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MgB_2 Superconducting Whiskers Synthesized by Using the Hybrid Physical−Chemical Vapor Deposition

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Since the discovery of superconductivity in MgB_2 in 2001,[1] tremendous research activities have been stimulated. Both understanding the basic properties and searching for mass production toward large scale applications are highly important for the study of MgB_2. MgB_2 has a remarkably high $T_c(0)$ of ~39 K, a relatively high coherence length[2] of ~5 nm compared with the high critical current density up to 1×10^8 A/cm^2 at 2 K and self-field,[3] and a larger energy gap[4] without a weak link between grain boundaries.[5] All these advantages make it a promising candidate for applications in superconducting devices operating in the temperature range 4−20 K. In the past few years, research and development of MgB_2 have been rapidly progressing. Up to now, study of the MgB_2 and its derivative has been mainly focused on the bulk,[6,7] thin films,[8,9] wires,[10,11] and only a few reports on the synthesis of MgB_2 nanowires and nanoparticles.[12−15] However, little has been reported on the synthesis of MgB_2 whiskers. Superconducting nanowires and other 1D nanostructure can be used as the ideal low-dissipated interconnections in superconducting devices; thus it is desirable to grow MgB_2 whiskers and other nanostructures on a substrate. Fabrication and investigations of the nanodevices based on MgB_2 provide a fundamental understanding of the effect of dimensionality and size effects on superconductivity. In this paper, we report on the synthesis of the MgB_2 superconducting nanowhiskers on copper and other substrates (see Figure S1 in the Supporting Information) by using the hybrid physical−chemical vapor deposition (HPCVD) technique. The HPCVD method can provide a sufficiently high Mg vapor pressure for the thermodynamic phase stability of MgB_2 at elevated temperatures, which is the most effective method for MgB_2 synthesis. The MgB_2 whiskers have a hexagonal conelike morphology and a length of ~4 μm. The onset transition temperature is ~39 K.

The HPCVD growth method used in this experiment is successful in making high quality MgB_2 film.[16,17] The principle of the HPCVD and the scheme of the setup were described elsewhere.[16] A quartz chamber with induction heating and a stainless steel chamber with resistivity heating are the two mostly employed HPCVD setups, and a quartz reactor is used.[16] Essentially, the substrate circled with the Mg ingots was placed on a stainless steel susceptor and heated to a desired deposition temperature inductively by an rf-generator. Boron decomposed from the B_2H_6 reacted with sufficient Mg vapor near the substrate and formed MgB_2. During the entire reaction process, pure H_2 was introduced as ambient gas. The sample was deposited at 650 °C for 4 min, and the surface of the copper substrate was polished using a very fine sand grounding paper. The ambient pressure in the reacting chamber was maintained at ~25 KPa. The flow rates of B_2H_6 (with concentration of 25% in hydrogen) and H_2 were 25 and 100 sccm, respectively.

After the deposition, MgB_2 nanostructures can be observed with the naked eye at the edge of the film on the substrates. The morphologies of the whiskers were analyzed using a scanning electron microscope (SEM, QUANTA 200 FEG) (Figure 1). The low and high magnification SEM images of the whiskers are shown in (a) and (b), respectively, indicating that the whiskers have an average length of ~4 μm. The morphology analysis reveals that the whiskers have a hexagonal cone shape and the top diameter is ~1 μm while the bottom is ~200 nm. It is noted that there also exist many thin whiskers at the bottom of the large ones, whose length is in the range 20 nm to 1 μm.

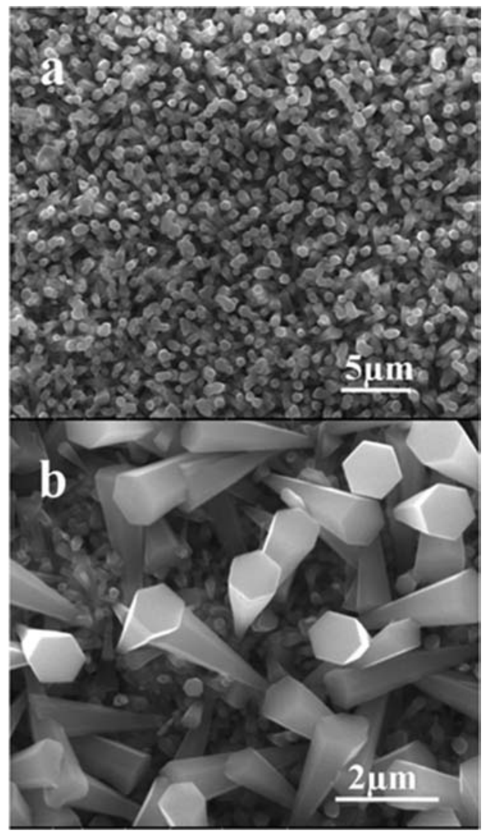

Figure 1. (a) Low and (b) high magnification SEM images of the MgB2 whiskers grown on the copper substrate.

The microstructure of individual MgB_2 whiskers was investigated by transmission electron microscopy (TEM, TECNAI F30). A bright-field TEM image of a single MgB_2 whisker is shown in Figure 2a. The incident electron beam is parallel to the $[\bar{1}\ 2\ \bar{1}\ 0]$ zone axis. The corresponding selected area electron diffraction (SAED) pattern taken from the MgB_2 whisker reveals that the whisker has a hexagonal single crystal structure. The electron diffraction pattern in the inset was indexed with the indices (10

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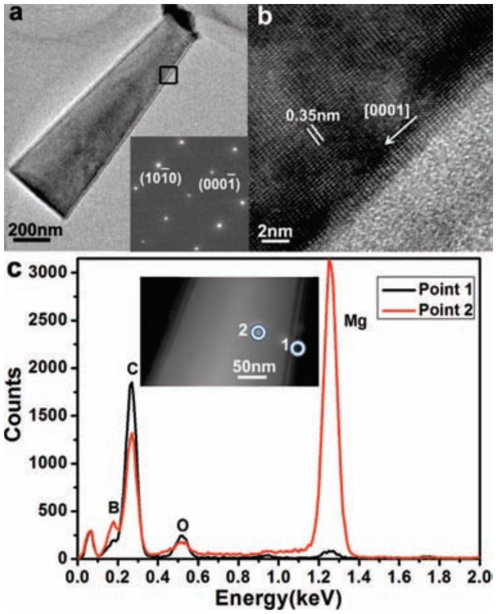

Figure 2. (a) TEM image of the MgB_2 whisker. The inset is the SAED pattern of the MgB_2 whisker. (b) High resolution TEM image of the MgB_2 whisker. (c) EDS analysis on individual MgB_2 whisker. The black curve is taken from point 1 and the red one from point 2, revealing that the sheathing layer consists of $Mg_xB_yO_z$.

$\bar{1}$0) and (000$\bar{1}$). The high resolution TEM image taken from the same MgB_2 whisker indicates that the whisker is grown along the [0001] c-axis and the lattice spacing is ~0.35 nm, corresponding to the (0001) plane of the MgB_2 (Figure 2b). The TEM image also shows that the whisker has an amorphous sheathing layer ~10 nm in thickness. Compositional analysis on individual MgB_2 whiskers was conducted by using energy dispersive spectroscopy (EDS) with TEM. The EDS spectra (Figure 2c) were collected from two selected points: the outer sheathing layer and the body of the whisker. Magnesium, boron, and oxygen were detected at both points. The ratio of oxygen to magnesium in point 1 is much higher than that in point 2, revealing that the sheathing layer consists of Mg and O with detected B. It is noted that, according to the above EDS results, the ratio of B over O in the body is much higher than that in the sheathing layer. Therefore, we can conclude that the amorphous sheathing layer of the whiskers is composed of $Mg_xB_yO_z$.

The whiskers were collected from the surface of the substrate, and their magnetic properties were measured with the magnetic property measurement system (MPMS, Quantum Design). The magnetization as a function of temperature ($M-T$ curve) reveals that the onset superconducting temperature is ~39 K (Figure 3), which is higher than the superconducting transition temperature of the bulk MgB_2 film on copper substrates.[18] This may be due to the fact that the MgB_2 whisker is of a single crystalline structure.

The growth mechanism of the MgB_2 whiskers is of great interest and deserves being discussed in detail. Since the MgB_2 whiskers can grow on different substrates like Cu, Mg, and stainless steel, the growth of MgB_2 may not need a catalyst. We believe the possible mechanism is dominated by self-seed growth. When the Mg ingots were heated to 650 °C, Mg melted and vaporized. Then, B_2H_6 decomposed and B atoms reacted with Mg vapor; as a result, a layer of dense MgB_2 film was formed on the substrate. This film can act as a seed layer, which can provide favorable nucleation sites (Figure S2). Due to the anisotropy growth rate, MgB_2 whiskers will grow on such a seed layer as cone-shaped whiskers close to

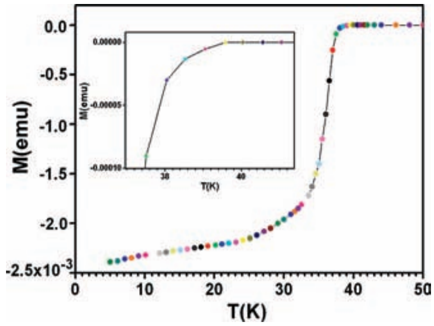

Figure 3. $M-T$ curve of the MgB2 whiskers measured under a magnetic field of 50 Oe. The inset shows the onset transition temperature ~39 K.

the Mg source where the Mg vapor concentration is higher. The above suggestion was confirmed by the fact that many smaller whiskers were observed to grow directly from the body of bigger ones, with no catalysts but the whisker itself, which proves that the mechanism of the MgB_2 whiskers is by self-seeded growth. A similar mechanism was also used to explain the growth of ZnO whiskers or nanowires without catalysts.[19,20]

In summary, by using the HPCVD technique, we demonstrated the superconducting MgB_2 whiskers synthesized on copper substrates. The cone-shaped MgB_2 whiskers have a hexagonal shape and grow along the [0001] direction with a single-crystal structure. An onset transition temperature of 39 K is observed. The possible mechanism is by self-seeded growth.

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Supporting Information Available: SEM images with full list of authors for refs 5 and 17. This material is available free of charge via the Internet at http://pubs.acs.org.

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