Superconducting NbSe$_2$ nanowires and nanoribbons converted from NbSe$_3$ nanostructures

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(Received 18 May 2005; accepted 22 August 2005; published online 27 September 2005)

We describe the synthesis of superconducting NbSe$_2$ nanowires and nanoribbons by the nondestructive removal of Se from one-dimensional NbSe$_3$ nanostructure precursors. We report scanning electron microscopy imaging, x-ray diffraction, and transmission electron microscopy analyses of the morphology, composition, and crystallinity of the converted NbSe$_2$ nanostructures. Transport measurements on individual nanowires/ribbons confirm their superconductivity with $T_c \sim 7.2$ K, and the appearance of current-induced resistance steps is attributed to localized phase slip centers, akin to those reported in other superconducting nanostructures. © 2005 American Institute of Physics. [DOI: 10.1063/1.2072847]

One-dimensional (1D) nanostructures in the form of wires, ribbons, and tubes have received steadily growing attention due to their unusual properties and application potentials which are superior to their bulk counterparts.\cite{1} Due to the confinement of Cooper pairs and supercurrent flows, new phenomena, such as quantum phase slips\cite{2–4} and quantum switch effects,\cite{5} are expected to appear in 1D superconductors. Furthermore, 1D superconducting nanostructures are also highly desirable in future nanodevices as electrical connections. Numerous efforts have been made to synthesize superconducting nanostructures.\cite{6–14} The most common approach is to use nanochannels in porous membranes as templates to form metal nanowires of Pb (Refs. 6–8) and Sn (Refs. 8 and 9) through electrodeposition. Other methods include the fabrication of MoGe (Refs. 3 and 4) and Nb (Ref. 10) nanowires by sputtering them onto bridges of carbon nanotubes. Progress has also been made in synthesizing Pb nanowires by thermal decomposition of lead acetate in ethylene glycol (Ref. 11) and directly growing Pb nanowires onto graphite substrates at high electrodeposition reduction potentials.\cite{12} Superconducting nanowires of MgB$_2$ have also been fabricated by annealing B nanowires in Mg vapors.\cite{13,14}

Superconducting NbSe$_2$ crystals have been used in recent years as a model system to study vortex dynamics.\cite{15–18} Therefore, it is of interest to pursue the physics of confinement effects in 1D superconducting NbSe$_2$ nanostructures. Furthermore, superconducting NbSe$_2$ nanostructures are far more stable at ambient atmosphere than oxophilic Pb, Sn, and Nb nanostructures, thus avoiding problems of surface oxidation that are normally encountered in metal nanowires.

NbSe$_2$ nanotubes and nanoribbons were observed when sintering NbSe$_3$ powders under inert gas flow, and NbSe$_2$ nanowires were also obtained through a solution-based synthesis approach.\cite{19,20} The NbSe$_2$ nanostructures synthesized with these methods are quite small (a few nm to tens of nm in diameters). Vortex confinement studies in superconductors require the sample cross section to be comparable with the penetration depth (230 nm at zero temperature and increases with increasing temperature). Recently, we developed a convenient and controllable way to synthesize monocrystalline NbSe$_2$ nanowires and nanoribbons.\cite{21} Here, we report the synthesis and characterization of a new class of 1D superconductors — NbSe$_2$ nanowires and nanoribbons by the transformation of NbSe$_3$ nanostructures. Their transverse dimensions range from about 10 nanometers to submicrometers. The synthesized NbSe$_2$ nanoribbons can provide a new platform for pursuing novel confinement phenomena, such as “few vortex rows” physics\cite{22} in 1D superconductors.

Crucial to this conversion process is the balance of two competing reactions. On the one hand, the removal of Se from NbSe$_3$ occurs at high temperatures, but on the other hand, these high temperatures can lead to the destruction of the nanostructures. Annealing NbSe$_3$ in flowing inert gas above 300 °C caused selenium to bleach out of the NbSe$_3$.\cite{19} However, there is no convenient way to monitor the composition change during annealing NbSe$_3$. Therefore, it is difficult to control the conversion of NbSe$_3$ into NbSe$_2$ nanowires with this approach. In fact, we typically obtained nanowires and nanoribbons of NbSe$_3$, when annealing NbSe$_3$ nanostructures in flowing argon or nitrogen atmospheres, probably due to the unavoidable residual oxygen in the argon gas or to oxygen outgassing from the quartz tube itself.

The controlled conversion from NbSe$_3$ into NbSe$_2$ nanostructures was realized in an evacuated quartz tube containing a stoichiometric proportion of NbSe$_3$ nanostructures and Nb powder which satisfied the chemical equilibrium reaction $2\text{NbSe}_3 + \text{Nb} \rightarrow 3\text{NbSe}_2$. Upon heating, the selenium bleaches out of NbSe$_3$ and is absorbed by the Nb powder. The bleaching automatically terminates once the Nb powder is completely consumed. In experiments, we placed NbSe$_3$ nanostructures\cite{21} on one end of the quartz tube and a stoichiometric amount of Nb powder at the center of the tube, approximately 5 cm away from the NbSe$_3$ nanostructures. The tube was evacuated and purged repeatedly with ultrahigh-purity argon gas. The ampoule was then sealed under an inert gas and heated to a fixed temperature at the rate of 3 °C/min, held at a temperature for various times, and then cooled down at 2 °C/min to room temperature.

We found that a temperature between 600 °C and 700 °C enabled the conversion from NbSe$_3$ to NbSe$_2$ while preserving the shapes of the NbSe$_3$ nanostructures. Figure 1 depicts the x-ray diffraction (XRD) patterns of the NbSe$_3$ nanostruc-

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The highest temperature for preserving the shapes of NbSe$_3$ nanostructures is about 700 °C. At higher temperatures, microrods and platelike structures can be observed. This maximum temperature coincides with the decomposition temperature of NbSe$_3$.

However, it can also be the decomposition temperature of NbSe$_2$ nanostructures, though bulk NbSe$_2$ decomposes at 840 °C. According to the above discussions on the conversion at low temperatures, NbSe$_2$ shells should start to form on NbSe$_3$ wires at 600 °C. It takes about 30 min to ramp up to 700 °C with the applied ramping rate of 3°C/min. Therefore, NbSe$_2$ shells should be thick enough to maintain the shapes of the NbSe$_3$ nanostructures after NbSe$_3$ cores decompose at 700 °C. A lower decomposition temperature of the converted NbSe$_2$ nanostructure can be caused by a high density of defects, such as dislocations and/or grain boundaries, which can appear because the atoms have to adjust their positions during the conversion. Although nearly perfect patterns, as shown in Fig. 3(a), were observed in the selected area electron diffractions (SAEDs), we did found a high density of grain boundaries through high-resolution transmission electron microscopy (TEM) imaging. The convergent beam electron diffraction (CBED) patterns and Kikuchi lines, as shown in the insets of Fig. 3(b) also identify the existence of misoriented microcrystallines with respect to the background along the thickness direction, e.g., in the area a of the nanoribbon. We found similar microcrystallines distributed throughout the sample.

A superconducting quantum interference device magnetometer was used to characterize the superconductivity of the converted NbSe$_2$ nanostructures (in an amount of mg). The critical temperature ($T_c$) for samples annealed at temperatures of 630 °C and above, was found to be close to 7.2 K, the typical value for bulk samples. For samples which show a small percentage of NbSe$_3$ phase in the XRD patterns, $T_c$ decreases with increasing amount of NbSe$_3$. This can be considered as indirect evidence of the formation of the NbSe$_2$/NbSe$_3$ shell/core structure which leads to lower $T_c$ due to the proximity effect.

Transport measurements were conducted to investigate the superconductivity of individual nanowires. The inset of Fig. 4(a) shows a NbSe$_2$ nanowire with two gold contacts. The applied magnetic field is perpendicular to the plane. Figure 4(a) shows the temperature dependence of resistance at various applied magnetic fields. The critical temperature of this single NbSe$_2$ nanowire is 7.05 K at zero field. From these resistance versus temperature curves, one can determine the critical temperature of NbSe$_2$. The traces of 630 °C and above, was found to be close to 7.2 K, the typical value for bulk samples. For samples which show a small percentage of NbSe$_3$ phase in the XRD patterns, $T_c$ decreases with increasing amount of NbSe$_3$. This can be considered as indirect evidence of the formation of the NbSe$_2$/NbSe$_3$ shell/core structure which leads to lower $T_c$ due to the proximity effect.

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shown in Fig. 4(b), resistance steps also occur in the $R$-$I$ curves of the converted NbSe$_2$ nanowires.

In conclusion, we have successfully converted NbSe$_3$ nanowires and nanoribbons into superconducting NbSe$_2$ nanostructures through a controlled Se-reduction approach. The conversion takes place in the narrow reaction temperature range of 600 °C–700 °C. Both magnetization and transport measurements confirm the superconductivity of the converted NbSe$_2$ nanostructures, which have critical temperatures reaching the bulk value of 7.2 K. Confinement-induced enhancement of the critical fields and resistance steps in the $R$-$I$ characteristics were observed in the synthesized NbSe$_2$ superconducting nanowires and nanoribbons.

This work was supported by the US Department of Energy, BES-Materials Science, Contract no. W-31-109-ENG-38. One of the authors (Z. L. X) also acknowledges support from the U.S. Department of Education. The scanning/transmission electron microscopics were performed in the Electron Microscopy Center at Argonne.

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