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Local structure around Fe in the diluted magnetic semiconductors $Ga_{1-x}Fe_xAs$ studied by x-ray absorption fine structure

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Extended x-ray absorption fine structure and near-edge x-ray absorption fine structure techniques are employed to investigate the local structure and valency about Fe atoms in the diluted magnetic alloy semiconductor system $Ga_{1-x}Fe_xAs$ prepared by molecular-beam epitaxy under various conditions. This experiment is aimed at elucidating possible correlations between the microstructures in these diluted magnetic semiconductors and some physical properties. Our x-ray results offer direct evidence of Fe substitution for Ga sites in GaAs prepared at relatively low substrate temperatures, wherein the $Ga_{1-x}Fe_xAs$ compound is mainly paramagnetic. However, the Fe impurity atoms could form small Fe clusters and/or Fe-As complexes when the samples are grown at high temperatures.

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I. INTRODUCTION

Recent studies of diluted magnetic semiconductors (DMS's) provided unprecedented opportunities for the development of magnetoelectronic/optic heterostructures and devices. Some physical properties of the DMS can be changed in an external magnetic field of only moderate intensity.[1,2] Spin-polarized materials are very important for pursuing physics and technologies such as photocarrier-induced magnetism[3,4] and spintronics.[5] Of special interest are in III-V DMS's obtained by incorporating metal atoms in InAs and GaAs.[6] In contrast to II-VI DMS's, incorporating a large amount of magnetic impurities into III-V semiconductors without phase separation has been relatively difficult, until the successful demonstration of substitutional Mn doping into InAs achieved by Munekata and co-workers.[7–11] To obtain direct evidence that magnetic impurities are indeed successfully incorporated into the host semiconductor, and to understand the underlying mechanisms responsible for the special physical properties of these III-V DMS's, detailed information about the local structures around the magnetic impurities is needed. Since in principle the dilute magnetic impurities in the compound semiconductor do not show long-range structural order, the conventional x-ray-diffraction method is not useful for determining the location of the impurity atoms. On the other hand, the short-range-order probing technique of x-ray absorption fine structure (XAFS), which includes both extended XAFS (EXAFS) and near-edge XAFS (NEXAFS), is uniquely suited for this purpose.

Using the XAFS technique, our previous results[11] provided clear evidence of substitutional doping of Mn impurities in $In_{1-x}Mn_xAs$ DMS's with Mn concentrations as high as 12%. We follow this successful approach in the present work, and investigate the local structures and valency about Fe impurities in a $Ga_{1-x}Fe_xAs$ DMS system with this technique. Some basic properties of the $Ga_{1-x}Fe_xAs$ DMS were recently been studied by Haneda *et al.*[12]

II. EXPERIMENT

Six $Ga_{1-x}Fe_xAs$ samples prepared by molecular-beam epitaxy under different growth conditions were investigated in the present experiment. Two ''high-temperature samples'' with $x=0.004$ (DMS169) and 0.02 (DMS167) were grown at a substrate temperature $T_S=580\,°\mathrm{C}$, while two ''low-temperature samples'' with $x=0.015$ (DMS76) and 0.04 (DMS126) were prepared at $T_S=350$ and 260 °C, respectively. To study the effects of thermal annealing, two additional samples were also investigated both with $x=0.023$ grown at 260 °C but followed by annealing at 350 °C for 30 min (DMS187) and at 580 °C for 10 min (DMS186), respectively. Some characteristics of the samples studied in the present experiment are summarized in Table I.

The XAFS experiments were performed at beamline X3B1 of the National Synchrotron Light Source in Brookhaven National Laboratory. A conventional x-ray fluo-

TABLE I. Some characteristics of $Ga_{1-x}Fe_xAs$ samples studied in the present experiment. X is the Fe fraction and T_s is the substrate temperature in °C.

Sample	x	T_s(°C)	Annealing temperature (°C)	Annealing time (min)
DMS169	0.0014	580	-----	-----
DMS76	0.015	350	-----	------
DMS167	0.035	580	-----	-----
DMS126	0.04	260	-----	-----
DMS187	0.023	260	350	30
DMS186	0.023	260	280	10

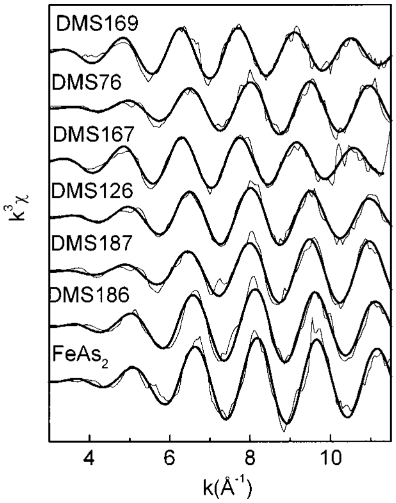

FIG. 1. Weighted Fe *K*-edge EXAFS χ functions. Fine lines: experimental. Coarse lines: theoretical.

rescence detection mode was used to obtain the XAFS data. Experimental details about these measurements can be found in our previous papers.[11–13] To extract the EXAFS χ functions from the raw data, a well-established background-subtraction and correction method was used.[13,14] These χ functions were then weighted with k^3, and Fourier transformed into real space for direct comparison.[15] Quantitative information of the local structures around Fe in the $Ga_{1-x}Fe_xAs$ samples was obtained by a curve-fitting procedure using the backscattering amplitude and phase-shift functions extracted from theoretical models calculated with a well-known FEFF program.[13,16] The EXAFS χ functions and Fourier transforms for the six samples DMS169, DMS76, DMS167, DMS126, DMS187, and DMS186 studied in the present experiment are shown in Figs. 1 and 2 along with fitted curves obtained from theoretical calculations, respectively. The local structural parameters determined by this curve-fitting procedure are listed in Table II. The *K*-edge NEXAFS data for Fe in $Ga_{1-x}Fe_xAs$ are shown in Fig. 3, together with those of model compounds with known valency for comparison. From a simple effective charge argument, the absorption-edge threshold shifts to higher energies as the effective valency of the x-ray absorbing atoms in the material increases.[15,16] Thus, by comparing the threshold energy of the III-V DMS samples with those of the model compounds, the effective valency of the DMS samples can be reasonably estimated.[17]

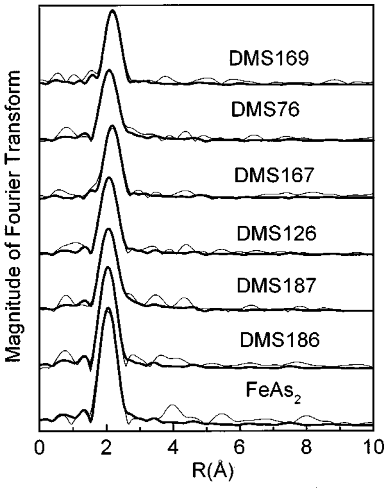

FIG. 2. Fourier transform of Fe *K*-edge EXAFS χ functions. Fine lines: experimental. Coarse lines: theoretical.

TABLE II. Parameters of local structure around Fe atoms obtained from curve fitting the Fe *K*-edge EXAFS. The amplitude reduction factor S_0^2 representing the central atom shake-up and shake-off effects was obtained from tabulated values published by Stern (Ref. 17). *N* is the coordination number. *R* is the bond length. σ^2 is the Debye-Waller-like factor serving as a measure of local disorder. ΔE_0 is the difference between the zero-kinetic-energy value of the sample and that of the theoretical model used in FEFF. Uncertainties were estimated by the double-minimum residue ($2\chi^2$) method.

Sample	nn atom	N	R (Å)	σ^2 (10^{-3} Å^2)	ΔE_0 (eV)	S_0^2
DMS169	Fe	5.1 ± 0.8	2.55 ± 0.02	6 ± 1	-1 ± 4	0.69
DMS76	As	3.6 ± 0.6	2.41 ± 0.01	5 ± 1	-1 ± 4	0.69
DMS167	Fe	5.1 ± 0.8	2.54 ± 0.02	7 ± 1	-1 ± 4	0.69
DMS126	As	5.7 ± 0.6	2.40 ± 0.01	7 ± 1	-1 ± 3	0.69
DMS187	As	3.0 ± 0.3	2.40 ± 0.01	3 ± 1	-5 ± 4	0.69
DMS186	As	6.2 ± 1.1	2.38 ± 0.01	6 ± 1	-1 ± 3	0.69
FeAs$_2$	As	6.1 ± 1.3	2.37 ± 0.01	5 ± 1	1 ± 4	0.69

III. RESULTS AND DISCUSSION

As shown in Fig. 1, the EXAFS χ functions for samples DMS76 and DMS126 both exhibit a phase and amplitude similar to those of EXAFS oscillations, obviously different from those for samples DMS169 and DMS167. The Fourier transforms for DMS76 and DMS126 shown in Fig. 2 demonstrate that the position of the first peak, representing the distance between the central x-ray absorbing Fe atom and the nearest-neighbor (nn) shell, is also apparently different from that in DMS169 and DMS167. From the detailed curve-fitting results (Table II), the first prominent peaks in the Fourier transforms for samples DMS76 and DMS126 are identified as arising from As neighbors around the Fe impurities with coordination numbers 3.6 and 5.7 and bond lengths 2.41 and 2.40 Å, respectively. Based on the known crystal struc-

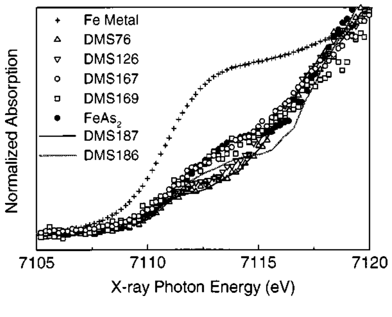

FIG. 3. Normalized x-ray absorption spectra near the Fe *K*-absorption edge.

ture of GaAs,[18] each Ga atom in the host is coordinated with four nn's of As atoms at a distance of 2.45 Å. Considering the inevitable local lattice distortion when a Ga atom is replaced by a smaller Fe atom, a decrease of the nn bond length to 2.41 Å seems quite reasonable; also, with a typical 20% uncertainty in the determination of coordination number by the EXAFS method, the results for DMS76 and DMS126 given in Table II can therefore be viewed as direct evidence of the fact that the Fe impurity atoms in these samples most likely have substituted for the Ga sites in the GaAs host. Within the sensitivity limit of our EXAFS detection, there are no Fe clusters present in these two samples. On the other hand, the first Fourier transform peaks for samples DMS169 and DMS167 are identified as due to Fe neighbors with an average coordination number 5.1 and bond length 2.54–2.55 Å, indicating the formation of small Fe clusters.

Possibilities other than Fe substitution for Ga in DMS76 and DMS126, such as the formation of Fe_2As, FeAs, or $FeAs_2$, which should give rise to nn Fe-As distances of 2.49, 2.44, and 2.36 Å, and average first-shell (As) coordination numbers 4.5, 6, and 6, respectively,[18] can be ruled out by a direct comparison of the Fe NEXAFS spectra shown in Fig. 3. As demonstrated in this figure, the samples DMS76 and DMS126 not only reveal a distinctly higher effective valency than the model compound $FeAs_2$ (in which the Fe valency is higher than that in Fe_2As and FeAs), but the spectra also show features clearly different from those of $FeAs_2$. Hence the possibilities for Fe in DMS76 and DMS126 to form other phases of Fe_2As, FeAs, or $FeAs_2$ can be safely ruled out. It should also be noted that DMS169 and DMS167 both show a threshold energy clearly lower than that of samples DMS76 and DMS126. This lowering of effective valency is probably caused by an admixture of some small Fe clusters (valence 0), and some traces of Fe-containing complexes in the material. The local structure(s) around the Fe atoms in these small complexes could be highly disordered, hence only the Fe nn bonds are found in the EXAFS spectra of DMS169 and DMS167.

For a study of the effects of thermal annealing on the Fe-doped GaAs, similar XAFS measurements were carried out for the two annealed samples DMS187 and DMS186, molecular beam epitaxy (MBE) grown at a low substrate temperature of 260 °C and followed by annealing at different temperatures. In these samples, as found from detailed EXAFS analysis (Table II), the Fe impurity atoms are surrounded by 3.0 and 6.2 As neighbors at distances of 2.40 and 2.38 Å, respectively. The sample DMS187 was annealed at a relatively low temperature 350 °C, in which the local structure around Fe is found to be similar to that in DMS76, indicating clear Fe substitution for Ga. On the other hand, the Fe local structure in the 580 °C annealed sample DMS186 appears similar to that in $FeAs_2$, suggesting that annealing at this higher temperature has resulted in the departure of Fe atoms from the Ga sites, and form small $FeAs_2$ complexes in the material. The NEXAFS spectra also support this observation. The NEXAFS spectrum for DMS187 shown in Fig. 3 almost coincides with those of samples DMS76 and DMS126, while that of DMS186 appears similar in shape to that of $FeAs_2$. Both the EXAFS and NEXAFS results indicate that annealing of the low-temperature-grown samples at a sufficiently high temperature (580 °C) tends to incur the formation of $FeAs_2$ clusters in the sample, while annealing at a lower temperature (350 °C) can hardly change the basic structure even with a much longer annealing time.

In conclusion, our XAFS results have shown that magnetic Fe impurities in $Ga_{1-x}Fe_xAs$ III-V diluted magnetic semiconductors can indeed substitute for cation sites by using low substrate temperatures (not higher than 350 °C) in the MBE process. Formation of FeAs complexes and Fe-Fe clusters can occur when the substrate temperatures are relatively high (580 °C). In comparison, this result is different from that in the other III-V DMS systems $In_xMn_{1-x}As$ and $Ga_yMn_{1-y}As$ in which the microstructures of ferromagnetic MnAs are found but not metallic Mn clusters. Annealing of the DMS thin films, where magnetic ions have substituted for the cation sites in GaAs, can lead to the formation of $FeAs_2$ phases at a sufficiently high (580 °C) temperature. Further studies of controllable doping of magnetic impurities in other III-V compounds using the XAFS approach can be of great interest for further development of diluted magnetic semiconductors.

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