Synthesis of Magnesium Borate ($Mg_2B_2O_5$) Nanowires by Chemical Vapor Deposition Method

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Metal borates are remarkable ceramic materials with excellent mechanical properties and high resistance to corrosion and they possess attractive thermal properties.[1−6] Magnesium borate has been shown to be a thermoluminescence phosphor,[7,8] a good antiwear, and a reducing friction additive.[9] $Mg_2B_2O_5$ is also a ferroelastic material.[10] Thus, one-dimensional metal borate nanostructures can have potential applications in the fields of nanocomposites, nanomechanics, and nanoelectronics. Aluminum borate nanowires including $Al_{18}B_4O_{33}$ and $Al_4B_2O_9$ have been synthesized by heating a mixed powder of B, B_2O_3, and Al_2O_3 with catalysts to elevated temperature.[2,3] Recently, MgB_4O_7 nanowires have been synthesized by a similar method of heating a mixed powder of MgO, B_2O_3, and B at 1050 °C.[11] The metal borate nanowires reported in the literature usually were mixtures of the precursor powders or fiberlike boron oxide agglomerates.[2,3,11] Thus, purification processes are needed to separate the metal borate nanowires. Furthermore, it is difficult to grow metal borate nanowires with controllable size and locations using the reported methods. Herein, we report the growth of single-crystal $Mg_2B_2O_5$ nanowires on MgO substrates by a chemical vapor deposition (CVD) method, which uses boron triiodide and boric acid (BI_3/H_3BO_3) vapor with Ar as the carrier gas. Pt/Pd nanoparticles are employed as the catalysts. $Mg_2B_2O_5$ nanowires are grown directly out of MgO substrates. No other powder or fiberlike contamination is found around the nanowires. Controlling of the nanowire size and locations is possible using this CVD method.

MgO ((100) or (111), one side or double side polished, Coating & Crystal Technology Inc.) substrates are sputter-coated with 2−3-nm Pt/Pd film on the polished side using a Cressington 208 HR Sputter Coater with a Pt/Pd foil (80% Pt, 20% Pd, Refining Systems Inc., Las Vegas) as the target. A coated MgO substrate and a bare MgO substrate (used as control) are placed on a quartz boat in the center of a tube furnace. The tube furnace is heated to 750−1100 °C under Ar flow. Once the temperature of the tube furnace reaches the desired temperature, BI_3/H_3BO_3 vapor with Ar gas is introduced. BI_3/H_3BO_3 vapor is introduced through a sublimator, which is kept around 40 ± 1 °C. BI_3/H_3BO_3 source is produced by exposing 2 g of BI_3 (98+%, Aldrich) to air (30% relative humidity and 23 °C) for about 2−5 min. The gas tubing between the sublimator and the tube furnace is heated to 60 ± 1 °C to prevent the vapor from condensing. Ar gas acts as both the carrier gas and the diluting gas. The typical flow rates of carrier Ar gas and diluting Ar gas are 19 and 20−400 sccm, respectively. The reaction time is varied from 0 to 3 h. After reaction, the tube furnace is cooled to room temperature under Ar gas flow.

Scanning electron microscope (SEM) observations are carried out in a Hitachi S-4500 FE-SEM. Nanowires on the substrate are transferred onto holey carbon grids (400 mesh Cu, SPI supplies) by gently dragging the grids along the surface of the samples. Transmission electron microscopy (TEM, Hitachi H8100 and Hitachi HF2000), selected area electron diffraction (SAD, Hitachi H8100), electron energy-loss spectrometry (EELS, JEOL JEM-2010F with a Gatan imaging filter (GIF) system) and X-ray energy-dispersive spectrometry (XEDS, JEOL JEM-2010F with a Noran Vista XEDS system) are used to characterize the structures present on the grids.

An SEM study of all the samples shows that straight nanowires with uniform diameter distribution are synthesized on the MgO substrates coated with Pt/Pd film, if the reaction temperature is between 850 and 1050 °C. Only very rough surfaces are observed for the bare MgO substrates in the same temperature range. The average size of the nanowires can be manipulated by varying the growth time, the growth temperature, and the BI_3/H_3BO_3 vapor concentration. The nanowires can vary in the range of 30−150 nm in diameter and 1−10 μm in length. Increasing the growth time while keeping the growth temperature and the BI_3/H_3BO_3 vapor concentration constant leads to longer nanowires. Elevating the growth temperature, while keeping the other two parameters unchanged, produces larger and longer nanowires. Raising the BI_3/H_3BO_3 vapor concentration alone produces larger diameter but shorter nanowires. Parts (a) and (b) of Figure 1 show the SEM images of the nanowires synthesized at 1000 °C with

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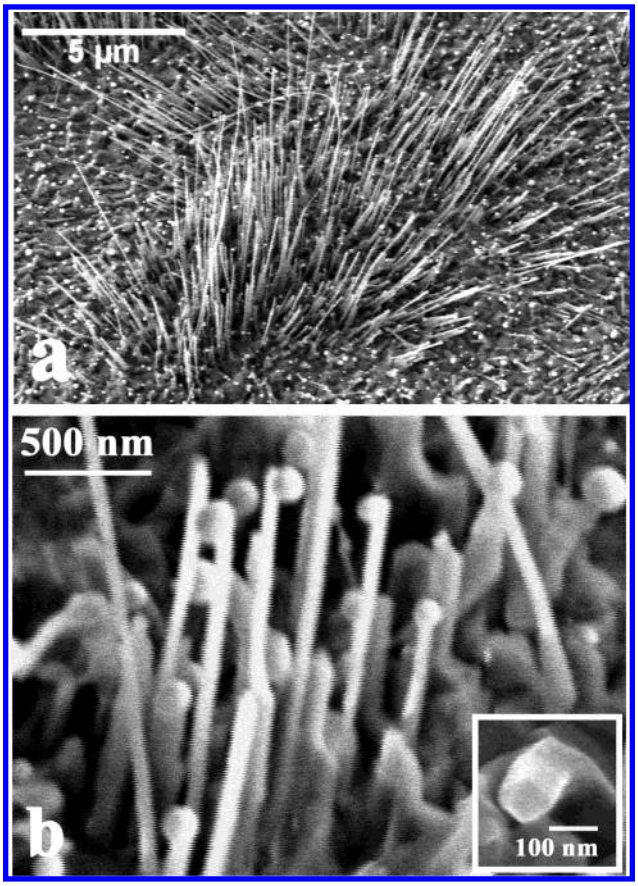

Figure 1. (a) SEM image of the nanowires grown on Pt/Pd-coated MgO substrate. (b) Enlarged SEM image showing the particles attached to the top or the bottom of nanowires, a typical cross-sectional SEM image of a nanowire.

19 sccm carrier Ar and 200 sccm diluting Ar gas flowing for 2 h. Figure 1a reveals that large amounts of nanowires grow out of the rough MgO substrate. The average diameter and length of the nanowires are about 70 nm and 3 μm, respectively. Each nanowire usually has a particle attached to its top or bottom, as shown in Figure 1b. To obtain cross-sectional SEM images of the nanowires, a sample is put into a 2-mL ethyl alcohol solution and ultrasonically oscillated for 15 min; the sample is then taken out and observed by SEM. The inset of Figure 1b shows a typical cross-sectional SEM image of a nanowire, which indicates that the cross-sectional shape is a parallelogram.

Figure 2a shows a typical low-magnification TEM image of a nanowire, which has a particle attached to one of its ends. The insets in Figure 2a show the SAD pattern and the corresponding HR-TEM image taken from part of a nanowire. The SAD pattern can be indexed as a triclinic $Mg_2B_2O_5$ phase[12,13] recorded from a [100] zone axis. The HR-TEM image clearly displays the 0.447-nm *d* spacing of the (020) planes. The axis direction of these nanowires is along the ⟨001⟩ direction. Both the SAD pattern and the HR-TEM image imply that the nanowires are single crystals. A typical EELS spectrum taken from part of a nanowire is shown in Figure 2b, which indicates that the nanowire is mainly

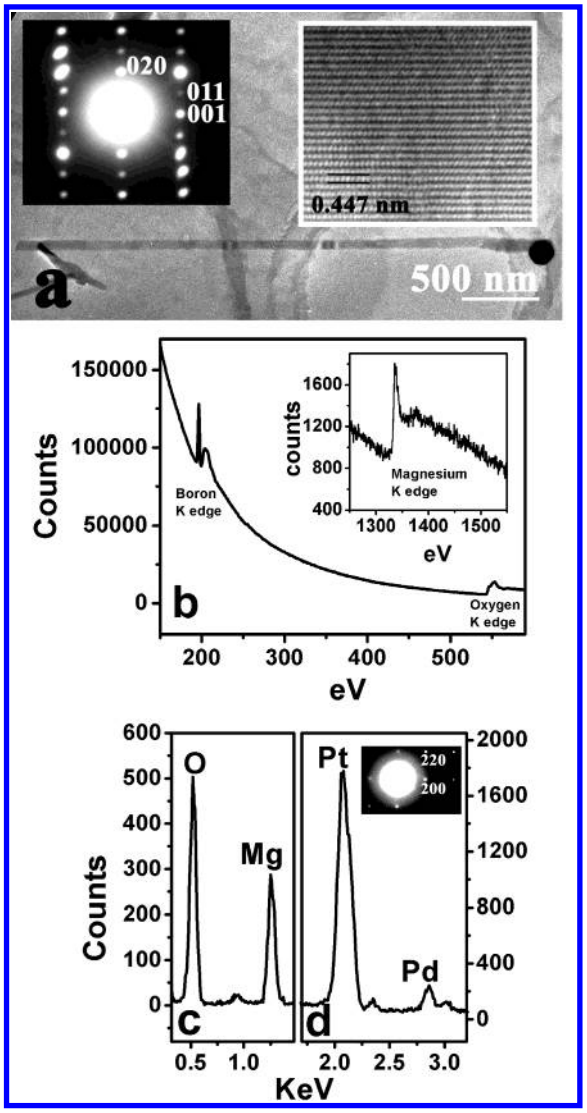

Figure 2. (a) A typical low-magnification TEM image, SAD pattern, and HR-TEM image from a nanowire. (b) EELS spectrum from part of a nanowire. (c) XEDS spectrum from part of a nanowire. (d) XEDS spectrum and SAD pattern from the particle attached to one end of a nanowire.

composed of B, O, and Mg. The shape of the boron K edge shown in Figure 2b is similar to the one taken from B_2O_3 powder,[14] suggesting the B−O bond in the nanowire. XEDS spectra taken from part of a nanowire and from the particle attached to the nanowire are shown in parts (c) and (d), respectively, of Figure 2. The XEDS spectra show that the nanowire does contain Mg and O, while the particle is mainly an alloy of Pt and Pd. The SAD pattern (the inset in Figure 2d) taken from the particle can be indexed as a face-centered cubic phase (fcc) with a lattice constant of 4.0 Å. Since both Pt and Pd have fcc lattice structures with a lattice constant around 4.0 Å, the particle can be considered as a substitutional solid solution of Pt and Pd.

The existence of a particle at one end of a nanowire suggests that the growth mechanism could be the vapor−liquid−solid (VLS) growth process.[15] It has been

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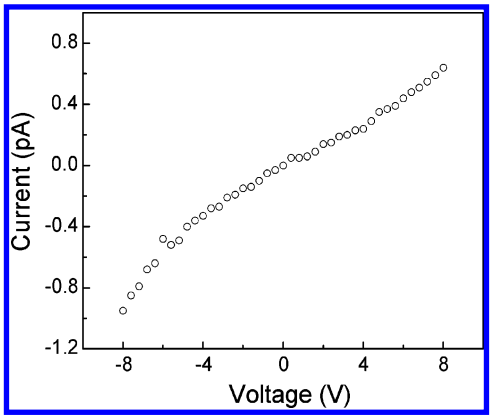

Figure 3. $I-V$ curve of a nanowire. The conductance and conductivity are derived to be 10^{-4} nS and 10^{-4} Ω^{-1} m^{-1}, respectively.

known that H_3BO_3 decomposes into B_2O_3 and H_2O at around 500 °C:[16] $2H_3BO_3 \rightarrow 3H_2O + B_2O_3$. BI_3 then absorbs H_2O to provide more H_3BO_3:[16] $BI_3 + 3H_2O \rightarrow H_3BO_3 + 3HI$. BI_3 can also decompose into B and I_2 at elevated temperature (800−1000 °C):[16] $2BI_3 \rightarrow 2B + 3I_2$. So the chemical vapor in the center of the tube furnace could contain B_2O_3, B, BI_3, I_2, and HI. As mentioned earlier, the smooth surface of a MgO substrate turns into a very rough surface after a reaction at high temperature (850−1050 °C), which suggests that the MgO substrate reacts with B_2O_3 vapor:[17] $B_2O_3 + 2MgO \rightarrow Mg_2B_2O_5$. The MgO substrate may also react with B vapor:[16] $2B + 3MgO \rightarrow 3Mg + B_2O_3$ to provide more B_2O_3 vapor. Pt and Pd both can form boron eutectics at relatively low temperature (Pt: 830 °C,[18] Pd: 960 °C[19]), which may serve as the liquid agent in the VLS method. The surface of the liquid has a large accommodation coefficient[16] and is therefore a preferred site for the growth of $Mg_2B_2O_5$. Further experiments are being carried out to study how the relative concentration of H_3BO_3 and BI_3 vapor can influence the growth of $Mg_2B_2O_5$ nanowires.

To characterize its electrical transport property, contact electrodes (Au/Ti) to an individual $Mg_2B_2O_5$ nanowire are fabricated using the electron beam lithography technique. Room-temperature electrical measurement is done using a semiconductor parameter analyzer (HP 4156C). Figure 3 shows the $I-V$ curve of the nanowire. The conductance of this nanowire is derived to be 10^{-4} nS, which is obtained from the linear region of the $I-V$ curve [±2 V]. With the diameter of the nanowire (36 nm) and the nanowire channel length between the electrodes (1.28 μm), the conductivity is obtained to be $\sim 10^{-4}$ Ω^{-1} m^{-1}. Theoretical calculation shows that bulk $Mg_2B_2O_5$ crystal has a wide band gap of 5.44 eV;[20] the measured low conductivity is consistent with the theoretical calculation.

Single-crystal $Mg_2B_2O_5$ nanowires have been synthesized at high temperature (850−1050 °C) on MgO substrates coated with a thin film of Pt/Pd. BI_3 and H_3BO_3 vapor with Ar gas are used as the precursors. The growth mechanism of the $Mg_2B_2O_5$ nanowires is shown to be the VLS-type process. Electrical transport measurement on a single nanowire indicates that the $Mg_2B_2O_5$ nanowires are wide band gap semiconductor nanowires. The results demonstrate that metal borate nanowires can be synthesized by introducing boron and boron oxide sources to a metal oxide substrate coated with a thin film of some catalyst.

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Supporting Information Available: Schematic of the CVD apparatus, the preliminary analysis of BI_3/H_3BO_3 powder, AFM image of a $Mg_2B_2O_5$ nanowire contacted with Au/Ti electrodes, and the device fabrication process (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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