

The optical properties of a- $(\text{GeS}_2)_{100-x}\text{Ga}_x$ thin films

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Abstract

Thin films whose compositions can be expressed by $(\text{GeS}_2)_{100-x}\text{Ga}_x$ ($x=0, 6,12,18$) formula were obtained by thermal evaporation technique of bulk material at a base pressure of $\sim 10^{-5}$ torr. Optical transmission spectra of the films were taken in the range of 300-1100 nm then the optical band gap, tail width of localized states, refractive index, extinction coefficient were calculated. The optical constants were found to increase at low concentration of Ga (0 to12%) while they decreases with further addition of Ga. The optical band gap was found to change in opposite manner to that of optical constants. The variation in the optical parameters are explained in terms of average bond energy of the system.

Key words

Chalcogenide glasses, absorption coefficient, optical band gap, average bond energy.

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الثوابت البصرية لأغشية $(\text{GeS}_2)_{100-x}\text{Ga}_x$ الرقيقة

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الخلاصة

تم تحضير أغشية المركب $(\text{GeS}_2)_{100-x}\text{Ga}_x$ وبنسب مختلفة من المحتوى (0,6,12,18%) بواسطة التبخير الحراري تحت ضغط مقداره 10^{-5} torr. تم الحصول على طيف النفاذ للأغشية المحضرة ضمن المدى 300-1100 nm ومن ثم تم حساب فجوة الطاقة البصرية، عرض الحالات الموضعية، و الثوابت البصرية. لقد أظهرت الثوابت البصرية ازديادا عند إضافة الكاليوم بنسب واطئة (من 0 الى 12 %) لكنها تناقصت بعد زيادة نسبة الكاليوم. فجوة الطاقة البصرية أظهرت سلوكا معاكسا لسلوك الثوابت البصرية. تم تفسير تغير المعلمات البصرية بدلالة تغير طاقة أصرة المنظومة.

Introduction

Although many different materials have been grown using the oblique angle deposition (OAD) technique [1–6], very few have been synthesized using infrared transparent or glass forming materials. Among these materials, chalcogenide glasses have been successfully deposited by OAD [7], thus adding extra functionality to their unique properties as to expand their range of optical and morphological properties [8,9] and, in turn, their applications. Chalcogenide

glasses are of great technological importance, since their high transmission in the infrared (IR) region [10], together with the possibility of modifying their optical band gap and index of refraction by illumination [11], make them very attractive materials in the areas of infrared optics, optical signal imaging, and data storage. Moreover, optical materials transparent in the mid-IR spectral region offer access to fundamental fingerprint absorptions of organic

molecules and bimolecular [12,13]. In this respect, mid-IR sensors are currently receiving increased attention because of their inherent molecular selectivity.

The chalcogenide glasses are one of the most widely known families of amorphous materials and have been extensively studied for several decades because of their interesting fundamental properties and because of their potential applications in optical imaging, optical recording and integrated optics, microelectronics and optical communications. Most of these applications are based on the wide variety of light-induced effects exhibited by these materials [14-19]. The novel bulk glasses from the chalcogenide Ge-S-AgI system have been synthesized [20].

Ge₂₈Sb₁₂Se₆₀ glassy matrix doped with metal impurities has been used for the determination of copper (II) in aqueous solution[21].

The surface plasmon resonance phenomenon has been studied in a chalcogenide glass-based optical system[22]. Investigation of the diffusion products occurring after photodiffusion of Ag in GeS₂films at room temperature and after annealing up to 603K[23].

Experimental procedure

Quenching technique. The materials (5N pure) were weighed in accordance with their atomic weight percentage. The weighed materials were sealed in evacuated ($\sim 10^{-2}$ mbar) quartz ampoules and heated up to 1273K in a rocking furnace at a heating rate of 3-4 °C/min. Ampoules were frequently rocked at the highest temperature for 5 hours. The quenching was done in water immediately after taking out the ampoules from the furnace. The polycrystalline nature of the bulk samples was confirmed by the x-ray

The determination of the optical constants is of great importance for understanding the mechanism of the optical processing and for their application in practice. A number of works exist which trace the influence of composition and preparation conditions of thin films on the physico-chemical properties, and the changes in them induced by light. The structural changes in these materials are related to the changes in their optical properties. Various methods exist for determining the optical constants of thin films from the coefficient of transmission, T, and reflection, R, or via their combination [24-29]. All these methods are based on the Swanepoel's method [30] and on different computer programs for calculation of the optical constants and film thickness. As the layer structure depends strongly on the conditions of the film deposition it is difficult to make some comparison between the published data in the literature.

The present work deals with the study of absorption coefficient and optical band gap ,extended of localized states, and optical constants of (GeS₂)_{100-x}Ga_x (x=0, 6, 12, 18 at.%) thin films. The transmission spectrum of the thin films is taken in the range of 300-900nm. Bulk samples (GeS₂)_{100-x}Ga_x (x = 0, 6, 12, 18) were prepared by melt diffusion technique when checked with ASTM cards[31].

Thin films of the bulk samples were prepared on cleaned glass substrates by thermal evaporation technique [Vacuum coating unit EDWARD Model] at base pressure of $\sim 10^{-5}$ Torr. Optical Interference Fringes was used to measure film thickness and Fizeau fringes of equal thickness are obtained in an optical apparatus of the type, the film thickness (d) is given by:

$$d = \frac{\lambda \Delta x}{2 x} \quad (1)$$

where Δx is the shift between interference fringes, λ is the (Na) wavelength (5893\AA) and x is the distance between interference fringes. The samples having almost thickness of about $300 \pm 10\text{nm}$.

Amorphous nature of thin films was also checked by x-ray diffraction technique[31]. The normal incidence transmission spectra of $(\text{GeS}_2)_{100-x}\text{Ga}_x$ ($x=0, 6, 12, 18$ at.%) thin films have been taken by a double beam UVVIS-NIR spectrophotometer [Hitachi-330] in the transmission range 300-1100 nm. All measurements were taken at room temperature.

Results and Discussion

Fig.1 shows the transmission spectrum of a- $(\text{GeS}_2)_{100-x}\text{Ga}_x$ ($x=0, 6,$

12, 18 at.%) thin films. It has been found from the investigation of the optical transmittance of amorphous Ge-S-Ga thin films that introduction of Ga to GeS_2 sample causes a red shift, i.e the absorption edge shift towards longer wavelengths which is accompanied by substantial decrease of the transparency of the thin films. Optical transmission is a very complex function and is strongly dependent on the absorption coefficient (α) the absorption coefficient of the thin films is calculated by using the expression [32]:

$$\alpha = (1/d) \ln(1/T) \quad (2)$$

where d is the thickness of the thin film and T is the transmittance .

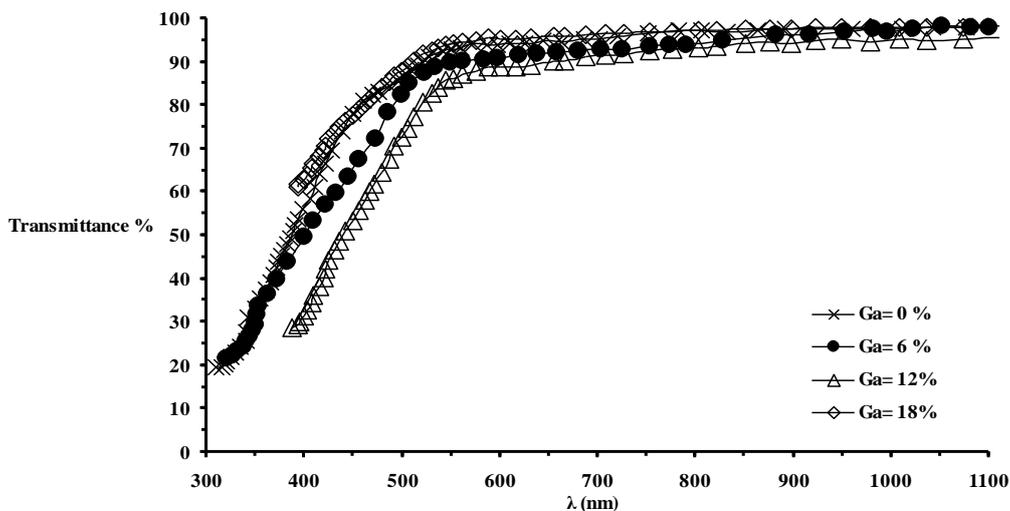


Fig.1: Transmittance spectra of $(\text{GeS}_2)_{100-x}\text{Ga}_x$ thin films deposited at R.T.

The optical band gap has been estimated from absorption coefficient data as a function of wavelength by using Tauc Relation [32]:

$$(\alpha h\nu)^{1/r} = B (h\nu - E_g^{\text{opt}}) \quad (3)$$

where $h\nu$ is the photon energy, α is the absorption coefficient, E_g^{opt} the optical band gap, B is band tailing parameter and $r = 1/2$ for direct band gap and $r=2$ for indirect band gap. This is observed

from the plot (as shown in Fig.2) between $(\alpha h\nu)^{1/2}$ and $(h\nu)$ for $(\text{GeS}_2)_{100-x}\text{Ga}_x$ that the nature of graph is non linear which shows that transition in the forbidden gap is indirect in nature [15]. Optical band gap E_g^{opt} can be determined by the extrapolation of best fit line between $(\alpha h\nu)^{1/2}$ and $(h\nu)$ to intercept the $(h\nu)$ axis ($\alpha = 0$).

Fig.2 shows graphically the variation of

optical band gap with increasing % of gallium content. It is found that the optical band gap decreases with increase in concentration of gallium up to 12 at. % and at higher concentration of gallium (>12 at.%), it increases. The gallium additives in $(\text{GeS}_2)_{100-x}\text{Ga}_x$ must bring about a compositional change of host network of Ge-S i.e. the alloying effect, as the optical band gap is found to vary with gallium concentration. This change in optical band gap may be understood in terms of the structure of Ge-S system or on the basis of the change in average bond energy as a function of composition.

The bond energies values exclude the application of random covalent network model for structure explanation where Ge-Ge bonds are possible. Bonds such as Ga-S and S-S have also lower possibility of existence due to their lower bond energy (213 and $217\text{kJ}\cdot\text{mol}^{-1}$). We suggest that most favorable structural units are $\text{GeS}_4/2$ and Ga. The tetrahedral $\text{GeS}_4/2$ units are corner bridged with Ga clusters through three-coordinated Ga atoms.

The increase in the Ga amount is

associated with an increase in the number of Ga clusters. Thus the lower transparency of films with ≤ 12 at.% Ga can be explained. The almost linear decrease of the band gap with Ga content is attributed also to the structural transformation in the films after Ga introducing. The incorporation of Ga clusters in the Ge-S matrix is connected with an increase of the disorder and an increase in the number of localized states within the band gap. According to Davis and Mott [33] the presence of high density of localized states in the band structure is responsible for lower values of the optical gap. It seems that our experimental data agree well with Davis and Mott suggestion. While the incorporation of Ga into the Ge-S glassy at high concentration (>12at.%), leads to partial compensation of structural defects which is correlated with decreasing of localized states concentration in the band gap. Thus, the optical band gap expands (see Table1) that agree with the results reported by Boycheva et al[34].

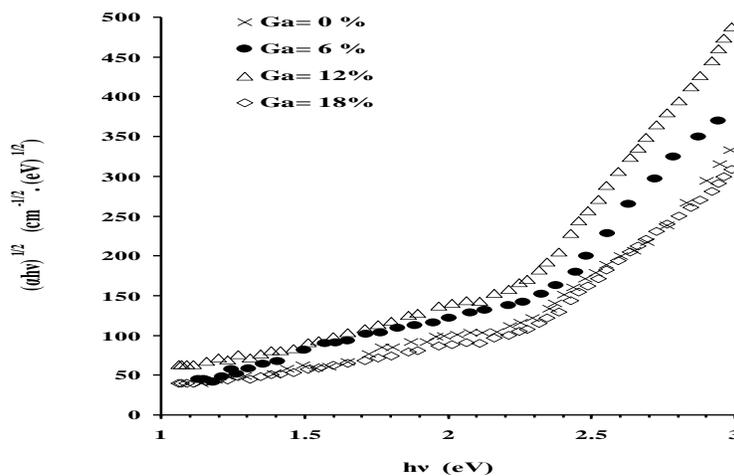


Fig.2: Variation of $(ahv)^{1/2}$ with (hv) of $(\text{GeS}_2)_{100-x}\text{Ga}_x$ thin films deposited at R.T.

For amorphous semiconductors, the basic absorption edge slightly differs from crystalline structure. In this case, the value of the optical absorption coefficient could be expressed by the following mathematical relation [31]:

$$\alpha = \alpha_0 \exp \frac{h\nu}{E_e} \quad (4)$$

where α_0 is the correlation constant, and E_e represents the tail width of localized states within the optical energy gap which can be determined from

the plot of $\ln \alpha$ versus $h\nu$ as shown in Fig.3. The data show that E_e increase with gallium addition to GeS_2 , moreover E_e increases from 0.7651 to 0.9458 eV when Ga increases from 0 to 12% but then decrease to 0.8491 when Ga concentration increases to 18% (see Table 1), this explain the variation of E_g with the increase of Ga concentration, on the other hand increase of E_e give indication about the defect states accompanies the introduction of Ga to GeS_2 system.

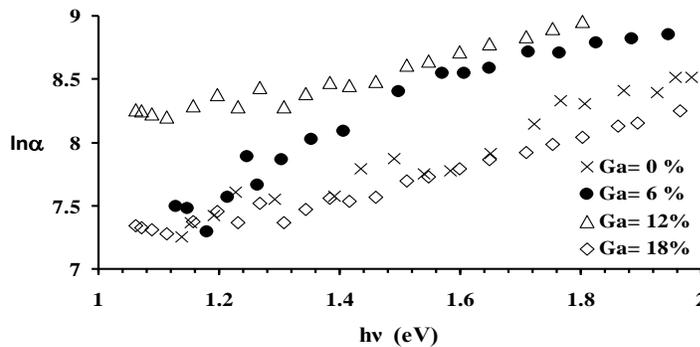


Fig.3: Variation of $\ln(\alpha)$ with photon energy for $(\text{GeS}_2)_{100-x}\text{Ga}_x$ thin films deposited at R.T

Moreover, the optical properties of semiconductors can also be expressed by using the concepts of refractive index (n) and extinction coefficient (k) through the following relations:

$$n = \left[\left(\frac{4R}{(R-1)^2} - k^2 \right) \right]^{1/2} - \frac{(R+1)}{(R-1)} \quad (5)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (6)$$

where λ is the wavelength of incident photon, and R the reflectance, which could be calculated from the relation: $R + A + T = 1$, where A represents absorption.

The refractive index n and the extinction coefficient k change in the

same way and its spectral distribution as shown in Fig.4 and 5. It is obvious that n and k increases with increase of Ga concentration up to 12%, but then decreases, moreover (n) and (k) increases from (1.4116 to 1.6012) and from (0.0238 to 0.0453) when Ga concentration increases from 0 to 12% at $\lambda = 650$ nm (see Table 1). The behavior of (n) can be explained as addition of Ga leads to make GeS_2 more dense (increasing the packing density) which in turn decreases the propagation velocity of light through the sample which resulting in increasing of n values since n represent the ratio of light velocity through

vacuum to velocity through any medium, while the behavior explanation of k is the increases of Ga increases the absorbance or the absorption coefficient consequently k will be increase, while the decrease of n and k with the further increase of Ga concentration(i.e. to 18%) result from

the lowering of packing density of absorption coefficient respectively. The spectral distribution of ϵ_r and ϵ_i are shown in Fig.6 and 7 It is obvious that ϵ_r and ϵ_i exhibit in the same manner of n and k respectively and the same explanation can be given.

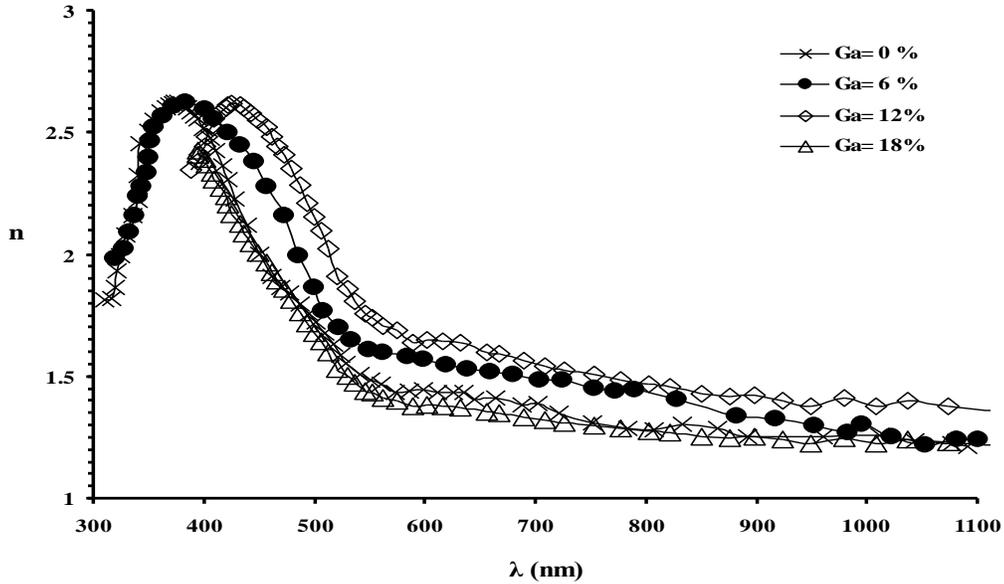


Fig.4: Variation of n with wavelength for $(GeS_2)_{100-x}Ga_x$ thin films deposited at R.T

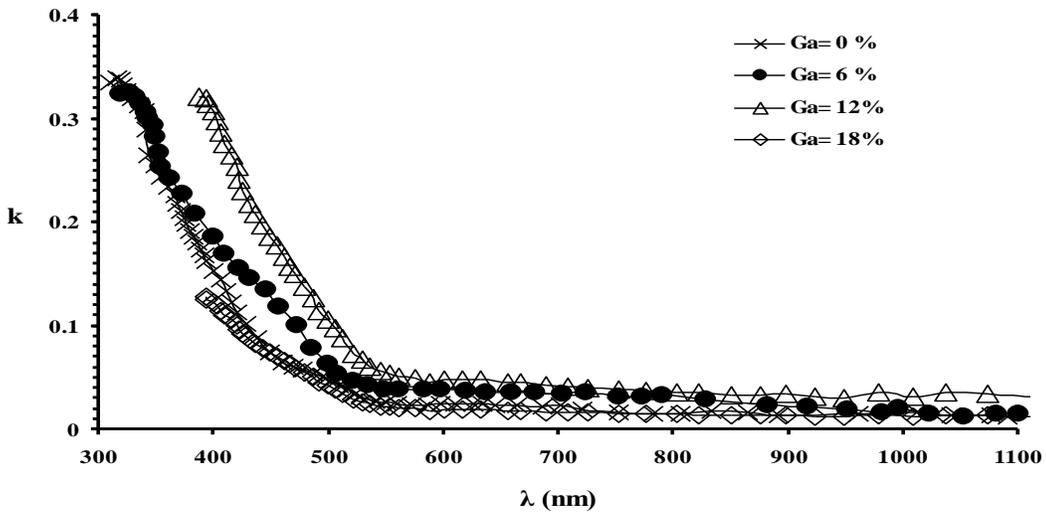


Fig.5: Variation of k with wavelength for $(GeS_2)_{100-x}Ga_x$ thin films deposited at R.T

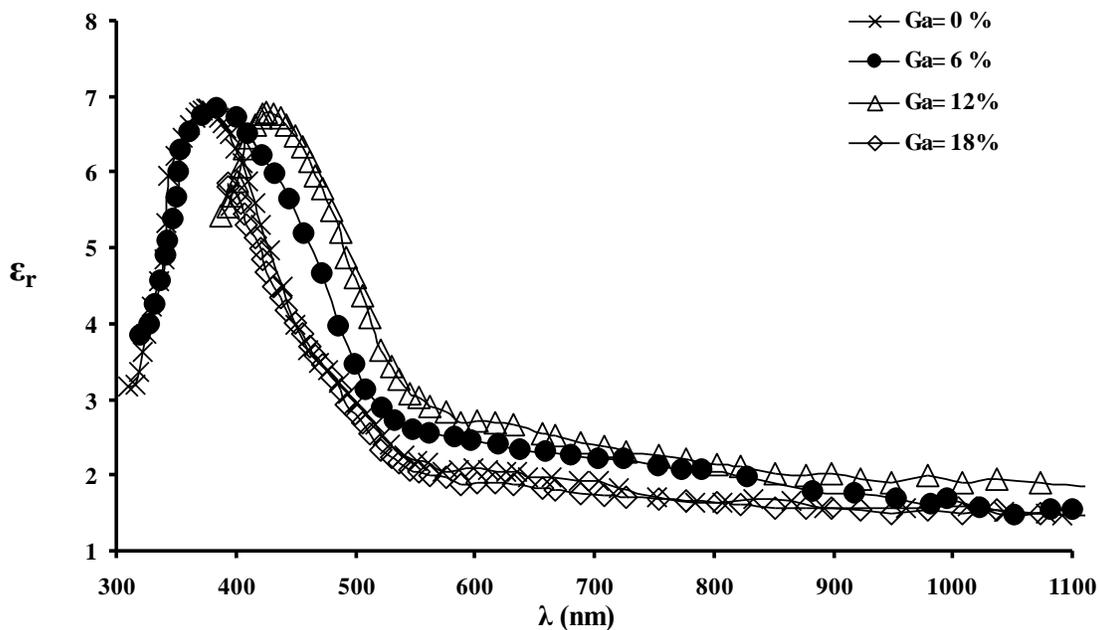


Fig.6: Variation of ϵ_r with wavelength for $(GeS_2)_{100-x}Ga_x$ thin films deposited at R.T

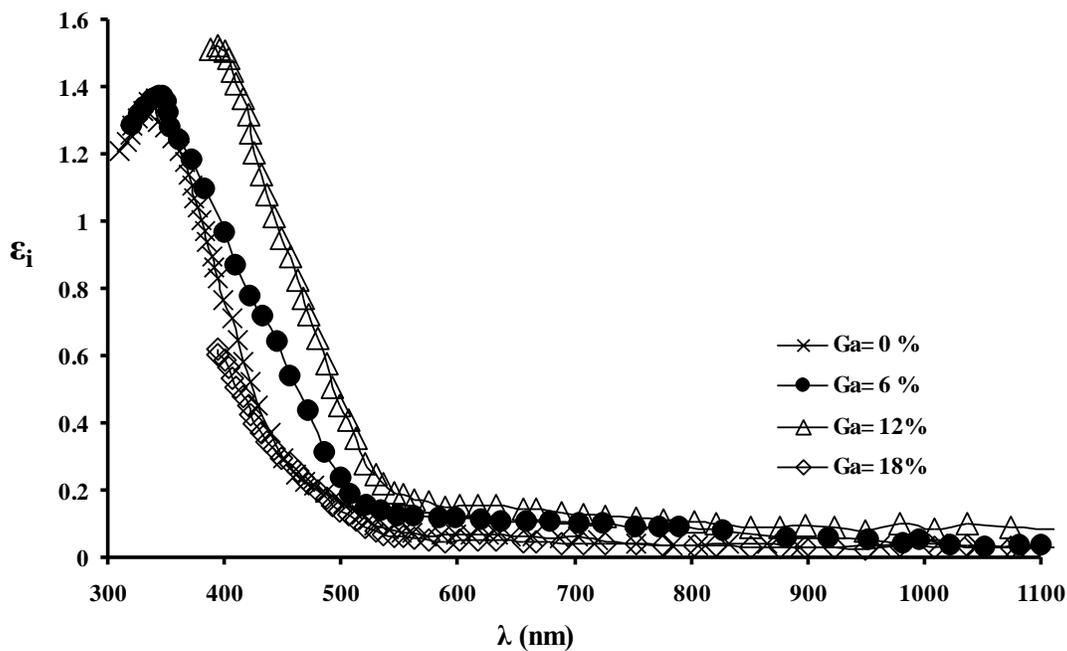


Fig.7: Variation of ϵ_i with wavelength for $(GeS_2)_{100-x}Ga_x$ thin films deposited at R.T

Table1: Basic optical constants at $\lambda=650$ nm and E_g and E_e for $(\text{GeS}_2)_{100-x}(\text{Ga})_x$ thin films.

Composition	T%	n	k	ϵ_i	ϵ_r	$E_g(\text{eV})$	$E_e(\text{eV})$
GeS_2	95.1363	1.4116	0.0238	1.9923	0.0641	2.30	0.7651
$(\text{GeS}_2)_{92}(\text{Ga})_6$	92.9330	1.5205	0.0355	2.3107	0.1082	2.20	0.6720
$(\text{GeS}_2)_{88}(\text{Ga})_{12}$	92.0356	1.6012	0.0453	2.5620	0.1451	1.90	0.9458
$(\text{GeS}_2)_{82}(\text{Ga})_{18}$	95.3615	1.3545	0.0181	1.8343	0.0491	1.94	0.8491

Conclusions

Optical constants of the thin films of $(\text{GeS}_2)_{100-x}\text{Ga}_x$ ($x = 0, 6, 12, 18$) has been calculated using the transmission spectrum in the range 300-1100 nm. The optical band gap decreases with the increase of gallium concentration up to 12% and then increases. This behavior is explained on the basis of average bond energy of the system.

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