Cole- Cole Diagrams of Ge_xS_{1-x} Thin Films

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Abstract

The germanium sulfide Ge_xS_{1-x}thin films with different germanium concentration (0.1 0.2,and0.3) weight %have been prepared by thermal evaporation under vacuum of (10^{-5} Toor) with thickness (0.15µm) at room and annealed at(373and 423K). Measurements of The dielectric properties are carried out over frequency range (10^2-10^7 Hz) for all the prepared films .It was found that all samples displayed dielectric dispersion thus the curves log ε_1 versus log w, log ε_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 (α) decreases while microscopic relaxation time (τ_0)increases with the increasing of germanium content and temperature of thermal treatment . The dielectric constant ε_1 decreases sharply with the increasing of germanium content in the prepared Ge_xS_{1-x} films **.**

Keywords: AC Conductivity; dielectric permittivity and relaxation, Ge_xS_{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 $(GeS_2)_{1-x}$ $(AgI)_x$ 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 Ge:S=1:2 ratio and different amount of AgI (x= 5, 10, 15,20 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_g^{Tauc} has been determined from the Tauc plot $\alpha h\upsilon=B(E_g^{Tauc}-h\upsilon)^2$.The calculated Eg valued show decreasing with increasing silver content.

Structure and thermal properties of Ge-In-S chalcogenide glasses whose compositions can be expressed by $(GeS_2)_{100-x}(In_2S_3)_x$ (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 μm) to mid infrared region (10μm). Main structural units of studied glasses are GeS_4 tetrahedra connected to each other by corners and edges, InS_4 tetrahedra and 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 ~ temperature of glass transition, T_x ~ temperature of onset of crystallization, T_c ~ temperature of crystallization, T_m ~ temperature of melting.

A.C conductivity(σ a.c(w)) gives informatics 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 (ε_1)and imaginary part (ε_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 polaizability α or distribution parameter and the relaxation time τ.

Experimental details

In the present work, Ge_xS_{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, and0.3). 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_xS_{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 and423K) for one hour. To study measure the effect of germanium concentration, annealing temperature ,and frequency of the applied electric field on the real (ε_1)and imaginary part (ε_2) of dielectric constant of Ge_xS_{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 (R_T), total capacitance (C_T) and dissipation factor tanδ 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] :

$$\sigma(\omega, T) = \sigma_{DC}(T) + a(T)\omega^s, \qquad (1)$$

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 ω, and s is an exponent in the range $0 \leq s \leq 1$. Equation (1) predicts that if (at certain temperature) σ_{DC} is much less than the second term, then $\sigma(\omega, T) \propto \omega^s$, so that a log log plot of σ against ω describes a straight line with slope s. On the other hand, if σ_{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 σ_{DC}, and a plot of σ against ω in log-log scale should give a horizontal straight line. The real and imaginary parts of the complex dielectric constant, ε_1 andε_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 ε_2 in terms of an AC conductivity defined as:

$$\sigma = (d/A)G = \varepsilon_0 \omega \varepsilon_2 \qquad (2)$$

Results and Discussion

Cole –Cole diagrams of Ge_xS_{1-x}Thin Films

A direct evidence of the existence of multi-relaxation time in the as depositedGe_xS_{1-x} films treated at temperature in the range (303-433K) is obtaining by plotting Cole-Cole diagrams as shown in Figs(1A,B,and C).It has been observed that for all films reported here ε_1 versus ε_2 curves represent the arc of circles having their centers lying below the absicca axis .This confirms the existence of distribution of (τ) in all films. By measuring the angles ($\alpha\pi/2$)the vales of the polarizability (α) had been determined and were listed in table(1).We can notice that the values of (α)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 (α) with the increasing of heat treatment results from rise of the forces of the intermolecular, while the increase of (α)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 α increases with the increase of annealing temperature at the first bet it get to reduce with further increase of annealing temperature , i.e. α increase from 0.6 to 0.63 when T_a increases from 298to 373K for $Ge_{0.1}S_{0.9}$. the most noticeable remark is the value of α

decreases with the increasing of germanium addition to sulfide indeed i.e. α decreases from 0.4444to 0.02222 for as deposited Ge_xS_{1-x} thin films when x increase from 0.1 to 0.3(see table (1)).The value of microscopic relaxation time τ_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 τ_0 for as deposited Ge_xS_{1-x}thin films increases with thermal treatment for low germanium content but with further addition τ_0 get to decrease with the increasing of thermal treatment ,the behavior of τ_0 attains the same sequence for high germanium content ,moreover τ_0 increases from $2.68x10^{-4}$ to $5.45x10^{-4}$ then decreases from $8.45x10^{-4}$to$1.74x10^{-4}$ but it get to rise from $13.35x10^{-4}$ to $16.67x10^{-4}$for when

thermal treatment increases from 313to 433K fore x=.1,0.2and 0.3 respectively, from same table one can notice that τ_0 increases with the increasing of germanium content in
Ge_xS_{1-x}films i.e. τ_0 increases from $2.68x10^{-4}$ t0 $13x10^{-4}$ for x=0.1and 0.3 respectively. On the other hand It is clear that for all x values namely (0.1,0.2and 0.3) τ_0 values increases with Ge addition ,this result was estimated since the addition of germanium results in the formation of barrier while the decreasing of τ_0 attributed to rising of intermolecular force[7].
The increment of τ_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]:
Ge – S 551 $kJ.mol^{-1}$,S-S 213 $kJ.mol^{-1}$,Ge-Ge 185 $kJ.mol^{-1}$
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_xS_{1-x}Thin Films

The dielectric constant (ε_1)of Ge_xS_{1-x}films with various concentrations namely (0,1 ,0.2 and 0.3) were measured within the employed frequency range(10^2-10^7Hz) , from the spectrum of (log ε_1) versus (log w)in Figs.(2-4A,B,and C), it is obvious that (ε_1) tends to increase with increase treatment temperature while it decreased with increase frequency to reach lower values this 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 (ε_1) are affected greatly by the germanium addition, moreover (at frequency =10^2 Hz)(ε_1) decreases rapidly one order of magnitude with germanium addition , i.e. ε_1 decreases from 13.686 to 1.982 when x increases from 0.1 to 0.3 . The

decreasing in ε_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_xS_{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 τ_0 and Cole – Cole diagrams of Ge_xS_{1-x} films with different germanium concentrations had been conducted and several significant results have emerged from this experimental study:-

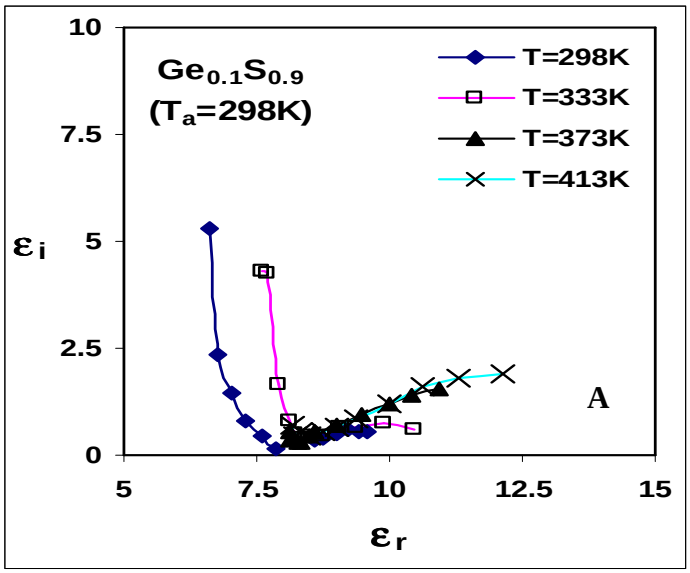
1- The values of ε_1 affected strongly by the germanium addition .

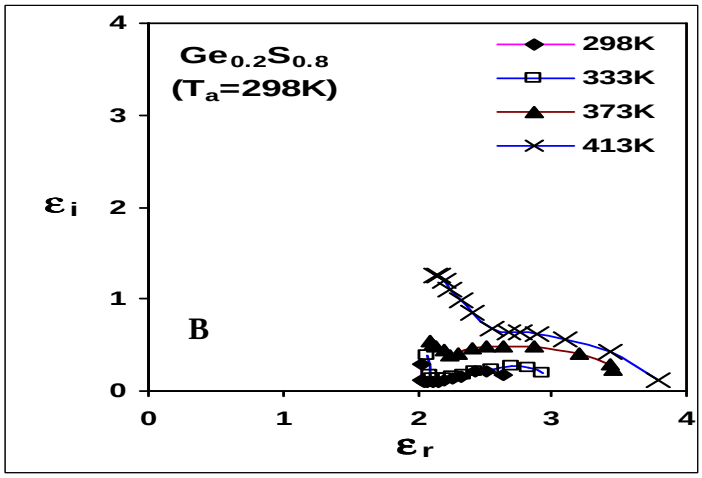
2-The values of (α and τ_0) are found to change in an opposite manner with addition of germanium content in Ge_xS_{1-x} films.

3-It is found that α decrease and τ_0 increases when the Ge addition reduces the force of the intermolecular i.e. formation a barrier while α increases and τ_0 decrease when Ge addition increases the force of the intermolecular .

3-The sharp reduction in the ε_1 values explained in the light of Maxwell-Wagner model .

4- Ge_xS_{1-x} films more convenient to use as resistor in electronic circuits since the values of Polarisability in general($\alpha<0.5$) .


Ge0.1S0.9
(Ta=298K)
T=298K
T=333K
T=373K
T=413K
εi
εr
A


Ge0.2S0.8
(Ta=298K)
298K
333K
373K
413K
εi
εr
B

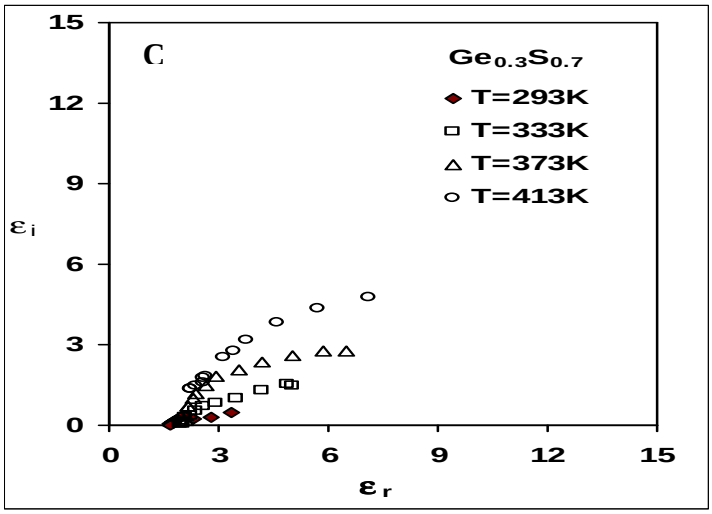
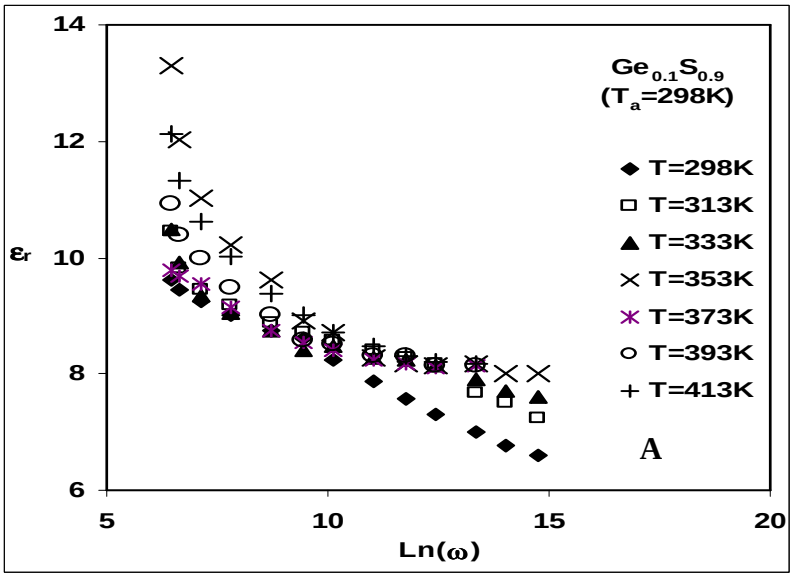
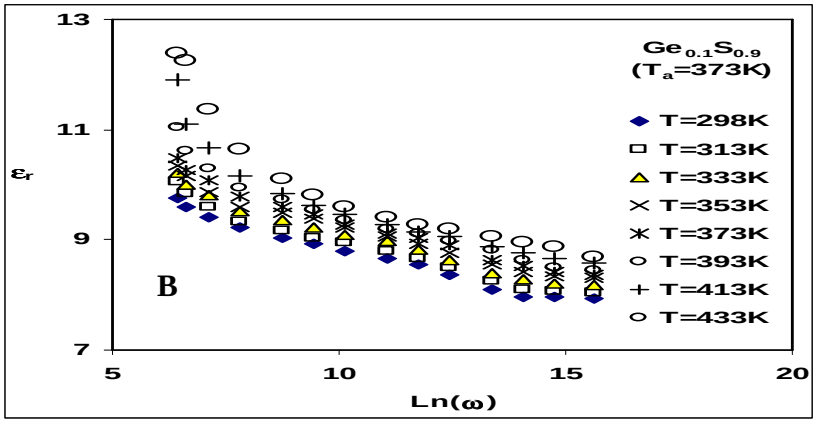


Fig.(1A,B.and C)Cole – Cole diagrams of for as deposited Ge_xS_{1-x}thin films treated at different temperatures.





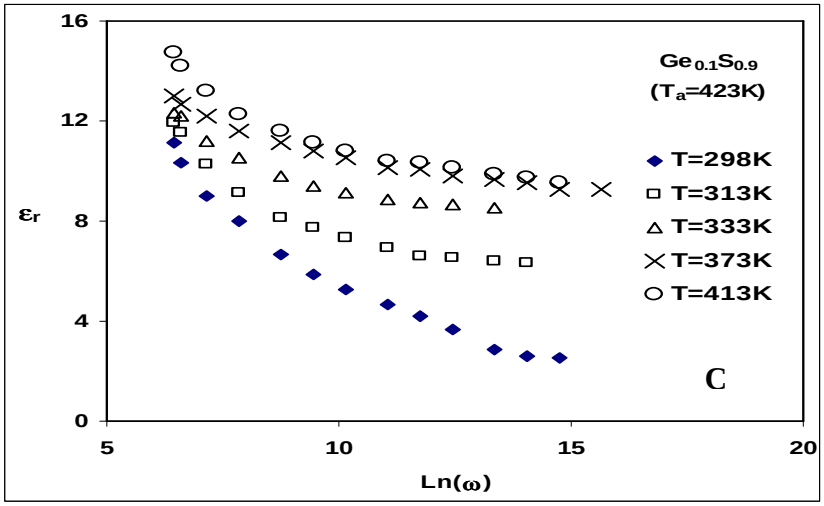
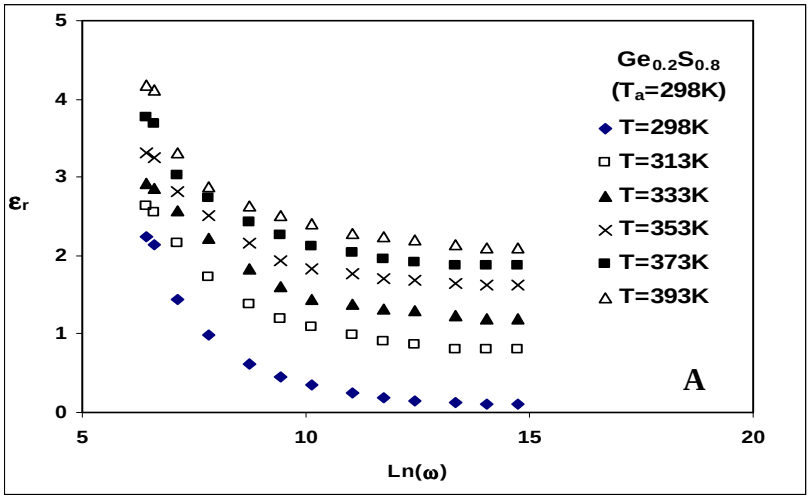
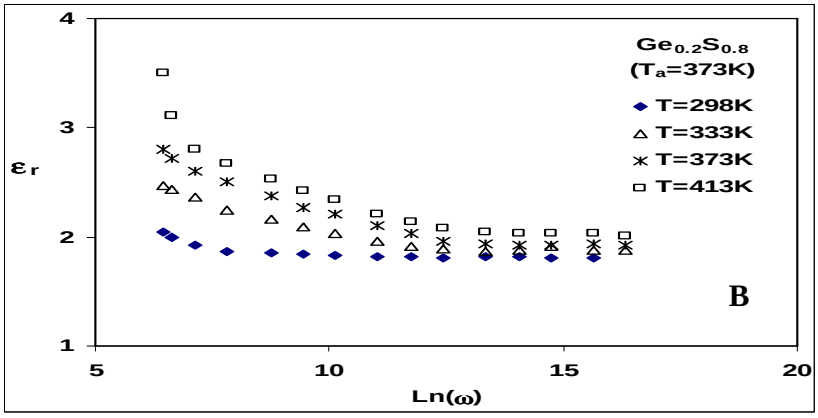


Fig.(2 A,B,and C) The variation of ε_r with ln (w) for as deposited $Ge_{0.1}S_{0.9}$thin films and annealed at different temperatures.


Ge0.2S0.8
(Ta=298K)
T=298K
T=313K
T=333K
T=353K
T=373K
T=393K
A
εr
Ln(ω)


Ge0.2S0.8
(Ta=373K)
T=298K
T=333K
T=373K
T=413K
B
εr
Ln(ω)

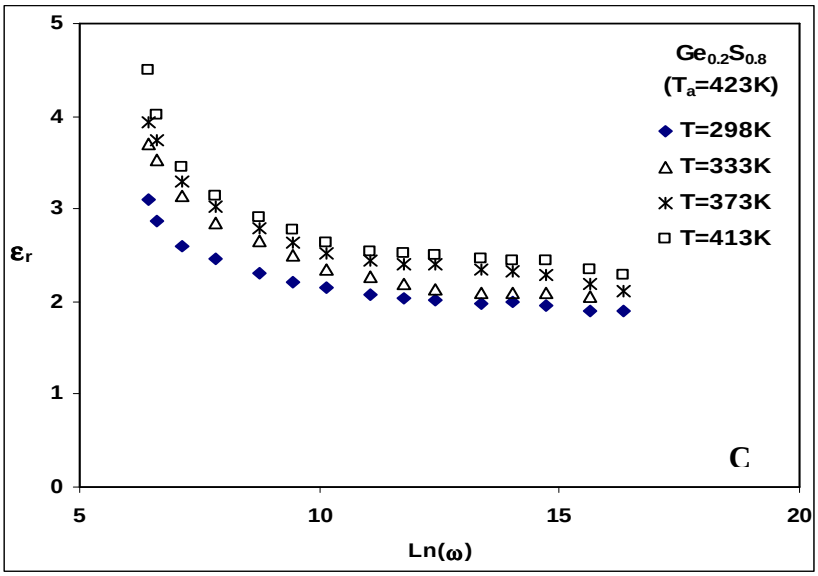
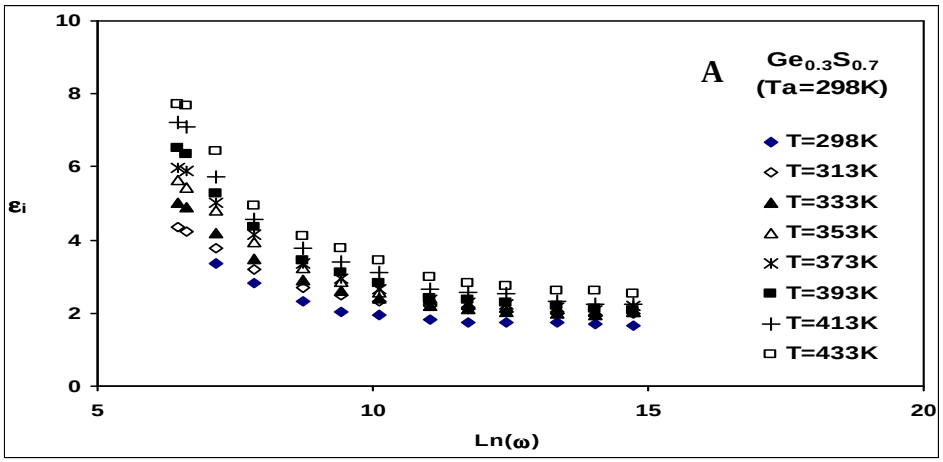
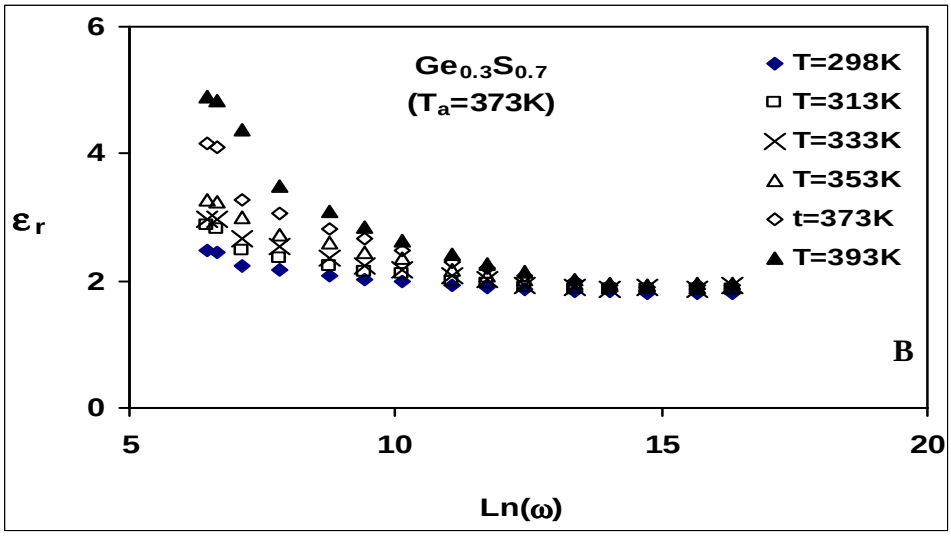


Fig.(3 A,B,and C) The variation of ε_r with ln (w) for as deposited $Ge_{0.2}S_{0.8}$thin films and annealed at different temperatures.





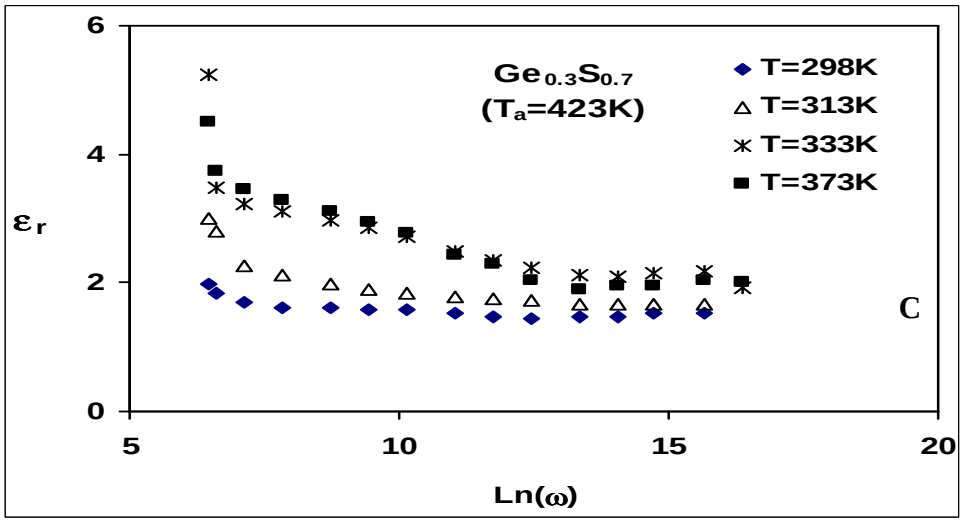


Fig.(4 A,B,and C) The variation of ε_r with ln (w) for as deposited $Ge_{0.3}S_{0.7}$thin films and annealed at different temperatures.

References

[1] K. Tanaka, Reviews of Solid State Science (World Scientific Publishing Company,p.641, (1990).

[2] K. Tanaka, Y. Kasanuki, A. Odajima, Thin Solid Films, 117, 251 (1984).

[3] T. Kawaguchi, S. Maruno, K. Masui, J. Non-Cryst. Solids, 97&98, 1219 ,(1987).

[4]B. Moncheva, P. Petkova*, T. Petkovab, andC. Popovc J. Opto and Advanced Mat., 7, 3, p. 1293 , (2005).

[5] M. Rebkov, P. Nemec, and M. Frumar,J. of Opto. and Advanced Mat. ,8, 5, , p. 1796,(2006)

[6]J.O.Lopez and R.G.Aguila,RevistaMexicana De Fiisica,49,6,529,2003

[7]I.M.EIAmwar,A.K.Mohammad and F.F.Hammad ,Egypt,J. Chem,42,527,(1999).

[8]-R.Sathymoorthy,"Phys.Stat.Sol.(a)",117,495,(1990).