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Structural, morphological, electrical and optical properties of PbSe thin films sputtered at various pressures

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ABSTRACT

Optical band gap control of lead selenide (PbSe) thin films is essential for realizing the practical applications. In this paper, PbSe thin films have been deposited by radio frequency (RF) magnetron-sputtering with varied sputtering gas pressures from 0.5 to 4.0 Pa. A systematical investigation of the film properties was carried on. X-ray diffractometry, atomic force microscopy, Hall effects measurements and UV–vis spectroscopy analyses were performed to investigate the crystal structural, morphological, electrical and optical properties of the films. The sputtering pressure has a significant effect on the structure and properties of the PbSe thin films. The intensity of the preferred orientation (200) increases with sputtering pressure up to 3.0 Pa, and then decreases at 4.0 Pa. The films are composed of equiaxed spherical crystals, whose roughness tends to increase with pressure. According to the Hall effect measurements, the resistivity linearly decreases from 1.6 Ω cm to 0.02 Ω cm, and the carrier concentration decreases from 1.19×10^{20} cm^{-3} (0.5 Pa) to 4.0×10^{17} cm^{-3} (4.0 Pa). The optical band gap ranges from 1.22 to 1.52 eV. The suitable pressure range is 2.0–3.0 Pa in this study.

1. Introduction

Owing to their versatile optical and electrical properties, especially the multiple exciton generation (MEG) effect [1], nanocrystalline IV-VI compound semiconductors have captured considerable attention. Among those materials, lead selenide (PbSe) has been intensively pursued not only for its fundamental scientific interest, but also for many technological applications [2]. Generally, the structure, especially the narrow band gap (0.28 eV [3]) of PbSe thin films could be tuned by varying their composition [4] and deposition parameters [5,6], to fulfill the higher conversion efficiency of solar cells based on PbSe films. These studies have established the correlation between the band gap structure and deposition mechanisms [7]. Therefore, it is achievable that control over the deposition parameter can consequently allow for control over the properties of PbSe thin films [8].

By far, a multitude of deposition techniques have been employed to prepare PbSe films, such as chemical bath deposition [9], electrochemical deposition [10], thermally evaporation [2,11], and so on. Compared with these above methods, magnetron sputtering has been focused as one of the most competitive techniques, by virtue of the lower costs, easier handling and higher quality products.

In the case of sputtering, transport of the sputtered species is controlled by parameters like device geometry and gas pressure [12,13]. Control over films crystal grain shape, size and orientation, intrinsic stress, defect densities and morphologies by varying the sputtering parameters is critical for obtaining high quality semiconductor films with expected structure and physical properties [13,14].

Accordingly, the working gas pressure is considered as one of the most crucial parameters to tailor films structure and properties [15]. Zhu et al. [16] have reported that decrease of pressure improved the crystallinity and orientation of the sputtered fresnoite thin films, due to the increase of the mean free path and the impacting energy of ions at low working pressure. Flickyngerová [17] found that both working gas pressure and RF power significantly influence crystalline size, roughness and electrical properties in ZnO: Ga thin films. There, however, has been no attempt performed about the effect of argon gas pressure on structure and properties of PbSe thin films. It is still confused whether higher or lower pressure is more favorable. In this paper, we report RF magnetron sputtered PbSe films at various pressures. The dependences of deposition rate, structural, electrical and optical properties on argon (Ar) pressure (P_{Ar}) have been addressed in detail.

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2. Experimental

2.1. Films deposition

PbSe thin films with different P_{Ar} (0.5, 1.0, 2.0, 3.0, and 4.0 Pa) were grown on glass substrates under 9.5×10^{-4} Pa base pressure by the HPVD magnetron sputtering system equipped with the SY-500W radio frequency power source. The hot-pressed PbSe target with 99.99% purity was used in this paper. During the deposition process, high purity Ar gas (99.99%) used as the sputtering ions was introduced into the vacuum chamber with a constant flux of 25 standard cubic centimeters per minute (sccm) controlled by a mass flow controller. The other deposition parameters were target-substrate distance (50 mm), RF power (80 W), substrate temperature (200 °C), deposition time (60 min).

2.2. Characterization

The thickness of the thin films was measured by a step profiler (Dektak 150, Veeco Instruments). X-ray diffraction (XRD) analysis of the as-deposited films was performed on Bruker D8-Focus diffractometer using Cu Kα radiation (λ = 0.15406 nm), which was generated at 40 kV voltage and 40 mA current. XRD patterns were recorded from 10° to 80° (2θ) with 4°/min scanning rate. Surface morphology of the films was observed on a Shimadzu SPM9500-J3 atomic force microscopy (AFM). The images were acquired at 256 × 256 pixels. The electrical resistance, carrier concentration and mobility of the PbSe thin films were investigated by the Hall effect measurements using Keithley 2000 and 2400 with 6150 Gs magnetic field intensity. UV–Vis spectra were recorded by Gangdong UV-3501 Spectrophotometer from 300 to 1100 nm. The Energy Dispersive X-ray Spectrometer (SEDX 500, Shimadzu) attached to the Scanning Electron Microscope (SEM, SSX-550, Shimadzu) was adopted for composition analysis of the films. During process, the area was excited with 15 keV X-ray for 60 s. For quantitative analysis, the ZAF correction method was used, and the error of measurement is about 0.1%. All measurements were performed at room temperature.

3. Results and discussion

3.1. Film deposition rate

The variation of film deposition rate with P_{Ar} was given in Fig. 1. The plot reveals that the deposition rate decreases linearly from 18.2 nm/min (0.5 Pa) to 9.58 nm/min (4.0 Pa) with P_{Ar}, dropped about 47.4%. It is interesting that the deposition rate slightly decreases at the beginning (up to 2.0 Pa), and then rapidly reduces at further increase of pressure. Generally, as P_{Ar} is increasing, mean free path of the species reduces due to more frequent collisions [18]. This results in the decrease in the fluxes of the sputtering ions arriving at the target and the sputtered atoms arriving at the substrate. As a consequence, the deposition rate decreases. Similar results have been reported by other authors for various films [19,20].

3.2. Crystal structure

The XRD patterns of PbSe films sputtered with diverse P_{Ar} are shown in Fig. 2. All patterns correspond to the FCC cubic chalcogenide phase, which is consistent with the standard JCPDS 65-0327. According to the patterns, all films show predominant (200) orientation at around 2θ = 29.24°. In order to distinguish the (200) peak of the patterns at pressures between 1.0 and 4.0 Pa, it is highlighted as presented in the inset of Fig. 2. Obviously, as P_{Ar} rises from 1.0 to 3.0 Pa, the dominant (200) peak is intensified. At further increase of pressure from 3.0 to 4.0 Pa, however, the dominant (200) peak becomes less intense. The most obvious preferred orientation in (200) at 2.0 and 3.0 Pa highlights

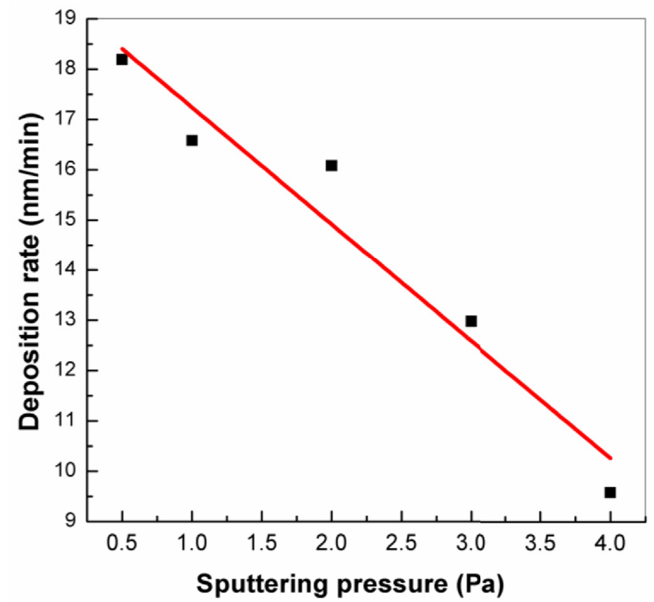

Fig. 1. Variation of the deposition rate of PbSe thin films as P_{Ar} increases from 0.5 Pa to 4.0 Pa.

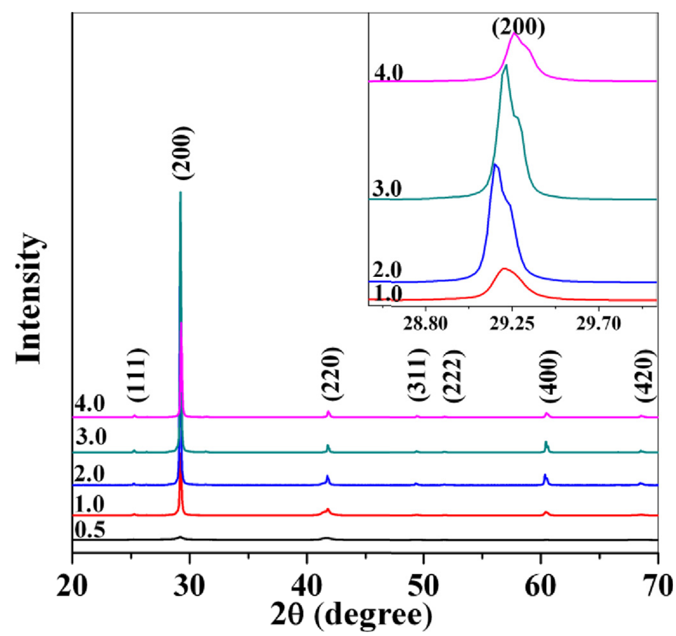

Fig. 2. XRD patterns of PbSe thin films deposited at different P_{Ar}. The (200) peak at pressures between 1.0 and 4.0 Pa in the 2θ range of 29.2–30.6° is highlighted as an enclosed plot.

the best crystallinity, which demonstrates 2.0–3.0 Pa P_{Ar} favors the preferred growth in (200) direction.

In principle, the Bragg peak broadening in an XRD pattern is due to a combination of grain refinement and lattice strain. The average crystallite size, D, for the (200) reflection was estimated based on the Williamson–Hall method [21].

$$\beta \cos \theta = \left(\frac{0.89\lambda}{D}\right) + (4\varepsilon \sin \theta) \tag{1}$$

where λ denotes the wavelength of the X-ray radiation, β represents the full width at half maximum (FWHM) of the (200) peaks and θ is the angle of the diffraction peaks. Here, $\sin\theta$ and $\beta\cos\theta$ act as horizontal and vertical coordinates, respectively. Thus, the values of microstrain