Structural and optical properties of gallium sulfide thin film

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Abstract: Structural, morphological, and optical properties of gallium sulfide film grown by chemical bath deposition have been investigated by XRD, SEM, AFM, and optical absorption techniques. The XRD spectrum indicated that the gallium sulfide film grew in crystalline form and the phase was identified as GaS. Gallium sulfide film had an island-like structure with a random distribution on a glass substrate. The particle size of the crystallites and surface roughness of the film were found to be 28–48 nm and 11.84 nm, respectively. The direct and indirect band gaps of gallium sulfide thin film were calculated from the absorption spectra as 2.76 and 2.10 eV, respectively.

Key words: Gallium sulfide, chemical bath deposition technique, XRD, SEM, AFM

1. Introduction

As members of the layered chalcogenides, bulk gallium sulfide crystals (GaS and Ga_2S_3) are wide band gap semiconductors and they have potentials for the fabrication of optoelectronic devices applied in the blue visible region [1–5]. The indirect band gap energy of GaS is about 2.59 eV, approximately 0.45 eV below the direct band gap energy [6]; on the other hand, the direct band gap energy of Ga_2S_3 is 3.40 eV [7]. The exciton Bohr radius of bulk GaS crystal is 1.4 nm [8]. GaS is a diamagnetic semiconductor that possesses a crystal lattice with hexagonal structure (space group D_{6h}^4 for β-type GaS) [9,10]. GaS crystallizes in the stacking type of layers, each monolayer consisting of two gallium and two sulfur close-packed sublayers in the stacking sequence of S – Ga – Ga – S along the c axis [11–13]. Goodyear et al. found that Ga_2S_3 crystal cells contained four molecules, and they concluded that the sulfur atoms must be nearly hexagonally close-packed in layers perpendicular to the c axis [14].

GaS and Ga_2S_3 have also been investigated as thin films in the literature. Several deposition techniques were used in the growth of GaS thin films, including microwave glow discharge [15], chemical vapor deposition [16], modulated flux deposition [17], and thermal evaporation [18]. It is known that deposition conditions/techniques may affect the structural, optical, and electrical properties of thin films. For instance, Suh et al. and Sanz et al. deposited GaS thin films by using chemical vapor deposition and modulated flux deposition techniques, and they found the direct band gap energies of thin films as 3.47 eV and 3.4 eV, respectively [16,17].

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On the other hand, Micocci et al. found the direct band gap energy of gallium sulfide thin film deposited by using thermal evaporation as 2.55 eV [18].

The purpose of this paper is to report the preliminary structural, morphological, and optical characterizations of gallium sulfide thin films, grown by chemical bath deposition (CBD), through XRD, SEM, AFM, and linear absorption measurements. To the best of our knowledge, GaS thin films were not grown by CBD technique before in the literature. The CBD method offers the following advantages over other techniques: 1) films can be deposited on all kinds of hydrophilic substrates; 2) it is a very simple and inexpensive method, suitable for large-area deposition; and 3) impurities in the initial chemicals can be made ineffective by suitably complexing them [19]. However, the solution deposition of gallium sulfide has the following fundamental problems: 1) aqueous solutions of gallium(III) salts are subject to extensive hydrolysis; and 2) sulfides are hydrolytically unstable [20].

2. Experimental

Gallium sulfide thin film was deposited onto glass substrate by the CBD method. The glass substrate was washed in HNO_3 and bidistilled water prior to the growth process. Because of the difficulties in growing gallium sulfide film by CBD, several experiments were conducted by varying experimental parameters like pH, temperature, sulfide source, and concentrations. Relatively good film was obtained by using the following parameters: 0.5 M gallium sulfate $[Ga_2(SO_4)_3]$, 0.25 M sodium thiosulfate pentahydrate $[Na_2S_2O_3.5H_2O]$, 1 M tartaric acid $[C_4H_6O_6]$, pH $\sim$10.6, and 27 °C bath temperature. Tartaric acid was used to adjust the pH of the solution. Finally the chemically cleaned glass substrate was immersed vertically into the chemical solution. Immersing processes were carried out for 120 min.

The structure of the film grown on glass substrate was analyzed by grazing incidence X-ray diffraction (GIXRD) measurements carried out with a Panalytical X'Pert PRO-MRD diffractometer using Cu K α radiation. The GIXRD pattern was obtained in the $10°$–$50°$ range with a step size of $0.1°$. The surface morphology of the film was probed using an FEI Nova Nanosem 430 model scanning electron microscopy and a PSIA XE-100E atomic force microscopy. The optical absorbance spectra were recorded using a PerkinElmer Lambda 25 UV/Vis spectrophotometer between 400 and 1100 nm.

3. Results and discussion

Despite the difficulties/problems of growing gallium sulfide thin film by CBD given in the introduction, we were able to grow gallium sulfide thin film on glass substrate by CBD. The film had a yellowish color.

The X-ray spectrum of gallium sulfide thin film is given in Figure 1, which indicates that the gallium sulfide film grows as a polycrystal on the glass substrate. Analysis of the XRD spectrum yields that the phases grown on the glass substrate are GaS and Ga_2S_3. Different phases can be obtained under different growth conditions in some semiconductor crystals and this is one of the main characteristic properties of the A^{III}–B^{VI} semiconductors [21].

SEM images of gallium sulfide thin film with different magnifications are given in Figures 2a and 2b. It is seen from Figure 2a that the gallium sulfide film grown on glass substrate by CBD in this study is not continuous. It looks like the film grew as islands distributed over the glass substrate and there are not any cracks and/or fissures at the thin film's surface. When we look inside these islands, we see that they consist of particles of different shapes and sizes (Figure 2b). The grain size of the film is calculated from the XRD data using the Scherrer equation [22,23]:
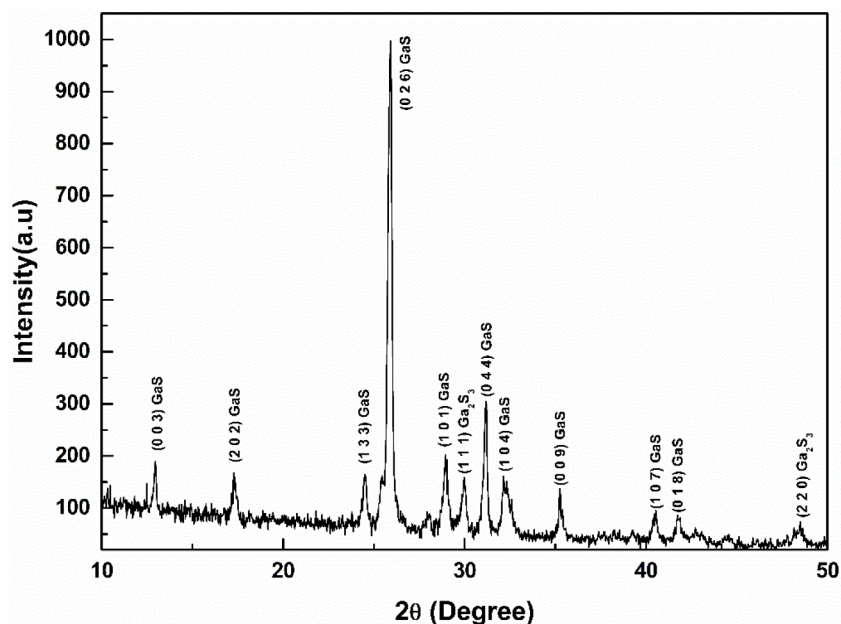
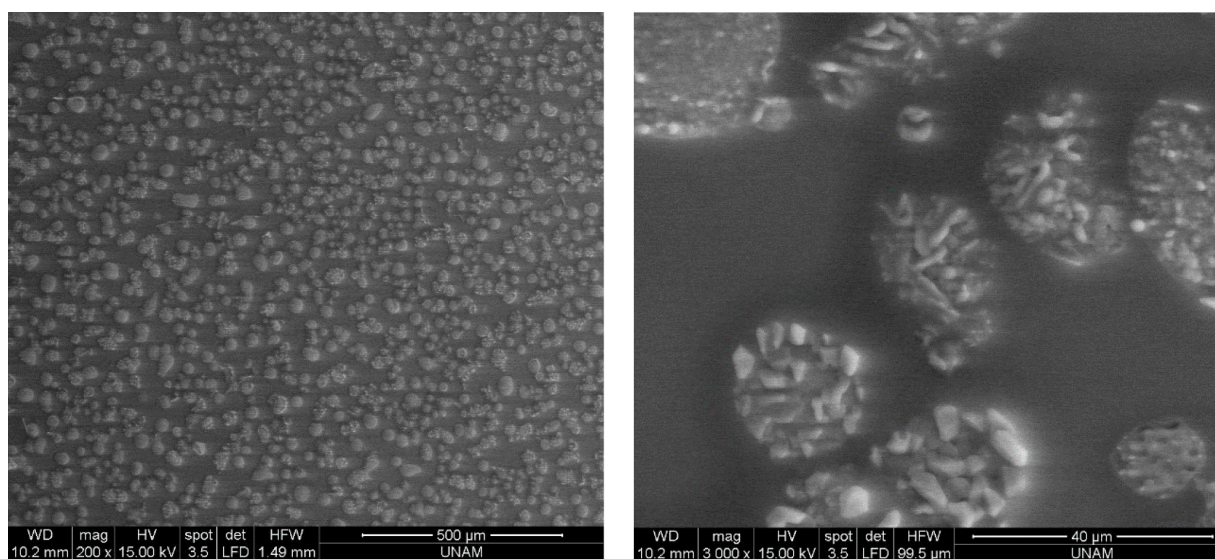**Figure 1.** XRD pattern of CBD-grown gallium sulfide thin film.

Figure 2. SEM images of gallium sulfide thin film: a) 200× and b) 300 × magnifications.

$$D = k\lambda/(\beta\cos\theta),$$

where λ is the wavelength of the Cu K$_\alpha$ radiation, k is the Scherrer constant, θ is the Bragg angle of the diffraction peak considered, and β is the full width at half maximum of the diffraction peaks corresponding to (003), (133), (026), (101), and (044) crystal planes. The crystallite size of the GaS film was determined to be 28–48 nm, indicating that the film is nanocrystalline. Atomic force microscopy has been used to access the surface quality of the gallium sulfide thin film grown by CBD method. A large-scale (5 × 5 μm^2) AFM image of the film is given in Figure 3. By visual inspection of the morphology of the film it is possible to see that granules with different size and shapes exist and are distributed homogeneously over the substrate in some

regions, although the overall distribution is not homogeneous. By quantitative analysis of the AFM image, the standard deviation of the surface height, i.e. the root mean square value of surface roughness of the film, was determined to be 11.84 nm.
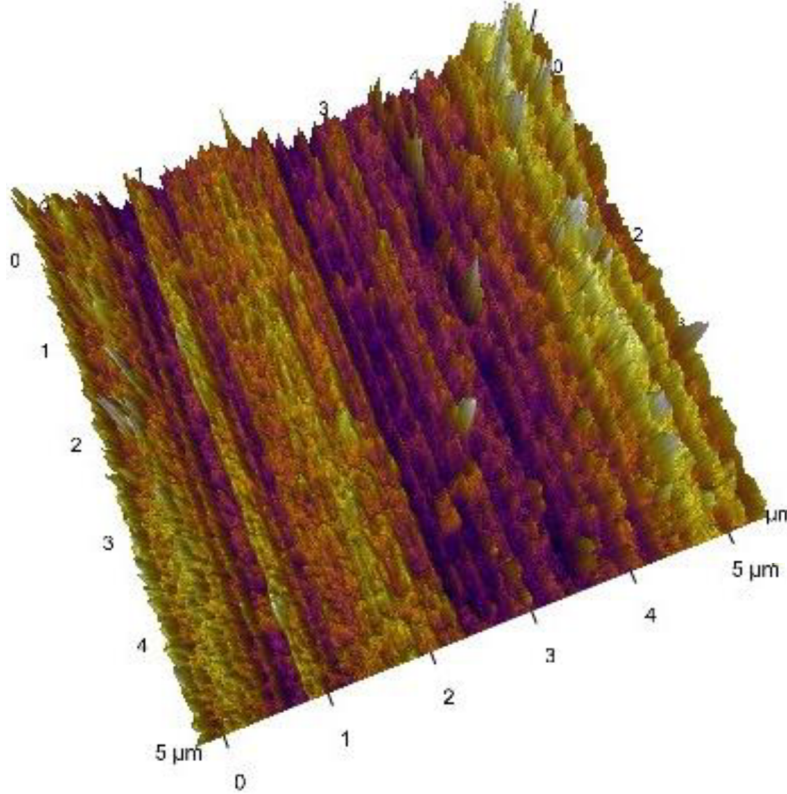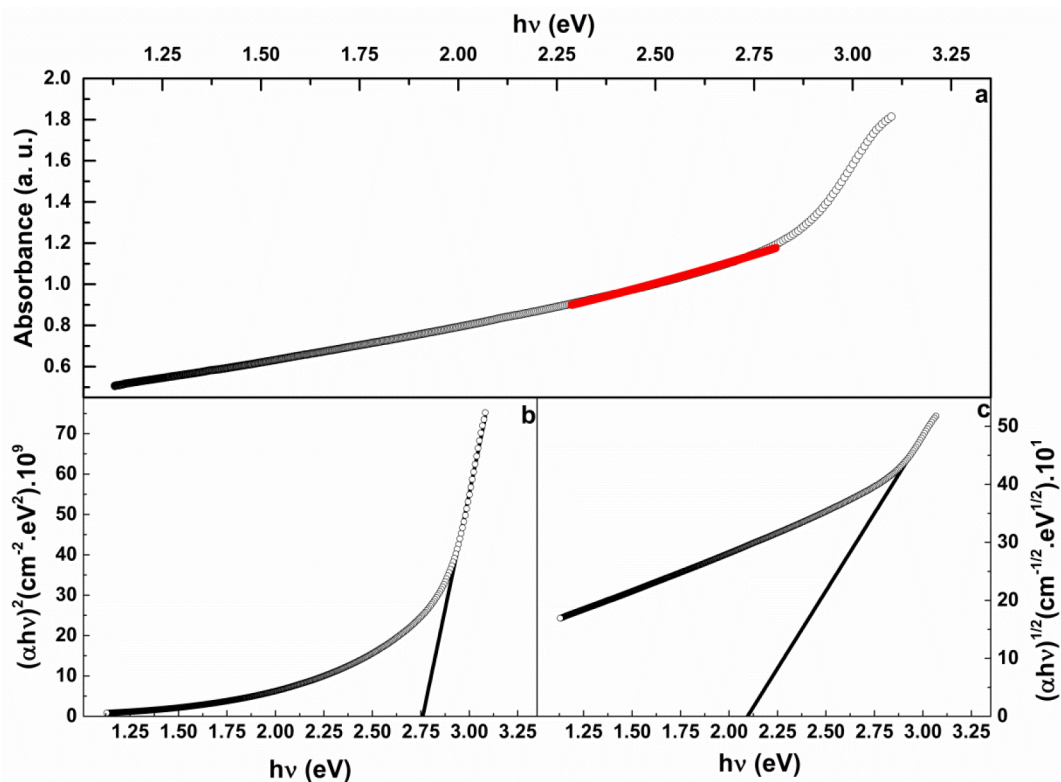

Figure 3. AFM image of gallium sulfide thin film.

The optical absorption spectrum of gallium sulfide thin film is given in Figure 4a. The slight increase at the absorption edge indicates the presence of the defect states at the band gap. The band gap energy (E_g) of thin film was estimated on the basis of the recorded optical spectra using the following relation [24]:

$$\alpha h\nu = A \left(h\nu - E_g^{opt} \right)^n,\tag{1}$$

where A is a constant, α is the absorption coefficient, $h\nu$ is the photon energy, and n depends on the nature of the transition. For direct band transitions $n = 1/2$ or $3/2$, and for indirect band transitions $n = 2$ or 3, depending on whether they are allowed or forbidden transitions, respectively [24]. In this study, absorption spectra were fitted according to direct and indirect transitions and the best fits to the experimental data were obtained for $n = 1/2$ and 2. The band gap energies for direct and indirect transitions of the gallium sulfide thin film were determined with the help of plots of $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ versus $h\nu$ (eV) shown in Figures 4b and 4c, respectively. The band gap energies of gallium sulfide thin film for direct and indirect transitions were calculated from the fits as 2.76 and 2.10 eV, respectively. These values are less than the band gap values of bulk gallium sulfide crystal. This behavior is thought to be due to the blurring of the band gap by the defect

Figure 4. a) Linear absorption spectra and Urbach fit, b) Tauc's plot for indirect band gap, c) Tauc's plot for direct band gap transitions of gallium sulfide thin film.

states [25,26]. Steepness of the exponential absorption tail is determined from the absorption spectrum as:

$$\alpha = \alpha_0 \exp\left[(\frac{\sigma(T)}{k_B T})(h\vartheta - E_g)\right],$$

where k_B is the Boltzman constant, T is the temperature, and υ is the frequency of the incident photons. The Urbach energy is also determined with the steepness of the tail, $E_u = k_B T/\sigma$ [27,28]. Urbach energy of gallium sulfide thin film was calculated by fitting the long wavelength tail of the experimental absorption data with the above equation. The fit given in Figure 4a yielded a value of 1.93 eV for the Urbach energy. Generally, Urbach energies of thin films are bigger than those of bulk crystals [29–31].

The band gap energy of gallium sulfide thin films is known to depend on the thin film growth technique and conditions. As we mentioned in the introduction, direct band gap energies of GaS thin films grown by different techniques and under different growth conditions have been reported between 2.55 and 3.6 eV [16–18]. Although the direct band gap energy obtained in this study for CBD-grown gallium sulfide film is different from the reported values, it falls in the reported interval and it is close to the band gap energy given for GaS grown by thermal evaporation [18]. The fact that GaS thin films can have band gap energies in a relatively large energy interval makes these films worthy of investigation for electronic, optic, and optoelectronic applications.

4. Conclusion

Gallium sulfide thin film was grown on glass substrate by CBD technique for the first time and structural, morphological, and optical properties of the film were studied by means of GIXRD, SEM, AFM, and optical absorption measurements. Analysis of the GIXRD pattern showed that the film grew in crystalline form and the crystalline phase was identified as GaS. Morphological analysis indicated that GaS film has an island-like growth and random distribution on glass substrate. The band gap energies for direct and indirect band transitions were calculated from the optic absorption spectra as 2.76 eV and 2.10 eV, respectively. These values of direct band gap energy are comparable to the reported band gap energies for gallium sulfide films grown by different methods.

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