Manganese Doping in Lead Sulfide Nanowires

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Abstract

Lead sulfide nanowires were synthesized using a Vapor-Liquid-Solid method, and a similar procedure with the addition of a manganese doping agent was used to potentially fabricate Mn doped PbS wires. A reaction between $PbCl_2$ and sulfur under nitrogen gas at 635 ^{o}C produced PbS nanowires and and identical synthesis with the addition of the doping agent $MnCl_2$ at a variable temperature between 645 ^{o}C and 665 ^{o}C was used to dope the wires. Various growth formations were fabricated and examined. The wires were analyzed by an X-ray diffractometer, and an electron paramagnetic resonance spectroscopy was performed to determine if the wires were doped with manganese. Once characterized, these wires may have applications in Spintronics and solar cells.

Introduction

Lead chalcogenides have been studied recently for a variety of applications. Lead sulfide (PbS) was chosen for this research because it has a narrow band gap that allows more photons to be absorbed than many other materials. It has been demonstrated that PbS shows multiple exciton generation, which makes it ideal for photovoltaics [1] and spintronics applications.

In conventional electronics, information is stored and transported using the charge of electrons then a current moves the electrons along a wire. Spintronics works by storing the information on the electrons' spin orientations, which is either up or down. The information is then sent along the wire by switching the orientation of the electrons. This requires less energy than conventional electronics because the charge carriers need a current to move the information. Spintronics simply flips the spins to carry the information [2].

PbS is a semiconductor that has no unpaired electrons. For our applications, we want to use dilute magnetic semiconductors, which are essentially the same as traditional semiconductors except they are doped with transition metals that makes them useful for spintronics [3]. The best doping materials contain many atoms with unpaired spins. Manganese was chosen because it has five unpaired electrons which is the most that you can have according to Hund's Rule.

We were interested in how magnetic fields change conductance in our nanowires;

we need as many unpaired electrons with measureable spin as possible.

Doping Procedure

The wires used for this study were grown using a vapor, liquid, solid (VLS) method. The setup to fabricate PbS wires is shown in Fig. 1.

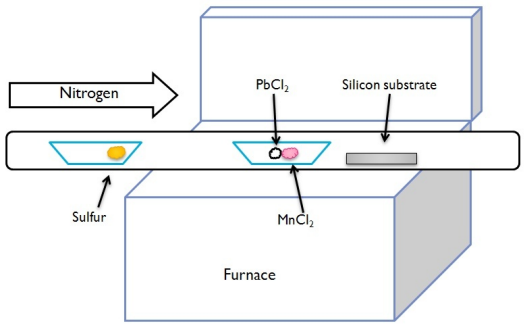

Figure 1: Setup for VLS method.

The setup consists of a furnace and a quartz tube connected to a pressure guage, multiple gas flow controller, and a vacuum pump. For this experiment, the gas flows from left to right through the quartz tube.

A silicon substrate was cleaned and thoroughly dried. 30 mg of $PbCl_2$ was placed in a ceramic combustion boat along with 60 mg of $MnCl_2$. This boat was loaded into the quartz tube and placed at the center of the furnace. The silicon was placed in the quartz tube such that the center of the substrate was 9 cm to the right of the $PbCl_2$. 60 mg of Sulfur was placed in a second combustion boat and also placed in the quartz tube, this time to the left of the $PbCl_2$, and kept outside of the furnace. We found that these quantities were not crucial, but they produced nice wires and most of the chemicals were completely vaporized during the growth. Manganese was the only chemical that left any residue in the combustion boat.

Quartz wool was placed inside the tube downstream to capture stray particles before they could enter the vacuum pump.

The left end of the tube was connected to the gas flow controller and the right end was connected to the vacuum pump. The tube was pumped to purge air and water from the system. Between pumping, N_2 gas was allowed to flow to bring the system back to atomspheric pressure. Once a significantly small base pressure (0.5 torr) was reached and brought back to atmospheric pressure with N_2, the quartz tube was heated to between 645 ^{o}C and 665 ^{o}C (depending on the run) in 15 minutes with the N_2 flow at 150 sccm. We found that tem-

peratures above 665 ^{o}C did not produce results, and $MnCl_2$ does not melt until 654 ^{o}C so a growth below this temperature would be less likely to contain the doping agent. Most of the growths performed in this experiment were done at 660 ^{o}C.

During the heating, the $PbCl_2$ and $MnCl_2$ gradually evaporated and was pushed over the substrate by the N_2 flow. When the peak temperature was reached, H_2 gas was introduced at 1 sccm for 1 minute in addition to the N_2 flow. We found that the exact timing and length of the hydrogen flow was crucial to the growth results. If the H_2 was introduced too soon or too late, no wires resulted. If the flow length was too short then the wires were small, and if it was too long then no wires resulted.

The H_2 gas reacts with the $PbCl_2$ and creates HCl vapor which is promptly blown out of the system by the N_2. This leaves behind the lead to form lead droplets on the substrate. The lead droplets act as a seeding for the nanowire growth.

Once the droplets were present, sulfur vapor was introduced. The liquid droplets absorbed sulfur and lead vapor until they were saturated. A PbS "whisker" began to grow out of the bottom of the droplet and raised it off of the substrate. The whisker continued to grow as the droplet was consumed.

The wires branched as they were grown and consumed more lead and sulfur vapor from the system. It has previously been suggested by Bierman et. al. that hydrogen vapor lingering in the system continues to reduce $PbCl_2$ [1] but it is our speculation that defects on the whisker are responsible for the branching.

The growth temperature was held constant for 15 minutes then the system was cooled to room temperature. The N_2 continued to flow for the entire cool down to remove any lingering vapors before opening the tube.

It should be noted that the same procedure was used to fabricate PbS nanowires except the $MnCl_2$ doping agent was omitted from the combustion boat and the peak temperature was 635 ^{o}C.

Growth Results

The wire growth was visible as a cloudy layer on the substrate and the quartz tube. When viewed through the microscope, we found the wires growth to change dramatically as you examine different regions of the substrate. Most good wires were produced in a network approximately 9 cm from the $PbCl_2$ and the wire clusters shrank as you moved away towards the edges. An example of wire networks can be seen in Figure 2 a.

There were a variety of wire shapes, but most common was cross shaped with a dense center region as shown in Figure 2 b. These wires are good for our applications because the branches are mostly long and straight. We did find some wires that grew in "spider" formations with curved wires (see Figure 2 c). At the time of this writing, we cannot conclude which parameters allowed this type of growth. It has been suggested that the substrate was not entirely clean or dry, or the system was not properly sealed, but that is only a speculation.

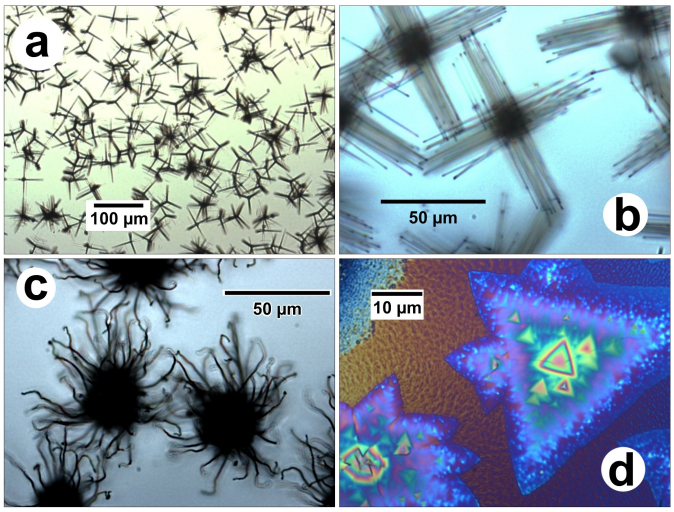

Figure 2: (A) Standard PbS growth on Si. Viewed at 40x magnification. (B) Mn doped growth on SiO_2 viewed at 80x magnification. (C) Abnormal doped growth on Si viewed at 80x magnification. (D) Mn and PbS crystal structures on Si viewed at 100x magnification.

All parameters between the good "cross" wires and the bad "spider" wires were identical.

In an attempt to produce more wires, the growth time was raised from 15 minutes to one hour. This did not produce more wires, and in fact, it did not produce wires at all. Instead PbS crystals were formed on the substrate as shown in Figure 2 d.

We were also able to examine some of the wires with a scanning electron microscope (SEM). From the SEM data (see Figure 3), we were able to measure one group of wires' diameter; the average diameter was 63.5 μm.

Growth Analysis

The samples were scanned using an X-ray diffractometer (XRD) to determine if the wires had been successfully doped. The data from a doped sample was compared to an undoped sample. No peak shift was detected, indicating that there was no difference in the crystalline structure between the two samples. This is not the anticipated result, which could be due to an experimental error, so the doped data was then compared to known peak patterns to see if Mn was present in the nanowires. Several Mn compounds' peak patterns were examined, and the best result showed that the doped data matched five of the twelve known peaks for MnS but is still inconclusive. Although this showed some progress, we did not want separated PbS and MnS, rather we wanted to show $Pb_{1-x}Mn_xS$.

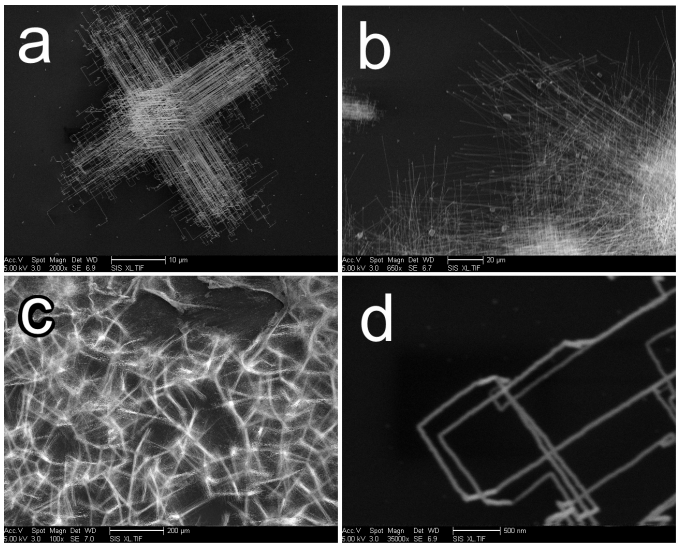

Figure 3: SEM imaging showing various growth formations. (a) standard growth showing wire formation (b) fine wire growth with large central network (c) standard network (d) magnification for measuring nanowire diameter

If the XRD matched more data peaks with known peak patterns, or a peak shift could be detected, then the data would be more conclusive. The XRD data can be observed in Figure 4.

The undoped wires were also compared to known peak patterns and PbS was confirmed.

Next, the samples were scanned using electron paramagnetic resonance (EPR) spectroscopy to see if they were successfully doped. The samples were sonicated and kept in a solution of isopropyl alcohol for the analysis. The EPR data was taken in a variable 7-10 K region with 8 Gauss modulation amplitude and the frequency was 9.47 GHz. The results were not as expected (Figure 5), but there were obvious errors during the scan. The EPR tube containing the sample had not been sealed properly and had apparently leaked air into the tube. When the cryogens were introduced, the tube shattered and the sample was lost.

The problem was that the density of the nanowires in solution was not high enough to get an accurate reading. The preferred method is to have a "powder" of nanowires, but scraping the nanowires off of the substrate was not an option so sonication was used and the wires were left in solution. In the future, more wires should be used for the EPR scan. It should be noted that longer growth time in the furnace does not produce more wires; it made crystals seen in Figure 2d.

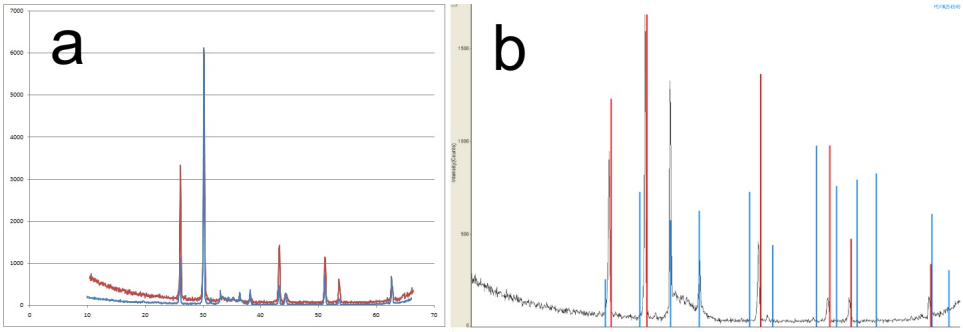

Figure 4: XRD data (a) compareson between undoped wires (blue data) and doped wires (red data). As shown, the peaks' position on the x-axis have not shifted. (b) XRD data compared to known peaks. Vertical lines represent where the peaks should be. Blue peaks are MnS and red peaks are PbS.

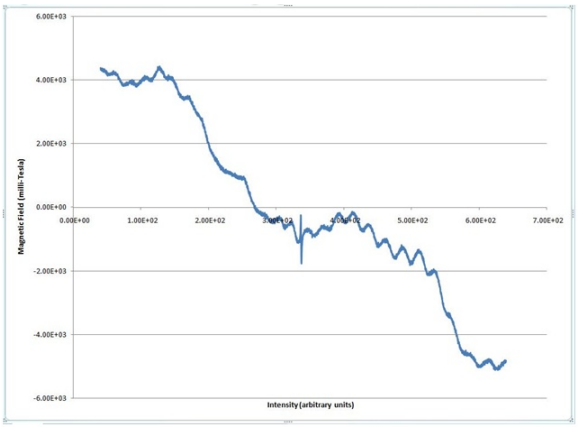

Figure 5: EPR data. These results are not accurate and do not reflect the manganese content in the wires

Future Plans

Since the XRD and EPR were both unsuccessful in proving or disproving the presence of Mn in the wires, we will examine our wires with Magnetically Induced Circular Dichroism (MCD). By performing spectroscopy with left and right circularly polarized light, a characteristic signal unique to the composition should be seen.

In addition to MCD, we will make single nanowire devices to measure the electrical conductivity of our wires as a function of magnetic field or light. The undoped wires should be different from the doped wires because Mn introduced local spins that should react differently in the magnetic field.

Once the conductivity and other properties of doped wires are known, they will be characterized for spintronic applications. We also plan on investigating other lead chalcogenides such as lead selenide (PbSe) doped with Mn. For the undoped wires, we plan to characterize them and see how light affects the wires for use in photovoltaics.

Conclusion

PbS nanowires were synthesized using VLS mechanism. A reaction between $PbCl_2$ and sulfur under nitrogen gas at 635 ^oC produced PbS nanowires and and identical synthesis with the addition of the doping agent $MnCl_2$ at a variable temperature between 645 ^oC and 665 ^oC potentially produced Mn doped PbS nanowires. Various growth formations were fabricated and examined. Although manganese was present for the doping procedure, it is still unclear if the wires had actually been doped. The results from the XRD were inconclusive and the results from the EPR scan had a severe problem. MCD spectroscopy will be performed in the future, and single nanowire devices will be made. The single nanowire devices will examine the conductivity of the wires as a function of magnetic field and wavelength, intensity, and location of the laser spot so the wires can be characterized for applications in spintronics and solar cells.

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