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Ellipsometric study of optical properties of GaS_xSe_{1-x} layered mixed crystals

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ABSTRACT

Spectroscopic ellipsometry measurements were performed on GaS_xSe_{1-x} mixed crystals ($0 \leqslant x \leqslant 1$) in the 1.2–6.2 eV range. Spectral dependence of optical parameters; real and imaginary components of pseudodielectric function, pseudorefractive index and pseudoextinction coefficient were reported in the present work. Critical point (CP) analyses on second-energy derivative spectra of the pseudodielectric function were accomplished to find the interband transition energies. The revealed energy values were associated with each other taking into account the fact that band gap energy of mixed crystals rises with increase in sulfur content. The variation of CP energies with composition (x) was also plotted. Peaks in the spectra of studied optical parameters and CP energy values were observed to be shifted to higher energy values as sulfur concentration is increased in the mixed crystals.

1. Introduction

Gallium selenide (GaSe) and gallium sulfide (GaS) compounds belong to the class of highly anisotropic layered semiconductors. The layers have a thickness of four atoms and contain covalent bonds, whereas between them only weak forces of mainly van der Waals type are present. The layers are stacked along the crystallographic ***c*** axis; cleaving parallel to them is easily possible. Optical and electrical properties of these compounds have been investigated to have a foresight about the potential usefulness in relevant technological areas. The band gap energy of GaSe has been reported as ~2.0 eV [1,2]. The studies on the far-infrared conversion applications of GaSe showed that crystals transmitted light between 0.65 and 18 μm wavelength range which is wider and more appropriate than the range of other nonlinear optical materials, such as $AgGaSe_2$, $ZnGeP_2$ and Tl_3AsSe_3 crystals [3]. GaS is a wide band gap semiconducting material having indirect and direct band gap energies of ~2.55 and 2.89 eV, respectively, at room temperature [4].

GaSe and GaS form a continuous series of mixed crystals GaS_xSe_{1-x} with x ranging from 0 to 1. By varying the composition its energy gap covers a wide range of the visible spectrum. Taking into consideration the technological applications of GaSe and GaS, GaS_xSe_{1-x} mixed crystals can be important candidate to be used in the fabrication of long-pass filter, light emitting devices and optical detecting systems [5–11]. Although there are lots of papers concerning the characterization of GaSe and GaS compounds, the studies on GaS_xSe_{1-x} mixed crystals are limited. Optical properties of GaS_xSe_{1-x} mixed crystals ($0 \leqslant x \leqslant 0.5$) grown by Bridgman method were studied by transmission and piezoreflectance measurements [12]. The analysis of the obtained spectra showed that band gap energy increases from 1.986 eV ($x = 0$) to 2.37 eV ($x = 0.5$). Photoluminescence measurements showed full-range luminescence of 625–480 nm from mixed crystals for $0 \leqslant x \leqslant 1$ at room temperature [13]. The Raman spectra of the mixed crystals for a wide range of composition ($0 \leqslant x \leqslant 1$) were obtained at 300 and 10 K [14]. Previously, we have performed the spectroscopic ellipsometry measurements on GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) in the energy range of 1.2–6.2 eV at room temperature [15,16]. Analysis of the second derivative of real and imaginary parts of the pseudodielectric constant revealed four ($x = 0.5$) and five ($x = 1$) critical point energies which have been assigned to interband transitions according to theoretical study of band structures available in the literature.

In the present work, we investigate the spectral dependence of optical parameters; pseudodielectric function, pseudorefractive index and pseudoextinction coefficient of GaS_xSe_{1-x} mixed crystals ($0 \leqslant x \leqslant 1$) by means of ellipsometry measurements carried out in the 1.2–6.2 spectral range. Moreover, the interband transition energies of the studied crystals were established from the analysis

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of the second-energy derivative of components of pseudodielectric function.

2. Experimental details

GaS_xSe_{1-x} polycrystals were synthesized using high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Each single crystals in the studied composition (x) range were grown by the Bridgman method 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) showed good optical quality and were easily cleaved along the planes that are perpendicular to the c-axis of the crystal.

The ellipsometric measurements on the GaS_xSe_{1-x} single crystals were carried out at room temperature in the 1.2–6.2 eV spectral range using SOPRA GES-5E rotating polarizer ellipsometer. The incidence angle of the light beam was 70°. For measurements the samples with thickness about 1 mm were used. Since the freshly cleaved platelets (along the layer plane (0 0 1)) were mirror-like, no further polishing and cleaning treatments were required.

3. Results and discussion

Ellipsometry measurements have been accomplished to investigate the optical properties of GaS_xSe_{1-x} single crystals. The change of an incident polarized light after reflection from the surface of a sample is measured and analyzed in the ellipsometry experiments. Ψ and Δ representing the amplitude ratio and phase shift of the parallel and perpendicular components of the reflected light, respectively, are taken as an experimental data. Pseudodielectric function ($\langle\varepsilon\rangle$) is obtained from air/sample model defined as [17]

$$\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle = \sin^2(\varphi)\left[1 + \left(\frac{1-\rho}{1+\rho}\right)^2 \tan^2(\varphi)\right], \quad (1)$$

where φ is the angle of incidence and $\rho = \tan(\psi)\, e^{i\Delta}$ is the complex reflectance ratio of the polarized light. Fig. 1 shows the spectra of real and imaginary parts of the pseudodielectric functions of each studied crystal in the 1.2–6.2 eV range. There exist two peaks in each spectrum. It is known that band gap energy values of GaS_xSe_{1-x} mixed crystals shift to higher values (1.99 eV for GaSe and 2.59 eV for GaS) as sulfur composition increases in the mixed crystals. Similar shift was also observed for peaks arising in the spectra of real and imaginary parts of the pseudodielectric function. The spectra of real components of $x = 0.3$, 0.5 and 0.8 samples exhibit oscillations in the below band gap energy region. These oscillations are probably due to the thickness interference from back-reflected component. The corresponding thickness values of these oscillations were calculated around 8–10 μm which is much smaller than the thicknesses (around 1 mm) of the used samples. The similar oscillations were also observed in our previously reported ellipsometry studies on ternary and quaternary semiconducting crystals [18,19]. This large difference between measured actual and theoretically determined thickness values is thought a result of the case that a group of layers (with around 8–10 μm) partially lose its binding to the remaining bulk due to weak interlayer binding energy when we cleaved the top few layers. The spectra of imaginary components of pseudodielectric function of crystals for compositions x = 0.3, 0.5 and 1.0 show a sharp decrease around at 2.11, 2.31 and 2.45 eV, respectively. These values correspond approximately to the band gap energy of the crystals. The increasing behavior of the band gap energies with sulfur composition can be seen from the observed values.

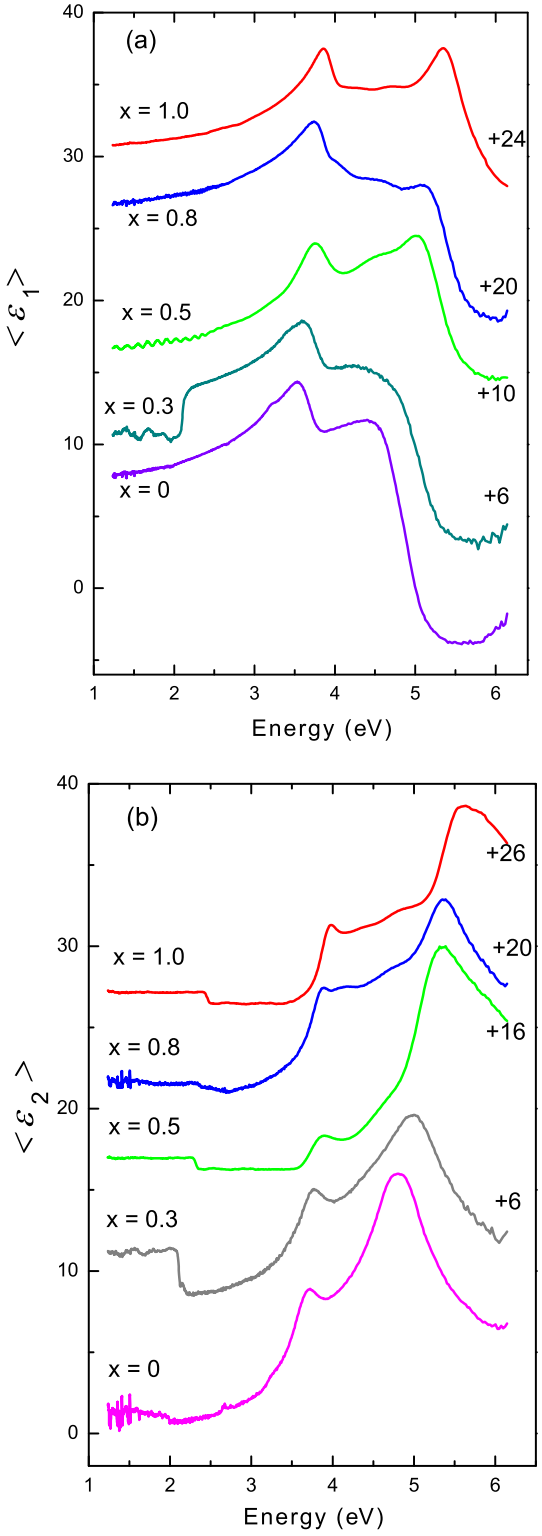

Fig. 1. Spectral dependencies of the real (a) and imaginary (b) parts of pseudodielectric function for GaS_xSe_{1-x} mixed crystals. The data for GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) are taken from Refs. [15,16].

Fig. 2 shows the spectral dependences of pseudorefractive index and pseudoextinction coefficient obtained from the relations [20,21]

$$\langle n\rangle = \left[\left(\langle\varepsilon_1\rangle + \left(\langle\varepsilon_1^2\rangle + \langle\varepsilon_2^2\rangle\right)^{1/2}\right)/2\right]^{1/2}, \quad (2)$$

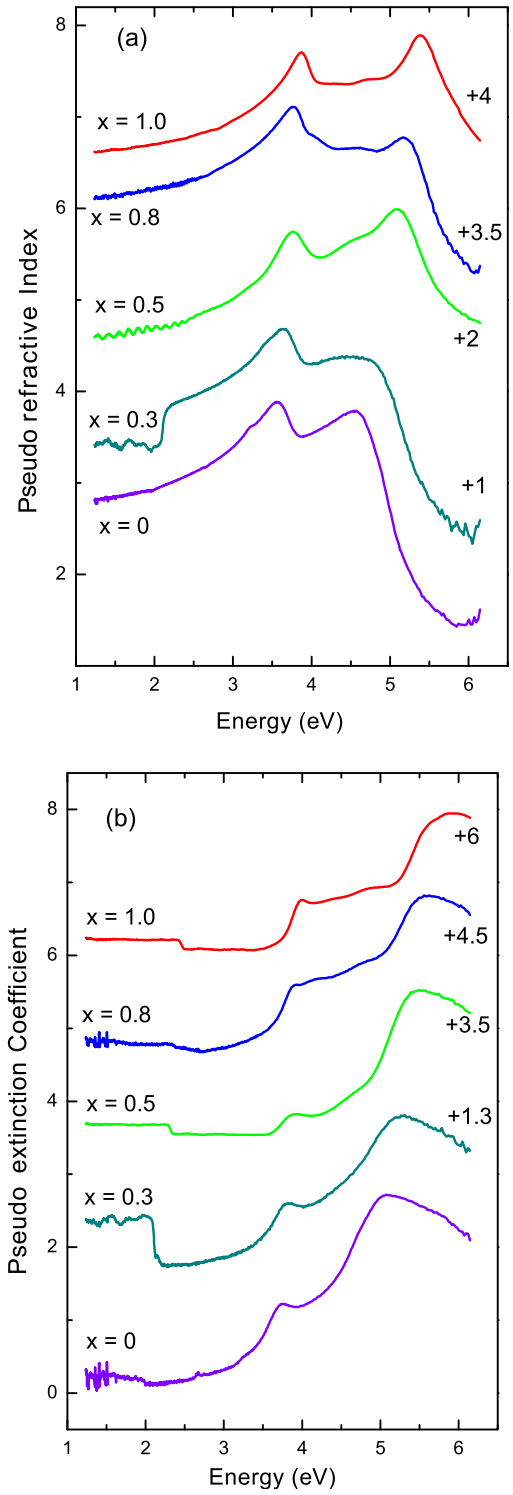

Fig. 2. Spectral dependencies of the pseudorefractive index (a) and pseudoextinction coefficient (b) for GaS_xSe_{1-x} mixed crystals. The data for GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) are taken from Refs. [15,16].

$$\langle k\rangle = \left[\left(-\langle\varepsilon_1\rangle + \left(\langle\varepsilon_1^2\rangle + \langle\varepsilon_2^2\rangle\right)^{1/2}\right)/2\right]^{1/2}. \quad (3)$$

As observed in the spectra of pseudodielectric function, spectra of ⟨n⟩ and ⟨k⟩ of studied crystals show some peaks which shift to higher energies as sulfur composition increases in the mixed crystals. The refractive indices of the crystals were found between 2.72 and 2.98. Moreover, the variation of the refractive index values for the studied crystals satisfies the fact that refractive index and band gap energy have inverse relation for semiconductors. The reflectivity R of GaS_xSe_{1-x} mixed crystals was determined using the following relation [20,21]

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \quad (4)$$

The spectra of R calculated from ellipsometric data are presented in Fig. 3.

The spectral dependence of the pseudodielectric function can also be used to find the interband transition energies (critical points). The second-energy derivative spectra of components of the pseudodielectric function are theoretically related to photon energy (E), amplitude (A), critical point energy (E_{cp}), broadening parameter (Γ) and phase angle (ϕ) by [17,21–23]

$$\frac{d^2\varepsilon}{dE^2} = m(m-1)A\exp(i\phi)(E - E_{cp} + i\Gamma)^{m-2} \quad (m \neq 0) \quad (5)$$

$$\frac{d^2\varepsilon}{dE^2} = A\exp(i\phi)(E - E_{cp} + i\Gamma)^{-2} \quad (m = 0), \quad (6)$$

where m is associated with the dimensions of wave vectors taking role in the optical transitions. The m values are equal to -1, $-1/2$, 0 and +1/2 for excitonic, one, two and three dimensional lineshapes, respectively. The second derivative spectra of real and imaginary components of the pseudodielectric functions of GaS_xSe_{1-x} mixed crystals are shown in Fig. 4. In each step (experimental data, first and second derivatives) of obtaining the second derivative spectra, low level binomial filtering was used to smooth the plots. The fitting of the spectra has been accomplished in the energy ranges in which smoothed data do not give any and/or considerable deviation from the experimental data. The case of excitonic optical transitions (corresponding to $m = -1$) resulted with the lowest mean-square deviations in the fitting studies. Arrows in Fig. 4 correspond to the critical point (CP) energy positions (see also Table 1) in the GaS_xSe_{1-x} mixed crystals. Since the band gap energy values for the GaS_xSe_{1-x} mixed crystals increase as amount of sulfur increases, the revealed CP energies were associated with each other taking

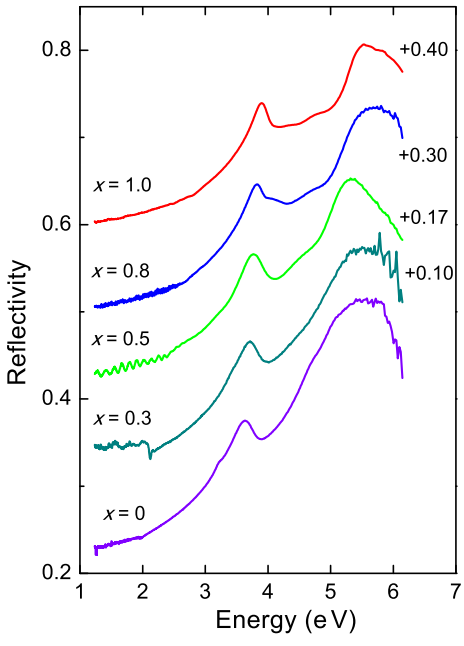

Fig. 3. The spectral dependence of reflectivity R of GaS_xSe_{1-x} mixed crystals. The data for GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) are taken from Refs. [15,16].

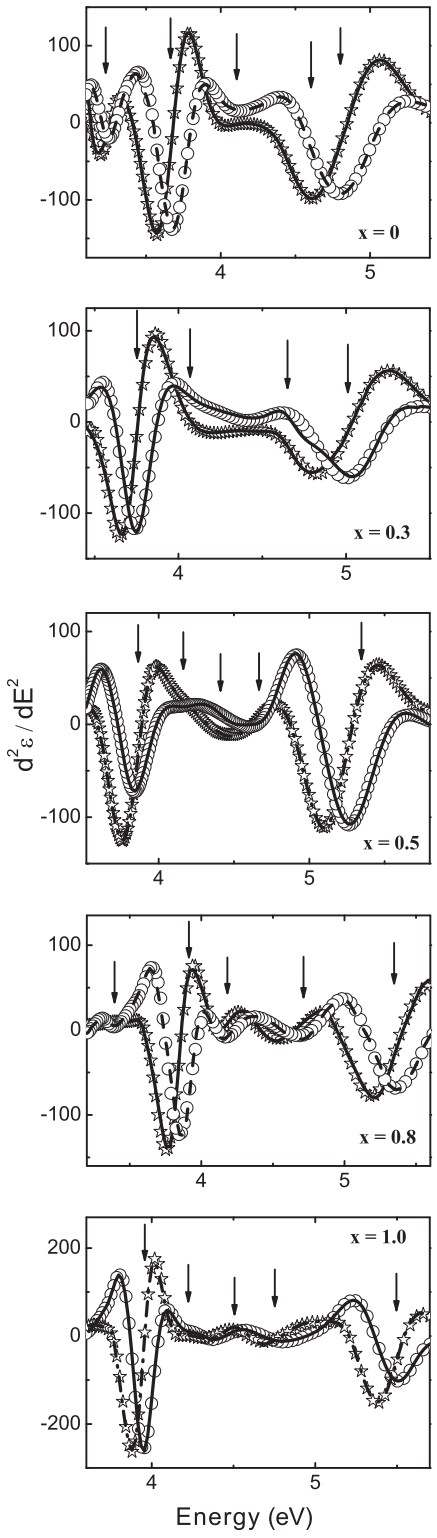

Fig. 4. Second-energy derivative spectra of the pseudodielectric function for GaS_xSe_{1-x} mixed crystals. Open circles and stars represent the second-energy derivative spectra of the real and imaginary parts of the pseudodielectric function, respectively. The solid and dot-dashed curves show the fit to the experimental data. For clarity only one-third of the circles and triangles are shown. The arrows represent the positions of the critical point energies. The data for GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) are taken from Refs. [15,16].

into account the similar increasing behavior. The average variations of the associated CP energies with composition are shown by solid lines in Fig. 5.

Table 1
Critical point energies (eV) for GaS_xSe_{1-x} mixed crystals.

Crystal (x)	E_A	E_B	E_C	E_D	E_E
0	3.23	3.67	4.10	4.60	4.80
0.3	–	3.75	4.13	4.64	5.01
0.5[a]	–	3.87	4.16	4.67	5.34
0.8	3.39	3.91	4.18	4.71	5.36
1[b]	3.60	3.95	4.22	4.75	5.50

[a] Ref. [15].
[b] Ref. [16].

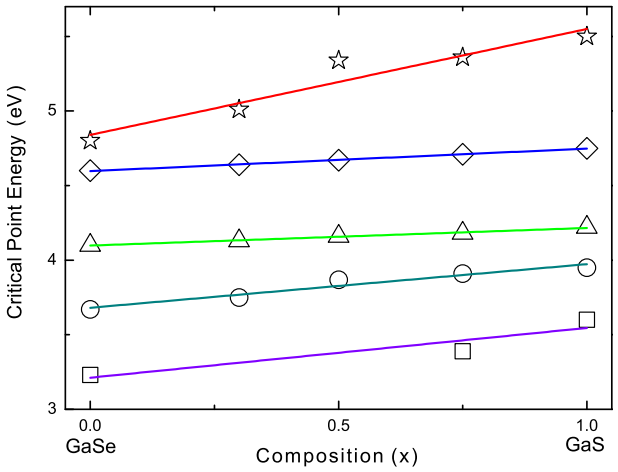

Fig. 5. Dependence of critical point energies on composition of GaS_xSe_{1-x} mixed crystals. Solid lines represent the average variations of the CP energies with composition. The data for GaS_xSe_{1-x} mixed crystals ($x = 0.5$ and 1) are taken from Refs. [15,16].

4. Conclusions

In this study, spectral dependence of optical parameters of GaS_xSe_{1-x} mixed crystals ($0 \leqslant x \leqslant 1$) was investigated by ellipsometry measurements. Spectra of pseudodielectric function, pseudorefractive index and pseudoextinction coefficient showed similarities in the way of existence of peaks. A shift of the exhibited peaks to higher energies was observed as sulfur percentage is increased in the mixed crystals. Critical point energies were also revealed from the analysis of second-energy derivative of components of pseudodielectric function. Compositional dependence of CP energies was plotted under the light of increasing behavior of energies with sulfur concentration.

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