Determining the Solid Solubility of Mn in Ge Nanowires Using Pulsed-Laser Atom Probe Tomography

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Abstract

Germanium (Ge) nanowires were grown via the vapor-liquid-solid growth mechanism and surface-doped with manganese (Mn). The nanowires were annealed at 350° C for 30 min to promote the Mn diffusion. Pulsed-laser local electrode atom probe tomography was used to determine the concentration and distribution of Mn in the Ge nanowires. Analysis showed that the amount of Mn in the Ge was ~10^{-3}–10^{-4}, depending on the sample and analysis volume in question. Mn-doped Ge nanowires have potential applications as magnetic semiconductors.

Introduction

The development of semiconducting nanowire structures may lead to dramatic advances in electronic technologies.[1] The fabrication of wires with diameters on the nanometer scale will facilitate the creation of smaller electrical devices, including transistors and diodes. As devices get smaller, an increased number can be used when designing circuits, which will result in improved performance.[1]

Further, nanowires can be created to construct spintronic devices. Contemporary electronic devices only transfer information through the charge of electrons that flow through conducting materials. Spintronic devices, though, transfer information both through the charge and the spin of an electron.[2] In order to convey and interpret this information, spintronic components must have magnetic as well as conducting properties.

Depositing surface dopants on semiconducting nanowires followed by annealing is one approach that can lead to the formation of structures with certain desired magnetic properties. These dopants diffuse and are incorporated into the bulk of the material. To study and refine this diffusion process, analysis can be conducted with the Local Electrode Atom Probe (LEAP). The LEAP is an advanced instrument that can determine the location of individual atoms in a sample with high precision.[3–5]

Background

Diffusion

Germanium (Ge) doped with manganese (Mn) is a material with appealing magnetic and semiconducting properties.[6] One method of creating such magnetic semiconducting structures is to deposit Mn on the surface of Ge nanowires. Upon heating, it is possible that the Mn will diffuse into the Ge. No previous literature describes the solid solubility of Mn in Ge at low temperatures, so the feasibility of this method of doping has not been established.

Nanowire Growth

The vapor-liquid-solid (VLS) mechanism is a well-documented growth process.[7] VLS growth is achieved by first depositing solid metal catalyst nanoparticles on a substrate in a reactor, and then introducing a gaseous precursor. In the case of Ge nanowires, gold (Au) is the metal catalyst, and germane gas (GeH_4) is the precursor. At the growth temperature, GeH_4 preferentially decomposes on the Au surface. As demonstrated in Figures 1 and 2, a liquid Au-Ge alloy will form at temperatures above the eutectic temperature. The Ge continues to be absorbed into the liquid until the alloy is supersaturated and nucleation of the solid semiconductor occurs. This nucleation takes place at the liquid-substrate interface. The growth continues in one direction, resulting in a structure that has a length much larger than its diameter.

It is possible to create nanowires with geometries that are favorable for device construction by introducing changes in the previously described procedure.[8] By sequentially introducing precursors into the reactor after a previous growth has finished, a different material can be grown from the end of an existing nanowire.[9] This procedure can create nanowires that have alternating lattice structures — a geometry that is conducive to creating transistors. Further, conditions can be established that facilitate chemical deposition on the surface of already existing nanowires, resulting in "shells" forming around the nanowires.

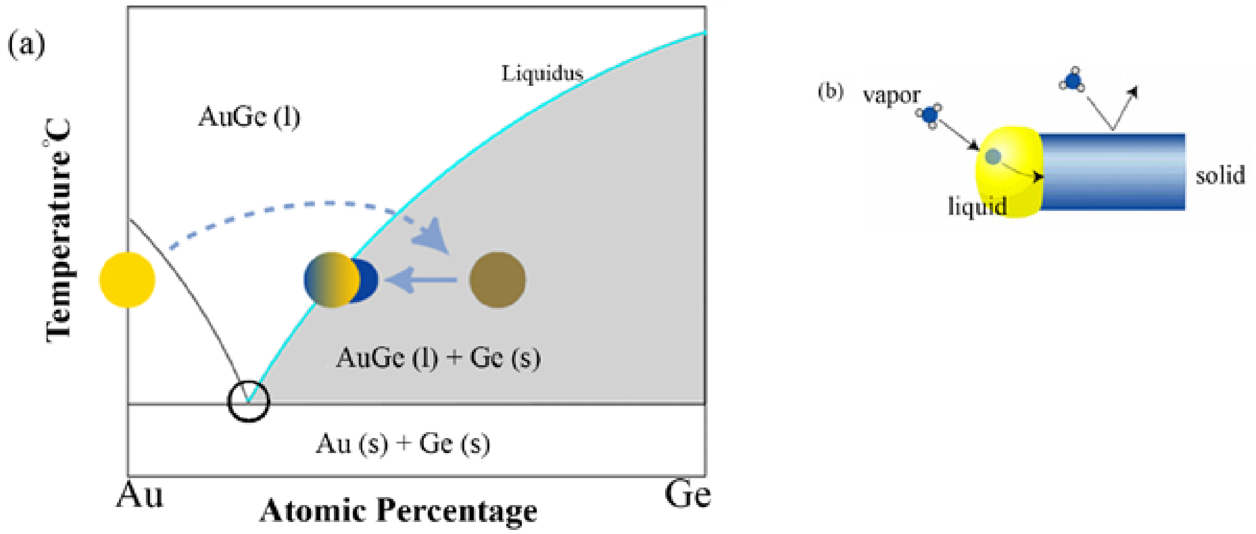

Figure 1: VLS growth of a Ge nanowire. a) Au-Ge binary phase diagram depicting the eutectic point (circled) above which a liquid alloy forms. As the composition increases beyond the liquidus line, shown in light blue, phase separation and Ge nucleation occurs. b) An illustration of the tip of a nanowire. The vapor is GeH_4, the liquid is an Au-Ge alloy and the solid is Ge.

Upon annealing (a heating process used to promote diffusion), the nanowire core and shell may be considered to be a nanoscale diffusion couple.[10] A diffusion couple is a system of two materials that are joined together and annealed, causing atoms to migrate from one component of the couple to the other. If materials A and B constitute a diffusion couple, three different situations may arise when they are annealed. It is possible that atoms from A will diffuse only into B, atoms from B will diffuse only into A, or that atoms from both materials will diffuse into each other. For example, in a copper (Cu) and nickel (Ni) diffusion couple, atoms from both metals begin to diffuse equally when a specific temperature is reached. As demonstrated by Figure 3, after a certain amount of annealing, the interface between the Cu and Ni becomes blurred as atoms from each metal diffuse across the boundary. Not all diffusion couples present the even composition profile demonstrated by the Ni-Cu system. When Ni and silicon (Si) form a diffusion couple, the Ni primarily diffuses into the Si.[11] The Ni-Si system is relevant because the Mn-Ge system may behave in a similar manner.

Chemical Identification

In order to study the diffusion process, it is necessary to be able to determine the chemical composition of individual nanowires. Several methods exist that can provide information about the chemical makeup of a material: electron energy loss spectroscopy (EELS), energy dispersive x-ray spectroscopy (EDX), secondary ion mass spectrometry (SIMS), and LEAP tomography.

EELS is conducted by first bombarding a material with electrons. When the incident electrons interact with electrons in the material, there is a chance that the energy from the interaction will push the electrons into excited states. If this happens, the incident electrons lose energy. By analyzing the amount of energy lost by the incident electrons (which will be scattered), certain properties of the material can be

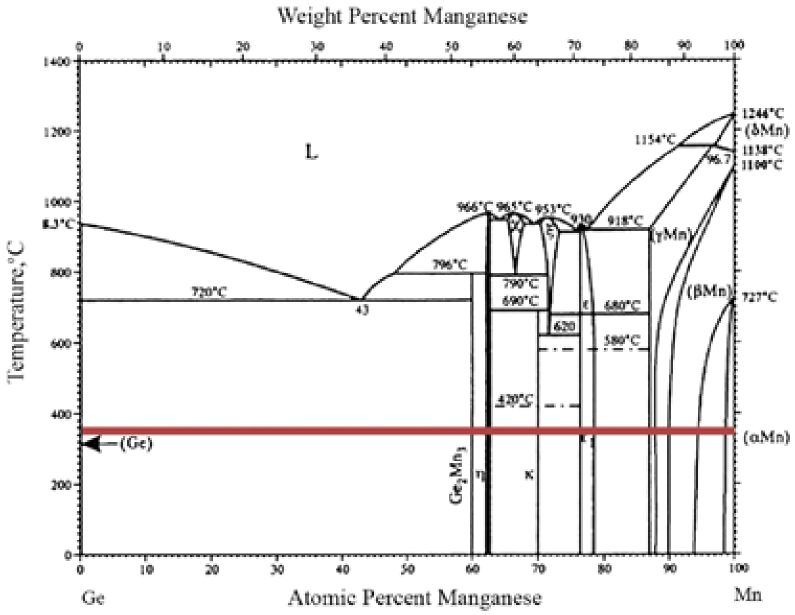

Figure 2: Binary Phase diagram of Ge-Mn showing possible phases. The anneal temperature used for this experiment is marked by the red line.

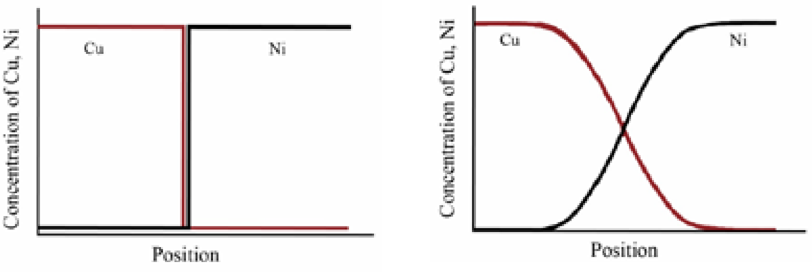

Figure 3: The Cu-Ni diffusion couple. a) Before heating, the Cu-Ni interface is sharp. b) After heating, Cu atoms diffuse into the Ni and Ni atoms diffuse into the Cu. Callister W.D. *Materials Science and Engineering: An Introduction;* John Wiley & Sons, Inc: New York, 2000: 92-107.

determined.[12] EDX spectroscopy functions in a similar manner, but the characteristic x-rays emitted upon electron bombardment are analyzed.[13] Both of these techniques are limited, however, in that they can detect only atoms that have concentrations higher than 1% of the total, and they have maximum spatial resolutions of ~1 nm.

When SIMS is used, an ion beam is directed at a material with such energy that it will liberate surface atoms from a material. The ejected atoms leave the surface as positive, negative, or neutral ions and are detected by a mass spectrometer. The information collected by the mass spectrometer can give insight into the chemical makeup of the material.[12] While the information obtained by SIMS can be used to form a 3D profile of a semiconductor, it has a limited resolution of 5 nm.[14]

LEAP tomography is a chemical identification method that possesses unique advantages for studying the atomic composition of nanowires. The LEAP functions by stimulating the field evaporation of individual atoms from a specimen with a nanometer-scale tip.[5] Using a time-of-flight measurement and a two-dimensional spatial detector, the apparatus measures the evaporated atoms and creates a three-dimensional reconstruction. Field evaporation is achieved by first applying a constant voltage to the nanowire sample. The voltage lowers but does not remove the potential energy barrier that prevents atoms from escaping the solid. For some materials, a pulsed voltage is then used to provide the energy necessary for atoms to evaporate. The voltage pulse technique is not feasible to use with semiconducting nanowires, however, because the semiconductors are brittle and often

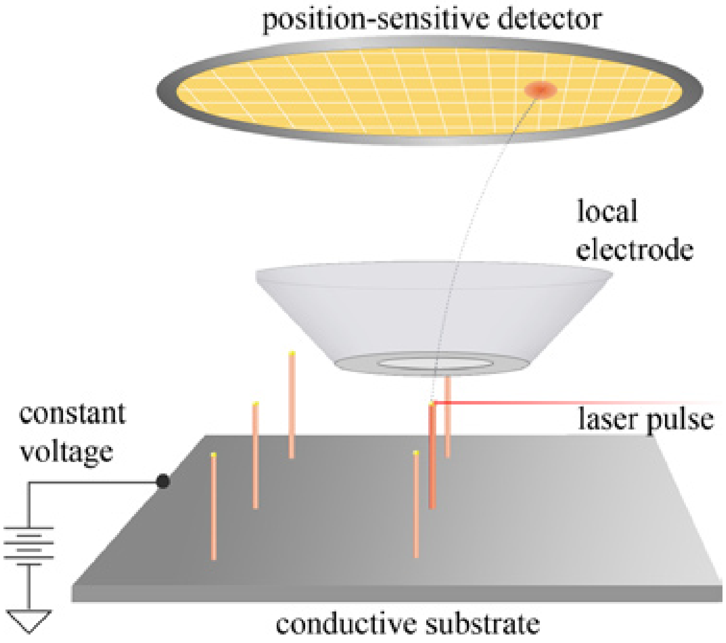

Figure 4: A laser pulse is administered to a nanowire tip which causes the field evaporation of a single atom. The atom's flight path is depicted as a dashed line. The 2D sensor records both the position at which the atom was detected as well as its time of flight.

fracture when exposed to high voltage. Instead, a laser pulse is administered to the tip of the nanowire (pulsed-laser local electrode atom probe tomography is referred to as PL-LEAP). The pulse provides the thermal energy necessary for a single atom to cross the potential energy barrier and break free of surface bonds. Once the atom is liberated from the solid, it is accelerated by a potential difference and detected by the previously mentioned position-sensitive sensor. This process is depicted in Figure 4. The sensor records both the location and the time the atom was detected. By comparing this recorded time with the time at which the laser pulse was administered, the mass-to-charge ratio of the atom can be determined. Using the information provided by the LEAP, a user can resolve the position and chemical identity of a high percentage of the atoms present in the nanowire sample.

The analysis performed by Lauhon et al. was the first example of LEAP analysis performed on semiconducting nanowires.[5] It was determined that the LEAP possesses several advantages over other chemical identification techniques. These advantages will be discussed in the next section.

Approach

The ultimate goal of this project was to determine the solid solubility of Mn in Ge in nanoscale structures. PL-LEAP was selected to perform the composition analysis. A series of 3D reconstructions provided the information necessary to draw conclusions about the solid solubility of the Mn that was deposited on the surfaces of the Ge nanowires.

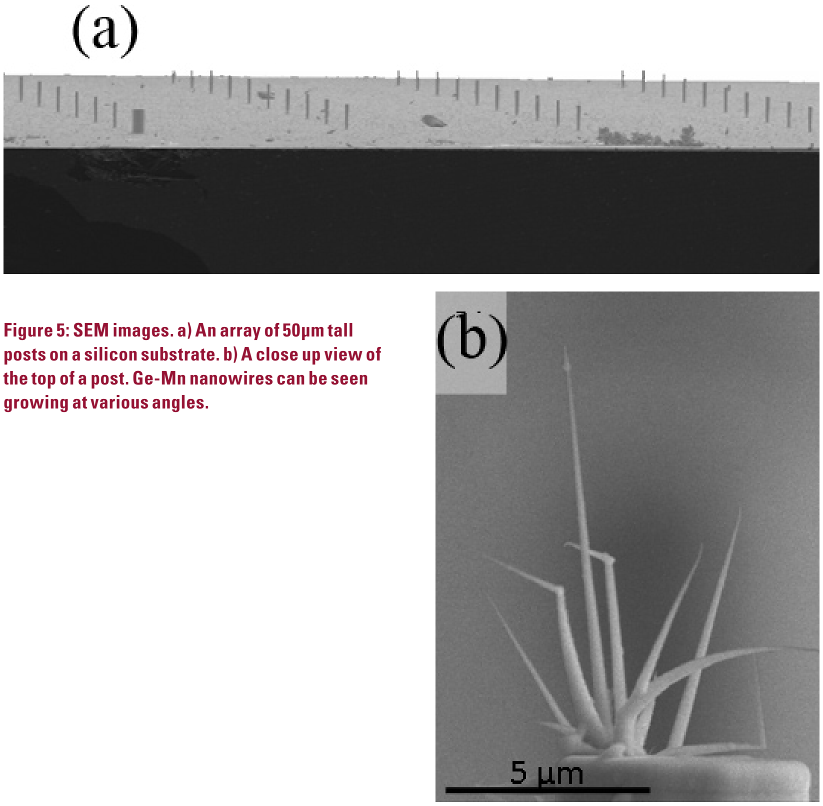

Figure 5: SEM images. a) An array of 50µm tall posts on a silicon substrate. b) A close up view of the top of a post. Ge-Mn nanowires can be seen growing at various angles.

The nanowires were grown from Au catalysts via the VLS mechanism using chemical vapor deposition (CVD) of GeH_4 in a hot-wall CVD reactor. The nanowires were taken out of the reactor after the initial growth, and all remaining Au was removed using a 10-sec tri-iodide etch. The Ge nanowire surfaces were passivated using 1 M HCl. After both cleaning processes were complete, the nanowires were placed back in the reactor for deposition of Mn using tricarbonyl methylcyclopentadienyl Mn (TCMn) as the precursor. The introduction of this precursor caused an Mn shell to form around the Ge core. Unlike other core-shell structures,[8] the Mn layer was not uniform, as determined by using AFM on planar substrates.[15] Because the phenomenon of interest was the incorporation of Mn into the Ge, it was only important that the Mn shell covered the entire nanowire. After the layer of Mn was deposited, the nanowires were annealed at 350° C for 30 min. PL-LEAP was then used to determine whether any Mn from the nanowire shell diffused into the Ge core.

As previously mentioned, the PL-LEAP technique has a unique set of advantages and disadvantages. These qualities must be discussed in detail to fully understand the analysis in this experiment. First, the spatial resolution of the PL-LEAP is 0.3 nm, significantly higher than the resolution provided by other methods.[4] Individual atoms can be spatially mapped because of this atomic-scale resolution. This capability is significant when trying to obtain the distribution of dopant atoms. Further, the resolution provides excellent information concerning interfaces in a nanowire.[5] The degree of abruptness of an interface is often a significant point to consider when

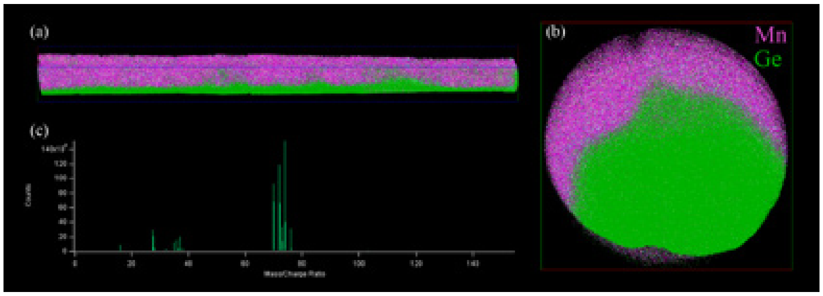

Figure 6: a) A three-dimensional reconstruction of data set 1, consisting of approximately 5.5 million atoms. The length of the reconstruction is 360nm. b) An end view of the reconstruction. The diameter is 30nm. c) The mass spectrum collected for the entire nanowire. O^+, Mn^{2+}, Ge^{2+}, and Ge^+ peaks can be seen.

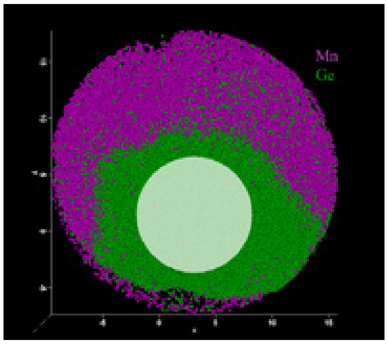

Figure 7: An end on view of the 3D reconstruction for the 0-25nm slice of data set 1. The white circle is a cylinder which has the same length as the slice and is used to take a mass spectrum from the Ge core away from the interface. 47% of the total Ge and 79% of the total Mn atoms are represented as spheres.

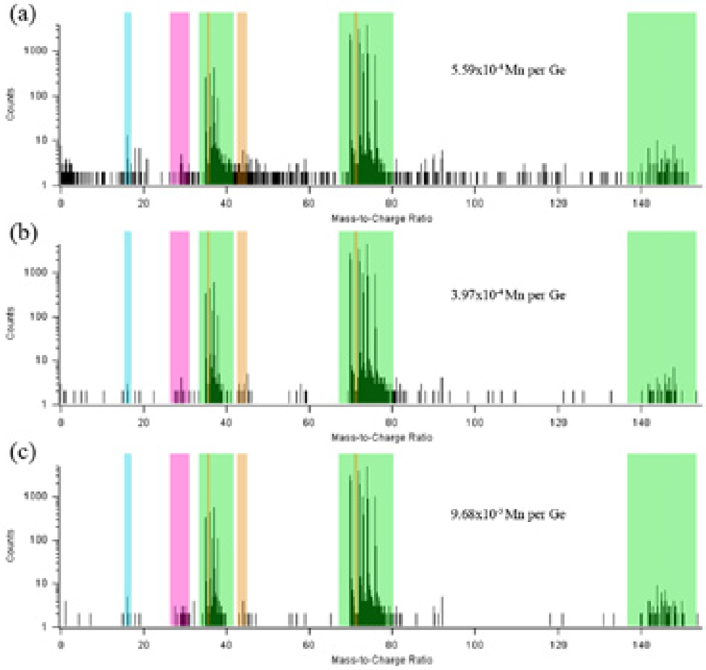

Figure 8: a) Mass spectrum collected for the 0-25nm slice of data set 1 and displayed on a semi-logarithmic plot. The O^+ peak is displayed in blue, the Mn^{2+} is in magenta, Ge, Ge^{2+}, and Ge_2 are displayed in green, and various Mn oxides are displayed in orange. b) Mass spectrum collected for the 210-235nm slice with the same ranges as (a). c) Mass spectrum collected for the 300-325nm slice with the same ranges as (a).

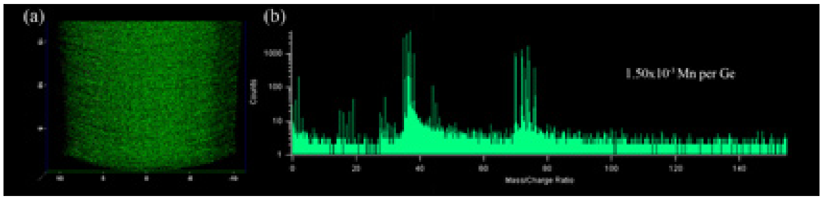

Figure 9: a) A 3D reconstruction of data set 2. b) The mass spectrum collected for data set 2 displayed on a logarithmic plot.

analyzing nanowires, and the PL-LEAP can create a graphical image that is helpful in determining this quality. Finally, because the technique analyzes nanowires from the top down, the PL-LEAP can effectively detect features buried within the structure.[4]

The PL-LEAP also has a specific set of limitations. First, field evaporation is a destructive tomography method, so each nanowire can be studied only once.[4] The destructive nature of the field evaporation can also cause certain properties of the wire to be altered. For this experiment, it was important to understand that the thermal energy provided by the laser pulse may have affected the diffusion of Mn into the Ge. The effect of the thermal energy on Mn diffusion could best be determined by analyzing many different nanowires of varying lengths and compositions. This possibility is further discussed in the conclusion.

Another restriction of PL-LEAP analysis is that the nanowire being studied must be straight, vertical, isolated from other wires, and of sufficient length (≈10 μm). The VLS growth process creates nanowires that develop in various directions and sometimes group together. The nanowires are grown on arrays of posts 5 μm in diameter and 50 μm tall. There are typically about 100 per substrate, and each may contain several nanowires growing on the top. Usually only 4 or 5 of these posts contain nanowires that are valid candidates for LEAP analysis. Figure 5 shows scanning electron microscope (SEM) images of a micropost array and a close-up view of several nanowires growing on top of a post. Finally, field evaporation puts great mechanical strain on the samples that frequently causes them to fracture prematurely. When the nanowire samples break, the experiment has to be terminated. Even though it has several limitations, the PL-LEAP possesses enough unique advantages for it to be considered a powerful analysis tool for this experiment.

Results

Two Mn-Ge nanowires were successfully analyzed using PL-LEAP. For the first set of data, approximately 5.5 million atoms were evaporated and collected by the LEAP; approximately 239,000 were collected for the second set. Once the data were collected, they were analyzed using Imago Visualization Software (IVAS).

The larger data set will be referred to as data set 1. The 3D reconstruction for this data set is displayed in Figure 6 and clearly showed a Mn-Ge interface. The atoms that were collected were from a region that contained both a Ge core and an oxidized Mn-Ge shell. It was not surprising to find various oxide species present on the shell of the nanowire because Mn oxidizes easily. Since data set 1 contained so many atoms, the data set was cut into three 25 nm thick regions. The ranges from the tip of the nanowire of these regions were 0–25 nm, 210–235 nm, and 300–325 nm. No Mn-Ge shell was observed in the reconstruction of the second data set.

To accurately obtain the amount of Mn in the Ge core of the nanowire, mass spectra were collected and displayed using IVAS. Three mass spectra are shown in Figure 8. For data set 1, a cylindrical region of interest of radius 10 nm and length 25 nm was created. This cylinder is an arbitrary construct that is set by the user in IVAS in order to analyze specific sections of the data. As can be seen in Figure 7, the cylinder (colored white) was positioned away from the core-shell interface of the nanowire. The cylinder was centered in the same location for each of the three 25 nm-thick slices being analyzed. Figure 7 depicts the location of the analysis cylinder in the 0-25 nm slice. Mass spectra were collected using the cylinder as an outside boundary. These spectra were analyzed using a background subtraction method to find the number of present Ge, Mn, O, and Mn oxide counts. Similar analysis was performed on data set 2, though it was not necessary to isolate the Ge core of the nanowire because there was no Ge/Mn-Ge boundary. Figure 9 shows the 3D reconstruction of data set 2, as well as the accompanying mass spectrum. The mass spectra for both sets of data revealed that the amount of Mn in the Ge ranged from ~10^{-3} to 10^{-4}. A 1D concentration profile taken from the Ge region of the entire 360 nm length of the reconstruction suggested there was no significant deviation in the amount of Mn found at any point along the length of the nanowire.

Discussion

The data showed there was a measurable amount of Mn present in the Ge core of the nanowire. Data from this experiment suggested that the level of Mn in a Ge nanowire was approximately 10^{-3}–10^{-4}. This measurement led to the conclusion that Mn demonstrates some solid solubility on the nanoscale. While this value may not be high enough for spintronic applications,[16] it is not trivial. The fact that a definite amount of Mn was found within the core of the nanowire suggests that certain experimental conditions can be altered to increase the amount of Mn in Ge nanostructures.

Conclusion

This project warrants further investigation to determine whether any factor can be adjusted to increase the amount of Mn in Ge. It should first be determined whether the equilibrium concentration was achieved. In order to make this determination, a series of 1D concentration profiles should be taken for each data set. Since the amount of Mn present in a nanowire is higher in the shell than in the core, each of the concentration profiles will display a concentration gradient. If equilibrium has been reached, the concentration gradient will decrease until a certain point and then remain at a constant level.

If it is determined that the concentration of Mn in the Ge has not reached equilibrium, varying the anneal time and temperature may increase the Mn concentration. The nanowires studied in this experiment were annealed at 350° C for 30 min. These conditions are ideal for VLS growth, but it is possible to heat the nanowires at much higher temperatures. Varying these two parameters will likely have a significant effect on the amount of Mn present in the Ge.

Also, the experiment must be performed many more times to ensure that the results discussed here are repeatable. As previously mentioned, when any kind of PL-LEAP experiment is performed, the diffusion properties of a structure may change as a result of the evaporation process. Only two nanowires were analyzed to obtain the data for this experiment. It must be established that the results obtained are not merely artifacts caused by the PL-LEAP analysis. If more nanowires are studied, the actual amount of Mn in the Ge core will become clear.

In this experiment, the solid solubility of Mn in Ge nanowires was studied in order to better understand a material that may have spintronic applications. The Ge nanowires were grown via the VLS mechanism, and the Mn was deposited using CVD. It was hypothesized that after annealing, a certain measurable amount of Mn from the outer shell would diffuse into the core of the nanowire. This hypothesis was tested using PL-LEAP tomography.

The data provided by the LEAP analysis demonstrated that Mn does have a measurable amount of solubility in Ge. The annealing conditions of this experiment were sufficient to cause Mn atoms to diffuse into the Ge core of the nanowires. While the solid solubility of the Mn was low, it is possible that it can be increased by changing various experimental factors. Ge nanowires doped with Mn may have spintronic applications in the future.

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References

(1) Lieber, C. M. *Sci. Am.* **2001.** 285, 58–64.

(2) Wolf, S. A.; Awschalom, D. D.; Buhrman ,R. A.; Daughton, J. M.; von Molnar, S.; Roukes, M. L.; Chtchelkanova, A. Y.; Treger, D. M. *Science.* **2001,** *294,* 1488–1495.

(3) Perea, D. E.; Lensch, J. L.; May, S.cJ.; Wessels, B.cW.; Lauhon, L. J. *Appl. Phys. B* **2006,** *85,* 271–275

(4) Kelley, T. F.; Miller, M. K. *Rev. of Sci. Instrum.* **2007,** *78,* 20.

(5) Perea, D. E.; Allen, J. E.; May, S. J.; Wessels, B. W.; Seidman, D. N.; Lauhon, L. J. Nano. *Lett.* **2006,** 6, 181–185.

(6) Gokhale, A. B.; Abbaschian, R. *Bull. of Alloy Phase Diagrams* **1990,** *11,* 460–468.

(7) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964,** 4, 89–90.

(8) Lauhon, L. J.; Gudiksen, M.S.; Wang, C.L.; Lieber, C.M. *Nature* **2002,** 420, 57–61.

(9) Gudiksen, M. S.; Lauhon, L. J.; Wang, J.; Smith, D. C.; Lieber, C. M. *Nature* **2002,** 415, 617–620.

(10) Callister, W. D. *Materials Science and Engineering: An Introduction;* John Wiley & Sons, Inc: New York, 2000: 92–107.

(11) Zheng, L. R.; Hung L. S.; Mayer J. W.; Majni G.; Ottaviani G. *Appl. Phys. Lett.* **1982,** 41, 646–649.

(12) Chung, Y. W. *Practical Guide to Surface Science & Spectroscopy;* Academic Press: New York, 2001: 69–80.

(13) Kittel, C. *Introduction to Solid State Physics;* John Wiley & Sons, Inc: New York, 2005: 447–448.

(14) McPhail, D. S. *J. Mater. Sci.* **2006.** 41, 873–903.

(15) Lensch-Falk, J. L.; Hemesath, E. R.; Lopez, F. J.; Lauhon, L. J. *J. Am. Chem. Soc.* **2007,** in press.

(16) Kazakova, O.; Kulkarni, J. S.; Holmes, J. D.; Demokritov, S. O. *Phys. Rev.* **2005** 72, 094415.