Studies of impurities in magnetic semiconductors: an example of important XAFS applications

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The x-ray absorption fine structure (XAFS) technique has been employed to investigate the local structure and valency about Mn and Fe ions in the III-V diluted magnetic semiconductors $In_{1-x}Mn_xAs$ and $Ga_{1-x}Fe_xAs$, prepared by molecular-beam-epitaxy under various growth conditions. These new systems are promising magnetic materials of considerable current interest and with important technical applications including *photo-carrier induced magnetism* and *spin-polarized current* devices. The local structure around the magnetic ions can play a pivotal role in affecting the magnetic properties of these semiconductors. Local structure information obtained from XAFS has provided the *first* direct evidence that the magnetic impurities can indeed substitute for the cation host atoms in samples prepared under appropriate conditions.

Keywords: Diluted Magnetic Semiconductors, EXAFS, NEXAFS

Diluted magnetic semiconductors (DMS) exhibit many unique physical properties that are of great potential for applications in developing novel magneto-electronic devices. For example, compound semiconductors doped with considerable amount of magnetic Mn ions have demonstrated an appreciably enhanced Zeeman splitting effect when subjected to an external magnetic field of merely moderate magnitude (Brandt & Moshchalkov, 1984). Recently, the advent of new technologies such as *photo-carrier induced magnetism* (Munekata *et al.*, 1997; Koshihara *et al.*, 1997) and *spintronics* (Kikkawa & Awschalom, 1998), where electron spin states can be manipulated to perform specific roles usually played by electrical charges in conventional electronics, have attracted even more interest in the development of III-V compound DMS. Substitutional doping of controllable large amount of magnetic Mn ions into III-V compound semiconductor InAs was first accomplished by H. Munekata *et. al.* using molecular beam epitaxy (MBE) techniques (Munekata *et al.*, 1989; Munekata *et al.*, 1990; Ohno *et al.*, 1991; von Molnar *et al.*, 1991; Soo *et al.*, 1996). Synthesis of Mn-doped GaAs thin films with Mn substituting Ga has also been reported recently (Ohno *et al.*, 1996; Shioda *et al.*, 1998). To increase the transition temperature of ferromagnetic III-V DMS, incorporation of Fe, whose transition temperature is higher than that of Mn, seems to be a reasonable approach.

The location of magnetic ions in the III-V semiconductor host serves as an indication for a successful doping process and an important prerequisite for understanding the physical properties of the material. Since the magnetic dopant ions in the host do not possess long-range structural order, conventional x-ray diffraction techniques cannot be used for this purpose. On the other hand, the short-range-order x-ray absorption fine structure (XAFS) methods are uniquely suited for this task. In this paper, our previous XAFS results on the $In_{1-x}Mn_xAs$ systems are summarized and compared with those of the more recent $Ga_{1-x}Fe_xAs$ systems.

Samples of $In_{1-x}Mn_xAs$ were prepared by MBE with various growth conditions including two high-concentration films with x=0.12 grown at substrate temperatures (T_S) of 280ºC (R1141) and 210ºC (R1144). A low-T_S film (R1144A) was then annealed at 480ºC for 74 minutes to study the effect of annealing. Two low-concentration films with x=0.014 (R1126) and 0.017 (R1264) were also grown at T_S=200ºC and 300ºC, respectively. Samples of $Ga_{1-x}Fe_xAs$ with x=0.004 (DMS169) and 0.02 (DMS167) were grown at T_S=580ºC while two low-temperature samples with x=0.015 (DMS76) and 0.04 (DMS126) were prepared at T_S=350ºC and 260ºC, respectively. To study the effect of annealing, two samples grown at 260ºC with x=0.023 were annealed at 350ºC for 30 minutes (DMS187) and 580ºC for 10 minutes (DMS186), respectively. The XAFS measurements were performed at beamline X3B1 at the National Synchrotron Light Source. All samples were measured in the fluorescence mode using an energy dispersive solid state Si(Li) detector.

An established background-subtraction method was used to extract the EXAFS χ-functions from the raw experimental data (Newville *et al.*, 1993). The χ-functions were then weighted with k or k^3 and Fourier-transformed into real space (Lee *et al.*, 1981) for detailed comparison. Fourier transforms of the experimental curves are shown as fine lines in Figure 1. The experimental data were then analysed and compared with theoretical calculations by a curve fitting method (Soo *et al.*, 1994). Cumulants were used to account for the non-Gaussian disorders when needed (Sayers & Bunker, 1988). The magnitude of the backscattering amplitude and the corresponding phase shift are extracted from theoretical EXAFS functions calculated by FEFF (Rehr *et al.*, 1991).

Fourier transforms of weighted χ-functions calculated from final values of curve-fitting parameters are shown as heavy solid lines in Figure 1. As calculated from published crystal-structure data (Wyckoff, 1960), the MnAs model compound has As near neighboring shells at distances of 2.57, 4.51 and 4.78Å with coordination numbers of 6, 6 and 6 and Mn near neighboring shells at distances of 2.85, 3.71 and 4.68Å with coordination numbers of 2, 6 and 12, respectively. Except for some minor bondlength variations, our EXAFS curve-fitting results show that the majority local structure around Mn in samples R1201, R1144A, and R1141 are similar to that in MnAs while those in the samples R1144, R1126 and R1264 show good agreement with the model of Mn substitution for In sites in the zinc-blende structure. However, 7.5% of Mn atoms in R1144A are found to substitute for the In sites in the InAs host and 25.5% of Mn atoms in R1144 are in the form of MnAs minority phase. Also, an additional In shell is found in the samples R1144 and R1264.

For the $Ga_{1-x}Fe_xAs$ systems, the first prominent peak in the Fourier-transforms of the low-temperature-grown samples DMS76 and DMS126 were identified as arising from As neighbors around the Fe impurities with coordination numbers of 3.6 and 5.7 and bondlengths of 2.41Å and 2.40Å, respectively. On the other hand the first peak of the high-temperature-grown samples DMS169 and DMS167 are determined to be due to the Fe neighbors of a coordination number of 5.1 and bondlengths of 2.54-2.55Å. As calculated from published crystal-structure data (Wyckoff, 1960), the Ga sites in GaAs have a nearest neighboring shell of 4 As atoms at a distance of 2.45Å. Considering probable built-in distortion on the bondlength needed (Mikkelsen & Boyce, 1983) when the smaller Fe ions are incorporated into the GaAs structure and a 20% uncertainty of coordination number in the EXAFS method, we

suggest that Fe atoms in samples DMS76 and DMS126 most likely substitute for the Ga sites in the GaAs host. Other possibilities include formation of Fe_2As, FeAs, and $FeAs_2$ in which the Fe atoms has Fe local structure resembling that in the $FeAs_2$ model compound. The similarities between samples DMS187 and DMS76 are also exhibited in the NEXAFS data. Although NEXAFS of DMS186 does not coincide with that of Fe_2As, their general shapes are nevertheless similar to each other.

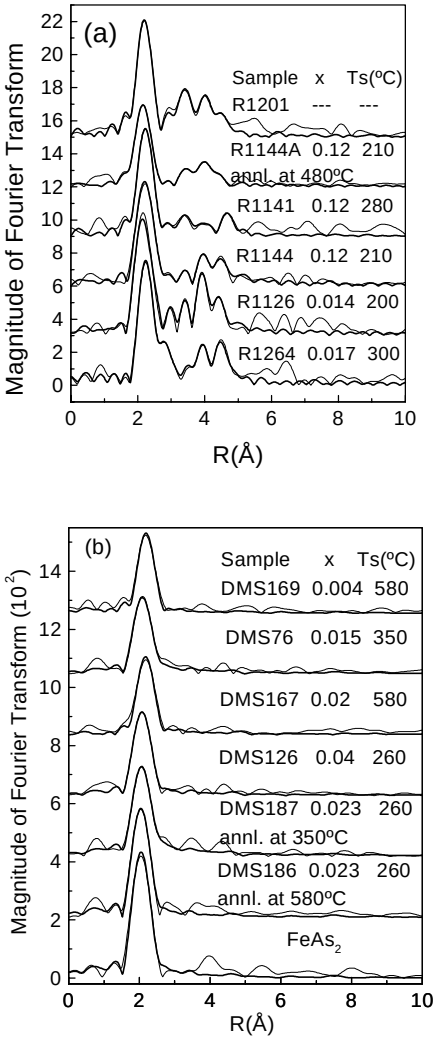

Figure 1
Fourier transforms of experimental data (fine lines) and theoretical calculation (heavy solid lines) for (a) $In_{1-x}Mn_xAs$ (3.0-12.0 $Å^{-1}$ for R1201 and R1141, 3.0-11.7 $Å^{-1}$ for R1144A, 3.25-10.8 $Å^{-1}$ for R1144, and 3.0-10.8 $Å^{-1}$ for R1126 and R1264) and (b) $Ga_{1-x}Fe_xAs$ (3.0 -11.5 $Å^{-1}$) DMS and model compounds. Curves have been shifted vertically for the sake of clarity.

have average first-shell (As) coordination numbers and Fe-As bondlengths of 4.5, 2.49Å; 6, 2.44Å; and 6, 2.36Å; respectively. However, the Fe NEXAFS spectra plotted in Fig. 2 show that the samples DMS76 and DMS126 not only have higher effective valencies than the model compound $FeAs_2$, in which the Fe valency is higher than those of Fe_2As and FeAs, but their curves also possess different features from the model compounds. Hence, the possibilities for Fe in the samples DMS76 and DMS126 to form Fe_2As, FeAs, or $FeAs_2$ phases can be ruled out by our Fe NEXAFS data. In the annealed low-temperature-grown samples DMS187 and DMS186, Fe atoms are surrounded by 3.0 and 6.2 As neighbors at distances of 2.40Å and 2.38Å, respectively. In contrast to the 350ºC-annealed sample DMS187 in which the local structure around Fe is similar to that in DMS76, the 580ºC-annealed sample DMS186

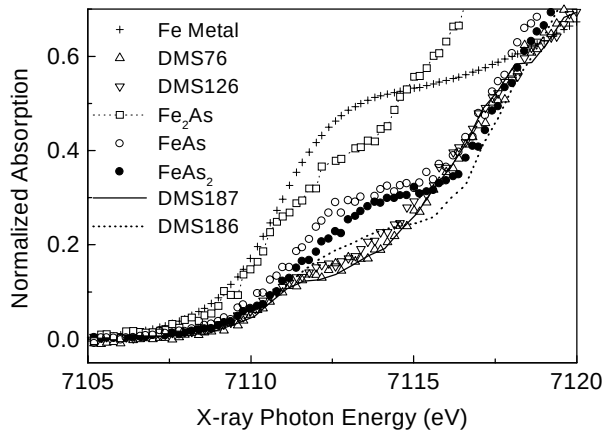

Figure 2
Near edge x-ray absorption fine structure (NEXAFS) data for $Ga_{1-x}Fe_xAs$ DMS and model compounds. Curves are normalized to the edge-step height.

In conclusion, our XAFS results have shown that the magnetic Mn ions in the $In_{1-x}Mn_xAs$ and Fe ions in the $Ga_{1-x}Fe_xAs$ III-V diluted magnetic semiconductors can indeed substitute for the cation sites by using lower substrate temperatures in the MBE process. Formation of MnAs and Fe-Fe clusters can also occur when substrate temperatures are relatively high. Annealing of DMS films where magnetic ions substitute for cation sites can lead to formation of MnAs and $FeAs_2$ phases at sufficiently high annealing temperatures in the $In_{1-x}Mn_xAs$ and $Ga_{1-x}Fe_xAs$ systems, respectively. We have thus demonstrated an important application of the XAFS technique in the study of new magnetic materials.

The present research at SUNY-Buffalo is supported by NEDO and DOE.

References

Brandt, N. B. & Moshchalkov, V. V. (1984). *Advances in Physics* 33, 193-256
Kikkawa, J. M. & Awschalom, D. D. (1998). *Phys. Rev. Lett.* 80, 4313-4316
Koshihara, S., Oiwa, A., Hirasawa, M., Katsumoto, S., Iye, Y., Urano, C., Takagi, H. & Munekata, H. (1997). *Phys. Rev. Lett.* 78, 4617-4619
Lee, P. A., Citrin, P. H., Eisenberger, P. & Kincaid, B. M. (1981). *Rev. Mod. Phys.* 53,769-803
Mikkelsen, J. C., Jr. & Boyce, J. B. (1983), *Phys. Rev.* B 28, 7130-7140
Munekata, H., Abe, T., Koshihara, S., Oiwa, A., Hirasawa, M., Katsumoto, S., Iye, Y., Urano, C. & Takagi, H. (1997). *J. Appl. Phys.* 81, 4862-4864
Munekata, H., Ohno, H., von Molnar, S., Segmüller, Armin, Chang, L. L. & Esaki, L. (1989). *Phys. Rev. Lett.* 63, 1849-1852
Munekata, H., Ohno, H., von Molnar, S., Segmüller, Armin & Chang, L. L (1990). *Vac. Sci. Technol.* B 8 , 176-180
Newville, M., Lïvin, P., Yacoby, Y., Rehr, J. J. & Stern, E. A. (1993). *Phys. Rev.* B 47, 14126- 14131

Ohno, H., Munekata, H., von Molnar, S & Chang, L. L (1991). *J. Appl. Phys.* 69, 6103–6108
Ohno, H., Shen, A., Matsukura, F., Oiwa, A., Endo, A., Katsumoto, S. & Iye, Y. (1996). Appl. Phys. Lett. 69, 363-365
Rehr, J. J., Mustre de Leon, J., Zabinsky, S. I. & Albers, R. C. (1991). *J. Am. Chem. Soc*. 113, 5135-5142
Sayers, D. E. , Bunker , B. A. (1988). *X-ray Absorption*, edited by D. C. Koningsberger and R. Prins, pp.211-252. New York: Wiley.
Soo, Y. L., Huang, S. W., Ming, Z. H., Kao, Y. H., Munekata, H. & Chang, L. L. (1996). *Phys. Rev*. B 53, 4905-4909
Soo, Y. L., Ming, Z. H., Huang, S. W., Kao, Y. H., Bhargava, R. N. & Gallagher, D. (1994). *Phys. Rev*. B 50, 7602-7607
Stern, E. A. (1988). *X-ray Absorption*, edited by D. C. Koningsberger and R. Prins, pp. 3-49. New York: Wiley.
von Molnar, S, Munekata, H., Ohno, H. & Chang, L. L (1991). *J. Magn. Magn. Mater*. 93,356-364
Wyckoff, Ralph W. G. (1960). *Crystal Structures*, New York: Interscience Publisher Inc.

 Received 31 July 2000 • Accepted 8 November 2000