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Preparation of ZnSe quantum dots embedded in SiO_2 thin films by sol–gel process

Haiqing Jiang*, Xi Yao, Jun Che, Minqiang Wang, Fantao Kong

Electronic Material Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

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Abstract

In this paper, ZnSe quantum dots embedded in SiO_2 thin films was successfully prepared with H_2SeO_4 as selenium source and $Zn(Ac)_2{\cdot}H_2O$ as zinc source by a sol–gel process. Reaction mechanism of synthesizing ZnSe nanocrystallites embedded in silica thin films also was discussed through the XRD and DTA–TG analysis. In the process of synthesizing ZnSe nanocrystallites, $ZnSeO_4{\cdot}H_2O$ crystallites precipitated in organic solvent was prepared first, then the crystallites were reduced with carbon monoxide atmosphere. The XRD analysis reveals the structure of ZnSe phase is sphalerite (cubic ZnS). XPS results show that the atomic ratio of Se/Zn was smaller than the nominal atomic ratio of the sample, which means the selenium element was volatilized seriously. The AFM images show that the size of $ZnSeO_4$ crystallite was increased with the concentration of selenium element. This approach to synthesis of ZnSe nanocrystallites has the potential application in the preparation of optical composite thin films from sol–gel process.

Keywords: A. Films; D. SiO_2; ZnSe; Quantum dots; Reduction

1. Introduction

In addition to quantum wires and quantum wells, fabrication of semiconductor quantum dots is very important for realization of new functional quantum devices due to their large optical nonlinearity. Especially, the II–VI group semiconductor ZnSe quantum dots embedded in strained system has attracted much more attentions for the fabrication of visible semiconductor laser. Yin et al. [1] fabricated the ZnSe quantum dots in glass matrix thin films by pulsed laser evaporation. Li and Nogami [2] prepared the ZnSe crystallites doped in borosilicate glass films by sol–gel method. Lipovskii et al. [3] successfully prepared the II–VI semiconductor nanocrystals in a novel phosphate glass. And also, Huang and Birman [4] investigated a new hybrid exciton state which arises when a regular array of semiconductor quantum dots is placed in a molecular organic medium and numerical estimates ZnSe dots embedded in a typical organic host. Tohge et al. [5] prepared Cd and Zn chalcongenide microcrystals in silica glasses.

In recent years, with the improvement of techniques of preparation of ZnSe single crystal, the transition metal doped the II–VI semiconductor ZnSe single crystal have attracted much attention as a promising IR laser crystal which demonstrate the high quantum radiation efficiency, broadly tunable mid-IR and room-temperature operation [6–9]. And there are lots of achievement have been made on the applications of the transition metal doped ZnSe single crystal as a mid-IR laser material. The combination of quantum dots and this novel laser material provided a new direction of preparation of functional devices.

This paper reports the fabrication of $ZnSe/SiO_2$ composite thin films through the sol–gel method under the carbon monoxide reduction atmosphere. This method is one of the in situ techniques which is quite convenient for preparing composite thin films with lower cost. And it is different with the work of Li who use hydrogen and nitrogen as the reduction medium. Li prepared $ZnSe/SiO_2$ thin composite films using H_2SeO_4 and $ZnCl_2$ as source materials. They prepared $ZnSe/SiO_2$ thin composite films by sol–gel process adding $ZnSeO_4{\cdot}H_2O$ into TEOS sol–gel system under nitrogen and hydrogen reduction atmosphere. But our research works revealed that selenium element would escape from the samples seriously because the reaction between selenium and

* Corresponding author. Fax: +86-29-82668794.
E-mail address: jianghaiqing@vip.sina.com (H. Jiang).

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hydrogen was at rather low temperature, 215 °C, which is the reason why ZnO phase and H_2Se emerged in the samples. In this paper, we successfully synthesized ZnSe/SiO_2 composite thin films using relatively cheap H_2SeO_4 as selenium source and $Zn(Ac)_2{\cdot}2H_2O$ as zinc source under carbon monoxide atmosphere in 500 °C. The synthesis process of ZnSe can solve the problems of the emergence of ZnO phase.

2. Experiment

2.1. Preparation of ZnSe/SiO_2 composite thin films

There are two steps of fabrication of ZnSe/SiO_2 composite thin films [10]. At first, the sol of TEOS was prepared using TEOS, H_2O, NH_4OH. The TEOS was mixed with water under NH_4OH catalysis without adding ethanol which meant there was no occurrence of the flocculation phenomenon when PVA was added later. The ratio of the composition is TEOS : H_2O : NH_4OH = 5 : 30 : 2(ml). After stirring for 24 h and filtrating, we can obtain a transparent and homogeneous solution. Then acetic acid was added in this solution to adjust PH of this solution to 2.5 which will slow down the speed of condensation and to delay the growth of gel particles. Meanwhile, the $Zn(Ac)_2{\cdot}2H_2O$ as zinc source was added to this solution. Then H_2SeO_4 as selenium source was added to the solution after $Zn(Ac)_2{\cdot}2H_2O$ dissolved completely. Finally, a 5.5 wt.% PVA water solution was added to the solution to coat the SiO_2 gel particles in order to obtain a stable gel solution and restrict the growth of the gel particles.

Usually, the hydrogen bond between PVA and silica depends strongly on the PH value. When pH 2.5, strong hydrogen bond is be formed between PVA and silica. The acetic acid is also helpful to stabilize the gel solution. The amount of PVA is one main factors in the preparation of the high quality, crack free, porous SiO_2 thin films.

Fig. 1 described the procedure of preparation of sol and ZnSe/SiO_2 composite thin films. Firstly, the wet films was prepared by spin coating method. To prevent the excessive crystallization of $ZnSeO_4{\cdot}H_2O$, the wet films must be heat treated in 70 °C quickly. Then the thin films was annealed under air to make complete volatilization of organic solvent and PVA in 450 °C. The aforementioned composite thin films will be heat treated under carbon monoxide reduction atmosphere in 500 °C to obtain the ZnSe/SiO_2 composite thin films.

2.2. Characterization

The phase structure of synthesized thin solid films was characterized by XRD (Rigaku, D/MAX-2400, Cu Kα). The surface configuration of films was investigated by AFM (DI-IIIA). DTA–TG (TA-2000) analysis was used to record the thermal effect in the process of heat-treatment. The atomic ratio of Se/Zn/Si was analyzed by XPS (VG ESCALAB, MK II, Mg Kα).

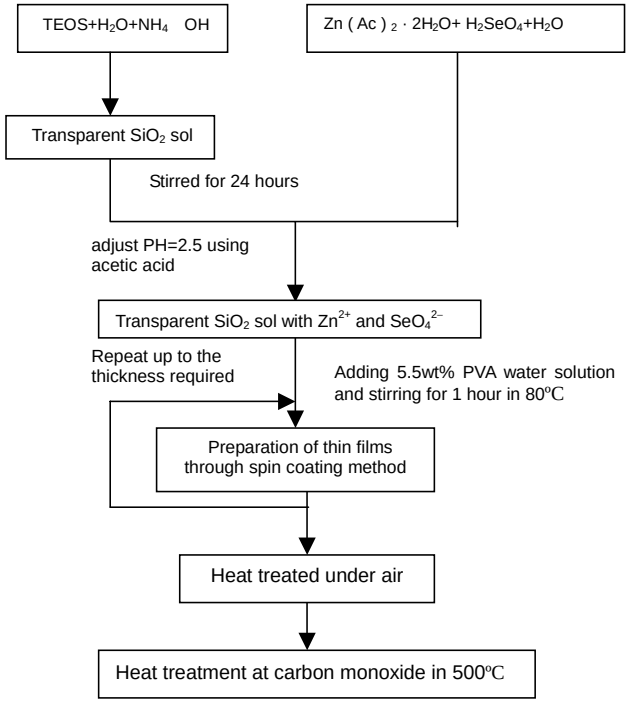

Fig. 1. The schematic description of preparation of ZnSe/SiO_2 composite thin films by sol–gel method.

3. Results and discussion

3.1. The XRD analysis

The XRD of ZnSe/SiO_2 thin films synthesized at 500 °C under carbon monoxide atmosphere using $ZnSeO_4{\cdot}H_2O$ was shown in Fig. 2. The XRD pattern indicated that the structure of ZnSe is sphalerite (cubic ZnS).

In experiment results showed that overlong time and un-sufficient heat treat time is disadvantage to prepare of ZnSe/SiO_2 thin solid films. Our further research works revealed that the reaction between selenium and oxygen at lower temperature is to occur, which means selenium element will escape seriously from the samples. At the same time, the selenium dioxide also easily decompose in relatively lower temperature. That is the reason why the over long time is disadvantage to the synthesis of ZnSe/SiO_2 thin solid films. To ensure the partial pressure of selenium element, small amounts of metal selenium also sealed in quartz tube stove. In the reduction course, oxygen must be removed as far as possible under the condition of low temperature. That is the important step to ensure ZnSe phase.

3.2. XPS analysis

Fig. 3 is the XPS curve of $ZnSeO_4{\cdot}H_2O$ crystal samples heat-treated under air condition in 450 °C without reduction process. Table 1 is the analysis results of the narrow XPS spectrum of each element in the sample.

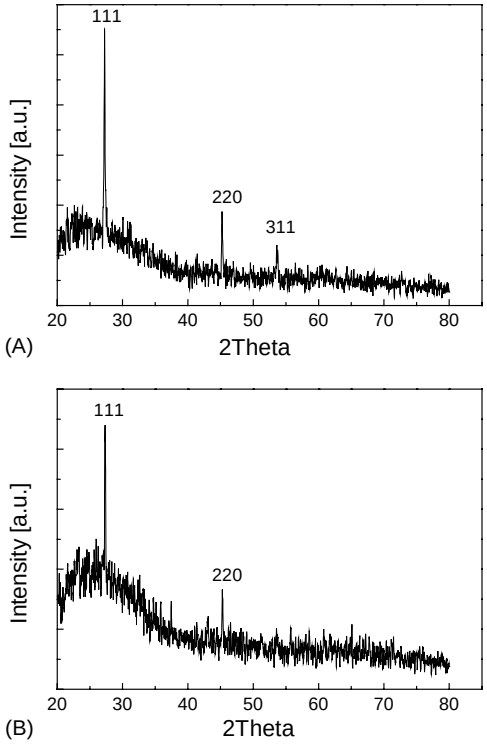

Fig. 2. The XRD patterns of $ZnSe/SiO_2$ composite thin films (synthesized at 500 °C under carbon monoxide atmosphere for (A) 20 min and (B) 15 min).

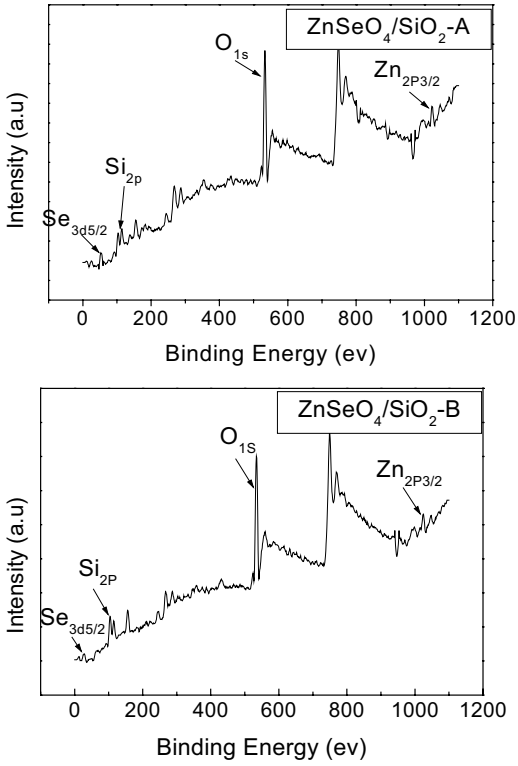

Fig. 3. The XPS of $ZnSeO_4/SiO_2$ composite thin films.

The results of the XPS analysis show that the volatilization of selenium element was very seriously in the heat-treatment process, even through further heat-treatment under reduction atmosphere has not yet been performed. This disadvantage is most important factor considered in the process of preparation of the sample containing selenium element. The concentration control of selenium element must be considered. The nominal atomic concentration and actual atomic concentration are different.

3.3. DTA–TGA analysis

Fig. 4 is the DTA–TG curve of TEOS sol and PVA water solution without adding H_2SeO_4 and $Zn(Ac)_2{\cdot}2H_2O$. The curve revealed that there are two exothermic peaks in 342 and 465 °C, respectively. The exothermic peak in 342 °C be likely to the fracture of C–O–Si and the formation of Si–O–Si. The exothermic peak in 465 °C represents the combustion of PVA, which means that we must heat-treat the samples under air condition in 465 °C before treating under

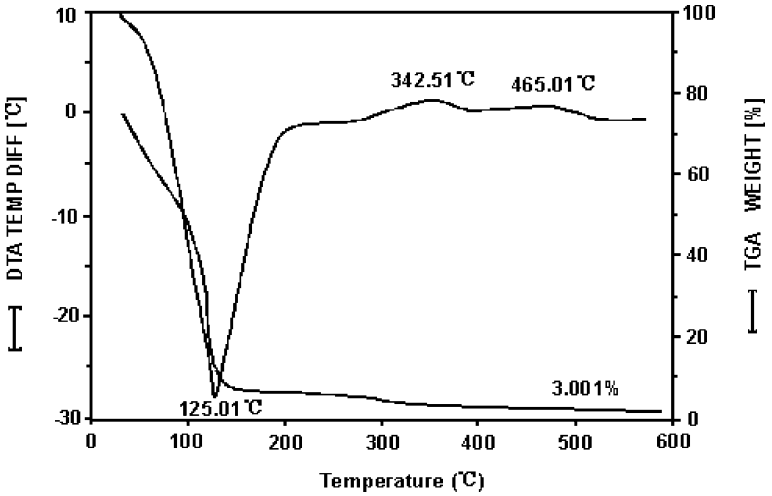

Fig. 4. The DTA–TGA curve of TEOS sol and PVA water solution.

Table 1
The result of the narrow XPS spectrum of each element

Sample	Element	Sensitivity factor	Integral area	Calculated relative atomic ratio (%)
A	Si_{2p}	0.270	1317	83.06
	$Zn_{2p3/2}$	4.800	3908	13.8
	$Se_{3d5/2}$	0.670	121	3.4
B	Si_{2p}	0.270	1313	85.82
	$Zn_{2p3/2}$	4.800	2874	10.56
	$Se_{3d5/2}$	0.670	137	3.6

The nominally relative atomic ratio of Si:Se:Zn in sample A is 1:0.5:0.5 and in sample B is 1:0.4:0.4.

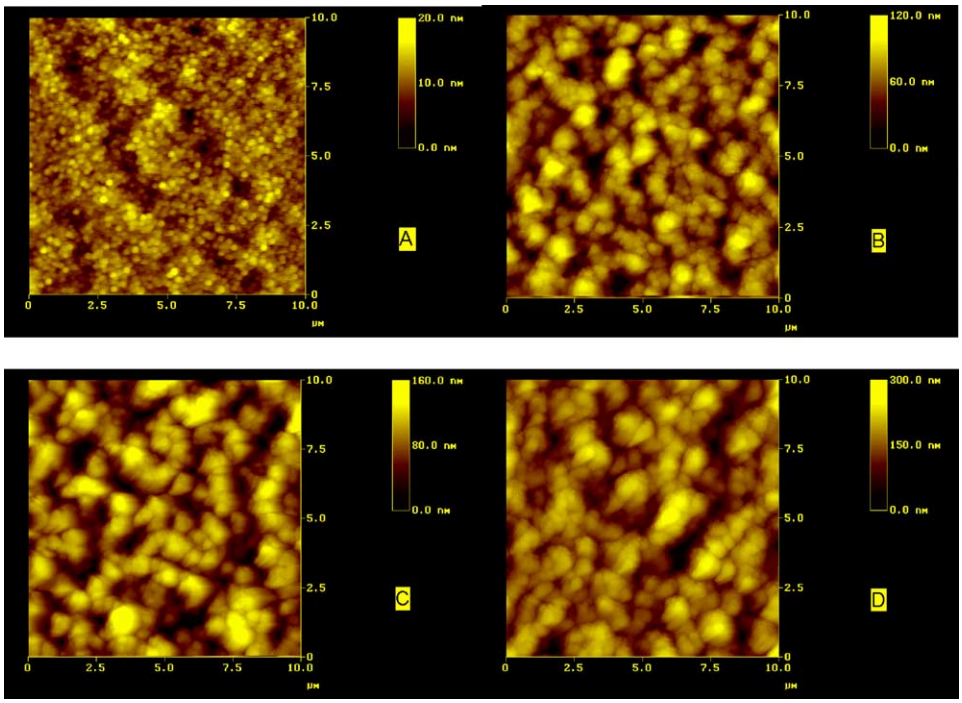

Fig. 5. The AFM pattern of $ZnSe/SiO_2$ thin solid films with different ratio of Zn/Si: (A) 20 (B) 30 (C) 40 and (D) 50%.

reduction atmosphere. Otherwise, the carbon element will exist in the films.

3.4. AFM

The surface configuration of thin films heat-treated under air conduction was shown in Fig. 5. The results reveal that the size of crystal of ZnSe will increase with the ratio of Zn/Si increasing. The conflict between size-control and the minimization of volatilization must be concerned. This will increase the complexity of synthesis processing.

4. Conclusion

In conclusion, the ZnSe quantum dots embedded in SiO_2 thin films was successfully prepared by a sol–gel process under carbon monoxide atmosphere at 500 °C, which is a new in-situ method to fabricate the $ZnSe/SiO_2$ thin solid films. This approach to synthesis of $ZnSe/SiO_2$ thin solid films has the advantages to reducing the amount of volatilization of selenium element.

Acknowledgements

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