



Characterization and properties of Zn–O–Se ternary system thin films deposited by radio-frequency (rf)-magnetron sputtering

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ARTICLE INFO

Article history:

Received 3 May 2009

Received in revised form 16 December 2009

Available online 13 January 2010

Keywords:

Alloys

II–VI semiconductors

Electron diffraction/scattering

UPS/XPS

Sputtering

Absorption

Luminescence

Short-range order

ABSTRACT

Zn–O–Se alloy films were grown on quartz substrate by radio-frequency (rf)-magnetron sputtering ZnSe single crystal target, with high pure Ar and O₂ as working gas. X-ray diffraction and transmission electron microscopy characterizations indicate that the films are amorphous state. Energy disperse spectroscopy and X-ray photoelectron spectroscopy measurements verify the amorphous Zn–O–Se alloy was Se doped ZnO₂ (Zn_{1–x}Se_xO₂), in which both Zn and Se atoms are bound with O atom. Absorption spectra exhibit that the optical band gap of Zn_{1–x}Se_xO₂ films are 4–5 eV. After annealing at 673 K in Ar ambient for 15 min, Zn_{1–x}Se_xO₂ film was decomposed to ZnO and SeO₂, and SeO₂ sublimed while annealed. The band gap energy decreased to the 3.2 eV, which is similar to the value of ZnO film directly deposited on quartz substrate. Room-temperature photoluminescence spectrum of the film after annealed shows NBE emission at 3.26 eV.

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1. Introduction

Semiconductor alloy containing component elements with distinctly different properties have attracted significant attention. These alloys are always highly mismatched semiconductor alloys (HMAs). Nonlinear dependence of fundamental band gap on the composition of semiconductor alloys is widely observed in HMAs. It has typically been assumed that the deviation from a linear dependence predicted by the virtual crystal approximation (VCA) [1,2] can be accounted for by including effects of disorder on the conduction- and valence-band edge. HMAs shows composition dependent optical band gap bowing. When the composition of the doped element was increased, the band gap energy of such semiconductor alloys firstly decrease, then increase. III–N–V alloy system is the most extensively studied HMAs [3–6]. The effect has been rationalized by the band anti-crossing (BAC) between a single N level and extended states of conduction band (CB) of the host [3]. Recently, similar effect has also been observed in O, S and Se doped II–VI compounds [7–10]. A series of ZnO_{1–x}S_x alloy films (0 ≤ x ≤ 1) have been deposited by reactive sputtering ZnS target, using Ar and O₂ as working gas [10]. The sputtered ZnO_{1–x}S_x films have wurtzite symmetry and the composition dependence of

band gap energy was observed in the ternary system, with a bowing parameter of 3 eV [10]. Both S and Se are VIA group elements, and they have similar properties. However, so far, ZnO_xSe_{1–x} alloy (x ≤ 1.3%) can only be fabricated in a very narrow composition range by molecular beam epitaxy (MBE) [8,9], due to the limited solubility of O and Se in ZnSe and ZnO, respectively. Because ZnSeO alloy films are extremely difficult to fabricated, Zn–O–Se alloy with larger composition of Se element, so far, has been rarely studied.

Here we present our work on Zn–O–Se alloy films with composition of Se about 13% via radio-frequency (rf)-magnetron sputtering high pure ZnSe single crystal target. We studied the structure, chemical bond, and optical properties of the Zn–O–Se alloy films in this paper. The electronic behavior of amorphous Zn–O–Se alloy is quite different from that of crystalline structure of ZnO_{1–x}Se_x alloy what has been reported. In amorphous Zn–O–Se alloy, O atom did not replace the lattice position of Se atom in ZnSe crystal lattice, but bonded with Se atom. Therefore, Zn–O–Se alloy exhibited thoroughly different optical property either form ZnO or ZnSe.

2. Experiments

ZnSeO thin films were grown on quartz substrate by radio-frequency (rf)-magnetron sputtering single crystal 99.99% ZnSe target, using high pure O₂ and Ar (99.99%) as working gas and oxidizing agent. The base pressure of the chamber was 5 × 10^{–4} Pa

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Table 1

Deposition parameters employed for the samples of investigated samples.

Sample	Sputtering pressure (Pa)	Sputtering power (W)	Substrate temperature (K)	Working gas ratio O ₂ (sccm)/Ar (sccm)	Deposition time (min)
A	0.6	70	610	15/30	120
B	0.6	100	610	20/20	90
C	0.6	100	610	30/10	90

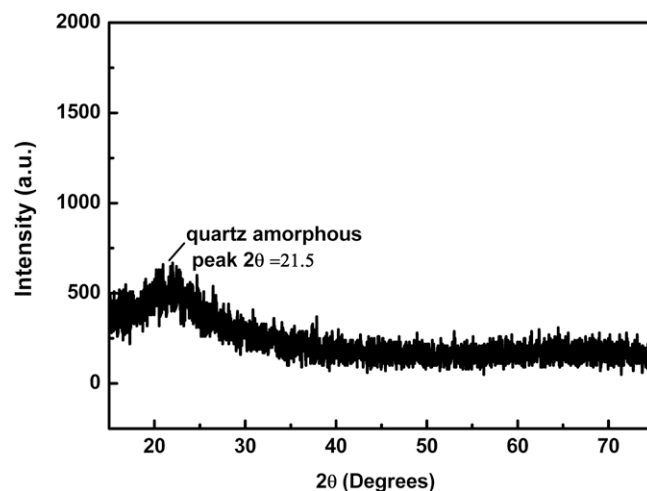
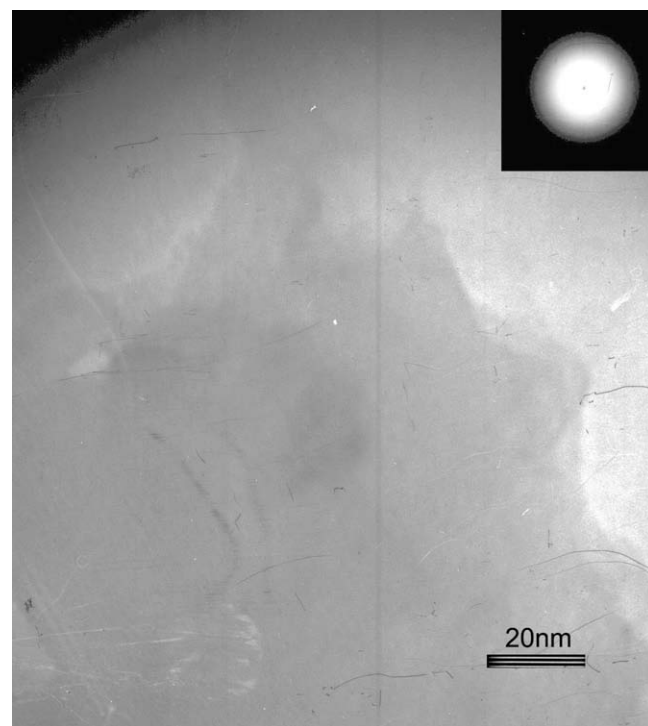
and the growth pressure was maintained at 0.6 Pa. The target to the substrate was 60 mm in the on-axis geometry. All the quartz substrates were ultrasonically cleaned in acetone, ethanol and deionized water for ten minutes, respectively, and N₂ blown dry. The temperature of substrate was set from 473 to 673 K; deposition time was changed from 40 to 120 min, and sputtering power was changed from 70 to 100 W. The structure and morphology of one film sample were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Energy disperse spectroscopy (EDS) was used to determine the composition of the films. X-ray photoelectron spectroscopy (XPS) using an Al K α as X-ray source was performed to determine the binding energy of Zn, Se and O in the film. UV–Vis–NIR scanning spectrophotometer, in which the Xenon lamp ranged from 900 to 190 nm was employed as incident ray, was used to indicate the optical band gap. The photoluminescence (PL) measurement was carried out at room temperature by the excitation from a 325 nm He–Cd laser.

3. Results and discussion

3.1. The structure of films

Table 1 presents the deposition parameters employed for the investigated samples. All the samples did not show any XRD peaks besides one amorphous peak of quartz substrate ($2\theta = 21.5^\circ$), and the XRD measurement result of the film is shown in Fig. 1. One possible reason is due to the poor crystalline quality of the films, which leads to that the intensity of diffraction peaks is too weak to be observed. But more possible reason is that the film is amorphous and has diffraction position close to the position of the quartz, which makes structure characterization of the film difficult by XRD. In order to further determine the structure of the samples, TEM was performed for the representative Sample A, and the result is present in Fig. 2. Fig. 2 suggests Sample A is amorphous state, for the electron diffraction pattern is circle halo. TEM image of the film indicates the surface morphology is very smooth and is consecutive. No grain can be seen, in despite of being enlarged 400 000 times, which is the very character of amorphous state. This result is different from films grown by molecular beam epitaxy (MBE) method by Shan et al. and Nabetani et al. [8,9]. They claimed that when O was doped into ZnSe, O substituted for the lattice position of Se atom, and they had obtained crystalline structure of ZnO_xSe_{1-x} alloy in a narrow range oxygen composition ($0 \leq x \leq 1.3\%$) in ZnO_xSe_{1-x} alloys.

In our study, amorphous state was always formed though the growth condition was changed. It is indicated that Gibbs free energy of amorphous state Zn–O–Se is smaller than crystalline state during the rf-magnetron sputtering. Therefore, according to thermodynamic rules, amorphous state Zn–Se–O is easier to form than crystalline state. In addition, rf-magnetron sputtering is a physical vapor deposition method, when oxygen is included in the working gas, furthermore as the reactive gas, Zn atom binding with Se atom will encounter competition of both Zn and Se atom binding with O atom, respectively. Based on the dynamics rules, Zn and Se atoms adsorbed on substrate would migrate hardly due to the priority

**Fig. 1.** The XRD patterns for the amorphous film.**Fig. 2.** The TEM morphology image and electron diffraction pattern for Sample A.

of binding with O atom, which also prevents the forming of crystal ZnO_xSe_{1-x} alloy, because that lower migration rate would easily lead to amorphous forming. To investigate the composition of the amorphous film, energy disperse spectroscopy (EDS) was carried out. Table 2 shows the EDS measurement results.

3.2. The composition of the films

Considering the 0.5% error bar of EDS measurement, which is referred to the use specification of the apparatus of the EDS we employed in the present work, the percentage ratio of Zn, Se, and O of EDS measurements indicate that the composition ratio of the amorphous films is subjected to Zn_xSe_{1-x}O₂, with composition of Se about 13%, which is much larger than what have been reported in ZnO_xSe_{1-x} alloy (up to 1.3%) previously. Nabetani et al. [9]

Table 2

The content of Zn, Se and O in the films measured by EDS.

Sample	Zn content (%)	Se content (%)	O content (%)
A	18 ± 0.5	13 ± 0.5	69 ± 0.5
B	20 ± 0.5	12 ± 0.5	68 ± 0.5
C	23 ± 0.5	14 ± 0.5	63 ± 0.5

considered that O atom substituted Se lattice position in ZnSe, when O atom was incorporated into ZnSe. However, according to the percentage ratio of Zn, Se, and O elements, it is obviously that O atom did not incorporate into ZnSe, neither did O atom substitute Se lattice position in ZnSe during the film growth process. Both O and Se are group-VI atoms, with a similar structure of electronic shell. But compared O with Se, the electronegativity of O is much larger than that of Se: 3.5 and 2.4, respectively [11]; and the atomic size of Se is much larger than that of O. Incorporation of O into ZnSe is quite difficult, due to large discrepancy between Se and O atoms. During sputtering process, atomic or ionic state of Zn, Se and O are all in the sputtering cavity. Binding energy between different elements must be confined. When O included in the reactive system, Se is more reactive to O than to Zn. Therefore, in our experiments, atomic or ionic state of both Se and Zn prefer to react with atomic or ionic state of O during the reactive sputtering process. The migration rate of Zn and Se is reduced due to binding with O atom, so Zn, Se and O would not have enough energy to adjust their position, which finally leads to the disorder of atoms in the alloy films. Therefore, when O is accessible in the growth condition, crystalline state $\text{ZnO}_x\text{Se}_{1-x}$ alloy could not be synthesized. Instead, amorphous $\text{Zn}_x\text{Se}_{1-x}\text{O}_2$ is obtained, and its local short-range order is like the structure of ZnO_2 . In order to validate our presumption, X-ray photoelectron spectroscopy (XPS) is performed.

3.3. The X-ray photoelectron spectroscopy of the films

Fig. 3 shows the XPS scanning spectrum of Sample A after Ar ionic etching 2 min to get rid of the pollution on the film surface. The fine XPS spectra of Zn 2p, O 1s and Se 3d are displayed in part (a), (b) and (c) of Fig. 3, respectively. Fig. 3(a) shows Zn 2p_{3/2} peak. The Zn 2p_{3/2} peak locates at about 1024 eV is fit as two peaks: 1023.08 ± 0.05 and 1024.45 ± 0.05 eV, which both are about 1–2 eV larger than binding energy of Zn 2p_{3/2} (1022 eV) in ZnO [12,13] and 1021.8 eV in ZnSe [14]. Bae et al. [15] reported that they had synthesized S-doped ZnO nanowires via chemical vapor deposition and had taken XPS measurement for the sample. They found Zn 2p_{3/2} peak was located at 1022 eV in S-doped ZnO, which was between 1021.7 eV in ZnS [16] and 1022 eV in ZnO [12,13]. It can be conferred that the binding energy of Zn 2p_{3/2} in crystalline structure Se doped $\text{ZnO}_{1-x}\text{Se}_x$ should also be between that of ZnO and that of ZnSe. Consequently, it is suggested that the structure of the samples we have synthesized would not be ZnO-like, or ZnSe-like $\text{ZnO}_{1-x}\text{Se}_x$. Chen et al. [17] calculated the band structure for ZnO₂ and found that there was a strong hybridization between Zn-d and O-p states in ZnO₂. So, if Zn atom bound with O atom like ZnO₂ not ZnO, it would deduce the large binding energy of Zn 2p. Splitting Zn 2p_{3/2} peak did not suggest two different phase in the sample, and the absorption spectrum later would prove it later. The 1023.07 ± 0.05 and 1024.45 ± 0.05 eV possibly are corresponding to Zn–O bond with Se–O bond around and without Se–O bond around, respectively. Fig. 3(b) shows two overlapped Se 3d peaks, corresponding to Se 3d_{5/2} and Se 3d_{3/2}. The Se 3d_{5/2} peak is centered at 59.07 ± 0.05 eV whereas the Se 3d_{3/2} peak is founded at 60.98 ± 0.05 eV with a spin energy separation of 1.9 eV. The Se 3d_{5/2} peak (59.07 eV) is about 5 eV blue shift, compared with Se 3d_{5/2} (54.0 eV) peak in ZnSe [14]. But it is quite similar to the bind-

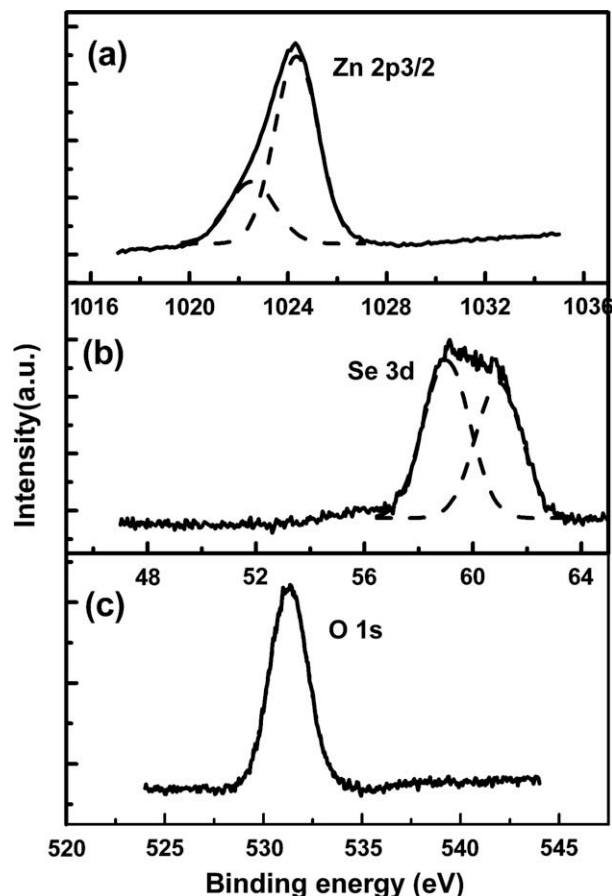


Fig. 3. The XPS scanning spectrum for Sample A. (a–c) show the spectra for Zn 2p, Se 3d and O 1s, respectively.

ing energy of Se 3d_{5/2} in SeO₂, H₂SeO₃ and selenite [18–20], in which Se binds with O. The electronegativity of O atom is 3.5 [11], which is much larger than that of Zn atom. Se–O bond will be combined much stronger than Se–Zn bond, which accounts for the blue shift of Se 3d peak position. Both blue shifts of Zn 2p and Se 3d peaks indicate that neither hexagonal structure ZnO nor face-centered cubic structure ZnSe was formed in Sample A. Fig. 3(c) shows O 1s peak centers at 531.29 ± 0.05 eV. The binding energy of O 1s is nearly the same with that in ZnO and SeO₂. Considering EDX and XPS results, it is concluded that the Sample A is probably amorphous ZnO₂, with partial Zn atom substituted by Se atom. In the amorphous network, Zn and O atoms were combined according to the short-range order in ZnO₂.

3.4. The optical properties of the films

To further verify our speculation, we also studied the optical property of the strange amorphous material. Fig. 4 shows room-temperature absorption spectra of the as-grown samples. The absorbance of a second phase cannot be found in Fig. 4, which means the samples possibly are single phase. The absorbance spectra have the characteristics of non-crystal, with an absorption tail. Furthermore, the absorption edge shows large blue shift compared with ZnO (3.2 eV at room temperature) and ZnSe (2.56 eV at room temperature). In the high absorption region where $\alpha \geq 10^4 \text{ cm}^{-1}$, the absorption coefficient α obeys the following relation according to Tauc et al. [21] and Davis and Mott [22],

$$\alpha(\omega) = B(\hbar\omega - E_{\text{opt}})^n / \hbar\omega, \quad (1)$$

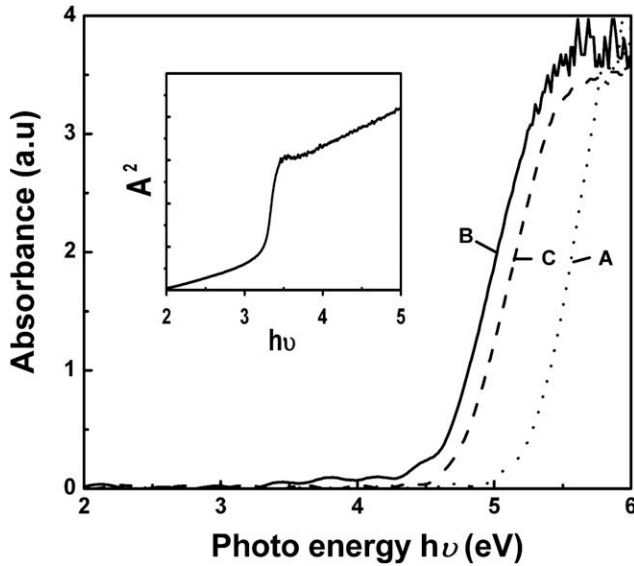


Fig. 4. Absorbance spectra for films A–C. The inset of Fig. 3 shows the absorption spectrum of film A after annealing at 673 K in Ar ambient for 15 min.

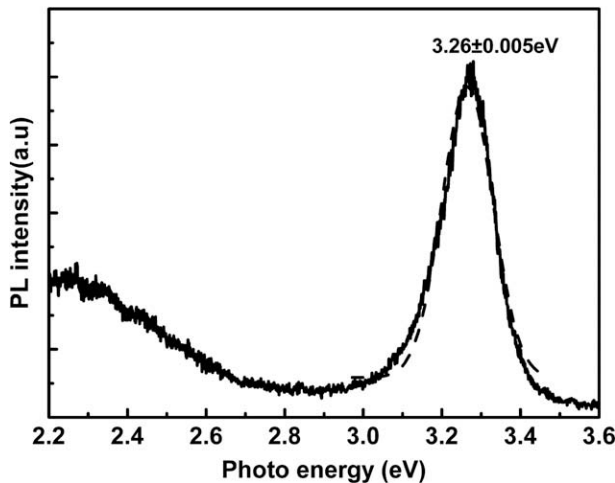


Fig. 5. Room-temperature PL spectrum for A after annealing at 673 K in Ar ambient for 15 min.

where B is a constant, E_{opt} is the optical energy gap of the material. The equation above with $n=2$ has been successfully applied to many amorphous thin oxide films [23]. The A (absorbance) and α both are function of T (transmission),

$$A = -\log T,$$

$$\alpha d = -\ln T / (1 - R)^2 \quad (R \text{ is the reflection coefficient, } d \text{ is the thickness of the films}). \quad (2)$$

In the present work the transmission is quite high (shown in Fig. 6), so reflection part of the incident ray can be approximately ignored, A (absorbance) can approximately take the place of α in Eq. (1),

$$A = B' (h\omega - E_{\text{opt}})^n / h\omega. \quad (3)$$

According to Eq. (3) with $n=2$, we calculated the optical band energy of Samples A–C: 5.00 ± 0.05 , 4.48 ± 0.05 , 4.32 ± 0.05 eV, respectively. They are consistent with 4.5(6) eV which is reported

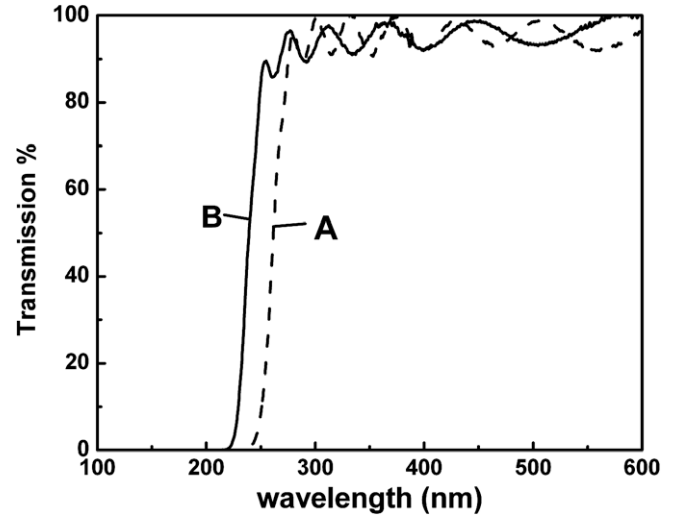


Fig. 6. The transmission spectra for films A and B.

by Chen et al. [17]. The distinction of the band energy of films is possibly caused by different measurement method, growth condition, or the displacement of Zn by Se atoms in our experiments. The result is deviated from the band gap bowing predicated in $\text{ZnO}_x\text{Se}_{1-x}$ alloy. This is possibly because when x is beyond one critical value in $\text{ZnO}_x\text{Se}_{1-x}$ alloy, this alloy would not be formed, instead of the forming of amorphous Zn–O–Se ternary, especially in non-equilibrium system of magnetron rf-sputtering. The electron behavior of the ZnOSe amorphous is different from that in ZnO, ZnSe and $\text{ZnO}_x\text{Se}_{1-x}$ alloy, which causes that its energy band structure is not $\text{ZnO}_x\text{Se}_{1-x}$ -like. After annealing at 673 K in Ar ambient for 15 min, the films of Samples B and C were cracked from the substrate as a result of coating instability, and the film of Sample A after annealing decomposed into ZnO and SeO_2 . SeO_2 sublimed while annealing. The inset of Fig. 4 is the absorption spectrum of Sample A after annealing, exhibiting that its optical band gap is about 3.2 ± 0.005 eV. PL measurement at room temperature is also carried out for Sample A after annealing. The PL spectrum of Fig. 5 shows NBE emission is at about 3.26 eV. Both absorption and PL spectrum accord with the NBE emission of ZnO. It should be noted that the as-grown amorphous films are remarkably transparent from visible range to deep ultraviolet range. Fig. 6 shows the transmission spectra for as-grown Samples A and B. The transmission of Samples A and B even reach 95% at 270 nm. This will possible have important application on deep ultraviolet device.

4. Conclusion

In summary, under the non-equilibrium system of rf-magnetron sputtering, we did not get O doped ZnSe films ($\text{ZnSe}_{1-x}\text{O}_x$ alloy) when O_2 and Ar as working gas. Whereas we obtained amorphous state $\text{Zn}_x\text{Se}_{1-x}\text{O}_2$, which is easier to form compared with the formation of O doped ZnSe $_{1-x}\text{O}_x$ alloy, according to the thermodynamic and kinetic restriction. Its band energy is about 4–5 eV, and it decomposed to ZnO and SeO_2 after annealing at 673 K.

Acknowledgments

The authors would like to acknowledge the financial support from the Key Project of National Natural Science Foundation of China under Grant No. 50532050, the ‘973’ program under Grant No. 2006CB604906, and the Innovation Project of Chinese Academy of Sciences and the National Natural Science Foundation of China

under Grant Nos. 10874178, 6077601, 60506014, 10674133 and 60806002.

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