Zn nanobelts: a new quasi one-dimensional metal nanostructure

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A large quantity of metal Zn nanobelts have been synthesized by a simple approach, which involves thermal decomposition of ZnS powder, followed by Zn deposition.

Low dimensional systems represent one of the most important frontiers in advanced materials research.1-3 Quasi one-dimensional (1D) nanostructured materials, such as nanowires and / or nanotubes, have been successfully synthesized and have received much attention due to their peculiar optical, electrical, thermoelectric properties and potential applications in nanodevices.4-7 Recently, semiconducting oxide nanobelts, a new group of 1D nanomaterials with a rectangular cross section, have been synthesized, and their morphology is distinctly different from those of nanowires and nanotubes.8 The nanobelts could be an ideal system for fully understanding dimensionally confined transport phenomena in functional oxides. Through confinement of metals to quasi one-dimension, a variety of changes in their characteristics are induced.9 Therefore, to fully study the fundamental physical and chemical properties of quasi-1D metal systems, the synthesis of metal nanostructures including nanowires, nanotubes and nanobelts are very important. Up to now, considerable effort has been focused on the synthesis of metal nanowires and nanotubes.9-14 However, there have been no reports about metal nanobelt synthesis. In this communication, we describe the fabrication of a new quasi-1D metal nanostructure: Zn nanobelts. Successful synthesis of Zn nanobelts will open up the possibility of fully studying physical and chemical properties of quasi-1D metal nanomaterial systems.

A silicon wafer (5 \times 10 mm) was used as a substrate for the growth of Zn nanobelts. The substrate was cleaned by a standard treatment in piranha solution (30% H₂O₂-20% H₂SO₄) and rinsed with de-ionized water. Yumoto et al. have used pure Zn metal bars as raw materials to fabricate Zn crystals.¹⁵ This method, however, can not produce quasi-one-dimensional Zn crystals such as ribbons or whiskers owing to the fast production of Zn vapor. The produced rate of Zn vapor formed from pure ZnS powder decomposition by thermal evaporation is much slower than the rate of Zn vapor from Zn powder.¹⁶ In order to control the produced rate of Zn vapor, pure ZnS and C powders were used as raw materials in our experiment to synthesize Zn nanobelts. The ZnS was mixed with graphite powder (mass ratio about 1:1) and placed in the middle of an alumina boat, and the cleaned Si substrate was placed next to the mixed starting raw powder along the downstream side of flowing argon. The alumina boat, covered with a quartz plate to maintain a higher vapor pressure, was placed in the center of a quartz tube that was inserted in a horizontal tube furnace. Prior to heating, the system was flushed with high purity Ar for 1 h to eliminate O₂, and pumped down to 5×10^{-5} Torr. Then, under a constant flow of high purity Ar gas (100 sccm), the furnace was rapidly heated to 1000 °C (about 5 min) and held at this temperature for 120 min, and subsequently cooled to room temperature. It was observed that white sponge-like products appeared on the surface of the Si substrate.

The synthesized products were characterized using scanning electron microscopy [(SEM) JEOL JSM-6300], X-ray diffraction diffractmetry [(XRD) MXP18AHF], high-magnification TEM [(HRTEM) JEOL-2010] and energy-dispersed X-ray

spectrometry (EDS). For HRTEM observation, the products were ultrasonically dispersed in ethanol and a drop of this solution was then placed on a Cu grid coated with a holey carbon film.

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SEM observation (Fig. 1a) revealed that the product consisted of a large quantity of wirelike nanostructures. XRD measurement (Fig. 1b) shows that the product is hexagonal structured Zn with lattice constants of a = 0.2655 nm and c =0.4928 nm, consistent with the standard values for bulk Zn.17 It should be noted that no diffraction peaks from ZnO or other impurities have been found in our samples. The morphology, structure and composition of the synthesized products have been characterized in detail using SEM, HRTEM, selected area electron diffraction (SAED) and EDS. A low-magnification SEM image (Fig. 2a) of the synthesized products shows that the wirelike nanostructures have typical lengths in the range of several to several tens of micrometers. A representative highmagnification SEM image (Fig. 2b) of a Zn wirelike nanostructure reveals that its geometrical shape is beltlike, distinct from previously reported nanowires and nanotubes, and its thickness is about 20 nm. It can be seen (Fig. 3a and b) that each nanobelt has a uniform width along its entire length, and the typical widths of the nanobelts are in the range 40-200 nm. No nanoparticles were observed at the ends of the nanobelts. The SAED pattern and HRTEM image (Fig. 3c) reveal that the Zn nanobelts are structurally uniform and single crystalline. The SAED pattern (Fig. 3c, inset) recorded perpendicular to the nanobelt long axis could be indexed for the [010] zone axis of



Fig. 1 (a) A typical SEM image of bulk of Zn nanobelts. A large amount of the nanobelts are distributed homogeneously on the Si substrate. (b) XRD pattern taken on the bulk of the Zn nanobelts. The numbers above the peaks correspond to the (hkl) values of the hexagonal structure.



Fig. 2 SEM images of the Zn nanobelts showing their geometrical shapes and thickness. (a) a low-magnification SEM image of the synthesized Zn nanobelts. (b) a high-magnification SEM image of a Zn nanobelt, revealing the shape characteristics of the belt.

single crystalline Zn and suggests that the nanobelt growth occurs along the <100> direction. In addition, Fig. 3c also shows a lattice-resolved HRTEM image of a Zn nanobelt with a width of *ca*. 100 nm; this image clearly reveals the (001) and (101) atomic planes with separations of 0.4894and 0.2099 nm, respectively. We have also used EDS to address the composition of the nanobelts. EDS analysis (Fig. 4) demonstrates that the nanobelts contain only Zn, and no any other element is found. The Cu peaks are generated by the copper grid.

The question arises as to how the Zn nanobelts are formed. There exist several models to explain the growth for crystalline whiskers including dislocation and vapor–liquid–solid (VLS) mechanisms.^{18–21} In the present case, however, none of the above mechanisms seem suitable to account for the growth of the Zn nanobelts. This is because first, no evidence of dislocations was found in our analysis, and second, there were no nanoparticles observed on any ends of the Zn nanobelts. In addition, the only source material used in our experiment is pure ZnS and graphite powder. Therefore, it is likely that the Zn nanobelts follow a growth mechanism similar to the vapor–solid



Fig. 3 TEM and HRTEM images of the Zn nanobelts: (a and b) images of several straight and twisted Zn nanobelts. (c) HRTEM image of a Zn nanobelt which shows that the nanobelts are single crystalline and free from dislocation and defects. (Inset) The corresponding electron diffraction pattern recorded with the electron beam perpendicular to the long axis of a belt, showing the growth direction to be < 100 >.



Fig. 4 EDX spectra recorded at the position of the white dot in Fig. 3b.

(VS) mechanism^{8–22} First, the unidirectional motion of the Zn atom cloud driven by the carrying gas is a key factor in the preferational 1D growth of the Zn nanobelts. Secondly, the relatively high-saturated vapor pressure of Zn guarantees the concentration of this element necessary for the further growth of the Zn nanobelts. The Zn vapor is generated by the reaction of eqn. (1) at high temperature (1000 °C):

$$ZnS(s) \rightarrow Zn(g) + S(g)$$
 (1)

$$C(s) + 2S(g) \rightarrow CS_2(g)$$
(2)

The Zn vapor is transported to, and deposited on, the surface of Si substrate in the relatively low temperature zone to form nanobelts due to the epitaxial growth of crystals. Meanwhile, the CS_2 vapor [eqn. (2)] is carried away from the furnace by the flowing Ar.

In conclusion, vapor transport has been employed to synthesize single crystalline Zn nanobelts with well-defined morphology distinct from those of metal nanowires and nanotubes. The synthesis of those single crystalline metal nanobelts may open up new possibilities for experimental and theoretical understanding of dimensionally confined transport phenomena of quasi-1D metal nanomaterials.

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