Effect of Germanium Content on the Optical Constants of \( \text{Ge}_x\text{S}_{1-x} \) Thin Films

Bushra A. Hasan\(^1\) and Mohammed Abidalhur Kadhim\(^2\)

\(^1\)Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
\(^2\)Department of Physics, College of Science, University of Kerbala, Karbala, Iraq

a)Corresponding author: bushra.ab@sc.uobaghdad.edu.iq

Abstract:
In this study the alloys \( \text{Ge}_x\text{S}_{1-x} \) with different Ge content (\( x=0, 0.1, 0.2, \text{and} 0.3 \)) wt.% have been successfully prepared by evacuated quartz tube under vacuum pressure \( (10^{-2}\text{Torr}) \), whereas \( \text{Ge}_x\text{S}_{1-x} \) thin films were prepared by thermal evaporation technique under vacuum \( (10^{-5}\text{Torr}) \) with \( (x=0, 0.1, 0.2, \text{and} 0.3) \). The optical properties measurements shows that the optical energy gap decrease from \( (3.4 \text{ to } 3 \text{ eV}) \) with the increase of \( x \) content, the optical constants declare significant variation with \( x \) content variation.

Keywords: \( \text{Ge}_x\text{S}_{1-x} \) chalcogene thin films, optical constants, energy gap.

Introduction
Chalcogenide semiconductors with amorphous structure have numerous remarkable phenomena, which show possibilities for using them in many applications like microelectronics and optoelectronics - as ovonic threshold and memory switching devices, inorganic photoresists, optical memory disks, etc. The growing 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. K. Tanaka \cite{1,2} was concerned with photo induced changes in band gap, which have been studied in detail. Especially, amorphous Ge-S thin films exhibit remarkable irreversible photo- and thermo-bleaching effects, resulted from illumination and annealing, respectively \cite{2,3}. On the other hand the amorphous semiconductors and particularly the chalcogenide and chalcohalide glasses attract strong scientific interest due to the advantages from practical point of view:
1- easy to prepare thin films because of no long-range order;
2- easy to design and modify their properties by small changes of the compositions;
3- attractive optical application due to excellent characteristics like wide region of optical transparency, high refractive index, photo induced effects. A great number of amorphous chalcogenide and chalcohalide materials are successfully applied for optical storage media \cite{4-7}, IR optical windows, sensors \cite{8-10} non-linear optical elements \cite{11}, solid state electrolytes \cite{12}, etc. Complicated glasses of Ge-S system have been extensively studied by many authors \cite{13,14}. Ge- chalcogenides have been recognized as promising material for optical application due to the wide range of transparency \cite{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 \cite{16} but also as photosensitive material suitable for IR optics \cite{17}. 

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Optical Chalcogenide glasses have been studied intensively [18-21]. GeS₂-based chalcogenide glasses containing Ga, La elements, have been shown to provide satisfactory optical and thermal properties [22-24]. Over oxide and halide glasses, GeS₂-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°C) predict high thermal stability of Ge-In-S chalcogenide system.

Generally, the structure of GeS₂-based glasses has been widely studied by various techniques such as Raman and infrared spectroscopy [28-30]. The structure of germanium based chalcogenide glasses was described as network of GeS₄ tetrahedral units connected to each other by corners and edges [31].

Among chalcogenide glasses, glassy germanium disulfide (g-GeS₂) has been heavily studied for many years [32] and was still the subject of recent experimental investigations [33,34] because of its interesting physical properties. Chalcogenide materials can be used as sensitive media for optical recording, as light guides, as high-resolution inorganic photoresists, or antireflection coatings [35]. Moreover, bulk glasses with, for example, Ag⁺ cations are good solid electrolytes with a high ionic conductivity at room temperature [36] and thin GeS₂ films are promising materials for submicron lithography when doped with silver [37]. The high quantum efficiency of these glasses appears as a consequence of the relative high masses of the elements involved [38]. All these potential applications of glassy GeS₂ have led many authors to study the physical properties of these chalcogenide glasses, and many experiments have been done on this topic [39,40]. Although cluster modeling simulations were performed on g-GeS₂ [41] it appears that GeS₂ compounds have not been the topic of extensive MD investigations yet, contrary to GeSe₂ [42] or SiSe₂ [43]. In order to perform such investigations one has to decide what kind of description is adequate for GeS₂. Taking mostly but not purely covalent bonding into account in g-GeS₂ a first-principles approach seems appropriate. In this paper we therefore present a theoretical study of the structural, pushing point of the system at 610°C and 840°C respectively. The main features of the reported phase diagram are: The existence of a Ge게-GeS eutectic at 650°C. The existence of two sulfides of germanium, (48 at. % S).

By analogy with tin sulfide (2) and selenide (3, 4) the above authors assume this transition to be a second order transformation. Several observations made in our laboratory could not be reconciled with the reported thermal properties of GeS, and it was found necessary to study this compound further by the technique of differential thermal analysis.

Chalcogenide glasses, especially sulphide glasses, are becoming more and important for the fabrication of optoelectronic devices in part because of the high nonlinearity, strong photosensitivity and other unique properties they have [44-47]. Traditionally, the sulfide glasses are made in bulk from by traditional melt quenching method in the quartz ampoule. The bulk glasses are then reprocessed form fiber or planar waveguide.
Chalcogenide glasses are based on the chalcogen elements S, Se and Te and the addition of other elements such as Ge, As and Sb leads to the formation of stable glasses [48]. The addition of halides leads to the formation of chalcohalide glasses [49]. Since the chalcogenide glasses transmit to longer wavelengths in the IR than silica and fluoride glasses, there are numerous potential applications in the civil, medical and military areas. These can be essentially divided into two groups, namely “passive” and “active” applications:

(a) Passive Applications: The fibers are used as a light conduit from one location to another without interacting with the light, other than that due to scattering, absorption and end face reflection losses associated with the fiber. (b) Active Applications: The light propagating through the fiber is modified by a process other than that due to scattering, absorption and end face reflection losses associated with the fiber. Examples of these include fiber lasers, amplifiers, bright sources, gratings and non-linear effects. This electrical, A.C conductivity and dielectric properties system had been investigated previously [50][51][52]. This work includes the results and analysis of the optical properties of Ge x S1-x films for as deposited Ge x S1-x thin films with different Ge content in the range (0.1,0.2 and 0.3) wt. % with 150 nm thickness and rate of deposition 4 Å/sec at R.T were measured.

Results and discussion

X-ray diffraction studies of Ge x S1-x alloys for (x=0.1 and 0.3) were made, the diffraction patterns in Figure 1 of the alloy for x=0.1 declared sharp diffraction peaks located at 23°, 26°, 28°, 35°, and 57° indicated the polycrystalline structure with hexagonal unit cell when compared with the American Slandered for Testing (ASTM) cards, noticeable remark from Figure 2 is the addition of Ge increases the polycrystalline degree which is obvious from the increasing of peak heights in the diffraction pattern of the alloy for x=0.3, also the increasing of Ge is responsible about the disappearing of the peak at 2θ≈36°.

![Figure 1: X-ray Diffraction for Ge 0.1S 0.9 alloy.](image-url)
The diffraction pattern of prepared thin films of Ge\textsubscript{x}S\textsubscript{1-x} for different x content are shown in figure 3. The pattern reveal no peaks indicating the amorphous structures of these samples.

![X-ray Diffraction for Ge\textsubscript{x}S\textsubscript{1-x} thin films](image)

**Figure 3:** X-ray Diffraction for Ge\textsubscript{x}S\textsubscript{1-x} thin films.

The variation of (\(\alpha h\nu\))\(^{1/2}\) with photon energy (h\(\nu\)) for Ge\textsubscript{x}S\textsubscript{1-x} films for (x=0.1,0.2, and 0.3) are shown in Figure 4. It is clear that (E\textsubscript{g}) for pure S film was (3.4 eV), while the Ge film has (E\textsubscript{g}) value (0.7 eV) this means that the increase of Ge content from (0.1-0.3) will reduce the (E\textsubscript{g}) value from (3.4 to 3 eV) which can be estimated from Figure 5 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.
Figure 4: 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.

Figure 5: Transmittance spectra as function to wavelength for Ge$_x$S$_{1-x}$ thin films with different (Ge) content deposited at room temperature.

Figure 5 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 Ge content in Ge$_x$S$_{1-x}$ 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 Figure 5, 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.
Figure 6: Variation of refractive index (n) versus photon energy for Ge\textsubscript{x}S\textsubscript{1-x} thin films with different (Ge) content deposited at room temperature.

Figure 7 shows the variation of extinction coefficient (k) for Ge\textsubscript{x}S\textsubscript{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.

Figure 7: Variation of extinction coefficient (k) versus photon energy for Ge\textsubscript{x}S\textsubscript{1-x} thin films with different (Ge) content deposited at room temperature.
The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) part of dielectric constant were calculated and plotted in the spectral range (300-900nm) in Figures 8A, B, and C. The real part 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 ($\varepsilon_2$) of dielectric constant in Figure. (9A, B, and C) declared the same behavior of that of (k) thus it can give the same explanation.
Figure 8: Variation of real part and imaginary parts of dielectric constant ($\varepsilon_1$, $\varepsilon_2$) versus wavelength for Ge$_x$S$_{1-x}$ thin films with different (Ge) content deposited at room temperature, (A) for Ge$_{0.1}$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 $E_g$, $n$, $k$, $\varepsilon_1$ and $\varepsilon_2$ at $\lambda=600$nm for Ge$_x$S$_{1-x}$ thin films deposited at room temperature.

| Germanium content($x$) | $E_g$(eV) | ($k$) | $n$ | $\varepsilon_1$ | $\varepsilon_2$ |
|------------------------|----------|-------|-----|----------------|----------------|
| 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      | 0.1301| 1.6976 | 2.8650         | 0.4419         |

Conclusion
Chalcogenide from Ge-S thin films were prepared and the investigation of optical properties were done. 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 $E_g$.

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