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DIELECTRIC STUDIES OF AMORPHOUS $As_{45}Te_{33}Ge_{10}$ Si_{12} FILMS

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Measurements of the dielectric properties of $As_{45}Te_{33}Ge_{10}$ Si_{12} thin films prepared by thermal evaporation technique were carried out in the frequency range 10^{2-} 10^{5} Hz and within the temperature range 303 – 383 K. The dielectric relaxation behavior has been investigated, and it is found to be a thermally activated process. The analysis of the temperature dependence of relaxation time gave the activation energy for the relaxation of about 0.69 eV and the characteristic relaxation time of the order of 10^{-11}s. The activation energies obtained from the capacitance and dielectric loss measurements are in good agreement. The dielectric constant ε_1 was measured for the film samples under investigation. It is found that ε_1 has a temperature and frequency dependence. The temperature and frequency dependences of the ac conductivity were investigated for the films under test. It is found that $\boldsymbol{\sigma}_{ac}(\omega)$ can be described by the relation $\boldsymbol{\sigma}_{ac}(\omega)$=A $\boldsymbol{\omega}^{s}$ with s<1. The obtained values of s were found to decrease with increasing temperature, which which is in agreement with the correlation barrier hopping (CBH) model. An activation energy from 0.11 to 0.061 eV is observed in the studied frequency and temperature ranges.

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Keywords: Dielectric studies, Amorphous $As_{45}Te_{33}Ge_{10}$ Si_{12} films

1. Introduction

Chalcogenide glasses have been recognized as a promising materials for many applications [1,2].Thin dielectric films have attracted much attention due mainly to the possibilities for applications to various electronic and optoelectronic devices . Most of the technological, electronic and optoelectronic applications utilize materials in thin film forms. Recently, there has been growing interest in the dielectric–like behavior of some ferroelectric materials in the amorphous state [3,4].

Cholcogenide glasses have recently attracted the researchers interest [5-9], since they exhibit several peculiar phenomena useful for devices such as electrical threshold and memory switching [10,11] image storage, and photoresistors.

The investigation of electron transport in disorder systems has been gradually developed. The investigation of gap states is of particular interest, because of their effect on the electrical properties of semiconductor materials [12,13]. Several concepts proposed by many workers [14-16] start from the premise that the contribution of carriers hopping between localized states to electrical conductivity is expected in amorphous semiconductors. The hopping conduction can be easily distinguished from that of the band conduction by measuring the frequency dependence of conductivity [17-20], which as expected, is due to conduction in localized states. Measurement of frequency dependent electrical conductivity of amorphous chalcogenides is, therefore, a powerful tool for obtaining information about these states. This led to adapt and to elaborate models allowing the electronic properties of these materials to be described [17-21]

Chalcogenide glasses and films, in common with other amorphous semiconductors, exhibit in a particular frequency range an ac conductivity σ_{ac} (ω), whose dependence on the frequency is given by [22] σ_{ac} (ω) = A ω^{s} with s ≤ 1, where ω is the angular frequency, A is a

constant and s is the frequency exponent. It is found that the ω^s dependence of ac conductivity σ_{ac} (ω) with $s \leq 1$ is a general characteristic for the chalcogenide glasses up to frequencies up to 10^6 Hz and s is temperature dependent.

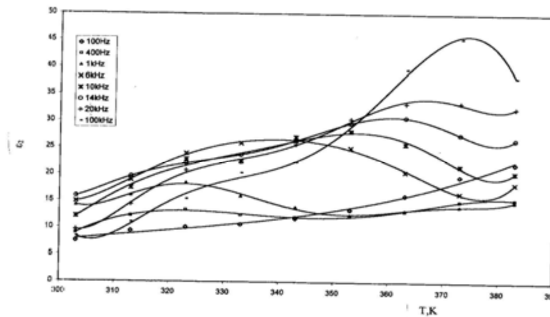

Fig.1. Dielectric loss ε_2Vs temperature T curves at different frequencies for As_{45} Te_{33} Ge_{10} Si_{12} films.

Few studies on the quaternary system As-Te-Ge-Si in the field of ac measurement have been reported in the literature. The composition $As_{45}Te_{33}Ge_{10}Si_{12}$ represented a new one of this system. The present work aims to shed light on the influences of ambient temperature and frequency on the ac conductivity and dielectric properties of amorphous chalcogenide composition $As_{45}Te_{33}Ge_{10}Si_{12}$ films. Our results are discussed in terms of different models of ac conductivity for semiconductors.

2. Experimental procedure

Bulk $As_{45}Te_{33}Ge_{10}Si_{12}$ glass sample was prepared by the well established melt quenching technique. Appropriate amounts of 99.999% pure constituent elements requiring 5 g were charged into a dry clean 8 mm inner diameter silica tube. The tube was sealed under vacuum of the order of magnitude 10^{-5} Torr.

Synthesis was carried out in an oscillatory furnace in the following sequence. The sample temperature was raised in steps in order to reduce the vapor pressure of As and Te as a result of their combination with other constituent component. At first it was raised from room temperature to 773 K(about 323 K higher than the melting point of Te)and then kept constant for 2 h . Then the temperature was raised in step of 373 K h^{-1} up to 1273 K over a long period of time (45-50 h).The long period of synthesis and rocking of the melt were necessary for homogenization of the material composition. The molten material was then rapidly quenched in iced water to obtain a sample in a glassy state. The mean rate of cooling in this case was about 573 K min^{-1}.

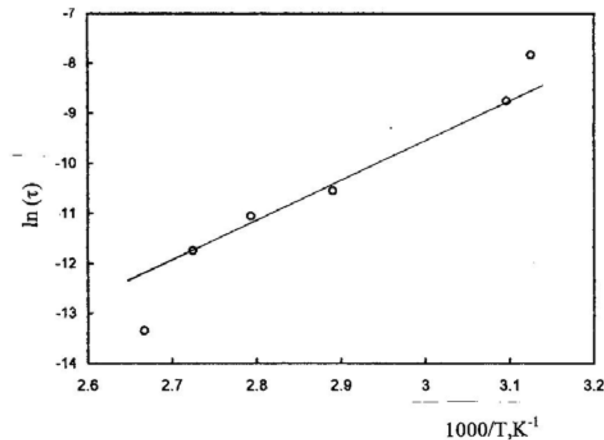

Fig. 2. Temperature dependence of the relaxation time τ Vs the reciprocal temperature for As_{45} Te_{33} Ge_{10} Si_{12} films.

Thin films of the obtained composition were then prepared by thermal evaporation technique using a high vacuum apparatus (Edward 306 A) on well cleaned glass substrate provided with Al electrodes in sandwich configuration for the ac measurements. Samples with different thicknesses were prepared under the same evaporation conditions. The substrate temperature was held below 323 K during deposition. The film thickness was established by Tolansky's method [22]) using multiple beam Fizeau fringes. The film thickness ranged from 105 to 340 nm

The amorphous nature of the films was confirmed by X-ray diffraction analysis (Philips PN 8203 diffractometer) [9].

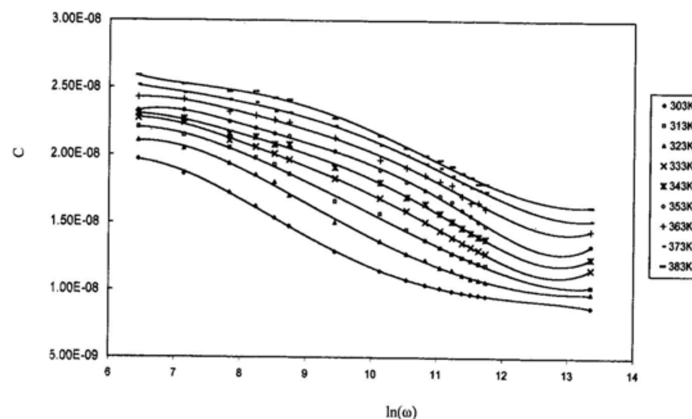

Fig 3. Capacitance Vs frequencies for the As_{45} Te_{33} Ge_{10} Si_{12} films for the measured temperature.

Ac conductivity σ_{ac}, dielectric constant ε_1, and dielectric loss ε_2 can be calculated according to the following relations $\sigma_{ac}(\omega)=\frac{1}{Z}\frac{h}{a}$, $\varepsilon_1 = C\, h / a\, \varepsilon_o$, $\varepsilon_2 = \varepsilon_1 D$ where h is the film thickness, a the sample area, ε_o the free space permittivity , and z ,C and D are the sample

impedance, capacitance, and dissipation factor of the film, respectively, which are measured directly using a programmable automatic RCL meter bridge (Philips PM 6304). The ac measurements were carried out in the temperature and frequency ranges (303 – 383 K) and (10^2 – 10^5 Hz), respectively.

3. Results and discussion

3.1 Studies on relaxation behavior

In an ac electric field the dielectric properties of the investigated composition will change with temperature and frequency. Figure (1) shows the variation of dielectric loss ε_2 with temperature at different constant frequency values. ε_2 exhibits slopes in the curves obtained, which corresponds to peaks. The positions of the peaks shift towards higher temperature as the frequency is increased. A simple Debye peak in ε_2 will be translated by the following equation [24]

$$\varepsilon_2(\omega) = (\varepsilon_s - \varepsilon_{ea})\omega\tau / (1+\omega^2\tau^2) \quad (1)$$

where ε_s is the static dielectric constant, ε_{ea} is the instantaneous value of the dielectric constant, and τ is the relaxation time. It is observed that the dielectric loss exhibits a maximum for $\omega\tau=1$, i.e for an angular frequency $\omega=1/\tau$. From the observed curves, the relaxation time can be determined at different temperature values.

The temperature dependence of the relaxation time τ can be controlled by a thermally activated process of the type [24, 25].

$$\tau_o = \tau_\infty \exp (E_o / k_B T) \quad (2)$$

where k_B is the Boltzmann constant, τ_∞ relaxation time at infinite temperature, and represents the time of a single oscillation of a dipole in the potential well and E_o is the free energy of activation for dipole relaxation .Fig.(2) represents the relation between the relaxation time τ versus the reciprocal of temperature T, and the obtained relation is linear. The values of τ_∞ and E_o are calculated and they are 4.39×10^{-11} s and 0.69 eV, respectively. The obtained data are in agreement with those obtained for other materials [24, 25].

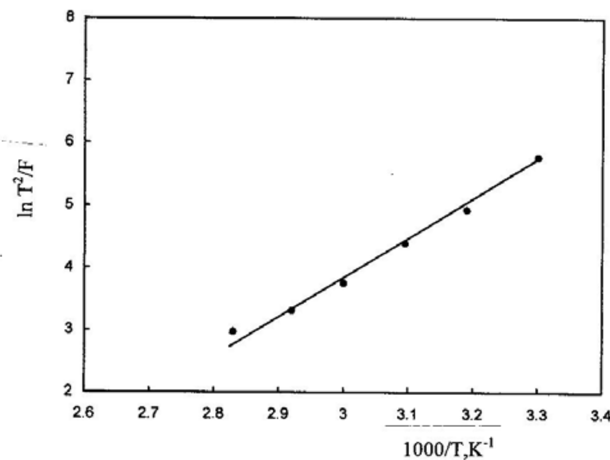

Fig. 4. Arrhenius plot of the capacitance for the As_{45} Te_{33} Ge_{10} Si_{12} films(C=0.18nF).

To explore the dielectric properties of As_{45} Te_{33} Ge_{10} Si_{12} films, the capacitance measurements were carried out over a frequency range of 10^2 -10^5 Hz and a temperature range of (303 – 383 K). Fig.(3)

illustrates the variation of the capacitance of film sample with thickness 340 nm as an example, as a function of test frequency and temperature . It is observed from this figure that the capacitance decreases with increasing test frequency. The same behavior was obtained for all other thicknesses under investigation. This effect may be attributed to the effect of charge redistribution by carrier hopping on defects [26,27] . At low frequency, the charge on defects can be rapidly redistributed so that defects closer to the positive side of the applied field become negatively charged, while defects closer to the negative side of the applied field become positively charged. This leads to screening of the field and an overall reduction in the electric field. Because capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed as the frequency is lowered. In case of high frequency, the defects no longer have enough time to rearrange in response to the applied voltage, hence the capacitance decreases.

As expected and observed in Fig. (3), at a given frequency the higher the temperature the more effective the carrier hopping because of the increase in the thermal emission of charges.

A plot of ln T^2/f vs $\frac{1000}{T}$ can be obtained from Fig. (3) at different values of the capacitance C, according to the following equation [28, 29]

$$\frac{1}{f} = K/T^2 \ \exp(E_c/k_B T) \tag{3}$$

where E_c is the activation energy of the carrier hopping, f is the test frequency and k is a proportionality constant.

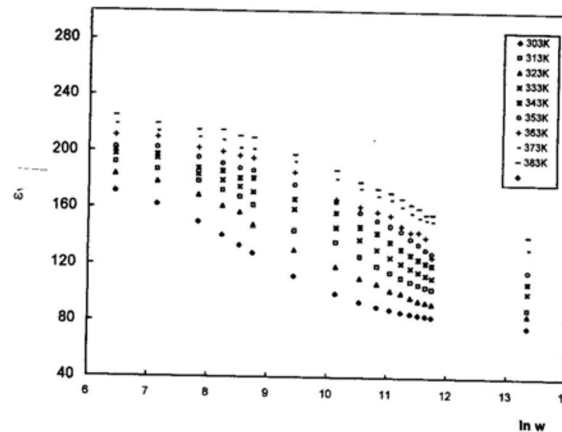

Fig. 5. Frequency dependence of the dielectric constant ε_1 for As_{45} Te_{33} Ge_{10} Si_{12} films at several temperatures.

The obtained relation shown in Fig. (4) represents typical Arrhenius plot of the frequency and the corresponding temperature at which the capacitance is equal to 0.18 n F. The activation energy E_c was determined from the slope of the straight line in Fig.(4). An average activation energy was determined by averaging the E_c values obtained from frequency and temperature corresponding to three different data of capacitance, and is equal to 0.647 eV. The activation energy obtained from the dielectric relaxation and capacitance measurements are in very good agreement. It is remarkable that the obtained value of the activation energy for relaxation E_o = 0.69 eV seems to be too high. This suggested that the relaxation in these amorphous films may be due to a dipolar type, where E_o is closer to the activation energy for conduction obtained before[9].

3.2 Dielectric constant

The dielectric constant ε_1 was measured as a function of frequency (10^2 – 10^5 Hz) in the temperature range (303 – 383 K). Fig. (5) shows the variation of the dielectric constant with frequency at constant temperature.

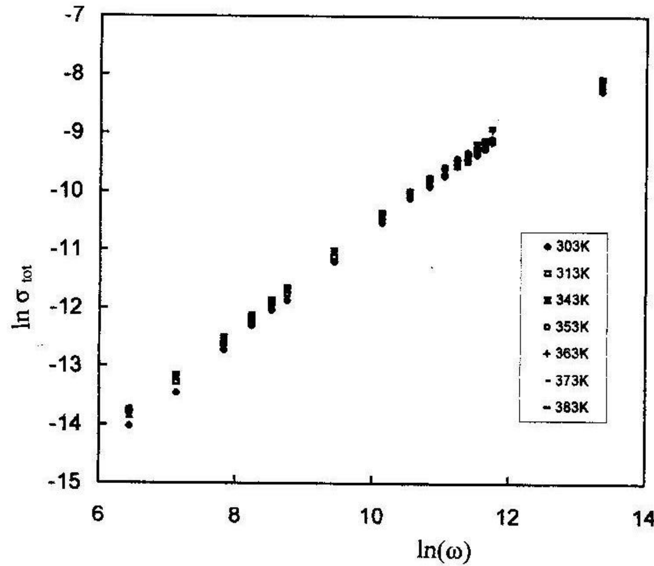

Fig. 6. Frequency dependence of the ac conductivity $\sigma_{ac}(\omega)$ for the As_{45} Te_{33} Ge_{10} Si_{12} films at several temperatures.

The dielectric constant ε_1 shows a decrease with increase in frequency for all measured temperature, but it increases with increasing temperature. The decrease of ε_1 with frequency can be attributed to the fact that at low frequencies ε_1 for polar materials is due to the contribution of multi component of polarization mechanisms(electronic, ionic, orientation and interfacial) [30] .When the frequency is increased, polarization will decrease and consequently the dielectric constant decreases. i.e as the applied frequency gets higher, the degree of polarization gets lower and thus a significant decrease in the values of ε_1 occurs.

3.3. AC conductivity

The measured total conductivity $\sigma_t(\omega)$ can be decomposed into two component σ_{dc} component is the direct current conductivity and a frequency dependent ac component according to the relation [31]

$$\sigma_t(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) \qquad (4)$$

The ac conductivity was calculated by using equation (1). However, for this particular composition, it is found that the measured total conductivity $\sigma_t(\omega)$ is much greater, by about three order of magnitude, compared to σ_{dc} conductivity. Therefore we are justified in plotting values of $\sigma_t(\omega)$ instead of $\sigma_{ac}(\omega)$. $\sigma_t(\omega)$ can be regarded as the typical values for ac conductivity.

The plot of ln $\sigma_t(\omega)$ versus ln (ω) at different constant temperature values for the composition under investigation is shown in Fig (6) for the film sample of thickness 340 nm as an

example.Similar dependence of ac conductivity has been observed for other films. It is evident that $\sigma_{ac}(\omega)$ fits the relation [32].

$$\sigma_{ac}(\omega) = A\,\omega^{s} \qquad (5)$$

which can be written as

$$\ln \sigma_{ac}(\omega) = \ln A + s \ln \omega \qquad (6)$$

At all the considered temperature values, the double logarithmic plot of $\sigma_{ac}(\omega)$ against ω describes a straight line with a slope s, verifying equation 6. This figure shows that the ac conductivity increases with increasing frequency. This behavior agrees with those obtained for other previously reported values [31].

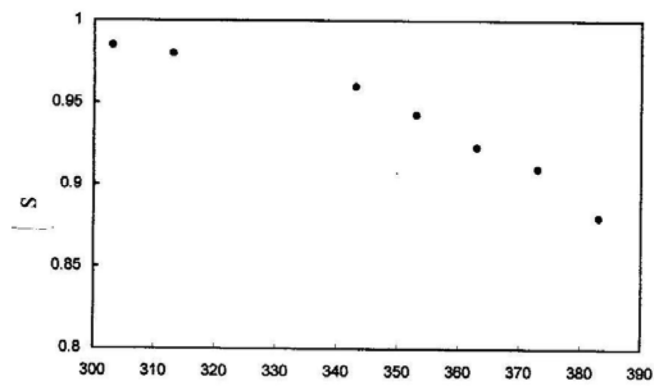

Fig. 7. Variation of the frequency exponent s with temperature for $As_{45}Te_{33}Ge_{10}Se_{12}$ films.

Values of the frequency exponent s for the investigated samples is shown in Fig.(7). It is clear from this figure that the exponent s decreases with increasing temperature through the studied range.

This behavior is in contradiction with the correlation barrier hopping model (CBH) describes charge carrier hops between sites over the potential barrier separating them and predicts that s decreases with increasing temperature[18,19,32].

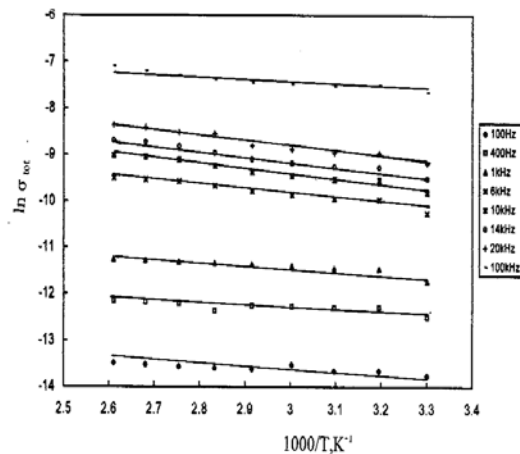

Fig. 8. Temperature dependence of ac conductivity of $As_{45}Te_{33}Ge_{10}Si_{12}$ films at different frequencies.

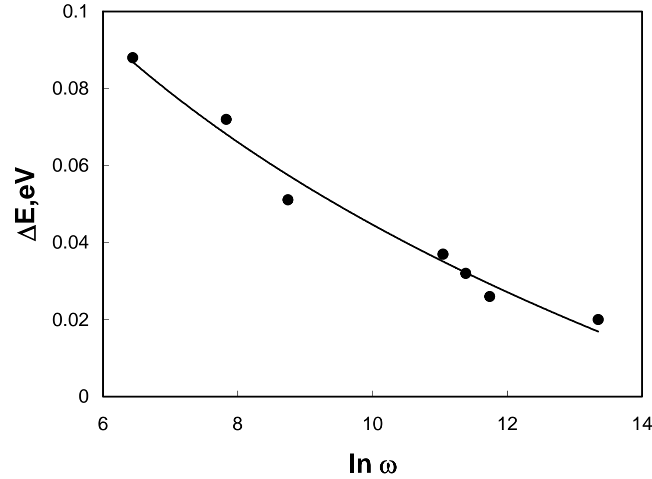

Fig. 9. Frequency dependence of ΔE_{ac} for $As_{45}Te_{33}Ge_{10}$ Si_{12} films.

The temperature dependence of σ_{ac} (ω) at different fixed frequency values for the film composition of thickness 340 nm is shown as an example in Fig. (8). The obtained relations indicate that σ_{ac} (ω) increases linearly with the reciprocal of temperature T. This suggested that the ac conductivity is a thermally activated process from different localized states in the gap or its tails. Thus, the application of an Arrhenius type relation is used to describe the temperature dependence of σ_{ac} (ω) as.

$$\sigma_{ac}(\omega) = \sigma_O(\omega) \exp.(-\Delta E_{ac}/k_B T) \quad (7)$$

where ΔE_{ac} is the activation energy, and σ_O (ω) is the pre-exponential factor. The activation energy of conduction is calculated at different frequencies from the slope of straight lines in Fig. (8) using equation (7). The frequently dependence of activation energy is shown in Fig. (9) for film sample of thickness 340 nm as an example. The same behavior is obtained for other films under test. The obtained ac activation energy is much lower than the dc activation energy obtained before [9]. The discrepancy between the dc and ac activation energies seems to be obvious since the charge carriers in the dc conduction choose the easiest path which include some large jumps, while this is not important in the ac conduction [33] . It can be also noted that ΔE_{ac} tends to decrease with increasing frequency. The increase of the applied field frequency enhances the electronic jumps between the localized states, consequently the activation energy ΔE_{ac} decreases with increasing frequency. The increase of the applied field frequency enhances. The discrepancy between the dc and ac activation energies, the smaller values of ac activation energy and the increase of σ_{ac} (ω) with the increase of frequency confirm the hopping conduction to be the dominated mechanism.

4. Conclusions

In summary, dielectric studies of As_{45} Te_{33} Ce_{10} Si_{12} thin films of different thicknesses in the thickness range (105-340 nm) obtained by thermal evaporation technique in the frequency range 10^2 – 10^5 Hz and at temperatures from 300 to 383 K have been investigated. The obtained results demonstrate a marked relaxation in the dielectric response in the studied temperature and frequency ranges. This behavior is attributed to the charge redistribution by carrier hopping among defects. The dependence of the relaxation time is of thermally activated type. The sample capacitance was found to decrease with increasing frequency.

The dielectric constant ε_1 shows frequency and temperature dependence. It decreases with increasing frequency, and increases as the temperature increases. This decrease in ε_1 is attributed to a decrease in some kind of polarization as the frequency increases. The ac conductivity was found to be both frequency and temperature dependent. The temperature dependence of the frequency exponent s was found to decrease with increasing the temperature, which follow the correlation barrier hopping (CBH) model.

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