Cole- Cole Diagrams of Ge\textsubscript{x}S\textsubscript{1-x} Thin Films

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Abstract

The germanium sulfide Ge\textsubscript{x}S\textsubscript{1-x} thin films with different germanium concentration (0.1 0.2, and 0.3) weight % have been prepared by thermal evaporation under vacuum of (10\textsuperscript{-5} Torr) with thickness (0.15µm) at room and annealed at (373 and 423K). Measurements of the dielectric properties are carried out over frequency range (10\textsuperscript{2}-10\textsuperscript{7} Hz) for all the prepared films. It was found that all samples displayed dielectric dispersion thus the curves log \( \varepsilon_1 \) versus log \( w \), log \( \varepsilon_2 \) versus log \( w \) gave direct evidence of the existence of Debye-type relaxation have a wide distribution of relaxation times. The results show that distribution parameters (\( \alpha \)) decreases while microscopic relaxation time (\( \tau_0 \)) increases with the increasing of germanium content and temperature of thermal treatment. The dielectric constant \( \varepsilon_1 \) decreases sharply with the increasing of germanium content in the prepared Ge\textsubscript{x}S\textsubscript{1-x} films.

Keywords: AC Conductivity; dielectric permittivity and relaxation, Ge\textsubscript{x}S\textsubscript{1-x} thin films.

Introduction

Amorphous chalcogenide semiconductors possess a lot of interesting phenomena, which reveal possibilities for using them in microelectronics and optoelectronics - as ovonic threshold and memory switching devices, inorganic photoresists, optical memory disks [1], etc. The increased interest in them has been connected mainly with their unique peculiarity to record information by irreversible or reversible structural transformations between a
disordered and a more ordered state. Exposure to band gap light causes photoinduced changes, which have been studied in detail [2]. Especially, amorphous Ge-S thin films exhibit remarkable irreversible photo- and thermo-bleaching effects, caused by illumination and annealing, respectively [2,3].

Thin films of glassy \( (\text{GeS}_2)_{1-x} (\text{AgI})_x \) system have been studied by Moncheva et al [4]. The films have been prepared from the respective bulk glasses previously synthesized from the elements with constant \( \text{Ge:S}=1:2 \) ratio and different amount of AgI \( (x=5, 10, 15, 20 \text{ mol.}%). \) The amorphous nature of the films has been proved by X-ray diffraction (XRD) and electron microscope investigation. Spectral distribution of the film transmission has been obtained. The optical energy gap \( E_{\text{g Tauc}} \) has been determined from the Tauc plot \( \alpha h\nu = B (E_{\text{g Tauc}} - h\nu)^2 \). The calculated \( E_g \) valued show decreasing with increasing silver content.

Structure and thermal properties of Ge-In-S chalcogenide glasses whose compositions can be expressed by \( (\text{GeS}_2)_{100-x}(\text{In}_2\text{S}_3)_x \) \( (x=0, 10, 20, 30) \) formula were obtained by the melt-quenching technique by Rebkova et al [5]. The glasses were homogeneous with high optical transmission from visible \( (0.65 \mu\text{m}) \) to mid infrared region \( (10\mu\text{m}) \). Main structural units of studied glasses are \( \text{GeS}_4 \) tetrahedra connected to each other by corners and edges, \( \text{InS}_4 \) tetrahedra and \( \text{InS}_6 \) octahedra interconnected by sulfur bridges. The thermal stability was evaluated using differential thermal analysis (DTA) combined with differential scanning calorimetry (DSC) for the determination of characteristic temperatures: \( T_g \sim \) temperature of glass transition, \( T_x \sim \) temperature of onset of crystallization, \( T_c \sim \) temperature of crystallization, \( T_m \sim \) temperature of melting.

A.C conductivity \( (\sigma_{\text{a.c}}(w)) \) gives informations about the nature of polarization mechanisms in dielectric, also provide information about the capacitance, interface and the amount of conductivity present.

In this paper the real \( (\varepsilon_1) \) and imaginary part \( (\varepsilon_2) \) of dielectric constant for germanium sulfide thin films with various germanium
concentrations were measured, the relation between them were discussed. An attempt had also made to interpret the results in terms of Maxwell-Wagner model. Cole-Cole diagrams were plotted and used to estimate the values of polarizability $\alpha$ or distribution parameter and the relaxation time $\tau$.

**Experimental details**

In the present work, Ge$_x$S$_{1-x}$ alloys has been synthesized using high purity elemental germanium and sulfide is about (99.9999%) with different $x$ content where ($x = 0.1, 0.2, \text{and} 0.3$). Stoichiometric amounts of the elements are placed in a quartz ampoule, which is evacuated to a vacuum of $10^{-2}$ Torr and then sealed. The sealed ampoule is placed in a furnace, and then heated at a rate of 333K per hour in steps up to 1000 K. The ampoule is maintained at this temperature for about five hours and then allowed to cool slowly to room temperature. The vacuum unit system, which is used to prepare thermally evaporated Ge$_x$S$_{1-x}$ films, was Edward Coating unit model 306A. Balzer CO. West Germany. All the prepared films are thermally treatment under vacuum of $10^{-2}$Torr at different temperature (373 and 423K) for one hour. To study measure the effect of germanium concentration, annealing temperature, and frequency of the applied electric field on the real ($\varepsilon_1$) and imaginary part ($\varepsilon_2$) of dielectric constant of Ge$_x$S$_{1-x}$ films, the (LRC) meter (model HP-4274A) and (HP-4275A) are used.

Electrodes were formed by applying silver paint or carbon conducting cement (Carbon Adhesive 30GM, Structure Probe, West Chester PA, USA) on both electrodes of the samples. The capacitance $C$ and conductance $G$ of the samples were measured (in parallel mode) with an automatic impedance meter Hewlett-Packard HP-4284A operated in the 100 Hz to 10 MHz frequency range, the specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). Three dielectric parameters were measured directly from above setup total resistance ($RT$), total capacitance ($CT$) and dissipation factor $\tan\delta$ with an accuracy of 0.1%. All measurements were performed under certain frequency
range $10^2$ - $10^6$ Hz., the temperature range between (293- 433)K, the
temperature was changed by constant rate of 2K/min, and constant
voltage of (0.08V) was applied in all frequency range and temperature
those are indicated in this work..
When the conductivity is measured with an AC technique of
frequency
$\omega = 2\pi f$, the response that characterizes a great variety of materials
with diverse chemical compositions, either crystalline or amorphous,
can be written as [6]:
\[ \sigma(\omega, T) = \sigma_{DC}(T) + a(T)\omega^s, \]
where $\sigma_{DC}(T)$ is the 'direct current' (or static, $\omega = 0$) conductivity,
$a(T)$ is a factor that depends on temperature but not on $\omega$, and $s$ is an
exponent in the range $0 \leq s \leq 1$. Equation (1) predicts that if (at certain
temperature) $\sigma_{DC}$ is much less than the second term, then $\sigma(\omega, T) \propto \omega^s$
so that a log log plot of $\sigma$ against $\omega$ describes a straight line with
slope $s$. On the other hand, if $\sigma_{DC}$ becomes larger than the second term
(by increasing temperature, for example), then $\sigma(\omega, T) \propto \sigma_{DC}(T)$, in
this case the AC technique renders a measurement of $\sigma_{DC}$, and a plot
of $\sigma$ against $\omega$ in log-log scale should give a horizontal straight line.

The real and imaginary parts of the complex dielectric constant, $\varepsilon_1$
and $\varepsilon_2$ respectively, are obtained from C and G according to:
$\varepsilon_1 = C/C_{0}$ and $\varepsilon_2 = G/\omega C_{0}$, where $C_{0}$ is the geometrical capacitance of the
sample ($C_{0} = \varepsilon_{0}A/d$, where $\varepsilon_{0}$ is the permittivity of free space, $A$ the
area of electrodes and $d$ the thickness of the sample), and $\omega = 2\pi f$
where $f$ is the measuring frequency. For materials having sizable
conductivity it is convenient to express the imaginary part $\varepsilon_2$ in terms
of an AC conductivity defined as:
$\sigma = (d/A)G = \varepsilon_{0}\omega\varepsilon_2$
Results and Discussion

Cole–Cole diagrams of Ge$_x$S$_{1-x}$ Thin Films

A direct evidence of the existence of multi-relaxation time in the as deposited Ge$_x$S$_{1-x}$ films treated at temperature in the range (303-433K) is obtained by plotting Cole-Cole diagrams as shown in Figs(1A,B,and C). It has been observed that for all films reported here $\varepsilon_1$ versus $\varepsilon_2$ curves represent the arc of circles having their centers lying below the absicca axis. This confirms the existence of distribution of ($\tau$) in all films. By measuring the angles ($\alpha\pi/2$) the values of the polarizability ($\alpha$) had been determined and were listed in table(1). We can notice that the values of ($\alpha$) declares a systematic reduction with the increasing of temperature thermal treatment especially at high temperature (373-433K), this is agreement with the concept of molecular relaxation, the decrease of ($\alpha$) with the increasing of heat treatment results from rise of the forces of the intermolecular, while the increase of ($\alpha$) value came from the weaken the forces as result of formation of barrier between sulfide and germanium atoms. On the other hand the results show that $\alpha$ increases with the increase of annealing temperature at the first bet it get to reduce with further increase of annealing temperature, i.e. $\alpha$ increase from 0.6 to 0.63 when $T_a$ increases from 298 to 373K for Ge$_{0.1}$S$_{0.9}$, the most noticeable remark is the value of $\alpha$ decreases with the increasing of germanium addition to sulfide indeed i.e. $\alpha$ decreases from 0.4444 to 0.02222 for as deposited Ge$_x$S$_{1-x}$ thin films when $x$ increase from 0.1 to 0.3 (see table (1)). The value of microscopic relaxation time $\tau_0$ estimated from the relation ($\tau_0 = \frac{1}{2\pi f(1+2\sin \pi \alpha)}$) also illustrated in table (1). It is clear that $\tau_0$ for as deposited Ge$_x$S$_{1-x}$ thin films increases with thermal treatment for low germanium content but with further addition $\tau_0$ get to decrease with the increasing of thermal treatment, the behavior of $\tau_0$ attains the same sequence for high germanium content, moreover $\tau_0$ increases from $2.68 \times 10^{-4}$ to $5.45 \times 10^{-4}$ then decreases from $8.45 \times 10^{-4}$ to $1.74 \times 10^{-4}$ but it get to rise from $13.35 \times 10^{-4}$ to $16.67 \times 10^{-4}$ for when
thermal treatment increases from 313 to 433 K for x = 0.1, 0.2, and 0.3 respectively. From the same table, one can notice that \( \tau_0 \) increases with the increasing of germanium content in Ge\textsubscript{x}S\textsubscript{1-x} films. i.e., \( \tau_0 \) increases from 2.68 \times 10^{-4} to 13 \times 10^{-4} for x = 0.1 and 0.3 respectively. On the other hand, it is clear that for all x values namely (0.1, 0.2, and 0.3), \( \tau_0 \) values increase with Ge addition, this result was estimated since the addition of germanium results in the formation of a barrier while the decreasing of \( \tau_0 \) attributed to rising of intermolecular force [7].

The increment of \( \tau_0 \) can be explained on the bases of difference in energy of the different bonds Ge – S, S-S, Ge-Ge, since it is well known that any system tends to form bonds of lowest energy, most likely bonds in the films under investigation have bond energy as follows [4]:

\[
\text{Ge – S} \quad 551 \text{ kJ.mol}^{-1}, \quad \text{S-S} \quad 213 \text{ kJ.mol}^{-1}, \quad \text{Ge-Ge} \quad 185 \text{ kJ.mol}^{-1}
\]

The bond energies values for structure explanation where Ge-Ge bonds are the most possible due to their lower energy while bonds like as Ge-S have lower possibility of existence due to their higher bond energy, consequently, the addition of Ge to Se reduces the force of intermolecular.

### 2-Dielectric Constant of Ge\textsubscript{x}S\textsubscript{1-x} Thin Films

The dielectric constant (\( \epsilon_1 \)) of Ge\textsubscript{x}S\textsubscript{1-x} films with various concentrations namely (0.1, 0.2, and 0.3) were measured within the employed frequency range \(10^2\text{-}10^7\text{ Hz}\), from the spectrum of \( \log \epsilon_1 \) versus \( \log w \) in Figs. (2-4A, B, and C), it is obvious that \( \epsilon_1 \) tends to increase with increase treatment temperature while it decreased with increase frequency to reach lower values ascribed to the fact that electrode blocking layer is dominated thus the dielectric behavior is affected by the electrode polarization, while at high frequency the dielectric signal is not affected by electrode polarization [8], also it can be noticed that the values of \( \epsilon_1 \) are affected greatly by the germanium addition, moreover (at frequency =10\textsuperscript{2}\text{ Hz})(\( \epsilon_1 \)) decreases rapidly one order of magnitude with germanium addition, i.e., \( \epsilon_1 \) decreases from 13.686 to 1.982 when x increases from 0.1 to 0.3. The
decreasing in $\varepsilon_1$ value may be attributed to the formation of a conductor or non linear capacitor with high energy barrier. On the other hand in heterogeneous materials like Ge$_x$S$_{1-x}$ or multiphase materials the motion of charge carriers take place through one phase and the some charge carriers may trapped and accumulated at interfaces and defects as a results the electric field will be distorted and the dielectric constant increased. this effect depends on the conductivity of the present phases .this type of polarization called Maxwell-Wagner effect.

**Conclusions**

Measurements of dielectric constants, microscopic relaxation time $\tau_0$ and Cole – Cole diagrams of Ge$_x$S$_{1-x}$ films with different germanium concentrations had been conducted and several significant results have emerged from this experimental study:-

1- The values of $\varepsilon_1$ affected strongly by the germanium addition .

2- The values of ($\alpha$ and $\tau_0$) are found to change in an opposite manner with addition of germanium content in Ge$_x$S$_{1-x}$ films.

3- It is found that $\alpha$ decrease and $\tau_0$ increases when the Ge addition reduces the force of the intermolecular i.e. formation a barrier while $\alpha$ increases and $\tau_0$ decrease when Ge addition increases the force of the intermolecular .

3- The sharp reduction in the $\varepsilon_1$ values explained in the light of Maxwell-Wagner model .

4- Ge$_x$S$_{1-x}$ films more convenient to use as resistor in electronic circuits since the values of Polarisability in general($\alpha<0.5$) .
Ge_{0.1}S_{0.9} (T_a=298K)

\[ \begin{array}{c}
\begin{array}{cccc}
T&=298K & T&=333K & T&=373K & T&=413K \\
\hline
\end{array}
\end{array} \]

\begin{align*}
\varepsilon_i & \quad 0 \quad 2.5 \quad 5 \quad 7.5 \quad 10 \\
\varepsilon_r & \quad 5 \quad 7.5 \quad 10 \quad 12.5 \quad 15
\end{align*}

Ge_{0.2}S_{0.8} (T_a=298K)

\[ \begin{array}{c}
\begin{array}{cccc}
T&=298K & T&=333K & T&=373K & T&=413K \\
\hline
\end{array}
\end{array} \]

\begin{align*}
\varepsilon_i & \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \\
\varepsilon_r & \quad 0 \quad 1 \quad 2 \quad 3 \quad 4
\end{align*}
Fig. (1A, B, and C) Cole–Cole diagrams of \( \text{Ge}_x\text{S}_{1-x} \) thin films treated at different temperatures.

\[ \varepsilon_r T=293K \]
\[ \varepsilon_r T=333K \]
\[ \varepsilon_r T=373K \]
\[ \varepsilon_r T=413K \]

\[ \ln(\omega) \]
\[ \varepsilon_r T=298K \]
\[ \varepsilon_r T=313K \]
\[ \varepsilon_r T=333K \]
\[ \varepsilon_r T=353K \]
\[ \varepsilon_r T=373K \]
\[ \varepsilon_r T=393K \]
\[ \varepsilon_r T=413K \]
Fig.(2 A,B,and C) The variation of $\varepsilon_r$ with ln (w) for as deposited Ge$_{0.1}$S$_{0.9}$ thin films and annealed at different temperatures.
\[ \varepsilon_r(T) \] for \( Ge_{0.2}S_{0.8} \) at different temperatures:

- A: \( T = 298K \) to \( 393K \)
- B: \( T = 373K \) to \( 413K \)

\[ \text{Ln}(\omega) \] vs. \( \varepsilon_r \) for each temperature range.
Fig. (3 A, B, and C) The variation of $\varepsilon_r$ with $\ln(w)$ for as deposited $Ge_{0.2}S_{0.8}$ thin films and annealed at different temperatures.
Fig. (4 A, B, and C) The variation of $\varepsilon_r$ with $\ln (\omega)$ for as deposited $\text{Ge}_{0.3}\text{S}_{0.7}$ thin films and annealed at different temperatures.
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431
References