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Quenched magnetic moment in Mn-doped amorphous Si films

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The absence of a Mn local moment was observed in Mn-doped amorphous silicon (a-MnSi$_{1-x}$) films. The magnetic susceptibility obeys the Curie-Weiss law for a wide range of $x$ ($5 \times 10^{-3}$ up to 0.175) but with extremely small moment. Magnetization measurements suggest that this behavior occurs because only a small percentage of Mn (Mn$^{2+}$ states with $J=S=5/2$) contribute to the magnetization. Thus, the magnetic moments are quenched for the majority of Mn atoms, contrary to the general belief of the existence of a localized Mn moment in Si. X-ray absorption spectroscopy suggests that the quenching of Mn moments is attributed to the formation of an itinerant but Anderson-localized impurity band, forming at $x$ as low as $5 \times 10^{-3}$.

Magnetic moments in semiconductors are important for spin electronics and for fundamental studies of interactions between magnetic and charge degrees of freedom, such as in Mn-doped GaAs (Ref. 1) and vacancy-doped Gd$_3$Si$_2$. In these crystalline magnetic semiconductors, carrier-induced magnetic ordering, large magnetotransport effects, or magnetic field-tuned metal-insulator (M-I) transitions were observed as a consequence of large moment-carrier interactions. Similar effects were discovered in Gd-doped amorphous Si (a-Gd$_3$Si$_2$) and Ge, including Ruderman-Kittel-Kasuya-Yosida–induced spin-glass (SG) freezing, enormous negative magnetoresistance (MR) [~$10^5$ at 1 K (Ref. 5)] and an M-I transition driven by magnetic field, providing evidence for strong local moment-carrier interactions. The coexistence of well-defined magnetic moments, charge carriers, and strong moment-carrier interactions is important prerequisites for magnetically doped semiconductors.

Mn-doped crystalline Si (c-Si) and Ge have been the focus of recent studies as potential spintronics materials. However, the observed ferromagnetism is controversial and seems to be extrinsic in origin, being attributed to nanocrystallites or chemical inhomogeneity, due to the extremely low thermodynamic solubility of Mn in c-Si ($x \sim 10^{-7}$).

We have prepared homogeneous Mn-doped amorphous Si (a-Si) to address the issue of the intrinsic magnetic state as well as to study the moment-carrier interactions. High-quality e-beam-evaporated a-Si consisting of a continuous random network of tetrahedrally bonded Si atoms possesses a local chemical environment similar to that of c-Si. Moreover, lower growth temperatures and the forgiving nature of the amorphous structure are conducive to homogeneous doping. Therefore, since charge and spin states are most sensitive to the local environment, Mn moments existing in c-Si should also be observable in a-Si.

The existence of a significant Mn moment in Si, key to ferromagnetic ordering, is predicted by the early model developed by Ludwig and Woodbury (the LW model) for isolated Mn in c-Si, as well as by more recent mean-field theory (Zener model) and first-principles calculations in the dilute doping range ($x \sim 10^{-2}$). The $s$-$d$ exchange interaction is expected to be larger than $s$-$f$ due to the delocalized nature of the 3$d$ moment compared to the 4$f$ moment. Thus, a local Mn moment in Si would be expected to lead to even larger MR than seen in a-Gd$_3$Si$_2$. Therefore, it is intriguing that the few reports on magnetotransport of Mn-implanted a-Si samples ($a$-Si$_{1-x}$, Mnx, $x \sim 0.07$–0.22) showed no large negative MR effect; magnetic properties were not reported.

In this Brief Report, we describe a systematic magnetization and magnetotransport study on Mn-doped a-Si ($a$-Mn$_x$Si$_{1-x}$) films (where $x$ ranges from $5 \times 10^{-3}$ to 0.175), covering both the dilute region and the M-I transition region. Films were grown by e-beam coevaporation from Si and Mn sources onto substrates held near room temperature under ultrahigh-vacuum conditions (base pressure of $\sim 8 \times 10^{-10}$ Torr). In situ thickness monitors were used to precisely control the real-time Mn and Si flux to achieve uniform doping profiles as well as the desired Mn concentrations. The resulting films have a more homogeneous and uniform Mn distribution compared to implanted samples, providing a better platform to probe the intrinsic Mn magnetic properties in Si. Film compositions and the absence of oxygen impurities inside the films were established by Rutherford backscattering (RBS) using the oxygen-resonance energy to enhance O sensitivity. No clustering or crystalline phases were observed by high-resolution cross-sectional transmission electron microscopy (HR-TEM) down to 2 nm, as shown in Fig. 1(a). There are a few regions with diameters of $\leq 2$ nm which show slight suggestions of poorly defined lattice fringes, but digital diffractograms show typi-
The low temperature magnetic moment \(M_t\) tuned for the \(x=0.135\) samples. Substitutional Mn \(M\) atoms acted like interstitial Mn \(M_{I}\) in \(a\)-MnSi\(_{1-x}\) (and therefore, located at sites with large Si coordination numbers and low symmetry). Substitutional Mn \(M_{S}\) on the other hand would have kept \(n_{\text{total}}\) constant and close to the pure \(a\)-Si density.

Figure 1(b) shows the \(T\) dependence of dc conductivity \(\sigma(T)\) for different \(x\). \(\sigma(T)\) increases monotonically with \(x\), indicating that Mn is an effective dopant. A concentration-tuned \(M-I\) transition is observed; samples are insulating for \(x\leq 0.135\), whereas they are metallic for higher \(x\). Based on the low temperature \(\sigma(T)\), the 0.135 sample is very close to \(x\), but slightly on the insulating side. This result is in agreement with the 0.137 found in Mn-implanted \(a\)-Si samples. Magnetotransport properties were measured for one sample on the insulating side \((x=0.135)\) and one sample on the metallic side \((x=0.175)\). A small positive \(\frac{\rho(H)-\rho(0)}{\rho(0)}\) was found down to 2 K at \(H=7\) kOe for both samples, as shown in Fig. 1(c): 27% and 16% for \(x=0.135\) and \(x=0.175\), respectively. No negative \(\rho\) was observed in any sample. The negative \(\rho\) found in Ref. 19 was attributed to magnetic clusters.

FIG. 2. (Color online) (a) Magnetization per Mn atom in units of \(\mu_B\) vs \(H\) for different Mn concentrations at 2 K, assuming all Mn equally contribute. Inset: same data on expanded scale. Lines are guides to the eye. (b) Normalized \(M\) vs \(H\) for various compositions \(x\) at 2 K. Lines show Brillouin function for free magnetic ions when normalized to the high field value, as shown in Fig. 2(b). The values of \(M\) at 6 kOe were within 2% of the saturation moment according to the Brillouin function and is used later to calculate the saturation moment per Mn \(\left(p_{\text{sat}}\right)\).

Both the zero-field-cooled (ZFC) and the field-cooled (FC) magnetic susceptibilities \(\chi_{\text{ZFC,FC}}(T)=M(T)/H\) were recorded in a dc magnetic field of 10 kOe. The diamagnetic background from the substrate was again subtracted. The resulting net ZFC and FC data are identical and follow the Curie-Weiss (CW) law very closely with a very low CW temperature \((\theta<2\) K). For \(x=0.04\), which had the largest raw magnetic signal, \(\chi_{\text{ZFC,FC}}(T)\) was also determined using smaller fields \((H=1000\) and 350 Oe). 10 kOe is a large field for measuring \(\chi\) and the reduction in \(\chi\) from its initial value is \(~20\%\), leading to a 10% underestimation of the effective moment \(\left(p_{\text{eff}}\right)\). This high field is necessary to obtain reliable sample signals (strongly \(T\) dependent) above the diamagnetic background (negligible \(T\) dependence) for our samples. No ferromagnetic or SG states were observed in the temperature range of \(2-40\) K. Above 40 K, the error bars were large due to the small signal. In order to probe further for possible antiferromagnetic (AFM) or spin glass states, the thermomagnetic moment (TRM) was also measured by cooling the sample in a 70 kOe field and then measuring during heating in zero field from 1.9 to 380 K: no significant signal was obtained. These results indicate that samples are purely paramagnetic.

Figure 3 shows the Mn concentration dependence of \(p_{\text{sat}}\) \((M\) at \(T=2\) K, \(H=6\) T), as described previously, and of \(p_{\text{eff}}\) deduced from the CW fitting constant \(A=M_{\text{sat}}p_{\text{sat}}^{2}H_{R}^{2}/3k_{B}\left(n_{\text{Mn}}\right)\). Both \(p_{\text{eff}}\) and \(p_{\text{sat}}\) decrease
FIG. 3. (Color online) $p_{\text{sat}}$ (from $A=n_{\text{Mn}}p_{\text{sat}}^m(\mu_B^2/3k_BT)$ and $p_{\text{sat}}$ from $M(H=60\text{ kOe})=n_{\text{Mn}}p_{\text{sat}}$) with different $n_{\text{Mn}}$ for each $x$. Lines are guides to the eye. Inset shows the concentration ($c_m$) of magnetic centers as a function of $x$.

... sharply from $x=5 \times 10^{-3}$ to $x=0.04$, becoming very small and negligible with increasing $x$.

The small magnetization ($p_{\text{sat}}$ and $p_{\text{eff}}$) of all samples strongly suggests that only a very small percentage of Mn atoms are magnetically active. Electron spin resonance (ESR) results suggest Mn is in a pure spin state ($g=2$). According to the LW model, there are two known MnI with a quenched orbital moment: MnI$^{2+}$ ($3d^3$, $J=S=5/2$) and MnI$^-$ ($3d^9$, $J=S=1$). Instead of assuming all Mn contribute equally (as done above to determine $p_{\text{sat}}$ and $p_{\text{eff}}$), the following equations can be solved assuming various fixed $J$ values:

$$p_{\text{sat}} = c_m\mu_B^2 J,$$

$$A = \frac{c_m n_{\text{Mn}} p_{\text{eff}}^m \mu_B^2}{3k_B},$$

where $p_{\text{sat}}$ and $A$ are experimentally determined as previously mentioned. Equation (1) gives $c_m$, the percentage of magnetically active Mn. Substituting $c_m$ into Eq. (2), we obtain a new effective moment (denoted as $p_{\text{eff}}^m$) based on $c_m n_{\text{Mn}}$ instead of $n_{\text{Mn}}$, as previously assumed. For a simple paramagnetic state, $p_{\text{eff}}^m$ should equal $g(J+1)$ [the same J as in Eq. (1)]. Table I shows the resulting $p_{\text{eff}}^m$ for $J=5/2$ is in excellent agreement with the calculated effective moment ($5.9\mu_B$) within experimental errors [~10% underestimated of $p_{\text{eff}}^m$ comes from determining $\chi(T)$ by using a 10 kOe field, as discussed previously]. This analysis does not work for the MnI$^-$ with $J=1$. This provides strong evidence that MnI$^{2+}$ ($3d^3$, $J=S=5/2$) is the magnetically active state, but only accounts for a small percentage of the $n_{\text{Mn}}$ (e.g., $c_m=35.2\%$ and 0.6% for $x=5 \times 10^{-3}$ and 0.175, respectively).

Using $J=5/2$, we plot $c_m$ vs $x$ (Fig. 3, inset). Its rapid decrease explains the low values of $p_{\text{sat}}$ and $p_{\text{eff}}$ in the main plot. The product of $x$ and $c_m$ (listed in Table I), which gives the atomic concentration of MnI$^{2+}$, is found to be a small constant value, on the order of $10^{-3}$, suggesting a constant limit for Mn ions with $J=5/2$ local moments. Above this limit, there is no increase in the number of Mn moments; the added Mn atoms contribute to the transport properties only. This is in sharp contrast to the previously studied magnetically doped system $a$-Gd$_2$Si$_{1-x}$, which had a SG ground state and showed enormous negative MR.\(^{13}\) These phenomena in $a$-Gd$_2$Si$_{1-x}$ are only consistent with each Gd acting as an electron dopant as well as having a large local moment. In contrast, $a$-Mn$_x$Si$_{1-x}$ behaves like a typical nonmagnetic disordered electronic system with small positive MR.\(^{23}\)

MnI in $a$-Si is believed to always have a local moment.\(^{15-18,24,25}\) This should be the same in $a$-Si since the Mn spin and charge states mainly depend on local environment. It is possible, but unlikely, that Mn moments exist but are completely canceled out by AFM interactions since AFM ordering is not robust to disorder so AFM interactions between local moments should lead to a magnetically frozen state, such as a SG phase (with $T_f$) or a clustered SG (with blocking temperature $T_B$), which would show magnetic hysteresis (differences between the FC and the ZFC states) and TRM. The CW behavior of our samples is reliably measured up to 40 K for $x$ up to 0.175. The known concentrated SG $a$-MnSi (x=0.5) has a $T_f$ only at 22 K,\(^{26}\) and $T_f$ ($T_B$) should decrease with decreasing magnetic concentration $x$. The crystalline MnSi compound has a magnetic ordering temperature ($T_C=30$ K). Above $T_f$ or $T_C$, in the paramagnetic states, they have comparable $p_{\text{eff}}$ of 2.2$\mu_B$ and 2.6$\mu_B$ for c-MnSi and a-MnSi, respectively, due to similar local environment and short-range order;\(^{27}\) both of these states would give significantly larger $\chi(T)$ than that observed in $a$-Mn$_x$Si$_{1-x}$.

Another possible source for vanishing Mn moment with increasing $x$ is the formation of local AFM clusters. Mn clusters in $a$-Si (which would be invisible in HR-TEM), such as Mn dimers or trimers, could potentially have an AFM configuration and zero moment. However, such complexes have never been observed in Si experimentally to the best of our knowledge and are theoretically found to have higher energy than FM-coupled configurations\(^{25,28}\) which would result in an enhanced $p_{\text{eff}}$. Only the neutral charge state of MnI favors AFM coupling in Si,\(^{28}\) which would not contribute to electrical transport, contrary to observation. Mn$^{0}$ (Ref. 15) and [Mn$_{3i}$]$^{0}$-MnI$^-$ (Ref. 29) clusters have large $S$ values. Therefore, pairs and polyclustering (up to four Mn atoms) are unlikely to be the reason for the absence of magnetism in

<table>
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<th>$x$</th>
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<th>$p_{\text{eff}}^m$/$\mu_B$</th>
<th>$x c_m$/$10^{-3}$</th>
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<tr>
<td>0.175</td>
<td>0.6</td>
<td>4.0</td>
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</tr>
</tbody>
</table>

$^a$Mn doping concentration from RBS: $a$-Mn$_x$Si$_{1-x}$

$^b$Magnetically active percentage from Eq. (1) for $J=5/2$.

$^c$Effective moment from Eq. (2) for $J=5/2$.

$^d$Atomic concentration of Mn$^{2+}$ in $a$-Si.

TABLE I. Sample atomic concentration, magnetically active percentage, effective moment, and atomic concentration of magnetic centers, and effective to atomic moment ratio.

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a-Mn$_x$Si$_{1-x}$. Existence of metallic Mn or Mn-rich clusters of larger scale are not supported by the HR-XTEM results and the atomic density analysis. Therefore, AFM clusters are unlikely to be the cause of the small magnetic moment.

We propose that the lack of Mn magnetization in a-Si is due to the formation of bandlike itinerant states. The existence of itinerant states in insulating samples is explained by Anderson localization in strongly disordered amorphous materials. States in the itinerant band are localized due to disordered momentum when $x \ll x_c$ (the localized length depends on $x$, but is generally much longer than an interatomic distance) and delocalized when $x > x_c$. These localized itinerant states have no magnetic moment. For some metallic Mn silicides, such as crystalline Mn$_4$Si$_7$, itinerant magnetism is found with tiny magnetic moment. For some metallic Mn silicides, such as crystalline Mn$_4$Si$_7$, itinerant magnetism is found with tiny $p_{\text{eff}}$ and $p_{\text{sat}}$: $0.365 \mu_B$ and $0.012 \mu_B$, respectively. The symmetry of the Mn site in this compound is low (space group P4c2) and may be a better representation of the local environment of Mn in a-Mn$_x$Si$_{1-x}$. It is also possible, given the usual strong s-d exchange interactions, that a Kondo effect plays a role in reducing the magnetic moment.

The model of a localized itinerant state is supported by x-ray absorption spectroscopy (XAS) studies. Samples with $x \geq 0.04$ show two broad Mn L edges, which resemble the spectra for transition metals with delocalized d bands. In the $x = 5 \times 10^{-3}$ sample, mixed electronic states are observed. Analysis shows that its Mn L$_3$ edge can be decomposed into two separate spectra: one with the broad edges found in the high Mn doping samples, and the other with Mn$^{2+}$ atomic multiplet structures, consistent with our magnetic data, indicating 35% Mn$^{2+}$, $S = 5/2$ centers. The broad absorption edges are therefore assigned to nonmagnetic Mn states and are characteristic of strong covalency and band formation.

In conclusion, an unexpected quenched Mn moment state has been observed in Mn-doped a-Si, forming at the lowest $x$ studied ($5 \times 10^{-3}$), which is not predicted by any existing model for transition metal dopants in Si. This result explains why MR for a-Mn$_x$Si$_{1-x}$ is positive and small, with typical values for disordered nonmagnetic electronic systems, unlike the enormous negative MR found in a-Gd$_x$Si$_{1-x}$. The nonmagnetic state is most likely due to the formation of an impurity band, subject to localization effects. The existence of the itinerant state is related to the local short-range Mn-Si covalency and may explain why the quest for discovering intrinsic dilute magnetic semiconductor based on Mn-doped Si has not been successful compared to Mn-doped III-V semiconductors. Our results also suggest that there is a concentration limit ($x \sim 10^{-3}$) where the LW model for Mn in Si is no longer valid due to formation of bands.

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31H. Wu and Matthias Scheffler (private communication).


