THE INFLUENCE OF SUBSTRATE TEMPERATURE ON DENSITY OF STATES AND OPTICAL PROPERTIES OF $GE_{0.2}TE_{0.8}$ THIN FILMS

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ABSTRACT

A systematic investigation on the effect of substrate temperature on the structure, optical absorption and density of states of vacuum evaporated $Ge_{0.2}Te_{0.8}$ thin films is reported.

The X-ray diffraction analysis shows a transformation occurrence from amorphous to polycrystalline structure in the films deposited at higher temperature substrates (473K).

The thickness of the film (3500+8 A^o) is measured by an optical interference fringes method.

Optical characteristics of the $Ge_{0.2}Te_{0.8}$ sample have been analyzed using reflection and transmission spectrum result. The absorption mechanism has been recognized as the allowed indirect transition for amorphous and polycrystalline films. The absorption coefficient (α) and the effect of substrate temperature (T_s) on it were investigated. The tail width for each prepared films was calculated.

The density of state (DOS) was calculated by depending on DC conductivity measurements; the density of extended state $N(E_{ext})$ increases with increasing the T_s, while the density of localized state $N(E_{loc})$ decreases with increasing the T_s.

Low field conduction enables one to determine the density of states near Fermi level $N(E_f)$ in amorphous and polycrystalline films, that needs measurements of the DC conductivity under low temperature by using liquid nitrogen. The experimental results are interpreted in terms of variations in the density of localized states due to progressive decrease of the unsaturated bonds during deposition.

INTRODUCTION

Chalcogenide glasses are attractive and widely investigated materials. Scientific and industrial interest exists since a long time, due to their unique properties. These glasses are used as optoelectronic device materials (Nandarumar & Philip, 1992), promising material in the IR optics, microelectronics, *etc*... (Lucas & Zhang, 1990; Vriens & Rippens, 1983) because of their excellent transmittance, reaching the far-infrared spectral region.

The study of the optical properties of materials is interesting for many reasons. First, the use of materials in optical fibers and reflected coating requires accurate knowledge

of their optical properties over wide ranges of wavelength. Secondly, the optical properties of all materials are related to their atomic structure, electronic band structure and electrical properties.

There are several models that are put to understand the structure of bands in the material, (Cohen-Fritizche-Ovshimsicy (CFO) model, Mott -Davis model and Marshal-Owen model (Brodsky, 1979)).

Mott-Davis is the model that agrees with the band structure of chalcogenide glass; by this model one can understand the phenomena of DC conductive and optical transition in it.

Mott-Davis suggested that the tails of localized states are rather narrow and extended few tenths of electron volts in the forbidden gap, which depend on the degree of disorder, the existence of dangling bonds in the amorphous semiconductors. The existence of dangling bonds and impurities produces a few localized states in the gap (Brodsky, 1979).

The structural bonding between the neighbors determines the optical properties, such as absorption and transmission of the amorphous material. The general features of the density of states of amorphous solids can be obtained from the model proposed by Mott and Davis (1971).

Chalcogenide glasses (GeTe) is a representative IV-VI semiconductor layers. It has typical characteristics of the layer semiconductor such as, (a) the low density of dangling bonds on the surface because of the almost complete chemical bonds within the layer, (b) intercalation and (c) the mechanical weakness due to the weak van der Waals force between the layers. Property (a) makes it possible to form heterojunction devices with a low interface density of states. Some investigations have been reported. They intend to make solar energy conversion systems by the use of layer semiconductors. Property (b) allows altering the electrical properties of the semiconductors, which will be convenient in device processing. However, because of disadvantage (c), it is almost impossible to form devices from layer semiconductor crystals. In order to overcome the disadvantage (c) and to utilize the advantages (a) and (b), epitaxial films of layer semiconductors are needed (Yudasaka & Nakanishi, 1988).

A layer of GeTe consists of four 2D mono-atomic sheets in the sequence of Ge-Te-Te-Ge, where atoms within each layer are tightly bound with a mixture of covalent ionic bonds, and the layers are held together by weak forces (Kuhn *et al*., 1975). The study of GeTe attracts broad attention in view of its number of positive properties for nonlinear applications in technology, the foremost among these being its extreme transparency. The GeTe has highly anisotropic transport, mechanical and optical properties (Levy, 1976), and high nonlinear optical coefficients in the infrared range, making it a candidate for second harmonic generation (SHG) materials (Catalan *et al*., 1978; Fernelius, 1994). While the optical properties of the bulk GeTe are quite promising, poor thermal and mechanical properties preclude its easy applications. These problems, however, may be overcome in thin film devices.

EXPERIMENTAL TECHNIQUE

To prepare the alloy of $Ge_{0.2}Te_{0.8}$, highly pure Ge and Te elements (99.999%) according to their relative atomic weight were used. The components of the alloy were placed in a quartz tube attached to the evacuated system. The tube was sealed at pressure 10^{-3} mbar and placed in an electrical furnace heated above the melting temperature for 2 hours. After that the tube was quenched rapidly in cold water.

The $Ge_{0.2}Te_{0.8}$ thin films of thickness 3500+8 A^o have been prepared from the alloy by thermal evaporation method at different substrate temperatures (T_s=R.T, 473 K) and at rate of 25 A^o/sec.

The structure of the films deposited on substrate temperatures 300K and 473K were examined by (XRD) method, Phillips X-ray differactometer system that records the intensity as a function of Bragg angle. The scanning angle (2θ) range was from 20° to 60° (CuKα line), radiation of wavelength =1.54 A^o, current =20 mA, voltage=40 kV, range=200 counts/s.

The optical interference fringes method was used to determine the thickness of films.

FTIR spectrophotometer was used to obtain the absorptions and transmittance spectra respectively.

The DC conductivity for each film is measured to use the result in calculating the DOS.

This type of conductivity measures the resistance of the films as a function of the temperatures from 303 to 473 K for $Ge_{0.2}Te_{0.8}$ films by using the equivalent circuit as shown in Fig. (1-A). The measurements have been done with sensitive digital electrometer type Keithley 616 and electrical oven.

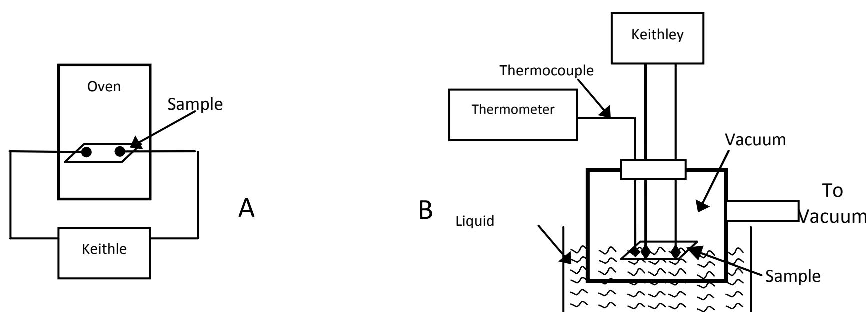

Figure 1. The circuit for measuring DC conductivity.

However, conductivity measures the resistance of the films as a function of temperature, ranging from 223 to 303 K for $Ge_{0.2}Te_{0.8}$ films, by using the equivalent circuit as shown in Fig. (1-B).

RESULTS AND DISCUSSION

Structural analysis

Thin films of $Ge_{0.2}Te_{0.8}$ prepared by vacuum evaporation onto glass substrates were found to be uniform and have very good adhesion to the substrate surface. The average thickness of the films was measured as 350 nm. XRD patterns were taken to study the structural of $Ge_{0.2}Te_{0.8}$ films. Fig. 2 shows the amorphous and polycrystalline nature of $Ge_{0.2}Te_{0.8}$ films deposited on substrates temperature 300 K and 473K respectively. Fig. 2 depicts the (200) and (220) ($\bar{2}$20) diffraction peaks observed in the film deposited at high substrate temperature. This result indicates the good crystalline in the film deposited at 473K with layer type growth and preferred orientation of basal planes parallel to the substrate. The lattice constant of poly-GeTe film calculated from these peak positions is 6.075 A^o, and the crystallite dimension in the direction of thickness was estimated using Scherrer equation (Warren, 1969). For polycrystalline film, the crystallite size (D), the dislocation density (δ), and the lattice spacing (d) are calculated as 206 A^o, 11.11 × 10^{14} lin m^{-2} and 2.148 A^o respectively.

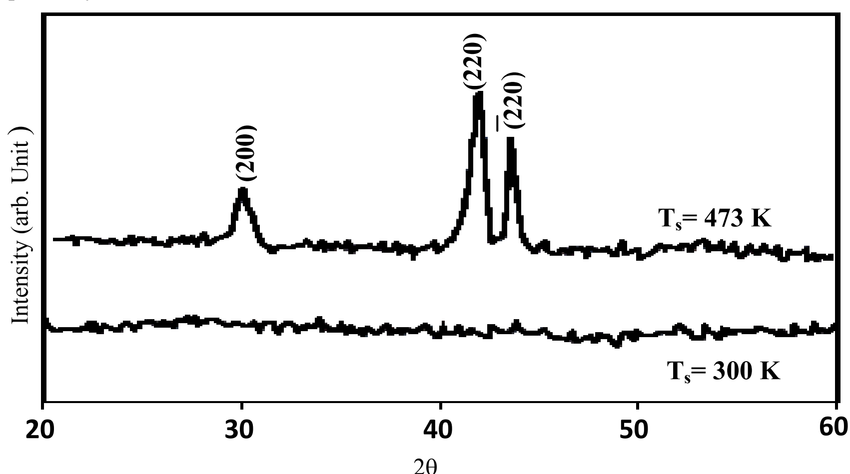

Figure 2. X-ray diffraction patterns for the $Ge_{0.2}Te_{0.8}$ films for different substrate temperatures.

Optical absorption

In a material free from any imperfections, only the direct but allowed transition can take place from the valence to the conduction band. In the presence of defects, impurities, dislocations and other imperfections, one has to consider the perturbation of the system due to their presence and also their interactions with phonons. All these give rise to the indirect and its other related transitions (Goswami, 1997).

In the present study, an analysis of the absorption coefficient spectra shows that the total absorption must be due to different optical transitions. The variation of the absorption coefficient (α) with phonon energy ($h\upsilon$) for the $Ge_{0.2}Te_{0.8}$ films which are deposited on substrate temperatures 300K and 473K is shown in Fig. 3.

In the fundamental absorption, an electron absorbs a photon (from the incident beam), and jumps from the valence band to conduction band. The phonon energy must be equal to the energy gap or larger (Jenkins & White, 1981).

The relation used to a given absorption coefficient (α) (Madan & Shaw, 1986):

$$\alpha = 2.303\left(\frac{A}{t}\right) \text{............ (1)}$$

where A is the absorptance and t is the thickness of the film.

Fig. 3 shows the variation of absorption coefficient ($\ln \alpha$) for $Ge_{0.2}Te_{0.8}$ films calculated by eq.(1), with phonon energy ($h\nu$) at different substrate temperature.

It is clear the effect of T_s shifts the absorption coefficient spectra to higher energies. In general the α value decreases with increasing T_s . Indeed, increasing T_s decreases defect structure of the film and increases the crystallization (Alwan, 2007) in accordance with Urbach (Catalan *et al*., 1978; Madan & Shaw, 1986):

$$\alpha = \alpha_o \exp\frac{h\nu}{\Delta E} \text{..................(2)}$$

where α_o is a constant, and (ΔE) width of tails.

The value of width of tails (ΔE) of localized state in the gap is obtained from Fig. 3, where $\ln \alpha$ is plotted as a function of $h\nu$, the value of ΔE extracted from the reciprocal slope of the linear part.

Where the tail width is decreasing due to the effect of substrate temperature.

The spectral variations of the absorption coefficient can also be perfectly fitted in the equation:

$$(\alpha h\nu)^{1/2} = B(E - E_g) \text{................(3)}$$

which is typical of allowed indirect transitions. The transition energy gap Eg is calculated from the plot of $(\alpha h\nu)^{1/2}$ *versus* ($h\upsilon$) (Fig. 4), the values of energy gap Eg are found to be 0.51 and 0.54 eV for amorphous and poly- $Ge_{0.2}Te_{0.8}$ films respectively.

The observed behavior of the optical gap in $Ge_{0.2}Te_{0.8}$ thin films investigated may be due to variations in the density of localized states as a result of substrate temperature induced modifications in the density of the unsaturated bonds. It is known that unsaturated bonds are responsible for the formation of gap states in the films. In particular, they contribute

to the effective spread in the localized states near the mobility edges. The presence of a high concentration of localized states is assumed to be responsible for the relatively low values of the optical gap in the as-deposited amorphous films. For the films deposited on the higher-temperature substrates (473K) the unsaturated bonds are annealed out, which in turn reduces the density of gap states and thus increasing the optical gap.

Density of states

Fig. 5 shows the variation between (ln σ) and (1000/T), when the path A in this Fig. intersect the (ln σ) axis at 1000/T =0 gives ($\sigma_{o(ext)}$), and path B gives ($\sigma_{o(loc)}$).

The density of extended states is measured by using the equation (Jassim, 1992):

$$N(E_{ext}) = \frac{6m}{e^2\hbar}\sigma_{\circ(ext)} \quad \text{.............(4)}$$

Where
$N(E_{ext})$= density of extended state
$(\sigma_o)_{ext}$ = conductivity at 0K
$\hbar = 1.0545 \times 10^{-34}$ J.s

The values of density of extended state are listed in Table 1, which shows the density of extended state $N(E_{ext})$ increasing with the increase of the substrate temperature from 2.36×10^{20} ($eV^{-1}.cm^{-3}$) at R.T to 7.18×10^{20} ($eV^{-1}.cm^{-3}$) at 473K .

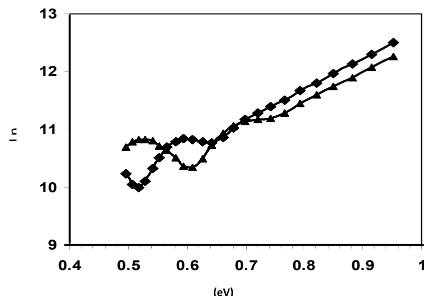

Figure 3. Variation of ln α *vs.* hν for $Ge_{0.2}Te_{0.8}$ thin film.

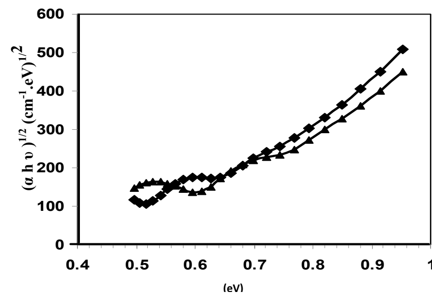

Figure 4. Variation of $(\alpha\ h\ \upsilon)^{1/2}$ *vs.* hν for $Ge_{0.2}Te_{0.8}$ thin film.

From this Table also see the effect of T_s on the density of localized state that is calculated by the eq. (Jassim, 1992):

$$N(E_{loc}) = \frac{6(\sigma_\circ)_{loc}}{e^2\upsilon_{ph}R^2} \quad \text{...........(5)}$$

Where
$(\sigma_o)_{loc}$= the conductivity at 0K
ν_{ph} = phonon frequency and of order 10^{13} s^{-1}
R = hopping distance and is give by

$$R = 0.7736\left|\frac{\Delta E\gamma^{-1}}{N(E_{ext})(K_B T)^2}\right|^{1/4} \quad \ldots\ldots\ldots\ldots(6)$$

ΔE= the tail width
γ^{-1}= 10 A
K_B = Boltzman constant

The density of localized state was decreased with increasing T_s from 2.009×10^{16} ($eV^{-1}.cm^{-3}$) at R.T to 5.659×10^{15} ($eV^{-1}.cm^{-3}$) at 473 K.

The increase in density of extended state and the decrease in density of localized state with increasing of substrate temperature, can be due to transformation occurrence from amorphous to polycrystalline structure.

Low field conduction was carried out to find the density of states (DOS) in the as-deposited and poly- $Ge_{0.2}Te_{0.8}$ films. In amorphous materials, Mott's variable-range hopping (VRH) conductivity is dominant. The phonons do not have enough energy for transferring to a nearest neighbor atom and the charge carrier hops from a neutral atom to another neutral atom situated at the same energy level, which can be many interatomic distance away (Sikha *et al*., 1985).

In polycrystalline materials, at low temperatures, the carriers can't be transferred into the grain by thermionic emission -they do not have enough energy to cross the grain barrier potential and the conduction involves the grain boundaries. In the grain boundary-trapping model, the trapping states, created by the disordered atoms and the incomplete bonding among them, are distributed in the band gap. Depending on the temperature and also on the distribution of these states in the gap, some of the trapping states are filled with carriers and are charged. The empty states may capture an electron from the charged state under favorable energy condition. Then a possibility for conduction is by the hopping of charge carriers from filled trap states to the empty trap states. The filled states may subsequently release the electrons and thus hop in conduction (Paul & Mitra, 1973).

A good fit of conductivity – temperature data is the eq. (Sikka *et al*., 1985):

$$\sigma T^{1/2} = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right] \quad \ldots\ldots\ldots..(7)$$

which will confirm the conduction mechanism of Mott's type. Fig. 6 shows the variation of ln $\sigma T^{1/2}$ with $T^{-1/4}$ (ln $\sigma T^{1/2}$ *vs* $T^{-1/4}$) for the amorphous and polycrystalline $Ge_{0.2}Te_{0.8}$ thin film samples. It is observed that the plot of $\sigma T^{1/2}$ *vs* $T^{-1/4}$ fits well and hence it can be concluded that at low temperature regions, the acting conduction mechanism may be the variable range hopping. The pre exponential factor σ_o and the characteristic temperature T_o are related to the density of localized states $N(E_f)$ and the wave function decay constant γ associated with these states by the following relation (Ka, 1991):

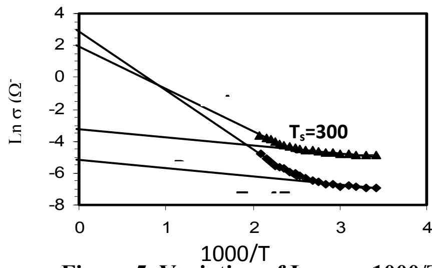

Figure 5. Variation of Ln σ *vs* 1000/T for $Ge_{0.2}Te_{0.8}$ thin film.

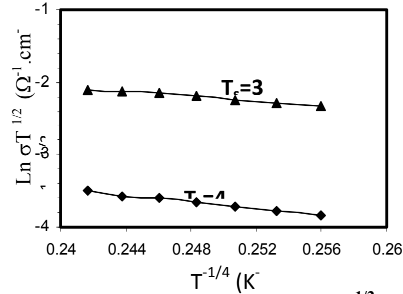

Figure 6. Variation of $\ln\sigma T^{1/2}$ *vs* $T^{-1/4}$ for $Ge_{0.2}Te_{0.8}$ thin film.

$$\sigma_o = 3e^2 \nu_{ph} \left(\frac{N(E_f)}{8\pi\gamma K_B} \right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots.(8)$$

and the characteristic Mott temperature in 3D is given by (Sikka *et al*., 1985; Ka, 1991)

$$T_o = \frac{18.1\gamma^3}{K_B N(E_f)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(9)$$

Simultaneous solution of equations 8 and 9 yields:

$$N(E_f) = 5.55416 \times 10^{13} (T_o)^{1/2} (\sigma)^3 \quad \ldots\ldots\ldots\ldots\ldots...(10)$$

The values of T_o and N (E_f) for the amorphous and polycrystalline $Ge_{0.2}Te_{0.8}$ thin film samples are calculated from the slope and intercept of the curves in Fig. 6 respectively and presented in Table 1.

TABLE 1

Density of States for the $Ge_{0.2}Te_{0.8}$ Films for Different Substrate Temperatures

$Ge_{0.2}Te_{0.8}$ Sample	T_s=300 K	T_s=473 K
$\sigma_{o(ext)}$ ($\Omega^{-1}.cm^{-1}$)	7.31	22.19
$N(E_{ext})$ ($eV^{-1}.cm^{-3}$)	2.36×10^{20}	7.18×10^{20}
$\sigma_{o(loc)}$ ($\Omega^{-1}.cm^{-1}$)	0.0407	0.0061
ΔE (eV)	0.21	0.18
R (cm)	8.70×10^{-7}	6.34×10^{-7}
$N(E_{loc})(eV^{-1}.cm^{-3})$	2.009×10^{16}	5.659×10^{15}
T_o K	6.945×10^{4}	2.842×10^{5}
$N(E_f)(eV^{-1}.cm^{-3})$	3.493×10^{15}	1.482×10^{16}

CONCLUSION

The effect of substrate temperatures is obvious on the structural parameters like crystallite size, dislocation density and lattice spacing were calculated from the XRD data.

One found the density of extended state increases with increasing T_s, while the density of localized state decreases with T_s increase. This affects the optical properties of $Ge_{0.2}Te_{0.8}$ films. At the same time, the optical energy gap increased with increasing T_s. The tail width decreases with increasing the substrate temperatures. It is observed that the optical gap of $Ge_{0.2}Te_{0.8}$ films depends on the substrate temperature that subsequently modifies the DOS. In the process of thermal treatment some of the unsaturated bonds are annealed out to some extent, reducing the density of gap states and consequently increasing the optical gap.

These results are confirmed with experimental data obtained from DC low field conduction and optical analysis, which are required to model the nonlinear optical devices, based on $Ge_{0.2}Te_{0.8}$, to determine the power threshold for optical bistability or the time response.

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