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AC CONDUCTIVITY AND DIELECTRIC PROPERTIES OF Al_2O_3 THIN FILMS

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Al_2O_3 thin films of different thicknesses were prepared onto clean glass substrates using ohmic aluminum electrodes. Their dielectric properties and ac conductivity have been investigated in the frequency range 0.1-100KHz and within the temperature range 100-400K. Oxide-layer thicknesses of the films range between 50-1550 Å. The dielectric constant ε_1 was found to decrease with increasing frequency and increase with temperature in the given intervals. Only ac losses have been investigated due to the smallness of dc losses. The ac conductivity satisfies the power law ω^s. Here the s parameter is in the vicinity of 0.8 and it decreases with increasing temperature. This behaviour of s can comply with CBH model. The activation energy values calculated from ac conductivity and dielectric loss factor measurements are in good agreement with each other. The obtained values agree with the model of hopping of charge carriers by thermal activation between two sites having a coulombic potential well. Film thickness dependence of Temperature Coefficient of Capacitance (TCC) and Temperature Coefficient of Permittivity (TCP) of the Al_2O_3 thin films were also determined.

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1. Introduction

There are many researches about dielectric properties of different thin films because of their electronic and optical usage [1-5]. Al_2O_3 films are frequently used for many purposes such as refractory coatings, antireflection coatings, anticorrosive coatings, microelectronic devices, capacitance humidity sensors and passivation of metal surfaces particularly in field effect transistors [6-11]. Therefore, much work has been reported on the dielectric properties of Al_2O_3 films, but especially studies of the dielectric properties of these films are rather rare at low frequencies. On the other hand, determination of the ac conductivity mechanism of materials is very important from the point of their usage in technology. Thus various models have been proposed to make clear the conduction mechanisms in amorphous semiconductors. These models are Quantum-Mechanical Tunnelling (QMT) model, small polaron tunnelling model, large polaron tunnelling model, atomic hopping model, and Correlated Barrier Hopping (CBH) model [12-15].

In our previous work on Al_2O_3 films, our aim was to determine the possible polarization mechanisms [2]. In this work, we are determining the dielectric properties and the frequency and temperature dependence of ac conductivity of Al_2O_3 films, prepared by anodic oxidation method and confront the results with ac conductivity models in amorphous semiconductors.

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2. Experimental techniques

A. Preparation of the samples: Aluminum base electrodes of thickness about 3000 Å were evaporated onto microscope slides at a pressure of approximately 10^{-5} Torr. The aluminum films were prepared by evaporating 99.99% pure Al. These evaporated aluminum films were partly anodized at room temperature in a solution of 3% tartaric acid made up to *p*H5.5 with NH_4OH. After anodization, they were cleaned in distilled water and left for drying in a desiccator for about 24h. The oxide film thickness was calculated from the anodizing ratio (13.5 Å V^{-1}) [2]. According to the applied voltage oxide-layer thickness in the range of 50-1550 Å are obtained. The Al counter electrodes were evaporated onto these anodized films at the same evaporation condition realized for the base electrodes. Hence $Al/Al_2O_3/Al$ capacitors are formed.

B. Experimental setup: A Gen-Rad 1615-A Scheering Bridge, a Gen-Rad 1232 Null Detector, and a Good Will GFG-8016D Generator were used for the capacitance and dissipation-factor measurements. These measurements were made in approximately 10^{-4} Torr vacuum. For each sample capacitor, we reversed the coupling and repeated the measurements twice; we chose those that gave the same results. The same experimental results were obtained under the same conditions. The areas of capacitors ~36 mm^2 were measured with a travelling microscope. Temperatures of the samples during the study were measured with a copper-constantan thermocouple.

3. Results

3.1. Ac conductivity

Ac conductivity is related to the energy loss obtained from the polarization mechanism that is suitable for the material and gives important information about the structure of the material. In all amorphous semiconductors and in some polymers, ac conductivity, $\sigma_{ac}(\omega)$, total conductivity, $\sigma_{tot}(\omega)$ and dc conductivity, σ_{dc} satisfy the following frequency relation [16,17]:

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} = A\omega^{s} , \quad (1)$$

where ω is the angular frequency, s is the frequency exponent and A is a constant independent of frequency.

Variation of ac conductivity of the 1550 Å film with frequency at various temperatures is shown in Fig. 1. In the worked thickness interval we obtained the same behaviour. According to this figure $\sigma_{ac}(\omega)$ increases linearly with frequency and from the slope of these lines the frequency exponent is determined. It is known that the value of this exponent yields the type of conductivity mechanism. As an inset we present the temperature variation of s. For all worked thicknesses s decrease as temperature increases.

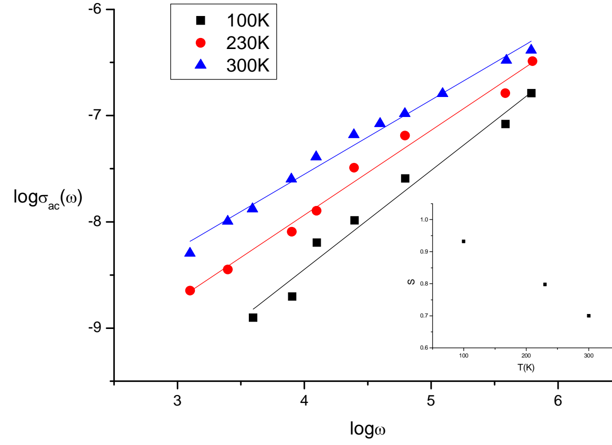

Fig.1: Frequency dependence of $\sigma_{ac}(\omega)$ at various temperatures. The inset figure shows the temperature dependence of s for 1550Å thick Al_2O_3 film.

Several conductivity mechanisms have been proposed for amorphous semiconductors. According to the QMT model s is about 0.8 and it either increases rather slowly or stays the same as temperature increases. Our experimental results disagree with such a behavior hence the mechanism responsible from the conductivity of Al_2O_3 cannot be QMT. OLPT conductivity mechanism requires both a frequency and temperature dependence of s. According to this dependence, s starting from 1 at room temperature, must first decrease and after passing a minimum again increase. It is clear that our results do not follow such a behaviour. On the other hand, for CBH model, the behaviour of s ought to be just the behaviour that we deduced from our experimental results [18,19]. In this model s is given by

$$s = 1 - \frac{6k_B T}{E_g}, \tag{2}$$

where k_B is the Boltzmann constant, T is the temperature in Kelvin and E_g is the optical band gap of the material. From this equation one can obtain the value of s at room temperature by using the energy gap value $2.6\,\text{eV}$ determined by Shiki *et al.* [20]. The thus calculated value (0.98) is in good agreement with our experimental value (0.93) within 5%.

The Austin-Mott formula [21] derived within the CBH model, gives

$$\sigma_{ac}(\omega) = \frac{\pi}{3} k_B T e^2 \frac{[N(E_F)]^2}{\alpha^5} [\ln \frac{\nu_{ph}}{\omega}]^4 \omega \tag{3}$$

where $N(E_F)$ is the density of states at the Fermi level, α is the exponential decay parameter of localized states wave functions and ν_{ph} is the phonon frequency. Assumptions involved in this formula have been discussed by Pollak [22]; the main one of which is that hopping is between pairs of centres *i.e.*, multiple-hopping processes can be neglected [23]. By using $\nu_{ph} = 10^{12}$ Hz and $\alpha^{-1} = 10\ \text{Å}$ [24], the density of states have been calculated: $N(E_F) \approx 10^{25}\ \text{eV}^{-1}\text{cm}^{-3}$. Fig. 2 shows the frequency dependence of $N(E_F)$ at different temperatures. $N(E_F)$ increases with frequency and temperature as is seen from Fig. 2. This result agrees well with the behaviour described by eq. (3) obtained from CBH model.

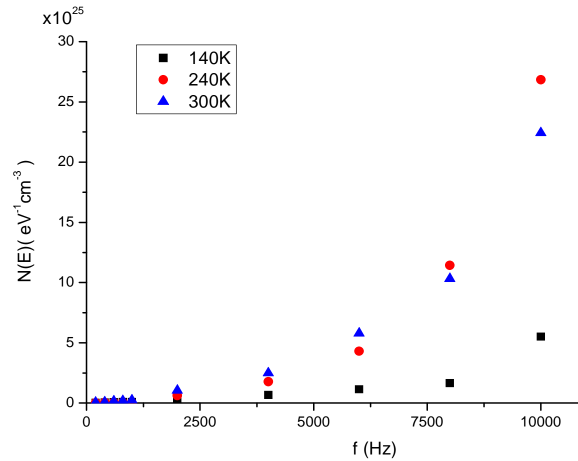

Fig.2: Frequency dependence of density of states at different temperatures for Al_2O_3 film 1450 Å thick.

Fig. 3 shows the temperature dependence of $\sigma_{ac}(\omega)$ at different frequencies for the 1550 Å thickness film. Similar results were determined in the investigated film thickness region. It can be seen from Fig. 3 that $\ln\sigma_{ac}(\omega)$ decreases linearly with decreasing temperature. This behaviour shows that there is a thermally supported process between the localized states at the band gap of ac conductivity or valance and conductivity band tails.

$$\sigma = \sigma_0 e^{-\frac{\Delta E_\sigma}{k_B T}}$$

The above formula defines the relation between the ac conductivity and activation energy. Thus activation energy is calculated from the slope of $\ln\sigma_{ac}(\omega)$ versus $\frac{10^3}{T}$ curve. The calculated value at different frequencies is $0.02 \pm 9\%$ eV within the experimental error.

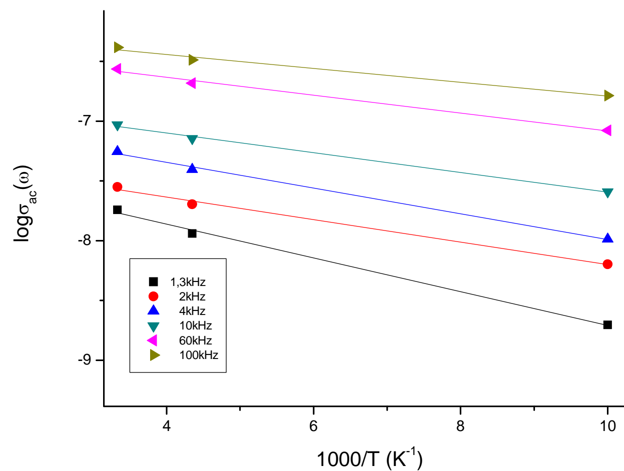

Fig.3: Temperature dependence of $\sigma_{ac}(\omega)$ for 1550 Å thick Al_2O_3 films at different frequencies.

On the other hand, Fig. 4 shows the frequency dependence of activation energy for the studied films. $\Delta E_{\sigma}(\omega)$ decreases with increasing frequency and is independent of film thickness. In one of our works, we proposed that electronic hopping mechanism was dominating at high frequencies. Therefore by increasing the frequency of the applied electric field we increase the hopping number in one second [25, 26]. This means that thermal activation energy belonging to hopping between two local sites decreases with increasing frequency.

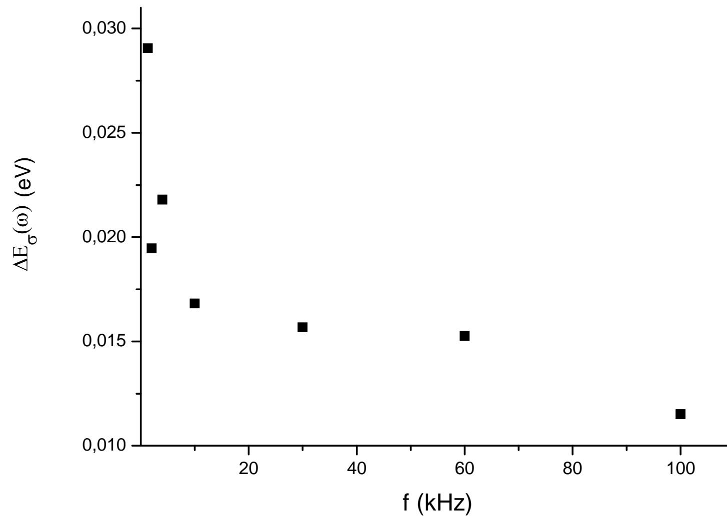

Fig.4: Frequency dependence of $\Delta E_{\sigma}(\omega)$ for Al_2O_3 thin films of thickness 1450 Å.

3.2. Dielectric constant

Our specimens are in the form of parallel plate capacitors. Therefore we calculated the dielectric constant ε_1 from the usual parallel plate capacitor equation

$$\varepsilon_1 = \frac{Cd}{\varepsilon_0 A},$$

where C is the capacitance, d is the oxide layer thickness, ε_0 is the free space permittivity and A is the area of the dielectric layer. Film thickness is an important parameter affecting the dielectric properties of the material under investigation, particularly in thin films. The thickness dependence of the dielectric constant ε_1 at different frequencies and different temperatures in the Al_2O_3 thin films in the thickness range of 50-1550 Å are shown in Figs. 5 and 6. ε_1 is almost independent of thickness and has a constant value of about 9 for the films whose thicknesses excess □ 1500 Å. Towards lower thicknesses, ε_1 is directly proportional with thickness. The effective thickness of insulators decreases with increasing density of void [27, 28]. The decrease in ε_1 can be explained by saying that the effective medium decreases as thickness decreases [29]. The frequency dependence of ε_1 at different temperatures for the film of thickness 270 Å is shown as a representative example in Fig.7. From this figure, it is clear that ε_1 decreases as frequency increases but increases with increasing temperature.

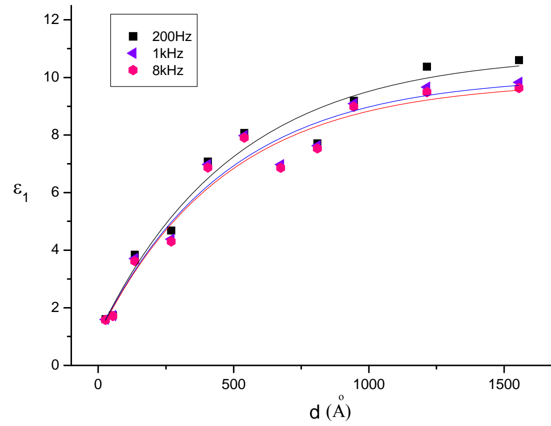

Fig.5: Thickness dependence of ε_1 for Al_2O_3 thin films at different frequencies at 300 K.

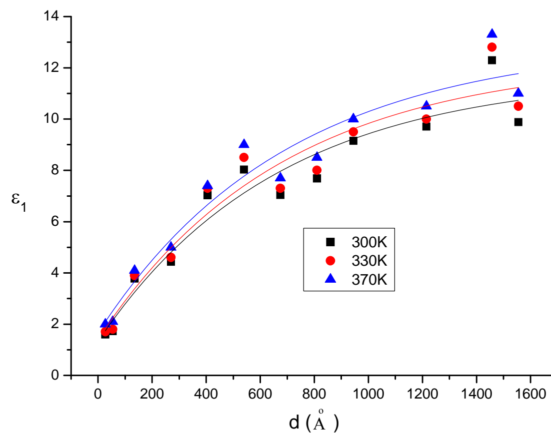

Fig.6: Thickness dependence of ε_1 for Al_2O_3 thin films at different temperatures at 400 Hz.

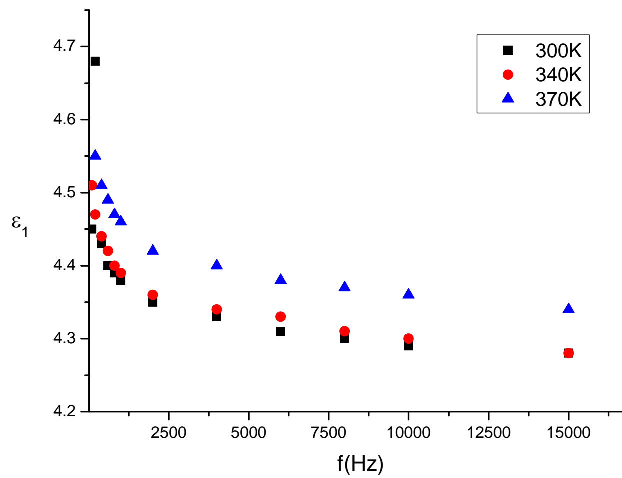

Fig.7: Frequency dependence of the ε_1 for Al_2O_3 thin films of thickness 270 Å at different temperatures.

In a material placed in an electric field, several different polarization mechanisms arise, such as electronic, ionic, dipolar and interfacial polarizations. The total polarization is due to the sum of these ones. Each mechanism may dominate in different frequency regions. In one of our works [2], we proposed that the ionic mechanism is dominant at low frequency region. When the frequency is increased the relaxation time decrease and dipolar mechanism lost its effect since it necessitates longer time with reference to electronic and ionic ones. Thus the total polarization goes down and this causes ε_1 to decrease with increasing frequency. This decreases the value of dielectric constant with frequency approaching a constant value at higher frequency corresponding only to interfacial polarization [26, 30]. When the temperature is increased, the structure relaxes and the orientation of the polarized units become easier and hence the value of orientational polarization increases. Dielectric constant increases as expected [31].

We calculated both the thickness dependence of the Temperature Coefficient of Capacitance (TCC) and Temperature Coefficient of Permittivity (TCP) of Al_2O_3 thin films using the following expressions, respectively

$$\mathrm{TCC} = \frac{1}{C_s}\frac{\mathrm{d}C}{\mathrm{d}T} \qquad \mathrm{TCP} = \frac{1}{\varepsilon}\frac{\mathrm{d}\varepsilon}{\mathrm{d}T}$$

The calcuated values are given in Table 1 as a function of the film thickness at 1KHz frequency and 300K temperature.

3.3. Dielectric loss

As is seen from Fig. 8, ε_2 increases with temperature at all frequencies [30, 32]. This behaviour of ε_2 can be reasoned as follows: The behaviour of charge carriers under the effect of constant and variable electric fields yields energy lost. Energy lost due to dc conductivity under the effect of constant electric field increases with temperature. This energy lost could be thought to be calculated by $\varepsilon_2 = \frac{\sigma_{dc}}{\varepsilon_0 \omega}$. As an example, $\sigma_{dc} = 2.7\times10^{-9}\,\Omega^{-1}\mathrm{m}^{-1}$ for the 1000 Å Al_2O_3 thin film, at room temperature and at 1KHz frequency; the energy lost for dc conductivity has been calculated to be 0.0485×10^{-5}. But this value is smaller from the experimentally determined one. Hence the reason for this energy lost cannot be the dc conductivity [30]. Therefore the energy lost is related to the dielectric relaxation appearing due to alternating electric field [31]. In order to understand the reason of the energy lost under alternating electric field one has to study the dielectric relaxation.

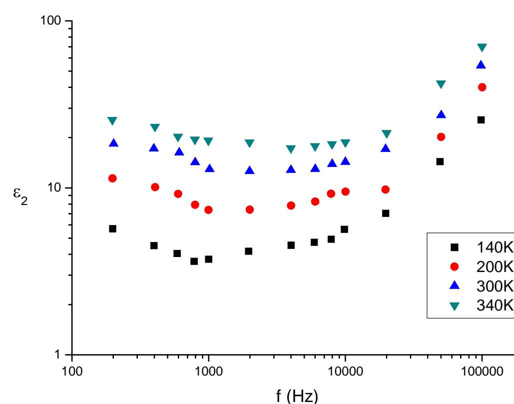

Fig.8: Frequency dependence of ε_2 for Al_2O_3 thin film of thickness 810 Å at different temperatures.

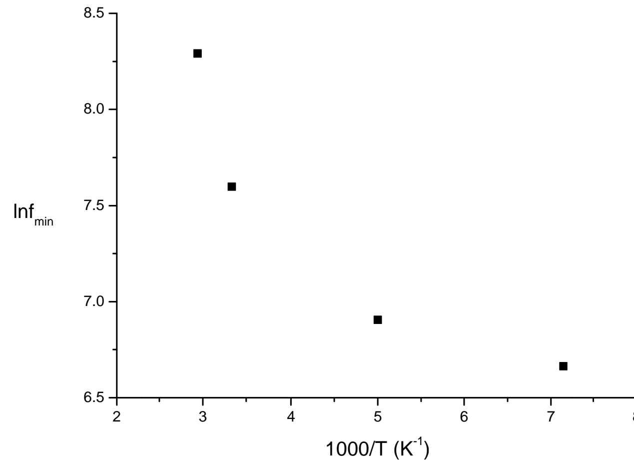

Fig.9: The plot of $\ln f_{min}$ *versus 1000/T.*

Table 1: The thickness dependence of TCC and TCP at 1kHz and 300K.

d(Å)	TCC(ppm/K)	TCP(ppm/K)
135	162.22	166.67
270	245.88	254.67
405	283.43	281.11
540	562.78	660.74
810	201.90	197.33
945	570.57	569.20
1215	2399.75	2407.68
1458	2315.30	2096.01
1555	2656.55	2620.95

The losses related to relaxation are the heat energy originated as the result of interaction between electric field induced polarizing charge carriers with lattice and is directly proportional with $\sigma_{ac}(\omega)$. With the increase of temperature the structure relaxes and the polarization gets easier. Hence $\sigma_{ac}(\omega)$ increases and ac conductivity losses increase. This means that ε_2 gets higher with temperature [32-33].

The frequency dependence of dielectric loss ε_2 at various temperature values is shown for 1450 $\overset{o}{\mathrm{A}}$ thick Al_2O_3 film in Fig. 8 as a typical example. It can be seen from this figure that as frequency increases ε_2 decreases and reaches a minimum and thereafter increases. As temperature goes higher the frequency at which ε_2 reaches a minimum shifts towards higher frequencies. The activation energy for the observed relaxation process was evaluated from

$$f_{\min} = f_0 \mathrm{e}^{-\frac{\Delta E}{k_B T}},$$

where $f_{\min}$ is the frequency at which ε_2 is minimum and ΔE is the activation energy. The plot of $f_{\min}$ versus T^{-1} is shown in Fig. 9. From the slope of the straight line the activation energy evaluated as 0.029eV. The activation energy values calculated from ac conductivity and dielectric loss factor measurements are in good agreement with each other. Furthermore, these values agree with the model of hopping of charge carriers by thermal activation between two sites having a coulombic potential well [19, 34].

4. Conclusion

Amorphous thin films of Al_2O_3 in the thickness range 50-1550 $\overset{o}{A}$ were prepared by anodic oxidation technique. The dielectric constant ε_1 was found to decrease with increasing frequency but increase with temperature in the given intervals. The ac conductivity obeys the ω^s law with a temperature dependence s ($s < 1$) which goes down as temperature increases. The temperature dependence of s is attributed to the correlated barrier hopping model. The activation energy values calculated from the ac conductivity and dielectric loss factor measurements are in good agreement with each other. The obtained values agree with the hopping model of charge carriers by thermal activation between two sites having a coulombic potential well. The film thickness dependence of TCC and TCP of the Al_2O_3 thin films have also been determined.

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