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Template Synthesis of MoN Superconducting Nanowires

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We have demonstrated a new facile method for the controllable synthesis of high quality single-phase MoN nanowires with T_c 10.5 K from $Mo_6S_2I_8$ nanowires templates. The MoN nanowire diameters were controlled exclusively by the $Mo_6S_2I_8$ nanowires template diameters, which were in the range between several tens and several hundreds of nanometers in this study. Furthermore, we have demonstrated that Ohmic contacts can be prepared on δ_3-MoN nanowires with ion beam induced platinum deposition using an FIB, allowing detailed characterization of the superconducting and transport properties of MoN nanowires. In addition, we have demonstrated straightforward synthesis of porous δ_3-MoN nanowires and nanotubes from MoS_2 nanotubes. X-ray diffraction, scanning electron microscopy with wave dispersive analysis, transmission electron microscopy, four probe electrical transport measurements and SQUID were used to characterize the starting nanowires and nanotubes and the final products.

Keywords: Nanowires, Superconductivety, Nitride, Molybdenum

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1. INTRODUCTION

The unique physical and chemical properties of the transition metal nitrides prove them as an important class of materials for the fundamental and technological applications in diversified areas [1,2] Among these nitrides, molybdenum nitrides have been extensively studied as well-known transition-metal nitrides for applications of superconducting devices [3,4] and active catalysts [5,6].

Molybdenum forms several crystalline nitrides including γ-Mo_2N (cubic), β-Mo_2N (tetragonal) and hexagonal β-MoN [7,8]. Among these, hexagonal δ_3-MoN is on the most interesting due to its potential uses in capacitors [9] and wear protective surface coatings [10] and because of its relatively high superconducting critical temperature of 12–14 K in the bulk [11,12]. Molybdenum nitrides have been synthesized in a number of different ways [12, 13, 14]. δ_3-MoN can be prepared by a reaction of Mo metal with ammonia at 700 °C and has been characterized by Hägg [15] with a hexagonal unit cell. Furthermore, bulk δ_3-MoN was prepared by ammonolysis of $MoCl_5$ or MoS_2 at 825 °C [12]. Recently there have been reports of synthesis of different phases of MoN nanoparticles [16,17], short nanowires [18] and nanotubes [19], but reliable single-phase synthesis is still not available. Novel synthesis routes for obtaining phase-pure material, and particularly superconducting δ_3-MoN nanowires, are thus of great interest from a fundamental point of view, as well as for diverse potential applications.

The properties of thin superconducting nanowires are also of great fundamental interest, in particular for investigations of, possible increases of T_C due to confinement [20] and superconductor to metal/insulator transition due to pair breaking [21]. It has been shown previously that MoSI nanowires have unique optical and electronic properties [22] and can act as precursor material for bulk production of several types of molybdenum-based nanowires and nanotubes, including Mo nanowires [23], MoS_2 nanotubes [24] and MoO_{3-x} nanowires [25]. Here we report on the synthesis and characterization of superconducting δ_3-MoN nanowires produced by a novel, yet straightforward, template-based transformation from $Mo_6S_2I_8$ molecular wire bundles and MoS_2 nanotubes.

2. EXPERIMENTS AND METHODS

MoSI nanowires based on $Mo_6S_2I_8$ material were used as precursor crystals. We synthesized the $Mo_6S_2I_8$ nanowires directly from elements at 1070 °C as described previously [24]. The reaction resulted in several-millimetre-long needles having a diameter from several tens to a few hundred nanometres. $Mo_6S_2I_8$ nanowires were sulphurized at 800 °C for two hours in flowing Ar gas containing 1% of H_2S and 1% of H_2 resulted in coaxial MoS_2 nanotubes [24]. To synthesize MoN nanowires, $Mo_6S_2I_8$ bundles and MoS_2 nanotubes were placed inside a tube furnace and annealed to temperatures between 700 and 825 °C in a constant flow of argon and ammonia in different volume ratio. Total flowing rates of gas mixtures passed through the quartz tube were around 40 cm³/min, and controlled by mass flow controllers (MKS). The final temperatures were kept for next few hours, and left to cool down to room temperature. After cooling, the samples were removed from the argon/ammonia atmosphere and placed inside a dry box. Materials were observed and analyzed by scanning electron microscope (SEM, Jeol JSM-7600F) equipped with energy dispersive spectrometer (EDS), high-resolution transmission electron microscope (HR-TEM, Jeol JEM-2100F, 200 keV) equipped with energy dispersive spectrometer (EDS). TEM grids were prepared with immersion of Formvar/carbon coated copper grid directly in nanowire dispersions. The x-ray powder diffraction pattern, obtained on a Siemens D-5000 diffract meter (Cu Kα radiation, Bragg–

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Brentano geometry, variable divergence and antiscatter slits). For electrical measurements, wires with different diameters were dispersed in isopropanole for 10 min in an ultrasonic bath and centrifuged at 300*g* to have the heavy agglomerates removed through sedimentation. The remaining dispersion was spray-cast on a silica substrate and examined under SEM. Focused ion beam (FIB)—induced platinum deposition was performed using beams with 30 kV acceleration voltage and a current of 80–430 pA with an FEI Helios NanoLab 600i. The thickness of the deposition was roughly 1 μm and was chosen to make the circuit robust enough to withstand the mechanical strain caused by the differential contraction of the sample and substrate during cooling to low temperatures. The temperature electrical measurements were performed with an Oxford 7 T Spectromag PT in the range from 300 to 2 K. The resistance measurements were carried out with the four-contact method using a Keithley 6221/Keithley 2182A setup. Magnetization measurements were performed with a Quantum Design MPMS-XL-5 SQUID magnetometer.

3. RESULTS AND DISCUSSION

Molybdenum nitride nanowires fabricated with annealing of $Mo_6S_2I_8$ nanowires at temperatures between 730 ºC and 825 ºC and fabricated at relatively low ammonia gas flow 10 - 15 ml/min are composed of several different crystal structures. XRD spectra of these nanowires revealed δ_3-MoN, Mo_5N_6 and Mo_2N crystal structures, where hexagonal δ_3-MoN phase was the main component (Fig.1a,b). After the temperature was adjusted to 825 ºC, similar to the previously published data [12], ammonia gas flow was increased to 30 ml/min and the reaction time was prolonged to 5 hours, XRD spectra confirmed that the obtained material was δ_3-MoN phase [12] with only very small amount of impurities as shown in Fig, 1c.

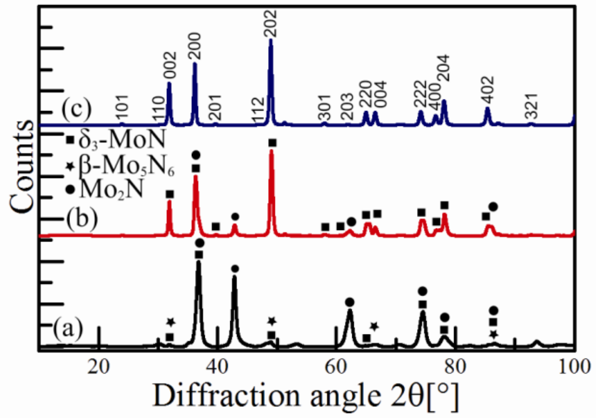

Fig. 1 – XRD spectra of MoN nanowires synthesised at different temperatures and ammonia flows

The quasi-one-dimensional morphology is preserved during the transformation from $Mo_6S_2I_8I$ nanowires to δ_3-MoN nanowires, but a change in the shape of the wire has been observed. While MoSI bundles nanowires have more round cross section, MoN nanowires seem to have rhomboid cross section, which is an indicator of a hexagonal crystal structure.

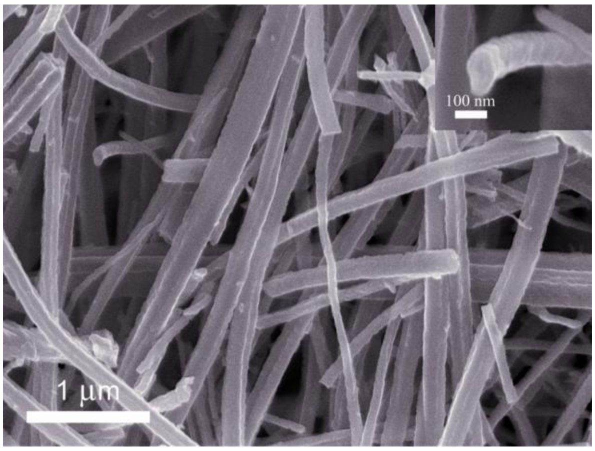

Fig. 2 – SEM images bundles of δ_3-MoN nanowires

MoS_2 nanotubes annealed at the same conditions for five hours resulted porous δ_3-MoN nanowires and open-end MoN nanotubes as shown in Fig. 3. Also during this process of transformation the diameters of the nanotubes were preserved. The XRD spectrum of the resulted material confirmed the presence of δ_3-MoN crystal structure.

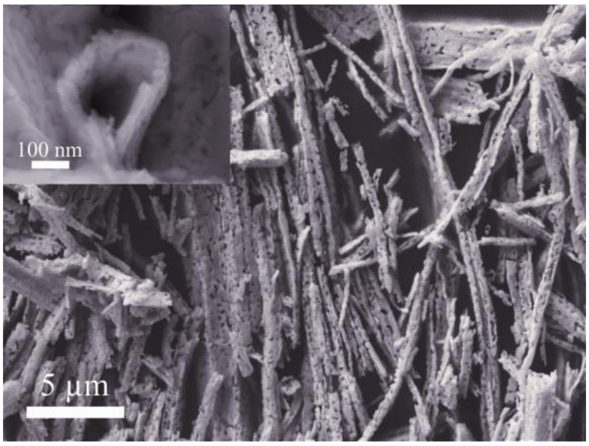

Fig. 3 – SEM images of porous δ_3-MoN nanowires and nanotubes fabricated from MoS_2 nanotubes

The nanowire samples fabricated from MoSI nanowires were compressed using a pneumatic press. The brittle nature of the material prevented us from obtaining high density pellets, without the addition of an adhesive, so the density of the compressed wires was ~3.7 $mg\,mm^{-3}$, considerably lower than the bulk theoretical density of 9.2 $mg\,mm^{-3}$. The corresponding magnetization measurements and calculated susceptibility as $\chi = M/H$ are shown in figure 3. Magnetic susceptibility measurements were performed in the measuring field of 100 Oe and the results revealed a superconducting transition at 10.5 K with a strong diamagnetic signal. We estimate that the percentage of the SC phase for the δ_3-MoN material produced from MoSI approaches 100%. The actual percentage of the SC phase is higher because we were unable to completely compress the wire material to obtain a truly bulk sample for susceptibility measurements.

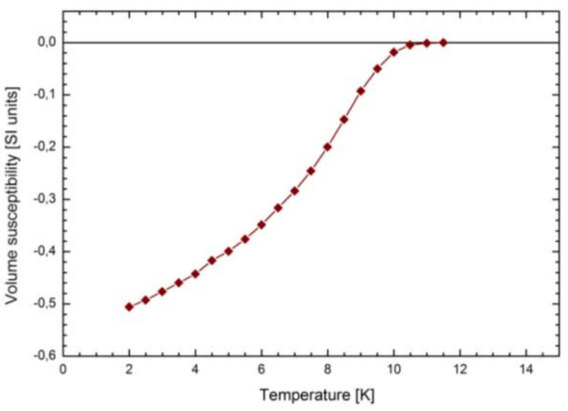

Fig. 3 – Magnetic susceptibility measurement of high density MoNnanowires pellet obtained from $Mo_6S_2I_8I$ precursor

For electrical measurements of individual nanowires the MoSI nanowires were dispersed in isopropanole as decribed previously and sprayed on a silica substrate. These substrates were annealed under the same conditiones as bulk material resulted δ_3-MoN nanowires. We chose FIB deposition of the electrodes to avoid the contamination of the wires with various chemicals used during standard e-beam/laser lithography procedures that could alter properties of the wires. An SEM image of a typical circuit with FIB-deposited around 900 nm thick Pt electrodes on top of a single MoN wire with dametrs around 200 nm is shown in Fig.4.

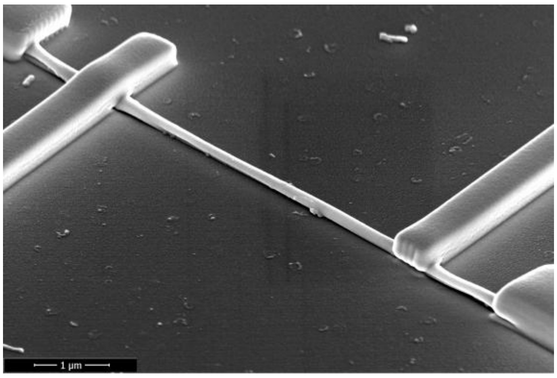

Fig 4 – An SEM image of a circuit with FIB-deposited around 900 nm thick Pt electrodes on top of a single MoN wire with dametrs around 200 nm.

Four-point resistance measurements (Fig.5) show a zero field SC transition at 10.5 K and confirmed the superconductivety of the individual MoN nanowires.

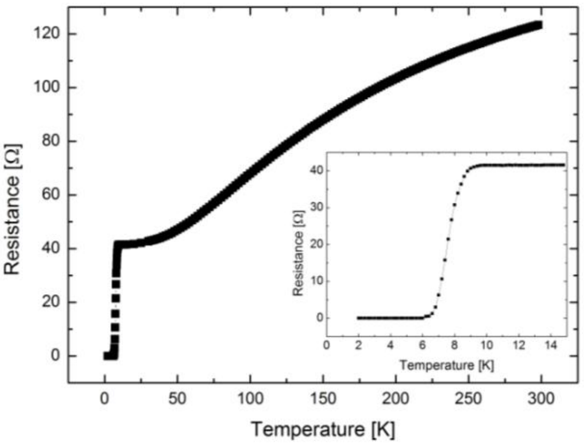

Fig. 5 – Temperature dependence of the resistivity of a wire in the range from 300 to 2 K

Comparison of two and four probe measurements shows that the Pt/MoN contacts prepared by FIB exhibit no Schottky barriers (*I*–*V* characteristics are linear), and have a contact resistance of around several kΩ.

4. CONCLUSION

We have demonstrated a new facile method for the controllable synthesis of superconducting high quality single-phase δ_3-MoN nanowires from $Mo_6S_2I_8$ nanowires templates and MoS_2 nanotubes by annealing in flowing ammonia gas at temperature around 825 ºC. The MoN wire diameters were controlled exclusively by the MoSI and MoS_2 template diameters. Furthermore, we have demonstrated that Ohmic contacts can be prepared on δ_3-MoN nanowire with ion beam induced platinum deposition using an FIB, allowing characterization of the superconducting and transport properties of δ_3-MoN nanowires. The investigationes of the nanowire diameter effect on the magnetic susceptibility and measurements of resistivity in a magnetic field (parallel and perpendicular to the wire direction) are in progress.

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