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Spectroscopic ellipsometry investigation of optical properties of β-Ga_2S_3 single crystals

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ABSTRACT

Ga_2S_3 single crystals were studied by x-ray diffraction (XRD), energy dispersive spectroscopy and spectroscopic ellipsometry measurements. XRD pattern of the sample is well-matched with reported hexagonal structure of β-Ga_2S_3. The spectra of real and imaginary parts of complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and refractive index ($N = n + ik$) were plotted in the 1.2–6.2 eV range according to results of ellipsometric data. The ε_2-spectrum and analyses of absorption coefficient pointed out that studied sample has band gap energy of 2.48 eV which is consistent with that of β-Ga_2S_3. Critical point energies of β-Ga_2S_3 were also reported in the present study.

1. Introduction

Ga_2S_3 is one of the significant members of III_2-VI_3 type binary semiconductors. There exist three main polytype phases of this compound known as monoclinic α-Ga_2S_3 with lattice parameters of $a = 1.1094$ nm, $b = 0.9578$ nm, $c = 0.6395$ nm and $\gamma = 141^\circ$, hexagonal β-Ga_2S_3 with wurtzite type of lattice parameters $a = 0.36785$ nm, $c = 0.60166$ nm and cubic γ-Ga_2S_3 with lattice parameter of $a = 0.517$ nm [1]. The band gap energies of these phases also remarkably differ from each other as 3.44 eV (α-Ga_2S_3), 2.48 eV (β-Ga_2S_3) and 2.96 eV (γ-Ga_2S_3) [1–3]. Wide band gap semiconducting compound Ga_2S_3 is an encouraging material for optoelectronic applications such blue-light emitting devices [4], heterojunctions [5,6], terahertz [7], solar energy [8], oxygen sensing and UV photodetection [9]. Ga_2S_3 is known as defective semiconductor and the trapping center energies associated with different intrinsic and/or extrinsic defects provide this material various emission characteristics. Photoluminescence (PL) experiments carried out on undoped Ga_2S_3 crystal at 96 K resulted in presence of green emission peak at 520 m and broad red emission band ranging from 590 to 826 nm with slight peaks at 629 and 725 nm [10]. Ag, Cu and Ge doped Ga_2S_3 crystals exhibited PL emissions at 496, 514 and 590 nm, respectively, at 94 K [11]. PL spectra of undoped and Fe-doped Ga_2S_3 presented emissions at 424 nm (blue), 643 nm (red) and 400 nm (violent), 643 nm (yellow), respectively [4]. The properties of good optical transparency in the infrared region (0.44–25 μm), covering the important band ranges of 3–5 and 8–14 μm of atmospheric transparent windows, and very high laser induced damage threshold values of Ga_2S_3 single crystals make them promising practical infrared nonlinear optical materials [12]. The investigations on p-Ga_2S_3/n-GaAs heterojunctions showed that they have significant potential in sensor applications for high power lasers [13]. Another paper on heterojunction structure of Si/Ga_2S_3 indicated that it behaves as solar cell with power conversion efficiency of 8.3% [8]. Ga_2S_3 compound is also effectively used in glass technology applications. Non-toxicity, chemical stability, high glass transition temperature and high rare-earth solubility characteristics of Ga_2S_3 based glasses makes them attractive infrared optical fiber materials [14,15].

Optical characterization of semiconducting materials which are significantly used in optoelectronic device technology gets an important place. Optical constants; refractive index, dielectric constant, band gap energy, extinction, and absorption coefficients are essential parameters in the characterization of these materials. To our knowledge no spectroscopic ellipsometry data are available on Ga_2S_3 crystals. For this purpose, in the present paper, spectroscopic ellipsometric investigations of Ga_2S_3 were given to optically characterize the sample in the 1.2–6.2 eV range. The analyses of the ellipsometric data were accomplished and spectral dependencies of some optical constants of Ga_2S_3 were reported. Moreover, band gap energy and interband transition energies were revealed according to results of analyses.

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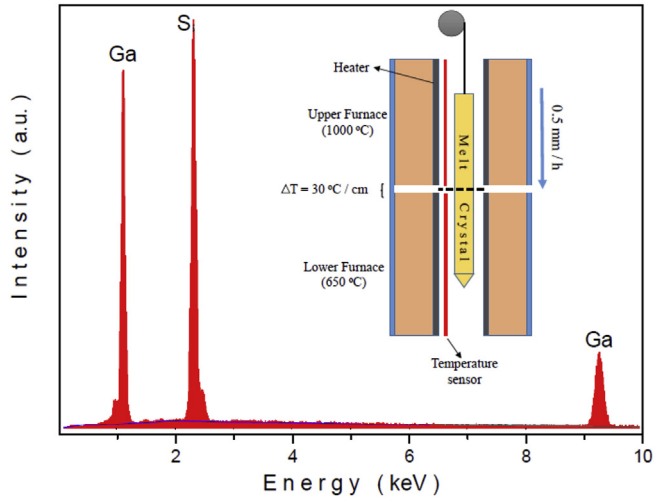

Fig. 1. EDS spectrum of Ga_2S_3 single crystals. Inset shows the schematic representation of the Bridgman method set-up.

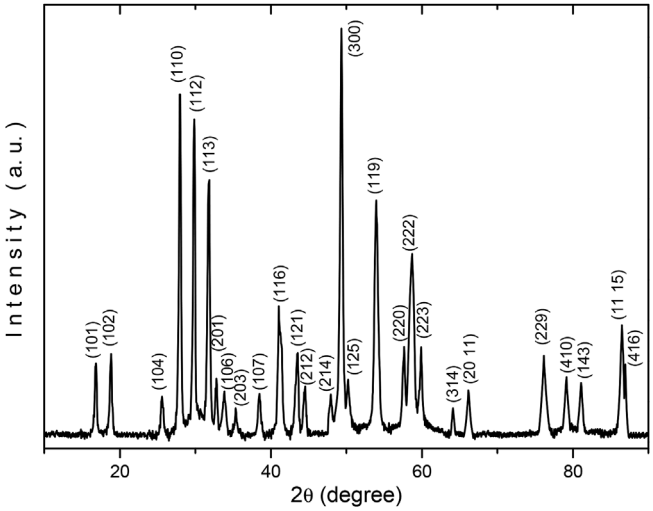

Fig. 2. X-ray powder diffraction pattern of Ga_2S_3 crystal.

2. Experimental details

Ga_2S_3 crystals were synthesized using high-purity elements (at least 99.999%) taken in stoichiometric proportions. Ga_2S_3 single crystals 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 (yellow in color) showed good optical quality. The chemical composition of the synthesized crystals were determined by carrying out energy dispersive spectroscopy (EDS) experiments using scanning electron microscope (Nova NanoSEM 430). Fig. 1 and its inset present EDS spectrum and schematic representation of the Bridgman method set-up, respectively. EDS measurements resulted in atomic compositions of the studied samples (Ga: S) as 40.8: 59.2 which is well consistent with chemical formula of Ga_2S_3.

Crystalline characteristics were revealed by x-ray diffraction (XRD) measurements performed on powder form of the crystal 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°. The ellipsometry measurements on Ga_2S_3 were carried out at room temperature in the 1.2–6.2 eV spectral range by SOPRA GES-5E rotating-polarizer ellipsometer. The angle of incidence of the light beam was 70° which is nearly equal to Brewster angle of Ga_2S_3 crystal. The crystal thickness was measured by standard micrometer as 3.24 mm which is acceptable to apply air-sample optical model.

3. Results and discussion

Crystalline structure of Ga_2S_3 crystals were identified by x-ray diffraction measurements which resulted in diffraction pattern presented in Fig. 2. XRD pattern of the sample was compared with those given in JCPDS card. As pointed above Ga_2S_3 have three polytype phases (α, β and γ) which possess different crystal structure. When observed diffraction pattern was compared with those given in database, it was seen that XRD pattern is in good agreement with that of JCPDS (Joint Committee on Powder Diffraction Standard) 84–1440 [16] which belongs to hexagonal β-Ga_2S_3 with lattice parameters of $a = b = 0.6385$ nm and $c = 1.8040$ nm. The Miller indices associated with XRD peaks were also indicated in the figure.

Ellipsometric measurements are utilized to optically characterize the materials. After a linearly polarized light beam is irradiated onto the sample, the reflected light is collected. The amplitude ratio (ψ) and phase shift (Δ) of parallel (p) and perpendicular (s) components of the reflected light were measured as ellipsometric data. The parameters ψ and Δ are related to the complex reflectance ratio ρ of the polarized light by the following equation:

$$\rho = \frac{r_p}{r_s} = \tan(\psi)\exp(i\Delta) \tag{1}$$

where r_p and r_s are Fresnel reflection coefficients of the polarized light. The simple air-sample optical model defined by the expression [17]

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

is used to find the dielectric constants of the bulk, flat crystals. In Eq. (2), ε_1 and ε_2 symbolize the real and imaginary parts of dielectric constants, respectively, and φ is the angle of incidence.

Fig. 3 indicates the spectra of ε_1 and ε_2 components of complex dielectric function obtained from the analyses of ellipsometric data according to air-sample optical model. The ε_2-spectrum exhibits a

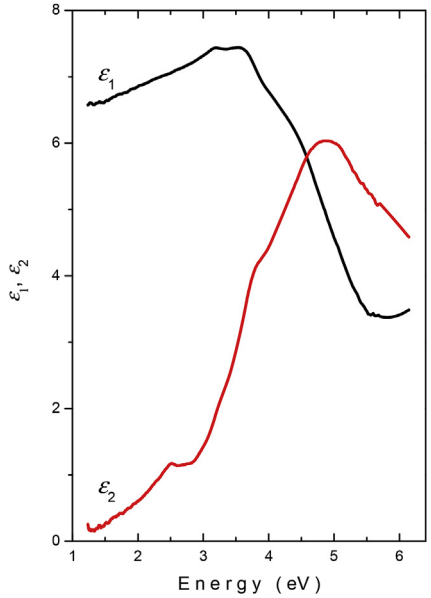

Fig. 3. Spectral dependencies of real (ε_1) and imaginary (ε_2) components of dielectric function of Ga_2S_3 crystal.