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Growth optical and magnetic properties of $Cd_{1-x}Fe_xS$ films prepared on Al_2O_3 (0001)

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Abstract

Diluted magnetic semiconductor $Cd_{1-x}Fe_xS$ ($0<x<0.4$) films were grown by the low-pressure metal organic chemical vapor deposition on c-Al_2O_3 substrates. All the films were fabricated at 633 K under a hydrogen pressure of 10^4 Pa. Structure and composition analysis revealed that the Fe was alloyed into the lattice structure of CdS, forming solid solution instead of precipitation. The room temperature optical band gap of $Cd_{1-x}Fe_xS$ films can be tuned from 2.454 to 2.310 eV with increasing Fe concentration from $x=0$ to 0.37. A typical Van Vleck-type paramagnetism of $Cd_{0.88}Fe_{0.12}S$ film was observed using superconduction quantum interference device magnetometer below 6 K.

Keywords: Diluted magnetic semiconductor; CdFeS; Band gap

1. Introduction

Diluted magnetic semiconductors (DMSs) [1] have attracted much attention due to the wealth of scientific information and potential technological applications. DMSs are semiconductor alloys formed by randomly replacing a fraction of the cations with magnetic ions, e.g., Fe^{2+} in CdS to form $Cd_{1-x}Fe_xS$. In these materials, the large sp–d exchange interaction between magnetic ions and electrons in valence band [2–4] can lead to a number of unusual electronic, optical and magneto-optical properties including the ability to magnetically tune the band gap. These properties make DMSs promising candidates for fabricating magneto-optical devices such as magnetic field sensors, isolators and magneto-optical switches [5]. Much work has so far been done on Mn doped II–VI semiconductors recently [5–9]; however, little is known about II–VI DMSs that contain other transition metals ions such as Fe ions [10–14]. The physical situation in the materials based on Fe differs completely from that of Mn: substitutional Fe^{2+} possesses both spin and orbital moment ($S=2$, $L=2$). It leads to some special properties such as typical Van Vleck-type paramagnetism and isolated Fe ion contribution to the specific heat in the absence of a magnetic field [15–17]. Furthermore, we could also adjust the band gap of semiconductor in a wide range by changing the Fe concentration. These phenomena already make Fe-based DMS worth studying.

Semiconductor CdS, with band gap energy of 2.454 eV at room temperature, is one of widely studied materials for its wide applications in solar cell and electroluminescent devices. Fe-doped CdS single crystal in bulk form has been synthesized by the Bridgman method [15–17]. Specimens fabricated by this method showed hexagonal structure for $x<0.1$. The d–d exchange interaction and thermodynamic properties have been studied. T.Q. Vu et al. [16] found that the magnetization for H // c-axis of $Cd_{0.9841}Fe_{0.0159}S$ is larger than that for H ⊥ c-axis at low fields, but at high fields the anisotropy is reversed. A. Twardowski et al. have measured the magnetic susceptibility of $Cd_{1-x}Fe_xS$ ($x<0.9$) and found a typical Curie–Weiss behaviour above 100 K. Meanwhile, energy levels resulting from the

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splittings of 5E ground term of the Fe^{2+} in $Cd_{1-x}Fe_xS$ were studied by Raman scattering at $T=2$ K. However, no more information about the growth, optical and magnetic properties of $Cd_{1-x}Fe_xS$ films can be observed.

In this paper, $Cd_{1-x}Fe_xS$ ($0<x<0.4$) films with a typical thickness of 900 nm were fabricated by low-pressure metal organic chemical vapor deposition (LP-MOCVD) on c-Al_2O_3 substrates. $Cd_{1-x}Fe_xS$ thin films were found to possess preferred *c*-axis orientation and exhibited hexagonal structure even Fe concentration up to $x=0.37$. Optical and magnetic properties of the films have been investigated.

2. Experiment

$Cd_{1-x}Fe_xS$ thin films were grown by an LP-MOCVD system with a horizontal rectangular quartz reactor. The ironpentacarbonyl [$Fe(CO)_5$], dimethylcadmium (DMCd) and hydrogen sulphide (H_2S) gas were used as source materials for Fe, Cd and S, respectively. Ultrahigh purity hydrogen was selected as a carrier gas. The sapphire with (0001) orientation was used as the substrate. Before loaded into the reaction tube, the substrates were cleaned by acetone and ethanol for 5 min in an ultrasonic bath and etched in a acid solution ($3H_2SO_4+1H_3PO_4$) for 5 min at 433 K, followed by a de-ionized water rinse. Then the substrates were heated at 873 K for 10 min in H_2 gas flow. During deposition, DMCd (268 K) precursor is transported into the reactor at 8 ml/min. H_2S gas is introduced separately into the reactor and the flow rate is kept at 11.6 ml/min. The flow rate of $Fe(CO)_5$ (273 K) is changed to obtain $Cd_{1-x}Fe_xS$ films with different Fe concentration x. All the depositions were operated at the pressure of 1×10^4 Pa and the growth temperature (T_g) was kept at 633 K. The thickness of all the films is about 900 nm and the growth rate is ~15 nm/min.

The structure of $Cd_{1-x}Fe_xS$ films was characterized by X-ray diffraction (XRD) with Cu Kα radiation ($\lambda=0.154178$ nm) (Ringaku O/max-RA). Photoluminescence (PL) was also measured at room temperature using with an He–Cd laser with 325 nm excitation to study optical properties of the films. The magnetic properties of the films were investigated using a superconduction quantum interference device (SQUID) magnetometer with the applied field parallel to the surface of the films. The Fe concentration x of the $Cd_{1-x}Fe_xS$ films have also been determined by the energy dispersive spectroscopy (EDS) (GENESIS 2000 XMS 60S) based on the scanning electron microscopy (HICACHI, S-4800). All EDS spectra of the samples were obtained under following conditions: 20 kV acceleration voltage, 100 s live time and 5% dead time.

3. Result and discussion

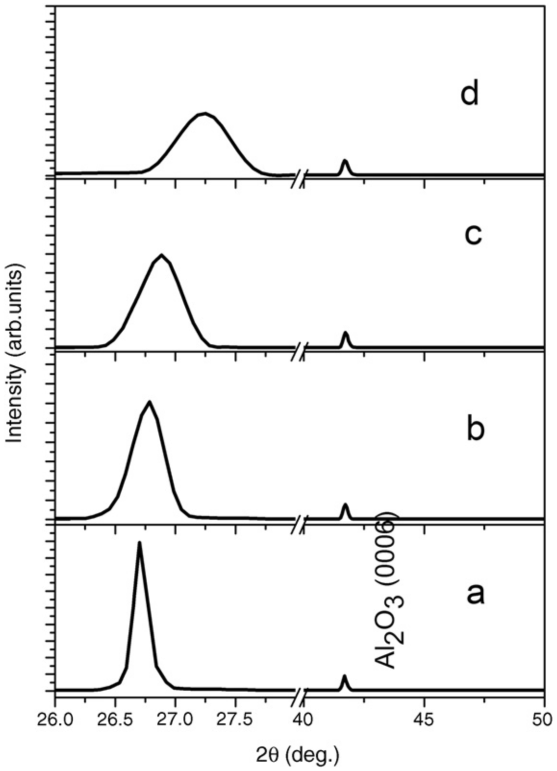

Fig. 1. XRD patterns of $Cd_{1-x}Fe_xS$ films with different Fe concentrations: a, $x=0$; b, $x=0.12$; c, $x=0.16$; d, $x=0.37$.

Fig. 1 shows the XRD patterns of the $Cd_{1-x}Fe_xS$ films with different Fe concentrations x. All the samples exhibit preferential orientation with c-plane perpendicular to the substrate surface. The peaks at 26.84°, 26.91° and 27.24° correspond to the diffraction from (0002) plane of $Cd_{1-x}Fe_xS$ films, depending on the Fe concentration x. The values of x of samples a, b, c and d are 0, 0.12, 0.16 and 0.37, respectively. The corresponding full width at half maximum (FWHM) of (0002) diffraction peaks broadens with increasing x. From Fig. 1, it is also observed that Fe was doped into the lattice site of CdS by replacing Cd, forming solid solution instead of precipitation even Fe concentration up to $x=0.37$. Furthermore, all the (0002) diffraction peaks in Fig. 1 showed broader FWHM and this result may be caused by the defects in the samples. The *c*-axis lattice constant of the $Cd_{1-x}Fe_xS$ films can be obtained from the diffraction angle by the formula: $2\ d\ \sin\theta=n\ \lambda$. In Fig. 2, we plot the lattice parameter as a function of Fe concentration x of the $Cd_{1-x}Fe_xS$ films. From this figure, a relative change in the *c*-axis lattice constant, resulting from the difference of the ionic radius between Cd^{2+} (0.97 Å) and Fe^{2+} (0.76 Å), has been found. The lattice parameter decreases linearly with Fe concentration x, and can be expressed as a function of x by the following equation:

$$a(x) = (6.7034\pm0.0002) - (0.4209\pm0.0002)x \qquad (1)$$

Meanwhile, EDS spectra have been used to determined the Fe concentration x of the $Cd_{1-x}Fe_xS$ and no other atoms like O and C were observed in the samples (see inset of Fig. 2).

The room temperature absorption spectrum of the $Cd_{0.92}Fe_{0.08}S$ film was shown in the inset of Fig. 3. The sharp absorption edge confirms the good optical property of the samples. The approximate room temperature optical band gap for $Cd_{1-x}Fe_xS$ films was obtained with the help of absorption spectra. To calculate the energy band gap from absorption spectra, Tauc relaxation is used, where $\alpha\ h\ \nu=A(h\ \nu-E_g)^n$; $h\ \nu$

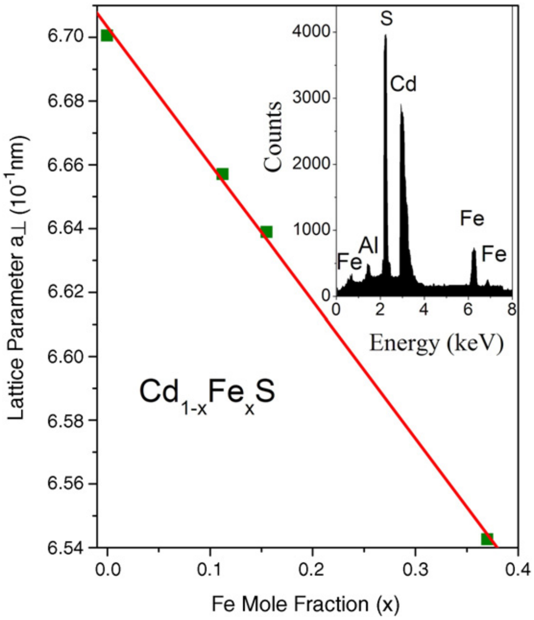

Fig. 2. Perpendicular lattice parameter as a function of Fe concentration x of the $Cd_{1-x}Fe_xS$ films.

is the photo energy; α is absorption coefficient; E_g is the band gap; A is a constant and $n=1/2$ for direct band gap material. In Fig. 3, it can be observed that the energy band gap (E_g) of $Cd_{1-x}Fe_xS$ films decreases with the Fe concentration x. We note that the band gap does not decrease linearly with Fe concentration for $0<x<0.4$. An abrupt decreasing of the E_g occurred in high Fe concentration $Cd_{1-x}Fe_xS$ films ($0.12<x<0.4$), but small change was found for low Fe concentration ($0<x<0.12$). Such phenomenon was also found in the data of other DMSs, such as $Cd_{1-x}Mn_xS$ [19] and $Zn_{1-x}Mn_xSe$ [20,21]. The upward bowing at small values of x ($x<0.12$) in Fig. 3 was suggested to be related to the s–d and p–d exchange interacting with the Fe magnetic moments.

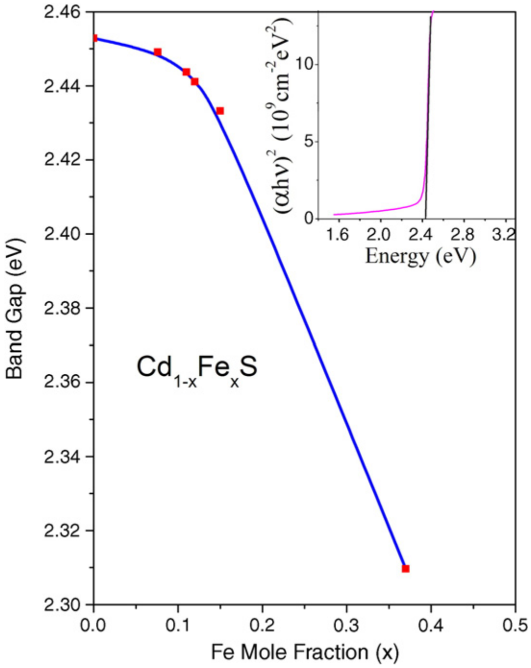

Fig. 3. Optical band gap at room temperature as a function of Fe concentration x of the $Cd_{1-x}Fe_xS$ films. The inset shows the absorption spectrum of $Cd_{0.88}Fe_{0.12}S$.

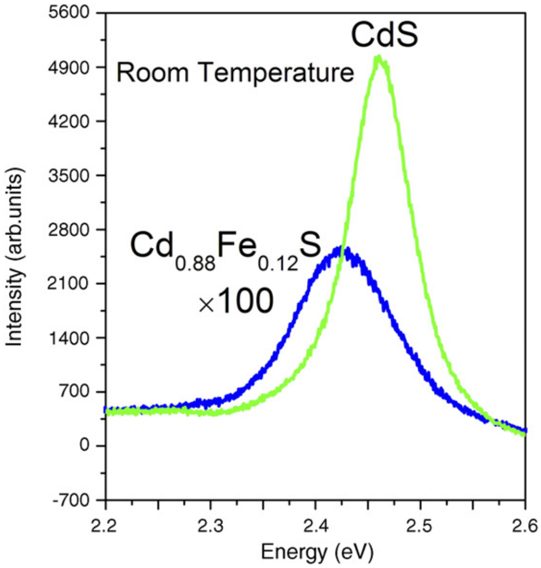

Fig. 4. PL spectra of $Cd_{0.88}Fe_{0.12}S$ and CdS films at room temperature.

The optical properties of the films were examined at room temperature using a He–Cd (325 nm) laser as the excitation source. It is known that Fe could act as a luminescent quencher in CdS. However, in our experiment $Cd_{1-x}Fe_xS$ films with low Fe content ($x=0.12$) still has a clear emission peak even at room temperature, just as shown in Fig. 4. Compared with the PL spectra of the CdS film, one can see that the emission peaks position of $Cd_{0.88}Fe_{0.12}S$ film shift to the low energies, and the full width at half maximum of the peaks becomes broader. From the band-edge absorption spectra of $Cd_{0.88}Fe_{0.12}S$ film (inset in Fig. 3) and the PL spectra of $Cd_{0.88}Fe_{0.12}S$ film at room temperature, it is observed that the PL spectra of $Cd_{1-x}Fe_xS$ can

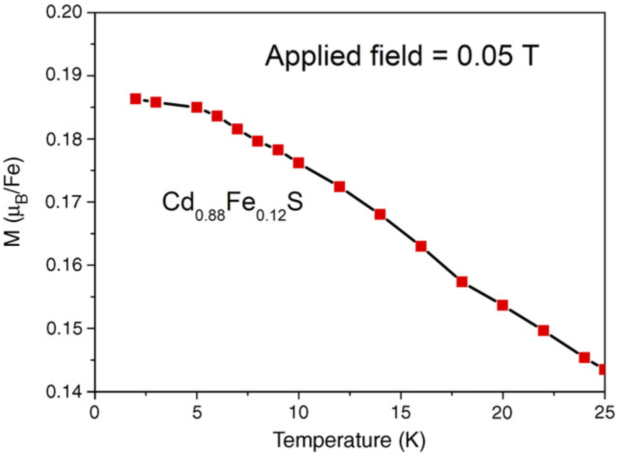

Fig. 5. The temperature dependence of the magnetization at fixed magnetic field for $Cd_{0.88}Fe_{0.12}S$.

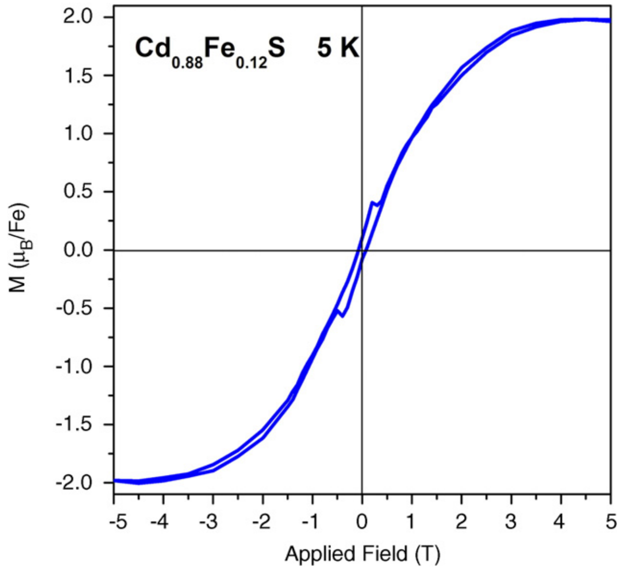

Fig. 6. M–H relationship of the $Cd_{0.88}Fe_{0.12}S$ film at 5 K.

be attributed to band-edge emission. The emission peak intensity of $Cd_{0.88}Fe_{0.12}S$ film is much weaker than that of CdS film at room temperature. The Fe doping could lead to remarkable change in energy band gap. The broadening of the band-edge luminescence peaks could be attributed to the fluctuation of Fe content and the defects in the film.

The magnetic properties of the diluted magnetic semiconductor $Cd_{1-x}Fe_xS$ films were investigated using a SQUID magnetometer with a magnetic field applied parallel to the film surface. We noted that when Fe^{2+} ($3d^6$) substitutes for Cd^{2+}, the ground manifold of the Fe^{2+} is ^5E. In second order, this is split by the spin–orbit interaction into five levels. The lowest lying state is a singlet A_1 which has no permanent magnetic moment. When a magnetic field is applied, it mixes other states of the ^5E manifold into the A_1 state so that a field and temperature dependent Van Vleck magnetic moment is produced. One characteristic feature is that the moment becomes independent of temperature (but not field) when k_BT is small compared to the A_2 (singlet)–A_1 (singlet ground state) separation [10,16,18]. The separation of A_2 to A_1 which was measured for Fe^{2+} in CdS using Raman scattering [17] is 1.45 meV. Therefore, Van Vleck paramagnetism is expected below 17 K for $Cd_{1-x}Fe_xS$. In Fig. 5, typical magnetization (M) versus temperature (T) curve was measured during cooling in an applied magnetic field of 0.05 T for $Cd_{0.88}Fe_{0.12}S$ film. The temperature independence of M for $T<6$ K shows that the $Cd_{0.88}Fe_{0.12}S$ film exhibited a typical Van Vleck-type paramagnetism. Ferromagnetic behavior of $Cd_{0.88}Fe_{0.12}S$ film was further investigated as a function of the applied magnetic field. The field dependence of magnetization (M–H curve) of the $Cd_{0.88}Fe_{0.12}S$ films was measured at 5 K, and revealed an obvious hysteresis loop, indicating the ferromagnetic ordering existing in the materials at low temperature (Fig. 6). Furthermore, the M–H curve indicates that the sample consists of two magnetic phases (paramagnetic and ferromagnetic). Meanwhile, the $Cd_{0.88}Fe_{0.12}S$ films showed a typical paramagnetism at room temperature, indicating that no other ferromagnetic phase like Fe or Fe oxide occurred in the films. Therefore, the ferromagnetism of the samples at 5 K may come from $Cd_{0.88}Fe_{0.12}S$ diluted magnetic semiconductor or little of Fe–S compounds. The detailed reason needs to be further studied.

4. Conclusions

$Cd_{1-x}Fe_xS$ films have been prepared on c-Al_2O_3 substrates by LP-MOCVD at the temperature of 633 K for a wide range of Fe concentrations ($0<x<0.4$). The Fe was doped into the lattice structure, forming solid solution instead of precipitation even Fe concentration up to $x=0.37$. The formation of $Cd_{1-x}Fe_xS$ films leads to a decrease of band-gap with the increasing of Fe content. At the same time one can observe a decrease of luminescence intensity and broadening of emission peak. Typical Van Vleck-type paramagnetism was observed below 6 K for $Cd_{0.88}Fe_{0.12}S$ and the hysteresis loop measured at 5 K indicates that the sample consists of two magnetic phases (paramagnetic and ferromagnetic).

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