NANO LETTERS

2008
Vol. 8, No. 5
1382-1385

Extracting Superconducting Single-Crystal Nb Mesowires Out of $NbSe_2$ by a Crystal-Lattice Collapse Method

Jian-Min Li†

Department of Physics, Zhejiang University, Hangzhou 310027, People's Republic of China

Received January 14, 2008; Revised Manuscript Received March 1, 2008

ABSTRACT

The author reports a conceptually new approach to superconducting niobium (Nb) mesowires in high yields from layered compounds ($NbSe_2$) by solid-state pyrolysis. High-resolution transmission electron microscopy and selected-area electron diffraction demonstrate that the mesowires are single crystalline, grow along the [001] direction, and have specific facets. Unlike the previous electrodeposition routes within templates, a possible vapor−solid interaction mechanism was first proposed for component-selective epitaxial growth of one-dimensional Nb lattices where vapor-assisted collapse of $NbSe_2$ crystal structure occurs through disposing of Se vapor phase matrix at enhanced temperatures.

Superconducting wires, well-known as carrying electricity without any loss of power, are extremely important for the current quest of low-dissipation electronics miniaturization.[1] Compared to the early development of commercial superconducting wire (Nb-47 wt % T_i being most common) by Westinghouse in 1962, nanostructuring of superconductors,[2,3] particularly creation of tiny dimension low-temperature superconducting wires with existing materials, e.g., Pb,[4] Nb,[5] Zn,[6] Sn,[7] and Bi[8] nanowires, remains a key materials challenge for superconducting nanowire-based quantum-state engineering.[9,10] Nb is a known type II metallic element superconductor with maximum superconducting transition temperature (T_c) of around 9.3 K,[11] which is attractive for making the so-called nanoSQUIDs (superconducting quantum interference devices).[12] However, until now, it has failed to obtain high-quality monocrystalline element superconducting nanowires because the high melting point of element Nb (2477 °C) entails that it probably cannot be evaporated by conventional thermal evaporation. Here, we report that superconducting single-crystal (SC) niobium (Nb) ultrafine wires, of diameter on the nano-to-mesoscale ($10^{-9}-10^{-6}$ m), were thermally extracted from inorganic layered compound niobium diselenide ($NbSe_2$) powders. In contrast to previously followed routes to superconducting nanowires or whiskers, for example, by electrodeposition routes within templates,[6–10] and "top-down" nanolithographic technique,[13] this novel cost-efficient "bottom-up" approach enables cheap and mass productionof one-dimensional (1D) mesoscopic SC superconductor feasible. Methodologically speaking, the simple templateless or lithography-free technique with meso- and nanostructuring capabilities is technologically interesting where the pure element superconducting Nb ultrafine wires were selectively "pulled out" from bulk $NbSe_2$ precursor during a reactive heating process, accompanied by vapor-assisted collapse of $NbSe_2$ crystal structure by expelling Se. Because of small size, these ideal superconducting SC mesowires can be predictably used as nanoengineered components for smaller electrical power conversion applications and at the same time allow us to explore mesoscopic and nanoscale physics.

We synthesized Nb mesowires by a standard iodine chemical vapor transport method[14] starting with a mixture (10:10:1 by weight) of commercial powders of $NbSe_2$ (Alfa-Aesar 99.8%), iodine (Fluka AG) and activated charcoal (Fluka). An ampule (10 mm diameter × 120 mm in length), fabricated from a quartz tube which had been cleaned, was vacuum sealed (1.5×10^{-5} Torr) and placed in the central part (high-temperature zone) of a horizontal tubular electric furnace (Supporting Information). The addition of activated charcoal is to produce a reductive environment avoiding the possible oxidization. After the growth, almost all gaseous species (e.g., iodine, Se) in an evacuated quartz ampule were deposited on the inside wall of the ampule by rapid quenching to room temperature. The optimal growth condition was found when the furnace (temperature gradient of 10 °C cm^{-1}) was slowly heated (rate of 4 °C/min) from

† E-mail: phyjmli@zju.edu.cn or jmli_yn@yahoo.com.

10.1021/nl0801273 CCC: $40.75
Published on Web 04/02/2008

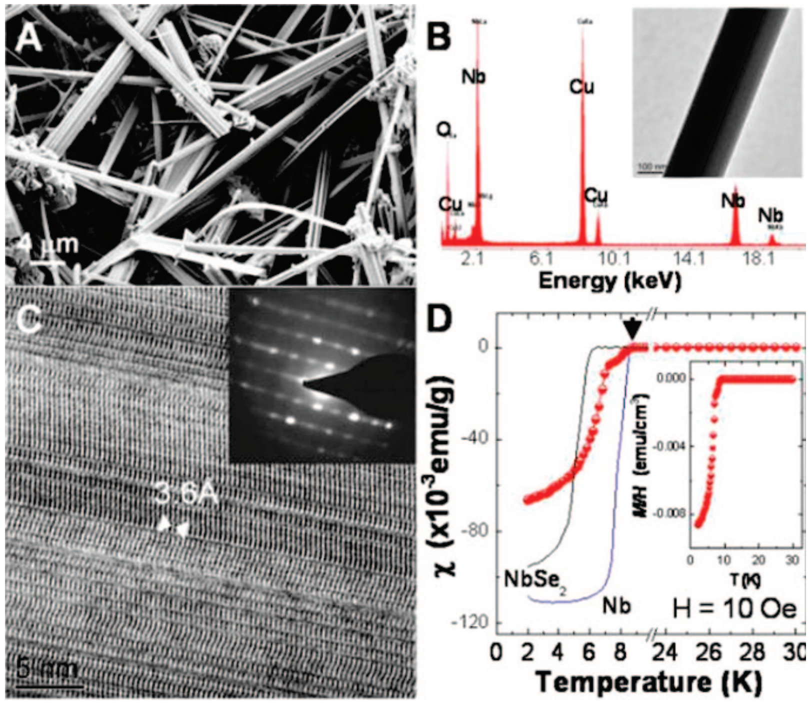

Figure 1. Production of Nb monocrystalline superconducting mesowires with faceted morphologies in high yields. A, Scanning electron micrograph (LEO SUPRA55VP) of the mesowires (note the material's resistance to bending). B, A typical EDAX spectrum of a single Nb mesowire. Cu signals are from copper grid supporting the mesowire. Inset, low-magnified TEM image from a single Nb mesowire. C, Typical atomic-resolution HRTEM (Philips CM120-FEG at 120 kV) image of an individual Nb mesowire, showing the perfect cubic packing structure (space group $Pm3m$, $a = 3.3$ Å). Inset, SAED pattern from a single Nb mesowire indicates single-crystallinity. D, Mass susceptibility as a function of temperature ($\chi(T)$ plot with red half-open/solid marks) of a bundle of Nb mesowires powder. The dark arrow represents T_c. Inset, Volume susceptibility as a function of temperature for zero field cooled Nb mesowire sample.

ambient temperature up to 830 °C for 2.5 h; subsequently the ampule was dragged out of the furnace.

Figure 1A shows the scanning electron microscopy (SEM) image obtained from a dark-gray sample collected from the high-temperature region. These 1D mesowires have uniform diameters mostly of 200 nm to 2 μm and lengths of 60−100 μm. The elemental chemical analysis via energy dispersive X-ray spectroscopy (EDAX) spectrum taken from an individual mesowire shows that the synthesized products are pure, containing mainly Nb, and very little oxygen (Figure 1B). The corresponding selected area electron diffraction (SAED) pattern (the inset of Figure 1C showing a SC feature) can be indexed to a body-centered-cubic (bcc) structure. A representative high-resolution transmission electron microscopy (HRTEM) image of a vapor-grown mesowire crystal's longitudinal edge reveals a defect-free structure where disorder is notably absent in the image (Figure 1C). The adjacent lattice planes were about 3.6 Å, indicating preferential growth along the crystallographic [001] direction. Moreover, it should be noted that the Nb wires seem to have specific facets, these being the lowest energy facets. In general, the driving force for spontaneously sidewall faceting of metastable crystals is the surface free energy. For Nb, a bcc metal, it is common for {110} to be the planes of least surface free energy.[15] To the best of our knowledge, this 1D faceted Nb nanowire morphology has never been reported, which is probably due to the synthesis method. Despite the nanofaceting of the sidewall, further nanocharacterization (while tilting) reveals the mesowire is SC in nature (Figure 2 and Figure S3).

The magnetization measurements were performed by the zero-field-cooling method in a commercial dc Quantum Design SQUID magnetometer (MPMS2) in an applied field of 10 Oe. The experiments were carried out using the as-prepared sample (without any purification with quantity of 1.35 mg in total) which is inside a capsule. As shown in Figure.1D, the existence of superconductivity of the resultant Nb mesowires is confirmed by the strong *Meissner* effect[11] at $T_c \sim 8.8$ K, which is slightly below the T_c of bulk Nb. Compared to well-known bulk superconductivity, the broadening and depression of the T_c could be due to the nanosize effect[16,17] and contamination by impurities such as O, respectively. For reference, measurements of starting materials $NbSe_2$ (solid line) and pure Nb (Alfa-Aesar 99.99%) powders (blue line) were made. From the inset of Figure 1D, the yield of Nb mesowires is quantitatively estimated by dimensionless volume susceptibility to approximately 10.4% (of $-1/4\pi$).

Without any purification, all the resultants for further characterization were dissolved in an ethanol solvent while iodine was cleaned. The powder X-ray diffraction (PXRD) measurements of the reactant, resultant, and remains were performed using a Japan Rigaku RU200 D/MAX 2400 type rotating anode X-ray generator (40 kV, 150 mA) with Cu K_a radiation ($\lambda = 1.518$ Å) at a fixed incident angle ($\theta = 4°$). A highly textured (001) reflection peak was observed

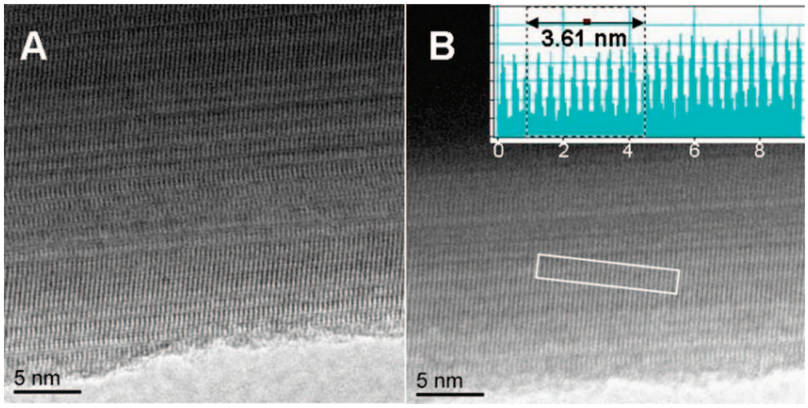

Figure 2. HRTEM images of an individual Nb mesowire, taken at different tilting angles of 0° (A) and +20° (B). The cubic lattice feature of the edge of a mesowire can be clearly visible in (A and B). Inset in (A) represents its corresponding in situ fast Fourier transform. Inset in (B) is the line profile of the frame area in (B) showing an interlayer spacing of 3.61 Å.

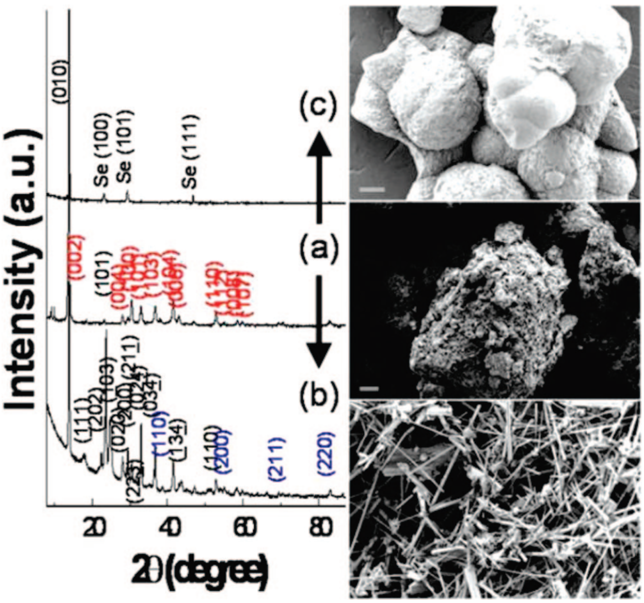

Figure 3. PXRD patterns of (a) starting stoichiometry materials, (b) remaining products collected at high-temperature region, and (c) evaporation products collected at the low-temperature region. The black, blue, and red diffraction peaks are indexed from Nb_2Se_9 (JCPDS 33-0968), Nb (JCPDS34-0370), and $NbSe_2$ phases (JCPDS, 19-0872), respectively. Right columns, corresponding SEM images from (a−c), respectively. Scale bars represent 10 μm.

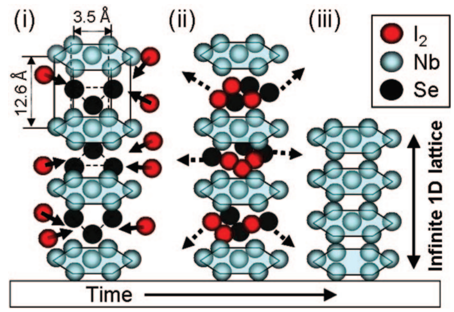

Figure 4. Component-selective epitaxial growth of Nb 1D nanostructure by vapor-assisted crystal-lattice collapse route of layered compound $NbSe_2$. (i) I_2 (as transporting agent) vapor invasion or intercalation into $NbSe_2$ (space group *P*63/*mmc*, the precise chemical formula is 2*h*-$NbSe_2$, ideally a local ABAB stacking arrangement of the basal planes in 2*h*-$NbSe_2$, *h* stands for hexagonal) hexagonal unit cell made easy because of the spacious room $c/a \geq 3.64$ (with lattice constants $a = 3.446 \pm 0.005$ Å and $c = 12.55 \pm 0.01$ Å). (ii) The formation of “liquid-like” Se−I mixture layers presumed in the structure of $NbSe_2$ and subsequently rapid removal of partial Se atomic sheets by evaporation. (iii) Collapse of $NbSe_2$ crystal structure into infinite 1D Nb lattice after Se vapor phase matrix extraction at enhanced temperatures.

in the as-grown Nb mesowires, which is consistent with the HRTEM result. The phase analysis demonstrates that Se is missing from the starting material, and phase separation happens in the Nb-rich phase (e.g., Nb precipitation) and Se-rich phase (e.g., Nb_2Se_9 remaining), that is, $NbSe_2 \rightarrow$ Se (evaporation) + Nb (left) + Nb-deficient phase (e.g., Nb_2Se_9).

The precise nature of the faceted superconducting Nb mesowires growing out of Nb atoms in reactant $NbSe_2$ precursor is not yet well understood. Because no metal catalysts or any other type of additive was used during synthesis in this work, the growth is different from the traditional vapor−liquid−solid mechanism.[18] Considering that hexagonal sandwich-type layered compound $NbSe_2$ are weakly coupled by van der Waals forces,[19] based on the above experimental results, we propose the following possible vapor−solid interaction mechanism for the production of mesoscopic superconducting Nb SC wires from $NbSe_2$, as depicted schematically in Figure 4. The noncatalytic vapor transport process includes the following: (i) When both iodine and $NbSe_2$ particles are heated in this closed-tube vacuum environment, the iodine particles first start to melt at 113.7 °C and then diffuse on the surface and penetrate into large lattice-spaced $NbSe_2$ particles through an injection of small radius iodine vapor-phase (I_2, boiling point, 184.3 °C). The “liquid-like” Se−I mixture layers are presumed to form in the structure of $NbSe_2$. (ii) Because Se has also a lower melting point (221 °C), the enhanced interdiffusion and immediate coevaporation of the “liquid-like” Se−I melts occur since the reaction temperature is above the boiling point. As a result, it leads to a fast selective removal of Se atomsheets, separated by hexagonal layers of Nb atoms, from the starting material by vapor extraction at elevated temperatures, and subsequent condensation on the low-temperature end of the quartz tube. (iii) At 830 °C, the melting point of

Nb is too high (2477 °C) to be evaporated, and the remaining Nb atoms in the starting $NbSe_2$ become supersaturated and dissociate continuously. At the suitable temperatures, Se atoms evaporate without replenishment, and eventually the component of Se can be almost completely expelled and only pure Nb left in principle provided that the efficient carrier iodine and time are met. Due to interfacial surface energy minimization, Nb atoms accumulate and grow into 1D Nb mesowires along the [001] direction of a bcc structure.

In conclusion, as a potentially cheap and easy way, we report the first preparation of superconducting single-crystal Nb mesowires pulled from transition-metal dichalcogenide 2*h*-$NbSe_2$ by crystal-lattice collapse. The discovery of iodine chemical vapor removal of Se in $NbSe_2$ demonstrates the possibility of making 1D mesoscopic element Nb superconductors directly from pyrolytic $NbSe_2$ compound precursors. The superconducting mesowires hold great promise as basic components for developing potential nano/mesocryoelectronics that require "cool" high-current transporting capability. Finally, and most significantly, we are trying to determine whether this meso-fabrication can be applied to other superconductive-element-containing layered families of materials.

Acknowledgment. This work was financially supported by PCSIRT (Grant No. IRT0754), the "Qianjiang Talent Project" (Grant No. QJD0702003) of Zhejiang Province, the PhD Programs Foundation of the Ministry of Education of China (Grant No. 20070335208), SEM, SRF for ROCS, SEM, and Education Office of Zhejiang Province (Grant No. 20070052). The author acknowledges the hospitality of Professor R. Tenne while visiting the Weizmann Institute of Science, Israel, and the technical help from Dr. Gregory Leitus for the SQUID measurements.

Supporting Information Available: Figures showing the schematic diagram of the temperature profile, diagram of the apparatus used for the mesowire growth, SEM and TEM images of the Nb mesowires, and SAED pattern images of an individual mesowire at different tilting angles. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Foltyn, S. R.; Civale, L.; MacManus-Driscoll, J. L.; Jia, Q. X.; Maiorov, B.; Wang, H.; Maley, M. *Nat. Mater.* **2007**, *6*, 631.
(2) Bezryadin, A. C.; Lau, N.; Tinkham, M. *Nature* **2000**, *404*, 971.
(3) Rogachev, A.; Wei, T.-C.; Pekker, D.; Bollinger, A. T.; Goldbart, P. M.; Bezryadin, A. *Phys. Rev. Lett.* **2006**, *97*, 137001.
(4) Yi, G.; Schwarzacher, W. *Appl. Phys. Lett.* **1999**, *74*, 1746.
(5) Rogachev, A.; Bezryadin, A *Appl. Phys. Lett.* **2003**, *83*, 512.
(6) Wang, J. G.; Tian, M. L.; Kumar, N.; Mallouk, T. E *Nano Lett.* **2005**, *5*, 1247.
(7) Tian, M. L.; Wang, J. G.; Kurtz, J. S.; Liu, Y.; Chan, M. H. W.; Mayer, T. S.; Mallouk, T. E. *Phys. Rev. B* **2005**, *71*, 104521.
(8) Tian, M.; Wang, J.; Kumar, N.; Han, T.; Kobayashi, Y.; Liu, Y.; Mallouk, T. E.; Chan, M. H. W. *Nano Lett.* **2006**, *6*, 2773.
(9) Doh, Y. J.; van Dam, J. A.; Roest, A. L.; Bakkers, E. P. A. M.; Kouwenhoven, Leo, P.; Franceschi, S. De *Science* **2005**, *309*, 272.
(10) Hopkins, D. S.; Pekker, D.; Goldbart, P. M.; Bezryadin, A. *Science* **2005**, *308*, 1762.
(11) Bennemann, K. H.; Ketterson, J. B. *The Physics of Superconductors*; Springer-Verlag: Berlin, Heidelberg, 2004; Vol. *II*.
(12) Troeman, A. G. P.; Derking, H.; Borger, B.; Pleikies, J.; Veldhuis, D.; Hilgenkamp, H. *Nano Lett.* **2007**, *7*, 2152.
(13) Sadki, E. S.; Ooi, S.; Hirata, K. *Appl. Phys. Lett.* **2004**, *85*, 6206.
(14) Kershaw, R.; Vlasse, M.; Wold, A. *Inorg. Chem.* **1967**, *6*, 1599.
(15) Herring, C. *Phys. Rev.* **1951**, *82*, 87.
(16) Giordano, N. *Phys. Rev. Lett.* **1988**, *61*, 2137.
(17) Bose, S.; Raychaudhuri, P.; Banerjee, R.; Vasa, P.; Ayyub, P. *Phys. Rev. Lett.* **2005**, *95*, 147003.
(18) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(19) Lévy, F. *Physics and Chemistry of Materials with Layered Structures*; D. Reidel Publishing Co.: Dordrecht, 1979; Vol. 6.

NL0801273