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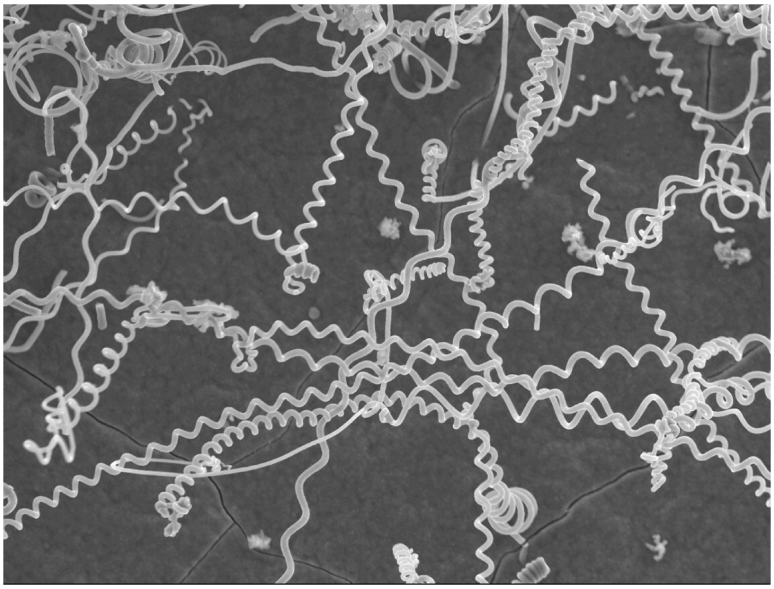

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Superconducting MgB_2 Nanohelices Grown on Various Substrates

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The discovery of superconductivity in the binary metallic boride, MgB_2,[1] has led to a flurry of research activities directed mainly toward understanding the fundamental properties and fabrication of wires,[2] tapes,[3] and thin films[4] of this material for practical applications. The remarkably high T_c (39 K) of this material coupled with the advantages of a high coherence length (50 Å),[5] weak-link-free grain boundaries,[6] high critical current densities in the range of 4−20 K, and large energy gap,[7] makes MgB_2 a promising candidate for applications in superconducting devices. Superconducting nanowires, and other 1D nanostructures, can ideally be used as low-dissipation interconnects in superconducting devices making it desirable to grow MgB_2 nanowires and other nanostructures on a substrate. However, the high volatility of Mg compared to that of B makes it difficult to control the stoichiometry and morphology of the product phase. There have been only a few reports on the synthesis of MgB_2 nanowires.[8,9] In addition to nanowires and nanotubes, new 1D nanostructured morphologies, nanocoils, nanosprings, and nanohelices, are of special interest owing to their unique periodic and elastic properties resulting in structural flexibility that provides additional opportunities for nanoengineering.

Herein we present the first examples of superconducting MgB_2 nanohelices grown by a combination of physical and chemical vapor deposition on Si and other substrates by the reaction of Mg metal with diborane at 770−800 °C under a flow of N_2 and H_2 (details in Supporting Information). After the reaction, black regions containing the MgB_2 nanostructures could be seen with naked eye on Si and the other substrates. The nanohelices cover the substrate and, in some areas of the substrate, were formed along with long MgB_2 nanowires. Some nanohelices are more than two hundred micrometers long and could be seen under an optical microscope. Si (with or without native oxide layer) was the primary substrate for growth; however, other substrates including sapphire, porcelain surface, Ta foil, and even thin Mg ribbons were also used to grow these nanostructures (see Figure S1 in Supporting Information).

Powder X-ray diffraction of the material in the black regions on the Si wafer showed the characteristic d(101) diffraction line of MgB_2 (Figure S2) along with the diffraction lines due to the substrate. The low intensity of the diffraction lines suggests that the nanohelices are not highly crystalline. When the black region was observed under a scanning electron microscope (SEM), a high density of nanohelices could be seen (Figure 1a). The nanohelices typically exhibited round tips and circular cross-section with diameters of 100−600 nm and lengths exceeding 50−100 μm. EDS analysis on individual nanohelices revealed the presence of Mg and B with a nominal atomic ratio of 1:2 (see Figure S3). The diameters of the helices varied widely in the range of 1−14 μm resulting in both very tightly wound springs (Figure 1b) and loosely wound coils (inset). The pitch of the nanohelices does not show any clear dependence on the diameter of the nanowire or the coil diameter. However, the diameter of the nanowires is very uniform along the length irrespective of the coil diameter. Careful control of growth conditions and positioning of the Si substrate allowed for uniform

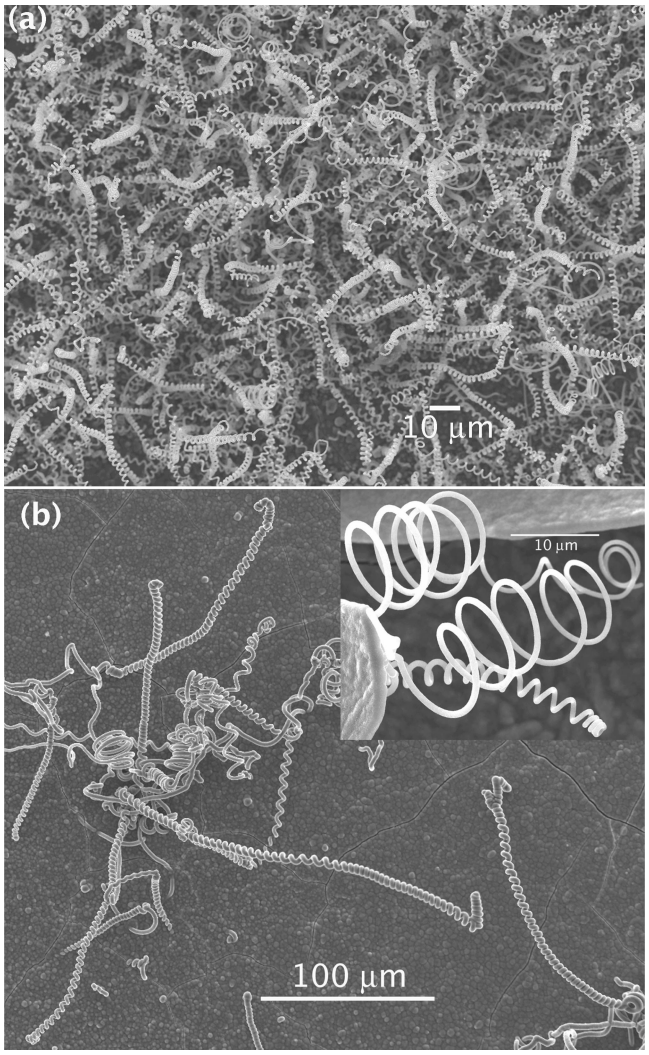

Figure 1. SEM images of MgB_2 nanohelices grown on Si substrates: (a) large area on the Si substrate covered with nanohelices; (b) tightly wound nanosprings, inset shows loosely wound coils.

growth of helices over a several hundred micrometer square area. The nanohelices exhibit both right-handed and left-handed turns and in rare cases showed a change of direction along the length of the helix. EDS analysis of the nanohelices did not pick up any Si signal indicating that there was little or no diffusion from the substrate into these growing nanostructures. TEM analysis showed that most of the nanohelices had a smooth surface and uniform diameter, and some showed rounded or bulbous tips. However, the nanohelices did not show any clear lattice fringes even at 500 000 magnification, but some electron diffraction (ED) patterns with spots corresponding to d(101) spacing (see Figure S4) were observed. The streaking in the ED pattern was indicative of crystal disorder in the structure of the nanohelices.

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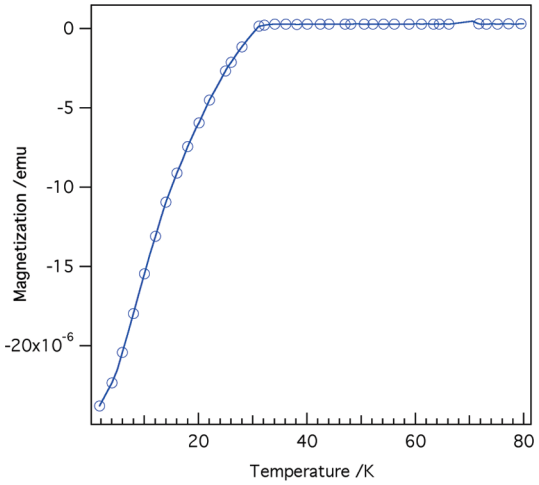

Figure 2. DC magnetization as a function of temperature for the MgB_2 nanohelices under an applied field of 25 Oe.

The samples for the magnetic measurements were prepared by carefully "peeling" off the film containing the nanohelices from the surface of the substrate. Magnetic studies were performed with a SQUID magnetometer on samples containing an ensemble of predominantly nanohelices. The DC magnetization as a function of temperature shows a repulsion of magnetic flux with an onset temperature of ~32 K (Figure 2), indicating superconducting behavior of the nanohelices. Estimation of the Meissner fraction in the sample yielded a value of around 40%. The transition is very broad when compared to that observed with our previously reported bulk-grown nanowires with a T_c of 39 K.[9] We are in the process of determining whether the shift of T_c is a result of the coiled geometry of the product or due to impurities or other factors.

Nanocoiling has been often observed in carbon nanotubes[10] and other inorganic materials including BC,[11] SiO_2,[12] SiC,[13] AlN,[14] ZnO,[15] InP,[16] SnO_2,[17] GeTe,[18] and ZnS[19] among which ZnO is the most widely studied. Unlike the piezoelectric ZnO helices that have a rectangular cross-section and are formed from flat nanobelts, the MgB_2 nanohelices are primarily composed of circular nanowires, implying that the growth mechanism might be different from the polar surface driven kinetic model proposed for ZnO. We briefly discuss the plausible formation mechanism of the MgB_2 nanohelices in the following. However, it should be noted that since the nanohelices did not show clear fringes in the HREM, it is difficult to estimate the growth direction and exact mechanism of helix formation at this stage.

The chemical reaction for MgB_2 formation can be written as

$$Mg + B_2H_6 \rightarrow MgB_2 + 3H_2$$

Mg metal melts at ~650 °C and forms droplets of melt where the Mg chips touch the Si wafer. These Mg droplets on the Si surface or on the Mg chip act as *self-catalysts* for vapor−liquid−solid (VLS) growth that controls the dimensionality of the growing MgB_2 phase. We propose that the helical geometry of the product is the result of perturbations caused by introduction of screw dislocations (SD) at the catalyst−wire interface combined with the offsetting of the catalyst droplet from the axis of the nanowire, thus creating a nonzero torque at the interface and leading to an asymmetric growth front. As the catalyst particle is offset from the axis of the nanowire following the formation of an SD, a contact angle is created at the interface. It has been suggested by McIlroy et al.[11] that the contact angle between the catalyst particle and the growing nanostructure determines whether a nanowire or nanocoil will be grown from the catalyst particle. Further reaction and self-catalyst-assisted growth from this stage leads to the formation of the MgB_2 nanohelices. The helices show a circular cross-section and several have bulbous or beaded tips (see Figure S5), providing support for this kind of catalyst mediated growth. The SD can be formed at any stage during the growth resulting in a variety of coil morphologies encountered in the product such as coil(s) emanating from a straight nanowire, branched coils, and intertwined loops. The SD can be oriented either clockwise or counter-clockwise resulting in the formation of both right and left-handed helices. Previous studies suggest that certain growth conditions can introduce SDs into the MgB_2 lattice.[20] The continuous growth of the B layer, which contains the strongest bonds in the material, via the SD provides a facile nanowire growth mechanism; however, the built up strain associated with the misalignment of the layers away from the SD causes the nanowire to bend and reduces the crystalline order in the nanowire. The structural distortion may also be a factor in the slightly lower T_c of the nanohelices.

In conclusion, we have grown superconducting nanohelices of MgB_2 ($T_c \approx 32$ K) on various substrates. An interesting and useful feature of the MgB_2 nanohelices is that their growth does not require any foreign catalyst particle as in classical VLS growth (the growth is self-catalyzed by Mg), thus minimizing the possibility of catalyst substitution (possibly altering T_c). Superconducting nanocoils and solenoids (with iron nanorod cores) may have practical applications as nanoactuators or in flexible superconducting cable.

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Supporting Information Available: Powder XRD, EDS analysis along some additional SEM images of the MgB_2 nanohelices. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Nagamatsu, J.; Nakagawa, N.; Muranaka, T.; Zenitani, Y.; Akimitsu, J. *Nature* **2001**, *410*, 63.
(2) Jin, S.; Mavoori, H.; Bower, C.; van Dover, R. B. *Nature* **2001**, *411*, 563.
(3) Kumakura, H.; Matsumoto, A.; Fujii, H.; Togano, K. *Appl. Phys. Lett.* **2001**, *79*, 2435.
(4) Zeng, X.; Pogrebnyakov, A. V.; Kotcharov, A.; Jones, J. E.; Xi, X. X.; Lysczek, E. M.; Redwing, J. M.; Xu, S.; Li, Q.; Lettieri, J.; Schlom, D. G.; Tian, W.; Pan, X.; Liu, Z-K. *Nat. Mater.* **2002**, *1*, 1.
(5) Finnemore, D. K.; Ostenson, J. E.; Bud'ko, S. L.; Lapertot, G.; Canfield, P. C. *Phys. Rev. Lett.*, **2001**, *86*, 2420.
(6) Larbalestier, D. C.; Cooley, L. D.; Rikel, M. O.; Polyanskii, A. A.; Jiang, J.; Patnaik, S.; Cai, X. Y.; Feldmann, D. M.; Gurevich, A.; Squiteri, A. A.; Naus, M. T.; Eom, C. B.; Hellstrom, E. E.; Cava, R. J.; Regan, K. A.; Rogado, N.; Hayward, M. A.; He, T.; Slusky, J. S.; Khalifah, P.; Inumaru, K.; Haas, M. *Nature* **2001**, *410*, 186.
(7) Tsuda, S.; Yokoya, T.; Kiss, T.; Takano, Y.; Togano, K.; Kito, H.; Ihara, H.; Shin, S. *Phys. Rev. Lett.* **2001**, *87*, 177006.
(8) (a) Wu, Y.; Messer, B.; Yang, P. *Adv. Mater.* **2001**, *13*, 1487. (b) Yang, Q.; Sha, J.; Ma, X.; Ji, Y.; Yang, D. *Supercond. Sci. Technol.* **2004**, *17*, L31. (c) Ma, R.; Bando, Y.; Mori, T.; Golberg, D. *Chem. Mater.* **2003**, *15*, 3194.
(9) Nath, M.; Parkinson, B. A. *Adv. Mater.* **2006**, *18*, 1865.
(10) Amelinckx, S.; Zhang, X. B.; Bernaerts, D.; Zhang, X. F.; Ivanon, V.; Nagy, J. B. *Science* **1994**, *265*, 635.
(11) (a) McIlroy, D. N.; Zhang, D.; Kranov, Y.; Norton, M. G. *Appl. Phys. Lett.* **2001**, *79*, 1540. (b) McIlroy, D. N.; Alkhateeb, A.; Zhang, D.; Aston, D. E.; Marcy, A. C.; Norton, M. G. *J. Phys.: Condens. Matter* **2004**, *16*, R415.
(12) Qu, Y.; Carter, J. D.; Guo, T. *J. Phys. Chem. B* **2006**, *110*, 8296.
(13) Zhang, H. F.; Wang, C. M.; Wang, L. S. *Nano Lett.* **2002**, *2*, 941.
(14) Wang, H.; Northwood, D. O.; Han, J.; Du, S. *J. Mater. Sci.* **2006**, *41*, 1697.
(15) Gao, P. X.; Ding, Y.; Mai, W.; Hughes, W. L.; Lao, C.; Wang, Z. L. *Science* **2005**, *309*, 1700.
(16) Shen, G. Z.; Bando, Y.; Zhi, C. Y.; Yuan, X. L.; Sekiguchi, T.; Golberg, D. *Appl. Phys. Lett.* **2006**, *88*, 243106.
(17) Yang, R.; Wang, Z. L. *J. Am. Chem. Soc.* **2006**, *128*, 1466.
(18) Yu, D.; Wu, J.; Gu, Q.; Park, H. *J. Am. Chem. Soc.* **2006**, *128*, 8148.
(19) Moore, D.; Ding, Y.; Wang, Z. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 5150.
(20) Liao, X. Z.; Serquis, A.; Zhu, Y. T.; Peterson, D. E.; Mueller, F. M.; Xu, H. F. *Supercond. Sci. Technol.* **2004**, *17*, 1026.

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