THE ELECTRICAL PROPERTIES OF AMORPHOUS THIN FILMS OF Al–In$_2$O$_3$–Al STRUCTURE DEPOSITED BY THERMAL EVAPORATION

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A discussion of electrical properties of amorphous thin films of Al–In$_2$O$_3$–Al structure is presented. Particular attention has been given to the question of film thickness, substrate temperature during deposition and post deposition annealing, since these conditions are known to have a profound effect on the structure and electrical properties of the films. The effects of temperature on the $V$--$I$ characteristics and effects of frequency on conductivity and capacitance of the Al–In$_2$O$_3$–Al structure are also reported. Activation energies for conduction processes are estimated and the results are discussed in terms of hopping model. The conduction at higher temperature is seemingly a contact limited $i.e.$ Schottky type process, so a transition from hoping to free band conduction takes place. The capacitance decreases with the rise of frequency and lowering of temperature. The values of dielectric constants are estimated and the results are discussed in terms of Schottky type of conduction. The increase in conductivity with the increase in temperature during measurement of electrical properties, film thickness, substrate temperature and post deposition annealing is reported and results are discussed in terms of current theory.

Key words: electrical conduction mechanisms; carrier density; trapped electrons; indium interstitials; electron donors; oxygen vacancies; lower oxidation state.

1. INTRODUCTION

Electronic conduction in amorphous solids has received considerable attention in recent years because of its importance in electronic devices. Charge transport measurements in disordered semiconductors and insulators can provide information about the electronic structure of these materials. The disorder in the atomic configuration is thought to cause localized electronic states or groups of states within the material. Stoichiometric films of compound insulators are difficult to prepare by evaporation, because of decomposition and preferential evaporation of the lower vapour pressure constituent atomic species. Such
insulators are extrinsic in nature rather than intrinsic. Adurodija et al. [1] have reported that if excess metal atoms exist within the insulator, then as a result of dissociation, they could act as donor centres.

There are various d.c. electronic conduction mechanisms by which electrons are transported under the influence of an applied field [2]. Generally, one mechanism will dominate the observed current but more than one conduction mechanisms may possibly operate at one particular voltage. In the process of conduction by field assisted thermal excitation the electrons are transported from the cathode into the conduction band of the contact barrier (Schottky emission). Electrons may also be transported by field-assisted thermal excitation over the lower coulombic potential barrier (Pool-Frenkel emission).

A.C. measurements are important means for studying the dynamic properties (capacitance, conductance, permittivity and loss factor) of a dielectric. The advantage of a.c. measurements are firstly that they permit investigations of time-dependent properties such as a carrier hopping and also of other processes taking place in the insulator, i.e. in the region of relatively low conductivity existing between the Schottky barriers, even though the conduction process may be electrode-limited. Moreover the a.c. voltage bias need never exceed a few hundred millivolts. Thus the maximum field within the insulator film is kept to a minimum and there is a little danger of more than one conduction processes being active. This measurement also helps to distinguish between localized and free band conduction. In the case of localized conduction the conductivity (σ_{a.c}) increases with frequency ω, while in the free band conduction the conductivity decreases with frequency. A number of investigations have been carried out on the frequency dependence of conductivity in many glassy and amorphous semiconductors [3–8]. It has been pointed out by Elliott [4] that a variety of conduction mechanisms can yield the ω^s behaviour for the a.c. conductivity, but in general, it is difficult to establish which of the above effects determines a given observed conduction process. A careful study of the temperature dependence of s (s is an index) can provide us more information in order to make a choice between the different theories for explaining the law \( \sigma_{a.c}(\omega) \propto \omega^s \).

Indium oxide is very important material for microelectronic applications. It is an insulator in its stoichiometric form, whereas in its non-stoichiometric form it behaves as a highly conducting semiconductor with a wide optical band gap (3.7 eV), providing high transparency in the visible light range and high reflectivity in the infrared light range. This unique combination of electrical and optical properties has led numerous researchers to a thorough investigation of growth and characterization of semiconducting \( \text{In}_2\text{O}_3 \) thin films. Klein [9] has reported that the structure of \( \text{In}_2\text{O}_3 \) greatly depends upon substrate temperature and annealing. An amorphous to polycrystalline transition occurs by increasing substrate temperature. Annealing of the amorphous films of \( \text{In}_2\text{O}_3 \) at 473 K gives
rise to the polycrystalline transition, while further annealing of the polycrystalline phase at temperature higher than 673 K may cause a change in microstructure of the films (both in size and shape of the crystallites).

There is relatively less information about In$_2$O$_3$ because of the considerable difficulties in preparing specimen suitable for the investigation of electrical properties. Due to complicated crystal structure, the conduction in In$_2$O$_3$ is still not fairly understood. The interesting feature of In$_2$O$_3$ films is that depending upon the growth conditions, films can be prepared having totally different properties. Asbalter et al. [10] and Palmer et al. [11] have reported that the transport properties strongly depend upon their structure (grain size and shape as well as the characteristic of the contact between them and structural absorbed gases etc). Heating of the films may modify these structural characteristics and consequently the transport properties of the respective films may vary too. Therefore the study of temperature dependence of electrical conductivity during the heat treatment may provide information on the processes taking place in the films.

The objective of this work is to look at amorphous thin films of In$_2$O$_3$ from the point of view of electrical conduction. Particular attention has been given to the question of film thickness, substrate temperature during deposition and post deposition annealing, since these conditions are known to have a profound effect on the structure and electrical properties of the films. The effects of temperature on the conductance, capacitance and $V$–$I$ characteristics of the Al–In$_2$O$_3$–Al structure are also reported.

2. EXPERIMENTAL WORK

2.1. SAMPLE FABRICATION TECHNIQUE

Amorphous thin films used in this study were prepared by vacuum evaporation of high purity In$_2$O$_3$. This oxide was evaporated from an electrically heated molybdenum boat in a Balzers BA 510 coating unit. The oxide was deposited at a pressure of $1.33 \times 10^{-4}$ Pa. Film thickness in the range 100–400 nm was attained at a deposition rate of 0.75 nms$^{-1}$ with the substrates at 293 K. Some 300 nm thick samples were fabricated with substrates in the temperature range 293–543 K. Al–In$_2$O$_3$–Al samples were prepared on clean corning 7059 glass substrate by the sequential vacuum deposition of aluminium as the bottom electrode, In$_2$O$_3$ as the insulator and aluminium as the top electrode in a crosswise fashion having width $\approx$ 3 mm so that the film capacitor has an affective area of 0.1 cm$^2$ approximately. Aluminium electrodes were made sufficiently thick so that their resistance was less than 2–3 $\Omega$. The substrates were heated to the required temperature by the heater mounted at the inner top of
the bell jar. The thickness of the film was estimated using a quartz crystal monitor and finally the exact film thickness was determined by multiple beam interferometry. Some samples were annealed in vacuum for 4 hours at different temperatures and allowed to cool down at the rate of 2 K/min.

2.2. ELECTRICAL MEASUREMENTS

2.2.1. D.C. measurements

D.C. electrical measurements were made by a conventional method with the sample in a subsidiary vacuum system at a pressure of the order of $1.33 \times 10^{-4}$ Pa. The d.c. bias voltage was provided by a Coutant LA 11.2 power supply and the current was measured by an electric meter EA113. The voltage across the sample was monitored by a digital voltmeter. The lowering of the sample temperature was achieved by firmly attaching the sample to the brass base of a stainless steel tank containing liquid nitrogen. Heating the sample above room temperature was initiated by using a resistance heater inserted in the holes made through the brass base. A chromel–alumel thermocouple was attached to the substrate close to the metal-insulator-metal (MIM) capacitor under test, so as to measure the device temperature accurately. A Comark electronic thermometer type 1601 was used for measurement of the temperature. Silver paste was used to make good electrical and thermal contacts.

2.2.2. A.C. electrical measurements

A Hewlett-Packard Impedance Analyzer type L. F. 4192, was used for the measurement of conductance and capacitance of the samples, in the frequency range 200 Hz to 1 MHz using an a.c. signal of 500 mV applied across each sample. The relative dielectric constant $\varepsilon_r$ was calculated from the well-known expression $C = \varepsilon_r \varepsilon_0 A/d$ where $A$ is the active area of the device, $d$ the thickness of the film, $C$ the capacitance of the film capacitor and $\varepsilon_0$ is the permittivity of free space. The area of the film capacitor was determined by a simple travelling microscope.

2.3. STRUCTURAL INVESTIGATION

For electron microscopic studies, samples were deposited on Carbon-coated mica sheets. The oxide thickness was ≈ 20 nm and the structure of the films was studied using a transmission electron microscope Model JEM 7 working at 80 KV with a magnification of 3800. Electron microscopic studies demonstrate that freshly evaporated films of In$_2$O$_3$ deposited at room temperature
and those prepared on substrates at 543 K are amorphous in structure. On annealing in vacuum the films become polycrystalline at 773 K and many of the defects associated with the films are annealed out.

3. RESULTS AND DISCUSSION

3.1. D.C. CONDUCTION

The voltage current characteristics at different temperatures in the range 193–393 K (during measurement in a subsidiary vacuum system) for a 300 nm thick Al–In$_2$O$_3$–Al sandwich sample deposited at substrate temperature 293 K are shown in Fig. 1(a). The results indicate an increase in current with voltage at all temperatures. At low fields ohmic behaviour was observed in our samples by considering the linear portion of the $I$–$V$ curves. Four samples deposited at substrate temperature 293 K, having film thickness in the range 100–400 nm were studied at 293 K (during measurement in a subsidiary vacuum system) and their voltage current characteristics are shown in Fig. 1(b). Four samples in the substrate deposition temperature range 293–543 K each having thickness 300 nm were studied at 293 K (during measurement in a subsidiary vacuum system) and their voltage current characteristics are shown in Fig. 1(c). Five samples deposited at substrate temperature 293 K and annealed in the temperature range 473–773 K each having thickness 300 nm were studied at 293 K (during measurement in a subsidiary vacuum system) and their voltage current characteristics are shown in Fig. 1(d). The interpretation of these curves based on the assumption of a simple Poole-Frenkel or Schottky effect requires the logarithm of the circulating current to be proportional to $V_b^{1/2}$. The analyses of these results are shown in Figs. 2(a), (b), (c) and (d) where log $I_c$ is plotted as a function of $V_b^{1/2}$. These plots suggest that mechanism of high field conduction is either Schottky or Poole–Frenkel. One can differentiate some times between the two types of conduction mechanisms by comparing the values of their dielectric constants with the value of the high-frequency dielectric constant through capacitance measurements. Both mechanisms show the same fundamental dependence of circulating current on the applied voltage, i.e.

$$I_c \propto \exp(\beta V_b^{1/2} \kappa T d^{1/2})$$

where $I_c$ is the circulating current, $d$ being the sample thickness, $\kappa$ the Boltzman constant, $T$ the absolute temperature and $\beta$ the barrier-lowering coefficient. The experimentally determined value of $\beta$ can be compared with the theoretical values of $\beta_s$ (Schottky barrier-lowering coefficient at the metal/insulator interface).
Fig. 1(a). – The voltage current characteristics of a 300 nm thick Al–In$_2$O$_3$–Al assembly, at various temperatures during measurements, (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K. ($V_b$ is applied voltage, $I_c$ is circulating current).

Fig. 1(b). – The voltage current characteristics of Al–In$_2$O$_3$–Al samples at room temperature during measurement, having various thicknesses, (1) 100 nm, (2) 200 nm, (3) 300 nm, (4) 400 nm.
Amorphous thin films of Al-In$_2$O$_3$-Al structure

Fig. 1(c). - The voltage-current characteristics of 300 nm thick Al-In$_2$O$_3$-Al samples at room temperature during measurement, having various substrate temperatures, (1) 293 K, (2) 373 K, (3) 473 K, (4) 543 K.

Fig. 1(d). - The voltage-current characteristics of 300 nm thick Al-In$_2$O$_3$-Al samples at room temperature during measurement, having various annealing temperatures, (1) as evaporated, (2) 473 K, (3) 773 K, (4) 673 K.
Fig. 2(a). Plot of $I_c$ against $1/2bV_0$ for Al–In$_2$O$_3$–Al assemblies, at various temperatures during measurement, (1) 193 K, (2) 233 K, (3) 273 K, (4) 313 K, (5) 353 K, (6) 393 K.

Fig. 2(b). Plot of $I_c$ against $1/2bV_0$ for Al–In$_2$O$_3$–Al samples, at room temperature during measurement, having various thicknesses, (1) 100 nm, (2) 200 nm, (3) 300 nm, (4) 400 nm.
Amorphous thin films of Al-In$_2$O$_3$-Al structure

Fig. 2(c). Plot of $I_c$ against $V_b^{1/2}$ for 300 nm thick Al-In$_2$O$_3$-Al samples, at room temperature during measurement, having various substrate temperatures, (1) 293 K, (2) 373 K, (3) 473 K, (4) 543 K.

Fig. 2(d). Plot of $I_c$ against $V_b^{1/2}$ for 300 nm thick Al-In$_2$O$_3$-Al samples, at room temperature during measurement, having various annealing temperatures, (1) as evaporated, (2) 473 K, (3) 573 K, (4) 673 K, (5) 773 K.
or $\beta_{PF}$ (the Poole-Frenkel barrier-lowering coefficient of donor centers) in order to distinguish between the two types of effects. The theoretical values of $\beta_s$ and $\beta_{PF}$ are determined from the following relation,

$$
\beta = \left( \frac{e^3}{n\pi\varepsilon_o \varepsilon_r} \right)^{1/2}
$$

(2)

where $\varepsilon_o$ is the permittivity of free space, $\varepsilon_r$ is the relative permittivity of the dielectric and $e$ is the electronic charge. The difference between the two effects is expressed by $n = 1$ for Poole-Frenkel effect and $n = 4$ for Schottky emission. The experimental values of barrier lowering coefficient $\beta$ and the relative dielectric constants $\varepsilon_r$ are shown in the Tables 1–4, (i) for 300 nm thick sample (deposited at substrate temperature 293 K) at various temperatures during measurements in a subsidiary vacuum system, (ii) for various sample thicknesses deposited at 293 K, (iii) for 300 nm thick samples deposited at substrate temperature in the range 293–543 K and (iv) for 300 nm thick samples deposited at 293 K and annealed in the temperature range 473–773 K respectively. The values of relative dielectric constant for Schottky type of conduction lie in the

**Table 1**

Experimental values of some parameters of 300 nm thick Al–In$_2$O$_3$–Al sample at various temperatures during measurement

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>$\beta_{exp}$ $10^{-4}$ eV V$^{-1/2}$ cm$^{1/2}$</th>
<th>Relative permittivity $(n = 4$, Schottky$)$ estimated</th>
<th>Relative permittivity $(n = 1$, Poole–Frenkel$)$ estimated</th>
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<tbody>
<tr>
<td>193</td>
<td>2.56</td>
<td>3.0</td>
<td>12.0</td>
</tr>
<tr>
<td>233</td>
<td>2.60</td>
<td>2.5</td>
<td>10.0</td>
</tr>
<tr>
<td>273</td>
<td>3.20</td>
<td>2.1</td>
<td>8.4</td>
</tr>
<tr>
<td>313</td>
<td>4.30</td>
<td>1.7</td>
<td>6.8</td>
</tr>
<tr>
<td>353</td>
<td>5.62</td>
<td>1.4</td>
<td>5.6</td>
</tr>
<tr>
<td>393</td>
<td>6.10</td>
<td>1.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>

**Table 2**

Experimental values of some parameters of 300 nm thick Al–In$_2$O$_3$–Al samples at various thicknesses

<table>
<thead>
<tr>
<th>Sample thickness [nm]</th>
<th>$\beta_{exp}$ $10^{-4}$ eV V$^{-1/2}$ cm$^{1/2}$</th>
<th>Relative permittivity $(n = 4$, Schottky$)$ estimated</th>
<th>Relative permittivity $(n = 1$, Poole–Frenkel$)$ estimated</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.70</td>
<td>2.4</td>
<td>9.6</td>
</tr>
<tr>
<td>200</td>
<td>3.10</td>
<td>2.2</td>
<td>8.8</td>
</tr>
<tr>
<td>300</td>
<td>4.20</td>
<td>1.9</td>
<td>7.6</td>
</tr>
<tr>
<td>400</td>
<td>5.12</td>
<td>1.2</td>
<td>4.8</td>
</tr>
</tbody>
</table>
range 1.2–3.0 and for Poole-Frenkel type of conduction in the range 4.8–12 (Table 1). The values of the high frequency dielectric constant through capacitance measurement lie in the range 1.6–2.8 suggesting that the high-field conduction mechanism is predominantly of Schottky type. The variation of current with inverse temperature for a 300 nm thick In$_2$O$_3$ sample at various biasing voltages in the range 0.2–2 V is shown in Fig. 3.

The conductivity in In$_2$O$_3$ is believed to have two components, electronic and ionic. It is argued that ionic conduction is characterized by low mobilities and high activation energies, while electronic conduction is associated with relatively high mobilities and lower activation energies. These conditions are indeed applicable in crystalline materials. But in the case of amorphous materials the mobility is very low, so the conduction is by hoping between localized states. It is not possible to give definite limits for the activation energy. As a general rule, values less than, say 0.2 eV would be considered as indicating undoubted electronic conduction, values in excess of, say, 0.6 eV would often be associated with ionic transport.

The mechanism of conduction in amorphous solids can be explained on the model put forward by Jonscher [6], which lets amorphous solids conduct electri-
city by means of electron motion either in localized levels (hopping) or in free bands. The effective mobility in the latter is very much higher than in the former. The localized levels are donor-like, depending on their ability to donate or accept electrons, and their characteristic determines their role in the conduction process. The level of conductivity depends on the density and mobility of charge carriers in the vicinity of the Fermi level. If the letter falls near the valence or conduction band, free band conductivity prevails; otherwise conduction is by carrier hopping. We explain our results on the basis of this model. The conduction in most insulators is controlled by the bulk of the sample since insulators obey Ohm’s law at low fields. The variation of the current with temperature at a low applied field is given by

\[ I_c = I_0 \exp\left(-\Delta E/kT\right) \]  

where \( \Delta E \) is the activation energy for donors or traps and

\[ I_0 = e\mu N_d V A d \]  

where \( e \) is the charge on an electron, \( \mu \) is the mobility, \( N_d \) is the carrier density, \( V \) is the bias voltage, \( d \) is the sample thickness and \( A \) is the active area of the

Fig. 3. – Circulating current as a function of inverse temperature at five applied voltages for a 300 nm thick Al–In$_2$O$_3$–Al assembly.
sample. Mott and Davis [12] agree on a lower limit for the free band mobility $\mu = 100 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$. According to Equ. 3, the activation energy can be obtained from the gradient of the slope of the straight portion of the curves in Fig. 3. In our results such a transition takes place within the temperature range $218–300 \text{ K}$. This suggests that more than one conduction mechanisms are involved. The low-temperature values of activation energy lie in the range $0.03–0.07 \text{ eV}$. This low value of activation energy in the low temperature region can be attributed to an electronic hopping process. The straight parts of the curves in the high-temperature region correspond to an activation energy of $0.20–0.32 \text{ eV}$. The conduction at higher temperature is seemingly a contact-limited i.e. Schottky type process and so a transition from hopping conduction to free band conduction takes place. The gradual transition from hopping to free band conduction is due to overlapping of localized levels and the free band. The value of carrier density as derived from Fig. 3 is $2.7 \times 10^{16} \text{ cm}^{-3}$. The hopping mobility as derived from eq. 3, is $\mu_H = 2 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$. This low value of hopping mobility, $\mu_H$, at low field and low temperature indicates that conduction is by hopping of electron between localized states.

In $\text{In}_2\text{O}_3$, oxygen vacancies are formed when an oxygen atom in a normal lattice site is removed, which is usually equivalent to a transformation of an oxygen atom in a normal site to the gaseous state. Considering that in binary oxides the oxygen ions in the regular sites have a valency of $-2$, in this process two electrons of the oxygen ion are left in the vacant site. If both of these electrons are localized at the oxygen vacancy, though neutrality is present and the oxygen vacancy has zero effective charge. If one or both of the localized electrons are excited and transferred away, from the vacancy, the oxygen vacancy becomes singly or doubly ionized respectively. Since electrons are removed, the ionized oxygen vacancy will have an effective positive charge to conserve the electrical neutrality of the material. The charged oxygen vacancy becomes an electron trap site but in this process one or two electrons are available for conduction.

In the present work the electrical properties of amorphous thin films of $\text{In}_2\text{O}_3$ have been studied, for $300 \text{ nm}$ thick samples deposited at $293 \text{ K}$ in the temperature range $193–393 \text{ K}$ (during measurement in the subsidiary vacuum system), for samples in the thickness range $100–400 \text{ nm}$ with the substrates at room temperature during deposition. Some samples $\approx 300 \text{ nm}$ have been studied in the substrate temperature range $293–543 \text{ K}$ and some samples $\approx 300 \text{ nm}$ thick have been studied in the annealing temperature range $473–773 \text{ K}$.

The observed results can be explained as follows:

It is generally accepted that defects responsible for electron production in pure $\text{In}_2\text{O}_3$ are oxygen vacancies. Oxygen vacancies, which capture one or two electrons, act as donors in which one electron of a doubly charged centre may be
ionized thermally and other only optically. Normal ionization gives rise to two charge carriers: an electron and a singly charged oxygen vacancy. The number of free electrons is balanced by an equivalent number of singly charged oxygen vacancies, which correspond to donors in an impurity semiconductor giving rise to electronic and ionic defect conductivity. The increase in conductivity due to increase in temperature during measurement of electrical properties of the sample is likely due to increase in the formation of oxygen vacancies and to the high mobility of the donors. As the mobility of donors is high, the electronic part of the conductivity is higher than the ionic part. When a d.c. voltage is applied across the sample, the positive effective charges (vacancies) travel continuously toward the negative electrode and the concentration of vacancies increases near the negative electrode. Thus conductivity in these samples is attributed to oxygen vacancies.

The thickness is one of the most important parameters, which affect the electrical properties of the films. Thermal evaporation of In₂O₃ in vacuum introduces oxygen vacancies in the oxide. When the thickness of amorphous thin films of In₂O₃ is increased, the concentration of oxygen vacancies is increased. Oxygen vacancies act as doubly ionized donors and contribute two electrons as charge carriers [13]. Thus initially when the thickness is increased, oxygen vacancies generate carriers in the films. The degree of localization of electrons increases with the increase in cation concentration thereby increasing the number of donor centres. A large concentration of donor centres, effectively increase the electrical conductivity in thicker samples.

The increase in electrical conductivity due to an increase in substrate temperature may be due to the release of trapped electrons by thermal energy or by the outward diffusion of the oxygen-ion vacancies, which are quite mobile even at low temperature. As the substrate temperature is increased, less interstitial oxygen and more oxygen vacancies and indium interstitials are incorporated in the oxide. An increase in electrical conductivity due to an increase in substrate temperature is ascribed to the increasing concentration and higher mobility of these effective donors.

In the amorphous materials, the forbidden band has a specific concentration of localized energy states, which originate from the statistical disordering of the atoms. During the annealing process, the degree of such disordering decreases or some voids are removed and this may cause a decrease in the number of unsatisfied bonds. More-over the films relax to a lower energy configuration, the volume densities of gaseous impurities fall, and the bond lengths and angles redistribute them-selves. At higher annealing temperature the point defects are removed in which oxygen plays an important role. Thus the increase in electrical conductivity due to annealing may be due either to the rearrangement and elimination of point defects, which lead to the decrease in carrier scattering or to the formation of indium species of lower oxidation state (In²⁺).
3.2. A.C. CONDUCTION

The frequency dependence of a.c. conductivity for amorphous thin films of In$_2$O$_3$, at various temperatures (during measurement in subsidiary vacuum system) in the range 193–393 K, for various film thicknesses in the range 100–400 nm, for various substrate deposition temperatures in the range 293–543 K and for various annealing temperatures in the range 473–773 K are shown in Figs. 4(a)–(d) respectively.

The experimental results are interpreted in terms of a model initially proposed by Pollak [14] and modified by Elliott [4]. This model involves a thermally assisted hopping conduction mechanism between localized states. It was observed that the a.c. conductivity in all the samples is increased monotonically with temperature and at high frequencies increased more rapidly.

Like many disordered materials, the films of In$_2$O$_3$ follow the frequency dependence of a.c. conductivity given by the relation:

$$\sigma_{\text{a.c.}} = \sigma_{\text{total}} - \sigma_{\text{d.c.}} = A\omega^s$$  \hspace{1cm} (5)

where $\omega$ is the angular frequency $A$ is a complex parameter that is weakly temperature dependent and $s$ is an index which is temperature dependent. The value of $s$ tends to unity as temperature is lowered; such behaviour can be observed from Fig. 5. At higher frequencies the a.c. conductivity at room temperature shows a square-law dependence on frequency with a relatively small dependence on temperature. Fig. 5 shows the variation of the conductivity with frequency at different temperatures for a 300 nm thick sample of Fig. 4(a). From the plot of Fig. 5 can be shown that:

$$s = \frac{\text{d} \log \sigma}{\text{d} \log f} = -AT + B$$ \hspace{1cm} (6)

where $A$ and $B$ are constants, $f$ is the frequency ($\omega/2\pi$) and $T$ is the absolute temperature. Hence $\sigma_{\text{a.c.}} \propto f^{-(AT - B)}$.

Fig. 6 shows the a.c. conductivity at different frequencies as a function of reciprocal temperature. Table 5 shows the activation energies, both d.c. and a.c. at 0.2 V and at various applied frequencies. It is seen from Table 5 that the a.c. conductivity seems to approach the d.c. conductivity asymptotically with increasing temperature. At low temperature the d.c. conductivity has an activation energy different from that corresponding to high temperature, and it is probable that hopping conduction at the Fermi level prevails at low temperature.

Fig. 7 shows the variation of capacitance with frequency for 300 nm thick sample of In$_2$O$_3$ at various temperatures in the range 193–393 K.

It has been noted that the conductivity shows a strong frequency dependence leading to a square law at high frequencies. This is also coupled with
Fig. 4(a). – Variation of a.c. conductivity with frequency at various temperatures for a 300 nm thick sample of In$_2$O$_3$: (1) 193 K; (2) 233 K; (3) 273 K; (4) 313 K; (5) 353 K; (6) 393 K.

Fig. 4(b). – Variation of a.c. conductivity with frequency at various sample thicknesses of In$_2$O$_3$: (1) 100 nm; (2) 200 nm; (3) 300 nm; (4) 400 nm.
Fig. 4(c). – Variation of a.c. conductivity with frequency at various substrate temperatures during deposition for a 300 nm thick sample: (1) 293 K; (2) 373 K; (3) 473 K; (4) 543 K.

Fig. 4(d). – Variation of a.c. conductivity with frequency at various annealing temperatures for a 300 nm thick sample: (1) as evaporated; (2) 473 K; (3) 573 K; (4) 673 K; (5) 773 K.
Fig. 5. – Temperature dependence of the slope of conductivity- frequency characteristics of the sample shown in Fig. 4(a).

Fig. 6. – Conductivity plotted as a function of $1000/T$ for fixed frequencies for a 300 nm thick sample of Fig. 4(a).
Amorphous thin films of Al-In$_2$O$_3$-Al structure

Table 5
Activation energies for two ranges of temperature of a 300 nm thick sample of In$_2$O$_3$ at various applied frequencies

<table>
<thead>
<tr>
<th>Frequency [kHz]</th>
<th>Activation energy [eV]</th>
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<tbody>
<tr>
<td></td>
<td>193–210 K</td>
</tr>
<tr>
<td>0 d.c. (at 0.2 V)</td>
<td>0.070</td>
</tr>
<tr>
<td>0.2</td>
<td>0.065</td>
</tr>
<tr>
<td>10</td>
<td>0.060</td>
</tr>
<tr>
<td>100</td>
<td>0.020</td>
</tr>
<tr>
<td>1000</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Fig. 7. – Variation of capacitance with frequency at various temperatures for a 300 nm thick sample of In$_2$O$_3$: (1) 193 K; (2) 233 K; (3) 273 K; (4) 313 K; (5) 353 K; (6) 393 K.

low activation energies at low temperature (Table 5). All these are indicative of electronic hopping conduction. The transport of the carriers between localized
states is mainly due to hopping over the barrier separating two nearest neighbouring sites, rather than tunnelling through the potential barrier. This process in general involves many polarons because of barrier height. The localized site potentials are taken to be of拄omic form. The barrier height and the distance separating these two sites are $W$ and $R$ respectively and $W_m$ is the maximum barrier height (the energy difference between the ground states and extended states). The equation relating these parameters is given by

$$W_m - W = \frac{e^2}{\pi \varepsilon_o \varepsilon_r R}$$  \hspace{1cm} (7)

Elliott [4] extended this theory to the a.c. conduction of amorphous chalcogenides materials. Assuming a Coulombic interaction, the barrier height over which a carrier hops is given by

$$W = W_m - 4ne^2 / (\varepsilon_r R)$$  \hspace{1cm} (8)

where $n$ is the number of carriers that hope (e.g. $n = 2$ for bipolarons and $n = 1$ for single polaron). The a.c. conductivity according to Elliott [4] model is given by;

$$\sigma(\omega) = (\pi^2 N^2 \varepsilon_r / 24)(8e^2/\varepsilon_r W_m)^6 (\omega^s / \tau_0^6)$$  \hspace{1cm} (9)

where $N$ is the concentration of localized sites, $\tau_0$ is the effective relaxation time ($\approx 10^{13}$ s), $s = 1 - \beta$ at low temperature, $\beta = 6kT/W_m$ and $W_m$ is the barrier height separating distant pairs. The pair relaxation time is assumed to be,

$$\tau = \tau_0 \exp(W/kT)$$  \hspace{1cm} (10)

The exponent $s$ is related to $W_m$ by

$$1 - s = 6kT/W_m$$  \hspace{1cm} (11)

where $k$ is the Boltzmann’s constant and $T$ is the absolute temperature. The parameter $W_m$ is approximately equal to the band gap of the material, measured optically. We substitute the measured value of optical band gap (2.5 eV) [15] of 300 nm thick sample deposited at 293 K in eq. (11). The value of $s$ is found out to be 0.94 at room temperature which is consistent with the measured value (0.92) as derived from Fig. 5 which is plotted from the room temperature data of Fig. 4(a) and at a frequency of $\approx 10^5$ Hz. The eq. (9) also predicts a frequency dependence of a.c. conductivity ($\sigma_{a,c} \propto \omega^s$) with $s$ increasing and tending to unity as the temperature is lowered. The gradual increase in the value of $s$ with the decrease in temperature has been observed experimentally in our samples (Fig. 4a). Figs. 4(b)–(d) show the conductivity versus frequency graphs at different film thicknesses, substrate temperature during deposition and annealing.

It is observed that a.c conductivity is increased with increase in temperature during measurement of electrical properties, film thickness, substrate temperature
Amorphous thin films of Al-In$_2$O$_3$-Al structure

and annealing. Oxygen vacancies in oxide compounds have already been reported by Kiriakidis et al [7] and Klein [9]. Oxygen deficiency results in the formation of dipoles, which contribute to the conductivity in In$_2$O$_3$ films. The observed behaviour of a.c. conductivity may also be attributed to defects in In$_2$O$_3$ films caused by decomposition during the evaporation process and by movement of dipoles under the influence of an external field.

The variation of capacitance with both frequency and temperature in In$_2$O$_3$ films can be explained by using the model proposed by Goswami and Goswami [16] of a circuit containing a single capacitance element together with a discrete resistance $R$ in parallel with the capacitor and a series lead resistance $r$. The effect of temperature on capacitance can be considered from the following equation:

$$C_s = \frac{1}{\omega^2 R^2 C} + C = \left(1 + D^2\right)C$$

where $D = \frac{1}{\omega RC}$ and $C_s$ is the equivalent series capacitance of the circuit; if however, $\frac{1}{\omega^2 R^2 C}$ is much smaller than $C$, then $C_s = C$. This condition can be obtained in a capacitor system either by increasing $R$ or by raising $\omega$. A suitable combination of these parameters along with an appropriate value of $C$ will lead to the frequency independent capacitance.

The capacitance generally decreases not only with the rise of frequency but also with the lowering of temperature and in our results never attains a constant value even at the highest frequency (10$^6$ Hz). The variation of $C$ with $f$ for a 300 nm thick sample of In$_2$O$_3$ is shown in Fig. 7. According to Kiriakidis et al. [7] normal ionization in doubly charged oxygen vacancies in In$_2$O$_3$ gives rise to two charge carriers, an electron and a singly charged oxygen vacancy. The number of free electrons is balanced by an equivalent number of singly charged oxygen vacancies, which correspond to donors in impurity semiconductors giving rise to electronic and ionic conductivity. When an a.c. voltage is applied to the structure, the ionic component of conductivity gives rise to space-charge polarization. There are two general types of dispersion processes relevant to these low frequencies and amorphous insulators. One is an orientation polarization mechanism and other is some form of interfacial mechanism, which is believed to be caused by blocking of charge carriers at the electrode giving rise to a space-charge region. In In$_2$O$_3$ at low temperature and low frequencies the contribution to the capacitance from dipole orientation and interfacial polarization would be insignificant because of the hindrance to rotation. Hence the major contribution to capacitance arises from the atomic and more probably from ionic polarization. However, with the increase of temperature the contribution from dipolar orientation would increase considerably and hence the capacitance would also increase. The increase in capacitance with the decrease in frequency
may be attributed to interfacial polarization in that region. The charge carriers existing in the dielectric film can migrate from some distance under the influence of electric field. When they are blocked at electrodes a space charge region is developed, which in turn leads to a substantial increase in a capacitance at the lower frequency.

REFERENCES