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Optical characterization of Ga_2SeS layered crystals by transmission, reflection and ellipsometry

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Optical properties of Ga_2SeS crystals grown by Bridgman method were investigated by transmission, reflection and ellipsometry measurements. Analysis of the transmission and reflection measurements performed in the wavelength range of 400–1100 nm at room temperature indicated the presence of indirect and direct transitions with 2.28 eV and 2.38 eV band gap energies. Ellipsometry measurements were carried out in the 1.2–6.0 eV spectral region to get information about optical constants, real and imaginary parts of the pseudodielectric function. Moreover, the critical point (CP) analysis of the second derivative spectra of the pseudodielectric constant in the above band gap region was accomplished. The analysis revealed the presence of five CPs with energies of 3.87, 4.16, 4.41, 4.67 and 5.34 eV.

Keywords: Semiconductors; optical properties; ellipsometry; absorption.

1. Introduction

GaSe and GaS semiconducting compounds have been attractive materials used in optoelectronic devices in red and blue regions.[1–3] The large optical nonlinearity properties of these crystals make them very promising materials in the areas of optical switching devices[4] and photodetectors.[5,6] The structural and optical characterization of GaSe revealed that the crystal has hexagonal structure with lattice parameters of $a = 0.375$ and $b = 1.595$ nm[7] and band gap energy of ~ 2.0 eV.[8,9] GaS semiconducting material has indirect and direct band gap energies of ~ 2.59 eV and 3.04 eV, respectively, at room temperature.[10] The researches on both crystals

showed that GaSe can be especially used in nonlinear optical applications[11] whereas GaS is a promising material for near-blue light-emitting devices.[12]

Ga_2SeS is one of the GaS_xSe_{1-x} mixed crystals formed from GaSe and GaS. Taking into consideration the role of constituent compounds GaSe and GaS in the technological applications, Ga_2SeS mixed crystal can be thought as a promising candidate to be used in the fabrication of long-pass filter, light emitting devices and optical detecting systems. Since Ga_2SeS is the most distinctive one showing properties of GaSe and GaS among GaS_xSe_{1-x} crystals, the characterization of this crystal takes additional importance for researchers studying on relevant areas. The Ga_2SeS crystals, like binary compounds GaSe and GaS, have a layered structure.[13] Each layer has four atomic planes with the sequence Se(S)–Ga–Ga–Se(S). The weak interlayer bonding is van der Waals like and strong intralayer bonding is covalent. The crystal structure of GaSe shows four modifications (ε, β, γ and δ) while GaS crystallizes only in the β-modification. Therefore, the crystal structure of GaS_xSe_{1-x} mixed crystals mainly depends on the composition x. Ga_2SeS crystal structure is a mixture of the ε and β-polytypes.[14]

Previously, our research group reported studies on the characterization of GaS_xSe_{1-x} mixed crystals. Ga_2SeS studies among these reports have been focused on Raman,[15] photoluminescence,[16] optical absorption[17] and thermally stimulated current measurements.[18] The aim of the present paper is to expand studies on Ga_2SeS mixed crystal by investigating its optical properties by transmission, reflection and ellipsometry measurements. The band gap energy and transition type were found from the analysis of transmittance and reflectivity experiments. The extensive knowledge about the spectral dependence of pseudodielectric function, pseudorefractive index and pseudoextinction coefficient was acquired from ellipsometry measurements. Moreover, the energies of interband transitions in electronic band structure of Ga_2SeS crystals were found using the critical point (CP) analysis method.

2. Experimental Details

Ga_2SeS polycrystals were synthesized from high-purity elements (at least 99.999%) prepared in stoichiometric proportions. Single crystals of Ga_2SeS were grown by the Bridgman method in sealed 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°C and 650°C at a rate of 0.5 mm/h. The resulting ingots (orange in color) showed good optical quality and were easily cleaved along the planes that are perpendicular to the c-axis of the crystal. The chemical composition of the crystals was determined using the energy dispersive spectroscopy (EDS) experiments which were performed by JSM-6400 scanning electron microscope. The crystal structure properties were identified using X-ray diffraction (XRD) experiments. Measurements were performed using

"Rigaku miniflex" diffractometer with CuKα radiation (λ = 0.154049 nm). The scanning speed of the diffractometer was 0.02°/s. Experiments were accomplished in the diffraction angle (2θ) range of 10–90°.

Transmission and reflection experiments were performed at room temperature in the 400–1100 mm spectral range using Shimadzu UV 1201 model spectrophotometer which consisted of a 20 W halogen lamp, a holographic grating and a silicon photodiode. The resolution of the spectrophotometer was 5 nm. Transmission measurements were accomplished under normal incidence of light with a polarization direction along the (001) plane which is perpendicular to the c-axis of the crystal. The reflection experiments were carried out using a specular reflectance measurement attachment providing 5° incident angle.

The ellipsometry experiments on Ga_2SeS were performed at room temperature in the 1.2–6.0 eV spectral range with 0.01 eV increments using SOPRA GES-5E rotating-polarizer ellipsometer. The measurements were performed on the layer-plane (001) crystal surface (perpendicular to the optic axis c) with 70° angle of incidence of the light beam. The layered crystal structure of the compound makes it very difficult to accomplish experiments on other surfaces. The freshly cleaved surfaces of the used samples for measurements were mirror-like.

3. Results and Discussion

Figure 1 presents the EDS results used to determine the chemical composition of the crystal. EDS measurements showed that the atomic composition ratio of the studied sample Ga:Se:S was found to be 50.3:24.9:24.8, respectively.

XRD technique was used to obtain the structural parameters of the sample. Figure 2 shows the X-ray diffractogram of the Ga_2SeS crystal. The sharp diffraction peaks are an indication of the well crystallinity of the sample. Miller indices (h k l)

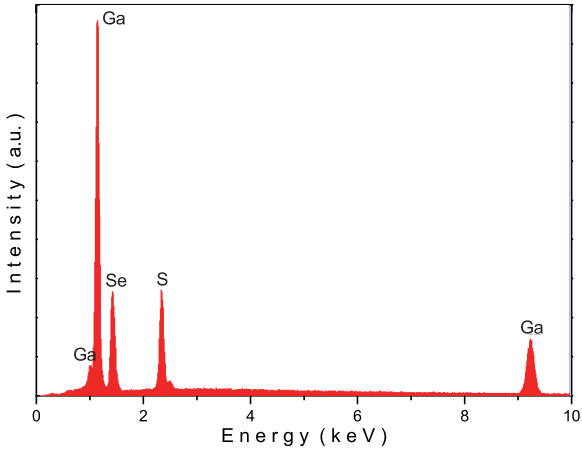

Fig. 1. Energy dispersive spectroscopic analysis of Ga_2SeS crystal.

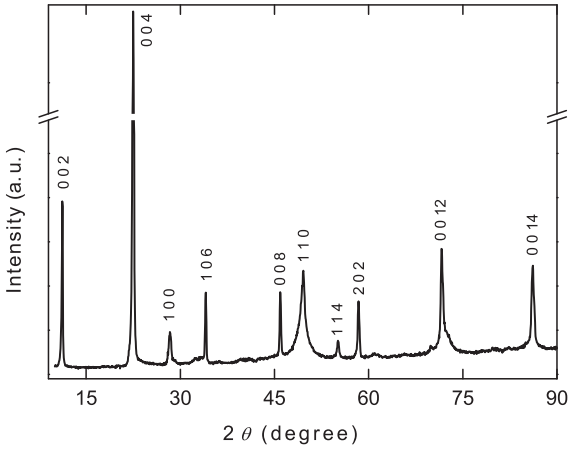

Fig. 2. X-ray powder diffraction pattern of Ga_2SeS crystal.

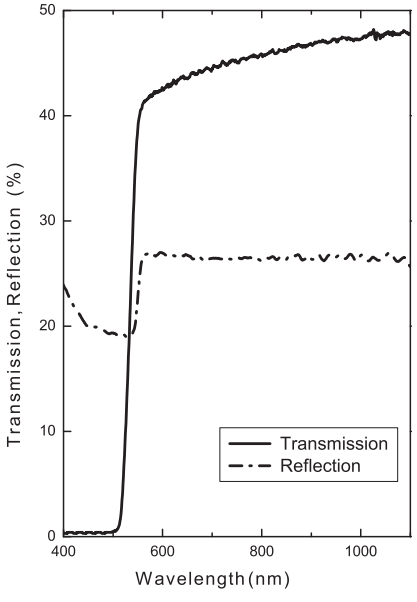

Fig. 3. The spectral dependence of transmission and reflection at room temperature for Ga_2SeS crystal.

are shown on the diffraction peaks. The lattice parameters of the hexagonal unit cell were found to be $a = 0.3671$ and $c = 1.5719$ nm.

Figure 3 shows the transmittance and reflectance spectra of Ga_2SeS crystals in the wavelength range of 400–1100 nm. The reflection measurements were accomplished using the samples with natural cleavage planes and the thickness (d) such that $\alpha d \gg 1$. Absorption coefficient (α) was calculated from the transmittance (T)

and reflectance (R) spectra using expression[19]

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

Photon energy dependency of the absorption coefficient is described as[20]

$$(\alpha h\nu) = A(h\nu - E_g)^p , \tag{2}$$

where E_g is band gap energy and A is a constant depending on the transition probability. The index p is equal to 2 and 1/2 for indirect and direct transitions, respectively. Equation (2) can be rewritten as[21]

$$\frac{d\left[\ln(\alpha h\nu)\right]}{d(h\nu)} = \frac{p}{h\nu - E_g} . \tag{3}$$

The plot of $d(\ln(\alpha h\nu))/d(h\nu)$ versus $(h\nu)$ is shown in Fig. 4. The figure exhibits two peaks positioned at 2.28 eV and 2.38 eV which corresponds to the band gap energies of the crystal. The p index was also obtained to find the type of transitions and support that these energies correspond to the band gap energies. For this purpose, $\ln(\alpha h\nu)$ versus $\ln(h\nu - E_g)$ graph was plotted and p values were found nearly as 2 and 1/2 from the slope of the obtained lines for 2.28 eV and 2.38 eV, respectively.

Ellipsometry measurements were also performed on the Ga_2SeS crystal to analyze the obtained experimental data to find the interband transition energies in the band structure. Ga_2SeS crystals having hexagonal layered structure are optically uniaxial. The spectra of the real and imaginary parts of the pseudodielectric

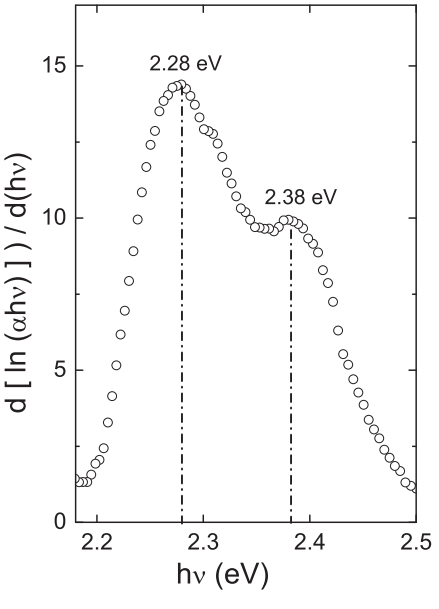

Fig. 4. The dependence of $d(\ln(\alpha h\nu))/d(h\nu)$ on $(h\nu)$ for Ga_2SeS crystal.

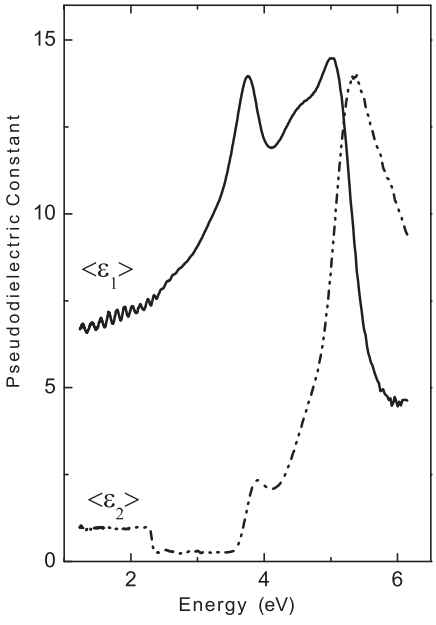

Fig. 5. Spectral dependence of the pseudodielectric function for Ga_2SeS crystals. Solid and dot-dashed curves represent the real and imaginary part spectra, respectively.

function of the Ga_2SeS crystal obtained from the ellipsometry measurements in the 1.2–6.0 eV range on the layer-plane (001) surface (perpendicular to the optic axis c), are shown in Fig. 5. According to the ellipsometric study on InSe layered crystal,[22] the spectra of dielectric constant obtained on an optically uniaxial crystal oriented with the optic axis perpendicular to the crystal surface are a close approximation to the ordinary component of the dielectric tensor of the crystal, since the c-axis contribution is reduced approximately by $1/\varepsilon$.[23,24] The spectra of imaginary component exhibit two peaks which is an indication of the strong absorption of photon energy at the corresponding critical points. This is also verified from the CP analysis. The obtained spectra of Ga_2SeS seem similar to those of GaS[25] and GaSe[26] as a shape and number of peaks but gets a position between these spectra in terms of energy. This is an expected result since the band gap energy value of Ga_2SeS is between those of GaSe and GaS. The spectra of the imaginary part shows sharp decrease nearly at 2.34 eV value which represents approximately the band gap energy of the Ga_2SeS crystal. The spectra of the real component of the pseudodielectric function presents oscillations below the fundamental absorption edge. The reason for these oscillations is attributed to the thickness interference from the back-reflected component. The thickness was calculated as 1.8 μm from the analysis of the oscillations period. This value is much smaller than the sample thickness of 320 μm. Similar oscillations were also observed in the ellipsometry analysis of GaSe layered crystal reported by Choi *et al.*[26] According to researchers, a group

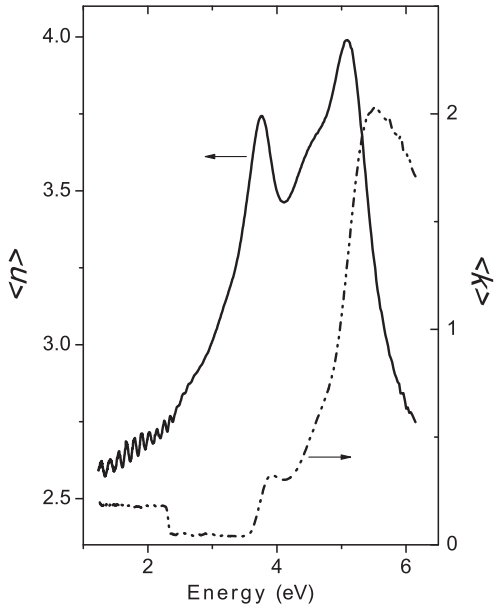

Fig. 6. Spectral dependence of the pseudorefractive index and pseudoextinction coefficient for Ga_2SeS crystals.

of layers partially lose its binding to the remaining bulk due to its weak interlayer binding energy when the top few layers are cleaved. 1.8 μm corresponds to the total thickness of group of layers mentioned in the explanation. The imaginary part of the pseudodielectric constant should be zero below the band gap energy. However, our measurements do not give spectra satisfying this condition. At present time, the origin of this below-band gap feature for Ga_2SeS crystals is not clear. Earlier, the absorption tails below the fundamental gap edge were also observed in the study on optical properties of $CuIn_5Se_8$ and $CuGa_5Se_8$ (Ref. 27) and $CuAl_xIn_{1-x}Se_2$ crystals by ellipsometric measurements.[28] According to the authors, these tails result from intrinsic contributions (alloy disorder) and deviation from stoichiometry. In Ga_2SeS crystals, one of the possible reasons may be the deviation from stoichiometry during the crystal growth process.

Once the real and imaginary parts of the pseudodielectric constant are obtained, the pseudorefractive index ($\langle n \rangle$) and pseudoextinction coefficient ($\langle k \rangle$) are calculated by means of the relations[19]

$$\langle n \rangle = [(\langle \varepsilon_1 \rangle + (\langle \varepsilon_1^2 \rangle + \langle \varepsilon_2^2 \rangle)^{1/2})/2]^{1/2}\,, \tag{4}$$

$$\langle k \rangle = [(-\langle \varepsilon_1 \rangle + (\langle \varepsilon_1^2 \rangle + \langle \varepsilon_2^2 \rangle)^{1/2})/2]^{1/2}\,. \tag{5}$$

The spectral dependencies of the pseudorefractive index and pseudoextinction coefficient are shown in Fig. 6. The refractive index value of Ga_2SeS has been found between 2.66 and 3.13 in the visible spectral range.

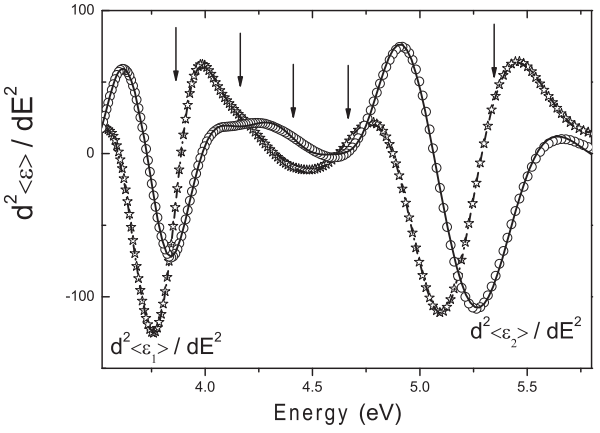

Fig. 7. Second-energy derivative spectra of the pseudodielectric function for Ga_2SeS crystals. Stars and open circles represent the second derivative spectra of the real and imaginary parts of the pseudodielectric function, respectively. The solid and dot-dashed curves show the fit to the experimental data.

Table 1. The comparison of critical point energies of Ga_2SeS and its constituents GaS and GaSe.

Crystals/critical points	CP1	CP2	CP3	CP4	CP5
GaS[a]	3.95	4.22	4.51	4.75	5.50
Ga_2SeS (this work)	3.87	4.16	4.41	4.67	5.34
GaSe[b]	3.75	4.03	—	4.69	5.02

[a]Ref. 25, [b]Ref. 26.

The pseudodielectric spectra given in Fig. 5 can be analyzed to get the critical points (interband transitions). The CP analysis method used to get knowledge about the band structure of the materials is based on the analysis of the second derivative spectra of the pseudodielectric constant.[29] Figure 7 shows the second derivative spectra of real ($d^2\langle\epsilon_1\rangle/dE^2$) and imaginary ($d^2\langle\epsilon_2\rangle/dE^2$) parts of the pseudodielectric constant calculated from the spectra given in Fig. 5. The graphs were smoothened without giving any distortion to the experimental curves using low level binomial filtering in each step of obtaining second derivative spectra. Smoothing process gives damage to the primary data for some energy ranges, especially below 3.5 eV energy value. The fitting of the spectra have been accomplished in the energy ranges giving successful smoothing results. In the studied energy ranges, least square fitting program revealed five interband transition structures with CP energies of 3.87, 4.16, 4.41, 4.67 and 5.34 eV which are indicated by arrows in Fig. 7. At this point, it is worthwhile to compare these values with those of GaS[25] and GaSe[26] crystals found from the CP analysis of the ellipsometry measurements. Table 1 presents the obtained CP energies of these three crystals. Since the E_g values for the GaS_xSe_{1-x} mixed crystals increase as amount of sulfur (S) increases,

the calculated CP energy values were related to each other considering the similar increasing behavior. The shift of the CP energies to higher values is thought due to the increase of content of smaller S atoms than selenium (Se) atoms in the composition.

4. Conclusion

Optical properties of Ga_2SeS crystals grown by Bridgman method were reported in the present paper. Transmission, reflection and ellipsometry measurements were carried out on the crystal at room temperature. Analysis of the transmission and reflection measurements resulted with 2.28 eV and 2.38 eV indirect and direct band gap energies, respectively. The spectra of pseudodielectric function, pseudorefractive index and pseudoextinction coefficient of the crystal obtained from the analysis of the ellipsometry measurements were given in the 1.2–6.0 eV spectral region. Moreover, the CP analysis of the second derivative spectra of the dielectric constant in the above band gap region was accomplished. Five critical points with energies of 3.87, 4.16, 4.41, 4.67 and 5.34 eV were revealed. Obtained CP energies of Ga_2SeS were compared with those of its constituents GaSe and GaS. It was reported that E_{cp} energies shift to higher values as the content of smaller sulfur (S) atoms increase in the GaS_xSe_{1-x} mixed crystals.

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