Thickness dependence of the dielectric properties of thermally evaporated \( \text{Sb}_2\text{Te}_3 \) thin films

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Abstract. \( \text{Sb}_2\text{Te}_3 \) thin films of different thickness (23 - 350 nm) were prepared by thermal evaporation technique. The thickness dependence of the ac conductivity and dielectric properties of the \( \text{Sb}_2\text{Te}_3 \) films have been investigated in the frequency range 10 Hz-100 kHz and within the temperature range 293-373 K. Both the dielectric constant \( \varepsilon_1 \) and dielectric loss factor \( \varepsilon_2 \) were found to depend on frequency, temperature and film thickness. The frequency and temperature dependence of ac conductivity (\( \sigma_{ac}(\omega) \)) has also been determined. The ac conductivity of our samples satisfies the well known ac power law; i.e.,
\[
\sigma_{ac}(\omega) \propto \omega^s
\]
where \( s < 1 \) and independent of the film thickness. The temperature dependence of ac conductivity and parameter \( s \) is reasonably well interpreted by the correlated barrier hopping (CBH) model. The activation energies were evaluated for various thicknesses. The temperature coefficient of the capacitance (TCC) and permittivity (TCP) were determined as a function of the film thickness. The microstructure of the samples were analyzed using X-ray diffraction (XRD). This results are discussed on the base of the differences in their morphologies and thicknesses. The tendency for amorphization of the crystalline phases becomes evident as the film thickness increases.

1. Introduction
Antimony Telluride is a semiconducting chalcogenide of the VB and VIB groups of elements. Due to its attractive photo conducting properties and its high Seebeck coefficient, low thermal conductivity, low electrical resistivity, low band gap, and long-term stability \( \text{Sb}_2\text{Te}_3 \) has wide industrial applications such as target material in television camera, microwave devices, switching devices and optoelectronic devices [1-4]. \( \text{Sb}_2\text{Te}_3 \) thin films have received considerable attention because of their potential application in the fabrication of integrated thermoelectric devices. To obtain \( \text{Sb}_2\text{Te}_3 \) thin films, a number of techniques have been used in the literature, such as thermal evaporation[5,6], atomic layer epitaxy(ALE) [7], sputtering [2,8], electrochemical method [9], flash evaporation [10] and metalorganic chemical vapor deposition (MOCVD) [11].

The electrical, thermoelctrical and optical properties of bulk samples \( \text{Sb}_2\text{Te}_3 \) were studied [12,13]. However, thickness dependence of the dielectric properties of films prepared from that compound were hardly investigated [5]. Therefore, at this study, the dielectric properties of the thermal evaporated \( \text{Sb}_2\text{Te}_3 \) thin films have been investigated with respect to frequency, temperature, and especially film thickness in detail, in the frequency range 10 Hz-100 kHz and in the temperature range 293-373 K and 23 - 350 nm film thickness.

2. Experimental Details
The \( \text{Al}[\text{Sb}_2\text{Te}_3]\text{Al} \) thin film sandwich structures were prepared by the following sequential evaporation procedure for dielectric measurements. The substrates were cleaned with detergent and flushed with copious amounts of de-ionized water. Finally the substrates were sequentially rinsed with acetone, methanol and isopropyl alcohol. The base and counter \( \text{Al} \) electrodes were deposited by thermal evaporation. The system was pumped to a base pressure of less than \( 1,333 \times 10^{-3} \) Pa. First \( \text{Al} \) was evaporated to serve as the bottom electrode on the Corning glass substrates. \( \text{Sb}_2\text{Te}_3 \) ingot of high purity (99.99%) were used as the starting material. The crushed ingot were evaporated from molybdenum boat at a vacuum better than \( 1,333 \times 10^{-4} \) Pa. \( \text{Al} \) was thermally evaporated to form the top electrode, finally. The evaporation temperature of \( \text{Sb}_2\text{Te}_3 \) ingot was about 600°C and the evaporation temperature of \( \text{Al} \) wires was about 1200°C. The resulting \( \text{Al}[\text{Sb}_2\text{Te}_3]\text{Al} \) thin film sandwich
structures have a capacitive configuration of effective area 6 mm². Films were aneled at 373 K for 1h. A HP 4192A 5Hz-13MHz LF Impedance Analyzer were used for the capacitance and dissipation factor measurements. The ohmic character of contacts were determined by applying front and reverse biases between bottom and top electrodes. For both of them, the resistance measurements gave same results [2]. These measurements were made in approximately 1,333x10⁻³ Pa vacuum and were carried out in the temperature range 293-373 K. Temperatures of the samples during the study were measured with a copper-constantan thermocouple. The thickness of films were measured by Tolansky interferometer method. The film thickness ranged from 23-350 nm. X-ray diffraction analysis was used to investigated the structure of the films. The total conductivity was calculated from the equation \( \sigma(\omega) = L/ZA \), where \( L \) is the thickness of the film and \( A \) is the cross-sectional area.

The dielectric constant was calculated from the equation: \( \epsilon_r = LC/A \epsilon_0 \), where \( C \) is the capacitance of the film, and \( \epsilon_0 \) is the permittivity of the free space. The dielectric loss was calculated from equation: \( \tan\delta = \epsilon_r \tan\delta \), where \( \delta = 90 - \Phi \), \( \Phi \) is the phase angle.

X-ray diffraction patterns of the films tell about their cristallinity. It is evident from Figs.1-a and b that increasing film thickness changes the film structure from being crystalline into amorphous. For the thinnest film (60 nm), all the diffraction peaks in Fig.1-a have been identified to belong to Sb₂Te₃ and Sb (JCPDS card no: 15-0874 and 85-1322). The peak values for this X-ray output are given in Table 1 where the 2θ values, calculated from the diffraction pattern of Fig.1-a, together with the standard 2θ values of the Sb₂Te₃ and Sb phase are also shown for comparison. A very good coincidence of these 2θ values with the standard ones is seen. Finally, Fig.1-b shows the completion of amorphisation.

3. Results

3.1 Structural investigations

Figs.1-a and b shows the X-ray diffraction patterns (XRD) of the thin films prepared on glass substrates. The X-ray diffraction patterns of the films tell about their cristallinity. It is evident from Figs.1-a and b that increasing film thickness changes the film structure from being crystalline into amorphous. For the thinnest film (60 nm), all the diffraction peaks in Fig.1-a have been identified to belong to Sb₂Te₃ and Sb (JCPDS card no: 15-0874 and 85-1322). The peak values for this X-ray output are given in Table 1 where the 2θ values, calculated from the diffraction pattern of Fig.1-a, together with the standard 2θ values of the Sb₂Te₃ and Sb phase are also shown for comparison. A very good coincidence of these 2θ values with the standard ones is seen. Finally, Fig.1-b shows the completion of amorphisation.

3.2 Dielectric constant

Fig. 2 shows the frequency dependence of dielectric constant, \( \varepsilon_r \), at different temperatures for of Sb₂Te₃ film of thickness 42 nm as a representative example. It is clear from the figure that \( \varepsilon_r \) with frequency can be attributed to the fact that at low frequencies \( \varepsilon_r \) for polar material is due to the contribution of multicomponents of polarizability, deformational (electronic, ionic) and relaxation (orientational and interfacial) as suggested by Farid A.M. et al. [5,15]. When the frequency is increased, the orientational polarization decreases since it takes more time than electronic and ionic polarization. This decreases the value of dielectric constant with frequency reaching a constant value at high frequency due to interfacial polarization.

The increase of \( \varepsilon_r \) with temperature can be attributed to the fact that the orientational polarization is connected with the thermal motion of molecules, so dipoles cannot orient themselves at low temperatures. When the

![Figure 1a. X-ray diffraction patterns of Sb₂Te₃ as-deposited films. Film thickness: 60 nm](image1)

![Figure 1b. X-ray diffraction patterns of Sb₂Te₃ as-deposited films. Film thickness: 85nm](image2)

| Table 1. XRD Diffraction results and JCPDS standarts |
|-----------------------------------------------|
| **Observed** | **Standart** |
| **20 from XRD (Deg.)** | **20 from JCPDS (Deg.)** | **Intensity** | **h** | **k** | **l** | **Number** |
| 23,520 | 23,656 | 5,6 | 0 | 0 | 3 | 85-1322 |
| 28,040 | 28,245 | 100 | 0 | 1 | 5 | 15-0874 |
| 41,120 | 41,903 | 32,7 | 1 | 1 | 0 | 85-1322 |
| 42,880 | 42,402 | 25 | 1 | 1 | 0 | 15-0874 |
temperature is increased the orientation of dipoles is facilitated and this increases the value of orientational polarization and this increases $\epsilon_1$ with increasing temperatures [16]. The thickness dependence of the dielectric constant, $\epsilon_1$ at different frequencies and different temperatures in the Sb$_2$Te$_3$ thickness range of 23-350 nm are shown in Fig. 3 and Fig. 4. Towards lower thicknesses $\epsilon_1$ decreases with decreasing thickness. This result is in agreement with the literature [17,18]. The observed decreases in $\epsilon_1$ is thought to arise from the increase in the density of voids for lower thicknesses. Deepha [19] and Kumar [20] have also reported that the effective thickness of insulators decreases with increasing density of voids causing the dielectric constant to decrease. Hence, the decrease in total polarization can be explained by saying that the effective medium decreases as thickness decreases. The frequency dependence of $\epsilon_1$ for different film thicknesses is shown in Fig. 5. It is known that the contribution of polarization mechanisms with long relaxation times increases at lower frequencies [17]. Furthermore, the temperature coefficient of the capacitance (TCC) and permittivity (TCP) were determined and are given in Table 2.

### Table 2. The thickness dependence of TCC (Temperature Coefficient of Capacitance) and TCP(Temperature Coefficient of Permittivity) for Sb$_2$Te$_3$ films at 293K and 1kHz

| $d$(nm) | TCC(ppm/K) | TCP(ppm/K) |
|---------|------------|------------|
| 23      | 2666.67    | 2673.15    |
| 42      | 6357.32    | 6351.91    |
| 120     | 4886.67    | 4917.13    |
| 240     | 7871.11    | 7782.18    |
| 270     | 7362.5     | 7420.2     |
| 350     | 6981.71    | 6985.31    |

3.2 Ac conductivity

A common feature to all amorphous semiconductors is that ac electrical conductivity $\sigma_{ac}(\omega)$ increases with increasing frequency according to the equation [21].

$$\sigma_{ac}(\omega) = \sigma_{dc} + \sigma_{ac} = A \omega^s$$  \hspace{1cm} (1)

where $\omega$ is the angular frequency ($\omega = 2\pi f$), $\sigma_{ac}(\omega)$ is the measured total electrical conductivity, $\sigma_{dc}$ is the dc electrical conductivity, $s$ is the frequency exponent ($s<1$) and $A$ is constant dependent on temperature. It is found that the $\omega^s$ dependence of ac conductivity $\sigma_{ac}(\omega)$ is a general characteristic for chalcogenide glasses up to a frequency of $10^6$ Hz where $\omega$ is the angular frequency, $s$ is the frequency exponent and $A$ is a constant independent of frequency [22]. Fig. 6-a shows the frequency dependence of ac conductivity $\sigma_{ac}(\omega)$ for Al$_2$O$_3$ film of thickness 270 nm at different temperatures as a representative example. It is clear from the figure that $\sigma_{ac}(\omega)$ increases linearly with frequency according to equation (1). The same behavior of the frequency dependence of $\sigma_{ac}(\omega)$ was obtained for all investigated films. Values of the frequency exponent $s$ were obtained from the slopes of these lines of the figure. The temperature dependence of $s$ for the investigated films is shown in Fig. 6-b. It is seen that $s$ decreases as the temperature increases, independent on film thickness in the investigated range.
According to the quantum mechanical tunneling (QMT) model [23], the exponent $s$ is almost equal to 0.8 and slightly increases with increasing temperature or independent on temperature. Therefore, QMT model is considered not applicable to the obtained results. According to the overlapping-large polaron tunneling (OLPT) model [24], the exponent $s$ is both temperature and frequency dependent. $s$ decreases with increasing temperature from unity at room temperature to a minimum value at a certain temperature then it increases with increasing temperature. Therefore, OLPT model is not applicable to the obtained results.

**Table 3.** The thickness dependence of Density of States N(E) for Sb$_2$Te$_3$ films at 1kHz

| Thickness (nm) | 0.293 | 0.323 | 0.333 | 0.343 | 0.353 | 0.373 |
|---------------|-------|-------|-------|-------|-------|-------|
| N(E) (1/eVcm$^3$) | 10$^{20}$ |
| 293K | 0.53 | 0.52 | 0.52 | 0.53 | 0.54 | 0.56 | 0.62 |
| 323K | 2.34 | 2.58 | 2.77 | 3.09 | 3.45 | 3.70 | 4.21 |
| 333K | 4.24 | 4.22 | 4.69 | 5.04 | 5.32 | 5.84 |
| 343K | 5.18 | 6.01 | 6.94 | 7.96 | 9.04 | 9.82 | 11.50 |
| 353K | 3.63 | 4.38 | 5.02 | 6.50 | 7.24 | 7.49 | 7.18 |
| 373K | 2,34 | 2,58 | 2,77 | 3,09 | 3,45 | 3,70 | 4,21 |

According to correlated barrier hopping (CBH) model, values of the frequency exponent $s$ is ranged from 0.7 to 1 at room temperature and is found to decrease with increasing temperature. This is in good agreement with the obtained results, so the frequency dependence of $\sigma_{ac}(\omega)$ can be explained in terms of CBH model. In most chalcogenide glasses the obtained values of $s$ ranged from 0.7 to 1 at room temperature, and have a tendency to decrease with increasing temperature. This means that the obtained experimental results agree with the CBH model. According to the Austin-Mott Formula [25], based on CBH model, ac conductivity $\sigma_{ac}(\omega)$ can be explained in terms of the hopping of electrons between pairs of localized states at the Fermi level. $\sigma_{ac}(\omega)$ is related to the density of states $N(E_f)$ at the Fermi level by:

$$\sigma_{ac}(\omega) = (\pi/3) \left[ N(E_f) \right] 2 K T e^2 \alpha^5 \omega \left[ \ln (\omega / \omega) \right]^4$$

(2)

where $\alpha$ is the exponential decay parameter of the localized states wave function, and $\nu$ is the phonon frequency. By assuming $\nu = 10^3$ Hz and $\alpha = 1$nm [26], the density of states is calculated and is given in Table 3. for the Se$_2$Te$_3$ at frequency 1kHz. Temperature dependence of the ac conductivity $\sigma_{ac}(\omega)$ at different frequencies was studied for the investigated films. Fig. 7 shows a plot of $\ln \sigma_{ac}(\omega)$ against 1000/T of thicknesses 270 nm as a representative example. It is clear from this figure that $\ln \sigma_{ac}(\omega)$ increases linearly with the reciprocal of absolute temperature. This suggested that the ac conductivity is a thermally activated process from different localized states in the gap or its tails. The activation energy of conduction, $\Delta E_{ac}(\omega)$ is calculated at different frequencies from the slopes of the straight lines, obtained for all investigated thicknesses using the well known equation

$\sigma = \sigma_0 \exp (-\Delta E_{ac}(\omega) / kT)$. The frequency dependence of the activation energy for the investigated films is shown in Fig. 8. It is clear that $\Delta E_{ac}(\omega)$ decreases with increase of frequency. It can also be seen that $\Delta E_{ac}(\omega)$ tends to decrease with increasing frequency as found for other amorphous materials [27].
The increase of the applied field frequency enhances the electronic jumps between the localized states, consequently the activation energy \( \Delta E_\zeta(\omega) \) decreases with increasing frequency. The activation energies, which value ~ 0.1 eV can be attributed as the activation energy for electronic polarization. The same behavior was obtained for all investigated films.

3.3 Dielectric Loss \( \varepsilon_2 \)

It was observed that \( \varepsilon_2 \) increases as the frequency increases and reaches a maximum and thereafter decreases as shown in Fig. 9.

As the temperature increases the frequency at which \( \varepsilon_2 \) reaches a maximum shifted towards higher frequencies. The increase in the dielectric loss may be due to an increase in both the residual current and absorption current. The dielectric loss caused by the dipole mechanism reaches its maximum value at a certain temperature for a definite frequency [28, 29]. The variation of dielectric loss with frequency and temperature represents the effects of various polarization mechanisms at different frequencies. Initially observed mechanism loses effective role with increasing frequency and increasing dielectric loss. At a maximum frequency another type mechanism or one of the mechanism, which the initial mechanism includes, becomes dominant in polarization process.

The activation process was evaluated from;

\[
f_{\text{min}} = f_0 \exp(-\Delta E/kT) \tag{3}\]

In Fig. 10 variation of the frequencies of minimum dielectric loss with temperature is observed. The activation energy obtained from temperature dependence of dielectric loss 0.06 eV as average.

The activation energy values evaluated from capacitance and dielectric loss factor measurements are in good agreement with each other. Depending on the obtained activation energy, this mechanism may be electronic polarization. Ionic dipole relaxations have been observed with activation energies between 0.5 and 1.0 eV. Electronic processes generally have associated low activation energies (~0.1 eV) and this presents a more favourable mechanism [30]. Temperature dependence of dielectric loss is shown in Fig. 11. Increase in
Temperature may activate or rise the effectiveness of dipolar (orientational) polarization in net polarization [31]. Fig. 12 is shown the frequency dependence of the $\varepsilon_2$ at different thickness. When the thickness dependence of dielectric loss is investigated, it is found to increase in thickness causes to increase in net polarization in structure. Higher thickness can be thought more charge carriers to be polarized, thus more dielectric loss may occur in structure.

4. Conclusion

Frequency, temperature and film thickness dependence of dielectric constant, dielectric loss factor and ac conductivity of Al|$\text{Sb}_2\text{Te}_3$|Al thin film sandwich structures were studied in detail. These factors are found to be frequency, temperature and film thickness dependent. The temperature dependence of ac conductivity and parameter $s$ is reasonably well interpreted by the correlated barrier hopping (CBH) model. The activation energies were evaluated for various thicknesses. The temperature coefficient of the capacitance (TCC) and permittivity (TCP) were determined as a function of the film thickness. The microstructure of the samples were analyzed using X-ray diffraction (XRD). This results are discussed on the base of the differences in their morphologies and thicknesses. The tendency for amorphization of the crystalline phases becomes evident as the film thickness increases.

Acknowledgement

This work was supported Research Fund of the University of Istanbul, Project No:2563 and UDP-7203/07052010.

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