Synthesis and Characterization of YB_{66} Nanowires

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The objective of the current research is to synthesize yttrium boride (YB_{66}) nanowires. Catalyst assisted growth of the nanowires under the vapor-liquid-solid (VLS) synthesis method was performed in a quartz tube furnace. The pyrolysis of diborane (B_{2}H_{6}) gas over yttrium oxide (Y_{2}O_{3}) powders with a thermally coated layer of nickel catalyst was carried out. The reaction conditions were at 925 °C and a pressure of 390 mTorr with varying reaction times. SEM analysis has shown the growth of nanowires with diameters around 400 nm. A catalyst particle was also seen at the tip of the nanowires, confirming growth by the VLS mechanism. Other analysis techniques that were used include Raman spectroscopy and TEM analysis. The Raman spectra of the nanowires were in good agreement with a Raman spectrum obtained on a YB_{66} single crystal. However, no other evidence was obtained that the nanowires contained yttrium or that the nanowires consisted of YB_{66}.

Introduction

The increased demand for energy calls for the development of new approaches towards useable energy sources. Notably, hydrogen is one of the most abundant energy carrier resources available. Thus, research towards the use of hydrogen in a hydrogen economy is crucial as it provides for a different type of energy carrier that may become both economically and environmentally favorable. In 2003, the Basic Energy Sciences Advisory Committee (BESAC) called for the research and development of hydrogen production, storage, and usage.\(^1\)

The objective is focused on the storage aspect of the hydrogen molecules. The objective is also to determine the optimal conditions, for example temperature and pressure, for which metal boride nanowires can be synthesized. Furthermore, nanowires are studied instead of bulk powder or crystalline materials because of the increased surface to volume ratio. This is beneficial in that more hydrogen can be stored per amount of the storage material. Also, the use of nanowires is beneficial because it is known to have an increased diffusion rate of the adsorbed material, which leads to more efficiency in obtaining the stored hydrogen.

Metal borides can hold high gravimetric densities of hydrogen, thus allowing more hydrogen storage as opposed to other materials. Particularly, YB_{66} is of interest because it has a low metal to boron content, which is favorable since boron is the element that will be bonding to the adsorbed hydrogen molecules. Theoretically, if each boron atom in a single YB_{66} unit were to bond to a single hydrogen atom, then there would be a 7.6 weight percent of hydrogen. Furthermore, the crystal structure of the boron unit in YB_{66} contains thirteen icosahedron units (B_{12}) in which twelve of the units surround a single icosahedral unit.\(^2\) This structure is unique and can be identified by comparison of electron diffraction patterns.

A proposed storage method is through the spillover mechanism. This mechanism involves the dissociation of diatomic hydrogen molecules over a metal catalyst particle, which is on top of a support.\(^3\) It is hypothesized that a similar spillover mechanism will apply to YB_{66}, with yttrium metal acting as the metal particle and the boron network acting as the support.

Methods

For the synthesis of YB_{66} nanowires, chemical vapor deposition (CVD) was used. Specifically, the vapor-liquid-solid (VLS) method was observed under these conditions. The CVD method is often used to produce solid materials at a high purity level. The products are often used in the semiconductor industry in applications such as electronic devices. The general process for chemical vapor deposition involves a solid substrate on a wafer where the pyrolysis of the gaseous reactant would occur. Precipitation of the desired product would occur as well as the production of byproducts, which can be pumped out of the reaction chamber. This process may require a catalyst, such as nickel, so that a one dimensional growth would be maintained. This process is explained in much greater detail in the discussion section.

To characterize the synthesized samples, scanning electron microscopy (SEM), Raman spectroscopy, energy dispersive x-ray (EDX) analysis, and selected area electron diffraction (SAED) analysis were used. SEM was first used to identify the basic structures of the samples. From the SEM analysis, it could be determined whether or not the desired structures were formed. For example, the synthesized sample may have consisted of nanoballs, crystalline structures, or nanowires. After the identification of the nanostructures, Raman analysis was performed. From this analysis, the composition of the sample can be determined by comparison with other reference spectra.

Another method to determine the elemental composi-
tion of the nanowires is EDX. Finally, SAED was used to obtain a unique diffraction pattern that can be compared with reference diffraction patterns of YB$_{66}$. This is important because the ratio of yttrium to boron should be 1:66, as the desired product is YB$_{66}$.

**Experimental**

For the synthesis of YB$_{66}$ nanowires, the chemical vapor deposition (CVD) catalyst assisted nanowire growth method was used. A silicon wafer with a 1 µm thick thermally grown silicon oxide layer was used to hold the sample where the deposition would occur. The wafers were cut with a diamond cutter in approximate dimensions of 2 cm by 0.5 cm. In order to remove the inorganic impurities, the wafers were first cleaned with sulfuric acid and hydrogen peroxide in a 1:1 ratio under ultrasonication for 20 minutes. In order to remove organic impurities, the wafers were then cleaned with a solution of ethanol and acetone in a 1:1 ratio under ultrasonication for 20 minutes.

After drying of the wafers, yttrium oxide (Y$_2$O$_3$) powder of 99.9999% purity was deposited over the wafers in a thin layer. Then, approximately 5-10 mg of nickel catalyst was evenly evaporated onto the yttrium oxide covered wafers. Previous experiments from this lab have shown that the exact amount of nickel catalyst used does not affect the growth of the nanowires. The nickel catalyst was thermally evaporated slowly onto the substrate in order to obtain smaller particles. The wafers were placed in a quartz boat, which was then placed in a quartz tube at the edge in a marked position.

Liquid nitrogen was placed into the liquid nitrogen trap as the pressure reached 25 mTorr due to pumping of the chamber. Then, the quartz tube was heated to 925°C under the flow of argon gas of ultra high purity at 5 sccm for a controlled time. The pressure of the reaction chamber was then 180 mTorr. Diborane gas (B$_2$H$_6$), of 1.08% purity in argon gas, was then introduced in the reaction chamber at 15 sccm for a controlled time under a pressure of 390 mTorr. Argon gas was again introduced into the chamber at 5 sccm for 4 hours until the reaction chamber was cooled to room temperature. The sample was then taken out of the quartz tube and set in a container for later analysis.

**Results and Analysis**

The synthesized samples were first analyzed with SEM (JEOL, model JSM-6320F). Upon identification of nanostructures, Raman spectroscopy (Renishaw Ramascope-2000; 514.5 nm argon ion laser excitation, spectral resolution of 2 cm$^{-1}$ and spatial resolution of 1 µm) was used to determine the compounds present in the sample. A transmission electron microscope (TEM) (JEOL, model 3010) was used to determine the diameter of each nanowire. EDX, a part of the JEOL-3010, was also used to determine the elemental composition of a particular nanowire. Finally, SAED, also a part of the JEOL-3010, was used to obtain a diffraction pattern.

The synthesis of YB$_{66}$ was performed by using the vapor-liquid-solid (VLS) method. For one dimensional nanowire growth, the solid substrate should be well defined crystallographically. The vapor phase in the VLS method is created by the pyrolysis of the gaseous reactant, diborane (B$_2$H$_6$). The pyrolysis of diborane may result in the production of different gaseous reactants such as boron, hydrogen, and borane radicals. The vapor phase is also created by the dissociation of yttrium oxide. The liquid phase in the VLS synthesis method is a liquid alloy catalyst droplet, which is formed when the temperature is at its eutectic point. In this case, the liquid droplet should be composed of the nickel catalyst, boron, and yttrium under a pressure of 390 mTorr. The center of the chamber was heated to 925°C under the flow of argon gas to reduce the amount of impurities and to create an inert environment. The liquid alloy droplets act as a nucleation site such that when the liquid droplet becomes supersaturated with boron, the YB$_{66}$ nanowires should precipitate. As boron continues to deposit at the solid-liquid interface, the nanowire would experience growth in the longitudinal direction. The desired product requires that yttrium and boron react in a 1:66 ratio, forming YB$_{66}$.

Another nanowire growth controlling factor is the size of the catalyst particle. This is because the size of the liquid alloy droplet remains unchanged throughout the growth of the nanowire, thus restricting the lateral size of the nanowire. The length of the nanowire is unrestricted. Thus, it was crucial to have the catalyst be smaller in size so that thinner nanowires are obtained.

To aid in the synthesis of the YB$_{66}$ nanowires, the
boron-yttrium phase diagram was employed. From the diagram, YB$_{66}$ has a eutectic temperature of 2100°C. From this, it can be inferred that the synthesis of YB$_{66}$ would occur at a lower temperature than that used to synthesize YB$_6$, which has a eutectic temperature of 2600°C. But, with the use of the nickel catalyst, the exact temperature for the synthesis of YB$_{66}$ is altered to a lower temperature.

To characterize the synthesized product, a scanning electron microscope (SEM) was first used to determine the structures of the nanowires. SEM images collected from a specific run are shown in Figures 1, 2 and 3. This particular synthesis was for a reaction time of 70 minutes. The nanostructures in Figure 1 were from wafer 1, which is the furthest wafer away from the main heat source and therefore experiences the coldest reaction temperature. The placement of the wafers is shown in Figure 5, where the left end of the quartz boat is closest to the heat source. Thus, wafer 3 experiences the highest temperatures, around 900°C. Also, the diborane gas flows from right to left so it is possible that wafer 1 experiences the highest amount of deposition. In wafer 1, there were nanowires present with diameters of about 400nm. Catalyst particles can also be seen at the tips of each nanowire, confirming the growth method through the VLS method. The nanostructures seen on wafer 2 are shown in Figure 2, which is the second furthest from the heat source. Nucleation sites were mainly observed on wafer 2, with little presence of the nanowires. Finally, in wafer 3, there are only bulk powder-like products (Figure 3), perhaps from the unreacted yttrium oxide powder. From this and similar experiments, it was determined that the ideal reaction temperature for the synthesis of the YB$_x$ nanowires occurs at a lower temperature, around 600°C, corresponding to the temperature at which wafer 1 was placed.

A separate synthesis trial, where the reaction time varied, resulted in the production of crystal structures. In this synthesis, the reaction time was 140 minutes and the synthesized product is shown in Figure 4. The desired nanowire structure was observed when the reaction time was 70 minutes, as opposed to the undesired crystal structures observed when the reaction time was 140 minutes. From this trial, it was determined that a shorter reaction time would better result in the desired products.

To ensure that the nanowires were synthesized using the VLS mechanism, a synthesis was performed without using the nickel catalyst. The reaction time for this synthesis was 70 minutes with all other conditions the same as the previous synthesis. SEM analysis has shown that there were no nanowires formed without the use of nickel catalyst, as shown in Figure 6.

To characterize the composition of the synthesized...
FIG. 5: Placement of three wafers on quartz boat. The left side of the boat is closest to the heat source and thus Wafer 3 experiences the highest temperatures. Also, the diborane gas flows from right to left of the quartz boat.

FIG. 6: SEM image of products synthesized without the use of nickel catalyst. Reaction time was 70 minutes and sample was placed at end of heating chamber. Image shows that no nanowires were present, confirming use of the VLS catalyst-assisted growth mechanism.

products, Raman spectroscopy was first used. Raman spectroscopy was performed on the sample with a reaction time of 70 minutes, grown with the use of nickel. A total of four spectra were taken from two different wafers with observed nanostructures from the SEM analysis. The results are shown in Figure 7 from wafer 1 middle region, wafer 2 hot region, wafer 2 cold region with islands, and wafer 2 cold region base. The assigned peaks are shown in Tables I, II, III and IV along with a comparison to values from the literature.

<table>
<thead>
<tr>
<th>Y-B units</th>
<th>Literature (cm$^{-1}$)</th>
<th>Experimental (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>B atoms in icosahedra unit</td>
<td>200-900</td>
<td>791</td>
</tr>
<tr>
<td>B atoms in icosahedra unit</td>
<td>200-900</td>
<td>897</td>
</tr>
<tr>
<td>Intericosohedral B-B bonds</td>
<td>1070</td>
<td>1084</td>
</tr>
<tr>
<td>B-H bond</td>
<td>2200-2600</td>
<td>2570</td>
</tr>
<tr>
<td>O-H in H$_2$O</td>
<td>3400</td>
<td>3471</td>
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TABLE II: Wafer 2 Hot Area

<table>
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<tr>
<th>Y-B units</th>
<th>Literature (cm$^{-1}$)</th>
<th>Experimental (cm$^{-1}$)</th>
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<tbody>
<tr>
<td>B atoms in icosahedra unit</td>
<td>200-900</td>
<td>816</td>
</tr>
<tr>
<td>B atoms in icosahedra unit</td>
<td>200-900</td>
<td>902</td>
</tr>
<tr>
<td>Intericosohedral B-B bonds</td>
<td>1070</td>
<td>1084</td>
</tr>
<tr>
<td>O-H in H$_2$O</td>
<td>3400</td>
<td>3479</td>
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TABLE III: Wafer 2 Cold Island Area

<table>
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<tr>
<th>Synthesized Nanowires Raman Shift (cm$^{-1}$)</th>
<th>YB$66$ Crystal Raman Shift (cm$^{-1}$)</th>
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<tr>
<td>Y-B units</td>
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<td>B atoms in icosahedra unit</td>
<td>791</td>
</tr>
<tr>
<td>B atoms in icosahedra unit</td>
<td>901</td>
</tr>
<tr>
<td>Intericosohedral B-B bonds</td>
<td>1084</td>
</tr>
<tr>
<td>B-H bond</td>
<td>2567</td>
</tr>
<tr>
<td>O-H in H$_2$O</td>
<td>3481</td>
</tr>
</tbody>
</table>

TABLE IV: Wafer 2 Cold Base Area

FIG. 7: Raman spectroscopy of all four samples at different positions in reaction chamber. Sample was synthesized with 70 minutes of reaction time.
There are many similarities in all four of the spectra. For example, there are similar peaks around 1084 cm\(^{-1}\) which corresponds to the vibrations of intericosahedral boron-boron bonds with a literature peak\(^6\) at 1070 cm\(^{-1}\). Also, in all spectra, there is a peak around 900 cm\(^{-1}\) which may correspond to the intraicosahedral vibration modes.\(^6\) Icosahedral boron units are present in YB\(_{66}\) with 12 B\(_{12}\) units surrounding another B\(_{12}\) unit. In the higher temperature regions of wafer 1 and wafer 2, there are prominent peaks around 800 cm\(^{-1}\), which may also correspond to intraicosahedral vibration modes. But, in the colder synthesis temperature areas of wafer 2, the peak at 800 cm\(^{-1}\) exists as a small shoulder. This suggests that the molecule corresponding to this peak is present in smaller quantities in the colder areas during synthesis. There is a peak centered around 555 cm\(^{-1}\) in all samples except for the cold base area of wafer 2. This peak corresponds to the YB\(_x\) intra and inter-unit vibrations.\(^7\) The proposed reason for not observing the 555 cm\(^{-1}\) peak in the base area of wafer 2 is because there are only small quantities of nanowires seen there with SEM.

Other possible peaks that might be seen in the Raman spectra include those for yttrium oxide, which include a strong peak\(^8\) at 379 cm\(^{-1}\). But, this peak as well as the other minor peaks were not observed in any of the samples, suggesting that there was no unreacted yttrium oxide powder in the samples. Also, there is a peak consistently around 3475 cm\(^{-1}\), corresponding to the presence of water. Finally, there were peaks observed at 2570 cm\(^{-1}\) in all samples again except for the cold base of wafer 2. This peak corresponds to boron-hydrogen bonds and is not present in the base of wafer 2 since there is only a small quantity of nanowires there.

As another source of reference, a Raman spectrum of the crystalline form of YB\(_{66}\) was obtained. This reference spectrum was compared with the spectra obtained from the cold areas of wafer 2, as shown in Figure 8. All three spectra seem to be identical in the positioning of the peaks, namely around 560 cm\(^{-1}\), 905 cm\(^{-1}\), 1092 cm\(^{-1}\), 2567 cm\(^{-1}\), and 3481 cm\(^{-1}\). The assignment of these peaks is similarly shown in Table V. Thus, the Raman analysis seems to support that the synthesized nanowires are of the YB\(_{66}\) composition.

In analyzing the same sample, EDX was used. Specifically, the nanowires on the cold region of wafer 2 were analyzed. The nanowires were scratched from the surface of the wafer and dissolved in ethanol for sonication for 10 minutes. A couple drops of the solution was then placed onto a holey carbon grid with the use of a micropipette. The grid was then dried under a heat lamp for ten minutes. The analyzed area consists of two wires, as shown in Figure 9. Both nanowires are about 400 nm in diameter. EDX analysis was performed on the same area and is shown in Figure 10. As expected, boron and nickel were detected. Silicon was also detected, possibly because the surface of the silicon wafer (used to synthesize the wires) was also scratched and sonicated along with the nanowires. Copper is present in abundant quantities since it is found in the grid used to hold the sample. Also, the sample appears to have little contamination since there is only a small amount of oxygen present. It is also noted that the EDX did not detect the presence of yttrium, which may suggest that the nanowires are purely boron and nickel.

Furthermore, SAED analysis was performed on the same area where the EDX was performed, as shown in Figure 11. The nanowires are of the same composition throughout the sample. The rings observed on the diffraction image suggest that the nanowires are of multi-
FIG. 10: EDX plotted data for nanowires in area #1. Sample taken from cold region of wafer 2 in nickel catalyzed synthesis with reaction time of 70 minutes. EDX spectra shows presence of B, Ni, Si, O, and Cu, all of which are expected.

FIG. 11: SAED image of the nanowires seen in the EDX image of area #1. Diffraction pattern shows a multi-crystalline product. Also, the distance between each ring in the diffraction pattern shows that this is a nanocrystalline product.

crystalline form. If the sample were of a single crystal, a clear diffraction pattern could have been obtained. Also, since the rings are a certain distance from one another, it was determined that the crystals are of the nano size. A reference electron diffraction pattern for YB$_{66}$ can be found in Huang et al. The reference image was taken from an YB$_{66}$ grain 350 nm thick in the [001] orientation. Since the diffraction pattern for the nanowires display ring structures, comparison with the reference cannot be made.

To determine how the spectra of nanowires of pure boron and nickel would compare to nanowires containing boron, nickel, and yttrium oxide, a separate synthesis was performed. The reaction time remained at 70 minutes and the wafers were placed in the same position as all other syntheses. SEM images were obtained and are shown in Figures 12 and 13. Both images were taken from wafer 1 and mixed structures of nanoribbons (from Figure 12) and nanowires (from Figure 13) were seen. The nanoribbon product was unexpected since the VLS experimental design was expected to occur. Raman analysis was performed on wafer 1, where the results are shown in Figure 14. The top graph shows the spectra taken on the island area and the bottom graph shows the spectra taken on the base area for comparison. These two graphs display the same peaks in the same positions around 901 cm$^{-1}$, 1106 cm$^{-1}$, and 3473 cm$^{-1}$.

FIG. 12: SEM image of nanoribbons on wafer 1. Synthesis was performed without use of yttrium oxide and at a time of 70 minutes. Thick nanoribbons were observed.

FIG. 13: SEM image of nanowires on wafer 1. Synthesis was performed without use of yttrium oxide and at a time of 70 minutes. Thick nanowires were observed.

FIG. 14: Raman spectra of wafer 1. The top graph shows the spectra taken on the island area and the bottom graph shows the spectra taken on the base area for comparison. These two graphs display the same peaks in the same positions around 901 cm$^{-1}$, 1106 cm$^{-1}$, and 3473 cm$^{-1}$.

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FIG. 14: Raman collected spectra of synthesized nanowires and nanoribbons of wafer 1. Reaction time was 70 minutes and quartz boat was placed at end of heating chamber. The top spectra is taken from the island area of wafer 1 and the bottom graph is taken from the base area of the same wafer. This corresponds to the peaks found in the boron bonds in an icosahedra unit, intericosahedral B-B bonds, and B-H bonds, respectively. But, unlike the Raman spectra taken of the nanowires synthesized with Y$_2$O$_3$, these spectra do not display a peak around 560 cm$^{-1}$, which corresponds to the presence of Y-B bonds.

**Conclusion**

Nanowires of about 400nm in diameter were synthesized using chemical vapor deposition. From the syntheses already performed, it was determined that when the wafers are placed at the low temperature region of the 925°C heat source, the precipitation of nanowires would occur. Also, it was determined that the reaction time ideally should be around 70 or less minutes, as a longer reaction time results in crystal structures. Raman spectroscopy was used to determine the compounds present in the synthesized samples. The Raman spectra of the crystal form of YB$_{66}$ was taken and compared to the synthesized nanowires, resulting in identical peak positions. Raman spectra of nanowires synthesized without the use of yttrium oxide were also taken. From this, it was found that there were at least three out of four matching peak positions compared with the nanowires synthesized using Y$_2$O$_3$. The missing peak in the spectra without using Y$_2$O$_3$ corresponds to Y-B bonds.

EDX analysis was then performed on the nanowires, showing the presence of Ni, B, Si, O, and Cu, all of which were expected. But, the EDX did not show the presence of yttrium, even though it was used to synthesize the nanowires. Finally, SAED was employed to obtain a diffraction pattern. Since the nanowires were multicrystalline, the obtained diffraction pattern cannot be compared with reference data.

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