3-D Atomic-Scale Mapping of Manganese Dopants in Lead Sulfide Nanowires

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ABSTRACT: Dopants in nanowires, whether intentional or unintentional, can ultimately control the material’s properties and, therefore, need to be understood on the atomic scale. We study vapor–liquid–solid grown manganese-doped lead sulfide nanowires by atom-probe tomography for the first time for lead salt materials. The three-dimensional chemical concentration maps at the atomic scale demonstrate a radial distribution profile of Mn ions, with a concentration of only 0.18 and 0.01 at. % for MnCl2 and Mn-acetate precursors, respectively. The ability to characterize these small concentrations of dopant atoms in Pb1−xMnxS nanowires (x = 0.0036 and 0.0002), important for spintronic and thermoelectric devices, sets a platform for similar analyses for all nanostructures. First-principles calculations confirm that Mn atoms substitute for Pb in the PbS structure.

INTRODUCTION

Dilute magnetic semiconductors (DMSs)† not only are an ideal test bed for exploring spin-related transport and magnetization but also have the potential to revolutionize the next electronics generation at faster speeds and reduced energy consumption by exploiting spins instead of charges as the main information carriers. To date, the main focus of the DMS research is on wide-band-gap semiconductors, where a high Curie temperature has been predicted theoretically‡ and observed experimentally. The ability to control the magnetic ions forming clusters result in secondary phases, which can strengthen the exchange interaction between impurity spins and conduction charges. The QDs, even in the absence of transition-metal ions, exhibit MR effects because of squeezing of electron wave functions§ and spin blockade. Addition of local spins into low-dimensional semiconductors can create an effective local magnetic field of 100–1000 T and a giant Zeeman splitting on the order of 10–100 meV.‡ NWs, at the smallest dimension with electrical connections, provide an ideal platform for studying magnetotransport.

In this article, we report on the successful vapor–liquid–solid (VLS) growth of Pb1−xMnxS NWs and their atomic-scale characterization in three dimensions using atom-probe tomography (APT). PbS has been employed in photodetectors and is recognized as a promising material for photovoltaics. PbS has several unique properties, such as a narrow band gap (0.41 eV at room temperature), high dielectric constant (190), and a large exciton Bohr radius (20 nm). Mn2+ ions are chosen as the dopants because (1) their half-filled d orbital yields a maximum sp–d exchange interaction with the conduction electrons and (2) Mn2+ ions act neither as donors nor as acceptors in PbS if Mn2+ substitutes Pb2+ and thus will not affect the carrier type and concentration in PbS.

Several routes to synthesize Mn-doped PbS and PbSe nanostructures have been attempted, including solution synthesis, molecular-beam epitaxy (MBE), and the fusion method in a glass matrix. One major difficulty of doping nanostructures is that the impurities tend to migrate to the surface by a self-purification process. Additionally, there has been a dearth of effective characterization techniques to determine the spatial distribution of the impurity ions, which has a great impact on the electronic and magnetic properties of the nanostructures. Specifically, magnetic ions that segregate at the surface have much weaker interactions with conduction electrons, and magnetic ions forming clusters result in second phases, which can
convolute the study of the DMS properties. Standard analysis tools, such as energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), electron paramagnetic resonance (EPR), and Fourier transform infrared spectroscopy (FTIR), have been used to investigate DMS nanostructures.17,18,23 These techniques are, however, not applicable to low dopant concentrations and/or the small quantity of samples from a typical VLS growth. Even when effective, these analysis instruments leave open questions concerning dopant location and uniformity. The atom-probe tomograph (APT) provides three-dimensional (3-D) chemical mapping of a single NW with atomic-scale spatial and chemical resolution and, therefore, is the instrument of choice for analyzing DMS NWs. In APT, a single NW is dissected atom-by-atom and atomic plane-by-plane employing either high-voltage pulses or picosecond ultraviolet (UV) laser pulses. A two-dimensional (2-D) position-sensitive detector records the spatial positions of the evaporated atoms in a NW and in parallel their chemical identities via time-of-flight mass spectrometry, that is, mass-to-charge state ratios. The depth scale (z dimension) is determined from the chronological sequence in which ions arrive at the detector. APT has been applied in several cases to study the nanoscale compositions of NWs,26 but no publication for this family of NWs using APT exists to date. The APT studies are complemented by first-principles calculations to confirm the substitutional site preference of Mn atoms within the PbS structure.

## METHODS

### Preparation of Mn-Doped PbS NWs.

MnCl$_2$·4H$_2$O (99%) and anhydrous 98% Mn(II) acetate are both purchased from Alfa Aesar. MnCl$_2$ does not contain carbon and thereby reduces the possible contamination of the NWs. Its melting point (654 °C) requires a high growth temperature, which often causes the NWs to kink.27 MnAc$_2$ with a significantly lower melting temperature (210 °C) yields straight and dense NWs even at a weight ratio of MnAc$_2$ to PbCl$_2$ as high as 1:1. In a typical growth procedure, a quartz tube was evacuated to a base pressure of 80 mTorr and then was filled with N$_2$ to ambient pressure. An alumina boat of PbCl$_2$ (99.999%, Alfa Aesar) was placed in the center of the quartz tube, and a boat of sulfur (99.999%, Alfa Aesar) was placed upstream near the mouth of the tube furnace (1:2 ratio of PbCl$_2$ to S). A Si wafer ((100) test grade, University Wafers) was placed at 8–12 cm downstream from the tube’s center. One of two precursors, MnCl$_2$ or Mn (II) acetate, was inserted between PbCl$_2$ and S (Figure 1a). N$_2$ flowing at 150 sccm was maintained during the entire growth procedure. Once a peak furnace temperature, $T_p$, was achieved, a short burst of H$_2$ (30–90 at 1 sccm) was flowed into the system to initiate the formation of Pb nanoparticles on the Si wafer: $T_p$ was varied from 600 to 670 °C, depending on the precursor. The sample was maintained at $T_p$ for a total of 15 min, and then the sample was cooled to room temperature over 3–4 h.

### Atom-Probe Tomography Measurements.

To prepare individual NWs for analysis by APT, a micromanipulator in a dual-beam FIB microscope was used to mount individual NWs on silicon microposts. To accomplish this, the NWs were first attached to the micromanipulator needle with a small (∼1 × 1 μm$^2$) patch of Pt that is deposited with the electron beam in the FIB from a Pt metalorganic precursor gas. Next, the NWs were removed from the silicon wafer by slowly translating the micromanipulator needle until the NWs detached. Figure 2a displays a pure PbS NW attached to the micromanipulator needle after having been detached from a hyperbranched NW bundle. The NW was then aligned with the long axis of a silicon micropost, and then attached to it, as shown in Figure 2b.

![Figure 1.](image1.png)  
**Figure 1.** Synthesis and characterization of (Pb$_{1-x}$Mn$_x$)$_2$S NWs. (a) Schematic of the tube furnace. (b) Scanning electron microscope image of hyperbranched NWs—a dense network of NWs. (c) X-ray diffraction pattern of pure PbS NWs and (Pb$_{1-x}$Mn$_x$)$_2$S NWs grown with different precursors. Note that the peak at $2\theta = 33^\circ$ and the broad shoulder near this peak, indicated by an asterisk, are from the Si substrate.

![Figure 2.](image2.png)  
**Figure 2.** Mounting procedure for attaching a NW to a prefabricated silicon micropost: (a) An individual PbS NW from a hyperbranched bundle is attached to the micromanipulator needle with an electron-beam deposited Pt patch and then detached from the bundle. (b) The NW is translated and then aligned axially with a silicon micropost and next affixed to it with an electron-deposited Pt patch.
picosecond ultraviolet (UV) laser pulses with a wavelength of 355 nm. During APT analyses, the MnCl₂ precursor grown NWs were maintained at 80 K, while the pure PbS and Mn-acetate precursor grown NWs were held at 30 K. The base pressure of the ultra-high-vacuum (UHV) chamber was 2 × 10⁻¹¹ Torr during the analyses, and a laser pulse energy of 25 pJ was employed at a pulse repetition rate of 100 or 250 kHz to achieve a target evaporation rate of 0.002–0.01 atom pulse⁻¹. Three-dimensional reconstructions and data evaluation were performed using Cameca’s IVAS3.4 code. The reconstruction parameters were fitted to the diameters of the NWs measured by scanning electron microscopy (SEM), 88, 80, or 110 nm for the pure PbS, MnCl₂, and Mn-acetate precursor grown NWs, respectively. Since the atom probe analyzes only the central part of the tip specimen, the actual reconstructions of the analyzed volumes have a smaller diameter.

**First-Principles Calculations.** Density-functional theory calculations are used to determine the Mn site preference in the PbS crystal structure, the substitutional energies for a Mn atom replacing a Pb or a S atom, respectively, which employ the plane-wave total-energy methodology with the generalized gradient approximation using the Vienna Ab initio Simulation Package (VASP). We employ projector augmented wave (PAW) potentials with spin-polarized technique. Unless otherwise specified, all structures are fully relaxed with respect to volume as well as all internal atomic coordinates. We carefully considered the convergence of results with respect to energy cutoff and k-points. A plane-wave basis set was used with an energy cutoff of 300 eV to represent the Kohn–Sham wave functions. The summation over the Brillouin zone for the bulk structures is performed on a 0.13 (1/Å) spacing Monkhorst–Pack k-point mesh for all calculations. We use a supercell with 2 × 2 × 2 unit cells with 32 Pb and 32 S atoms for calculating the substitutional energies. The total energies of the fully relaxed supercells are calculated before and after Pb substituting in either Pb or S sublattice site.

### RESULTS AND DISCUSSION

The synthesis of Mn-doped PbS NWs was performed using a modified approach of earlier research (Figure 1a). We have chosen MnCl₂ and Mn(II) acetate as precursors to dope PbS NWs, respectively. The growth yielded dense networks and/or hyperbranched NWs that have diameters of 50–100 nm and are tens of micrometers long (Figure 1b,c). XRD confirmed the crystallinity and composition of the Pb₁₋ₓMnₓS NWs (Figure 1d).

Individual NWs were mounted for APT analysis, on prefabricated silicon microposts in a dual-beam focused ion-beam (FIB) microscope with a direct mounting technique (see Figure 2) that does not involve any cutting with the Ga ion beam, unlike conventional lift-out techniques. The advantage is that the NWs do not need to be exposed to the Ga ion beam, and therefore, no protective cover layers need to be deposited. Figure 2a displays a pure PbS NW attached to a micromanipulator needle after having been detached from a hyperbranched NW bundle, and Figure 2b exhibits a NW attached to a micropost ready for APT analysis.

Figure 3a is an APT mass spectrum of a Mn-acetate grown NW. Sulfur is observed exclusively as molecular ions (32S+ 32S) and (32S+ 34S) and have 90.23% and 8.07% relative isotopic abundances, calculated from the isotopic composition of Pb₁₋ₓMnₓS NWs (Figure 1d). The mass spectra for MnCl₂ and Mn-acetate precursor grown NWs show distinctive peaks at 27.5 amu for (35Mn+2) and (35Mn+2) ions. A quantitative analysis of the peaks at 32 and 33 amu demonstrates that they are (32S+ 32S) and (32S+ 34S) dimeric ions: The two most abundant S isotopes are 32S and 34S with 94.99% and 4.25% molecular ions; the first is possibly from the Si substrate used for the NW growth and the latter possibly from residual gas in the UHV chamber. The mass spectra for MnCl₂ and Mn-acetate precursor grown NWs show distinctive peaks at 27.5 amu for (35Mn+2). A quantitative analysis of the peaks at 32 and 33 amu demonstrates that they are (32S+ 32S) and (32S+ 34S) dimeric ions: The two most abundant S isotopes are 32S and 34S with 94.99% and 4.25% isotopic abundances. Therefore, the most abundant molecular weights of S₂ are 64 (32S + 32S) and 66 (32S + 34S) and have 90.23% and 8.07% relative isotopic abundances, calculated from the isotopic abundances using the binomial permutations of the individual isotopes. In the doubly charged state, the dominant peaks are at 32 and 33 amu. The absence of a peak at 34 amu demonstrates that the peaks at 32 and 33 are exclusively S₂ dimeric ions.
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Table 1. Concentrations Measured by Atom-Probe Tomography for NWs Grown as (a) Pure PbS, (b) PbS Doped with Mn Using MnCl₂ Precursor Material, and (c) PbS Doped with Mn Using Mn-acetate as Precursor Material

<table>
<thead>
<tr>
<th>NW type</th>
<th>number of atoms</th>
<th>Mn concentration (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn¹⁺ Pb S</td>
<td></td>
</tr>
<tr>
<td>pure PbS</td>
<td>ND 3 467 888 3 606 598</td>
<td></td>
</tr>
<tr>
<td>MnCl₂ grown</td>
<td>5587 1 536 589 1 588 688</td>
<td></td>
</tr>
<tr>
<td>Mn-acetate grown</td>
<td>5461 23 619 551 24 379 463</td>
<td></td>
</tr>
</tbody>
</table>

```
MnCl₂ grown

|                  | Mn²⁺ Pb S       |                          |
| ND 48.61 0.02 51.39 0.02 |
| 0.18 0.02 50.43 0.03 |
| 0.0114 0.0002 50.79 0.01 |
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The concentration error given is the statistical uncertainty calculated from the total number of atoms collected using σ = [c(1 − c)/N]¹/₂, where c is the measured concentration and N is the number of atoms. ND = not detected. Trace impurities of 17 ± 2 at. ppm of either Si or N₂ were detected in this sample. Number of atoms corrected for time-of-flight mass spectrum cutoff effect: only 34% of the Pb and 48% of the S atoms were detected in the mass range below 200 amu.

The similarity between the ⁸⁴S₂²⁺ and ⁶⁸S₂²⁺ peaks in the three spectra is indicative of similar evaporation conditions for the different APT experiments. This fact is used to correct the overall compositions for samples for which the time-of-flights of the heavier (>200 amu) molecular ions were longer than the time-of-flight window. For instance, the mass spectrum for the MnCl₂ precursor grown NW was recorded up to 200 amu, therefore, capturing only 34% of the Pb and 48% of the S atoms. The concentration values for the MnCl₂ grown NW listed in Table 1 were calculated using the corrected number of atoms.

Table 1 presents the measured overall compositions for pure PbS, MnCl₂, and Mn-acetate precursor grown NWs. The measured PbS stoichiometry of the base material is Pb₄₈.₆S₅₁.₄ for the pure PbS NW, Pb₄₉.₄S₅₀.₄ for the MnCl₂ precursor grown NW, and Pb₄₉.₂S₅₀.₈ for the Mn-acetate precursor grown NW. The Mn concentration is 0.18 ± 0.02 at. % in the MnCl₂ grown NW, and 0.0114 ± 0.0002 at. % in the NW grown with the Mn-acetate precursor. Mn-acetate has a low melting point (210 °C) and may have completely evaporated prior to the formation of the NWs, leading to a lower Mn concentration. The 0.18% Mn concentration corresponds to an average distance of 4 nm between neighboring Mn ions.

Figure 4 displays the 3-D APT reconstructions obtained for the three types of NWs. The reconstruction volumes are 37 × 38 × 389, 35 × 35 × 166, and 50 × 50 × 1444 nm³ and contain 7 074 659, 1 267 365, and 48 004 475 atoms, respectively, for (a) pure PbS, (b) MnCl₂, and (c) Mn-acetate precursor grown NWs. The 3-D distributions of Mn atoms are displayed next to the reconstructions containing all elements for the Mn-doped NWs. Projections of the Mn atoms along the z axis of the reconstruction volumes are displayed in Figure 4d,e. It is seen that the Mn atoms are fairly uniformly distributed, with a possible higher concentration around the central axis of the NWs. This indicates that Mn is most likely incorporated through the catalytic droplet and not from the surface. The distribution of Mn atoms in the NWs is seen in greater detail in the concentration profiles (Figure 5). Figure 5a,b shows axial concentration profiles taken along the z axis of the NWs. The dashed line in the graphs is the average Mn concentration for each NW listed in Table 1, 0.18 ± 0.02 and 0.0114 ± 0.0002 at. % for the MnCl₂ and Mn-acetate precursor grown NWs, respectively. Figure 5a,b demonstrates that the Mn concentration along the z axis of the NW is uniform. Figure 5c,d displays radial Mn concentration profiles averaged over the entire analyzed length for (c) the MnCl₂ and (d) Mn-acetate precursor grown NWs. The Mn concentration is higher along the central portion of the NWs and continuously decreases toward the surface of the NWs. The dashed lines represent the overall average Mn concentrations. The radial distribution of Mn dopants with a higher concentration at the center is an unexpected result and one that will be explored more deeply in a future publication.

Understanding the distribution of Mn atoms on an atomic scale also requires knowledge of the site preference of Mn atoms within the PbS lattice. If Mn atoms dissolve interstitially, then charge balance should result in n-type doping, as each interstitial Mn atom donates two electrons. This is inconsistent with the experimental observation that Mn-doped PbS NWs remain p-type (Figure 6). Thus, we only consider the possibility that Mn atoms dissolve substitutionally. As a measure of the site preference, the substitutional energies $E_{\text{Mn-Pb}}^{\text{sub}}$ and $E_{\text{Mn-S}}^{\text{sub}}$ for a Mn atom replacing a Pb or a S atom, respectively, are...
calculated utilizing density functional theory. The substitutional energies, $E_{\text{Mn} \rightarrow \text{Pb}}$ and $E_{\text{Mn} \rightarrow \text{S}}$ in PbS are defined as by

$$E_{\text{Mn} \rightarrow \text{Pb}} = \left[ (E_{\text{tot}}^{\text{Pb}})_{(1-x)\text{Pb}-x\text{Mn}} + n\mu_{\text{Pb}} \right]$$

$$- \left( E_{\text{tot}}^{\text{PbS}} + n\mu_{\text{Mn}} \right)/n\text{Mn}$$

(1)

$$E_{\text{Mn} \rightarrow \text{S}} = \left[ (E_{\text{tot}}^{\text{S}})_{1-y\text{S} - y\text{Mn}} + n\mu_{\text{S}} \right]$$

$$- \left( E_{\text{tot}}^{\text{PbS}} + n\mu_{\text{Mn}} \right)/n\text{Mn}$$

(2)

where the $E_{\text{tot}}$s are the calculated total energies before and after substitution, $n$ is the number of substitutional atoms, and $x$ and $y$ are the fractions substituted. We utilize only one substitutional atom, so $x = 1/32$ and $y = 1/32$. The quantity $\mu$ is the chemical potential, and the values of Pb, S, and Mn are $-3.697$, $-0.512$, and $-1.053$ eV atom$^{-1}$. The calculated results demonstrate that Mn atoms prefer strongly to substitute for Pb on the Pb sublattice sites of PbS, as $E_{\text{Mn} \rightarrow \text{Pb}}$ is significantly smaller than $E_{\text{Mn} \rightarrow \text{S}}$ (Table 2).

The average atomic forces and displacements at the first nearest-neighbor distance associated with the local stresses and strains resulting from the substitution of Mn on the Pb and S sublattice sites are listed in Table 2. We note that no atomic force was measured for the relaxed PbS phase prior to Mn site substitution. The substitution of Mn on the Pb sublattice sites results in smaller values of the atomic force and displacement than substitution of Mn at the S sites, and therefore, Mn prefers the Pb sublattice sites. This result is also consistent with the electrical measurements of single (Pb$_{1-x}$Mn$_x$)$_S$ NW devices, which exhibit similar p-type carrier concentrations as pure PbS NWs (Figure 6).

### CONCLUSIONS

NWs of pure and Mn-doped PbS have been grown by the VLS technique and characterized with subnanoscale spatial resolution and atomic-scale chemical sensitivity in 3-D utilizing atom-probe tomography. The results indicate an absence of Mn for the pure PbS NW, and Mn dopant concentrations of 0.18 or 0.01 at. % for the NWs grown with MnCl$_2$ or Mn-acetate precursors, respectively. The Mn dopants are found to be distributed uniformly along the axial length ($z$ axis) of the NW but have a varying radial concentration, with the highest concentration in the center of the NWs and a decreasing concentration toward the surfaces of the NWs. This level of detailed characterization and sensitivity to the extremely small dopant concentrations in these nanostructures cannot be achieved by any other method. Furthermore, these are the first APT results reported on NWs of the lead salt family, and this article defines the conditions for their successful analyses. First-principles calculations confirm that Mn has a strong preference for occupying lattice sites on the Pb sublattice of the PbS structure. These measurements and calculations open the door to a new level of understanding of doped NWs and will contribute to the optimized synthesis and function of future nanodevices.

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### Notes

The authors declare no competing financial interest.
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