviour of absorbing In–O and transparent oxidised (In_2O_3) films. Since In–O films were easily oxidised to In_2O_3 in air, the former must have been a lower oxide or suboxide of indium resulting from the dissociation of In_2O_3 in vacuo during deposition in the manner Nb–O was formed from Nb_2O_5 (Goswami and Goswami 1974 *b*). Similar dissociations had also been previously reported by various workers (Mellor 1934, Goswami and Trehan 1957, Goswami 1965.) The dissociation of In_2O_3 during vacuum evaporation to species like InO, In_2O, In, etc., had also been previously reported (Thiel and Luckmann 1928, Burns 1966). It is therefore reasonable to conclude that the In–O films really consisted of In_2O_3 mixed with varying amounts of the above dissociated species thus leading to the formation of non-stoichiometric composition with the above species embedded in the In_2O_3 lattice matrices. The resulting oxide layer could then be considered to have a high concentration of impurities or doping agents. Consequently, the electrical behaviour will be similar to those of vacuum deposited molybdenum oxide films which also had a high doping concentration.

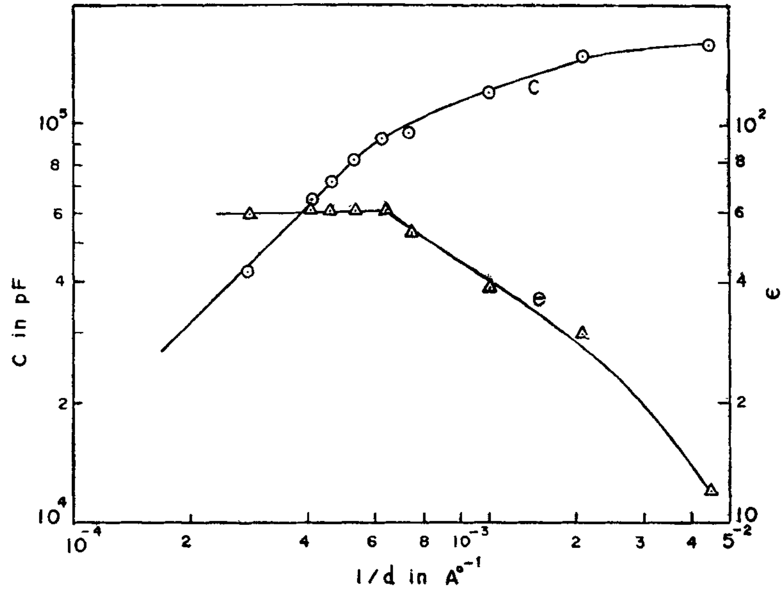

Figure 8. Variation of C and ϵ with $1/d$ at 1 kHz at room temperatur:

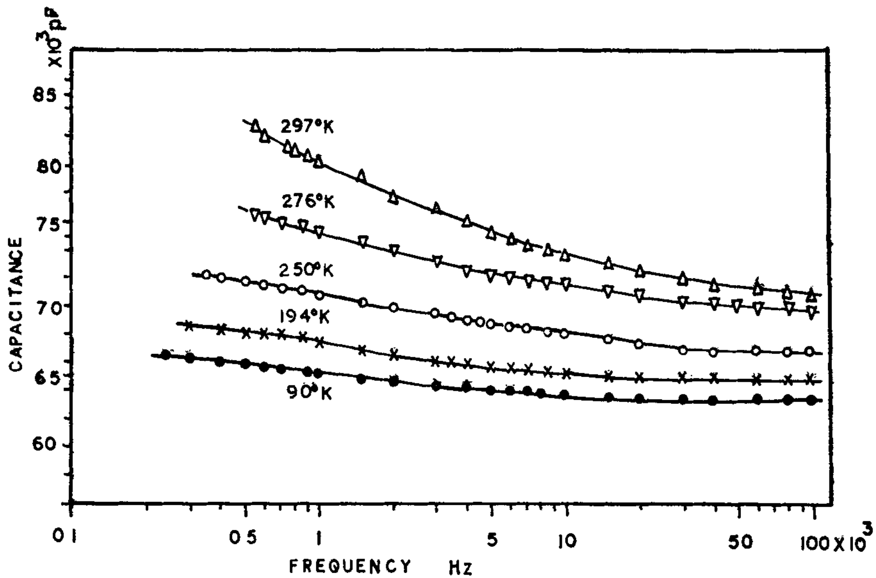

Figure 9. Variation of C with frequency at different temperatures (d = 1880 Å)a

Various features of In–O films namely the variations of ϵ with film thickness, invariant capacitance with the frequency at room temperature, ϵ'' vs. ϵ graphs lying on arcs tending to be on semi-circles with the change of temperature, etc., clearly demonstrated the relaxation effect. This could also arise either due to dipole orientations as a consequence of the classical theory (Debye 1912) or alternatively from the Maxwell-Wagner dispersion effects (Wagner 1914) where the system was supposed to be heterogenous involving a definite interface between the

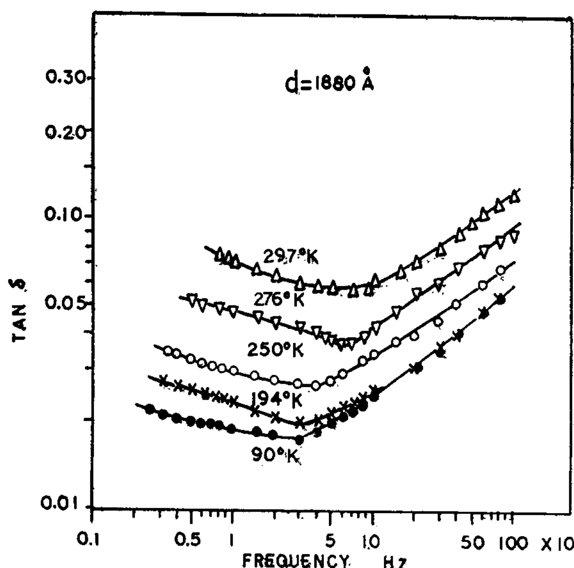

Figure 10. Variations of tan δ with frequency at different temperatures ($d = 1880$ Å).

various species and the medium as observed in the case of biological macromolecules or colloidal suspensions in water (Schwan *et al* 1962). Since electron microscopic examination of In–O films did not reveal any distinct interface or boundaries and in fact the films were homogenous without showing any distinctive features, the latter alternative, *i.e.*, dispersion effect was ruled out. Consequently, the relaxation phenomenon was due to the dipole orientations. Another possibility, *i.e.*, interfacial polarisation was also not likely since it could generally occur at an extremely low frequency range (0·01 to 1 Hz) (Weaver 1962, MacFarlane and Weaver 1966, Harrop and Campbell 1970). The relaxation frequency (f_{relax}) was also temperature sensitive. Since at low temperatures ($\sim 88\,°$K) no peak was observed even at a frequency as low as 15 Hz, it was concluded that the dipoles which could rotate at higher temperatures were frozen and became immobile thus suppressing the orientational effects.

The shift of the relaxation peak to the higher frequency region with the rise of temperature and *vice versa* was also in accordance with the Debye theory of dipole orientations. f_{relax} defined as the reciprocal of the relaxation time (τ), would be at the higher frequency region when τ was less and *vice versa.* Further, because of the inherent hindrance of the medium, the dipoles would require some definite interval of time to orientate themselves with the a.c. field to show the effect. Consequently with the increase of temperature, τ would decrease and f_{relax} would now occur at the higher a.f. range as observed by us.

It was also found during our optical studies that with the increase of the film thickness, both k and α increased thus suggesting a corresponding increase of the defect concentrations and hence of the dipoles. Since tan δ_{peak} or ϵ''_{peak} also increased with the film thickness this rise appeared to be due to the increase of the dipole concentration (Harrop and Wynklyn 1964).

The thickness effects on C and ϵ at room temperature and at 88 °K were similar to those of MoO_3 films. Because of the high impurity concentration, the dielectric

layers would show considerable conductivity even at room temperature and these would then act as shunt resistance or impedance in the a.c. field. Hence capacitance measured would no longer be the real one and ϵ thus evaluated would not be the characteristic of the material. However when chilled to $\sim 88\,^\circ$K, the mobile charge carriers introduced by the impurity would be frozen and the deposits would have the usual high resistivity leading to a constant ϵ which was close to that of bulk In_2O_3.

It is interesting to mention that similar conclusions can also be arrived at from the phenomenological consideration of the dielectric behaviour. At extremely low temperatures ($\sim 88\,^\circ$K) the dipoles could not contribute much to dielectric constant because of the hindrance to their rotation and hence the contribution would predominantly be due to atomic and electronic polarisation thus leading to a constant ϵ. However, with the increase of temperature the contributions from dipolar orientation would increase considerably and hence ϵ would also increase.

The a.c. behaviour of the oxidised film capacitors was very similar to those of the ZnS films studied by us earlier. The dependence of ϵ on the film thickness for thinner deposits could be attributed chiefly to the defects such as voids present in these films. For thicker films, however, ϵ was constant (~ 60) at 1 kHz at room temperature. The temperature variations of capacitance and tan δ, etc., can be explained with the help of eq. (9) of our paper on ZnS film capacitors (Goswami and Goswami 1973). The effect of frequency at different temperatures and also the occurrence of tan δ_{min} and its shift to higher frequencies with the increase of temperature are the direct consequences of our model proposed for ZnS film capacitors. With the help of eq. 9 *b* of our paper, the electrode lead resistance (r) was calculated and found to be about $1 \cdot 2$ ohm which was independent of frequency and temperature, a condition predicted from the theoretical model. From the ω_{min} value, the resistance (R) and the resistivity (ρ) of the dielectric films were evaluated. A similar calculation of resistance (R) were also made from the relation tan $\delta = 1/\omega RC$ at 1 kHz. Both these values were found to agree reasonably well and the resistivity at room temperature was found to be about 10^8 ohm cm. This is also consistent with the high value of energy band gap obtained from optical measurements.

It is interesting to note that whilst the dielectric constant of In_2O_3 in the audio frequency region was ~ 60, the contribution from the electronic polarisation was quite low ($n^2 = 3 \cdot 06$, estimated separately). As there was no peak in tan δ graph even at low temperatures and at low frequencies unlike the vacuum deposited films, the contributions from dipole orientational and interfacial polarisations, if at all present, would be insignificant. Hence the major contribution arose from the atomic and more likely from ionic polarisation.

ϵ of In_2O_3 films estimated from capacitance at room temperature would no doubt be slightly higher than that at lower temperature. Measurement near liquid air temperature led to a value around 50 thus suggesting ϵ obtained from so-called In–O film at $88\,^\circ$K was indeed mostly due to In_2O_3 film mixed with some amount of dissociated species acting as doping agents. The effect of these would be predominant at room temperature thus leading to the thickness independent C but dependent ϵ.

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