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Effect of Germanium Content on the Optical Constants of Ge_xS_{1-x} Thin Films

Mohmmed Abdulhor
University of Baghdad- College of Science –Department of physics
E-mail* : mhmdm25@yahoo.com

Abstract

In this study the alloys Ge_xS_{1-x} with different Ge content (x=0, 0.1,0.2and0.3) wt.% have been successfully prepared by evacuated quartz tube under vacuum pressure (10^{-2}mbar), whereas Ge_xS_{1-x} thin films were prepared by thermal evaporation technique under vacuum (10^{-5} mbar) with (x=0, 0.1,0.2and0.3).

The optical properties measurements shows that the optical energy gap decrease from (3.4 to 3 eV) with the increase of x content , the optical constants declare significant variation with x content variation.

الخلاصة

في هذا البحث تم تحضير سبائك Ge_xS_{1-x} بواسطة انبوبة من الكوارتز تحت ضغط فراغ (10^{-2}mbar) حضرت الاغشية الرقيقة باستخدام تقنية التبخير الحراري تحت ضغط فراغ مقداره (10^{-5}mbar) وبنسب جرمانيوم (x=0.1,0.2, and 0.3)
لقد بينت نتائج القياسات البصرية ان فجوة الطاقة لأغشية Ge_xS_{1-x} ولجميع قيم المحتوى من الجرمانيوم من نوع غير المباشروانها اظهرت تناقصا مع المحتوى حيث قلت من (3.4 الى 3) eV الثوابت البصرية تم ايجادها من طيف الأمتصاص والأنعكاس في مدى الطول الموجي
(300-900 nm) والتي أظهرت تغيرا ملحوظا مع تغير المحتوى.

Introduction

The increased interest in amorphous chalcogenide semiconductors possess 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 photo induced changes, which have been studied in detail by K. Tanaka [1,2]. Especially, amorphous Ge-S thin films exhibit remarkable irreversible photo- and thermo-bleaching effects, caused by illumination and annealing, respectively [2,3]. A great number of amorphous chalcogenide and chalcohalide materials are successfully applied or are of potential interest for optical storage media [4-7], IR optical windows, sensors [8-10] non-linear optical elements [11], solid state electrolytes [12], etc. Complicated glasses of Ge-S system have been extensively studied by many authors [13,14]. Ge- chalcogenides have been recognized as promising material for optical application due to the wide range of transparency [15]. Silver iodide as compound is at the boundary between an ionic crystal and a covalent one. The stable high-temperature form of AgI (a-AgI) is prominent ionic conductor. Complicated chalcogenide glasses with AgI additives are known as good transmitters of electricity [16] but also as photosensitive material suitable for IR optics [17].

Optical Chalcogenide glasses have been studied intensively [18-21]. GeS_2-based chalcogenide glasses containing Ga, La elements, have been shown to provide satisfactory optical and thermal properties [22-24]. Over oxide and halide glasses, GeS_2-based chalcogenide glasses are recognized as a frequently mentioned glass family with a wider transmission window from visible to infrared (IR) (0.5-10 µm)

[25]. Because of broader transmission window in IR spectral region, chalcogenide glasses are applicable for electronic and optoelectronic components not only in visible and near- IR, but also in mid-IR [19,20,26]. Chalcogenide glasses have been considered as promising hosts for doping with rare earth (RE) ions [22-24].

For the determination of thermal stability of glasses from ternary Ge-In-S chalcogenide system, differential thermal analysis was already used [27]. Boncheva-Mladenova et al. discussed the glass formation in Ge-In-S system, in terms of determination of glass-forming boundaries and consequently physical and electrical characteristics of prepared glasses. The calculated values of ΔT (162 – 365 ^{o}C) predict high thermal stability of Ge-In-S chalcogenide system.

The Aim of the Work

In this research the germanium sulfide alloys and thin films have been in series of germanium content have been prepared then the optical properties are studied in the wave length range (200-900nm)..In this work we shall shed light on the effect of germanium content on the optical parameters (Eg,n,k,ε_1, ε_2) and give the suitable explanation from the behavior of the prepared samples.

Experimental and measurements

The Preparation of (Ge_xS_{1-x}) alloys

In the present work, Ge_xS_{1-x} alloys has been synthesized using high purity elemental Lead, tellurium and selenium is about (99.9999%)

x = 0.1,0.2 and 0.3 .

Stoichiometric amounts of the elements are placed in a quartz ampoule, The quartz ampoule was cleaned carefully with water and alcohol, respectively to remove dust, grease, and other possible contaminants, 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 333 K per hour in steps up to 1000 K. The ampoule is maintained at this temperature for about 10 hours and then allowed to cool slowly to RT.

The Preparation (Ge_xS_{1-x}) Thin Films

Ge_xS_{1-x} thin films with (x = 0.1,0.2,and 0.3 percent) of 1500A^0 thickness were prepared using thermal evaporation by continuously feeding the material with a powder to a heated molybdenum boat of melting point about 1000 ^{0}K at this temperature instantaneous evaporation of the material will take place. Corning glass slides substrates were used, and the distance of the source to substrate was 15cm. The evaporation carried out using Edward coating unit (model E306A) that was evacuated by means of oil-diffusion and rotary pumps. During the evaporation of the films, the pressure in the system was 4×10^{-5} mbar. All the samples were prepared under constant condition :- pressure, rate of deposition (4-6A^0/sec), substrate temperature (RT) and thickness.

The Optical Properties Measurements

UV-Visible Spectrophotometer from Shimadzu was used to carry out the transmittance and the absorbance spectrum in the (200-1100 nm). The out put was obtained as a plot of the wavelength (nm) versus the % transmittance in the mentioned range. The absorption coefficient was calculated using eq. (8) , E_g(band energy) was obtained by plotting the$(\alpha h\nu)^{1/r}$ and (hv) The linear potion was best fitted with r=0.5 indicating direct transition type(k which mean extnshed coefficient) can be calculated using eq. (2),(n which mean reflective index) can be obtained using eq.(6) while ϵ_1(real dielectric constant) ,ϵ_2(image dielectric constant) is calculated using eqs. (9 and 10) respectively.

Results and discussion

1- The Optical Energy Gap (E_g)

The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for Ge $_x$ S_{1-x} films (x=0.1,0.2,and0.3) are shown in Fig.(2).It is clear that (E_g) for pure S film was (3.4 eV), while the Ge film has (E_g) value (o. 7 eV). This means that the increase of Ge content from (0.1 to 0.3) will reduce the (E_g) value from (3.4 to 3 eV) which can be estimated from Fig.(3) as a shift in the absorption band edge to longer wavelength (low energy values). This is ascribed to Ge addition to S which greatly enhanced the tailing of localized stats i.e creation of localized states which accompanied the addition of Ge to S.

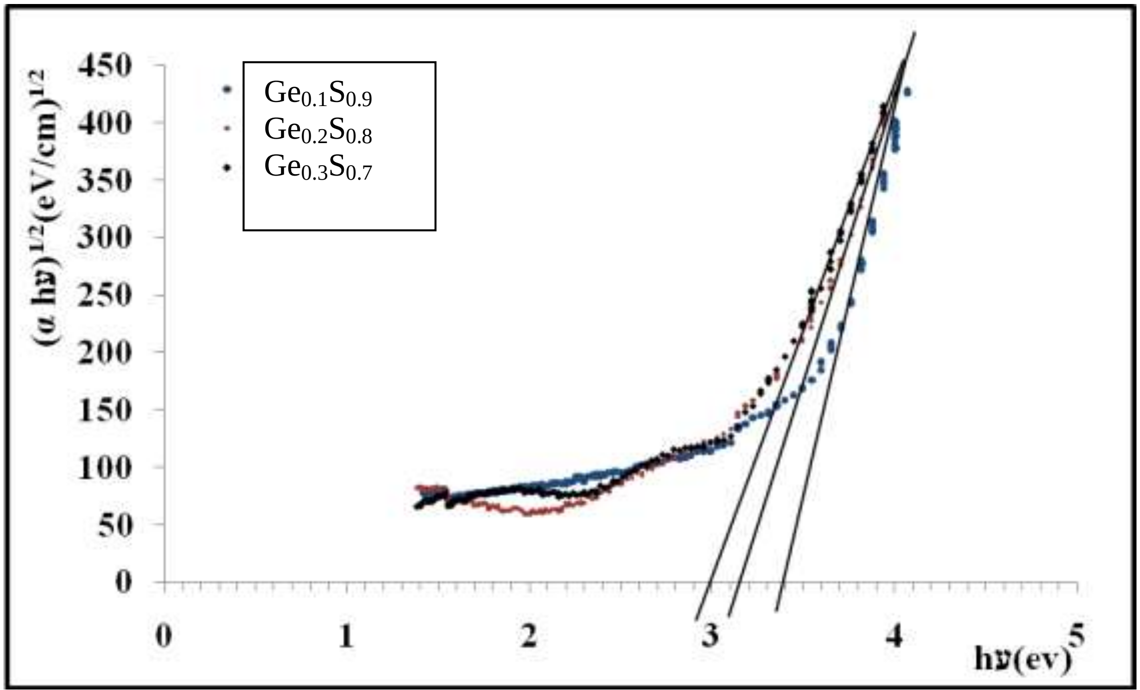


Fig.(2) The variation of $(\alpha h\nu)^{1/2}$ versus photon energy for Ge $_x$ S $_{1-x}$ thin films with different (Ge) content deposited at room temperature.

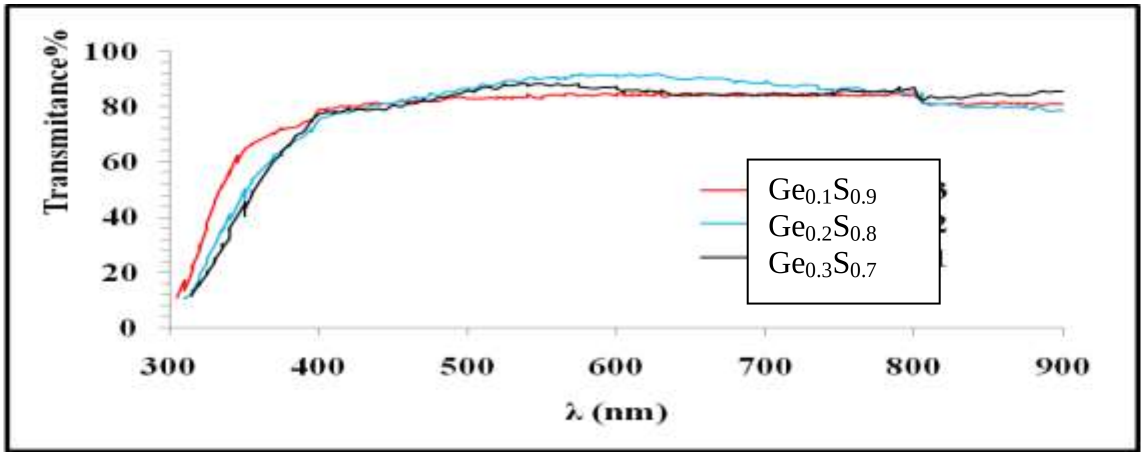


Fig.(3)Transmittance spectra as function to wavelength for Ge $_x$ S $_{1-x}$ thin films with different (Ge) content deposited at room temperature.

2-The Refractive Index (n)

Fig(4) declared the variation of (n) in the wavelength range (300-900nm) . It is obvious that n decreases with the increasing of wavelength ,on the other hand n decreases with the addition of Ge in the first stage while (n) get to increases when the X content of Ge_xS_{1-x} films increase to 0.3. The decrease in the (n) values when x increase from 0.1 to 0.2 is attributed to action of Ge addition since Ge atoms compensates the vacancies in the sulfide structure which in turn increases the transmittance of $Ge_x S_{1-x}$ films as shown in Fig .(1), while the continuous addition of Ge to the $Ge_x S_{1-x}$ samples latter will create anew states in the forbidden gap i.e make he samples less transparent resulting in the increasing of n values .

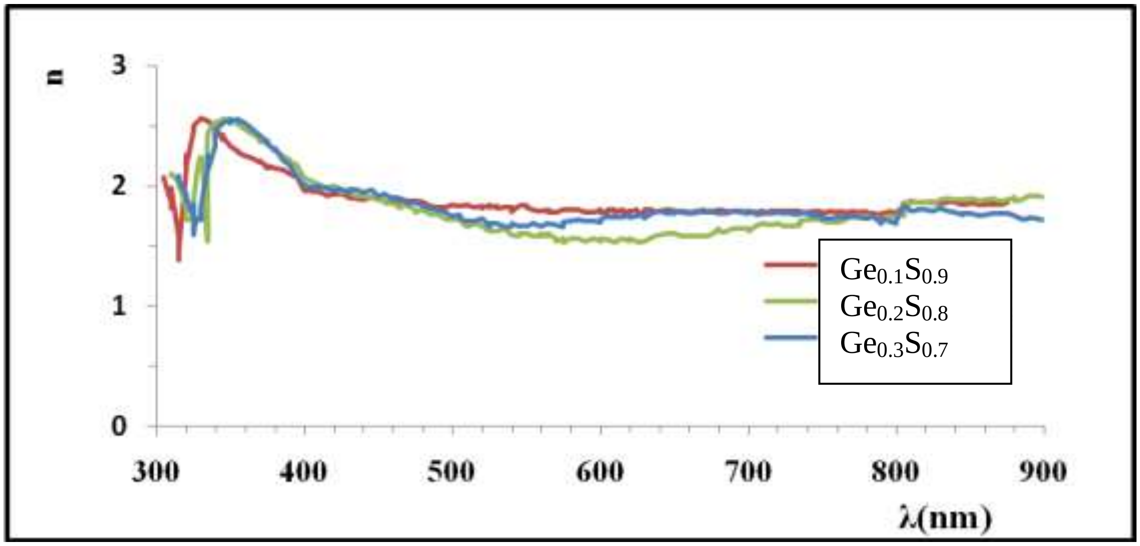


Fig.(4)The variation of refractive index (n) versus photon energy for Ge_xS_{1-x} thin films with different (Ge) content deposited at room temperature.

3-The Extinction Coefficient k

Fig. (5)hows the variation of extinction coefficient (k) for $Ge_x S_{1-x}$ thin films deposited at room temperature with different germanium content. One can observed that (k) values decreases when x content in the films increases from 0.1 to 0.2 ,while k increase for the residual x value ,moreover (k) decreases from (0.16481to 0.0825)when Ge content changed from (0.1 to0.2) at λ=600nm while k increase from 0.0825 to 0.1301 when x increase to 0.3 the decrease and the increase of k value related to the decrease and increase of absorption coefficient respectively.

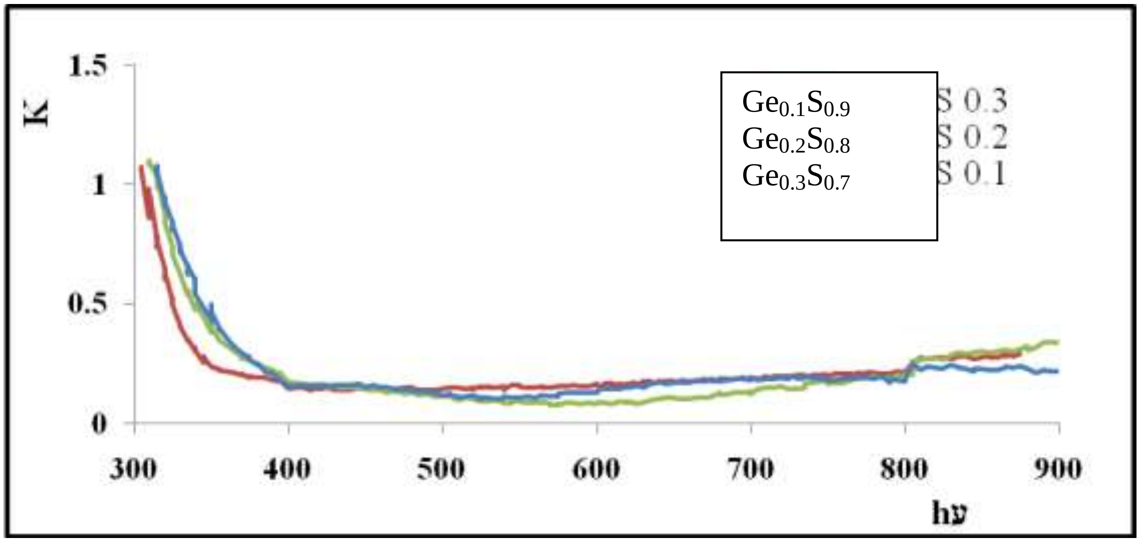
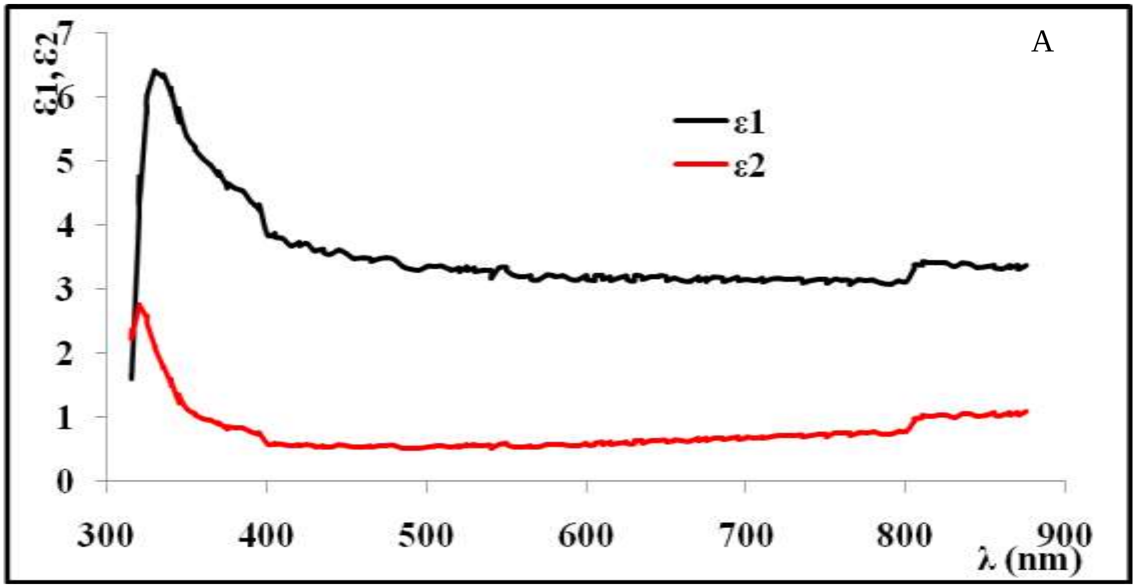
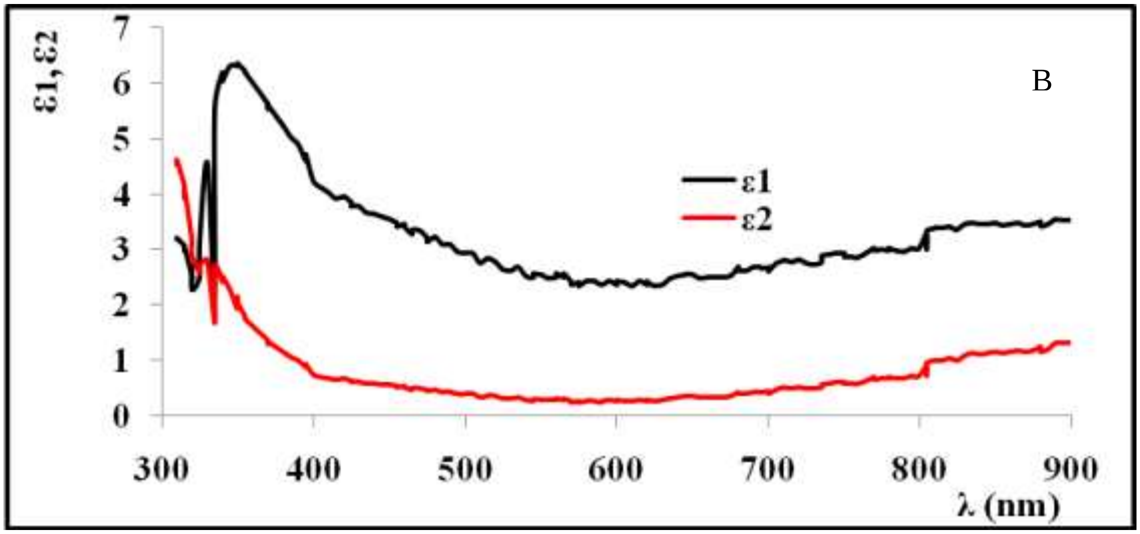


Fig.(5)The variation of extinction coefficient (k) versus photon energy for Ge_xS_{1-x} thin films with different (Ge) content deposited at room temperature.

4-TheRealand Imaginary Parts of Dielectric Constant ε_1, ε_2

The real part of dielectric constant (ε_1) in fig.(6) showed maximum values at values occurred at energies little higher than the energy gaps values ,moreover the location of the peaks shift to lower energy or to longer wavelength with increase Ge content. The variation of imaginary part (ε_2) of dielectric constant in Fig.(6A,Band C)declared the same behavior of that of (k) thus it can given the same explanation .





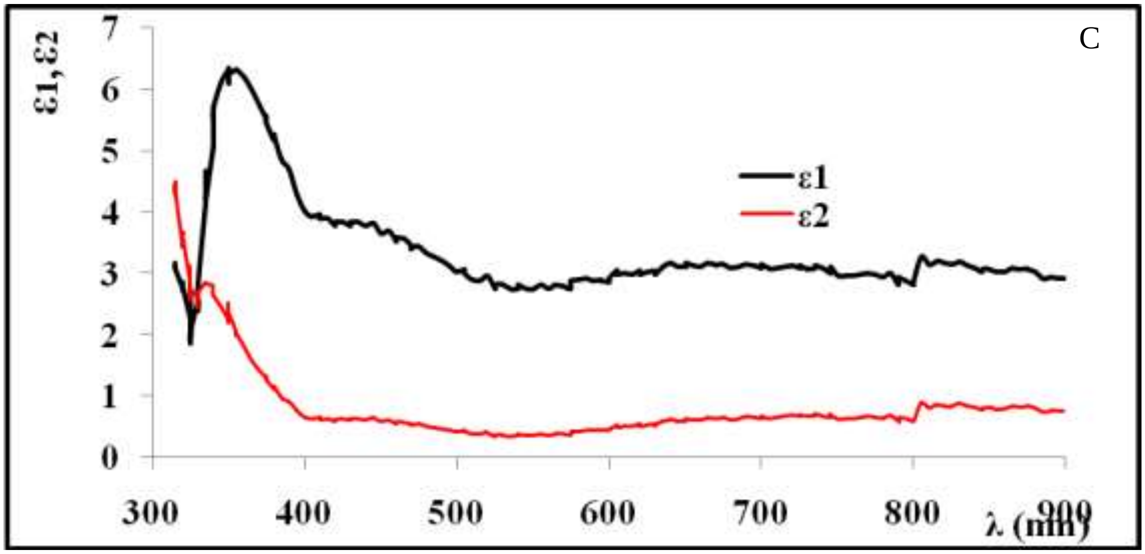


Fig.(6A,B and C) The variation of real part and imaginary parts of dielectric constant ($\varepsilon_{1,}$ ε_2) versus wavelength for Ge $_x$ S $_{1-x}$ thin films with different (Ge) content deposited at room temperature,(A)forGe $_{0.1}$ S $_{0.9.}$,(B) for Ge $_{0.2}$S $_{0.8}$ and (C)Ge $_{0.3}$ S $_{0.7}$

Table(1) Illustrates the values of (n(k, €$_1$ and € $_2$) at λ=600nm) for Ge_x S_{1-x} thin films deposited room temperature.

Germanium content(x)	E_g(eV)	(k)	n	(ε_1)	(ε_2)
0.1	3.4	0.1648	1.7983	3.2069	0.5931
0.2	3.15	0.0825	1.5374	2.3569	0.2539
0.3	3	0.1301	1.6976	2.8650	0.4419

Conclusion

Chalcogenide from Ge-S films were prepared and studied.The observed decrease of the optical energy gap with the increase of Ge resulting from the ordering and creation of new localized states .The formation of Ge- Ge bonds leads to creation of defect states resulting in reduction of Eg.

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