



Structure and composition effects on electrical and optical properties of sputtered PbSe thin films



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ABSTRACT

Lead selenide (PbSe) thin films were grown on Si (111) substrates using magnetron sputtering, and the structure and composition effects on the photoelectric and optical properties of the sputtered PbSe thin films were studied using field emission scanning electron microscope, energy dispersive X-ray detector, X-ray diffraction, X-ray photoelectron spectroscopy, physical property measurement system and Fourier transform infrared spectroscopy. The optical band gaps of all the sputtered PbSe thin films ranged from 0.264 eV to 0.278 eV. The PbSe thin film prepared with oxygen flux 1.0 sccm, deposition time 240 min, sputtering power 150 W and substrate temperature 150 °C showed the highest resistance change rate under illumination, about 84.47%. The variation trends of the photoelectric and optical properties with the average crystal size, lattice constant, oxygen content and lattice oxygen percentage were similar, respectively. The sputtered PbSe thin films showed poor photoelectric sensitivity, when the average crystal size was similar to the Bohr radius (46 nm), while the photoelectric sensitivity increased almost linearly with the oxygen content in the thin films, indicating that both deviating the average crystal size from the Bohr radius and increasing the oxygen content are two direct and effective ways to obtain high photoelectric sensitivity in PbSe thin films.

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1. Introduction

In 1874 Ferdinand Braun was the first to report electrical rectification with natural galena (lead sulfide, PbS) [1]. From then on, lead chalcogenides (PbS, PbTe and PbSe) and their alloys (PbSeTe, PbSnSe, PbSnTe and PbSnSeTe) were widely used as semiconductor devices, such as light emitting diodes [2], laser diodes [3], infrared photo-detectors [4], solar cells [5] and thermoelectric devices [6], due to their excellent photoelectric and thermoelectric properties.

Lead chalcogenides are typical narrow band gap materials (0 eV to 0.5 eV), leading to a remarkable spectrum absorption range from 3 μm to 30 μm for the lead chalcogenide devices [7]. On the other hand, the high permittivity of lead chalcogenides can effectively shield the charge carriers from the lattice defects, yielding superior fault-tolerant properties [8].

Compared with other lead chalcogenide materials, lead selenide (PbSe) has the largest exciton Bohr radius of about 46 nm and a relatively small effective mass of the excited electron–hole pair, which allows remarkable quantum confinement in large crystals [9]. In addition, the PbSe infrared detectors can maintain excellent detective ability in the

mid-wavelength infrared range, even at room temperature, which leads to a great interest in the fundamental studies of this material and its alloys [10–14].

The deposition of the PbSe thin films has been carried out by a variety of chemical and physical deposition techniques, such as chemical bath deposition [15], electrochemical deposition [16], thermal evaporation [17], atomic layer deposition [18], molecular beam epitaxy [19], sputter deposition [20] and several other improved methods [21–23]. In the present work, the magnetron sputtering technique was used to deposit the PbSe thin films due to its medium cost, easy handling, high quality products and the potential for mass production, compared with other methods. Moreover, multiple deposition parameters, such as the gas flux, sputtering power, distance between the target and the substrate, substrate temperature, deposition time and so on, can be varied to modify the physical and chemical properties of the sputtered PbSe thin films, which in turn affect the performance of the PbSe devices. Within this research, two parameters, oxygen flux and deposition time, were varied in order to prepare the different composition and structure PbSe thin films, while other parameters remained the same, based on the previous experiments.

The photoelectric and optical properties of the PbSe thin films are affected by several factors, including the film thickness, composition, and crystal structure. Barote et al. [24] found that the average crystal size, band gap, carrier mobility and concentration of the chemical bath

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deposited PbSe thin films all increased with the film thickness. On the other hand, Jung et al. [20] demonstrated that the oxidized surface of the radio frequency magnetron sputtered PbSe nanowires significantly influenced their optical properties and produced strong confined states. Moreover, Gautier et al. [25] found that the oxygen-induced sensitization in the polycrystalline PbSe could alter the microstructure, phase composition, and other material properties. However, most of the previous reports dealt with the sensitization treatment after the deposition of the PbSe materials, while the influence of the oxygen sensitization treatment during the preparation of the PbSe thin films has not been studied in detail yet.

In the present work, the PbSe thin films with different composition and structure were deposited on Si (111) substrates using magnetron sputtering technique with different deposition parameters. In order to identify the optimistic deposition parameters, the relationships between the composition, crystal structure, surface composition, photoelectric and optical properties of the sputtered PbSe thin films were studied using the field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and the physical properties measurement system (PPMS). Moreover, the effects of the structure (mainly average crystal size and lattice constant) and composition (mainly oxygen content and lattice oxygen percentage) of the sputtered PbSe thin films on the photoelectric and optical properties of the sputtered PbSe thin films were studied in detail, which provides guiding significance for the preparation of high quality PbSe thin films.

2. Experiment

2.1. Deposition equipment

PM500-S sputtering system equipped with the MF-5K medium frequency sputtering power source was used to deposit the PbSe thin films. The PbSe alloy targets were prepared by conventional powder metallurgy with the composition of $n_{\text{Pb}}:n_{\text{Se}} = 45:55$ (99.99% purity), based on the easier deposition of the Pb element than the Se element due to the high volatility of the Se element and different condensation coefficients for these two elements. The single-side polished Si (111) wafers with $15 \times 10 \times 0.5 \text{ mm}^3$ dimensions were chosen as the substrates. Prior to being fixed to the substrate holder, these Si substrates were ultrasonically washed in deionized water, ethanol and acetone for 15 min, respectively.

2.2. PbSe thin films deposition

The PbSe thin films were grown on the Si (111) substrates by the magnetron sputtering with different deposition parameters under $5 \times 10^{-3} \text{ Pa}$ base pressure. During the whole sputtering process, two different oxygen fluxes and three deposition times were used to prepare the PbSe thin films while other sputtering parameters remained the same, as listed in Table 1. Moreover, the argon flux was set to 30 sccm during the ion bombarding and magnetron sputtering process.

Table 1
Sputtering process parameters for the PbSe thin films.

Sample	Oxygen flux (sccm)	Time (min)	Sputtering power (W)	Substrate temperature (°C)
PbSe1	0.5	120	150	150
PbSe2	0.5	180	150	150
PbSe3	0.5	240	150	150
PbSe4	1.0	120	150	150
PbSe5	1.0	180	150	150
PbSe6	1.0	240	150	150

According to the previous research, the film thickness significantly affects the average crystal size and the lattice constant, which in turn affects the photoelectric and optical properties of the PbSe thin films [26]. In the present work, the deposition time was set to 120 min, 180 min, and 240 min, respectively.

The film surface oxidation technique during (or after) the deposition process, also known as “sensitization”, is essential to obtain remarkable photoelectric and optical properties in the PbSe thin films. Within this process, oxygen atoms act as acceptors, causing the appearance of the p-type charge carriers, whose presence can radically change the physicochemical properties of the thin films [27]. In addition, the oxygen atoms can create impurity levels in the forbidden band of the PbSe thin films, which can increase the density of states, and subsequently increase the charge carrier concentration during the activation process, such as illumination [28]. However, oxygen can react with the PbSe target, and the products will cover the target surface and create excess positive charges, which will increase the target surface positive potential and decrease the cathode dark space negative potential, and when the cathode dark space negative potential reaches zero, the sputtering process will be ceased. This process is also known as target poisoning [29]. Thus, the oxygen flux was set to less than 1 sccm, based on the previous research results.

2.3. PbSe property characterization

The field emission scanning electron microscope (FE-SEM, Zeiss Auriga) with 15 kV operating voltage was used to study the surface and cross-section morphology of the sputtered PbSe thin films.

The photoelectric properties of the sputtered PbSe thin films were characterized by the resistance change rate under certain illumination. The resistance of the films was recorded in the dark for 300 s and under illumination (using a 275 W infrared light source) for another 300 s with a step of 20 s. The resistance change rate under illumination, labeled as $\Delta \bar{R}_t$, was calculated as follows:

$$\Delta \bar{R}_t = \frac{R_D - R_{Lt}}{R_D} \times 100\% \quad (1)$$

where R_D represents the average value of the dark resistance recorded before the illumination treatment and R_{Lt} is the value of the light resistance of the sputtered thin films at the illumination time t . The dc electrical resistance of the sputtered PbSe thin films was measured using the four-probe method as a function of the film temperature from 25 °C to 100 °C using the physical properties measurement system (PPMS, Quantum Design, Inc., USA). A quick drying silver paste was used to bond the electrode line in order to decrease the ohmic contact.

The XRD studies were performed on the rotating anode diffractometer (Dmax-RB 12 kW, Rigaku, Japan) with the Cu radiation source, $\lambda = 1.5406 \text{ \AA}$. These measurements were undertaken at a scan rate of $8^\circ/\text{min}$ for the 2θ scanning angle ranging from 10° to 65° .

The surface composition of the sputtered PbSe thin films was analyzed by the X-ray photoelectron spectroscopy (XPS) measurements performed using the AXIS ULTRA^{DLD} (Shimadzu, Japan) X-ray photoelectron spectrometer equipped with the Al $K\alpha$ source, $h\nu = 1486.6 \text{ eV}$. The operating voltage and power were 12 kV and 200 W, respectively, and the vacuum was $1 \times 10^{-7} \text{ Pa}$. In order to study the thickness of the oxide layer and the difference of chemical states on and beneath the film surface, additional XPS analysis was performed on the PbSe6 sample after the film surface was etched for 60 s by Ar^+ with the etching energy of 3000 eV. The Ar^+ etching and XPS analysis cycle was conducted eleven times.

The optical properties of the sputtered PbSe thin films were studied using the infrared absorption spectra recorded on the Nicolet Nexus 470 Fourier transform infrared spectrometer (FT-IR) ranging from 4000 cm^{-1} to 400 cm^{-1} at room temperature.

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