Local Structures in ZnO/CoFe Multilayers

Diluted magnetic semiconductors (DMSs) have attracted a lot of attention for their potential applications in the field of spin-dependent semiconductor electronics, or so-called spintronics. A key work to realize spintronic devices is to develop DMSs with ferromagnetism above room temperature (RT). Transition-metal (TM) doped ZnO films have been predicted as promising DMSs for implementing spintronic devices. Ferromagnetism with Curie temperature above RT has been reported in ZnO films doping with Co and Fe. In spite of numerous reports of RT ferromagnetism in magnetically doped ZnO films, in many cases their ferromagnetic origins remain controversial whether they are resulting from the intrinsic property of DMSs or from the magnetic clusters, or from a mixed structure of DMS and magnetic clusters.

In this work we report detailed studies of $[ZnO(20Å)/Co_{0.7}Fe_{0.3}(xÅ)]_{25}$ multilayers (ZnO/CoFe MLs in the following) with nominal thickness x=1, 2 and 5. We focus on the magnetic properties of these MLs and their correlations with electronic states and local structures of the magnetic elements. The sample growth was carried out in an ion-beam sputtering system with base pressure of about 8×10^{-8} Torr. Deposition of ZnO/CoFe MLs was executed in a process pressure of about 2×10^{-4} Torr with Ar ion beam acting alternatively on ZnO and $Co_{0.7}Fe_{0.3}$ targets. The ZnO/CoFe MLs were deposited at room temperature. Most of the previous studies on ZnO based films have been restricted to polycrystalline samples, making the understanding of the interplay between structure and magnetism much difficult. In this work, high-quality (0001) oriented ZnO/CoFe MLs have been established on Al_2O_3 (0001) substrates. Note that epitaxial growth of the (0001) oriented ZnO/CoFe MLs cannot maintain (thus polycrystalline appears) for MLs with x reaches about 15, below which critical thickness discontinuous CoFe layer forms in the ZnO/CoFe MLs. This is confirmed by an *in-situ* resistance measurement of CoFe(x Å) on ZnO as a function of x. Thus, the three samples reported in this work can be considered MLs consisting of alternating continuous ZnO layer and discontinuous CoFe layer.

The magnetic properties were studied by a commercial superconducting quantum interference device (SQUID). Ferromagnetism has been observed up to RT for x=1 and x=2 MLs, while superparamagnetic behavior appears for x=5 ML.(not shown here) The field-cooling (FC) and zero-field-cooling (ZFC) M(T) measurements for x=1, 2 and 5 MLs are provided in Fig. 1. Both x=1 and x=2 MLs do not show any sign of blocking temperature (T_B) in ZFC data and their FC magnetizations do not go to zero up to 350 K, as shown in Fig. 1(a) and 1(b). This is in marked contrast to x=5 ML which clearly shows a blocking temperature with T_B=18K and the magnetization approaches to zero by 300 K. Nevertheless, the M(T) behaviors are quite different between x=1 and x=2 MLs in low temperature region. As shown in Fig. 1(b) for x=2 ML, the FC magnetization decreases rapidly from 6 to 25 K, which is not

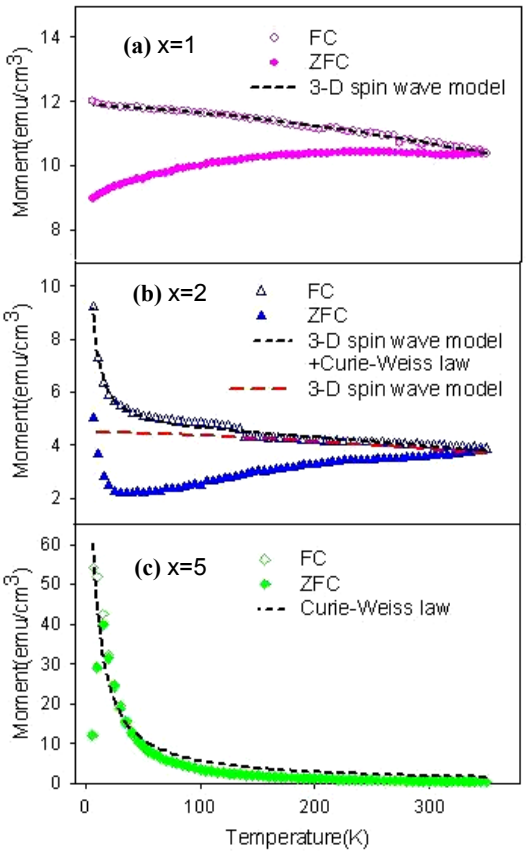

Fig. 1: *Magnetization of the multilayers [ZnO(20 Å)/$Co_{0.7}Fe_{0.3}$(x Å)]$_{25}$ (x=1, 2 and 5) as a function of temperature in a field of 50 Oe for zero field cooling (solid symbols) and field cooling (open symbols). The fitting results of the field-cooled data (as discussed in the text) are shown by the dashed curves.*

present for x=1 ML. The phenomenon of rapid decrease of FC magnetization in the low temperature region had been observed in Co(Fe) doped ZnO films by the other groups, but has not been clearly explained. Indeed, the rapid decrease of FC magnetization at low temperatures (6 to 25 K) mirrors the existence of CoFe clusters.

The FC M(T) data of ZnO/CoFe MLs can be fitted by different models, which sheds light on the magnetic origin in each case. The fitting results for x=1, 2 and 5 MLs are shown by the dashed curves in Fig. 1. The FC M(T) of x=1 ML can be well fitted by a standard 3D spin-wave model which leads to $M(T)=M_0 - 0.117\mu_B(k_BT/2SJd^2)^{3/2}$, where M_0 is the zero temperature magnetization, and d and J are the spacing and exchange interaction between magnetic ions, respectively. In contrast, the 3D spin-wave model fails to fit the low-temperature M(T) data for x=2 ML unless a Curie-Weiss model, $\chi=\chi_0 + C/(T-\theta)$, is also taken into account (Fig. 1(b)). For x=5 ML, the FC magnetization follows a simple Curie-Weiss model. The fit to a 3D spin wave model suggests a clear ferromagnetic phase for x=1 ML and a Curie-Weiss model fit indicates a predominant paramagnetic phase for x=5 ML. For x=2 ML, the combination of a 3D spin-wave and a Curie-Weiss model reveals a mixed magnetic phase, i.e. a ferromagnetic phase plus a paramagnetic one.

The distinct magnetic characteristics of x=1, 2 and 5 MLs imply different structural origin. To understand the correlation of structure and magnetism in details, we investigate the local structures of the ZnO/CoFe MLs using x-ray absorption (XAS) spectroscopy on Co, Fe and Zn K-edges. XAS is a fingerprint of the electronic states (using near-edge XAS, NEXAS) and local geometry (using extended x-ray absorption fine structure, EXAFS) around a specific absorbing atom. The XAS experiments were carried out in the wiggler-17C beamline of NSRRC. Figure 2 shows the NEXAS results of $[ZnO(20\ Å)/Co_{0.7}Fe_{0.3}(x\ Å)]_{25}$. The NEXAS spectrum of x=1 ML is in marked difference from those of x=2 and 5 MLs, particularly in pre-edge feature which is due to transition to bound state. The pre-edge feature of x=1 ML resembles much to the CoO reference, while that of x=5 ML is close to the CoFe (500 Å film) reference, as shown in Fig. 2(a). The NEXAS measurements reveal that most of Co atoms dissolve into ZnO and substitute Zn^{2+} ions for x=1 ML, while most of Co atoms form clusters for x=5 ML. The pre-edge curve of x=2 ML lies in-between that of the x=5 and x=1 samples but is closer to the former, suggesting that most of the Co atoms form clusters and the minority of Co atoms dissolve into the ZnO matrix for x=2 ML. The results are in consistence with the magnetic studies. Similar NEXAS results using Fe-edge were obtained for ZnO/CoFe MLs, as shown in Fig. 2(b).

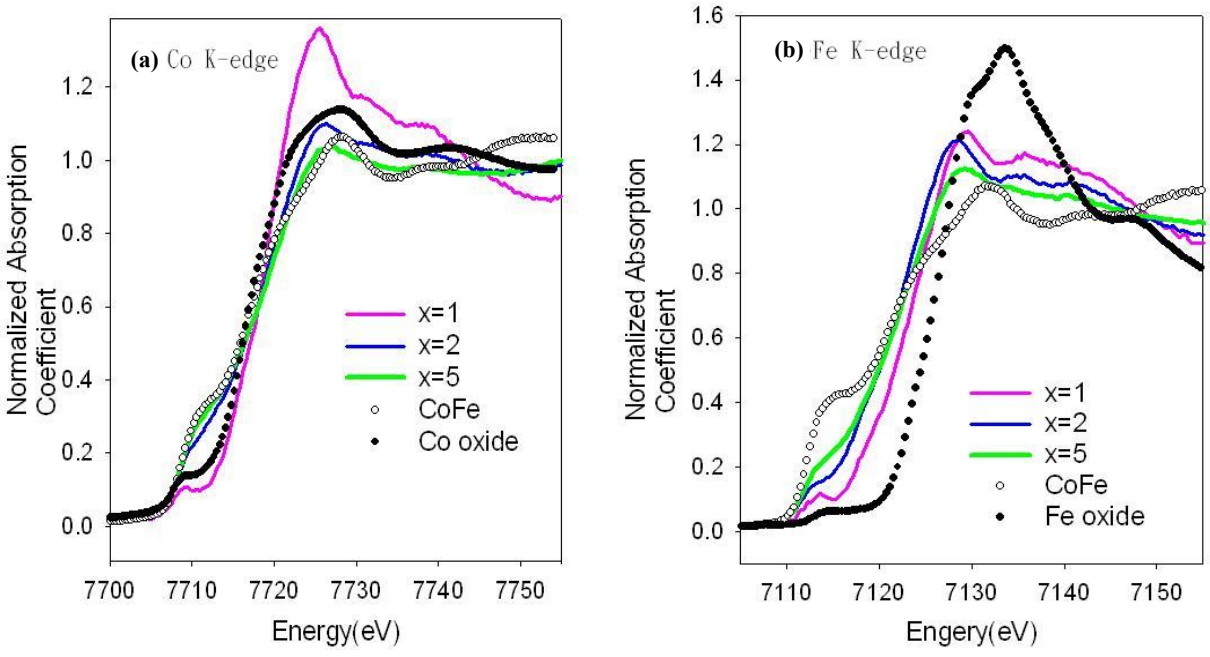

Fig. 2: *Normalized absorption spectra of the multilayers $[ZnO(20\ Å)/Co_{0.7}Fe_{0.3}(x\ Å)]_{25}$ (x=1, 2 and 5) at the (a) Co K-edge and (b) Fe K-edge. The spectra of CoFe (500 Å film), and Co and Fe oxides are also provided for reference. The ZnO/CoFe MLs and CoFe film were grown on α-Al_2O_3 (0001) substrate; Co and Fe oxides were powders.*

Figure 3 shows the radial distribution function (RDF), i.e. Fourier transform amplitude of EXAFS, at the Co K-edge of [ZnO(20 Å)/$Co_{0.7}Fe_{0.3}$(x Å)]$_{25}$ (x=1, 2 and 5) together with the Co K-edge of CoFe (500 Å) and Zn K-edge of ZnO(500 Å) for reference. Note that the first and second major peaks at the Co K-edge correspond to the nearest oxygen and Zn (or Co, Fe in the case of clustering), respectively, as viewed from a specific Co atom. For x=1 ML, the interatomic distances of the two major peaks of the Co K-edge RDF resembles much to those of ZnO as viewed from a specific Zn atom. This implies that in this case most of the Co atoms substitute for Zn ions in the ZnO matrix. The results support the magnetic studies that the origin of RT ferromagnetism for x=1 ML comes from an intrinsic property of a DMS multilayer. In contrast, the RDF spectra at Co K-edge for x=2 and x=5 MLs are similar to the CoFe reference, even though the two samples show different magnetic properties. Interestingly enough, the RDF spectrum of x=2 ML can be well fitted by a linear combination of those of x=1(25%) and x=5 (75%), as illustrated by the dashed curve in Fig. 3. We believe this is a reasonable estimation (~75%) of the amount of CoFe atoms incorporated in clusters for x=2 ML. Figure 4 shows the RDF spectra of x=1and 5 MLs from the Zn K-edge EXAFS data. The quantitative local structure information was obtained by fitting of the RDF curves using theoretical models generated by the FEFF program. The results also reveal that much less Co and Fe atoms substitute for Zn in spite of the more magnetic concentration for the x=5 ML. It is possible that most of the magnetic elements form clusters before reaching the saturation dissolution condition for x=5 ML.

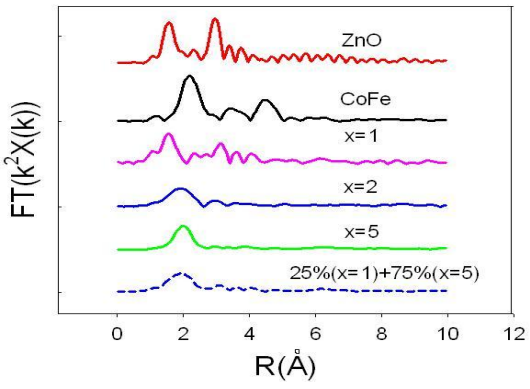

Fig. 3: Fourier transform amplitude of EXAFS at the Co K-edge of the multilayers [ZnO(20 Å)/$Co_{0.7}Fe_{0.3}$(x Å)]$_{25}$ (x=1, 2 and 5) and the Co K-edge of CoFe (500 Å) and Zn K-edge of ZnO(500 Å) for reference. All the samples were grown on α-Al_2O_3 (0001) substrate.

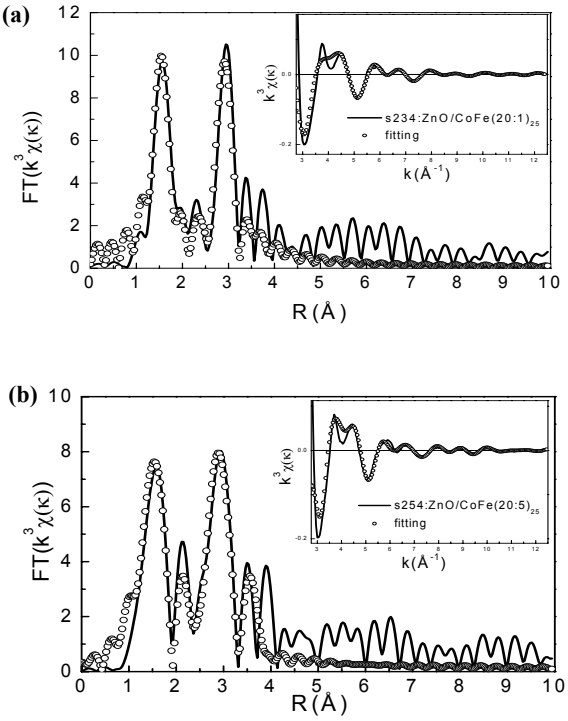

Fig. 4: The Fourier transforms of EXAFS at Zn K-edge (symbols) and fittings (curves) from FEFF code for (a) [ZnO(20 Å)/$Co_{0.7}Fe_{0.3}$(1 Å)]$_{25}$ (b) [ZnO(20 Å)/$Co_{0.7}Fe_{0.3}$ (5 Å)]$_{25}$.

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BEAMLINE
17C W20 XAS beamline.

EXPERIMENTAL STATION
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