

# Electrodeposition mechanism of ZnSe thin film in aqueous solution

Jun-Li Xu\* (iD 0000-0002-4572-311X), Wei-Ying Gong, Wei Wang, Hao Meng, Xia Zhang, Zhong-Ning Shi, Geir-Martin Haarberg

**Abstract** ZnSe is one of the important and excellent II-VI semiconductor materials, which has direct transition band structure. In this paper, ZnSe thin films were prepared by an electrochemical deposition method and the formation mechanism of ZnSe was studied systematically. Voltammetry and chronoamperometry combined with X-ray diffraction (XRD) and Raman techniques were used to analyze the deposition processes. It is found that the substrate and deposition potentials have a great influence on the phase composition of deposited thin film, and Zn substrate is beneficial to the preparation ZnSe films. Strong selenium substrate interaction results in the formation of selenium compounds involving electrode materials. The addition of Zn(II) source can affect the reduction potential of Se, and results in the change of reducing mechanism for Se(0) from Se(IV). Se(0) formed because of the formation of H<sub>2</sub>Se is more active than Se(0) formed directly from Se(IV), and it can recombine with the substrate material forming selenium-substrate compounds more quickly.

**Keywords** ZnSe; Thin film; Electrodeposition; Mechanism; Raman spectra

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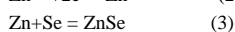
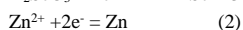
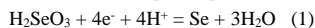
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## 1 Introduction

ZnSe is a promising photovoltaic material because of its optical band gap energy (2.7eV) and the high absorption coefficient for efficient energy conversions [1, 2]. In the last years, a variety of methods have been employed for the fabrication of ZnSe thin film, such as chemical bath deposition [3, 4], sol-gel deposition [5, 6], physical vapour deposition under vacuum [7], electrodeposition [8-29]. Among these, electrodeposition method is relatively inexpensive and simple [30]. Moreover, it is the only technique which can be used for depositing films on large and irregular surfaces, and it enables the fabrication at conditions near chemical equilibrium for ZnSe [31-34].

Electrolytes used for the ZnSe electrodeposition can be divided into three major types: aqueous solutions, organic solutions [15, 17, 27, 35] and high temperature molten salts [12]. Aqueous solutions have attracted much interest since it is safe and inexpensive. As the standard electrode potentials of Zn<sup>2+</sup>/Zn and SeO<sub>3</sub><sup>2-</sup>/Se are -1.005 and 0.5000 V vs. the standard saturated calomel electrode, respectively, the electrodeposition of ZnSe should be difficult because of the wide difference in the reduction potential of Zn and Se ions, and low concentration of selenous acid and high concentration of zinc salt are usually used for this approach. Moreover, it was found that the deposition potential of zinc is shifted towards positive values because of the contribution of Gibbs free energy change of ZnSe formation. Three different mechanisms of ZnSe electrochemical synthesis in aqueous electrolytes have been suggested. Bouroushian, Loizos and Gudage et al. suggested that Se and Zn species were deposited by cathodic electro-reduction first, and zinc selenide thin films were deposited according to chemical reactions as follows [16, 23]:



Chandramohan et al. [10, 20] suggested that H<sub>2</sub>SeO<sub>3</sub> was

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由于形成H<sub>2</sub>Se再转变得到的Se(0)比由从Se(IV)直接转变得到的Se(0)活性要高。

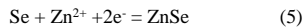
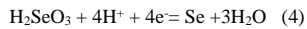
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It是指由形成H<sub>2</sub>Se而转变得到的Se(0)。这个句子可以变成如下:  
Active Se(0) can recombine with the substrate material forming selenium-substrate compounds more quickly. (把Se(0) formed because of the formation of H<sub>2</sub>Se is more active than Se(0) formed directly from Se(IV)删除)

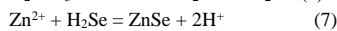
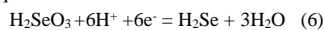
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first reduced to Se, and subsequently reacted with  $Zn^{2+}$  to form ZnSe on the cathode surface. The reactions for the formation of ZnSe were expressed as follows:



However, Dhanasekaran et al. proposed that Se was reduced to  $Se^{2-}$  state, forming  $H_2Se$ , which was highly reactive.  $H_2Se$  immediately reacted with  $Zn^{2+}$  which was adsorbed on the surface of the substrate and formed ZnSe [9, 29]. The reactions can be expressed by the following equations:



Moreover, a wide range of studied experimental conditions was examined in order to determine the best way of electro-synthesis of the material, such as pH, reagent concentration, deposition potential, temperature and substrates. The substrates used were Ag, Ti, indium tin oxide (ITO), glass carbon, stainless steel, aluminum and Cu. In this paper, Cu and Zn were used as the substrates for the electrodeposition of ZnSe. The aim of the present studies was to investigate the mechanism of ZnSe electrodeposition, and a new mechanism was proposed according to our results.

## 2 Experimental

Electrochemical tests were carried out in an acidic solution containing  $ZnSO_4$  and  $SeO_2$ . The concentrations of  $ZnSO_4$  and  $SeO_2$  were  $0.200$  and  $0.002\text{mol}\cdot\text{L}^{-1}$ , respectively, and pH was adjusted to 2 by sulfuric acid addition. All chemicals were analytical grade and used directly without further purification. The cyclic voltammograms (CV) and chronoamperometric measurements were performed using a potentiostat (CHI660). For all the electrochemical measurements, a conventional three electrode system was used. Zinc tablet or copper tablet was used as working electrode. A platinum wire was used as the counter electrode and a platinum wire served as the pseudo reference electrode. Prior to the measurements, the working electrodes were cleaned as follows: the copper and zinc plates (about  $3\text{cm}^2$  in geometric area) were polished with emery paper, rinsed with deionized water, then immersed for 30min in 98% alcohol solution and thoroughly rinsed with water.

The products were characterized by X-ray diffractometer (XRD, MAC Science X'PERT PRO) with  $Cu\ K\alpha$  radiation ( $\lambda=0.15406\text{ nm}$ ). Scanning electron microscopy (SEM) pictures were obtained using a Zeiss ultra plus FESEM apparatus. The Raman spectra of the products were recorded at ambient temperature on a 633nm He-Ne laser with a liquid helium cooling system (Jobin Yvon LabRAM HR800UV).

## 3 Results and discussion

Typical CV curves of aqueous solutions containing different solutes using a copper electrode at pH=2 are shown in Fig. 1. As seen in Fig.1(1), a reduction peak at about  $-0.6\text{V}$  and a small reduction peak at  $-0.75\text{V}$  are observed in  $0.002\text{mol}\cdot\text{L}^{-1}$   $SeO_2$  solution. With the addition of  $ZnSO_4$  to  $SeO_2$  solution, the reduction peaks move to the positive direction as seen from Fig.1(2). The reduction peak at  $-0.6\text{V}$  is shifted to  $-0.3\text{V}$ , and the second reduction peak at  $-0.75\text{V}$  appears at  $-0.6\text{V}$ .

Electrodeposition experiments were carried out for 2h at different potentials on Cu substrate to characterize the reduction reaction. XRD was used to characterize the phase of the deposits, and the results are shown in Fig. 2. As shown in Fig.2, there are Se, CuSe, and  $Cu_2Se$  phases in the deposits along with peaks for the Cu substrate. No ZnSe or Zn is detected in the deposited coating even when the deposition process was carried out at  $-1.0\text{V}$ .  $Cu_2Se$  is also detected for the electrodeposition of ZnSe when using copper as cathode by Skyllas Kazacos and Miller [36].

As there are  $Cu_2Se$  and CuSe in the deposits, and no Cu source is contained in the solutions, it can be deduced that the deposited Se may react with the Cu substrate, forming  $Cu_2Se$  and CuSe. Another possibility is that selenium atoms diffuse into substrate, and then form alloys. To prepare ZnSe, Cu substrate was changed to Zn substrate, and the electrodeposition processes were carried out at  $-0.6\text{V}$  in the same electrolyte composition. Figures 3 and 4 show the XRD pattern and Raman spectrum of the obtained thin films on Zn substrates. As shown in Fig.3, the diffraction peaks at  $2\theta = 27.60^\circ, 45.68^\circ, 84.03^\circ, 91.32^\circ$  are attributed to the (111), (220), (422), (511) planes of cubic ZnSe phase, respectively, which is confirmed using the standard JCPDS data card (No. 01-6920). Se and Zn are also detected in the deposits. Compared with the XRD results on copper substrate (Fig.2), the appearance of Zn in XRD pattern (Fig.3) should be attributed to the Zn substrate. Se is caused by the reduction of Se(IV) to Se(0) on Zn cathode. For the Raman spectrum shown in Fig.4, two peaks at  $252$  and  $235\text{cm}^{-1}$  are observed. As the spectrum of pure ZnSe consists of a longitudinal optical (LO) phonon at  $253\text{cm}^{-1}$  and the transverse mode (TO) at about  $204\text{cm}^{-1}$  [37, 38], the peak at  $252\text{cm}^{-1}$  indicates the existence of ZnSe in the thin film. The pronounced peak at about  $235\text{cm}^{-1}$  is attributed to a trigonal Se phase [38, 39]. These results are consistent with the XRD results.

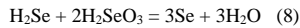
Figure 5 shows SEM images of ZnSe deposited on Zn substrate at  $-0.2$  and  $-0.6\text{V}$  vs. Pt for 2h, respectively. It is clearly seen that the deposited thin films are composed of nanoparticles which are homogenous and well cover the Zn substrate. Moreover, during the electrodeposition process, it is observed visually that the cathode becomes dark when using copper as cathode with prolonged electrodeposition time at  $-0.6\text{V}$ , while it turns to golden yellow color first, and

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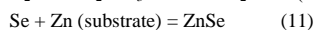
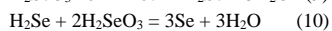
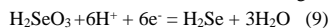
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then changes to red when using zinc as cathode. According to Pezzatini et al. [40, 21], the reduction process of Se (IV) occurs through two reaction paths,  $\text{Se(IV)} \rightarrow \text{Se(0)}$  and  $\text{Se(IV)} \rightarrow \text{Se(-II)}$ ; the product Se(-II) for the second path then reacts with  $\text{H}_2\text{SeO}_3$  through a reaction as follows:



Se obtained via Path 1 is the grey type of the selenium, which is recognized as electroinactive, while the latter step leads to red Se, which is the only electroactive form of Se(0) [21]. When using copper as cathode, Se(IV) is reduced to Se(0) directly at  $-0.6\text{V}$ , and the cathode appears gray and dark. As the reduction reaction shifts to positive (Fig.1), the electroactive form of Se(0) is formed because  $\text{H}_2\text{Se}$  is produced at  $-0.6\text{V}$ . The appearance of golden yellow color results from the formation of ZnSe. After the surface of zinc cathode is covered by ZnSe, electroactive Se(0) can not contact with the Zn cathode, and deposits on top of ZnSe instead, appearing as red. Compared to the CV results, it is deduced that the first reduction peak (at  $-0.6\text{V}$  in Fig.1(1)) belongs to the reduction of Se (IV) to gray Se(0) directly, and the second reduction peak (at  $-0.8\text{V}$  in Fig.1(1)) is due to the reduction of Se (IV) to Se(-II) and then red Se(0) is formed.

From the above results, it can be concluded that ZnSe can be obtained with the use of Zn substrate, while  $\text{Cu}_2\text{Se}$  is formed when Cu was used as substrate. It is deduced that the formation mechanism for ZnSe in this experimental condition can be described as following:



As pointed out above, ZnSe is formed by the reaction of reduced Se with Zn substrate.  $\text{ZnSO}_4$  does not seem to be essential for the formation of ZnSe. To verify this conclusion, electrodeposition processes were carried out using solutions which only contained Se source. Figure 6 shows the Raman result of the deposits obtained in  $0.002\text{mol}\cdot\text{L}^{-1}\text{SeO}_2$  acidic solution. The peaks at 145 and  $252\text{cm}^{-1}$  show the existence of ZnSe in the deposit, and this confirms the proposed ZnSe formation mechanism. However, the intensity of ZnSe characteristic peaks are smaller compared with the Raman result of deposits obtained at  $-0.6\text{V}$  on Zn substrate in  $\text{ZnSO}_4\text{-SeO}_2$  solution (Fig.4). This indicates that the addition of  $\text{ZnSO}_4$  can accelerate the formation of ZnSe. As shown in Fig.1, the addition of Zn(II) source results in the positive transfer of the reduce reaction, and it makes the change of mechanism for Se(0), forming  $\text{H}_2\text{Se}$  first, and then forming Se(0), which is more active.

#### 4 Conclusion

ZnSe thin films were successfully deposited on Zn substrate

using electrodeposition method. Strong selenium substrate interaction results in the formation of selenium compounds involving electrode materials. The presence of Zn(II) in the electrolytic bath is not essential for the deposition of ZnSe when using zinc cathode. However, The addition of Zn(II) source results in the positive transfer of the reduction reaction. It makes a change in the reducing mechanism of Se(0), from Se(IV) reduced to Se(0) directly to forming  $\text{H}_2\text{Se}$  first, and then forming Se(0), which is more active than Se(0) reduced by Se(IV) directly.

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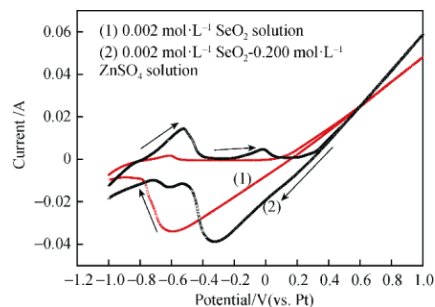
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## Graphical Abstract



The addition of ZnSO<sub>4</sub> results in the positive transfer of the reduce reaction. When the applied potential is set at -0.6V, the reduction process of Se (IV) to Se(0) occurs through Se(IV) → Se(-II) → Se(0) path in SeO<sub>2</sub>-ZnSO<sub>4</sub> acid solution, while it occurs through Se(IV) → Se(0) directly in SeO<sub>2</sub> acid solution.

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Figures

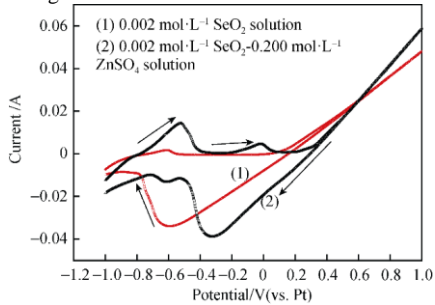
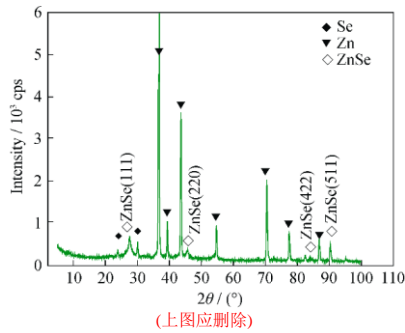


Fig.1 CV curves with a copper electrode in different aqueous electrolytic baths at 25°C and scan rate of 100mV·s<sup>-1</sup>



(上图应删除)

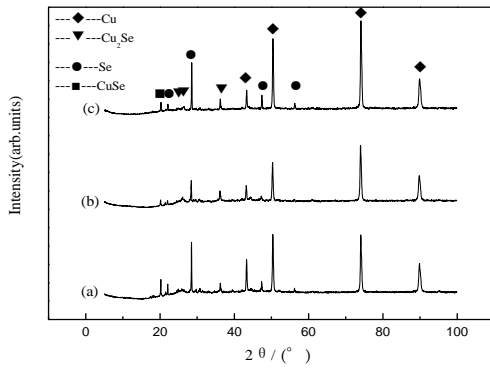


Fig.2 XRD patterns of films deposited at different potentials for 2h on copper cathode in ZnSO<sub>4</sub>-SeO<sub>2</sub> solution: a -0.2V, b -0.6V, and c -1.0V

**Commented [W用16]:** 按题图叙述，图中应该有三条曲线，但是只有一条，请检查并修改  
 (图2应该是放错修改后的图了，我检查我提交的初稿中的图不是这个，已重新添加上。紧接图1标题后的XRD(图中线条为绿线的)应删除。)

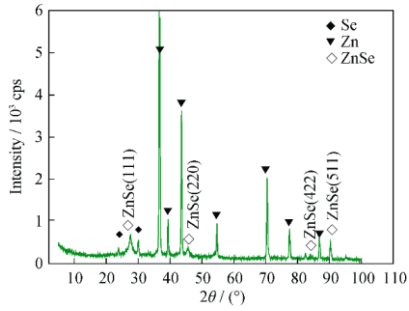


Fig.3 XRD pattern of electrodeposited ZnSe film obtained at -0.6V on Zn substrate in  $\text{ZnSO}_4\text{-SeO}_2$  solution

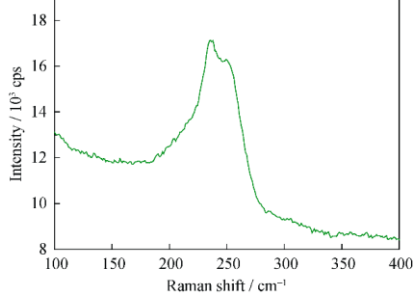


Fig.4 Raman spectrum of electrodeposited film obtained at -0.6V on Zn substrate in  $\text{ZnSO}_4\text{-SeO}_2$  solution

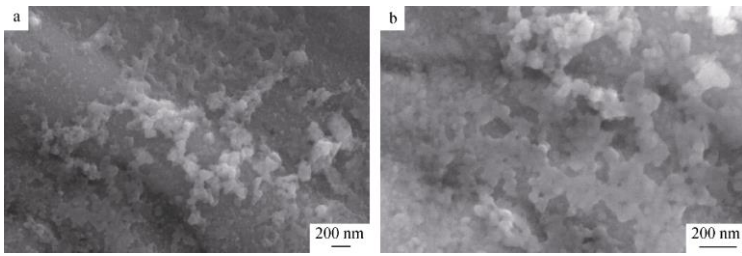


Fig.5 SEM images of ZnSe deposited at a static potential for 2h: **a** -0.2V and **b** -0.6V vs. Pt

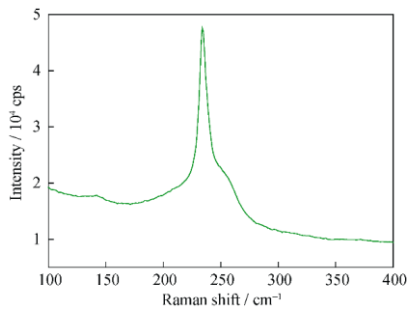


Fig.6 Raman spectrum of electrodeposited film obtained at -0.6 V on Zn substrate in  $\text{SeO}_2$  acidic solution