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Ellipsometry study of optical parameters of $AgIn_5S_8$ crystals

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ABSTRACT

$AgIn_5S_8$ crystals grown by Bridgman method were characterized for optical properties by ellipsometry measurements. Spectral dependence of optical parameters; real and imaginary parts of the pseudodielectric function, pseudorefractive index, pseudoextinction coefficient, reflectivity and absorption coefficient were obtained from ellipsometry experiments carried out in the 1.2–6.2 eV range. Direct band gap energy of 1.84 eV was found from the analysis of absorption coefficient vs. photon energy. The oscillator energy, dispersion energy and zero-frequency refractive index, high-frequency dielectric constant values were found from the analysis of the experimental data using Wemple-DiDomenico and Spitzer-Fan models. Crystal structure and atomic composition ratio of the constituent elements in the $AgIn_5S_8$ crystal were revealed from structural characterization techniques of X-ray diffraction and energy dispersive spectroscopy.

1. Introduction

I–III–VI ternary semiconductors with the general formula of AB_5C_8 (where A=Cu or Ag; B=Ga or In and C=S, Se or Te) have potentials as photo-absorbers in solar cells, optoelectronics devices, and photoelectrochemical cells. They are visible-light-active crystals with high-absorption coefficients, suitable band gaps, good radiation stability, and easy conversion between *n*- and *p*-type carrier types which permits a variety of potentially low-cost homo- and hetero-junction [1,2]. These crystals have been confirmed as materials suitable for use in high-frequency thin films convertors, infrared detectors and various types of heterojunctions [3].

The optical and electrical properties of $AgIn_5S_8$ have been studied in Refs. [4–8]. The energy band gaps for the direct optical transitions of $AgIn_5S_8$ were found as 1.78 and 1.88 eV at 295 and 96 K, respectively [8]. Infrared reflection and Raman scattering spectra of $AgIn_5S_8$ crystals have also been investigated and analyzed [9]. Photoluminescence (PL) spectra of $AgIn_5S_8$ crystals were studied in the temperature range of 10–170 K [10]. The observed PL band centered at 1.65 eV was attributed to the radiative recombination of charge carriers from donor (E_d=0.06 eV) to acceptor (E_a=0.32 eV) states. Recently, thermally stimulated current measurements were carried out on as-grown $AgIn_5S_8$ single crystals [11]. The investigations were performed in temperatures ranging from 10 to 70 K with heating rate of 0.2 K/s. The analysis of the data revealed the electron trap level with activation energy 5 meV.

The present paper expands the studies on the optical characterization of $AgIn_5S_8$ crystals by elllipsometry measurements. The spectral dependencies of optical constants were obtained from the analysis of ellipsometric data using sample/air optical model. Moreover, band gap energy, high frequency dielectric constant, carrier concentration, oscillator energy, zero frequency refractive index and dielectric constant were evaluated using appropriate relations in literature.

2. Experimental details

$AgIn_5S_8$ polycrystals were synthesized using high-purity (99.999%) elements taken in stoichiometric proportions. The single crystals were grown by the Bridgman method from polycrystalline ingots in evacuated (10^{-5} Torr) silica tubes (10 mm in diameter and about 15 cm in length) with a tip at the bottom in our crystal growth laboratory. The temperatures in the upper and lower zones of a vertical furnace were about 1130 and 840 °C. The ampoule was moved in a furnace through a thermal gradient of 30 °C/cm at a rate of 1.0 mm/h. The resulting ingot with 8.5 mm in diameter and about 3.5 cm and 13 g in length and mass, respectively, was air/moister stable.

The crystal structure properties were identified using X-ray diffraction (XRD) experiments. Measurements were performed using “Rigaku miniflex” diffractometer with CuKα radiation

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(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°. The ellipsometric measurements on the $AgIn_5S_8$ 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°. In order to carry out the ellipsometric measurements, the ingots were cut and the surfaces produced were ground and polished carefully according to optical techniques to have the highest optical quality.

3. Results and discussion

Atomic composition ratio and crystal structure of the $AgIn_5S_8$ were obtained from EDS and XRD analysis, respectively. Energy dispersive spectrum presented in Fig. 1 revealed the composition ratio, Ag:In:S to be 7.4:37.8:54.8, respectively.

The crystal system, Miller indices of the diffraction peaks and lattice parameter were evaluated from the analysis of the X-ray diffractogram of $AgIn_5S_8$ using least-squares computer program "TREOR90". Miller indices (h k l) corresponding to observed diffraction peaks are shown in Fig. 2. The computer program revealed the crystal structure of $AgIn_5S_8$ as cubic unit cell with lattice parameter of a=1.0827 nm. Obtained Miller indices and lattice parameters well correlate with that reported previously in Ref. [12].

Optical properties of $AgIn_5S_8$ crystals have been investigated using ellipsometry measurements. In the ellipsometry experiments, the change of an incident polarized light after reflected from the surface of a sample is measured and analyzed. Two parameters of Ψ and Δ representing the amplitude ratio and phase shift of the parallel and perpendicular components of the reflected light are measured in the experiments. Since the optical parameters are calculated from the usage of Ψ and Δ in an appropriate optical model, the word of "pseudo" is placed in front of these parameters. Pseudodielectric function ($\langle\varepsilon\rangle$) is obtained from air/sample model defined as [13]

$$\langle\epsilon\rangle = \langle\epsilon_1\rangle + i\langle\epsilon_2\rangle = \sin^2(\varphi)\left[1 + \left(\frac{1-\rho}{1+\rho}\right)^2 \tan^2(\varphi)\right] \quad (1)$$

where φ is the angle of incidence and ρ is the complex reflectance ratio of the polarized light. Fig. 3 shows the spectra of real and imaginary parts of the pseudodielectric function in the 1.2–6.2 eV range. The non-zero behavior of ε_2 in the below band gap region disobeys the theoretical fact. This behavior which is also observed previously in Refs. [14,15] is thought a result of intrinsic contributions and deviation from stoichiometry.

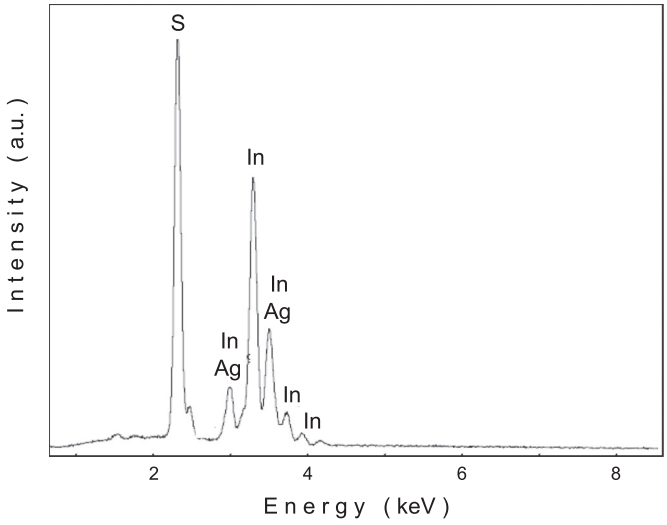

Fig. 1. Energy dispersive spectroscopic analysis of $AgIn_5S_8$ crystal.

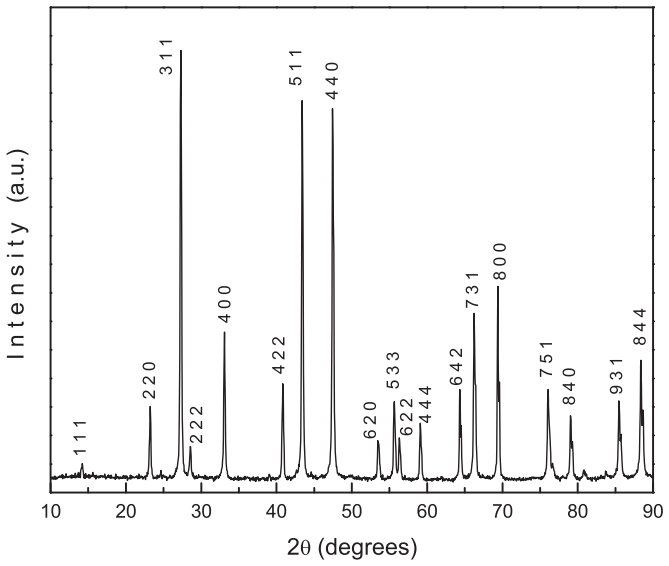

Fig. 2. X-ray powder diffraction pattern of $AgIn_5S_8$.

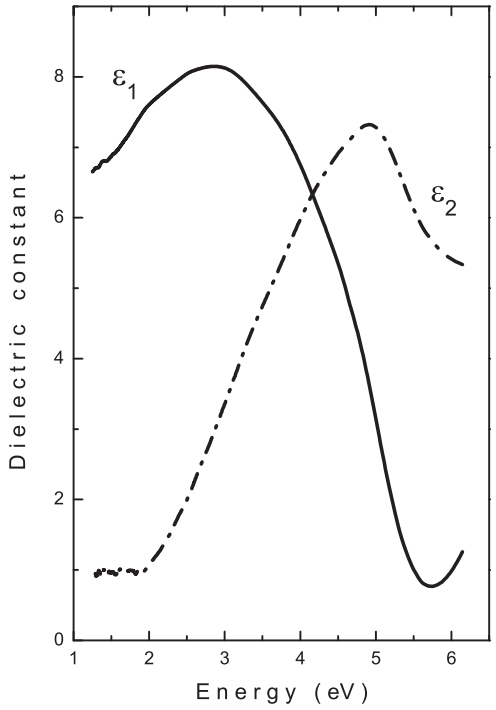

Fig. 3. Spectral dependencies of the pseudodielectric functions of $AgIn_5S_8$. Solid and dot-dashed curves represent the real and imaginary part spectra, respectively.

Fig. 4 shows the spectral dependencies of pseudorefractive index and pseudoextinction coefficient calculated from the relations [16]

$$\langle n\rangle = \left[\left(\langle\epsilon_1\rangle + (\langle\epsilon_1^2\rangle + \langle\epsilon_2^2\rangle)^{1/2}\right) / 2\right]^{1/2}, \quad (2)$$

$$\langle k\rangle = \left[\left(-\langle\epsilon_1\rangle + (\langle\epsilon_1^2\rangle + \langle\epsilon_2^2\rangle)^{1/2}\right) / 2\right]^{1/2}. \quad (3)$$

For semiconductors, refractive index and band gap energy (E_g) have typically inverse relation. Kumar and Singh relate these two

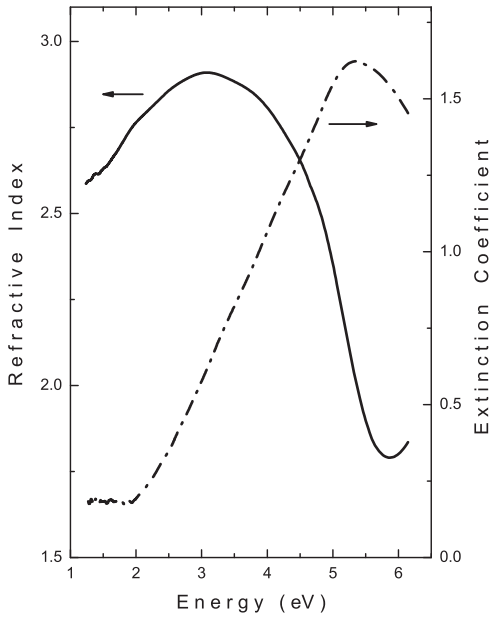

Fig. 4. Spectral dependencies of the pseudorefractive index (solid curve) and pseudoextinction coefficient (dot-dashed curve) of $AgIn_5S_8$.

optical parameters by the expression, $n = K E_g^C$, where constants K and C are equal to 3.3668 and −0.32234, respectively [17]. n value was calculated from this relation as 2.77. In another expression formulated by Herve and Vandamme, n and E_g are related by [18]

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \tag{4}$$

where A and B are constants as 13.6 and 3.4 eV, respectively. This expression resulted with 2.78 refractive index value. The spectrum of n shown in Fig. 4 exhibits its value as 2.73 at the band gap energy of E_g=1.84 eV. All these calculated and experimentally revealed n values show a good consistency.

Fig. 5 shows the spectra of absorption coefficient (α) calculated from well known equations relating α to refractive index and extinction coefficient. Spectra of absorption coefficient are utilized to obtain band gap energy from the relation [16]

$$(\alpha h\nu) = A(h\nu - E_g)^p \tag{5}$$

where A is a constant depending on the transition probability. The p is an index and equal to 2 and 1/2 for indirect and direct transitions, respectively. ($\alpha h\nu$) and ($h\nu - E_g$) relation showed that $AgIn_5S_8$ crystal has direct band gap energy of 1.84 eV (inset of Fig. 5). This value is in satisfactory agreement with previously reported band gap energy of 1.78 eV from absorption measurements [8].

The photon energy dependence of refractive index was also investigated using Wemple and DiDomenico single-effective-oscillator model which relates the n and $h\nu$ in the below band gap region ($h\nu < E_g$) by [19]

$$n^2(h\nu) = 1 + \frac{E_{so}E_d}{E_{so}^2 - (h\nu)^2} \tag{6}$$

where E_{so} and E_d represent the single oscillator energy and dispersion energy, respectively. The values of E_d, a measure of the intensity of the inter-band optical transition, and E_{so}, an average energy band gap, were obtained from the intercept and slope resulting from the extrapolation of the curve of Fig. 6 as 23.1 eV and 4.4 eV, respectively. The oscillator energy E_{so} is associated with

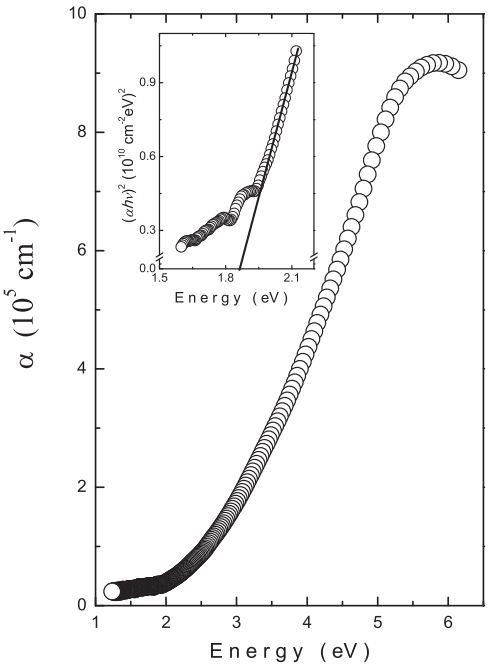

Fig. 5. Spectral dependency of the absorption coefficient of $AgIn_5S_8$. Inset: the dependence of $(\alpha h\nu)^2$ on photon energy.

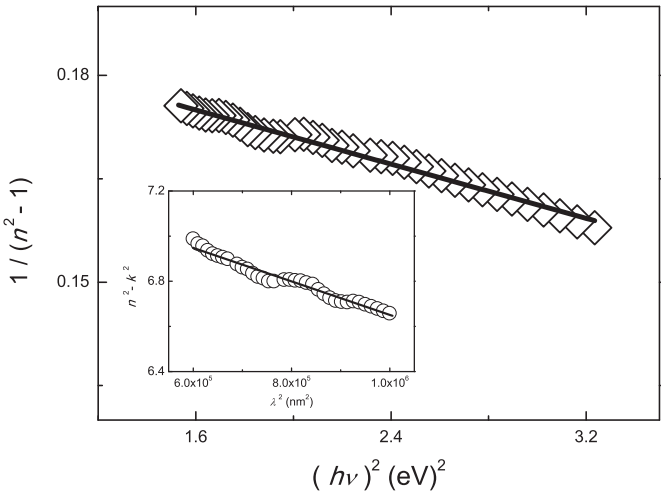

Fig. 6. The plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ in the $h\nu < E_g$ range. Rhombs are experimental data and solid line represents the linear fit. Inset: plot of ε_1 vs. λ^2. Circles are experimental data and solid line shows the linear fit.

direct band gap by the relation $E_{so} \approx 2.5\, E_g$ [20]. The ratio E_{so}/E_g for $AgIn_5S_8$ crystal was found as 2.4. The zero-frequency refractive index (n_0) and dielectric constant (ε_0) were also calculated as n_0=2.50 and $\varepsilon_0 = n_0^2$=6.25.

Real component of the pseudodielectric function is given in the Spitzer-Fan model as [21]

$$\varepsilon_1 = n^2 - k^2 = \varepsilon_\infty - \left[\frac{e^2}{\pi\, c^2}\right]\left(\frac{N}{m^*}\right)\lambda^2 \tag{7}$$

where ε_∞ is the high-frequency dielectric constant in the absence of any contribution from free carriers, N is the carrier concentration, m^* is the effective mass, c is the speed of light and e is the electronic charge. ε_∞ and N/m^* values were obtained as 7.4 and 9.1×10^{50} kg^{-1} cm^{-3}, respectively, from the analysis of ε_1–λ^2 dependency (inset of Fig. 6).

4. Conclusions

Ellipsometry measurements have been carried out in the 1.2–6.2 eV spectral range on $AgIn_5S_8$ crystals to get optical parameters. Applied air/sample optical model on ellipsometric data revealed the spectral dependencies of pseudodielectric function, pseudorefractive index, pseudoextinction coefficient and absorption coefficient. Analysis on absorption coefficient showed that $AgIn_5S_8$ crystals have direct band gap energy of 1.84 eV. The Wemple-Di-Domenico single-effective-oscillator model applied to refractive index dispersion data was used to determine the oscillator energy, dispersion energy and zero-frequency refractive index. The oscillator parameters were calculated as $E_{so}=4.4$ eV, $E_d=23.1$ eV and $n_0=2.5$. Spitzer-Fan model resulted with high-frequency dielectric constant of 7.4.

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