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An economical method for amorphous selenium thick films preparation: e-beam evaporation

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ABSTRACT

We report a controllable, economical and rapid preparation of amorphous selenium (a-Se) thick films by using e-beam evaporation technique. Characterization including X-ray diffraction, Raman and FTIR spectroscopy confirm the amorphous nature of the as-grown films. The films in thickness as high as 267 μm were obtained with a deposition rate of 2.11–2.3 μm/min. A Raman shift peak at 252.4 cm^{-1} and the absorption of the vibration band at 487.9 and 737.7 cm^{-1} in FTIR spectra are related to the disordered Se chains and Se_8 rings assigned to a-Se. All the results indicate that the e-beam evaporation is a promising technique for a-Se films fabrication.

1. Introduction

Amorphous selenium (a-Se) has drawn considerable attention because of its commercial importance as a high sensitivity photodetector, an avalanche solid-state imaging device and a direct conversion imaging x-ray detector material [1–4]. One of the distinguishing drawbacks of a-Se is a crystallization transition from the amorphous phase at 40–50 °C [5,6]. As a consequence, the temperature must be strictly regulated during the film preparation, device fabrication and application. Doped with a content of 0.2–0.5% arsenic (As) to create a-Se-As alloy and coated with some kind of polymer layer can improve the resistance of crystallization [5–8]. Generally, the pure a-Se and doped a-Se alloy films were prepared by conventional thermal evaporation with source temperature 300–400 °C while maintaining the substrate temperature at 65 °C or less. [9]. In the area of a-Se based flat panel detectors (FPD) the thickness of a-Se alloy layers is acquired above 200 μm to achieve sufficient absorption toward x-ray photons [1]. By using thermal evaporation, a considerable time is needed to deposit so thick a-Se films owing to the low evaporation rate. The substrate temperature will rise inevitably via the heat radiation from the elevated source, which would result in crystallization. Due to the material direct contact with the boat, it is possible to introduce contaminations during the evaporation and film deposition. Therefore, it is important to seek other techniques capable of economical and high-efficiency fabrication of a-Se thick films suppressing the temperature and contamination. The e-beam evaporation (eBE) method is considered for its controllable and high evaporation rate of about 1–5 μm/min without heat radiation from the source heating the substrate. Hardly any contamination from the crucible will be presented because the e-beam only heats the source material. In this work we prepare and evaluate the pure a-Se thick films deposited by using eBE. Highly smooth and uniform a-Se thick films were obtained. The characterization of morphology, structure and optical and electrical properties show that eBE is a potential technique for high-quality a-Se (pure and alloyed) films preparation.

2. Experiments

All the a-Se thick films were deposited by using eBE method. Selenium powder (99.99%, Emei semiconductor material institute, China) was loaded in a graphite crucible with continuous water cooling during the evaporation. The a-Se films were deposited on glass substrates with a source-to-substrate distance of 100 mm. The e-beam power was controlled from 280 to 300 W. The film growth was performed with the pressure maintained to 10^{-3}–10^{-4} Pa. The substrate temperature is maintained at room

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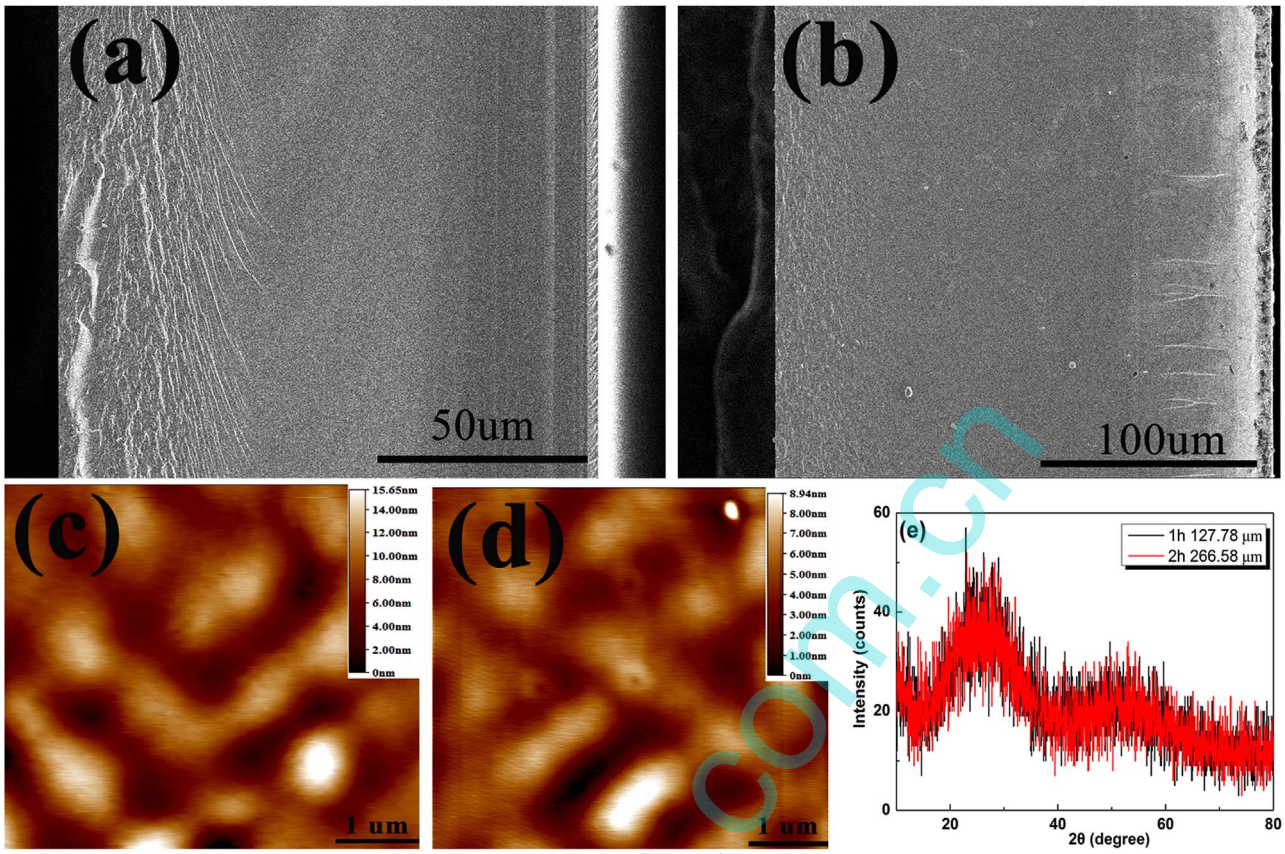

Fig. 1. Cross-sectional SEM images of the films deposition for (a) 1 h and (b) 2 h. Surface AFM images of the films deposition for (c) 1 h and (d) 2 h. (e) XRD pattern of the as-grown a-Se thick films.

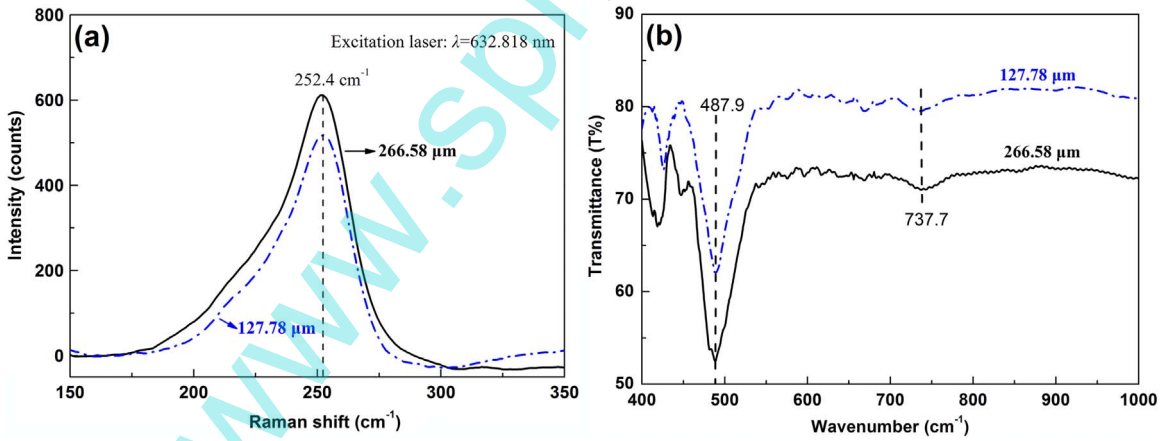

Fig. 2. (a) Raman and (b) FTIR spectra of the as-grown a-Se thick films.

temperature without any cooling measures. The morphology of the as-grown films was inspected by using a S-3400 N scanning electron microscope (SEM) for cross-section and a CSPM5500 contact mode atomic force microscopy (AFM) for surface observation. The amorphous structure was identified by X-ray diffraction (XRD), Raman and FTIR spectroscopy. The XRD was performed using a DX-2700 CuKα radiation (1.54 Å, 30 kV, 20 mA), varying the scanning angle from 10° to 80° with step of 0.03°. The room temperature Raman spectra were recorded using a LabRAM HR Raman spectrometer. A semiconductor laser used for excitation was 632.8 nm with a power of about 5 mW selected to prevent local heating effects. The optical property was analyzed using a Shimadzu UV-2550 spectrophotometer and a FTIR (IR Prestige-21) spectroscopy. The measurements of optoelectronic properties were performed by an Agilent B2912A precision source/measure unit as well as an integrated X-ray source (Optima 97,008, Oxford Instruments).

3. Results and discussion

The thickness of the as-grown a-Se films was measured from SEM cross-section view, as shown in Fig. 1(a) and (b). The films with 1 and 2 h continuous deposition are about 127.78 μm and 266.58 μm thick, respectively. The deposition rate is estimated about 2.11–2.3 μm/min, which is higher than that with conventional thermal evaporation [10,11]. Actually, the deposition rate is mainly controlled by e-beam power and as high as 5 μm/min can

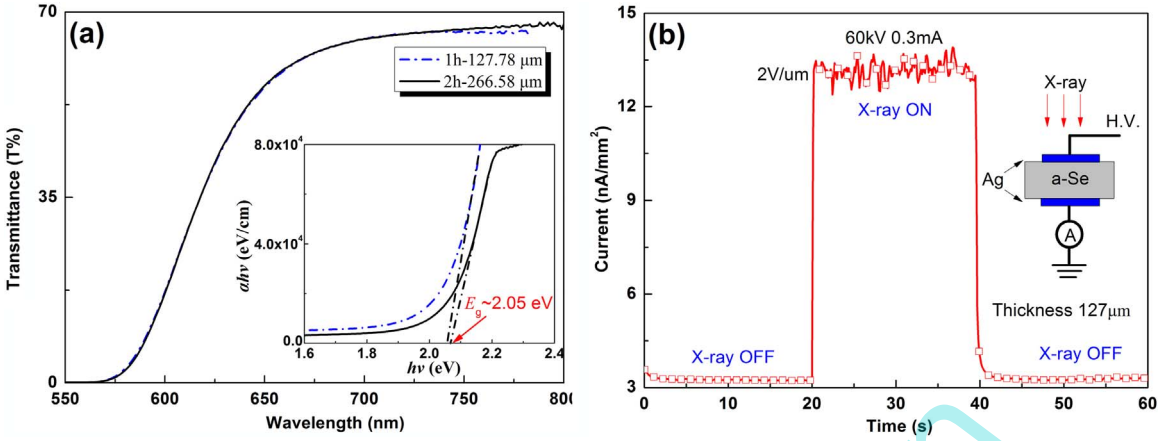

Fig. 3. (a) Optical transmittance spectrum and $\alpha h\nu$ versus $h\nu$ curves of the as-grown a-Se thick films. (b) X-ray response of the pure a-Se film (127 μm in thickness) with Ag electrodes. The X-ray tube voltage and tube current is 60 kV and 300 μA, respectively.

be obtained with e-beam power 450 W by using our current evaporator. A long deposition time also can thicken the films. From the cross-section view, one can find that the films are greatly dense without any grain boundary. The as-grown thick films present highly smooth and specular surface. From the AFM analysis, the maximum surface height is about 14 and 8 nm for 1 and 2 h growth time, respectively, as shown in Fig. 1(c) and (d). The surface roughness average decreases from 2.09 to 1.14 nm with the increasing growth time. Even this value was reduced to 0.383 nm when the film in thickness of about 1000 μm.

The structure of the as-grown a-Se films was analyzed by XRD, as shown in Fig. 1(e). No diffraction peaks present in the XRD pattern due to any extraneous and crystallographic phases. It is evident that there is only a broad envelope at $2\theta = 20–60°$ in agreement with published results [12,13]. This shows that amorphous structure films were obtained by using eBE technique.

Meanwhile, this amorphous structure was further confirmed from Raman and FTIR spectral analysis, as shown in Fig. 2. A relatively broad Raman shift peak at 252.4 cm^{-1} is assigned to amorphous nature, which is related to disordered Se chains with a minor contribution of Se_8 rings of the structure present in amorphous selenium [14]. The presented spectrum is in good agreement with the published data [15–17]. The absence of the 235 cm^{-1} indicates that trigonally crystalline Se (t-Se) chain structure which refers to the crystallization Se is not presented [15]. Besides, from the FTIR spectra, the absorption of the vibration band at the wavenumber 487.9 and 737.7 cm^{-1} is also related to Se_8 rings [10,18]. Fig. 3(a) shows the transmittance recorded from ultraviolet to visible light wavelength (300–900 nm). The transmittance is about 64% in 670–800 nm. The optical bandgap $E_g = 2.05$ eV is estimated from the $\alpha h\nu$–$h\nu$ curves, which is in agreement with the reported data [12,19]. The X-ray response measurement shows that the as-deposited a-Se films are sensitive to X-ray pulse, as shown in Fig. 3(b). The dark current is about 3 nA/mm^2 with 2 V/μm applied bias, which is higher than that with As doped and blocking layer coated [3,5].

4. Conclusion

The pure a-Se thick films were prepared by using e-beam evaporation method and characterized with SEM, AFM, XRD, Raman and FTIR spectroscopy. The films in thickness of 127.78 and 277.58 μm were obtained with deposition rate 2.11–2.3 μm/min by this technique, which is higher than that using conventional thermal evaporation. AFM analysis shows the highly smooth surface of the as-grown films with low surface roughness average 1–2 nm. The absence of diffraction peaks in XRD results indicates the amorphous structure nature. A relatively broad Raman shift peak at 252.4 cm^{-1} and the absorption of the vibration band at 487.9 and 737.7 cm^{-1} in FTIR spectra are related to the disordered Se chains and contribution of Se_8 rings assigned to a-Se. The film presents the dark current about 3 nA/mm^2 with 2 V/μm applied electric field and also is sensitive to pulsed X-ray exposure. All the results indicate that the e-beam evaporation technique is capable of controllable, economical and rapid preparation of a-Se thick films. The further works will be focused on fabricating large-area a-Se or alloyed a-Se thick films by using e-beam evaporation.

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