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Structural phase control of CdSe thin films by metalorganic chemical vapor deposition

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Abstract

Photoluminescence of CdSe thin films under different growth conditions was studied in this paper, and typical double emission peaks were observed at room temperature. Temperature and excitation intensity-dependent photoluminescence studies in combination with X-ray diffraction measurements revealed that the two emission peaks originate from cubic- and hexagonal-phased CdSe, respectively, which indicates that the crystalline phases of CdSe can be controlled by changing the growth conditions in metalorganic chemical vapor deposition process.

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1. Introduction

Cadmium selenide (CdSe) is a member of the II–VI semiconductors having a suitable band gap, a high absorption coefficient and high photosensitivity [1]. Along with some additives in it, CdSe can form an important class of semiconductor materials, which finds applications in many low-cost devices, such as light-emitting diodes [2], solar cells [3], photodetectors [4], electro photography [5] and lasers [6]. All these applications are associated with optical properties of CdSe; therefore, it is necessary to investigate the optical properties of CdSe films. Photoluminescence (PL) spectroscopy is suitable to achieve this goal, because it is a nondestructive method that can probe the electronic levels directly.

The PL of CdSe has been investigated in detail by a number of groups. For example, the luminescence spectrum of CdSe that consists of bound and free excitons as well as donor–acceptor pair (DAP) was fully resolved at 4.2 K [7]. An acceptor defect Se interstitial in CdSe has been reported by Halsted and Aven [8]. At 3 K, two distinct DAP transitions at 1.75 and 1.70 eV were observed in the PL spectra in addition to deep states at about 1.55 eV at 20 K [9]. As it is well known that CdSe can be crystallized in zinc blende (cubic), wurtzite (hexagonal) or wurtzite–sphalerite mixed phases, the transformation in crystalline phases of CdSe has attracted much attention in the past. Some researchers observed the phase transformation by annealing [10] or mechanically grinding CdSe samples [11]. However, the formation of different phases during growth process by changing the growth conditions is rarely reported. Furthermore, most of the phase transformations were characterized by X-ray diffraction (XRD) only [10], while very few reports can be found on the studies of different phases using PL spectroscopy [12].

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In our work, CdSe films were prepared on sapphire substrates by using metalorganic chemical vapor deposition (MOCVD) equipment. The PL emissions of the films consisted of two peaks, which can be assigned to the emission from cubic and hexagonal CdSe phases. That is, by changing the flux ratio of dimethylcadmium (DMCd) and H_2Se, wurtzite, sphalerite or mix-phased CdSe can be obtained intentionally.

2. Experiments

CdSe thin films were grown on *c*-plane sapphire substrates by LP-MOCVD using a homemade horizontal reactor with the growth pressure fixed at 150 Torr. In our experiment, high-purity hydrogen was used as carrier gas to carry the reactants into the growth chamber. 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, and then etched in the mixture solution of a H_2SO_4:H_3PO_4 = 3:1 at 160 °C for 10 min. The chemical-etched substrates were rinsed in DI water again and finally blown dry by nitrogen before being put into the growth chamber. The substrate was annealed at 600 °C in hydrogen ambient for 10 min, which is demonstrated to be an effective method to remove the residual surface contaminants. CdSe films were grown in the reaction chamber for 30 min. Three samples labeled by A, B and C were obtained, and the growth conditions were listed in Table 1. The luminescent properties of these thin films were studied in a PL system at room temperature and low temperature, employing the 488 nm line of an Ar^+ laser as the excitation source. A Rigaku Dmax-B X-ray diffractometer was use to characterize the structure of the thin films.

3. Results and discussion

Room temperature PL spectra of the three samples are shown in Fig. 1. Sample A was grown at 440 °C with the flow rate of H_2Se and DMCd fixed at 1.25×10^{-4} and 3.51×10^{-6} mol min^{-1}, respectively. It is very interesting to note that it contains double peaks that can be deconvoluted into two Lorentzian curves located at 1.67 and 1.74 eV. When the growth temperature is fixed at 360 °C while the flux ratio remained, only one emission peak at about 1.67 eV can be observed, as shown in Fig. 1B. When the flux ratio of H_2Se and DMCd was changed to another value (1.0×10^{-4} mol min^{-1}/3.51×10^{-6} mol min^{-1}) while the growth temperature was kept at 360 °C, only an emission peak at 1.74 eV was observed in sample C. For hexagonal CdSe, the near-band-edge (NBE) emission at room temperature is about 1.738 eV [13]. Therefore, the emission peak at 1.74 eV in sample A is attributed to the NBE emission of hexagonal CdSe, and sample C is a typical hexagonal CdSe thin film. Since sample B has an individual emission peak at 1.67 eV, it may have the same origin with the lower energy emission peak of sample A. To explore the origin of this peak, PL spectra of samples A and B at 82 K were studied, as shown in Fig. 2. For sample A, the two emission peaks are separated completely at 82 K. The higher energy peak located at 1.81 eV can be attributed to the NBE emission from hexagonal CdSe, for its position is very close to the reported band gap (1.82 eV at 77 K) [14]. The emission peak of sample B is very close to the lower energy emission peak, just as that observed in room temperature PL spectra, which further suggests that they have the same origin.

Table 1
The growth parameters of samples A, B and C

Sample	H_2Se (mol min^{-1})	DMCd (mol min^{-1})	Growth temperature (°C)
A	1.25×10^{-4}	3.51×10^{-6}	440
B	1.25×10^{-4}	3.51×10^{-6}	360
C	1.0×10^{-4}	3.51×10^{-6}	360

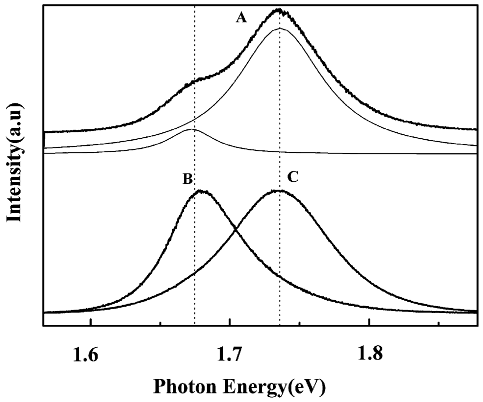

Fig. 1. Room temperature PL spectra of the three samples (A, B and C). For sample A, the above thick original peak is deconvoluted into two Lorentzaints of thin lines; the former is shifted up for clarity. The two vertical dotted lines is an aid to help see the alignment of peaks between above and bottom.

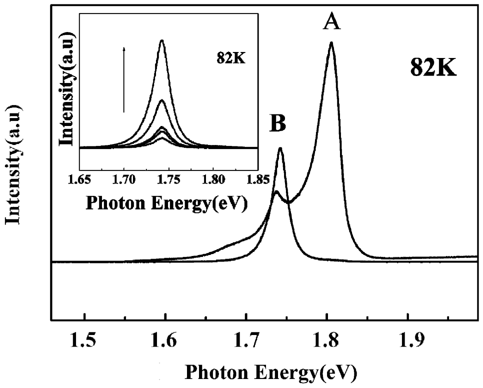

Fig. 2. PL spectra of samples A and B at 82 K. The inset is excitation dependence spectra for sample B at 82 K.

The possible origins of the lower energy peak are illustrated as follows. Firstly, it may come from the DAP emission. Secondly, it may be the two-longitudinal-optical

(2LO) phonon replica of the free exciton. Lastly, it is a phase transition between cubic- and hexagonal-structured CdSe. For the first possible origin, the energy position of the peak is very close to the reported DAP emission in CdSe [14]. However, it is well known that one of the typical characteristic of DAP emission is that it will blue-shift with increasing excitation density [15], but we did not detect this shift in PL spectra with increasing excitation density for sample B at 82 K, as presented in the inset in Fig. 2. This indicates this lower energy emission peak is not a DAP emission. The LO-phonon energy of bulk CdSe is 26 meV [16]. In our work, the energy splitting between the lower energy peak and the higher energy peak (NBE) is 66 meV, which is higher than 2LO-phonon replica (52 meV). Therefore, the 2LO replica of the free exciton can be excluded. Therefore, the origin of the peak at 1.67 eV is speculated to be from the cubic-phased CdSe. In order to verify the speculation, temperature-dependent PL measurement was conducted for sample A from 82 to 303 K, as shown in Fig. 3, in which all the spectra were normalized against their peak height to illustrate the PL spectroscopic lineshape and line width. We fit the two peaks position with the temperature by Varshni's equation [17]:

$$E_0(T) = E_0(0) - \frac{\alpha T^2}{\beta + T}, \tag{1}$$

where $E_0(0)$ is the optical band gap maximum at 0 K; α and β are fitting parameters. As shown in the inset, the solid and open triangles are experimental data and the lines are theoretical fits. They fit very well, and the fitting parameters are shown in Table 2. The band gap that obtained 1.818 eV is very close to the band gap at 1.6 K, which is 1.817 eV [18]; the peak located at 1.744 eV is very close to the band gap of cubic CdSe at 10 K reported by Samarth et al. [19]. Moreover, similar shrinkage (3.9×10^{-4} and 5.7×10^{-4} meV K^{-1}) of the band gap with temperature implies that they have similar origin [20]. Hence, it can be concluded that the emission peaks observed at 1.81 and 1.74 eV originate from the NBE emission of hexagonal and cubic CdSe, respectively.

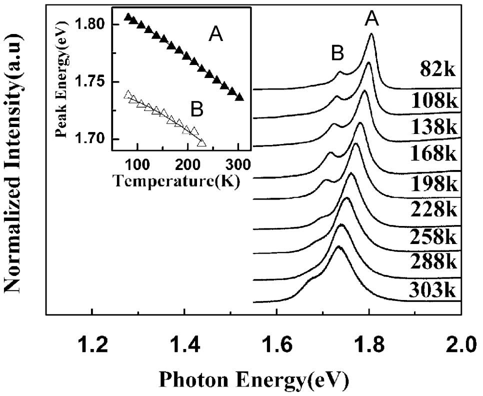

Fig. 3. Temperature-dependent PL spectra of sample A from 82 to 303 K.

Table 2
Parameters obtained by fitting the data in the inset in Fig. 3 with Eq. (1)

Emission peak	α ($\times 10^{-4}$ eV K^{-1})	β (K)	$E_0(0)$ (eV)
a	3.9	127	1.818
b	5.7	413	1.744

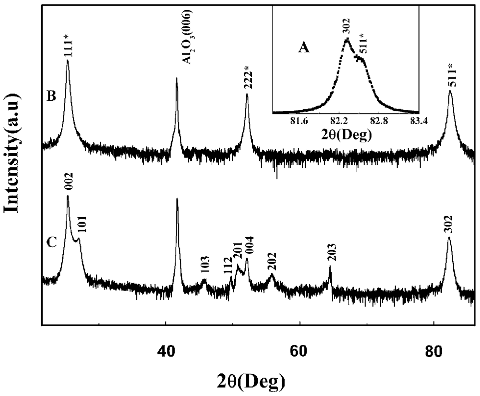

Fig. 4. XRD pattern of samples B (above), C (bottom) and A (inset).

XRD is an effective tool to determine the structure of the sample. Fig. 4 shows XRD diffraction pattern of samples A, B and C. The peaks labeled by *hkl** are attributed to the zinc blende structure, and those by *hkl* are identified as the wurtzite structure. No peaks belonging to other impurities are observed. Within our experiment resolution, there is some overlap of peaks belonging to the zinc blende and wurtzite-structured CdSe. For examples, the three usually strong zinc blende peaks (1 1 1), (2 2 0) and (3 1 1) overlap correspondingly with 002, 110 and 112 peaks of wurtizte [21]. However, the (5 1 1) peak (in sample B) can only be indexed to the zinc blende structure, which is different from the (3 0 2) diffraction peak (in sample A) of wurtzite structure as shown in Fig. 4. Furthermore, the XRD pattern of the sample C contains identifiable hexagonal characteristic peaks (1 0 1), (1 0 3), (2 0 1); and (2 0 3), therefore, sample B is a cubic phase and sample C is hexagonal phase. For sample A, both (5 1 1) and (3 0 2) can be observed in the XRD pattern as shown in the inset; in other words, sample A is crystallized in mixed phase of cubic and hexagonal CdSe. The results obtained from XRD are in good agreement with the analysis of PL spectra.

As depicted by both PL and XRD measurements, cubic, hexagonal or mix-phased CdSe have been obtained in our experiments by tuning the growth conditions. We can see that the flux ratio of the precursors can affect the phase of CdSe at lower growth temperature. For samples B and C, more Se flux will drive the film to cubic structure. The reason lies in that in our case, the flux of Se is far more than that of Cd, and more Se flux will lead to defects or dislocations in the films, which in turn drive the films to a metastable phase. As for the effect of growth temperature on the crystalline phase of CdSe, this will become the dominant factor when temperature is higher than 440 °C; it can be observed in samples A and B, that is, high temperature will lead to hexagonal structure. It is known that CdSe has a natural preference for wurtzite structure under normal conditions [22]. In our case, high growth temperature will be helpful for the reaction radical to move to the energy minimums; as a result, wurtzite-structured CdSe forms under higher temperature, which is confirmed by the fact that at 500 °C with the same Cd/Se of cubic phase to sample B, pure hexagonal-phased CdSe thin films have been obtained in our experiment (not shown in this paper).

4. Conclusion

The origin of the two emission peaks in CdSe thin films grown by MOCVD has been discussed. They are ascribed to the NBE emissions of cubic (lower energy)-and hexagonal (higher energy)-structured CdSe. This indicates that varying the flux ratio of the precursors under lower ($<400\,^{\circ}$C) growth temperature can control the phase of CdSe, which raises a number of exciting prospects. For instance, preliminary results show promise of growing wurtzite–zinc blende superlattices related to CdSe that are very interesting to both basic research and potential applications.

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