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Structural and Optical Properties of Ga_2Se_3 Crystals by Spectroscopic Ellipsometry

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Optical and crystalline structure properties of Ga_2Se_3 crystals were analyzed utilizing ellipsometry and x-ray diffraction (XRD) experiments, respectively. Components of the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and refractive index ($N = n + ik$) of Ga_2Se_3 crystals were spectrally plotted from ellipsometric measurements conducted from 1.2 eV to 6.2 eV at 300 K. From the analyses of second-energy derivatives of ε_1 and ε_2, interband transition energies (critical points) were determined. Absorption coefficient–photon energy dependency allowed us to achieve a band gap energy of 2.02 eV. Wemple and DiDomenico single effective oscillator and Spitzer–Fan models were accomplished and various optical parameters of the crystal were reported in the present work.

Key words: Semiconductors, optical properties, optical constants, critical points

INTRODUCTION

Many scientists are interested in group III_2–VI_3 (III = Ga, In, Tl and VI = S, Se, Te) compound semiconductors due to their importance in photovoltaic devices and possible applications in electrothermal devices.[1–5] Gallium chalcogenides belonging to this group have been successfully used for chemical and electrical passivation of the surface of III–V semiconductors and infrared (IR)/visible optoelectronic devices.[2] Ga_2Se_3 having attractive characteristics is one of the members of this group.[6–9] This compound takes interest for heterostructures with Al_2Se_3 which is another attractive member of group III_2–VI_3 compounds.[10] The heterostructures of these two materials offer potential to optoelectronic devices based upon AlAs, GaAs and $Al_xGa_{1-x}As$ compounds.[10] Previous studies indicated that Ga_2Se_3 having a gap energy between 1.9 eV and 2.6 eV, depending on phase structure, may be used in optoelectronic devices, memory switching and light-emitting diodes when Ga_2Se_3 layers were grown on GaAs and GaP substrates.[11,12] Moreover, Ga_2Se_3 being lattice-matched with silicon has potential to be used in silicon-based technologies[10] and can serve as suitable material for passivation of GaAs(100) surface.[13] Ga_2S_3-Ga_2Se_3 superlattices may also be used as blue light-emitting diodes.[14] Density functional calculations,[15] edge absorption,[6,16] photoconductivity,[16,17] IR absorption, and Raman[18] studies were previously carried out on Ga_2Se_3 crystal. Vacancy distributions of Ga_2Se_3 and structural and optical properties of Ga_2Se_3 thin films were studied.[19,20] Some scientists investigated electrical and optical properties of the Ga_2Se_3 bulk crystals.[21–26] Afifi et al. also performed transmission measurements for bulk and thin film Ga_2Se_3 crystals.[9] From the transmission measurements, the optical constants, refractive index and absorption index of Ga_2Se_3 thin films were identified. Indirect and direct band gap energies were determined as 2.056 eV and 2.65 eV, respectively, from study of

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the absorption index. Moreover, variation of optical constants with different temperatures was investigated. The change of direct current (DC) and alternating current (AC) photoconductivity of Ga_2Se_3 single crystal with light intensity, applied voltage and temperature is reported.[27] In addition, the band gap energy at room temperature and thermal coefficient of the energy gap were determined as 1.793 eV and -1.31×10^{-3} eV K^{-1}, respectively.

In this work, x-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and ellipsometric experiments were conducted to structurally and optically characterize the Ga_2Se_3 single crystal, respectively. The complex dielectric function of Ga_2Se_3 crystals was found by ellipsometric measurements conducted from 1.2 eV to 6.2 eV at 300 K. From the derivatives of the constituents of the complex dielectric function with respect to energy, interband transition energies (critical points) were determined. Moreover, refractive index and extinction coefficient were found. Band gap energy of the Ga_2Se_3 was determined from analysis of the absorption coefficient spectrum.

EXPERIMENTAL DETAILS

Ga_2Se_3 single crystals were grown by the Bridgman method using high-purity elements (at least 99.999%) arranged in stoichiometric proportions. The crystals were grown in silica tubes with a tip at the bottom in vacuum. The ampoule was moved in a vertical furnace through a thermal gradient of 30°C/cm, between the temperatures 1090°C and 650°C at a rate of 0.5 mm/h. The resulting ingots optically qualified were red-brown in color. The crystal area was 14×11 mm^2 and thickness was ~ 4 mm that is acceptable for application to an air-sample optical model. EDS measurements were performed using a "ZEISS EVO 15" scanning electron microscope to determine atomic compositions of the elements constituting Ga_2Se_3. The structural properties of the crystal were identified using XRD measurements performed using a "Rigaku miniflex" diffractometer with CuKα radiation (λ = 0.154049 nm). Experiments were conducted in the diffraction angle (2θ) range of 20°–90° with a scanning speed of 0.02°/s. The lattice parameters of the crystal were found using a least-squares computer program "DICVOL 04". Optical properties of samples were determined using ellipsometric measurements performed using a SOPRA GES-5E rotating polarizer ellipsometer with the angle of the incident light beam as 70º. Ellipsometry technique was conducted from 1.2 eV to 6.2 eV at 300 K.

RESULTS AND DISCUSSION

The atomic compositions of the constituent elements (Ga, Se) were identified using EDS measurements. Figure 1 indicates the EDS spectrum presenting several characteristic peaks at energies

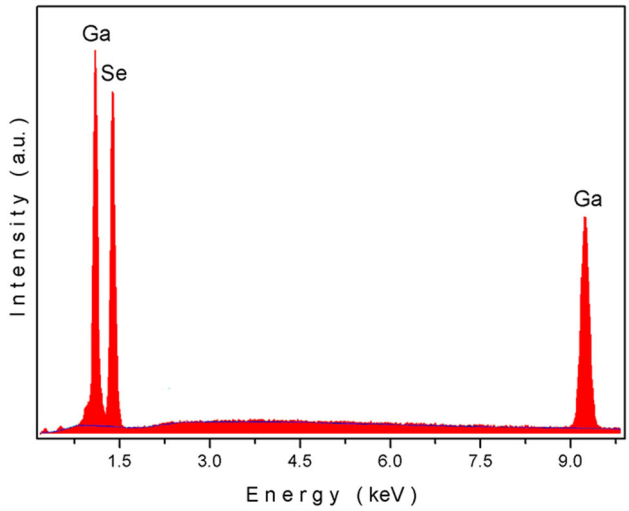

Fig. 1. Energy-dispersive spectroscopic analyses of Ga_2Se_3 crystal.

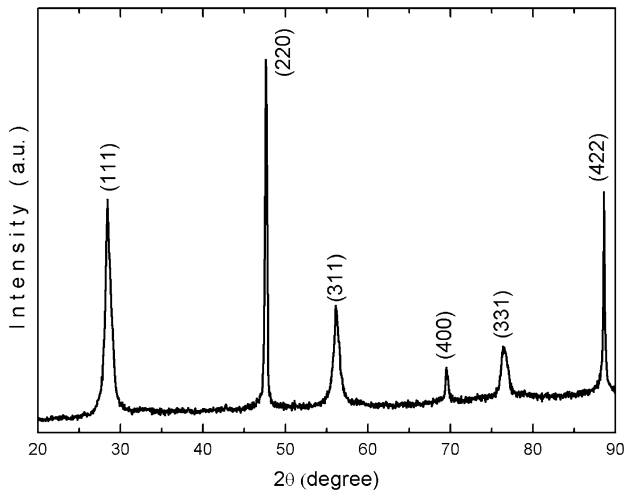

Fig. 2. X-ray powder diffraction pattern of Ga_2Se_3 crystal.

associated with x-rays emitted from the elements. The atomic compositions of the elements Ga:Se were obtained as 41.2:58.8 which nearly corresponds to the chemical formula of Ga_2Se_3. Figure 2 indicates the XRD pattern of Ga_2Se_3 single crystal. The lattice parameter of the cubic unit cell was found as a = 0.5397 nm. This lattice parameter is in good agreement with that given in the associated JCPDS card (0.5429 nm). The lattice parameter of Ga_2Se_3 is well matched with that of silicon reported as 0.5431 nm. As pointed above, this lattice-matching property makes Ga_2Se_3 an attractive material for silicon-based technologies.

Ellipsometric measurement is used to make optical characterization of the crystals. The output data of ellipsometry experiments were analyzed under the light of an ambient-substrate optical model detailed in Refs. 28–30. Figure 3 shows the spectra of components of the dielectric function of Ga_2Se_3

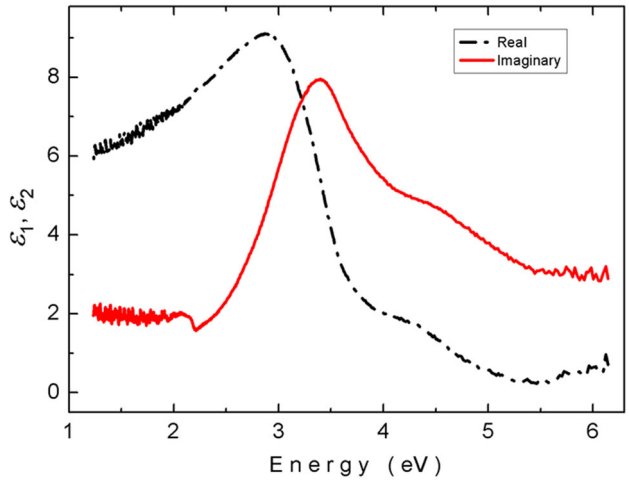

Fig. 3. Spectral dependencies of the components of the dielectric function of Ga_2Se_3 crystals.

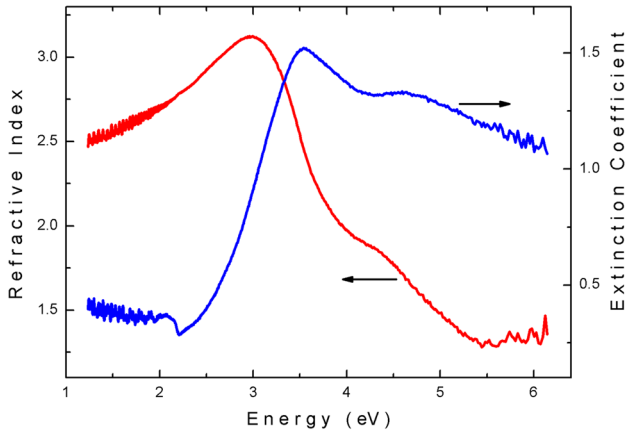

Fig. 4. Spectral dependencies of the refractive index and extinction coefficient of Ga_2Se_3 crystals.

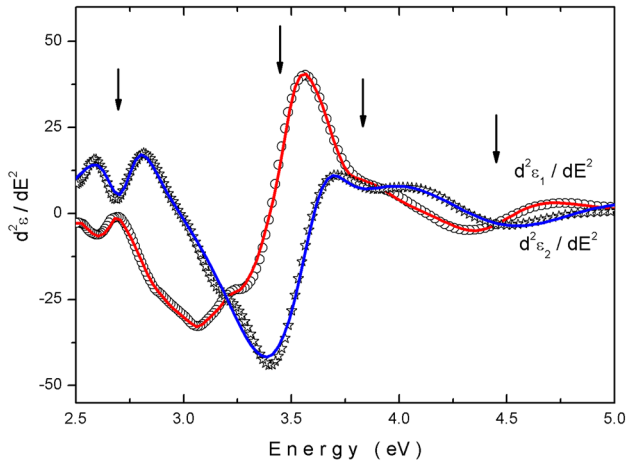

Fig. 5. Second-energy derivative spectra of the components of the dielectric function of Ga_2Se_3 crystals. The solid lines show the fit to the experimental data.

crystals from 1.2 eV to 6.2 eV. In the spectrum of the imaginary part, there is a sharp decrease at about 2.1 eV. This energy value more or less equals the band gap energy of Ga_2Se_3 crystals. Two peaks were observed at 3.40 eV and 4.50 eV in the spectrum of the imaginary part. According to reported Refs. 31 and 32, these peaks are associated with the sample that strongly absorbs photon energy at these critical points (interband transitions). In Fig. 3, the oscillations were observed below the absorption edges because interference occurred due to the thickness of the sample.[29] The imaginary component of the dielectric function does not reach a zero value below the absorption edge. This result was also presented for $CuIn_5Se_8$, $CuGa_5Se_8$[33] and $CuAl_xIn_{1-x}Se_2$[34] crystals. In these references, the authors associated this non-zero behavior to the intrinsic contributions and deviations from stoichiometry. Taking into account this idea, deviation from stoichiometry may be the possible reason for these tails.

Figure 4 presents spectral dependencies of refractive index (n) and extinction coefficient (k) acquired from the well-known following relations[29,30]:

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

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

The refractive index value of Ga_2Se_3 was obtained with a maximum value of 3.13 at 3.0 eV and 2.74 at a gap energy (E_g) of $\sim$ 2.1 eV. The relation between n and E_g can be found in literature; that is, they are inversely related with each other. This relation was reported in Refs. 35 and 36. According to the expressions relating n and E_g given by Moss,[37] Ravindra,[38] Kumar and Singh,[39] Herve and Vandamme,[40] refractive indices were calculated as 2.62, 2.70, 2.68 and 2.70, respectively, using a gap energy value of 2.1 eV for Ga_2Se_3 crystals. Among the applied relations, Ravindra and Herve–Vandamme expression gives the closest value of 2.70 with 2.74 obtained from ellipsometry plots.

The spectra of second derivatives of components of the dielectric function with respect to energy are utilized to obtain critical point energies (E_{cp}). Figure 5 presents related spectra for ε_1 and ε_2 of the Ga_2Se_3. In the studied energy range of 2.5–5.0 eV which does not yield deviation in the smoothing process, the fitting experience brought out E_{cp} energies of 2.70 eV, 3.45 eV, 3.83 eV, and 4.45 eV which are represented by arrows in Fig. 5. In literature, there are a few papers concerning theoretically investigating the band structure of Ga_2Se_3.[15,41,42] Taking into account the reported band structures in these studies, revealed critical point energies may be associated with band-to-band transitions from Se($3s$) and Se($3p$) states in the

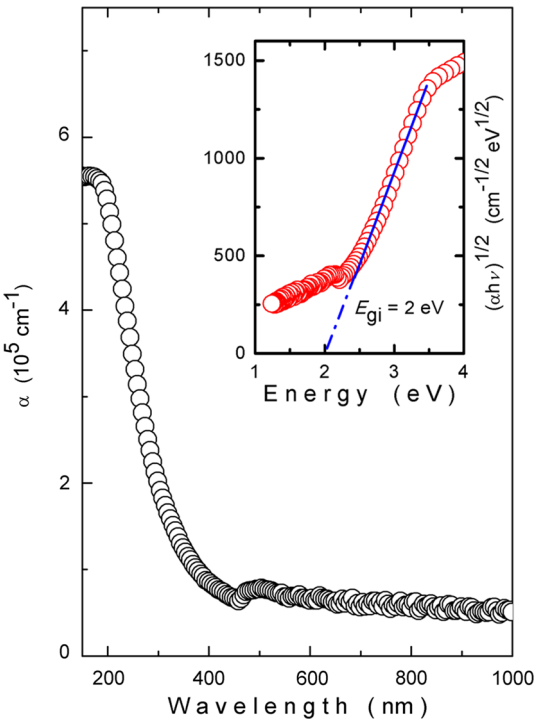

Fig. 6. Absorption coefficient as a function of wavelength for the Ga_2Se_3. The inset represents the dependency of $(\alpha h\nu)^{1/2}$ on photon energy. Circles represent the experimental data fitted to a linear equation (the solid line) to find the band gap.

valence band to the Ga(4*s*) states in the conduction band and transitions taking place between Ga(3*d*) and Ga(*s*) states.

The absorption coefficient (α) was calculated using k in the expression of $\alpha = 4\pi k/\lambda$. The determined absorption coefficient spectrum of Ga_2Se_3 crystals is shown in Fig. 6. Band gap energy E_g of the sample can be found by utilizing the relation of Ref. 35

$$(\alpha h\nu) = A(h\nu - E_g)^p \tag{3}$$

where A is a constant and p is either 2 for indirect or 1/2 for direct transitions. Analyses indicated that $(\alpha h\nu)$ and $(h\nu–E_g)$ dependency provides a good fit for $p = 2$. The inset of Fig. 6 indicates the dependency of $(\alpha h\nu)^{1/2}$ on $(h\nu)$. The value of indirect gap energy was reported as 2.02 eV from an energy correspondence of $(\alpha h\nu)^{1/2} = 0$ value of the fitted line. The indirect band gap energy has good agreement with 2.056 eV reported for Ga_2Se_3 thin film from analyses of the absorption measurements.[9] The A_2B_3 (A: Al, Ga, In; B: S, Se, Te)-type compounds have a wide range of gap energies between 0.64 (Ga_2Te_3) and 4.1 eV (Al_2S_3).[43] When the gap energy of Ga_2Se_3 was compared with those of other members of A_2B_3 group, it is seen that Ga_2Se_3 has a suitable gap energy value especially for optoelectronic devices. The 2.02-eV energy value falls into the visible spectral range of ~ 1.77–3.18 eV. This property

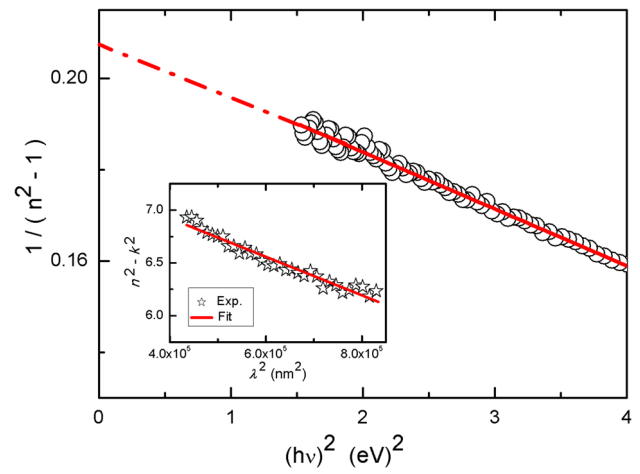

Fig. 7. Plot of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$. The solid line represents the linear fit according to Eq. 4. Inset: plot of $n^2 - k^2$ versus λ^2. The solid line shows the linear fit according to Eq. 5.

gains attractiveness to Ga_2Se_3 compound for visible light applications.

A dielectric model was proposed by Wemple and DiDomenico by taking into consideration the experimental results of over 50 nonmetallic and nonmagnetic compounds.[44,45] The results of experimental observations on dispersion energy (E_d), which is described as a measure of the intensity of interband optical transition, pointed out that E_d is independent of gap energy. In light of this behavior, Wemple and DiDomenico proposed a simple model (single effective oscillator model) for ε_2 spectrum and, as a result of theoretical investigations, the authors expressed the refractive index in the below band gap energy region as[45]

$$n^2(h\nu) = 1 + \frac{E_{so}E_d}{E_{so}^2 - (h\nu)^2} \tag{4}$$

where E_{so} symbolizes the single oscillator energy defined as the average gap energy. E_{so} and E_d energies were obtained from the linear fit of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ plot as 4.09 eV and 19.6 eV, respectively, using the slope and intercept of the fitted line (see Fig. 7). Similar analyses were previously applied on Ga_2Se_3 thin films.[9] The E_{so} and E_d values were reported as 3.86 eV and 19.3 eV, respectively. These values show good agreement with those revealed in our analyses. The zero-frequency ($\upsilon = 0$) refractive index (n_0) and dielectric constant (ε_0) were obtained using expressions $n_0 = (1 + E_d/E_{so})^{1/2}$ and $\varepsilon_0 = n_0^2$ as 2.41 and 5.79, respectively. In Ref. 9, n_0 and ε_0 values of Ga_2Se_3 thin film structure were also determined as 2.45 and 6.00, respectively. These optical parameters of bulk and thin film structures present good consistency with each other.

The Spitzer–Fan model relates the real component of the dielectric function to wavelength as[46]

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \left[\frac{e^2}{\pi c^2}\right]\left(\frac{N}{m*}\right)\lambda^2 \qquad (5)$$

Here, ε_∞ is the high-frequency dielectric constant, N is carrier concentration and m^* is effective mass. According to Eq. 5, the linear dependency of $\varepsilon_1 - \lambda^2$ can be used to determine ε_∞ and N/m^* which were found as 7.65 and 2.2×10^{51} kg^{-1} cm^{-3} (see inset of Fig. 7).

CONCLUSIONS

Ga_2Se_3 single crystals were optically characterized by conducting ellipsometry experiments. The complex dielectric function of Ga_2Se_3 crystals was spectrally plotted in the range of 1.2–6.2 eV. Interband transition energies (critical points) were found as 2.70 eV, 3.45 eV, 3.83 eV and 4.45 eV. The absorption coefficient was evaluated from the absorption index. As a result of absorption coefficient and photon energy dependency, the indirect gap energy of Ga_2Se_3 was obtained as 2.02 eV. Single oscillator energy, dispersion energy, zero-frequency refractive index and dielectric constant were found using the Wemple and DiDomenico single effective oscillator model as 4.09 eV, 19.6 eV, 2.41 eV and 5.79 eV, respectively. ε_∞ and N/m^* values were obtained with the help of the Spitzer–Fan model as 7.65 and 2.2×10^{51} kg^{-1} cm^{-3}, respectively.

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