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SnSe Thin Films Were Prepared by Electron Beam Deposition Technique

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Abstract

Tin selenide (SnSe) is a typical two-dimensional (2D) semiconductor material, which has attracted extensive attention in the field of new optoelectronics due to its excellent electrical and optical properties.In this paper, tin selenide (SnSe) thin films were successfully prepared on soda-lime glass substrates by electron beam deposition technology, and related tests were carried out using characterization equipment. The effects of different temperatures (25℃, 100℃, 150℃, 200℃, 250℃) on the phase and composition, surface morphology, transmittance and absorption rate of the obtained films were studied by temperature treatment. The results show that the peak intensity of SnSe decreases with the increase of temperature, and the peaks of $SnSe_2$ and SnO_2 appear at the same time. In addition, SnO was initially formed and gradually transformed into SnO_2 at 200℃, and the intensity of the SnO peak completely disappeared at 250℃. The absorptivity of SnSe thin films decreases with the increase of temperature, and the maximum absorptivity (about 1.4) is obtained in the visible light range. The absorptivity of the five groups of thin film samples is below 1.2 in the range of 900-1400nm. The transmittance of the film increases with the increase of temperature, and has a high transmittance in the near-infrared region. The transmittance of all samples in the visible light band remains below 25%.

Keywords

SnSe Thin Films; Electron Beam Deposition; Optical Property.

1. INTRODUCTION

Thermoelectric conversion technology is a technique of directly converting thermal energy into electrical energy using semiconductor materials. It is favored by researchers due to its small system volume, no pollution, no noise, zero emissions, and wide range of applicable temperatures. Using this technology, the temperature difference in nature and industrial waste heat can be converted into electricity for daily use, which is clean and pollution-free, and has good social benefits. The performance of thermoelectric materials is generally judged by the thermoelectric figure of merit (ZT). Excellent thermoelectric materials usually have higher ZT values. The definition of ZT is

$$ZT=S^2\sigma T/\kappa \quad (1)$$

In the formula , S, σ, κ and T are Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. $S^2\sigma$ is the power factor (PF). It can be seen that good thermoelectric materials should have excellent thermoelectric materials need to have

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a high Seebeck coefficient to generate a large potential difference, a high electrical conductivity σ to reduce Joule heat loss, and a low thermal conductivity κ to prevent heat loss, so as to have a high ZT value. The greater the ZT, the greater the thermoelectric conversion efficiency.

At present, people have found many thermoelectric materials with high application value through research. For example, PbTe (ZT=1.5) [1], Bi-Te thermoelectric materials (ZT=1.4)[2], and Cu_2Se (ZT=1.6)[3] have been widely used in the middle temperature region. However, considering the resource reserves, environmental compatibility and ZT value, the above materials do not have optimal characteristics. Therefore, a thermoelectric material with excellent performance, environmental friendliness and abundant reserves is urgently needed to meet the production and application of today 's society. In 2014, a research team from Northwestern University and University of Michigan[4] prepared single crystal tin selenide (SnSe) with good performance by using the Bridgman method, and found that single crystal SnSe has good photoelectric and thermoelectric properties. The ZT value of SnSe can reach 2.6 at 923K.This major discovery of performance has led researchers to turn their attention to SnSe materials. SnSe is a member of the IV-VI narrow band gap semiconductor[5]. It has become a research hotspot in the field of thermoelectric conversion due to its excellent photoelectric properties, non-toxicity, cheap raw materials and relatively abundant advantages. Because of its orthorhombic crystal structure[6], it has great application prospects in the field of solar cells. In addition, SnSe is also a p-type semiconductor with a moderate band gap (1.0-2.0eV) and a high absorption coefficient ($10^5 cm^{-1}$), which also ensures almost complete absorption of solar radiation[7] and is suitable for photovoltaic applications. There are four solid phases in the Sn-Se system (Se, Sn, SnSe and $SnSe_2$), which makes the phase composition of SnSe compounds easier to control during growth[8]. Tin selenide usually exists in the form of two phases, namely SnSe and $SnSe_2$. However, some researchers have observed a third phase in the experiment, namely Sn_2Se_3[9]. The experimental test shows that the phase of Sn_2Se_3 is the superposition of SnSe and $SnSe_2$.

In recent years, due to the poor mechanical properties of SnSe single crystals, strict crystal growth conditions, and high production costs, the preparation of polycrystalline SnSe cannot control its morphology, and the ZT value is much smaller than that of single crystal SnSe. It is difficult to achieve excellent thermoelectric properties in polycrystalline SnSe. Therefore, researchers gradually focus on the thin film SnSe. SnSe thin films have shown a wide range of applications in solar cells[10], photoelectrochemical cells[11], flexible devices[12], phase change memory[13] and other fields.

The performance of the film is affected by the preparation method. At present, SnSe thin films have been prepared by various deposition techniques, including chemical vapor deposition (CVD)[14] and physical vapor deposition (PVD). The CVD method mainly includes electrodeposition[15], spray pyrolysis[16], atomic layer deposition (ALD)[17] and chemical bath deposition[18]. The PVD method includes magnetron sputtering[19], gradient vapor deposition[20], pulsed laser deposition (PLD)[21], molecular beam epitaxy (MBE)[22] and thermal evaporation[23]. The films prepared according to different deposition techniques exhibit different characteristics. The method of preparing SnSe thin film by magnetron sputtering has the advantages of easy control of deposition rate and thickness. A wide range of material selection and other advantages, but its shortcomings are also very obvious, such as complex coating equipment, high cost, low utilization rate of target materials.

Although the chemical vapor deposition method has the advantages of easy control of purity, low production cost and flexible process, it is not suitable for the preparation of SnSe thin film because of its complex production equipment, and the commonly used reaction raw materials have certain corrosion to the equipment, and the residual gas after the reaction has the risk of easy combustion, explosion or toxicity. The thermal evaporation method has the advantages of

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relatively easy operation, fast film formation rate, good film quality, high purity, low pollution and low energy consumption, and the density of the film can be improved by electron beam deposition. Therefore, by comparing the advantages and disadvantages of various thin film preparation techniques, SnSe thin films were prepared on soda-lime glass substrates by electron beam deposition. The effects of different substrates, film thickness and high temperature on the structure, morphology and optical properties of the films were studied.

2. EXPERIMENTAL

Firstly, the sodium calcium glass and copper crucible bushing with a size of 25mm×25mm×2mm were ultrasonically cleaned in deionized water, acetone and anhydrous ethanol for 20 min, respectively. The natural oxides and pollutants on the surface were removed. The cleaning operation was repeated three times and the surface was dried with nitrogen. Tin selenide thin films were deposited on clean soda-lime glass substrates (cleaned by following standard procedures) using a vacuum coating machine. Domestic SnSe particles were used for deposition. Five groups of samples were prepared under the same deposition conditions. One group of samples was placed at room temperature, and the other four groups of samples were placed at different temperatures of 100°C, 150°C, 200°C, and 250°C for 1 hour (waiting for natural cooling). The samples treated at 25°C, 100°C, 150°C, 200°Cand 250°C were named S1, S2, S3, S4 and S5, respectively, as shown in figure 1. The main process parameters of vacuum coating are shown in Table 1.

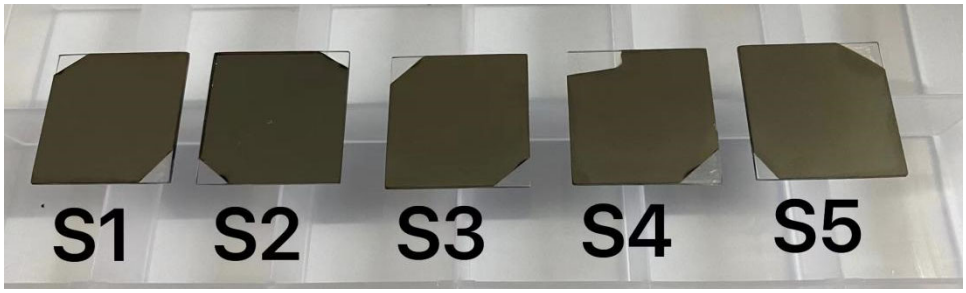

Figure 1. Films treated at different temperatures, 25°C (S1), 100°C (S2), 150°C (S3), 200°C (S4), 250°C (S5)

Table 1. Main process parameters of vacuum coating

Vacuum	Deposition Rate	Electron Beam Power	Baking Temperature	Film Thickness
2×10^{-3}Pa	8Å/s	1%-2%	150℃	1μm

3. RESULTS AND ANALYSIS

3.1. Phase analysis

In order to explore the changes of different components of SnSe thin films at different temperatures, Raman studies (50-350 cm^{-1} range) were carried out.

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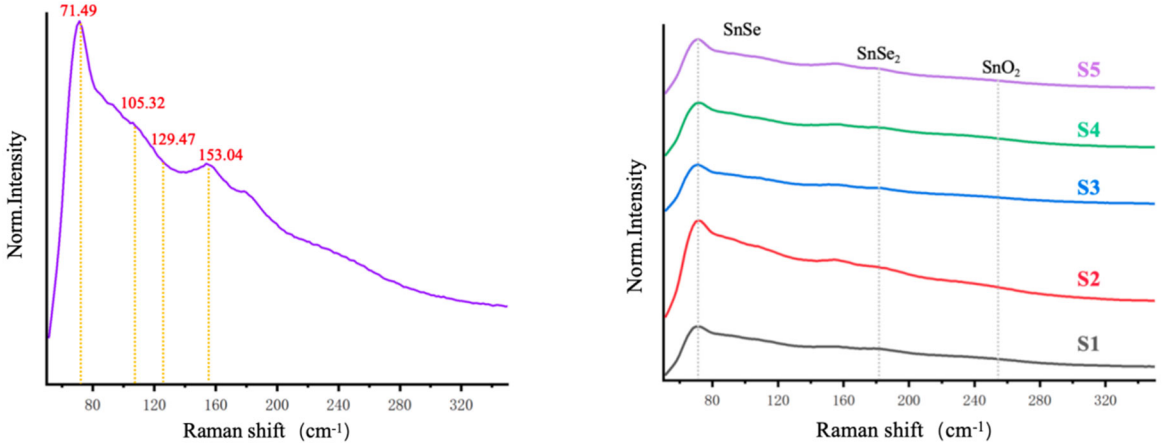
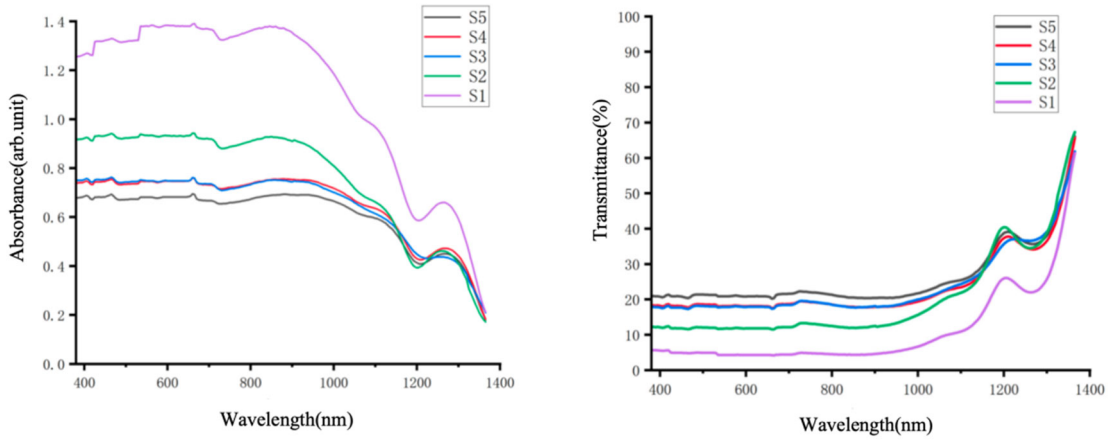


(a) (b)

Figure 2. Raman spectra of the films at 25°C (a) and comparison of Raman spectra at different temperatures (b)

At room temperature, as shown in Fig.2 (a), the characteristic peaks appear at 71.49 cm^{-1},105.32 cm^{-1},129.47 $cm^{-1}$and 153.04cm^{-1}, corresponding to the,, and modes of SnSe, respectively[24], and a very weak peak corresponding to $SnSe_2$ (116.92cm^{-1} and 185.44cm^{-1})[25] [26]. The exposure of Sn^{2+} in the air leads to surface oxidation, and Raman spectroscopy shows the presence of these compounds, so the trace presence of these compounds can be inferred in the sample (S1) at room temperature. As the temperature increases, as shown in Fig.2 (b). The intensity of the peak corresponding to SnSe in the film decreases, and $SnSe_2$ and SnO_2 appear in the Raman spectrum. The peaks associated with $SnSe_2$ and SnO_2 become sharper. The initial $SnSe_2$ and SnO_2 (disordered) amorphous phases gradually transformed into crystalline phases. In addition, SnO is initially formed and gradually transformed into SnO_2, and the intensity of the SnO peak increases at 200°C and disappears at 250°C.

3.2. Optical performance analysis



(a) (b)

Figure 3. Absorption spectra (a) and transmission spectra (b) of SnSe thin films treated at different temperatures.

Figure 3 (a) is the absorption curve of SnSe thin film at different temperatures with the wavelength range (380-1400) nm. It can be concluded from the curve law that the absorption rate of the film decreases with the increase of the wavelength, and the absorption edge of the film moves to the short wavelength direction after increasing the temperature. With the

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increase of temperature, the crystallinity of the film increases, which leads to the decrease of grain boundary and grain growth, thus reducing the light absorption of the film. It can be seen from 3 (a) that when the temperature is 250 °C, the SnSe thin film has a high absorption rate in the range of 380-900 nm, up to about 1.4, and the absorption rate of the five groups of thin film samples in the range of 900-1400 nm is below 1.2. The results show that SnSe thin films are indeed suitable for solar cells, lithium-ion batteries and photovoltaics.

The transmittance of SnSe thin films before and after different temperature treatment is shown in Figure 3 (b). It can be seen from the figure that the transmittance of the film increases with the increase of temperature, and the film has a high transmittance in the near-infrared region, up to about 70%. The transmittance of all samples in the range of 380-1000nm is below 25%. Therefore, the light absorption and transmittance of SnSe thin films are related to the change of crystal structure of thin films after temperature rise.

3.3. Micromorphology analysis

The morphology plays a crucial role in determining the physical properties. Therefore, the surface morphology of SnSe films was studied by scanning electron microscopy (SEM). The SEM image of the sample is shown in Figure 8. It can be seen from Figure 8 (a) that the surface of the SnSe thin film grown at room temperature is a small circular grain that gradually spreads along the horizontal direction of the substrate at a magnification of 50,000 times. The surface is uniform, flat and the particle size is uniform. The particles are densely arranged to form a continuous film layer. This morphology of SnSe film is beneficial to the diffusion and transport of carriers in the film and improves the thermoelectric figure of merit of the film. When the temperature at both ends of the thin film sample is different, a thermal electromotive force will be generated.

From Figure 8 (c), it can be seen that the surface of the layer has a slight wavy fluctuation and presents a certain concave and convex change, but the film is still relatively flat on the whole. The deposited SnSe grains are arranged neatly, and the grains are spherical, with a diameter of about 10-30 nm. The particles are arranged closely and neatly to form a dense film.

It can be seen from Fig.8 (e) that the diameter distribution range of the particles in the film continues to expand, and the small-diameter particles and large-diameter particles are interlaced and densely distributed. Small particles are densely filled between large particles, closely and evenly arranged with each other, and the density of the film is increased. At the same time, as the temperature increases, the flatness also increases, forming a denser grain morphology composed of nano-circles. This provides a better transport channel for the transport of electrons and holes.

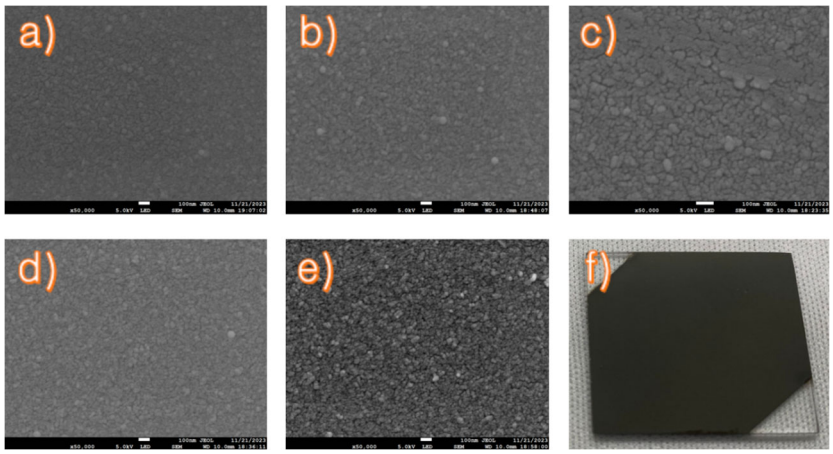

Figure 4. SEM images of SnSe (a) at 25°C (S1), (b) at 100°C (S2), (c) at 150°C (S3), (d) at 200°C (S4), (e) at 250°C (S5), (f) SnSe thin films deposited on soda-lime glass.

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4. CONCLUSION

In this paper, 1μm thick SnSe thin films were successfully deposited on soda lime glass substrates by electron beam thermal evaporation. In order to understand the possible applications of thin films in thermoelectric, photovoltaic, gas sensing and other aspects, the prepared thin films were studied at high temperature, and the effects of different temperatures (25°C, 100°C, 150°C, 200°C, 250°C) on the structure, optical properties and surface morphology of SnSe thin films were investigated. The results show that the average grain size of the films decreases with the increase of temperature. A part of SnSe phase transforms into $SnSe_2$ phase, and then evolves into SnO_2. The absorption rate of the film decreases with the increase of temperature, and the transmittance increases with the increase of temperature. As the temperature increases, the flatness of the film surface also increases, forming a denser grain morphology composed of nano-circles. This morphological feature provides a better transport channel for the transport of electrons and holes. In summary, the research shows that SnSe thin films are suitable for applications in photovoltaic and other fields.

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