Composition-tuned band gap energy and refractive index in GaS\textsubscript{x}Se\textsubscript{1-x} layered mixed crystals

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Abstract

Transmission and reflection measurements on GaS\textsubscript{x}Se\textsubscript{1-x} mixed crystals (0 \leq x \leq 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\textsubscript{x}Se\textsubscript{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 \textit{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
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$_x$Se$_{1-x}$ 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. GaS$_x$Se$_{1-x}$ mixed crystals form GaS$_x$Se$_{1-x}$ (0 ≤ x ≤ 1) mixed crystals with x ranging from 0 to 1. The optical properties of GaS$_x$Se$_{1-x}$ mixed crystals were investigated in the regions of (0 ≤ x ≤ 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 ≤ x ≤ 1 [11]. The compositional dependence of lattice parameters and higher energy interband transitions were revealed for GaS$_x$Se$_{1-x}$ mixed crystals in the compositional range of 0 ≤ x ≤ 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$_x$Se$_{1-x}$ 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$_x$Se$_{1-x}$ mixed crystals in the composition range of 0 ≤ x ≤ 1. As a result, variation of interband transition energies with composition was established. Interband transition energies of GaS$_x$Se$_{1-x}$ 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$_x$Se$_{1-x}$ mixed crystals by performing for the first time transmission and reflection measurements in the range of 0 ≤ x ≤ 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$_x$Se$_{1-x}$ 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...
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 ad ≫ 1 where a symbolizes the absorption coefficient. Thicknesses of the used samples for experiments were...
The band gap energy of GaSe is given as ~0.053 eV [21], it is not reliable to associate the type of transition structures in the present work as indirect transition. The obtained and estimated direct band gap energies of 2.37 and 2.13 eV for GaS0.5Se0.5 and GaS0.25Se0.75 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]

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

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

Here, \( d \) is the sample thickness. Eqs. (1) and (2) relate \( n \) to reflectance \( R \), absorption coefficient \( \alpha \) and wavelength \( \lambda \) (see Fig. 4). The shift of the absorption to higher energy values as sulfur 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 GaSxSe1−x mixed crystals were given in the same work as

\[
n^2(GaS_xSe_{1-x}) = x n^2(GaS) + (1 - x) n^2(GaSe)
\]

The intervals of refractive indices of GaSxSe1−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 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 GaSxSe1−x mixed crystals were given in the same work as

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Fig. 5 shows the compositional dependence of band gap energy

### Table 1

<table>
<thead>
<tr>
<th>Composition</th>
<th>( E_g ) (eV)</th>
<th>Refractive index (800–1000 nm)</th>
</tr>
</thead>
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<tr>
<td>x</td>
<td>( dT/d\alpha )</td>
<td>( dR/d\alpha )</td>
</tr>
<tr>
<td>0</td>
<td>1.99</td>
<td>1.97</td>
</tr>
<tr>
<td>0.25</td>
<td>2.13</td>
<td>2.12</td>
</tr>
<tr>
<td>0.5</td>
<td>2.24</td>
<td>2.25</td>
</tr>
<tr>
<td>0.75</td>
<td>2.39</td>
<td>2.39</td>
</tr>
<tr>
<td>1.0</td>
<td>2.55</td>
<td>2.61</td>
</tr>
</tbody>
</table>

Fig. 4. The dependences of the refractive index on the wavelength for different compositions of GaSxSe1−x mixed crystals.

Fig. 5. Compositional dependences of the refractive index and the energy band gap in GaSxSe1−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\textsubscript{1-x}Se\textsubscript{x} mixed crystals. The compositional dependence of band gap energy for semiconductor alloys are given by Ref. [24]

\[ E(x) = E(0) + bx + cx^2, \]

(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\textsubscript{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\textsubscript{1-x}Se\textsubscript{x} mixed crystals grown by Bridgman method were investigated using the room temperature transmission and reflection experiments for compositions of \(x = 0, 0.25, 0.75\) 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\textsubscript{1-x}Se\textsubscript{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.

References


