Local environment of Mn in Mn delta-doped Si layers

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Abstract. Dilute magnetic semiconductors combine both magnetic ordering and semiconducting behaviour, leading to potential spintronic applications. Silicon containing dilute Mn impurities is a potential dilute magnetic semiconductor. We have grown Mn delta-doped films by deposition of 0.7 of a monolayer of Mn on Si(001) by molecular beam epitaxy and capping the film with Si. The magnetic properties are likely sensitive to the distribution of Mn on substitutional or interstitial sites and the formation of metallic precipitates. We have used polarization-dependent XAFS to examine the local structure. We compare to a thicker MnSi film grown on Si(111) and also examine the influence of lead on the manganese environment when used as a surfactant in the growth process.

1. Introduction
One of the principle challenges in the field of dilute magnetic semiconductors (DMS) is the controlled incorporation of dilute concentrations of 3d transition metals into a semiconducting matrix. With a Mn concentration of a few percent, ferromagnetic order is produced in a number of semiconductors [1]. These concentrations, well above the solubility limits of the semiconductor, are created with far-from-equilibrium conditions provided by low-temperature molecular beam epitaxy (MBE). Appropriate growth conditions are needed to avoid the formation of metallic precipitates and to incorporate the impurities homogeneously into the semiconductor lattice. Ferromagnetic semiconductors based on MnₓGe₁₋ₓ have been successfully grown with their magnetism mediated by the hole carriers [2]. While high Curie temperatures are reported for MnₓSi₁₋ₓ, its magnetic properties are likely due to precipitates [3]. The growth of Si-based DMS is complicated by the high temperatures typically required for epitaxial growth, leading to the formation of precipitates [4]. A layer of segregating surface impurities, -surfactants- may enable epitaxial growth at lower temperatures than is otherwise possible on a clean substrate surface [5]. For creating a Si-based DMS, Pb is a potential surfactant. It has been used successfully to incorporate As in Si at low temperatures [6] and does not act as a dopant in Si.

One approach to achieving high concentrations of impurities in semiconductors is to deposit single atomic layers of impurities in the semiconductor matrix - δ-doping [7]. Here, we investigate the structure of Mn δ-doped Si(001). Delta-doping separates the Mn and Si growths, permitting the growth of a Mn layer at a lower temperature than the Si, to help reduce the formation of precipitates. XAFS is used to study the effect of the growth conditions, with and without Pb, on the distribution of Mn atoms inside three samples consisting of a Si layer δ-doped with a sub-monolayer of Mn.

2. Experiment
The Mn δ-doped Si samples were prepared by MBE on Si (001) substrates (p-type, 1-20 Ω.cm) ultrasonically cleaned in acetone and methanol followed by an RCA bath at 70°C. The native oxide
was removed in-situ by annealing at 800 °C until the Reflection High Energy Electron Diffraction (RHEED) system showed a (2×1) reconstructed surface. The depositions were performed in ultra high vacuum (base pressure of \(< 5 \times 10^{-11} \) Torr) and, for all samples, a 20 nm Si buffer layer was first deposited at 600 °C. Manganese was deposited at a substrate temperature of approximately -15 °C and lead was grown at 25 °C using thermal effusion cells. The growth sequences and deposition conditions for each layer are summarized in Table 1.

**Table 1. Structure of layers and deposition temperatures of epitaxial films on Si(001).**

| Sample | 1st Layer | Thickness | Growth Temp. | 2nd Layer | Thickness | Growth Temp. | 3rd Layer | Thickness | Growth Temp. |
|--------|-----------|-----------|--------------|-----------|-----------|--------------|-----------|-----------|--------------|
| A1     | Mn        | 0.7 ML    | \(<\) RT     | Si cap    | 12.4 nm   | 200°C        |
| A2     | Mn        | 0.7 ML    | \(<\) RT     | Pb        | 2 ML      | RT           | Si cap    | 12.4 nm   | 200°C        |
| A3     | Pb        | 2 ML      | RT           | Mn        | 0.6 ML    | \(<\) RT     | Si cap    | 12.4 nm   | 200°C        |
| K1b    | MnSi      | 5 nm      | 400°C        | Si cap    | 20 nm     | 50°C         |

a One monolayer (ML) is defined to be \(6.78 \times 10^{14}\) atoms/cm²

b The reference film was grown on a Si(111) substrate with a 20 nm buffer deposited at 600°C.

The order in which Mn and Pb were grown was interchanged in A2 and A3 in order to study how the Pb affects the incorporation of Mn. *In-situ* Auger and *ex-situ* x-ray photoelectron spectroscopy indicated Pb acts as a surfactant and segregates to the surface, while the Mn remains near the substrate-cap interface. The benefit of using a Pb surfactant is evident from RHEED observations. Samples A2 and A3, grown with 2 ML Pb, were crystalline. The original Si (2×1) disappeared during the initial deposition, but a (2×1) reconstruction reappeared after Pb deposition. They retained their (2×1) Pb reconstruction throughout the growth, whereas the Si capping layer in sample A1, which was grown at the same temperature without a surfactant, was amorphous. To identify possible signatures of MnSi precipitates in the XAFS measurements and to serve as a reference system for determination of EXAFS parameters, sample K1 was grown using solid phase epitaxy [Karhu E, Kahwaji S, Raffel R, Robertson M D, Maunders C and Monchesky T L, 2009 unpublished]. RHEED and X-ray diffraction show that K1 has a single crystal (B20) MnSi layer with a (111) orientation.

Fluorescence-mode x-ray measurements were made at the Mn K-edge with a Mn reference being monitored simultaneously [8] for energy calibration. The Si(111) double crystal monochromator on the PNC/XOR ID beamline [9], APS Sector 20, was detuned 20% at 6750 eV to reduce the harmonic energies in the x-ray beam. The x-ray beam was focussed to 3 x 5 \(\mu\)m² by Kirkpatrick-Baez mirrors. The samples were oriented such that the x-rays were incident on the single crystal substrates at an angle, slightly above the critical angle for total external reflection, selected to keep the Mn fluorescence intensity close to its peak value as the energy was changed in the XAFS scans. The electric field vector of the x-rays was aligned to within \(2^\circ\) of the \(<-110>\) or \(<110>\) substrate orientations for in-plane measurements (within the critical angle for out-of-plane scans). Small azimuthal in-plane adjustments were made to shift small Bragg peaks affecting the fluorescence signal and to facilitate the removal of these peaks during processing. The fluorescence intensity was monitored with a seven element Ge(Li) detector. Anomalous dispersion effects [10] were negligible due to the energy-discrimination of the detector, the ultra-thin nature of the samples and air-path. The data were normalized by using an ionization chamber to measure the incident x-ray intensity, \(I_0\).

### 3. Results and Discussion

XAFS interference functions, \(\chi(k)\), were extracted from averaged (20-80 scans in average, depending on sample) \(\mu(E)\) data using ATHENA [11]. Comparison of the near-edge for the films versus Mn foil reference indicated no chemical shift as well as consistency with Mn-implantation in Si near-edge results [12]. The \(k^2\)-weighted Fourier transforms were performed in WINXAS [13] using a \(\beta=4\) Bessel function window over the typical range 2.35 – 9.75 Å⁻¹ (nearst-zero-crossings thereto). Both \(\chi(k)\) and the magnitude of the Fourier transforms are shown in figure 1.
Figure 1. XAFS interference functions (left) and k²-weighted Fourier transform magnitudes (right) for one reference MnSi and three δ-doped Si(Mn) films.

Data were fit in R-space to FEFF7 [14] models using WINXAS [13] over the typical range 1.13 – 2.49 Å (single shell) or R max of 2.82 Å (two-shell). In the parent MnSi B20 crystal structure, Mn has 7 Si neighbours (1x2.305Å, 3x2.413Å, 3x2.523Å) and 6 Mn neighbours (N2) at 2.796Å. The limited k-space range imposed by the δ-doped films prevents resolving the 3 separate Mn-Si distances (average = 2.445Å, N1 = 7). Given the unknown character of the δ-doped films, unpolarized FEFF models were used, though the reference in-plane data could be fit to a polarized model. The reference film was fit initially to a model with the MnSi structure, K1 MnSi in table 2. For comparison between reference and samples, S o ² and E o shift were transferred to a fit using calculated amplitudes and phases from a Mn substitution in silicon model structure, K1 Si(Mn) in table 2. With these parameters transferred, N, R and σ ² were the variable parameters for fitting the film data. To reduce correlation between N and σ ², the data were fit simultaneously to k 1- and k 2-weighted transforms in WinXAS. Some correlation between N and σ ² still has influence, evident when comparing the K1 fits.

Table 2. Fit results and percent fit residual for the reference MnSi film measured with x-ray polarization in-plane (ip) and samples measured ip and out-of-plane (oop) relative to the Si substrates.

| Sample  | S o ²  | ΔE o (eV) | N1(Si) | R 1(Å) | σ ²1(Å²) | N2(Mn) | R 2(Å) | σ ²2(Å²) | R(%) |
|---------|-------|-----------|--------|--------|----------|--------|--------|----------|------|
| K1 MnSi | 0.70(2)| 2.8(6)    | 7      | 2.393(7)| 0.0099(9)| 6      | 2.788(7)| 0.0043(5)| 0.98 |
| K1 Si(Mn)| 0.7  | 2.8(4)    | 6.0     | 2.391(8)| 0.0081(1)| 5.7(3) | 2.785(6)| 0.0040(5)| 0.83 |
| A1 ip   | 0.7   | 2.8      | 2.371(7)| 0.0101(5)| 0.7(5)  | 2.81(6) | 0.010(6)| 1.64(3) | 1.47 |
| A1 oop  | 0.7   | 2.8      | 7.2(3)  | 2.371(6)| 0.0086(5)| 1.5(7) | 2.83(3) | 0.016(7)| 1.04 |
| A2 ip   | 0.7   | 2.8      | 7.3(2)  | 2.386(5)| 0.0108(5)| 2.5(6) | 2.76(4) | 0.024(5)| 2.52 |
| A2 oop  | 0.7   | 2.8      | 7.5(3)  | 2.389(5)| 0.0113(6)| 2.5(8) | 2.77(6) | 0.025(6)| 2.59 |
| A3 ip   | 0.7   | 2.8      | 2.4(3)  | 2.237(7)| 0.0056(6)| 6.7(2) | 2.427(4)| 2.59 |
| A3 oop  | 0.7   | 2.8      | 6.6(2)  | 2.389(5)| 0.0080(4)| --     | --     | 2.14(3) |     |

a strongly correlated with R max, but contributions constant at ~11% of main peak

Sample A1 is dominated by the first (Si) shell with contracted R 1 relative to K1 and higher N1. A weak second shell of Mn could also be fit, similarly for A2. The Si shell for A2 is less contracted than A1. Weak higher-R features near 4Å in A2 and A3 are present. Sample A3, where the Pb surfactant
was deposited prior to the Mn, distinguishes itself from the other samples by a detectable splitting in the in-plane Si shell. With $\sigma^2$ constrained to be the same for both, the ratio of coordination numbers of short to longer Mn-Si distances is $\sim$1:2.8. The shorter distance could not be detected in the out-of-plane fit, suggesting the short Mn-Si distances are largely an in-plane interaction. A second shell is present in A3 oop, but was not included in the fit since the identity of the component could not be decided between Mn (at 2.81Å) and Si (at 3.08Å) with both giving comparable fits.

The theoretical treatment by Hortamani et al. [15] discusses competition between different adatom sites for Mn deposition on Si(001). In that work, one possible site involves the breaking of a surface Si-Si dimer with Mn in between giving two short Mn-Si distances in-plane (short-bridge site B, figure 1 in [15]). Though the Pb deposition removes the Si reconstruction, it may facilitate the occupation of related sites by Mn in sample A3 and lead to defects at the interface between the Si buffer layer and cap. Though there is some evidence for Mn-Mn distances in A1 and A2 comparable to that in MnSi, the higher first-shell N values for the films and contracted $R_1$ distances, particularly for A1, may be an indication of a non-MnSi (B20) Mn environment. One possible alternative, also discussed by Hortamani et al. is a CsCl-like Mn site. Granted, correlations between N and $\sigma^2$ are likely present.

In summary, we have examined three Mn $\delta$-doped-in-Si systems comparing the effect of the use of Pb as a surfactant between films and a reference MnSi film. The three preparations (no Pb, Pb after Mn, Pb before Mn) yielded three distinct results. The sample with no Pb has Mn-Si neighbours contracted compared to MnSi and a Mn-Mn distance slightly expanded, possibly indicating a CsCl-like local environment rather than MnSi. The A3 sample, with Pb deposited prior to Mn, is distinct from the other two in having 2 resolvable Mn-Si distances in-plane.

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