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Magnetic properties and tunneling magnetoresistance effect in Fe–CdFeS granular films

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Granular thin film samples composed of Fe clusters embedded in CdFeS were prepared with using low pressure metal organic chemical vapor deposition. Temperature dependence of the resistivity of the granular film follows well the relationship for the tunneling transport between the iron granules. A large negative magnetoresistance of about 2.2% at 0.1 T was observed at room temperature due to the presence of Fe clusters. The hysteresis behavior observed in the magnetoresistance corresponded exactly to those of the hysteresis loop in the magnetization measurement, which evidently showed the correlation between the magnetoresistance and global magnetization in the sample. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2709892]

Hybrid ferromagnetic-semiconductor structures are of strong interest to the development of spintronic devices.[1] Up to now, much attention has been concentrated on fabricating high quality ferromagnetic films epitaxially on semiconductor substrates, such as Fe or manganese compounds on GaAs.[2–5] Heteroepitaxial growth of ferromagnetic metals on semiconductor can realize room temperature ferromagnetism, while it is usually difficult to regrow semiconductor[4,5] on metal to form trilayer structure. Dilute magnetic semiconductors (DMSs) have better compatibility with semiconductor, but they are usually paramagnetic or ferromagnetic with very low Curie temperatures (T_C). Ferromagnetic metal-semiconductor granular system, consisting of magnetic metal clusters embedded in semiconductor matrix, has received more and more attention due to its room temperature ferromagnetism and good compatibility with semiconductors.[6–8] Recently, increasing interests have been paid to the tunneling magnetoresistance (TMR) effects in granular systems because of their advantage in some aspects when compared to those of the trilayer magnetic tunnel junctions (MTJs). For example, the existence of pinholes in MTJs is a serious problem which will greatly minimize the TMR,[9] while it is not a problem in granular systems since the latter consists of thousands of tunnel junctions.[10]

Over the past decade, stimulating studies of the ferromagnetic granular films were carried out using III-V semiconductors such as GaAs or InGaAs as the matrix. A negative magnetoresistance (MR) about 1.5% was observed in GaAs with MnAs nanoclusters at 30 K in 1 T by Akinaga *et al.*[11] Pekarek *et al.*[12] reported a large negative MR effect (~3.2% at 5 K in 0.5 T) in an iron-doped InGaAs sample in which the MR was attributed to the superparamagnetic clusters embedded in the matrix. One big challenge for the previous reports on the granular films using III-V semiconductors is that large MR only appears at very low temperature which is not good for room temperature application. Furthermore, larger MR effect at smaller magnetic field is also preferred for device operation.

Here we have studied a granular system composed of Fe clusters embedded in CdFeS matrix. Since Fe is a good ferromagnetic material with low coercivety and high Curie temperature, it is expected to give better MR effect at room temperature with much lower magnetic field. Matrix using wide gap II-VI semiconductor instead of narrower gap III-V semiconductor is also an advantage to achieve better TMR performance. Considering the fact that the origin of the MR comes from the spin-related scattering or tunneling process, we believe the design using CdFeS instead of CdS as the matrix will give stronger scattering and thus larger MR effect is anticipated. We show that a large negative MR of about 2.2% at 0.1 T is achieved at room temperature due to the presence of Fe clusters in CdFeS matrix.

In this work, we report the growth, the magnetic properties, and the TMR effect of the Fe–CdFeS granular films prepared using low pressure metal organic chemical vapor deposition (LP-MOCVD) on sapphire substrates. The structure and the composition of the samples were characterized using x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS), respectively. The magnetic properties were investigated using a vibrating sample magnetometry (VSM). The magnetoresistance was measured using a two-probe method with annealed indium pads as Ohmic contacts.

The samples were grown using 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. Sapphire with (0001) orientation (C face) was used as the substrate. During deposition, DMCd precursor was transported into the reactor at 8 ml/min. H_2S gas was introduced separately into the reactor and the flow rate was kept at 11.6 ml/min. The flow rate of $Fe(CO)_5$ was 0.5 ml/min and the growth temperature (T_g) was kept at 360 °C. We find that uniform CdFeS films with homogeneous Fe distribution is easily obtained with the above

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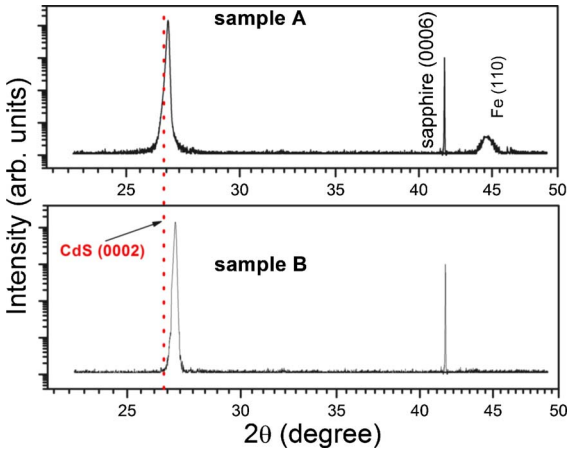

FIG. 1. (Color online) XRD patterns of the Fe–CdFeS granular film (sample A) and CdFeS DMS (sample B). The Fe composition in the CdFeS matrix of sample A is about 1.5% and is about 5% in sample B.

growth parameters fixed. By periodically changing the pressure in the chamber from 76 to 80 Torr for 30 s every 2 min, we find that the obtained thin film samples are with Fe cluster phases embedded in CdFeS DMS matrix. The phase separation is believed to come from the sensitive fluctuation of the flow rate of the $Fe(CO)_5$ source due to the pressure modulation. The two kinds of samples (Fe–CdFeS granular film and CdFeS DMS film), referred to as A and B hereafter, respectively, could be clearly identified by both XRD spectrum and magnetic measurements, as shown later. The thickness of the films is about 400 nm.

Figure 1 shows the XRD patterns of samples A and B which reveal the *c*-axis orientation of the CdFeS thin films. The main diffraction peaks of samples A and B shift to larger angles compared with that of the (0002) plane of pure CdS phase because of the smaller radius of Fe^{2+} than that of Cd^{2+}, indicating the incorporation of Fe elements into the lattices. Doping of Fe atoms into the lattice does not change the wurtzite structure of CdS. Meanwhile, the corresponding full width at half maximum of (0002) diffraction peak for sample A is broader than that of sample B, which may be caused by more defects in the film containing Fe phase. In addition to the main CdFeS related strong diffraction peak, it is noted that a broad and weak Fe (110) diffraction peak was detected in sample A but not in sample B. Though we cannot exclude the possibility of the existence of Fe cluster phases in sample B due to the sensitivity limit of XRD measurement, we believe it will not give significant MR effects since we also could not detect any ferromagnetic signal in the magnetization measurement. The existence of Fe cluster phase in sample A is further supported by the scanning electron microscope (SEM) measurement. Many pits are observed in sample A, as shown in Fig. 2(a); however, the surface of sample B is very smooth, as shown in Fig. 2(b). The formation of the pits is presumably attributed to the precipitation of metallic Fe clusters separating from the CdFeS matrix. In order to study the composition of the pits, energy dispersive spectroscopy (EDS) analysis was performed on sample A, as shown in Fig. 2(c). It can be found that the atomic ratio between Fe and Fe+Cd is 0.062 in the dark area and is 0.041 in the white regions. This result indicates that the pits are rich in Fe. From the XPS data, we can find the existence of Fe phase in sample A more clearly. Figure 2(d) shows the XPS spectra of samples A and B. The surfaces of the samples

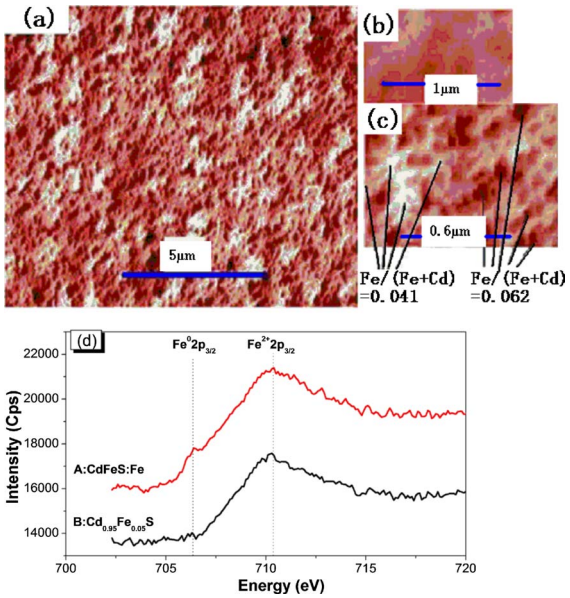

FIG. 2. (Color online) SEM image of the (a) Fe–CdFeS granular film and (b) CdFeS DMS. (c) is the EDS image of the granular thin film showing the existence of the Fe-rich clusters. (d) presents the XPS spectra of the Fe_{2p} for the Fe–CdFeS granular film and CdFeS DMS revealing the existence of metallic Fe phase in sample A.

were firstly cleaned with 3 keV Ar^+ for 5 min before analysis. For both samples, the peaks at 710.3 eV are related to $Fe^{2+}_{2p3/2}$ of Fe–S bonding state, which confirms that Fe atoms are doped into CdS crystal lattices. Meanwhile, it clearly shows that a peak at 706.4 eV which is related to metallic Fe appeared in sample A but not in sample B. So the XRD spectrum together with the SEM and XPS measurements evidently show that Fe clusters are incorporated into the CdFeS matrix in sample A.

The temperature dependent resistivity of both samples was characterized simply by conventional two-probe method. Figure 3(a) shows the resistivity ρ as a function of the root of reciprocal temperature ($T^{-1/2}$) for sample A. The data fit exactly to the well established relationship[13] of $\rho = a \exp 2(E/k_B T)^{1/2}$ for tunneling resistance where E means

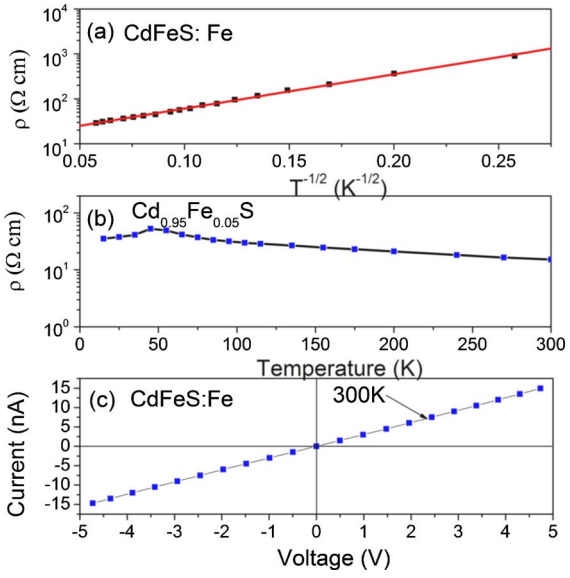

FIG. 3. (Color online) (a) Resistivity ρ in a logarithmic scale vs $T^{-1/2}$ for sample A. (b) Temperature dependent resistivity of sample B. (c) Current-voltage curves of sample A measured at room temperature.

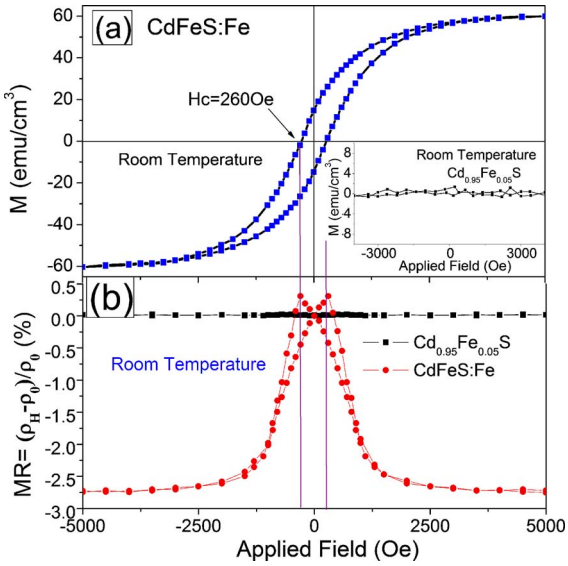

FIG. 4. (Color online) (a) Magnetization of the Fe–CdFeS granular film at room temperature with magnetic field perpendicular to the surface of the sample. The inset shows the *M-H* curve of the CdFeS DMS sample at room temperature. (b) Magnetoresistances of Fe–CdFeS granular film and CdFeS DMS thin film at room temperature.

the activation energy for tunneling between Fe granules. This agreement suggests that the electric transport in sample A is mainly due to a tunneling mechanism of electrons across the barrier between neighboring Fe clusters. The resistivity of sample B is shown in Fig. 3(b) which is only weakly temperature dependent. The resistivity slightly increases as the temperature drops from room temperature to low temperature which behaves as a degenerate semiconductor. The current-voltage (*I-V*) characteristics of sample A was measured at 300 K, as shown in Fig. 3(c). The linear *I-V* curve indicates that the tunneling current is proportional to the applied voltage. This is expected because the voltage drop between neighboring grains is too small to reduce significantly the height of the potential barrier since the current path between contacts in the granular films involves lots of small tunnel junctions,

The magnetization of sample A was measured using a VSM system at room temperature with an out-of-plane magnetic field, as shown in Fig. 4(a). A typical hysteresis loop with coercivity of about 260 Oe is observed, indicating that sample A is ferromagnetic at room temperature. Since CdFeS is a dilute magnetic semiconductor with paramagnetic property, the ferromagnetic behavior in sample A cannot originate from the matrix. The *M-H* curve of sample B measured at room temperature [see the inset of Fig. 4(a)] also supports that no ferromagnetic signal could be observed in CdFeS thin film. The only possible origin for the room temperature magnetization in the granular film is the Fe clusters. Furthermore, we find that the hysteresis loop for sample A is almost the same for different magnetic field directions. This is a key feature of granular systems distinctively different from that in multilayers, indicating that the Fe clusters are almost spherical and there is no strong coupling between neighboring magnetic particles.

The room temperature magnetoresistance of samples A and B was plotted in Fig. 4(b). The applied magnetic field is perpendicular to the current direction. Sample A shows a negative MR response and reaches about 2.2% when the applied magnetic field is 0.1 T. For sample B, a positive MR of about 0.02% is observed in the measured range, which suggests that the CdFeS matrix is not the origin for the observed large negative MR effect. The negative MR observed in sample A could be well explained by the magnetic tunneling resitance between neighboring Fe clusters. By simply comparing the *M-H* curve and the MR curve of sample A, we can clearly find that the increasing-field and the decreasing-field branches of MR correspond exactly to those of the magnetization hysteresis loop. The correlation between the MR and global magnetization is clearly shown. We also notice that the maximum of the resistance takes place exactly at the coercive field, which corresponds to the state of maximum disorder in the orientation of the neighboring magnetic particle moments. The lowest resistivity is realized at the saturation field where all the particles are ferromagnetically aligned. So the spin-related scattering or spin-dependent tunneling probability of carriers between neighboring Fe clusters is the origin for the large negative MR in the granular system. Since the magnetoresistance is a measure of the magnetic (or spin) disorder from ferromagnetic alignment, a large negative MR can be realized in a system that contains a high density of inhomogeneous and disordered small nonaligned magnetic entities (such as ultrafine magnetic particles). We believe that the observed large negative MR in our sample is due to the formation of large amount of small ferromagnetic Fe clusters. The small saturation field at room temperature will be beneficial for device application. Further optimization of the growth parameters for better control of the size and density of the clusters will be possible to improve the performance.

In conclusion, granular film composed of Fe clusters embedded in CdFeS was prepared by LP-MOCVD. The temperature dependent resistivity suggests the tunneling transport between Fe granules. A large negative magnetoresistance (MR) (about 2.2% at room temperature at 0.1 T) was observed. The mechanism is considered to originate from the spin-dependent tunneling process between the neighboring ferromagnetic Fe clusters.

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