A STUDY ON A.C PROPERTIES OF TIN SELENIDE THIN FILMS

Samsudi Sakrani, Zulkafli Othaman, Karim Deraman and Yussof Wahab

Thin Film Laboratory, Physics Department
Faculty of Science, University Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

ABSTRACT

A.c properties of tin selenide thin films prepared by an encapsulated selenization method are investigated. The measurements obtained from Al/SnSe/Al sandwich structures showed strong indication of frequency and temperature dependence of capacitance, dielectric loss and conductance over the ranges of 5-200 kHz and 228-373 K, respectively. Dielectric behaviour was expected to be due to space charge polarization which contributed to a.c conduction. This was generally explained in terms of hopping of the charge carriers between localized states with activation energies 0.03-0.08 eV. Parameters such as trap binding energy (0.94 eV) and minimum hopping distance (1.01 nm) were also predicted.

Keywords: selenide, thin film capacitance, dielectric loss, conductance, polarization

INTRODUCTION

Recent interest in tin selenide (SnSe) thin films has resulted, mostly from characterization measurements of electro-optic properties and applications of electronic devices, such as memory switching, photodiodes and heterojunctions [1-3]. SnSe is one of the IV-VI group semiconducting material in view of its covalent bonding [4] and positive electro-negativities existing in of both elements. Studies on d.c properties have been extensively covered, with the measured resistivities, 0.07-300 Ωcm and activation energies, 0.01-0.28 eV [6-11]. The different conduction phenomena in SnSe thin films was also observed, apparently due to hopping [12] and Poole-Frenkel [13] conduction at low and high temperatures, respectively. Prominent results in a.c properties of SnSe thin films was reported recently by Pejova and Grozdanov [14] using chemical synthesis. Attention on this matter is given in the present work in order to acquire some information obtained from the a.c measurements, in particular the extent of dielectric behaviour and conduction mechanisms. These studies are apparently similar to the works of Suguna *et al.* [15] and Sharma *et al.* [16] but different in the methods of thin film preparation.

EXPERIMENTAL PROCEDURE

Samples was prepared using a E306 vacuum coater with masking system and deposition parameters set for fabricating eight Al-SnSe-Al sandwich structures on glass substrates, each of active area, 5.89×10^{-6} m^2. The Al electrodes, of thickness 150 nm, were evaporated from tungsten filaments at the rates 1 nms^{-1}, while SnSe was prepared using an encapsulated selenization of the stacked layers [17]. In the latter method granular tin and selenium of purity 5N were evaporated from molybdenum boats at pressures less than 10^{-5} and rates 0.8 nms^{-1} (Sn) and 0.2 nms^{-1} (Se) mbar in order to form Sn/Se stacked layers of equal thickness ratio and placed them in a high grade carbon block. Annealing was performed in an evacuated chamber under the running argon gas at 240 °C for three hours to form stoichiometric composition of SnSe after room temperature cooling. These procedures were aimed at preventing material losses during heating and ensuring the optimum crystallization process; thus total film thicknesses of SnSe were typically 100-

500 nm. During each deposition, film thicknesses were monitored using a FTM 5 quartz crystal and the resulting films were later confirmed using a stylus. It was earlier confirmed that the contacts between Al-SnSe at both interfaces were ohmic, even after annealing in vacuum condition.

The capacitance of 100, 200, 300, 400 and 500 nm (thickness of SnSe) samples were measured using a Hewlett-Packard 4192A LCZ impedance analyzer (13.6 MHz) at a fixed frequency 100 kHz and room temperature in an evacuated container for the determination of dielectric constant. A.c measurements were also carried out on the 200 nm samples using a similar equipment at varying frequencies 5-200 kHz and temperatures 228-373 K; these were purposely for the establishment of graphs of capacitance, dielectric loss and conductivity as functions of frequency and temperature. All the measurements were carried out on the samples placed in a liquid nitrogen cooled cryostat at a pressure 10^{-2} mbar.

RESULTS AND DISCUSSION

Dielectric constant

The capacitance, C_d of two parallel metallic plates filled with a dielectric material of thickness, d is given by

$$C = \frac{\varepsilon_s \varepsilon_o A}{d}$$
(1)

where ε_s is a relative permittivity of a dielectric, ε_o permittivity in vacuum space and A an effective area. The dielectric constant is obtained by simply plotting a graph of C against $1/d$ (Figure 1) and equating the gradient of a straight line with $\varepsilon_s \varepsilon_o A$, in order to deduce ε_s. Nevertheless, the straight line is not passing the origin and it rather intersecting the C-axis at 5.73 nF. According to Gould *et al.* [18] there exist a parallel capacitance, C' with respect to C which can give rise to an equivalent capacitance,

$$C_e = C + C' = \frac{\varepsilon_s \varepsilon_o A}{d} + C'$$
(2)

The dielectric constant, obtained from Figure 1 is $\varepsilon_s = 14.52$, which is comparable to those of bulk SnSe, 13.38 [14, 15].
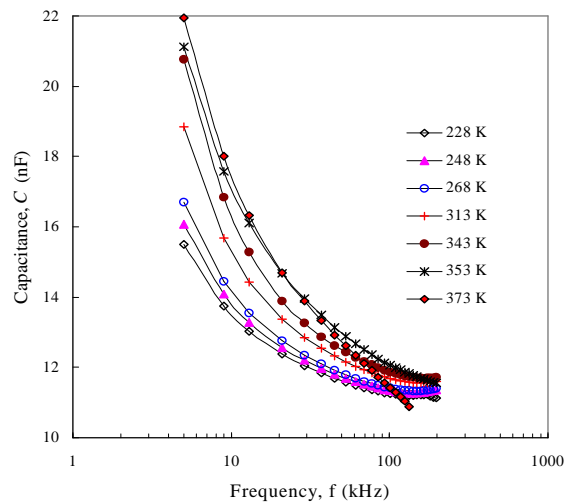
Capacitance

The graphs of capacitance as functions of frequency and temperature are shown in Figure 2 and Figure 3, respectively. Noticeably, the fall in capacitance is very rapid in the initial frequency, starting between 15-22 nF and then gradually attaining 11 nF at a frequency f = 100 kHz for all the temperatures (Figure 2).
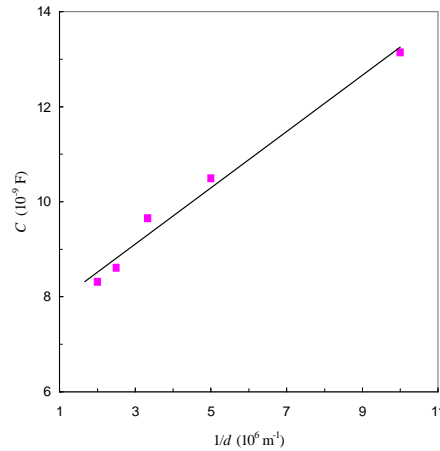
**Figure 1:** Capacitance plotted as a function reciprocal film thickness

In contrast, the temperature dependency of capacitance appears to be much significant at higher temperatures greater than 280 °C and lower frequencies (Figure 3). A marked 30% increase in capacitance is observed for a 5 kHz curve. These results give the approximate dielectric constants which vary with temperature in an increasing manner to that shown in Fig. 3 according to Equation (1).

Figure 2: Variation of capacitance with frequency at different temperatures.

Dielectric loss

Dielectric loss or $\tan\delta$ was obtained for different ranges of frequency 5-120 kHz and temperature 228-373 K. It is seen that, from the graphs shown in Fig. 4, the modes of variation are associated with the presence of loss minimum for all the temperatures. These values are observed to displace slightly to the right (for 228-313 K) and left sides (for 333-373 K) of the 100 kHz mark, with overall changes in $\tan\delta$ between 0.116-0.180 over the range of frequencies.
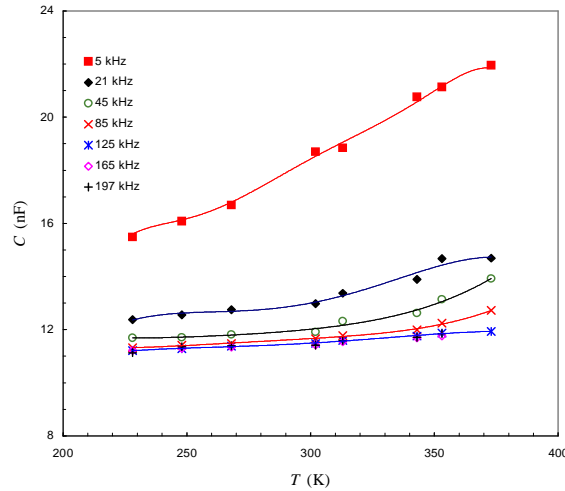
Figure 3: Variation of capacitance with temperature at different frequencies.

Using a Goswami and Goswami's model [19] the relationship between dielectric loss and frequency is given by

$$\tan\delta = \frac{\omega(1+\omega^2R^2C_p^{\,2})[R+r(1+\omega^2R^2C_p^{\,2})]}{(\omega^2R^2C_p)(1+\omega^2R^2C_p^{\,2})}$$

$$= \frac{1}{\omega RC_p} + \frac{r}{\omega R^2C_p} + \omega rC_p$$

$$= D\left(1+\frac{r}{R}\right) + \omega rC_p \qquad (3)$$

where $D = 1/\omega RC_p$, $\omega = 2\pi f$ is the angle frequency, R and r being the dielectric resistance and resistance due to electrode and connecting wires, respectively. Equation (3) gives the interpretation of $\tan\delta$ in terms of the parameters ω, R, C_p and r. Since $R \gg r$, then $rC_p = 1/\omega^2RC_p$ and the minimum dielectric loss occur at a frequency,
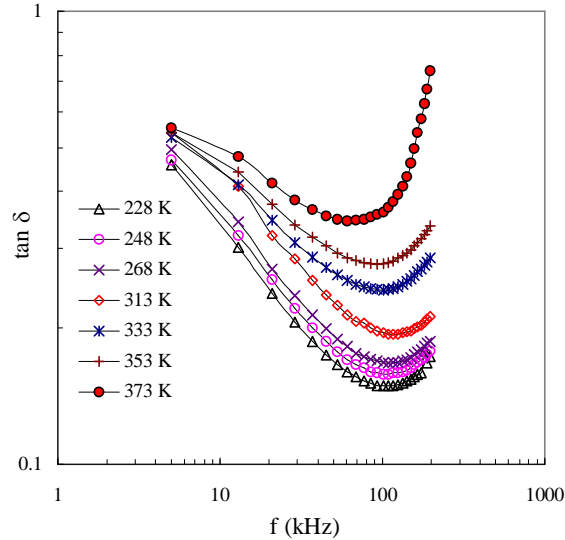
$$\omega_{min} = \sqrt{\frac{1}{rRC_p^{\,2}}} \qquad (4)$$

If $\omega R^2C_p \gg r$ or $r/R \ll 1$, then Equation (3) is simplified to

$$\tan\delta = \frac{1}{\omega RC_p} + \omega rC_p = (D + \omega rC_p) \qquad (5)$$

In case of smaller ω, $1/\omega RC_p \gg \omega rC_p$, thus the second term of Equation (5) becomes negligibly small, giving an equation of the first term,

$$\tan\delta = \frac{1}{\omega RC_p} = D \qquad (6)$$

Figure 4: Dielectric loss versus frequency for different temperatures

It is also possible that ω is considerably large, so that $1/\omega RC_p << \omega rC_p$, and elimination of the first term of equation (5) results in another expression,

$$\tan\delta = \omega rC_p \tag{7}$$

The treatments given in Equations (6) and (7) can be correlated to the curves plotted in Figure 4 where the lowering mode implies to the former equation, whilst the increasing mode refers to the later one. These results are only valid for a capacitor system comprising of capacitive element C_p in parallel with temperature-dependent resistive element R due to dielectric film, both in series with a constant low value resistance r. In addition, the metal-dielectric interfaces must be ohmic in order to satisfy Equation (2).

The effect of temperature can be explained indirectly using Equation (4), i.e. R decreases with increasing T, and the minimum angular frequency ω_{min} follows accordingly if r remains unchanged. This is consistent with slight shifts of minimum frequencies to the right-hand side of the curves for temperatures between 228-313 K. However, the trend is no longer applied to the graphs measured at higher temperatures (313-373 K) due to opposing shifts of ω_{min}, i.e. toward left-hand side. This contradiction is somewhat misunderstood and no quantitative explanation could be given at this stage of investigation. A possible reason may intuitively be predicted from the effect of contaminants, such as thin oxidized layers, oil grease, etc. which may give rise to the series and parallel resistance that eventually change equation (4) to a rather complex expression.

In review of the results obtained from Fig. 3 and 4 the lower values of ε_s and $\tan\delta$ at lower range of frequencies may be attributed to space charge polarization. It has been pointed out [20] that the influence of temperature on the dielectric constant is strongly attributed to the increase of lattice defects of the materials at high temperature, making space charge polarization dominant. Defects in SnSe thin films may be attributed from the polycrystalline nature such as grain boundaries, voids, etc. The dispersion in capacitance and dielectric loss were observed to be due to the metal-dielectric interface and crystal behavior of the material [14, 20].

A.c conductivity

The variation of a.c conductivity with frequency and temperature are shown in Figure 5 and Figure 6, respectively. It is observed that the frequency variations of conductivity in the former graph is strongly related to a power law, $\sigma = A\omega^s$, where the index, s is decreasing marginally between 0.46-0.40 for frequency $f = 10$-70 kHz and increasing between 0.91-0.99 for $f = 70$-120 kHz. These values are smaller than that of the majority of dielectric materials with $s = 2$ to 16. The temperature variations of conductivity shown in Figs. 6 and 7 is apparently temperature sensitive and becoming more pronounced at a higher range of $T > 280$ K. A general expression, $\sigma_{a.c} = A(T)\omega^{s}(T)$ was proposed by Anwar and Hogarth [21] where A is a complex parameter weakly temperature dependent. There is a possible electronic hopping which capable of inducing a.c conduction at low temperature, a similar phenomena occurring in the d.c conductivity of SnSe thin films [12]. The associated activation energy, ΔE is related to Arrhenius equation,

$$\sigma_{ac} = \sigma_o \exp\left(-\frac{\Delta E}{kT}\right) \tag{8}$$

where σ_o is a pre-exponential factor and k is Boltzmann constant. Fig. 7 shows linear graphs of ln σ_{ac} - $1/T$ which reasonably fit equation (8), and thus yielding ΔE. These results are tabulated in Table 1 as follows:

Table 1: Thermal activation energies at different frequencies and temperatures.

| f (kHz)	5	21	45	85	125	165	197
ΔE (eV)	0.033	0.079	0.124	0.200	0.293	0.406	0.529

Sakrani and Jabar [12] have studied the low temperature hopping conduction in SnSe thin films using current-voltage measurements and found activation energies 0.040-0.048 eV and 0.066-0.069 eV at temperature ranges 123-188 K and 188-270 K, respectively and these values are consistent with 0.04 eV on d.c measurements at temperatures 193-303 K [17]. The present results, i.e. 0.033-0.079 eV in the first two column of Table 1 seem to agree with the d.c conductivity measurements, and therefore, supporting the evidence of hopping conduction mechanism occurring in SnSe thin films at temperatures less than 270 °C.

Hutagalung [17] has indicated that SnSe thin film prepared by an encapsulated selenization method is of polycrystal type, and it is possible that imperfection of SnSe structure during the crystallization process leads to the establishment of defects and traps within the energy gap which may effect the nature of carrier transport. A.c conduction in SnSe thin films is best explained using Elliott's model in association with the trapping parameters, such as A.c angular frequency ω, effective relaxation time, τ, dielectric constant, ε_s, defect density of states, N and trap binding energy, E_b, and is given by [19]
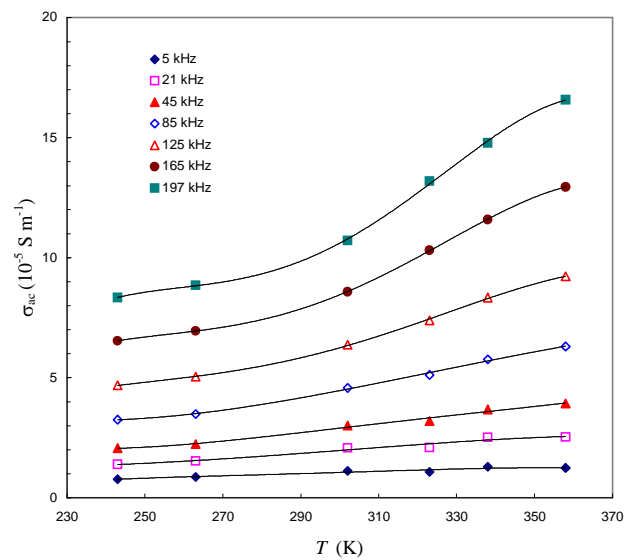
$$\sigma(\omega) = \frac{\pi^2 N^2 \varepsilon_s}{24}\left[\frac{8q^2}{\varepsilon_s E_b}\right]^6 \frac{\omega^s}{\tau^\beta} \tag{9}$$

where q is the electronic charge, $s = 1-\beta$ $\square$is the gradient of the linear portion of the ln σ_{ac}-ln f graphs shown in Fig. 5 and only valid for low temperature measurements. A set of s and thus β is obtained for frequency ranges $f < 70$ kHz. E_b is calculated using an expression,
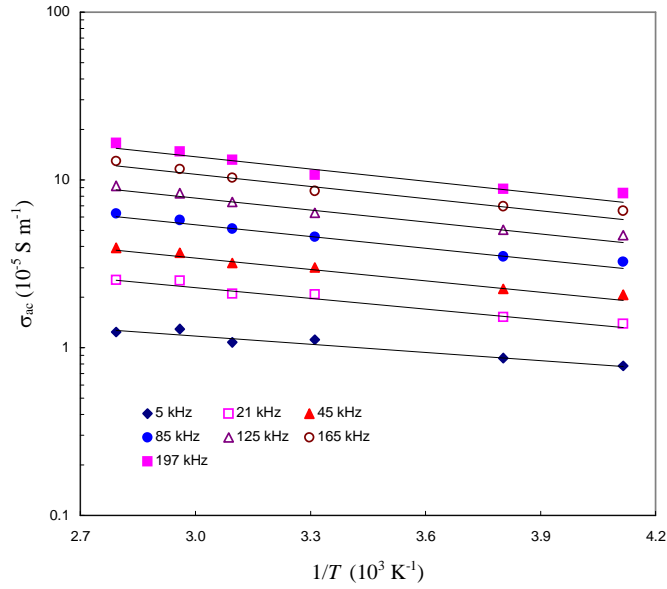
$$\beta = \frac{6kT}{E_b} \tag{10}$$
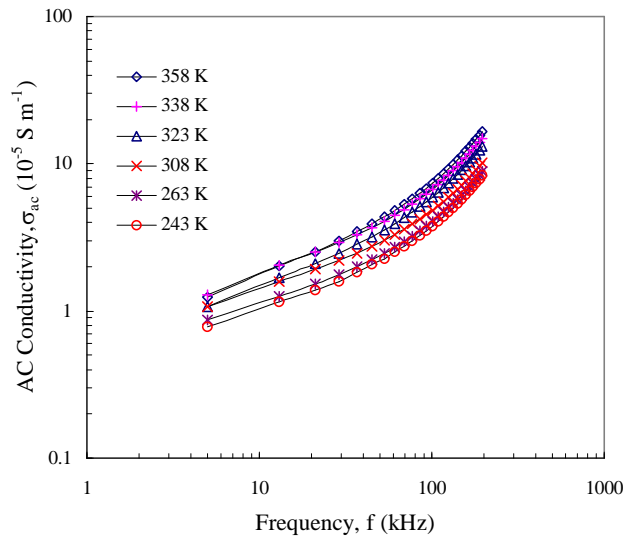
Figure 5:A.c conductivity versus frequency for different temperatures.

Figure 6: Variation of a.c conductivity with temperature at different frequencies.

**Figure 7:** A.c conductivity plotted as a function of reciprocal temperature at different frequencies.

Thus, by plotting β against T the trap binding energy E_b can be deduced from the linear relationship. The plot shown in Fig. 8 seems to be in a good agreement with equation (10), resulting in a gradient 5.50 x 10^{-4} and the trap binding energy of $E_b = 0.94$ eV for frequencies $f < 70$ kHz. It is also seen that the experimentally measured values of s = 0.46 at 50 kHz and s = 0.79 at 80 kHz are comparable to the predicted s = 0.72 when E_b = 0.80 eV [23] is substituted into equation (10). Furthermore, the parameter $E_b = 0.94$ eV lies within the range of optical band gaps E = 0.79-0.95 eV [24] measured on SnSe thin films prepared by encapsulated selenization and 0.95 eV [29], but still lower than 1.21 eV [25] and 1.30 eV [10] due to different in preparation techniques used. This suggests the validity of the Elliott's model at low temperatures less than 270 °C.

There exists a minimal condition between subsequent hopping via a distance, r_{min} that can be predicted using an equation,

$$r_{min} = \frac{2q^2}{\pi\varepsilon_s\varepsilon_o E_b} \qquad (11)$$

From Equation (11) the calculated value is $r_{min} = 1.01$ nm. It is a distance between pairs or trap levels encountered by hopping the carriers in order to overcome an energy barrier of $E_b = 0.94$.eV within the energy gap of SnSe.
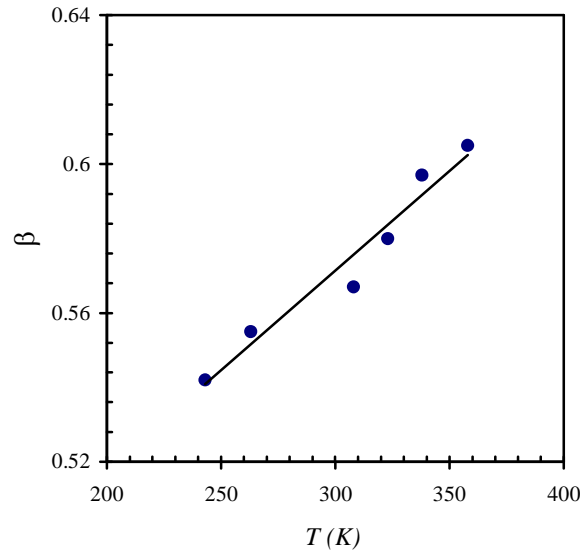
Figure 8: Temperature dependence of β =1-s which satisfies equation (10).

CONCLUSION

SnSe thin films exhibited some dielectric properties under a.c measurements. The computed dielectric constant of 12.13 was found to be consistent with those of bulk material. There were strong indication of both frequency and temperature dependency of capacitance, dielectric dissipation and conductivity within the measurable ranges 5-200 kHz and temperatures 228-373 K, respectively. The variation of capacitance with both frequency and temperature were found to follow the Goswami and Goswami's model. From the frequency variation of dielectric loss, there exist dielectric behaviour due to space charge polarization which occurred at low frequencies. A.c conductivity was observed to obey the Elliott's model and some of the computed trapping parameters showed a reasonable agreement with those measured earlier. Activation energies 0.03-0.08 eV were almost identical to d.c conductivity, and the low values were indicative of electronic hopping conduction at low frequencies and temperatures. Trap binding energy 0.94 eV was approximately equal to the band gap of SnSe thin film, with minimum hopping distance 1.01 nm.

ACKNOWLEDGEMENTS

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