



Metal organic chemical vapor deposition growth of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films

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ARTICLE INFO

Article history:

Received 30 November 2007

Received in revised form 7 September 2008

Accepted 17 September 2008

Available online 27 September 2008

PACS:

61.66.Dk

61.82.Fk

67.25.dp

Keywords:

$\text{Cd}_{1-x}\text{Fe}_x\text{Se}$

Thin film

PL

MOCVD

ABSTRACT

High quality $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films with different Fe content were grown on sapphire substrates by using low-pressure metal organic chemical vapor deposition (LP-MOCVD). The structural properties of these films were examined by X-ray diffraction (XRD). Temperature dependent spectra were also used to study the origin of the emission peak. Strong near band emission (NBE) without other defect related emission at room temperature demonstrates that the thin films have high optical quality. Absorption spectra were used to estimate the band gap of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ films.

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1. Introduction

Cadmium ferrous selenide is a kind of diluted magnetic semiconductor, which is obtained by doping Fe^{2+} into the lattice of CdSe matrix, the magnetic, electronic and magneto-optics of CdFeSe alloys has been studied by a number of researchers from 80s [1–6]. Among these, some interesting results have been reported. A. Petrou et al. studied the splitting of the bands of CdFeSe at low temperature under magnetic field, he concluded that $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ exhibits Van Vleck paramagnetism instead of the more usual Larmor paramagnetism [3]. The first observations of spin-flip Raman-scattering in CdFeSe were made by Suh et al. [7], and then Heiman et al. have reported a novel manifestation of the singlet ground state of Fe^{2+} in the spin-flip Raman-scattering spectrum of donor electrons in CdFeSe [8]. Recent years, Pawar et al. shown that Fe-doped CdSe thin films are more photo-sensitive than that of non-doped CdSe [9]. As a matter of fact, CdFeSe thin films have become one of the promising materials for photo-electrochemical solar cell applications [10]. The CdFeSe single crystal has been prepared earlier [11], however, the report about the growth of CdFeSe thin films is very few. CdFeSe thin

films have been deposited on the stainless steel by Rajapure et al., but the power conversion efficiency was only 0.41%. Such low power conversion efficiency is attributed to large scattering and recombination of the photo-generated carriers due to poor quality of the thin film [12]. As well known, the MOCVD technique has been widely used in preparing high quality thin films, for it can offer excellent control over the growth parameters, such as temperature, pressure, flow rate of the precursors, precisely and independently. Unfortunately, up to now, there is no report on the growth of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films by MOCVD. Fe is one of the famous PL quenching centers like Co and Ni, which is why a little attention was paid on the PL spectra of CdFeSe, however, the PL spectra can be a powerful and nondestructive method to characterize the crystal quality of these thin films.

In this paper high quality $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ ($0 < x < 9\%$) thin films were firstly prepared on sapphire substrate by MOCVD. We applied the PL spectra to investigate the optical quality of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films at room temperature and low temperature, respectively. The band gap of the thin films was obtained from absorption spectra.

2. Experiment

The $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin film was fabricated on Al_2O_3 (0 0 1) substrate by a low-pressure metal organic chemical vapor deposition (LP-MOCVD) system with a horizontal rectangular quartz chamber. The

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growth temperature was 713 K and the growth pressure was fixed at 2×10^4 Pa. Dimethylcadmium (DMCd), ironpentacarbonyl ($\text{Fe}(\text{CO})_5$) and hydrogen selenide (H_2Se) were used as precursors. Ultrahigh purity hydrogen was selected as carrier gas. The substrates were cleaned by acetone and ethanol for 5 min in an ultrasonic bath and etched in an acid solution ($3\text{H}_2\text{SO}_4 + 1\text{H}_3\text{PO}_4$) for 5 min at 433 K, followed by a de-ionized water rinse. Then the substrates were loaded into the LP-MOCVD chamber and heated to 873 K for 10 min in H_2 ambient. During deposition the DMCd precursor was transported into the chamber at 1.25×10^{-4} mol/min. H_2Se gas is introduced separately into the chamber and the flow rate was kept at 3.51×10^{-6} mol/min. The flow rate of $\text{Fe}(\text{CO})_5$ was changed to obtain $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ with different Fe content. We labeled them as samples A–D in the following discussion.

The structure of samples was studied by XRD with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154178$ nm) (Ringaku O/max-RA). The morphology and thickness (500 nm) of the thin films were examined with a scanning electron microscope (SEM) (HITACHI, S-4800). The composition of sample examined by an energy dispersive X-ray spectrometer (EDS) (GENESIS 200 XMS 60S) attached to the SEM. The absorption was recorded for the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films in the range of 190–850 nm using Shimadzu double beam spectrophotometer. The PL spectra were measured in the wavelength range of 500–800 nm using Ar^+ laser beam at an excitation wavelength of 488 nm with a variable temperature controller.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films with different Fe content x . All samples exhibit preferential orientation with c -plane perpendicular to the substrate surface with Al_2O_3 (0 0 6) diffraction peaks at $2\theta = 41.70^\circ$. It is well known that hexagonal CdSe (0 0 2) or cubic (1 1 1) diffraction peak located at $2\theta = 25.39^\circ$, previous work has demonstrated that the CdSe thin films under the same growth condition is crystallized in hexagonal form [13]. Therefore, the peaks at 25.44° , 25.47° , 25.49° and 25.55° correspond to the diffraction peak from (0 0 2) plane of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films, depending on the Fe content x . The x values of samples for A–D are 2, 4.1, 6.3 and 8.3%, respectively. It is well known that the crystallized quality is worse as the dopant increased for ternary compounds, which can be seen from Fig. 1(b). The full width at half maximum (FWHM) of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ diffraction peaks broadens with increasing Fe content. Fig. 1(c) shows the typical SEM image of CdFeSe samples, it can be seen that the thin film is very compact, hexagonal multilayer structure also is observed which indicates the high crystallized quality of the thin films.

In addition, the c -axis lattice constant d of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films can be obtained from the diffraction angle by the formula,

$$2d \sin \theta = n\lambda \quad (1)$$

The lattice parameter as a function of Fe content x of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ is plotted in Fig. 2(a), a relative change in the c -axis lattice constant has been found resulting from the difference of the ionic radius between Cd^{2+} (0.097 nm) and Fe^{2+} (0.076 nm). The lattice parameter decreases linearly with increasing Fe content x , and it can be expressed as a function of x by the following equation:

$$d(x) = 7.0152 - 0.4264x \quad (0 < x < 9\%) \quad (2)$$

Typical EDS spectra of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ is shown in Fig. 2(b), it can be seen that only Cd, Se, and Fe element was found, no other impurity like O and C were observed in all samples.

The optical properties were studied by PL spectra and absorption spectra, as shown in Fig. 3. Only a strong emission peak is observed in all samples. In order to study the origin of the emission peak,

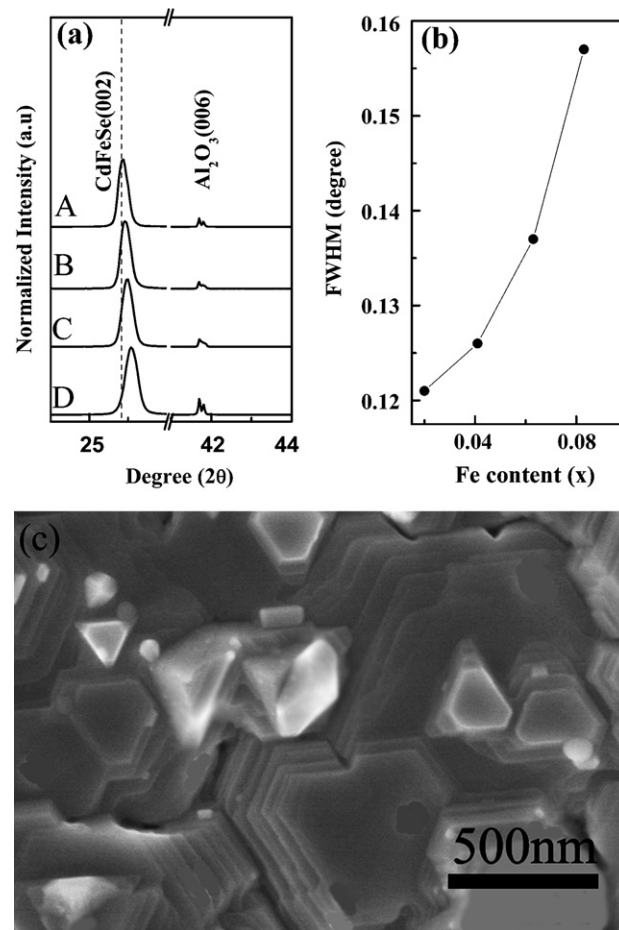


Fig. 1. (a) XRD patterns of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$, (b) the FWHM of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ (0 0 2) diffraction peak as a function of Fe content and (c) the typical SEM image of the CdFeSe samples.

temperature dependent PL measurement for sample C was conducted from 82 to 300 K in Fig. 4. We fit the peak position with the temperature by Varshni equation [14].

$$E_0(T) = E_0(0) - \frac{\alpha T^2}{\beta + T} \quad (3)$$

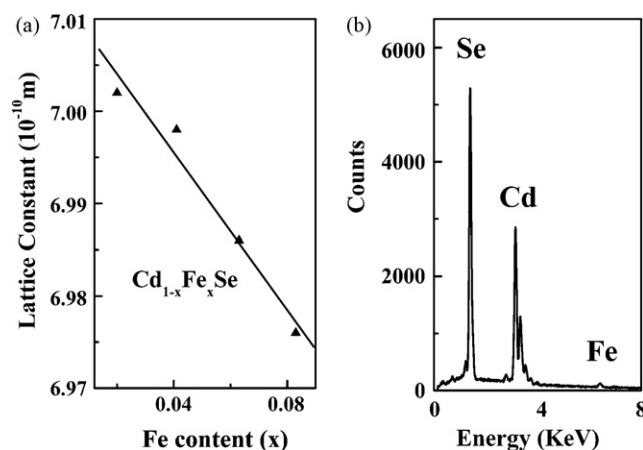


Fig. 2. (a) Lattice constant as a function of Fe content and (b) typical EDS spectra of the CdFeSe samples.

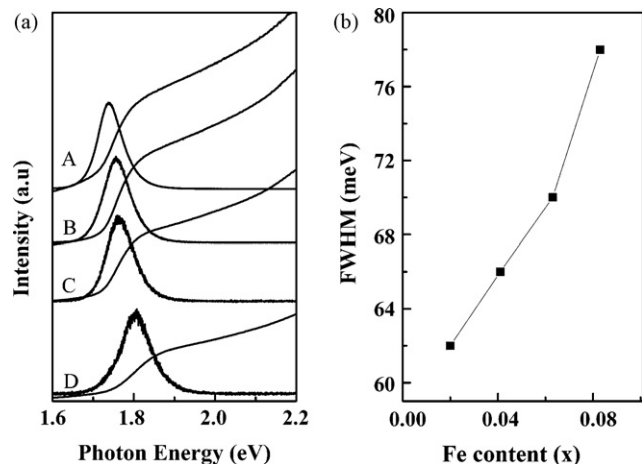


Fig. 3. (a) PL and absorption spectra of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ with different Fe content and (b) FWHM of emission peak with different Fe content.

where $E_0(0)$ is the optical bandgap maximum at 0 K, α and β are fitting parameters. As shown in the inset, the solid square is experiment data and the line is theoretical fits. They fit very well, the parameter $E_0(0)$ is 1.844 eV, and it is closed to the band gap of $\text{Cd}_{0.94}\text{Fe}_{0.06}\text{Se}$ (1.899 eV at 0 K) previous reported [15]. Hence, it can be concluded that the emission peak observed at room temperature originate from the NBE emission of CdFeSe . For samples A–D, both the NBE and absorption edge show a blue shift with increasing Fe content due to the widen of the band gap, which have been reported in bulk single crystal $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ by Stankiewicz et al. [15]. The FWHM of the emission peaks shown in Fig. 3(b) become wider and wider with increasing Fe content, which proves that much Fe incorporation will disorder the lattice of CdFeSe . However, no Fe and any other defect related emissions were found in our study range ($0 < x < 9\%$), which indicates the high optical quality of thin films.

It is generally accepted that for a material with direct band gap, the relation between the absorption coefficients and photon energy is expressed by the following formula [16]:

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (4)$$

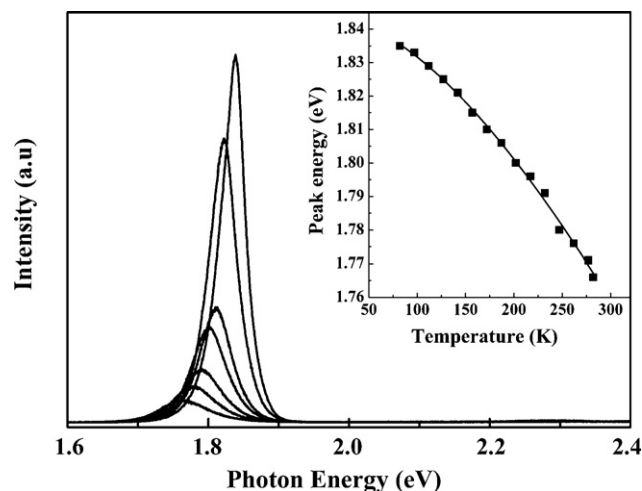


Fig. 4. The temperature dependent spectra of sample C from 82 to 300 K. (The inset shows the peak position varied with the temperature fitted by Varshni equation, the solid square is experiment data and the line is theoretical fits.)

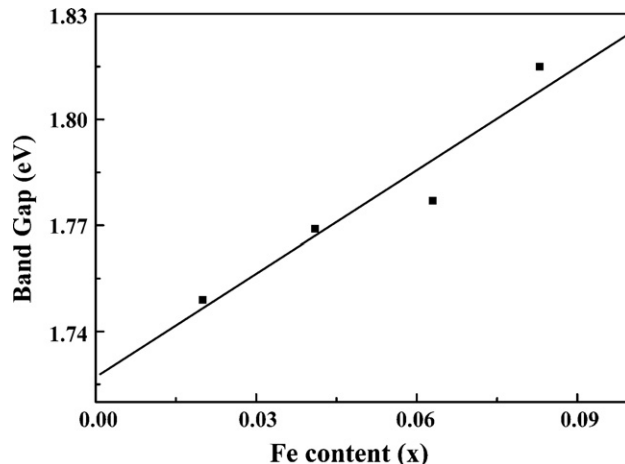


Fig. 5. Band gap of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films as a function of Fe content.

where the symbols have their usual meanings, A is a constant and $n = 1/2$ for allowed direct transition, $n = 2$ for indirect transition. The plot of $(\alpha h\nu)^2$ vs. $h\nu$ is used to estimate the band gap of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films. The results were shown in Fig. 5, it can be observed that the energy band gap (E_g) of $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films increases with the increase of Fe content x , the E_g as a function of x at room temperature can be expressed by the formula,

$$E_g(x) = 1.727 + 0.972x \quad (0 < x < 9\%) \quad (5)$$

4. Conclusions

High quality $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films grown on sapphire substrate were realized by LP-MOCVD. The lattice constant and energy gap of the $\text{Cd}_{1-x}\text{Fe}_x\text{Se}$ thin films varies linearly with Fe content in the range $0 < x < 9\%$. The temperature variation of the energy gap can be well fitted by the empirical Varshni relation. The PL spectra were used to examine the optical quality of the thin films at room temperature. The high optical quality of these thin films implies that the thin films have potential application in photo-electro-chemical solar cell.

Acknowledgements

This work is supported by the Key Project of National Natural Science Foundation of China under Grant Nos.60336020 and 50532050, the “973” program under Grant No.2006CB604906, the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos. 60429403, 60506014 and 10674133.

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