

Large Scale Synthesis of Highly Pure Single Crystalline Tellurium Nanowires by Thermal Evaporation Method

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Single crystalline tellurium nanowires were successfully synthesized in large scale by a facile approach of vaporizing tellurium metal and condensing the vapor in an inert atmosphere onto a Si substrate. Tellurium was evaporated by heating at 300 °C at 1 torr and condensed on the Si substrate at 100–150 °C, in the downstream of argon (Ar) gas at a flow rate of 25 sccm for 30 min. The as-synthesized nanowires have diameters between 100–300 nm and lengths up to several micrometers. The single crystalline nanowires grew in a preferred [0001] direction. The obtained nanowires were highly pure as only tellurium metal was used in the vaporization process, and no other reagent, surfactant, or template were used for the growth. This low temperature and high-yield approach to the tellurium nanowires synthesis may facilitate its industrial production for various applications.

Keywords: Single Crystalline Metal Nanowires, Tellurium, Vapor-Phase Synthesis.

1. INTRODUCTION

Owing to their possible novel applications such as fabrication of nanodevices, gas sensors, biosensors etc., single crystalline one-dimensional (1D) metallic nanostructures have attracted much interest.^{1–5} Among the reported methods for the synthesis of 1D nanostructures, vapour-phase synthesis is probably one of the most widely used.^{6–8} But it is mainly employed for the synthesis of metal oxides, metal sulfides or other systems, and only a few reports are available for metal 1D nanostructures.^{6–8} While several approaches have been reported for the synthesis of metal nanowires, most of these are based on wet chemical methods.^{1–5} Tellurium (Te) is a narrow-bandgap semiconductor with bandgap energy of 0.35 eV and it has been considered as an excellent candidate for the future high-efficiency photoconductors, thermoelectric and piezoelectric devices.^{2,9–19} Many functional materials such as CdTe, Bi₂Te₃ etc. can also be synthesized by the reaction of tellurium with other elements. The crystal structure of Te is highly anisotropic with covalently bonded atoms forming unique helical chains. These chains are bound through weak van der Waals interactions and form hexagonal lattices. This anisotropic crystal structure induces

tellurium towards a 1D growth leading to nanowires morphology.^{2,9–19}

Xia and coworkers reported the synthesis of various 1D Te nanostructures in wet chemical methods.^{2,9} Recently, several other approaches such as solvothermal synthesis,¹⁰ microwave assisted synthesis,¹¹ biomolecules assisted synthesis,^{12,13} and other wet chemical synthesis of 1D tellurium nanostructures are also reported.^{14–16} However, the vapor phase synthesis of 1D Te nanostructures is not common. In a particular vapor phase synthesis, tubular structures of Te with micrometer diameters were formed.¹⁷ Using a similar vaporization method, Geng et al. synthesized tellurium nanobelts by reacting Al₂Te₃ powder with H₂O in a horizontal tube furnace at a high-temperature of 500 °C.¹⁸ Metraux and Grobety have demonstrated the synthesis of Te nanotubes by a physical vapor deposition method, using an induction furnace.¹⁹

In this article, we report the synthesis of single crystalline tellurium nanowires by a facile low temperature (300 °C) vaporization method. Most of the reported 1D tellurium nanostructures were synthesized using surfactant, biomolecules, other precursors or some special experimental techniques.^{2,9–19} In the present method, we used only highly pure (99.99%) tellurium powder as precursor for the growth of the single crystalline nanowires. The nanowire morphology of tellurium could potentially improve or

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modify its fascinating electrical, electronic or thermoelectric properties.

2. EXPERIMENTAL DETAILS

The synthesis of the tellurium nanowires was carried out in a 1 inch diameter horizontal quartz tube furnace whose central temperature was held at 300 °C. The nanowires were deposited on the Si substrate placed downstream (about 2–3 inches) from an alumina boat filled with 0.3 g of tellurium powder (99.99%, Aldrich). Before the start of the reaction, the chamber was evacuated to 0.3 torr and then purged with argon (Ar) gas at a flow rate of 25 standard cubic centimeters per minute (sccm) for 30 minutes. In the steady state, the Ar flow rate and the pressure of the chamber were 25 sccm and 1.0 torr, respectively. Then the furnace was heated to 300 °C at a rate of 20 °C per minute. Grayish-black films were deposited all over the Si substrate after a deposition time of 30 min. The as-synthesized products were employed for various characterizations.

Field emission scanning electron microscope (FESEM) images of the as-synthesized Te nanowires were taken on a Phillips XL30S. Transmission electron microscope (TEM), high resolution TEM (HRTEM) images, selected area electron diffraction (SAED) pattern, and energy-dispersive X-ray spectrum (EDS) were studied on a Jeol JEM-2100F transmission electron microscope operated at 200 kV. X-ray diffraction (XRD) pattern of the specimen was recorded on a Rigaku D/max-rc (12kW) diffractometer operated at 40 kV voltage and 80 mA current with filtered 0.15405 nm $\text{Cu}_{K\alpha}$ radiation. X-ray photoelectron spectroscopy (XPS) measurements of the specimen were carried out on an ESCA 2000, V.G. Microtech UK, at a pressure of 1×10^{-9} torr using the Mg K_{α} line with a photon-energy of 1253.6 eV.

3. RESULTS AND DISCUSSION

Thermal evaporation of Te metal below its melting point and at a low pressure of 1 torr, and condensation of the vapor at a suitable temperature onto a substrate led to highly pure nanowires in high yield. Figure 1 is the FESEM image showing an overview of the as-synthesized nanowires. Their diameter varies between 100–300 nm with lengths extended up to several micrometers. Some of the nanowires are lying on the substrate where as most of them are close to vertical to the substrate with an inclined angle. The crystal structure of the obtained nanowires was studied with XRD. Figure 1(b) shows a typical XRD pattern of the obtained Te nanowires. All the peaks in the diffractogram were indexed as being due to the hexagonal crystal structure of Te (JCPDS file no 36-1452). The peak positions are fairly matched with the standard values. The most intense peak at interplanar spacing $d = 0.2343$ nm is due to the reflection from (102) crystal plane. The second

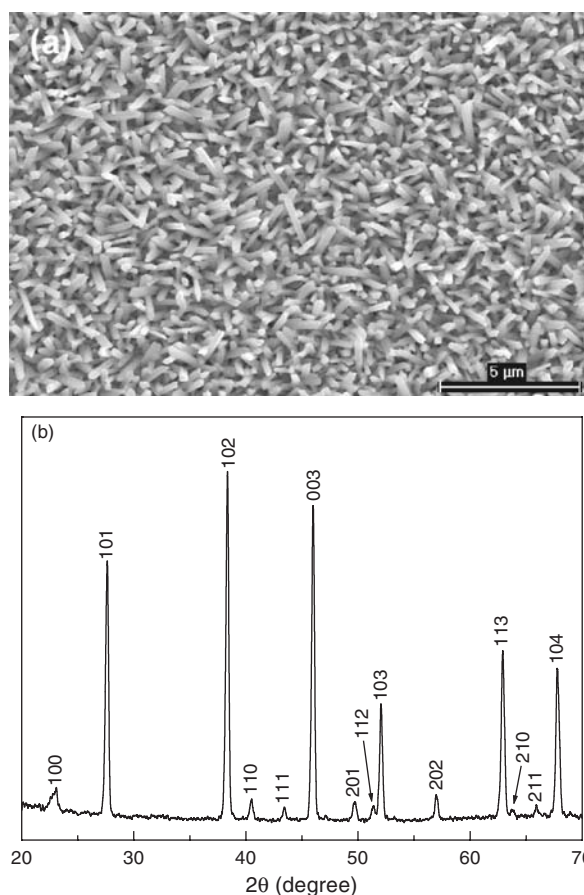


Fig. 1. (a) FESEM image of tellurium nanowires deposited on Si substrate kept at 100–150 °C by heating tellurium powder at 300 °C for 30 min. (b) XRD pattern of the as-synthesized tellurium nanowires.

most intense peak at $d = 0.1969$ nm is due to the reflection from (003) crystal plane. In the standard diffraction file the (003) peak is observed with an intensity of $\sim 9\%$ with respect to the most intense peak. But in the present case it appears as the second most intense peak with an intensity of $\sim 90\%$ compared to the most intense (102) peak. This enhancement of the intensity of (003) peak imply the possibility of growth of the nanowires along [0001] direction. In the next section of this article, the HRTEM image and the SAED pattern were used to study the single crystallinity and growth direction of the obtained tellurium nanowires.

The elemental composition of the as-synthesized nanowires was studied with EDS and the XPS spectrum. The EDS spectrum shown in Figure 2(a) indicates that the nanowires were highly pure. A few extra peaks were observed from copper and carbon because of the use of carbon coated copper grid for sample preparation. In the high resolution XPS spectrum shown in Figure 2(b), the presence of two peaks at 573.06 and 583.46 eV (as against the standard value of 573.1 and 583.49 eV) due to $3d_{5/2}$, $3d_{3/2}$ binding energies, respectively, confirms the purity of the nanowires. These two peaks have a separation

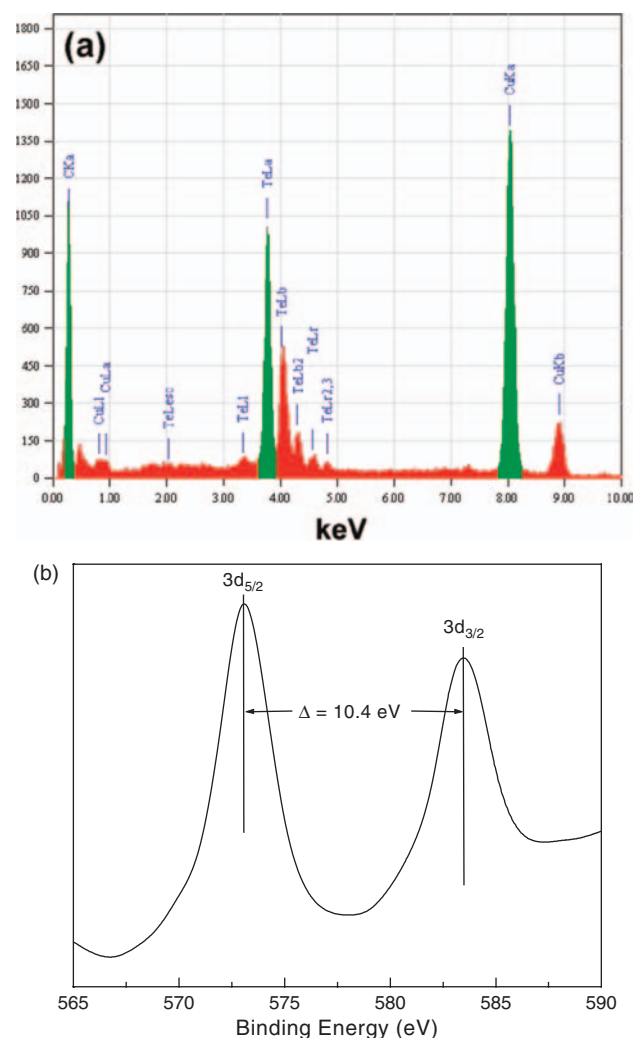


Fig. 2. (a) EDS pattern of the tellurium nanowires demonstrating the high purity of the specimen. (b) High-resolution XPS spectrum of the as-synthesized nanowires.

$\Delta = 10.4$ eV which agrees well with the standard value of $\Delta = 10.39$ eV in the elemental tellurium.²⁰

The TEM and the HRTEM micrographs of a representative nanowire are shown in Figure 3(a) and (b), respectively. The corresponding SAED pattern is given in the inset of Figure 3(a). The TEM image shows the morphology, and the HRTEM image and the SAED pattern were used in order to confirm the structure and the growth direction of the as-synthesized nanowires. The nanowire is straight with a diameter of ~ 160 nm which can be seen with the TEM image. The clear lattice fringes in the HRTEM image in Figure 3b indicate that the nanowire is structurally uniform and single crystalline. The interplanar spacing of ~ 0.59 nm is consistent with the (001) crystal plane and another interplanar spacing of ~ 0.22 nm is due to the (110) crystal plane which are perpendicular and parallel to the nanowire axis, respectively. These observations confirm that the nanowires are grown in the preferred

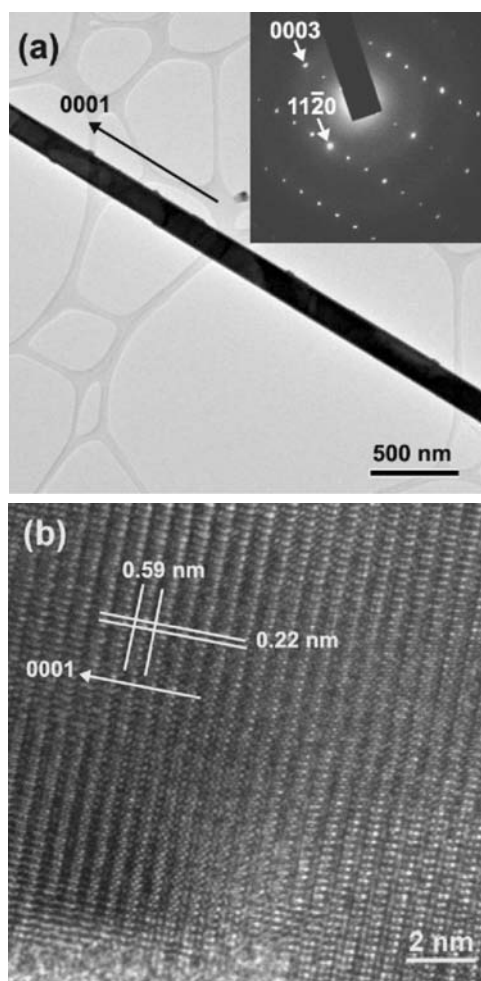


Fig. 3. (a) TEM and (b) HRTEM micrographs of a representative Te nanowire. The corresponding SAED pattern is given in the inset to (a). The nanowire grew along the [0001] direction as demonstrated with the HRTEM image and the SAED pattern.

direction of [0001]. This is further supported by the SAED pattern shown in the inset to Figure 3(a).

The formation of the Te nanowires can be explained through a vapor-solid (VS) growth mechanism. Typically, in a vapor-phase synthesis, the degree of the supersaturation controls the morphology of the obtained nanostructures.⁶ At a low degree of supersaturation nanowires were formed, and medium or high supersaturation favors growth of bulk crystal or powder, respectively.⁶ The supersaturation factor can be controlled by adjusting the experimental conditions such as temperature, pressure, and the proper dilution of Ar mixture. In the present case, the nanowires were formed through a VS mechanism because of the low degree of supersaturation of the tellurium vapor at the temperature region of 100–150 °C, which is much lower than the melting point (449.51 °C) of tellurium metal.⁶

Furthermore, the anisotropic crystal structure of Te induces a strong tendency towards the 1D growth. According to the Wulff facets theorem for the shape-control of a crystal growth, the relative specific surface energy of each

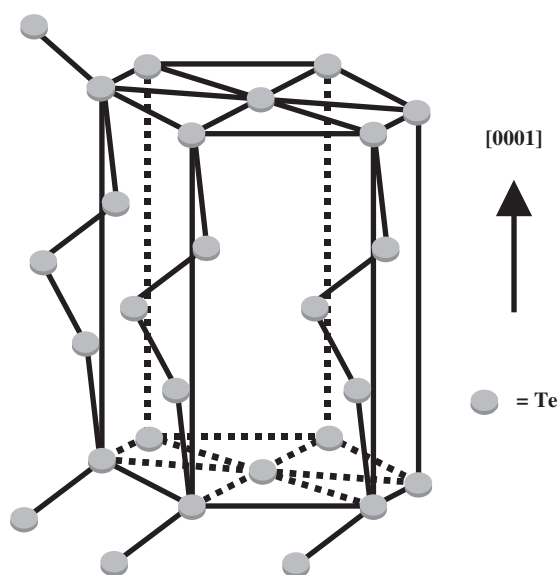


Fig. 4. Schematic representation of the tellurium crystal structure showing the anisotropy with a longer c -axis.

crystal facet determines the shape of the crystal, and favors the configuration with a minimum total surface energy.²¹ As shown with the schematic diagram in Figure 4, the crystal structure of Te is highly anisotropic with a longer c -axis. It has covalently bonded atoms forming unique helical chains which are bound through weak van der Waals interactions and form hexagonal lattices. Thus, the symmetry of basic crystal lattice of Te is reflected in single-crystalline nanowires with a preferred growth direction along c -axis.

4. CONCLUSION

In summary, we have successfully synthesized single crystalline tellurium nanowires by a vapor phase method. Free standing nanowires were grown in a regular [0001] direction on the Si substrate at a deposition temperature of 100–150 °C. The tellurium nanowires were very pure as only Te metal was involved in the growth process and no template or catalyst was used. The obtained nanowires can be potentially useful for the fabrication of nanodevices with

high performance and novel properties. Further studies on electrical transport and thermoelectric properties are under progress.

Acknowledgment: This work was supported by KOSEF(R01-2005-000-10711-0). TEM analysis was performed at the Korea Basic Science Institute in Daejeon.

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Received: 9 November 2005. Revised/Accepted: 11 February 2006.