

Preparation and Characterization of ZnSe Film Synthesized by Chemical Co-reduction

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Keywords: Zinc Selenide, phase, morphology, chemical co-reduction.

Abstract. Binary ZnSe thin films were prepared by spin-coating and chemical co-reduction, the effects of reaction conditions on thin films were investigated. The phases of obtained samples were characterized by X-ray diffraction (XRD). The size and morphology of the products were observed by scanning electron microscope (SEM). Experimental results show that, the product sample with high XRD peaks obtained at 200 °C has better crystallinity than those obtained at lower temperatures, which indicates that high temperature was in favor of crystallization; Longer reaction time and low speed spin-coating are also beneficial to crystallization of ZnSe films. Single phase ZnSe thin film with special morphology was prepared by low speed spin coating and reacting for 60 h with ethylene glycol as the solvent on the glass substrate.

Introduction

Zinc Selenide (ZnSe) with about 2.7 eV band gap can be used for optical windows, lenses, mirrors, prisms and optical blanks, slabs particularly for infrared applications due to its extremely low bulk losses, high resistance to thermal shock and stability [1-3]. The efficiency of the solar cell with Cu(In,Ga)(Se,S)₂ buffer layer prepared by chemical vapor deposition has reached 9.6% in 2000 [4]. The CIGSS/Zn(Se,OH)_x heterojunction with conversion efficiency 13.6% was reported by A.Ennaoui et al in the same year [5]. Indian Kale prepared yellow ZnSe thin film by chemical bath deposition with Zn(CH₃COO)₂ and Na₂SeSO₃ as raw materials, which has about 2.85 eV bandwidth and good combination with glass substrate [6]. ZnSe film with (111) preferential growth was successfully prepared by thermal evaporation technique at room temperature on the glass substrate [7]. In this work, the yellow ZnSe thin films with single phase were synthesized by spin coating and co-reduction. The effects of reaction temperature, time and the frequency of spin coating on ZnSe film and the film morphology were investigated.

Experimental

The substrates (glass or silicon) were cleaned in sulfuric acid for 30 min, and then cleaned by ultrasonic in acetone and ethanol respectively for 20 min. They were kept in ethanol and be dried before using. The precursor solution consists of ZnCl₂ and SeO₂ as raw materials with molar ratio of 1:1 in deionized water, ethanol or ethylene glycol. The precursor film with a certain thickness were prepared by repeated spin coating under conditions of low speed 400 r/min, high-speed 3000 r/min and rotation time 5 ~ 20 s for the spin coating machine. The precursor film on the substrate was placed in the reaction vessel with 1 mL hydrazine hydrate as reducing agent and reacted at 160~200 °C for 10~60 h. And then it was taken out for drying, the yellow ZnSe film can be obtained. The phases of obtained samples were characterized by X-ray diffraction (XRD) on a model of Bruker

D8 Advance XRD system with Nifiltered Cu-K α ($\lambda=1.5059$ Å). The size and morphology of the products were observed by JSM6380LA electron microscope (SEM).

Results and discussion

The effect of reaction temperatures on ZnSe phase formation

Fig.1 shows the XRD patterns of ZnSe thin film samples obtained with deionized water as solvent at different temperatures on the glass substrate, which reacting conditions are reacting time 20 h and at 180 °C for a) and 200 °C for b) respectively, Fig.1c is the pattern for the sample b that the peak of NaCl was removed. According to the standard PDF card (No.70-0777) of ZnSe, it can be known that the XRD peaks at 2θ angles of 27.4°, 45.5° and 53.9° are corresponding to (111), (220) and (311) crystal planes respectively. These three XRD peaks are similar to the results of ZnSe thin films prepared by Jeewan Sharma using inert gas condensation method, and the ZnSe films they obtained have preferential growth along (111) crystal plane [8]. From Fig.1 it can be seen that the XRD intensity of product ZnSe film with NaCl impurity is not high. Compared Fig.1a with Fig.1c, the crystallinity of the product film sample obtained at 200 °C is better than that obtained at lower temperatures, which indicates that high temperature is in favor of ZnSe crystallization.

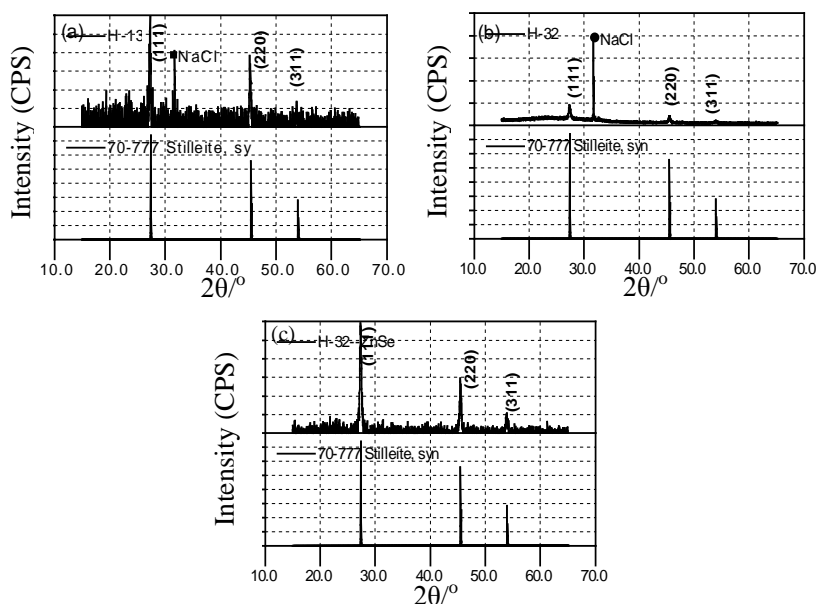


Fig.1 XRD patterns of ZnSe thin film samples obtained at different temperatures

The effect of reaction time on ZnSe phase formation

Fig.2 shows the XRD diffraction patterns of ZnSe thin films obtained under conditions of ethanol as solvent, silicon substrates, 200 °C for 10 h and 20 h respectively. The strong XRD peak at 2θ 32.9° belongs to NH₄Cl impurity phase along crystal plane (110) according to the PDF Card (No.1-1044). Compared Fig.2a with Fig.2b, it is clearly seen that the crystallinity of the product film reacted at 200 °C for 20 h was better than that reacted at 200 °C for 10 h, which demonstrates that longer reaction time is conducive to crystallization.

The effect of spin coating speed on product films

Fig.3 shows XRD patterns of ZnSe thin film samples prepared with different spin-coating speeds, 400r/min for Fig.3a with 30s, 3000r/min for Fig.3b with 30s. Other experimental conditions were 200 °C for 20 h, ethylene glycol as solvent, silicon substrates and spin coating eight times. Compared Fig.3a with Fig.3b, The product sample obtained with low spin coating speed has better crystallinity than that obtained with high speed.

Preparation of ZnSe thin film with single phase

By adjusting reaction temperature and prolonging reaction time, the product film with single phase ZnSe was obtained. Fig.4 shows the XRD pattern of the product film sample obtained at 180 °C for 60

h with ethylene glycol as solvent, it indicates that ZnSe thin film with single phase can be obtained with low spin coating speed on the glass substrate. The XRD peaks at 2θ angles of 27.4° , 45.5° and 53.9° are also corresponding to (111), (220) and (311) crystal planes respectively.

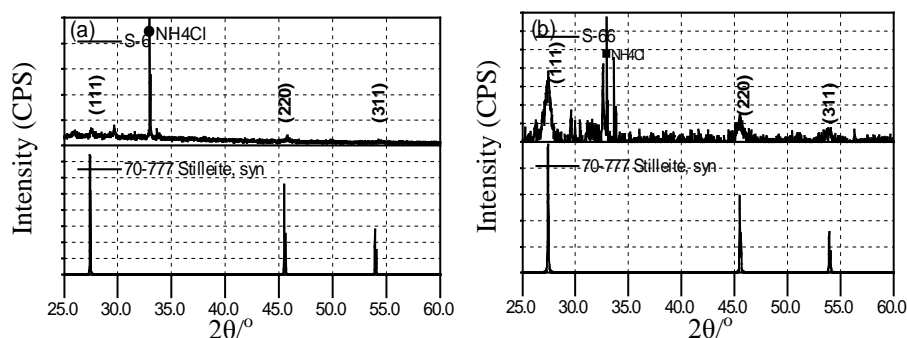


Fig.2 The XRD pattern of the ZnSe thin film sample obtained with different reaction time
a) 200 °C for 10 h b) 200 °C for 20 h

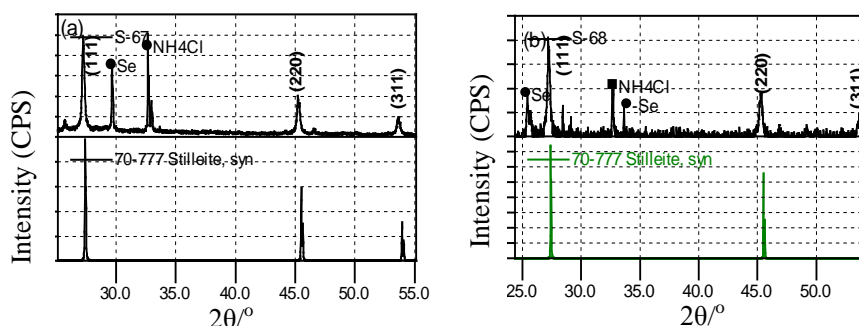


Fig.3 XRD patterns of ZnSe thin film samples prepared with different spin-coating speeds
a) 400r/min for 30s, b) 3000r/min for 30s

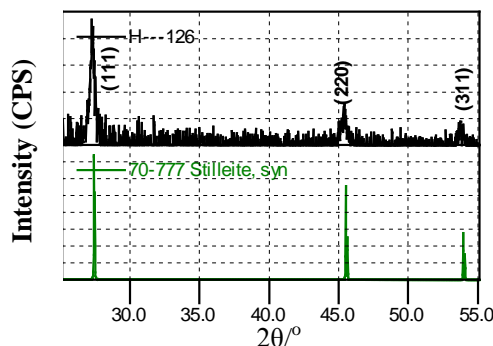
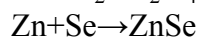
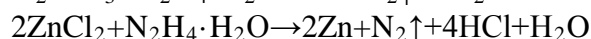
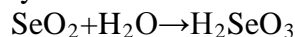


Fig.4 The XRD pattern of the ZnSe thin film sample obtained at 180 °C for 60 h

Fig.5 shows the SEM images of the product sample with single phase ZnSe obtained at 180 °C for 60 h. It can be seen that the film with special morphology is uncontinuous. There are many rings distributing on uniform circular particles. Among which a few of ring is not completely closed with radius of 0.1~1.5 μm and wall thickness about 0.2~0.4 μm .

Analysis of ZnSe thin film synthesizing mechanism

The reaction mechanism of this process, is that the precursor film sample was placed in a reaction vessel and heated, Zn and Se atoms were easily reduced by $\text{NH}_2\text{-NH}_2$, which were very active and easy to combine to form ZnSe compound. The main reactions are as follows.



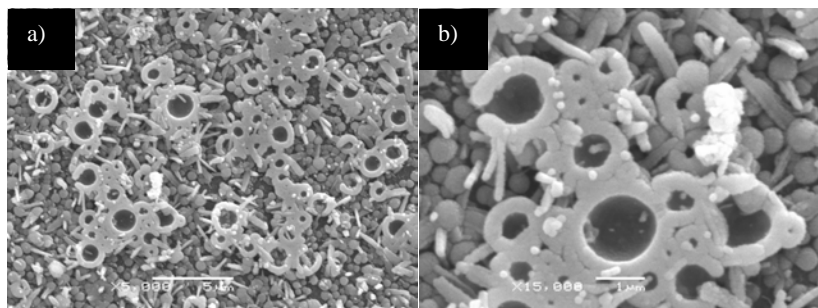


Fig.5 SEM images of the ZnSe thin film sample obtained at 180 °C for 60 h

Conclusions

Binary ZnSe thin films were prepared by spin-coating and chemical co-reduction, the effects of reaction conditions on thin films were investigated. The product sample with high XRD peaks obtained at 200 °C has better crystallinity than those obtained at lower temperatures which indicates that high temperature was in favor of crystallization; The crystallinity of ZnSe film sample obtained by reacting 20 h was better than those obtained by reacting 10 h which indicates that longer reaction time was also beneficial to crystallization of ZnSe films; The crystallization of ZnSe thin film obtained by low speed spin-coating is better than others. Single phase ZnSe thin film with special morphology was prepared by low speed spin coating and reaction 60 h with ethylene glycol as the solvent on the glass substrate.

Acknowledgment

This work was financially supported by the National Natural Science Foundation of China (No.51272140).

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