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Effect of annealing on the structural and optical properties of $AgGaS_2$ thin films prepared by pulsed laser deposition

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Abstract

The influence of annealing on the $AgGaS_2$ films grown by pulsed laser deposition has been investigated. The X-ray diffraction results show the $AgGaS_2$ films were found with preferential orientation (1 1 2) normal to the surface and silver droplets were diminished after the post-annealing. Photoluminescence (PL) measurements reveled the exciton energy is slightly red shifted that is possibly due to the thermal strain effect. The binding energy of the shallow donors is ~28 meV determined from temperature dependent PL spectra. In addition, the A-exciton and the B/C-exciton could be observed in the transmittance spectra at room temperature.

Keywords: X-ray diffraction; Photoluminescence; Optical properties

1. Introduction

The semiconductor compound $AgGaS_2$ has been extensively studied because of its potential use not only for nonlinear frequency converters but also for photonic devices [1–3]. It has a relatively large nonlinear coefficient in wide transparency region from 0.5 to 13 μm and it possesses a wide band gap energy of 2.68 eV at room temperature which is in the blue emission region [4]. For most applications of photonic device, a suitable technology for the thin film growth has to be developed. Various methods have been employed for the growth of $AgGaS_2$ films. Pulsed laser deposition (PLD) is a possible growth technique which has been widely used to fabricate high quality films of multi-element materials such as ferroelectrics and superconductors due to its high-energy flux. Uchiki et al. [5] first reported on the deposition of $AgGaS_2$ films where a target of consisting a stoichiometric mixture of Ag_2S and Ga_2S_3 powders has been used. The temperature range was 400–650 °C during the PLD experiment and a XeCl excimer laser was used. However, as shown, the quality of thin film is not good enough to observe exciton emission at low temperature through either photoluminescence (PL) or optical transmittance measurements. Silver particles were always responsible to form precipitates in the film. Recently, a much better film quality was obtained by PLD [6] and multisource evaporation [7]. These films showed exciton features in the PL spectra at low temperature PL and optical reflectance measurements.

As reported in this paper a suitable post-annealing can indeed diminish the silver precipitate formation. Hence, the quality of the PLD-grown $AgGaS_2$ films can be improved. The $AgGaS_2$ films were grown on quartz glass substrates using a KrF excimer laser. Stoichiometrically mixed targets of the binary compounds Ag_2S and Ga_2S_3 have been used. X-ray diffraction (XRD) results showed not only the silver XRD peaks have vanished during the annealing process but also the $AgGaS_2$ diffraction width is narrower as previously reported [5–7]. The observation of A- and B/C-excitons at room temperature by transmittance measurements also indicates an achievement of good film quality.

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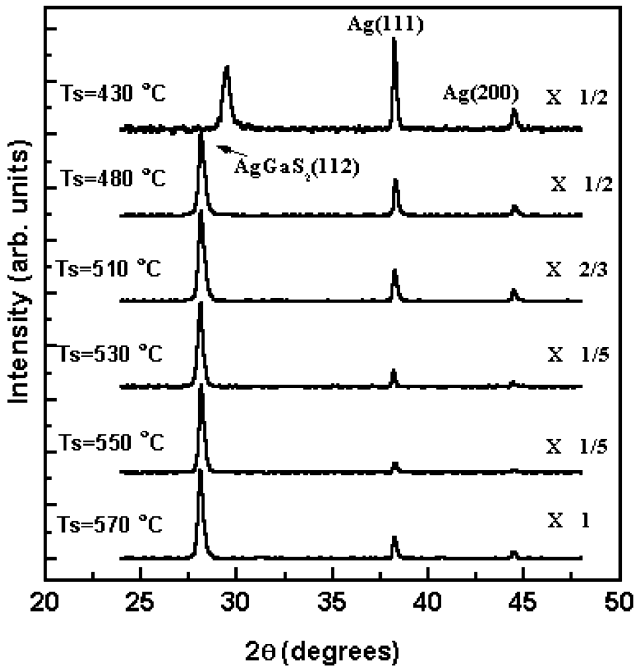


Fig. 1. XRD patterns of the films prepared at different growth temperatures.

2. Experiment

To grow high quality $AgGaS_2$ films, we used a KrF excimer laser (ATLEX-Spi 200) with the wavelength of 248 nm and a pulse duration 4 ns. The laser beam was focused on a target at 45° angle. The pulse energy density of the laser applied was 0.3–0.5 J/cm^2 and the pressure in the chamber was kept between 10^{-5} and 10^{-6} mbar. The target consists of a stoichiometric mixture of Ag_2S and Ga_2S_3 powders which had been pressed into a pellet of 10 mm in diameter. To ensure a good uniformity of the films, the laser beam was scanned over the target and the quartz glass substrate was placed parallel to the target at a distance of 30–40 mm. The substrate temperature varied in the range from 430 to 570 °C.

The surface morphology of the as-grown films was first examined by optical microscopy, and the crystalline quality was evaluated by XRD measurements using Cu Kα (λ = 1.5406 Å, Shimadzu XD-5) radiation. A scan rate of 4°/min in the range from 2θ = 24 to 48° was applied. The cryogenic PL spectroscopy was carried out using a He–Cd laser operating at 325 nm with the sample being mounted on the cold finger of a low temperature helium cryostat. The PL emission was detected by a monochromator (Jobin Yvon, U-1000) equipped with a cooled photo-multiplier tube (Hamamatu R955). The optical transmittance spectra were measured by means of a HP 8453 spectrometer within the range of 190–1100 nm at room temperature with respect to the bare glass substrate as the reference.

3. Results and discussion

3.1. XRD measurements

Fig. 1 shows the XRD pattern of as-grown films deposited at various substrate temperatures (T_s) in the range of 2θ = 24–48°. All of these films, except for the one grown at T_s = 430 °C, have a main peak at 2θ ~ 28°. They show single-phase of $AgGaS_2$ with chalcopyrite structure and preferred orientation with the (1 1 2) plane normal to the surface of the glass substrates. From JCPDS (Joint committee on Powder Diffraction Standards), we found two peaks at approximately 2θ ~ 38.3 and 44.5° which are attributed to silver islands that can be observed through an optical microscope as shown in Fig. 2a. We evaluated the film quality via the XRD intensity ratios of $AgGaS_2$ (1 1 2) to Ag (1 1 1). The effect of T_s on the XRD intensity ratio (I_{AgGaS_2}/I_{Ag}) and the full widths at the half-maximum (FWHM) of the main peak are listed in Table 1. We found that a good quality of films can be achieved for T_s ranging between

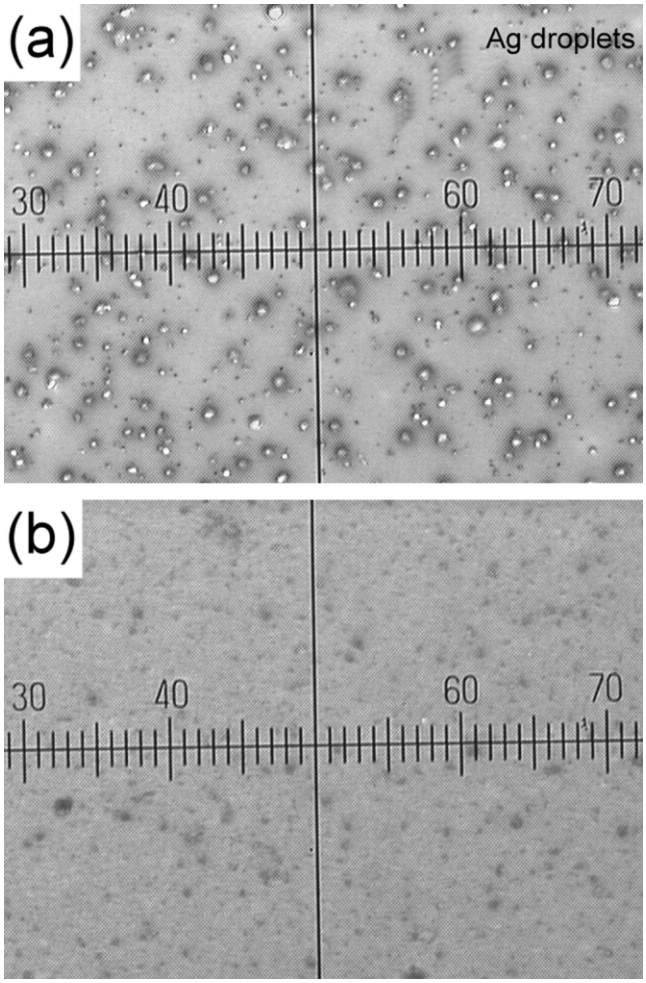


Fig. 2. Optical micrographs (1200× magnification) of the film surface of (a) as-grown and (b) annealed films.

Table 1
The data of T_s, I_{AgGaS_2}/I_{Ag}, and the FWHM of the main peak

T_s (°C)	I_{AgGaS_2}/I_{Ag}	FWHM (°)
510	2.84	0.347
530	5.44	0.318
550	9.14	0.281
560	10.48	0.342
570	4.47	0.343
550 annealed	–	0.32

550 and 560 °C. We deduced the grain size from XRD according to the Scherrer formula to be 32 nm. Comparing with the data of pervious work [5–7], this film seems to have a better quality.

After annealing of the film grown at 550 °C for 30 min, as shown in the optical micrograph of Fig. 2b, the silver droplets seem to disappear apparently. The XRD data also confirmed that the silver diffraction peaks disappeared after thermal annealing as shown in Fig. 3b. In addition, the FWHM of the annealed film (Fig. 3b) is narrower than that of the as-grown one (Fig. 3a). This indicates the film quality becomes better after heat treatment.

3.2. Photoluminescence measurements

The PL spectra of the as-grown and annealed films grown at $T_s = 550$ °C are shown in Fig. 4 for the measured temperatures ranging from 8.5 to 150 K. We found that the PL spectra of the as-grown films are dominated by a strong green emission below the band gap of the bulk that is centered approximately 506 nm or photon energy of 2.45 eV in Fig. 4a. This peak has been identified as the donor–acceptor pair (DAP) recombination [8] and was found to disappear above 150 K. Whereas, a weak emission approximately 2.69 eV aside the main peak is observable that can be

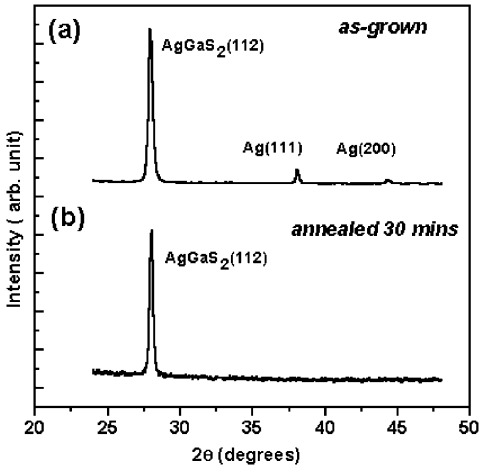
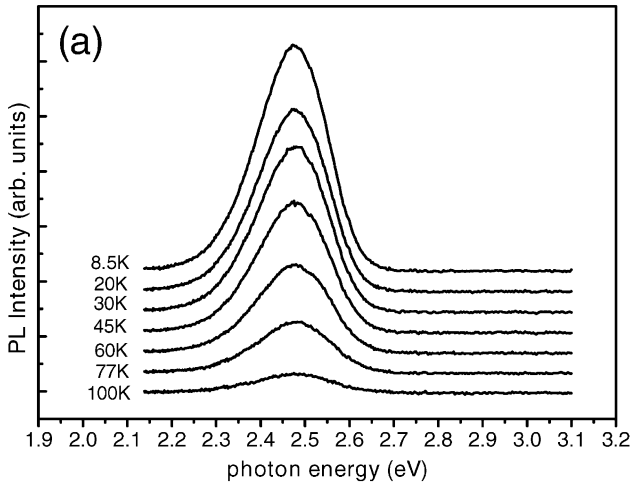


Fig. 3. XRD for the films as-grown and annealed at 550 °C for 30 min.



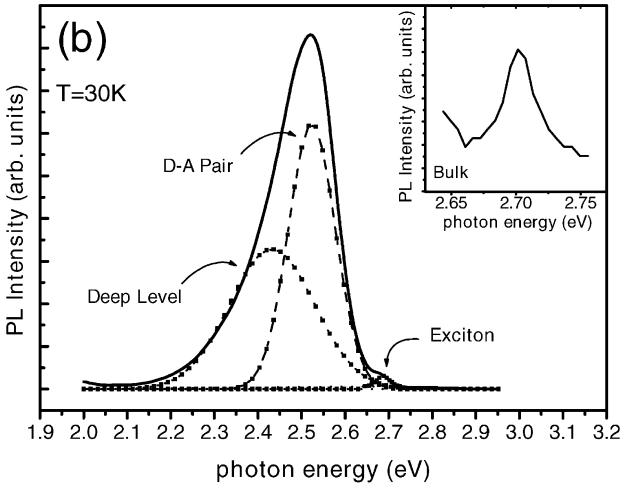


Fig. 4. (a) Temperature-dependence PL spectra of the as-grown film and (b) PL spectra of the annealed film at 30 K. The inset shows the PL spectra of the bulk crystal in the exciton region at 30 K.

attributed to the exciton emission in the annealed samples. All of the temperature dependent PL spectra (not shown in figure) reveal three main peaks. As shown in Fig. 4b in the PL spectrum measured at 30 K the exciton occurs, a peak caused by DAP, and deep level, respectively. The positions of the three peaks are nearly located at the same position independent of the temperature measured. The appearance of exciton emission indicates that the annealed films have better quality than the as-grown ones.

The Arrhenius plots of temperature dependent PL intensities for both as-grown and annealed films are shown in Fig. 5. They can be fitted by the expression: $I(T) = I(0)/[1 + \alpha \exp(-E_a/k_B T)]$ with $I(0)$, α, and E_a being the fitting parameters and k_B the Boltzmann constant. We calculated the activation energies E_a of

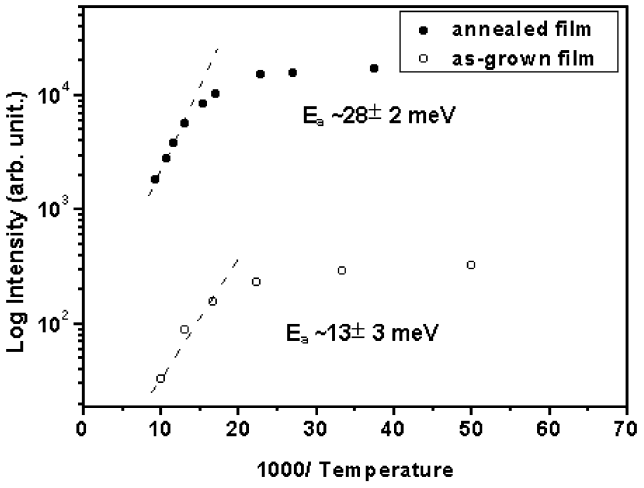


Fig. 5. Arrhenius plot of the intensities of the DAP peak at (a) as-grown film; (b) annealed film.

thermal decay channels of DAP emissions for the as-grown and annealed films as 13 ± 3 and 28 ± 2 meV, respectively. They can be attributed to the binding energies of the shallow donor levels below the conduction band. The binding energy of the annealed films is very close to that of $AgGaS_2$ bulk crystal determined at 26.8 meV [8].

In comparison with bulk $AgGaS_2$ where the exciton emission is located approximately 2.70 eV at 30 K, the exciton peak of the annealed film red shifts approximately 12 meV as shown in the inset of Fig. 4b. One may rule out the possibility of quantum size effect that induces blue shift of band edge rather than the observed red shift. Red shift of the exciton emission is consistent with the XRD result that the crystal size evaluated as large as 32 nm. The other reason is presumably the strain effect. The local strain may be induced between the substrate and the grown film during the cooling process due to different thermal expansion coefficients of the materials [9].

3.3. Optical transmittance

Fig. 6 shows the typical room temperature transmission spectrum of the annealed $AgGaS_2$ film grown at $T_s=560$ °C. We used the envelope method [10] to estimate the thickness of the film. It was found to be approximately 0.26 μm from the interference feature in the transmission spectrum between 1.25 and 2.5 eV photon energy range. The other two peaks located at 2.67 and 2.96 eV are attributed to the emission of A- and B/C-exciton, respectively. However, we were not able to resolve the spin–orbit splitting (~8 meV) of the lower valance bands, i.e. B and C excitons. The band structure of a typical chalcopyrite semiconductor is shown in Fig. 7. The uppermost valence band at the

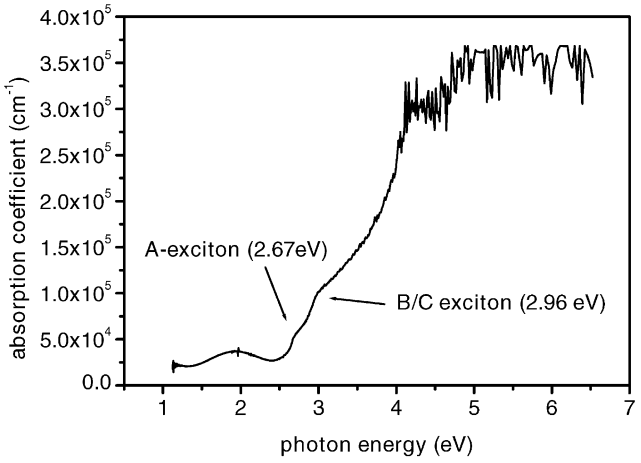


Fig. 6. The transmission spectrum of the annealed $AgGaS_2$ film measured at room temperature.

Γ point is characterized by the three split bands, Γ_7, Γ_6 and Γ_7. These splitting is due to the spin–orbit interaction (Δ_{so}) and the non-cubic crystalline field (Δ_{cf}) acting on the threefold degenerate p-like valence band. Under the uniaxial stress quasi-cubic model [1], the energy of the Γ_7 valence band relative to the Γ_6 valence band, E_1 and E_2, can be expressed as

$$E_{1,2}=\frac{\Delta_{so}+\Delta_{cf}}{2}\pm\frac{\left[(\Delta_{so}+\Delta_{cf})^2-\frac{3}{8}\Delta_{so}\Delta_{cf}\right]^{1/2}}{2}. \quad (1)$$

The three transitions from the valence bands to the Γ_6 conduction band are referred as A, B and C transition in order of increasing energy. In high-purity semiconductors, it is essential to consider the contribution of excitonic absorption from optical absorption spectra. In Fig. 6a, these peaks originate from three allowed direct transitions between the three upper valence bands to the conduction band called A-exciton, B-exciton and C-

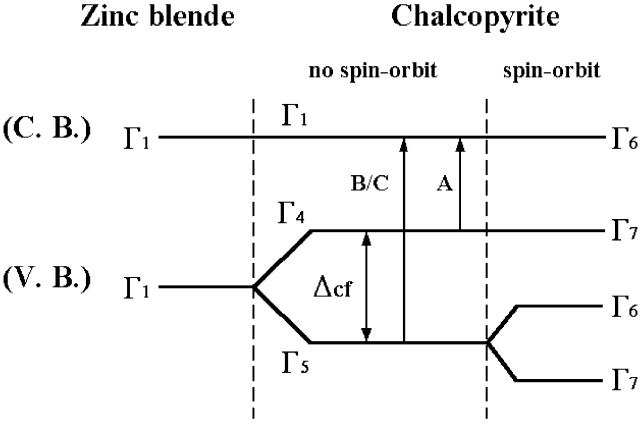


Fig. 7. The band structure of a typical chalcopyrite semiconductor.

exciton peaks. We evaluate the crystal field splitting to be 290 meV, which is very close to the film previously reported [11] and bulk [12,13] results. Since the binding energy of A-exciton is approximately 26 meV [14], we estimate the band gap of $AgGaS_2$ is approximately 2.696 eV at room temperature, which is similar to the finding of other authors [4,5,14,15]. It is indicated that the quantum size effect is not the dominant reason in our experiment.

4. Conclusion

The $AgGaS_2$ film has been successfully prepared by PLD using a KrF excimer laser on quartz glass from a target made of stoichiometric mixture of binary compound powders Ag_2S and Ga_2S_3. XRD studies showed that the deposited films were single-phase materials with chalcopyrite structure and preferential texture along (1 1 2). Moreover, the silver droplets vanished after heat treatment.

From PL measurement, we found the green emission resulted from the DAP transition. After annealing, the exciton energy is slightly red shifted due to the strain effect. We have determined the shallow donor binding energy in the $AgGaS_2$ films from the Arrhenius plot of temperature dependent PL which is very close to that of bulk crystal. In addition, the A- and B/C-exciton were estimated at room temperature by analyzing the observed transmittance spectra. It indicates that the post-annealing treatment improves the film quality.

Acknowledgments

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