Synthesis of crystalline boron nanoribbons and calcium hexaboride nanowires by low pressure chemical vapor deposition

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Abstract
Low pressure chemical vapor deposition was used to synthesize crystalline boron nanoribbons of 16 nm thickness by both uncatalyzed and nickel-catalyzed pyrolysis of diborane at relatively low temperatures. The nanoribbons were characterized with scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and Raman spectroscopy. Similar procedures were used to synthesize and characterize calcium hexaboride nanowires. The nanostructures reported here are compared with recent literature results for boron nanoribbons and CaB$_6$ nanowires grown by the same method.

1. Introduction
Boron and boron-rich solids possess unusual geometric and electronic structures that make them interesting from a fundamental perspective as well as uniquely suited to certain applications [1-3]. For this reason and the fact that boron and carbon share many properties, there has been much interest in recent years in exploring the properties of the boron analogs of fullerenes and carbon nanotubes. Based on an Aufbau principle, Boustani has predicted that novel layered, tubular, and quasi-crystalline boron nanostructures built from elemental subunits should be relatively stable [4-10]. Moreover, theoretical predictions indicate that boron-related nanostructures might be better candidates for applications as nanoscale interconnects than are carbon nanotubes. Unlike carbon nanotubes, boron nanoribbons do not roll-up to multiwall tubular forms and therefore the dangling bonds at their surfaces may be available for bonding to other elements, including hydrogen. For this reason, boron and boride nanostructures are of interest for hydrogen storage applications.

Calcium hexaboride (CaB$_6$) has a density of 2.45 g/cm$^3$, a melting point of 2235 °C, a resistivity of 222 $\mu$O·cm, and a Young’s modulus of 451 GPa [11]. Its electronic properties have been the focus of many recent studies, which have addressed whether CaB$_6$ is a high temperature ferromagnet [12-15], a semiconductor [16,17], or a semimetal [18-20]. Applications of CaB$_6$ as a high temperature material, a surface protector, and as a wear resistant material have all been considered [2,11]. Various methods of synthesising CaB$_6$ have been reported [21-24], but because high temperatures where calcium has a high vapor pressure are used, it is challenging to prepare the pure compound with a precise stoichiometry [25,26]. Recently, it was shown that a mixture of CaB$_6$ and CaH$_2$ will react with H$_2$ to produce Ca(BH$_4$)$_2$ [27]. Since the reverse reaction, the dehydriding of Ca(BH$_4$)$_2$ to produce CaB$_6$ and CaH$_2$, releases 9.6 wt% H$_2$, Ca(BH$_4$)$_2$ is of interest as a material that can reversibly store hydrogen at high gravimetric and volumetric densities. It is likely that the high surface-to-volume ratio of CaB$_6$ nanowires will greatly facilitate its reaction with H$_2$ to form Ca(BH$_4$)$_2$, thus making studies of the reaction of hydrogen with CaB$_6$ nanowires of great interest to the hydrogen storage problem. As a
prelude to such studies, methods to synthesize the appropriate boron and boride nanostructures must be established and the synthesized products well characterized.

2. Experimental set-up
A low-pressure chemical vapor deposition (LPCVD) system was designed and assembled for synthesis of boron-related nanostructures. It follows the design of the apparatus described by Xu et al for the synthesis of boron nanoribbons [28] and CaB$_6$ nanowires [29]. In this work, the nanostructures were deposited onto silicon (Si) substrates with a one-micron thick thermally grown SiO$_2$ layer (University Wafer). The Si substrates were cut from the wafers and ultrasonically cleaned first using H$_2$O$_2$ and concentrated H$_2$SO$_4$ and then with acetone and ethanol (time for each cleaning: 15 min). For the uncatalyzed growth of the boron nanoribbons, the cleaned substrates were simply loaded into a quartz boat and placed in the 1-inch diameter quartz tube, which in turn was placed into a tube furnace. As the ends of the quartz tube extend beyond the tube furnace, there is a temperature gradient from the middle of the furnace, where the temperature is highest, to the ends of the tube, which are near room temperature. Due to this temperature gradient, it was found that different results were obtained depending on the exact placement of the samples along the length of the quartz tube. For the CaB$_6$ synthesis, a thermal evaporator was used to deposit a Ni layer (6 nm) onto a randomly distributed powder of CaO (Alfa Aesar; 99.998% purity) placed on a Si substrate. For the Ni-catalyzed growth of the boron nanoribbons, the Ni layer was evaporated onto the bare Si substrates. The chamber was ramped up to 925 °C (center position temperature) in 45 min under a continuous flow of argon (BOC gases). A gas mixture of 1% diborane in argon (Matheson Trigas) at a flow rate of 20 sccm (standard cubic centimeter per minute) was then introduced into the chamber for 120 min. The total pressure for each run was ~ 400 mtorr. After reaction, several dark gray “puffy balls” (some visible to the eye) were found randomly deposited on the substrates, which were positioned in the 630-750 °C temperature zone region of the furnace. The substrates were removed, and the deposits were characterized by various techniques, including scanning electron microscopy (SEM), transmission electron microscopy (TEM) including energy dispersive X-ray spectroscopy (EDX) and selected area electron diffraction (SAED), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy.

3. Results and discussion
3.1. Uncatalyzed growth of boron nanoribbons
The SEM micrographs in figure 1 were recorded using a Nova NanoSEM 600 and JEOL JSM 6320 FE-SEM and show the different types of morphologies observed for nanostructures grown in the different temperature regions of the furnace. These morphologies can be designated as nanoribbons or nanoscrolls, as suggested by Xu et al [28]. The widths of these structures, including of the nanoscrolls calculated as if they could be unrolled, are more than a hundred nm with a thickness range of 15-20 nm. The inset in the right-hand panel of figure 1 shows the cross-section of one ~16 nm thick scroll. The “grass-like” nanoribbons, which are most common, display various features. For example, some are twisted or have zigzag edges and the tips (or ends) of some have slots in the middle, forming a “fork-like” structure. At the relatively higher temperature of formation of the wider nanoribbons, some break into narrower structures. Also, as seen in the inset of the upper left-hand panel, new ribbons seem to grow from the edge of a wide ribbon. This morphology was not described by Xu et al [28].
To characterize the boron nanoribbons with transmission electron microscopy (JEOL JEM-3010 TEM), some puffy balls were scraped off the substrates and ultrasonically dispersed in ethanol for 20 min. A drop of suspension was placed on a copper TEM grid covered with a holey carbon film (SPI Supplies). Figure 2 shows high resolution TEM micrographs of twisted nanoribbons. The spacing between atomic layers is about 0.26 nm (left) and 0.39 nm (right). The 0.39 nm value is a good match (within 10%) for the spacing between the (202) or (113) lattice planes of $\alpha$-tetragonal boron, while the 0.26 nm spacing likely corresponds to a higher index set of planes, such as (215). Selected area electron diffraction shows that the nanoribbons are crystalline. Measured d-spacings from the SAED pattern (figure 3) are well matched by those in JDPDS file #77-1275, which confirms that our product is $\alpha$-tetragonal boron, a conclusion also reached by Xu et al [28].
Further information on the nature of the boron nanoribbons is provided by the Raman spectra in figure 4. Table 1 compares the peaks reported by Xu et al [28] with those observed here. The peak at 520 cm$^{-1}$ is due to the silicon substrate. All of the peaks reported by Xu et al [28] are within a few cm$^{-1}$ of the peaks that we observe, with the exception of their peaks at 705 and 746 cm$^{-1}$, which are not seen in our spectra. Also, we observe additional peaks that are not apparent in their spectra, indicating that additional boron phases are present in our samples. However, the peaks we observe do not coincide exactly with those in the Raman spectra of α- or β-rhombohedral boron [30]. The preparation of pure elemental boron is difficult, because boron is very reactive toward other elements at the elevated temperatures required for reduction of its compounds. Moreover, the crystallinity of the final boron product is highly temperature dependent [2,3]. For example, amorphous boron powders are usually made at 600-800 °C; vitreous boron pieces are formed at 800-1100 °C; and various crystalline boron allotropes are commonly obtained above 1000 °C. Therefore it is not surprising to have peaks from different forms of elemental boron, some of which may be stabilized by impurities.

Table 1. Summary of Raman peak positions of boron nanoribbons

| Materials   | Raman Shift (cm$^{-1}$) |
|-------------|-------------------------|
| Xu et al    | 366 490 642 705 746 795 910 1100 |
| This work   | -- 493 646 683 -- 761 -- 789 911 1117 1170 |

The chemical composition of the nanoribbons was analyzed with EDX (figure 5) using a JEOL JEM 3010 TEM, which shows that they consist mainly of boron with only a small amount of oxygen detected. The oxygen peak is likely due to an amorphous oxide surface layer as boron is superficially oxidized in air at room temperature [2,3,31].
Figure 5. EDX spectrum shows that the boron nanoribbons contain oxygen.

The X-ray photoelectron spectra in figure 6 show that in addition to the boron and oxygen peaks, a peak due to carbon and a very weak nitrogen peak are also present. The possible source of the carbon and nitrogen impurities might be the gas precursor, which contains a small amount of CH₄, O₂, N₂, and CO₂ (all less than 10 ppm) in the ultra high purity diborane and argon used. Quantitative analysis revealed that within the XPS interrogation volume, the nanoribbons consist of ~70 at.% boron, ~14 at.% oxygen, ~14 at.% carbon, and trace amounts of other impurities including nitrogen. Like the oxygen, the carbon is likely present mainly at the surface. Since XPS is a surface analysis tool, it is not surprising that it yields higher apparent oxygen content than implied by EDX, if the oxygen is present only in a surface oxide layer. This observation can be confirmed from the Auger electron spectra of figure 7. Quantitative analysis of the AES data using the appropriate atomic sensitivity factors shows that the percentages of B, O and C in the nanoribbon sample are ~43%, ~13%, ~44%, respectively. As AES is slightly more surface sensitive than XPS, the higher carbon content from AES suggests that the carbon is present mainly in the topmost atomic layers.

Figure 6. XPS spectrum of a “puffy ball” showing carbon and nitrogen contamination in addition to a surface oxide.

Figure 7. Auger spectrum showing a higher carbon
concentration than detected with XPS.

The B 1s, C 1s, and O 1s regions of the XPS spectrum of the boron nanoribbons are displayed in figure 8. The B 1s peak shows two components at 187.0 and 188.2 eV. The larger and lower binding energy component is assigned to boron atoms bonded only to other boron atoms [31], whereas the less intense component at 188.2 eV is assigned to boron bonded to carbon [32,33]. The C 1s core-level spectrum is broad and asymmetric. It is composed of a peak at 285 eV due to the C-C bond from hydrocarbon contamination of the surface. The C 1s component at 286.6 eV was assigned as due to either a C-O bond or C-OH bond [34]. A corresponding O 1s component associated with the C-O (or C-OH) bond appeared at 531.7 eV. The main O 1s component is assigned to boron oxide. These assignments are generally in agreement with those of Xu et al [28].

There are several polymorphs of crystalline boron, including α-rhombohedral, β-rhombohedral, α-tetragonal, β-tetragonal, and others [2,3]. Among them, the first form to be discovered was α-tetragonal boron [35]. This form has a unit cell with a large number of holes, which in principle can accommodate both additional boron and impurity atoms [3]. A quantum mechanical calculation by Longuet-Higgins and Roberts [36] using the concept of a closed shell of boron icosahedra showed that the proposed B$_{50}$ structure is unstable. The tetragonal framework is stabilized through introduction of electron donor atoms, such as carbon, nitrogen, beryllium or aluminium [25,2,37]. A concentration of electron donor atoms of only 1 at.% can stabilize the structure [18]. Even though most of the carbon is concentrated on the surface, the XPS results in the B 1s region shows some evidence of B-C bonding. This carbon may serve to stabilize the α-tetragonal form of the nanoribbons, which is the crystalline form implied by the SAED results.

Figure 8. XPS of the boron nanoribbons shows that different components of the B, O and C 1s peaks can be resolved and assigned to B-O, B-C, C-H and C-O bonds.
3.2. Catalyzed growth of boron nanoribbons

By using nickel as a catalyst, boron crystalline nanoribbons and boron nanowire-catalyst-nanotube hybrid structures were synthesized. Although the growth mechanism of these nanostructures has not been fully explored, it is believed that the vapor-liquid-solid (VLS) growth mechanism plays an important role as catalyst particles can always be observed by SEM (figure 9) at the end of the nanowire. Xu et al. have worked with Au and Pt/Pd alloy catalysts and by reducing the thickness of the catalytic metal film, they have synthesized nanostructures with diameters of 8-10 nm [38]. Boron nanowires formed by the nickel catalyzed reaction are about 100 nm in diameter with bright metal particles at the tips. Some nanoribbons are also formed (figure 10), which have similar thicknesses of those formed by the non-catalyzed reaction. A Raman spectrum corresponding to the nanowires of figure 9, is shown in figure 11 and with only two wide peaks at 901 and 1106 cm$^{-1}$ it is quite different from the Raman spectrum shown in figure 5 of the crystalline boron nanoribbons. This suggests that these nanostructures are composed of amorphous boron.

![Figure 9. SEM images of the Ni-catalyzed boron nanotubes shows bright metallic particles on the tips. Diameters of the tubes are about 200 nm, which is controlled by the thickness of the deposited catalyst layer.](image)

![Figure 10. SEM images show that the Ni-catalyzed growth also leads to the formation of boron nanoribbons.](image)

![Figure 11. Raman spectrum encompassing all of the structures shown in figures 9 and 10.](image)
3.3. Synthesis and characterization of CaB$_6$ nanowires

As noted in the experimental section, with CaO placed on the substrate, wire-like CaB$_6$ nanostructures of various morphologies, depending on temperature region of the furnace, were observed to form. The nanowires are ~15-50 nm in diameter, and ~1-10 µm in length. Catalyst particles were observed on the tips of most of the nanowires. Figure 12 is a low-magnification SEM image of the as-synthesized nanowires which shows that similar to pure boron nanoribbons, CaB$_6$ also appears in the form of “puffy balls”. But unlike for pure boron, these balls are not visible to the naked eye. The higher magnification image in figure 13 shows the presence of catalyst particles on the tips.

![Figure 12. SEM image of “puffy balls” of CaB$_6$ nanowires.](image12)

![Figure 13. High magnification SEM image of the CaB$_6$ deposits shows straight stick-like wires with catalyst particles at the tips.](image13)

A low resolution TEM micrograph, figure 14, shows a portion of a nanowire with a catalyst particle on the tip. Figure 15 shows an EDX spectrum obtained in STEM mode with a 1 nm probe size, along with a TEM image showing a catalytic particle at the tip of the nanowires. The EDX spectrum shows the presence of only B, Ca, and Ni. The HRTEM image in figure 16 shows that the spacing between atomic layers is 0.27 nm. According to JDPDS file # 31-0254, the corresponding plane is (110), while growth is preferentially along the CaB$_6$ [001] direction.
Further information on the elemental composition was obtained with EELS line scans (STEM mode; probe size 0.2 nm). Figure 17 is a typical EELS spectrum, which shows the characteristic B and Ca ionization edges at ~188 and ~346 eV, respectively. Quantitative analysis of these results confirms the Ca:B ratio of 1:6.

Finally, figure 18 shows the Raman spectrum of the as-synthesized nanowires acquired at room temperature in ambient. As indicated by table 2, the peaks at 778, 1135, and 1280 cm$^{-1}$ match the Raman active modes $A_{1g}$, $E_g$ and $T_{2g}$, respectively, of CaB$_6$ as reported by Xu $et$ $al$ [29].
As mentioned by Xu, et al different morphologies were observed as a function of reaction chamber temperature.[29] As the CaB$_6$ nanowires grew in the presence of certain metal catalysts and catalytic particles were observed on the tip of most nanowires at a relatively low reaction temperature (860-900 °C), the growth probably occurs by the VLS mechanism [39]. Xu et al [29] speculated on the details of CaB$_6$ growth by this mechanism. The presence of a bulbous tip in some nanowires and bullet-like tips in other cases tells us that possibly both root-growth and tip-growth VLS took place. In addition to the VLS mechanism, it is also possible that growth occurred by the vapor-solid (VS) growth mechanism. The combination of different mechanisms may be responsible for the various morphologies observed.

4. Summary
The same LPCVD apparatus and general synthesis method involving the pyrolysis of diborane was used for the growth of both boron nanoribbons and CaB$_6$ nanowires. The uncatalyzed growth of boron nanoribbons led to a variety of structures with the appearance of blades of grass, ribbons, and rolled up scrolls. These different morphologies all feature locally flat boron sheets only 15-20 nm thick. The use of a Ni catalyst in the growth process gave similar structures but in addition yielded boron nanowire-catalyst-nanotube hybrid structures. The addition of CaO to the system resulted in the growth of CaB$_6$ nanowires with diameters of ~15-50 nm, and lengths of ~1-10 μm. Recently, we have extended the method to the growth of SrB$_6$ nanowires [40], with similar characteristics to those of the CaB$_6$ nanowires described here.

Acknowledgements
We thank R. S. Ruoff and T. Xu for advice and assistance in setting up the LPCVD apparatus and for help in interpreting our results. This work was supported by a grant from the US Department of Energy, grant no. DE-FG02-05ER15726.

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