X-ray absorption study of the electronic structure of Mn-doped amorphous Si

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The electronic structure of Mn in amorphous Si (a-Mn3Si1−x) is studied by x-ray absorption spectroscopy at the Mn L3,2 edges for x=0.005–0.18. Except for the x=0.005 sample, which shows a slight signature of Mn2+ atomic multiplets associated with a local Mn moment, all samples have broad and featureless L3,2 absorption peaks, corresponding to an itinerant state for all 3d electrons. The broad x-ray absorption spectra exclude the possibility of a localized 3d moment and explain the unexpectedly quenched Mn moment in this magnetically doped amorphous semiconductor. Such a fully delocalized d state of Mn dopant in Si has not been previously suggested. © 2008 American Institute of Physics. [DOI: 10.1063/1.2908050]

Mn is widely used as a magnetic dopant in diluted magnetic semiconductor (DMS) systems. The value of the Mn moment changes in different matrices due to different local environments. For Mn in crystalline Si (c-Si), both mean-field theory (Zener model) (Ref. 1) and first-principles calculations2,3 predict the presence of large Mn moments (≥5μB) due to partially filled localized 3d levels. Experimentally, ferromagnetism is reported in Mn-doped crystalline group-IV semiconductors.4,5 However, homogeneous doping of Mn is difficult, largely due to the extremely low solubility of Mn (x≈10−7) in crystalline group-IV semiconductors near room temperature.6 These issues were addressed by preparing Mn-doped Si in the amorphous form, enabling the study of the intrinsic Mn moment in the amorphous Si (a-Si) environment. Surprisingly, a quenched local Mn moment was observed by magnetic measurements.7

Ideal transition metal-doped ferromagnetic semiconductors rely on robust local moments associated with partially occupied 3d levels, which align via coupling through a low-density carrier system.8 Magnetization studies on Mn-doped a-Si(a-Mn3Si1−x) have shown that Mn in a-Si has an unexpectedly small magnetization for the wide range of x=0.005–0.18. Even for the most dilute sample (x=0.005), the majority (∼65%) of the Mn atoms are magnetically silent.7 This low magnetization can be a result of Mn low spin states, antiferromagnetic clusters, or the overlapping of 3d atomic orbitals resulting in a nonmagnetic band. With magnetic measurements alone, it is hard to distinguish between these alternative possible explanations.

In this letter, x-ray absorption spectroscopy (XAS) of Mn L edges is used to probe the 3d states of Mn in a-Si by measuring the transition from occupied 2p core levels to the unoccupied 3d states. Since the magnetic states are closely related to the electronic structure, the local 3d moment can be deduced and compared to magnetization measurements. The measured Mn L edges have a very broad absorption feature, even at a very dilute Mn concentration (as low as x=0.005). The XAS results conclusively show that the d levels are fully extended into bands for doping concentrations x greater than 10−3 in a-Si, even for samples deep on the insulating side of the insulator-metal (I-M) transition.

a-Mn3Si1−x thin film samples were prepared by e-beam coevaporation of Mn and Si sources under ultrahigh vacuum conditions. High-resolution cross-sectional transmission electron microscopy with energy dispersive spectroscopy shows a homogeneous amorphous structure with no sign of any crystallinity, even at the nanoscale, and no sign of any Mn clustering. More detailed sample information can be found elsewhere.7,9 X-ray absorption (XA) and x-ray magnetic circular dichroism (XMCD) spectra at the Mn L edges were taken at the Advanced Light Source (ALS) beam line 6.3.1, in total electron yield mode. All measured thin film samples, including a control sample of a pure Mn metal film, were capped with 2–4 nm Al and stored in a vacuum desiccator to avoid oxidation. Commercially available Mn oxide powders with different Mn valences (MnO, Mn2O3, and MnO2, corresponding to d3, d4, and d5 configurations, respectively) were used as references.

Figure 1 shows the Mn L3,2 spectra for all samples as well as a simulated Mn2+ spectrum. The atomic multiplet features of the Mn ion in different oxides can be well resolved. The spectra of the oxides are consistent with standard atomic multiplet simulations.10 We use the main Mn2+ L3 absorption peak as our energy reference, which occurs at 639.0 eV in our data [Fig. 1(g); the feature at ∼641.0 eV comes from Mn2O3 impurities in the MnO powder].11 The XA spectra of a-Mn3Si1−x [Figs. 1(a)–1(d)] have, in general, very broad L3 and L2 peaks, and no XMCD signal is observed in applied external fields up to 0.2 T at T=8 K, which is consistent with the lack of magnetization reported in Ref. 7. For x=0.04, the spectra scale very well with x. The spectra of the sputtered Mn metal film and a-Mn3Si1−x both show no distinct atomic multiplets, but they differ from each other in peak positions and peak widths: the main absorption peak of the Mn metal has a lower energy (639.4 versus 639.9 eV) and a narrower line width.

Figure 2 shows the detailed analysis of the L edges of a-Mn3Si1−x. For x=0.04, the inset of Fig. 2 shows their collapse into a single curve after normalizing to the concentration-dependent postedge steps. The spectrum of the x=0.005 sample is normalized by the L3 peak height since the signal/noise ratio is low at/beyond the L2-edge energy
due to the small Mn concentration. However, the $x=0.005$ sample obviously exhibits a different line shape at the $L_3$ edge with the $L_3$ peak at 639.0 eV, which is 0.9 eV lower in energy (with less broadening compared to the $x\geqslant 0.04$ samples) and aligned with the main Mn$^{2+}$ $L_3$ peak, as marked with a dashed line in Fig. 1.

Besides the 639.0 eV peak, the $L_3$ edge of the $x=0.005$ sample also shows a broad shoulder at $\sim 639.9$ eV, which is an energy quite similar to the broad peak seen in all samples with $x \geqslant 0.04$. This strongly suggests that this spectrum consists of a mixture of a Mn$^{2+}$ multiplet and another broad XA peak centered at $\sim 639.9$ eV, which is most likely the Mn XA spectra observed in the $x \geqslant 0.04$ samples. We test this idea by performing a weighted superposition of the broad spectrum of $x=0.18$ [Fig. 3(a)] and the Mn$^{2+}$ spectrum [Fig. 3(d)] to match the measured spectrum for the $x=0.005$ sample [Fig. 3(c)] at the $L_3$ edge. The simulated spectrum [Fig. 3(b)] reproduces the features of the $x=0.005$ sample’s spectrum well. The broad absorption peak found in high Mn doping samples develops even at a Mn concentration as low as $x=0.005$, with a significant fraction (>60%) of the incorporated Mn, which is reminiscent of the nonmagnetic Mn portion (~65%) found in a similar low Mn concentration in the previous magnetization study. These results link the broad XA spectra with the nonmagnetic Mn state. The consistency between the XA data and the magnetization results strengthens the two-state model we proposed for $a$-$\text{Mn}_x\text{Si}_{1-x}$.

The surprising nonmagnetic states seen in $a$-$\text{Mn}_x\text{Si}_{1-x}$ thus seem to be associated with the broad XA spectra seen here and strongly argues against Mn ions with a low spin state, or atomic force microscopy (AFM) coupled Mn moments because in either case, the XA spectra would have shown multiplet structures. Moreover, a large crystal field (CF) splitting is a prerequisite for low spin states, but CF splitting is a small effect in Si, as stated by the Ludwig–Woodbury model. Disorder in $a$-Si would introduce randomness in the CF strength. We therefore performed multiplet simulations with varying CF strengths. The CF of Mn oxides was used as an upper bound of the CF strength in Si, which is found to be $\approx 2$ eV (for Mn$^{4+}$ in MnO$_2$) according to our simulations. A varying CF between 0 and 2 eV pro-

FIG. 2. (Color online) $L_3$ edges of all $a$-$\text{Mn}_x\text{Si}_{1-x}$ samples. Spectra were normalized to the $L_3$ peak height to illuminate the differences in peak positions and peak widths. Inset: The normalized spectra (described in the text) show how the overall spectrum shapes of both $L_3$ and $L_2$ scale with $x$ for $x=0.04$, 0.14, and 0.18 but do not scale for $x=0.005$.

FIG. 3. Demonstration of the existence of mixed states in the $x=0.005$ sample [curve (c)] by superposition of the calculated $L_3$ edge of Mn$^{2+}$ [curve (d)] and of the $x=0.18$ sample [curve (a)]. The dashed-dotted curve (b) is the best match to curve (c). The uncertainty in the spectral weight of curves (a) and (d) is $\sim 10\%$. 

FIG. 1. XAS of the Mn $L$ edges for the samples and standards. $a$-$\text{Mn}_x\text{Si}_{1-x}$ were prepared by $e$-beam coevaporation. The Mn metal film was prepared by magnetron sputtering at 4 mTorr, all at room temperature. All thin film samples were capped with 2–4 nm Al. Mn oxides are commercially available chemicals powders. Compared to Ref. 11, both MnO and MnO$_2$ samples have an extra feature $\sim 641.0$ eV, indicating a small Mn$^{4+}$ contribution.
uces small effects (~0.5 eV shift) on the main L peak. Thus, even if a random distribution of CF strengths exists due to disorder, linear combinations of the corresponding weighted spectra would not yield the observed smooth and broad XA peaks (full width at half maximum ~5 eV).

Mixed Mn valence states can lead to a significant XA broadening, such as found in (La,Ca)MnO$_3$ (LCMO) and MnSi crystalline compounds. In LCMO, the L-edge broadening is due to the coexistence of Mn$^{3+}$ and Mn$^{4+}$ sites, and in crystalline MnSi, it is proposed to be the mixed-valence ground state, which consists of different multiplets. However, the underlying features from the atomic multiplets are still clearly visible in those spectra.

In a p-d hybridization scenario, as for the well-studied FM Mn-doped III-V DMS systems, multiplet structures are compressed and shifted due to the charge transfer effect and screening. This leads to narrower XA peaks due to disorder, linear combinations of the corresponding edges of the Mn$^{3+}$ and Mn$^{4+}$ sites, and in crystalline MnSi, it is proposed to be the mixed-valence ground state, which consists of different multiplets. However, the underlying features from the atomic multiplets are still clearly visible in those spectra.

We propose instead that the smooth broad L edges of a-Mn$_{2-x}$Si$_{1-x}$ are most likely due to the formation of an itinerant impurity band of the 3d electrons. Mn metallic clusters are excluded by previous materials characterization. The atomic density obtained from Rutherford backscattering and film thickness measurements linearly increases with Mn doping, suggesting that Mn are at interstitial-like positions with high Si coordination numbers, as in other crystalline MnSi silicides. The Mn centers and Mn–Si covalent bonds can lead to delocalized states and the formation of an itinerant impurity band. Moments associated with metallic bands are usually small, if present at all, such as in the Mn$_3$Si$_2$ silicide and the itinerant helimagnet MnSi. The existence of a well defined band with the electrons being localized due to disorder in these insulating samples (defined as vanishing conductivity at $T \to 0$ K in $I$-$M$ transition physics; $x=0.005$ and 0.04 samples are on the insulating side) is consistent with the Anderson localization theory. Furthermore, the formation of a band by the Mn 3d electrons, perhaps as a hybridization with Si s or p electrons, is possible without long-range order and explains the broad shape of the XA spectra. Also, the evidence of a well defined band in this system can be viewed as a precursor to the MnSi helimagnet with the disorder breaking the long-range order needed for a true magnetic ground state.

In conclusion, we have demonstrated that the XAS of a-Mn$_{2-x}$Si$_{1-x}$ for $x=0.005$–0.18 can be modeled by a superposition of two distinct electronic states that are associated with a small fraction of Mn$^{2+}$ magnetic states and a dominant Mn nonmagnetic state, which is in good agreement with previous magnetization data. The L edges corresponding to the nonmagnetic states have very broad and smooth absorption peaks, which argues against the existence of Mn low spin states and AFM clusters. Instead, the broad XA spectra are evidence of a fully delocalized d state and the formation of impurity bands, which explain the absence of magnetic Mn in the a-Si matrix previously observed.

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