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Composition-tuned band gap energy and refractive index in GaS_xSe_{1-x} layered mixed crystals

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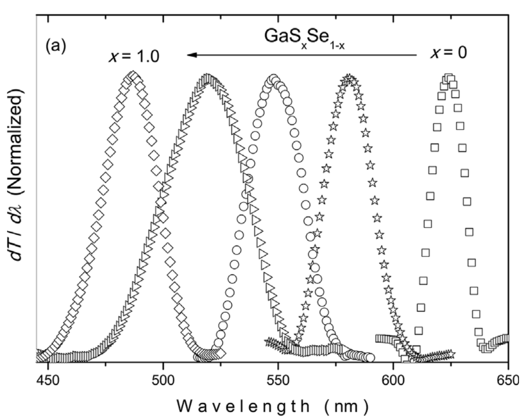
HIGHLIGHTS

- Transmission and reflection experiments were performed on GaS_xSe_{1-x} mixed crystals.
- Derivative spectra of transmittance and reflectance were used for analyses.
- Compositional dependence of band gap energy and refractive index were reported.

GRAPHICAL ABSTRACT



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ABSTRACT

Transmission and reflection measurements on GaS_xSe_{1-x} mixed crystals ($0 \le x \le 1$) were carried out in the 400–1000 nm spectral range. Band gap energies of the studied crystals were obtained using the derivative spectra of transmittance and reflectance. The compositional dependence of band gap energy revealed that as sulfur (selenium) composition is increased (decreased) in the mixed crystals, band gap energy increases quadratically from 1.99 eV (GaSe) to 2.55 eV (GaS). Spectral dependencies of refractive indices of the mixed crystals were plotted using the reflectance spectra. It was observed that refractive index decreases nearly in a linear behavior with increasing band gap energy for GaS_xSe_{1-x} mixed crystals. Moreover, the composition ratio of the mixed crystals was obtained from the energy dispersive spectroscopy measurements. The atomic compositions of the studied crystals are well-matched with composition x increasing from 0 to 1 by intervals of 0.25.

1. Introduction

The semiconducting materials, GaSe and GaS, have taken the attention of researchers due to their attractive properties in

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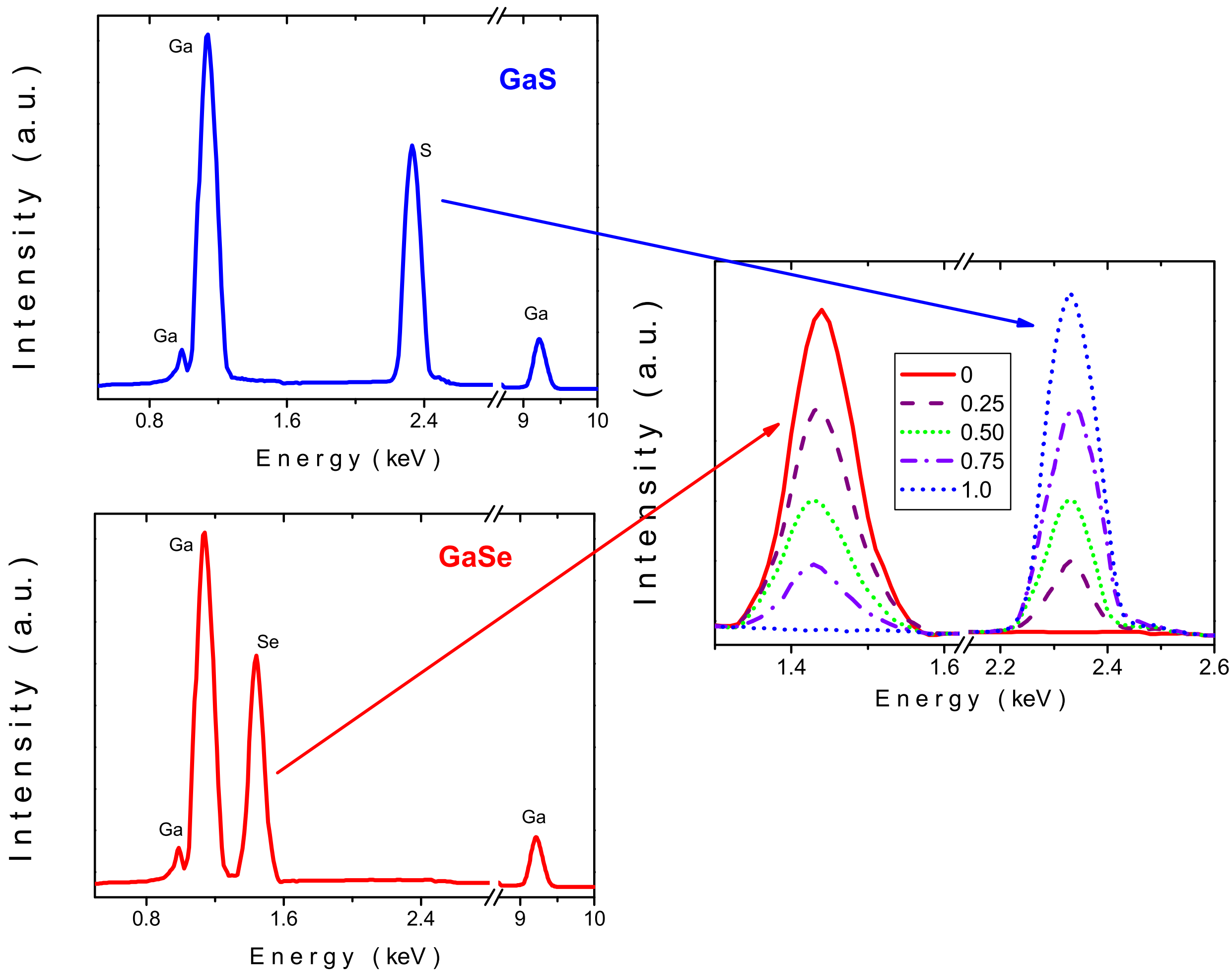

Fig. 1. Energy dispersive spectroscopic analysis of GaS_xSe_{1-x} mixed crystals.

technological applications such as field-effect transistors, photovoltaic, optoelectronic, thermoelectric, energy conversion and storage, topological insulators, nonlinear optical devices and photodetectors [1–5]. Moreover, investigations on GaSe/GaS revealed the potential usage of the structure as ultrathin layer transistors [6]. Taking into consideration the technological applications of GaSe and GaS, GaS_xSe_{1-x} mixed crystals have potential to be used in the fabrication of long-pass filter, light emitting devices and optical detecting systems [7,8]. In Refs. [9,10], it was established that GaSe and GaS single crystals have indirect band gap energies of 1.988 and 2.55 eV, respectively. GaSe and GaS crystals form GaS_xSe_{1-x} ($0 \leq x \leq 1$) mixed crystals with x ranging from 0 to 1. The optical properties of GaS_xSe_{1-x} mixed crystals were investigated in the regions of ($0 \leq x \leq 0.5$) by transmission and piezoreflectance measurements [10]. Room temperature Raman and photoluminescence spectra of the mixed crystals were reported for twelve different compositions in the range of $0 \leq x \leq 1$ [11]. The compositional dependence of lattice parameters and higher energy interband transitions were revealed for GaS_xSe_{1-x} mixed crystals in the compositional range of $0 \leq x \leq 0.5$ [12]. It was ascertained that band gap energy of the studied crystals increased from 1.99 eV ($x = 0$) to 2.37 eV ($x = 0.5$). In Ref. [13], band gap energies of the GaS_xSe_{1-x} mixed crystals were reported. The analyses of the transmission measurements resulted in energies of 1.976 eV ($x = 0$), 2.015 eV ($x = 0.05$), 2.026 eV ($x = 0.1$) and 2.307 eV ($x = 0.4$). Previously, in Ref. [14], ellipsometry measurements were carried out on GaS_xSe_{1-x} mixed crystals in the composition range of $0 \leq x \leq 1$. As a result, variation of interband transition energies with composition was established. Interband transition energies of GaS_xSe_{1-x} mixed crystals were also presented from the analyses of reflectivity and wavelength-modulated reflectivity measurements in the energy range of 3–6 eV [15]. The compositional dependence of transition structures were also given in this study.

The aim of the present work is to expand the optical studies on the GaS_xSe_{1-x} mixed crystals by performing for the first time transmission and reflection measurements in the range of $0 \leq x \leq 1$ at room temperature. The transmittance and reflectance spectra were used to obtain the band gap energy and refractive indices of the studied crystals. The effect of sulfur/selenium composition in the mixed crystals on the band gap energy and refractive index was investigated. The composition ratio (Ga:Se:S) in the mixed crystals were obtained from energy dispersive spectroscopy.

2. Experimental details

GaS_xSe_{1-x}polycrystals were synthesized using high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals were grown by the Bridgman method [16] in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 25 cm in length) with a tip at the bottom in our crystal growth laboratory. The ampoule was moved in a vertical furnace through a thermal

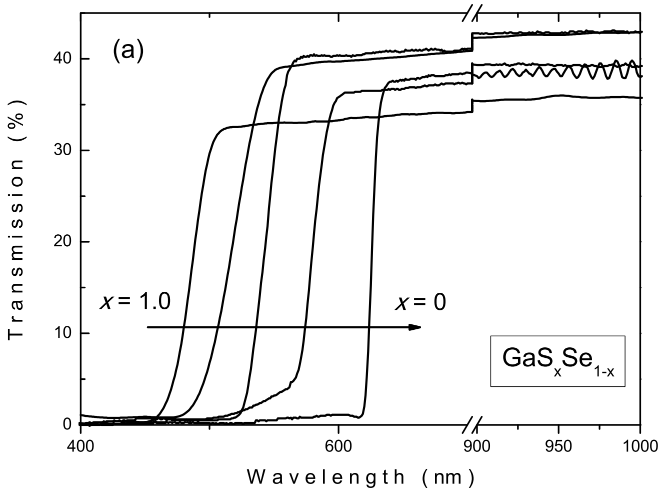

Fig. 2. The spectral dependence of (a) transmission and (b) reflection for GaS_xSe_{1-x} mixed crystals.

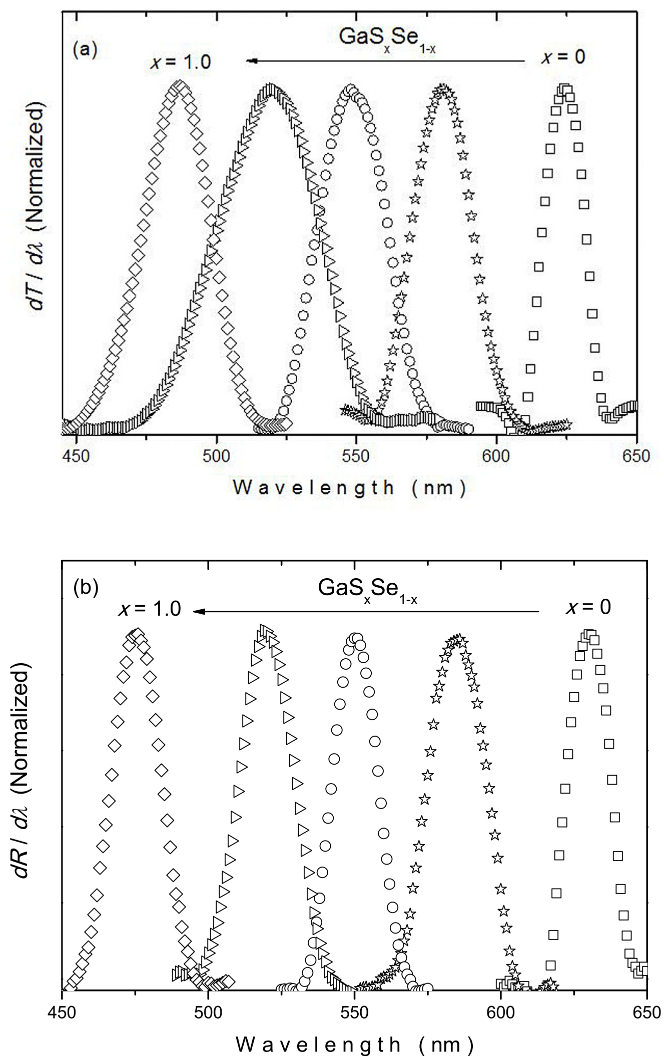

Fig. 3. The dependence of (a) $dT/d\lambda$ and (b) $dR/d\lambda$ on photon energy for GaS_xSe_{1-x} mixed crystals.

gradient of 30 °C/cm, between the temperatures 1000 and 650 °C at a rate of 0.5 mm/h. The resulting ingots (from yellow-green to red in color) had no cracks and voids on the surface. The samples for optical measurements were taken from the middle part of the ingot. The freshly cleaved platelets (along the layer plane (001)) were mirror-like. That is why no further polishing and cleaning treatments were required. The determination of the chemical composition of GaS_xSe_{1-x} mixed crystals was done using the energy dispersive spectral analysis (EDSA). The experiments were performed using JSM-6400 scanning electron microscope. NORAN System6 X-ray Microanalysis System and Semafore Digitizer were basic equipments to analyze the chemical composition of the studied crystals.

Transmission and reflection measurements were carried out in the 400–1000 nm spectral range using Shimadzu UV 1201 model spectrophotometer (Japan) with resolution of 5 nm, which consisted of a 20 W halogen lamp, a holographic grating and a silicon photodiode. Transmission measurements were performed under normal incidence of light with a polarization direction along the (001) plane. This plane is perpendicular to the c-axis of the crystal. For the reflection experiments, a specular reflectance measurement attachment for 5° incidence angle (P/N 206-14046, Japan) was used.

3. Results and discussion

Fig. 1 shows the EDS spectra of the studied samples to get the chemical composition of the crystals. The EDS analyses are based on the relative counts of the detected X-rays which are emitted from the radiated sample and characteristics for every element having unique energy levels [17]. The emission energies for Ga, S and Se elements are (1.098, 1.125, 1.144, 1.171 and 9.241 keV), (0.163, 0.164,2.307, 2.464 and 2.470 keV) and (1.379, 1.419, 1.434 and 1.475 keV), respectively [18]. As can be seen from the figure, intensity of the peak at 1.475 keV related with Se decreases and intensity of the peak at 2.307 keV related with S increases as the sulfur (selenium) composition increases (decreases) in the GaS_xSe_{1-x} mixed crystals. EDS analyses showed that atomic composition of the studied crystals are well-matched with composition x increasing from 0 to 1 by intervals of 0.25.

Fig. 2 shows the spectral dependencies of transmittance (T) and reflectance (R) of GaS_xSe_{1-x} mixed crystals. Reflectance spectra were obtained using samples with natural cleavage planes and thickness (d) such that $\alpha d \gg 1$ where α symbolizes the absorption coefficient. Thicknesses of the used samples for experiments were

Table 1
Band gap energies and refractive indices of GaS_xSe_{1-x} mixed crystals.

Composition	E_g (eV)		Refractive index (800–1000 nm)	
x	$dT/d\lambda$	$dR/d\lambda$	Present work	Ref. [23]
0	1.99	1.97	2.86–2.88	2.81–2.86
0.25	2.13	2.12	2.76–2.82	2.77–2.81
0.5	2.24	2.25	2.75–2.77	2.72–2.76
0.75	2.39	2.39	2.65–2.70	2.68–2.71
1.0	2.55	2.61	2.57–2.61	2.63–2.66

in the range of 80–120 μm. Transmittance and reflectance spectra can be used to get the absorption edge of the crystal under the light of different analyses methods. One of these methods, derivative spectrophotometry (DS), has been a powerful technique used in literature for three decades. DS is an attractive method used to obtain the qualitative and quantitative information of distinct spectra of overlapped peak signals in the experimental curve under the light of values revealed from the maxima and minima positions of the derivative curve [19]. In the present paper, we have used the derivative spectra of transmittance and reflectance spectra to obtain the band gap energies. Fig. 3 shows the first derivatives of each spectrum. Photon energy dependence of $dT/d\lambda$ and $dR/d\lambda$ presents peaks at energies corresponding to band gap energy. Table 1 gives the obtained energy values of GaS_xSe_{1-x} crystals from each spectrum. They indicate that band gap energy shows an increasing behavior with increase (decrease) of sulfur (selenium) composition. This increasing behavior of band gap energies is in agreement with reported observation of that E_g increases with increasing concentration of the smaller cation or anion [20]. At this point, it will be worthwhile to compare obtained energies with previously reported values. The indirect band gap energies of end crystals, GaSe and GaS, were reported as 1.988 and 2.55 eV, respectively [9,10]. Reported energy values show a good consistency with values obtained from derivatives of transmittance and reflectance spectra. Moreover, taking into account the type of band gap energies reported in the referenced papers, E_g values obtained from our analyses can be strongly associated with indirect transition structures. Wu et al. communicated the direct band gap energies of GaS_xSe_{1-x} mixed crystals for $0 \leq x \leq 0.5$ increasing from 1.986 (GaSe) to 2.37 eV ($GaS_{0.5}Se_{0.5}$) [10]. The band gap energy of GaSe in this paper is nearly same with our obtained value. Since the difference between the direct and indirect band gap energies of GaSe is given as ~0.053 eV [21], it is not reliable to associate the type of transition structures obtained from different studies with each other. The obtained and estimated direct band gap energies of 2.37 and 2.16 eV for $GaS_{0.5}Se_{0.5}$ and $GaS_{0.25}Se_{0.75}$ in Ref. [10] are larger than the values of 2.24 and 2.13 eV, respectively. This discrepancy thought due to the difference between direct and indirect band gap energies also strongly confirms the type of transition structures in our analyses as indirect transition.

The refractive index (n) spectra were plotted using the equations [22]

$$\alpha = \frac{1}{d}\ln\left\{\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2\right]^{1/2}\right\} \tag{1}$$

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R^2)} - \left(\frac{\alpha\lambda}{4\pi}\right)^2\right]^{1/2} \tag{2}$$

Here, d is the sample thickness. Eqs. (1) and (2) relate n to reflectance (R), absorption coefficient (α) and wavelength (λ) (see Fig. 4). The shift of the absorption to higher energy values as sulfur

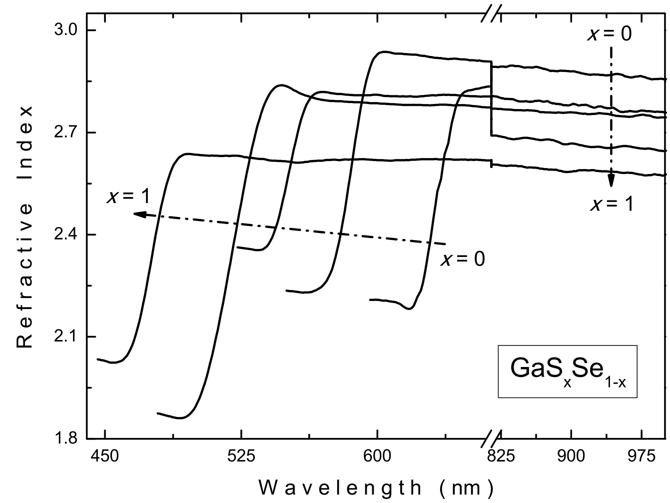

Fig. 4. The dependences of the refractive index on the wavelength for different compositions of GaS_xSe_{1-x} mixed crystals.

concentration is increased (selenium concentration is decreased) can also be seen from the figure. In the $h\nu < E_g$ region, refractive index shows normal dispersion behavior. The abnormal behavior in the refractive index only occurs in the vicinity of absorption bands of the crystals. Moreover, in the below band gap energy region, it is also seen that refractive index decreases with increase of band gap energy. This observation is in good agreement with the results of previously reported studies. According to Ref. [23], the refractive indices of GaSe and GaS in the 800–1000 nm spectral region, which is the common range of present and referenced works, vary in the 2.81–2.86 and 2.63–2.66 nm range, respectively. Refractive index values of GaS_xSe_{1-x} mixed crystals were given in the same work as

$$n^2(GaS_xSe_{1-x}) = xn^2(GaS) + (1-x)n^2(GaSe) \tag{3}$$

The intervals of refractive indices of GaS_xSe_{1-x} mixed crystals in the common spectral range of 800–1000 nm calculated from the above given equation and from Fig. 4 are shown in Table 1. The estimated values in Ref. [23] and determined refractive indices in the present work are observed in consistency with each other.

Fig. 5 shows the compositional dependence of band gap energy

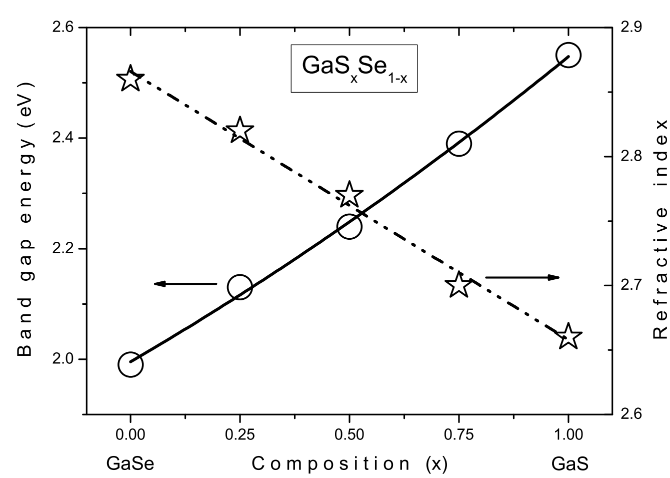

Fig. 5. Compositional dependences of the refractive index and the energy band gap in GaS_xSe_{1-x} mixed crystals. The solid and dashed-dotted lines show the fitted line according to Eq. (4) and linear fit, respectively.

and refractive index for GaS_xSe_{1-x} mixed crystals. The compositional dependence of band gap energy for semiconductor alloys are given by Ref. [24]

$$E(x) = E(0) + bx + cx^2, \tag{4}$$

where $E(0)$ and b are parameters determined from the band gap energies of pure semiconducting compounds, and c is the bowing parameter. The solid line shown in Fig. 5 is the fitted curve according to Eq. (4). The fitting parameters were obtained as $E(0) = 1.994$ eV, $b = 0.51$ eV, and $c = 0.046$ eV. The compositional dependence of refractive index, defined by Eq. (3), points out the nearly linear decrease of refractive index with composition ranging from 0 to 1. The dashed-dotted line related with refractive indices (stars) in Fig. 5 shows the linear fit considering the linear behavior ($n = lx + m$) of n–x dependency for GaS_xSe_{1-x} mixed crystals. The fitting parameters were found as $l = -0.208$ and $m = 2.866$.

4. Conclusions

Spectral dependencies of band gap energy and refractive index of GaS_xSe_{1-x} mixed crystals grown by Bridgman method were investigated using the room temperature transmission and reflection experiments for compositions of $x = 0$, 0.25, 0.5, 0.75 and 1.0. Derivative analyses of transmittance and reflectance spectra of the mixed crystals showed that band gap energy increases quadratically from 1.99 eV to 2.55 eV as selenium is replaced by sulfur. Compositional dependence of band gap energy of GaS_xSe_{1-x} mixed crystals were analyzed using the $E(x) = E(0) + bx + cx^2$ expressed for semiconductor alloys. Refractive index spectra of the studied crystals were plotted utilizing reflectance spectra. It was observed that refractive index gradually decreases with increasing wavelength in the $h\nu < E_g$ region and increases almost linearly from ~2.57 to ~2.86 as the composition x decreases from 1 to 0.

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