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Phase transition of cadmium selenide thin films in MOCVD growth process

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Abstract

Cadmium selenide (CdSe) thin films were fabricated on *c*-sapphire and GaAs (1 0 0) substrates by low pressure metal organic chemical vapour deposition. The structural properties of these CdSe thin films were investigated by x-ray diffraction and photoluminescence spectroscopy. The effects of growth temperature (T_g) on the structural phase of the CdSe thin films were discussed. Phase transition of CdSe thin films grown on sapphire substrates from zincblende (ZB) to wurtzite (W) was observed with increasing T_g , and the transition critical temperature is 440 °C. However, the CdSe films grown on GaAs (1 0 0) keep ZB form in the whole range of T_g investigated from 300 to 500 °C.

1. Introduction

Cadmium selenide is a very important II–VI semiconductor, which has numerous applications in optoelectronic devices such as solar cells [1], thin film transistors [2], photoconductors [3], gamma ray detectors [4] and large screen liquid crystal display [5]. One of the hot spots in the investigations of CdSe is the ZB–W dimorphism. The two forms have their own advantages, ZB–CdSe has been considered as an important development in the context of II–VI heterostructures [6], while W–CdSe has a higher photoabsorbance and provides much needed stability against corrosive electrolyte in photoelectric cells [7]. When grown in bulk, the overwhelming preference of CdSe is hexagonal structure. Moreover, Yeh *et al* have calculated the energy difference $\Delta = E_{W-ZB}^{LDF}$ between the cubic and hexagonal phases of cadmium selenide [8]. In fact, CdSe can exist in either ZB or W form in the solid state. It is widely accepted that ZB–CdSe is a metastable phase [9]. A variety of techniques have been employed to synthesize CdSe, either in pure W form or W and ZB mixed phase. Systematic study on structural properties of CdSe thin films has been done by Kale and Lokhande [10], but the CdSe they studied is in nanocrystalline form. Moreover, a number of researchers have reported the phase transition (from ZB to W) for chemically synthesized CdSe with x-ray diffraction (XRD) stud-

ies [11]. The phase transition in CdSe is usually incurred by thermal annealing [11], mechanical grinding [12], or applied pressure [13], while reports on the phase transition of CdSe occurring in the preparation process avoiding post-processing are very few.

In this work, CdSe thin films were prepared by low pressure metal organic chemical vapour deposition (LP-MOCVD). We studied the phase transition of CdSe films grown on sapphire and GaAs substrates at different T_g , both XRD and photoluminescence (PL) spectroscopy were applied to study this phase transition behaviour.

2. Experiments

The growth of the CdSe thin films was carried out using LP-MOCVD with a homemade horizontal reactor with the growth pressure fixed at 2×10^4 Pa. In our experiment, high purity hydrogen was used as the carrier gas to carry the reactants into the growth chamber. Dimethylcadmium (DMCd) and H_2Se were used as reaction precursors. The substrates were cleaned by ultrasonic with a sequence of trichloroethylene, acetone, ethanol and deionized (DI) water. Then Al_2O_3 was etched in the mixed solution of H_2SO_4 (98%): H_3PO_4 (85%) = 3 : 1 at 160 °C for 10 min, and GaAs in the mixed solution of H_2SO_4 (98%): H_2O_2 : H_2O = 3 : 1 : 1. The chemical etched substrates were rinsed with DI water again and finally blown

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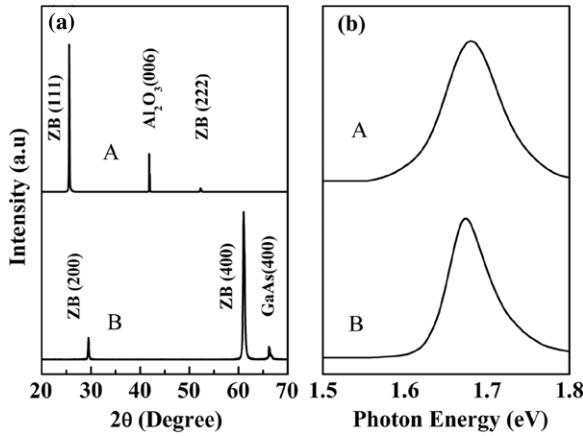


Figure 1. (a) XRD patterns of samples A (on sapphire, $T_g = 400^\circ\text{C}$) and B (on GaAs, $T_g = 400^\circ\text{C}$), (b) PL spectra of samples A and B at room temperature.

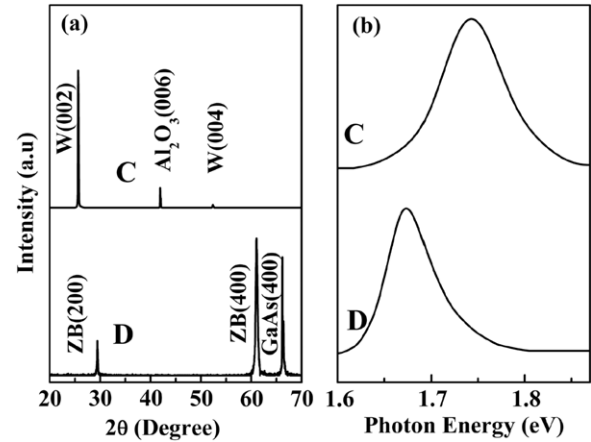


Figure 2. (a) XRD patterns of samples C (on sapphire, $T_g = 500^\circ\text{C}$) and D (on GaAs, $T_g = 500^\circ\text{C}$), (b) PL spectra of samples C and D at room temperature.

dry by nitrogen before being put into the growth chamber. The substrates were annealed at 600°C in hydrogen ambient for 10 min, which is demonstrated to be an effective way to remove the residual surface contaminants. CdSe films were grown in the reaction chamber for 30 min. The thickness of the samples was from 500 to 700 nm as examined by a scanning electron microscope (SEM). The T_g was changed and all the other parameters were kept constant. In this way, four samples, labelled A, B, C and D, with their growth conditions are listed as follows: sample A (on sapphire, $T_g = 400^\circ\text{C}$), B (on GaAs, $T_g = 400^\circ\text{C}$), C (on sapphire, $T_g = 500^\circ\text{C}$) and D (on GaAs, $T_g = 500^\circ\text{C}$).

A Rigaku Dmax-B XRD was used to characterize the structure of the thin films. The luminescent properties of these thin films were studied by a PL system at room temperature, employing the 488 nm line of an Ar⁺ laser as the excitation source. SEM (Hitachi, S-4800) was used to examine the thickness of the samples.

3. Results and discussion

Figure 1(a) illustrates the XRD patterns of samples A and B. For sample A, a strong and sharp diffraction peak located at 25.4° was observed along with a weak one at around 52° . In this case, the main diffraction peak can either be attributed to the (111) along with the (222) of ZB–CdSe or the W (002) along with the (004) diffraction peak. This is due to the very small difference between the ZB (111) and the W (002) diffraction peaks, which cannot be distinguished in our experiment resolution. However, PL spectrum can be another powerful and nondestructive method to identify the crystalline structure since the near band edge emission of ZB–CdSe is located at about 1.67 eV, while that of W–CdSe is at 1.74 eV at room temperature [14]. Figure 1(b) shows the PL spectrum of samples A (on sapphire, $T_g = 400^\circ\text{C}$) and B (on GaAs, $T_g = 400^\circ\text{C}$). For sample A, only a near band emission without defect related emission was detected at 1.678 eV. Considering the very small difference of the PL peak with the reported near band edge emission of ZB–CdSe, the diffraction peak in

sample A is attributed to the ZB (111) instead of the W (002). Meanwhile, the ZB characteristic diffraction peak (400) at 61° along with (200) appears in sample B. Hence, there is no doubt that sample B is crystallized in the ZB phase. The PL spectrum of sample B shown in figure 1(b) shows only one emission peak at 1.674 eV, which is very close to the band gap emission of ZB–CdSe, confirming the ZB phase of sample B.

Figure 2(a) shows the XRD patterns of samples C (on sapphire, $T_g = 500^\circ\text{C}$) and D (on GaAs, $T_g = 500^\circ\text{C}$) grown at 500°C . For sample C it exhibits a main diffraction peak at about 26° . The peak can be assigned to the (002) diffraction peak of W–CdSe according to the PL spectrum displayed in figure 2(b). For sample D, the characteristic diffraction peak (400) of ZB–CdSe is presented at 61° , and the PL emission peak is located at 1.674 eV. Both the XRD pattern and the PL spectrum indicate that sample D is crystallized in ZB form.

In light of the above discussion, ZB–CdSe is preferred to form at 400°C and the orientation is determined by the substrates used; that is, on Al₂O₃ (006), ZB–CdSe with (111) orientation is obtained, while on GaAs (400), ZB–CdSe with (400) orientation is formed. When the T_g increases to 500°C , the XRD patterns and PL spectra shown in figures 2(a) and (b) reveal that W–CdSe is formed on the Al₂O₃ substrate, while for sample D grown on the GaAs substrate, the CdSe is ZB, just as that observed in sample B.

As depicted above, when the T_g is at 400°C , the CdSe films grown on both sapphire and GaAs show ZB structure, but their orientations are consistent with the orientation of the substrates. While at 500°C , the CdSe films grown on GaAs show ZB structure, those on sapphire show W structure. The above phenomenon may be understood in terms of the atomic topologies as shown in figure 3. The atomic configurations in figures 3(a), (b) and (d) are all hexagons. Therefore, either W–CdSe with (002) or ZB–CdSe with (111) orientation is geometrically possible to grow on the Al₂O₃ substrate without producing miscoordinated atoms. The similar square lattice presented in figures 3(c) and (e) reveals that ZB–CdSe with

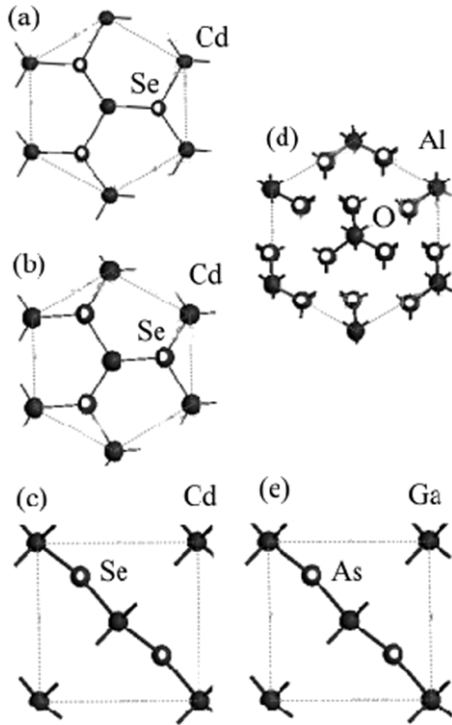


Figure 3. The atomic topology of CdSe thin films and substrates: (a) W-CdSe (002) with lattice constant $a = 4.299$, (b) ZB-CdSe (111) with lattice constant $a = 4.287$, (c) ZB-CdSe (400) with lattice constant $a = 6.050$, (d) Al_2O_3 (006) with lattice constant $a = 4.759$ and (e) GaAs (400) with lattice constant $a = 5.653$.

(400) orientation matches geometrically with GaAs (400). However, one cannot find square lattices in any orientations of W-CdSe. Therefore, we conclude that CdSe with the ZB (111) or the W (002) orientation can only be epitaxially grown on a substrate with W atomic topology like Al_2O_3 (006). And when GaAs (100) is used as the substrate, only the ZB (400) orientation can be obtained for its ZB atomic topology.

For samples A and C, which were grown on sapphire substrates with different T_g , they show different phases. In order to study the effect of T_g on the crystalline phase, CdSe thin films with different T_g from 300 to 550 °C were prepared on sapphire substrate by LP-MOCVD. The PL spectra of four samples are shown in figure 4(a). When T_g is lower than 400 °C, it can be clearly seen that only one emission peak near the band gap of ZB-CdSe was observed. When the T_g was increased to 440 °C, two emission peaks appeared. This phenomenon has been studied by our group previously [15]. The lower energy peak was from ZB-CdSe, while the higher energy one from W-CdSe. When T_g was above 500 °C, only one emission peak was detected at 1.744 eV, which corresponded to the near band edge emission of W-CdSe. The above facts meant that a phase transition from single-ZB to ZB and W mixed and finally to single-W phased CdSe occurred with increasing T_g . The effect of T_g on the crystalline structure of the CdSe films is shown in figure 4(b). It can be seen that CdSe thin films grown on sapphire substrates preferred to crystallize in the ZB phase at lower T_g , while in the W phase at higher T_g . The critical T_g for the phase transition is about 440 °C. This T_g is higher than the reported

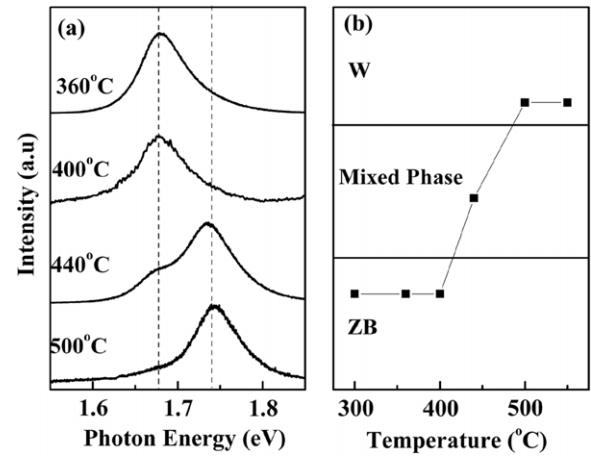


Figure 4. (a) PL spectra of CdSe with different T_g . (b) The crystalline phase of CdSe thin films with the T_g ranging from 300 to 550 °C grown on Al_2O_3 substrate.

300 °C in nanocrystalline thin film [9], but lower than the value for bulk CdSe (>1004 °C) [16]. The mechanism for this phase transition has been proposed by Lozada-Morales *et al* [17]. In the transition process, the atoms must pass through a potential barrier. At lower T_g (below 400 °C) the atoms did not have enough energy to go through the barrier. Therefore, the CdSe thin film was grown in the metastable ZB phase. When T_g increased to 440 °C, partial atoms would obtain enough kinetic energy and go over the barrier. Consequently, the sample grown at 440 °C showed a ZB and W mixed phase. When the T_g was above 500 °C, most of the atoms would have enough kinetic energy to get a minimum energy position. As a result, W-CdSe thin films were formed. However, the phase transition did not occur in the CdSe grown on GaAs (100) substrates. This is due to the fact that both ZB (111) and W (002) CdSe are geometrically possible to grow on sapphire substrates, while only ZB-CdSe can be formed on GaAs (100), as demonstrated by the atomic configuration shown in figure 3.

4. Conclusion

ZB and W phased CdSe thin films have been obtained by MOCVD. The substrate can affect both the crystalline phase and the orientation of CdSe thin films. The phase transition from the ZB phase to the W phase is observed on the CdSe thin films grown on sapphire. The dependence of the crystalline phase on the T_g is studied, and the critical T_g for the phase transition is 440 °C.

Acknowledgments

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