Synthesis and Growth of the Facet-tipped In_2O_3 Nanowires

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We report novel structures of the facet-tipped In_2O_3 nanowires (FTIONs) via a chemical vapor deposition (CVD) process. The FTIONs grow along [001] direction. These In_2O_3 nanostructures with special morphologies can be potentially useful in a variety of fields such as nanoelectronic devices and high-sensitivity gas sensors.

One-dimensional nanostructures including semiconductor oxide nanostructures have stimulated great interests due to their fundamental significance to the study of morphology-, size-, and dimensionality-dependent chemical and physical properties.[1,2] Among various semiconductor oxides, indium oxide (In_2O_3) is an important wide-band-gap transparent semiconductor ($E_g = 3.6\,eV$),[3] which has been widely used in window heaters, solar cells, gas sensors, and flat panel displays.[3] With the ongoing synthesis and applications based on the In_2O_3 nanowires, some complicated nanostructures, such as In_2O_3 nanobelts, In-filled In_2O_3 nanotubes, In_2O_3 nanopyramids, have been reported. However, studies on the fabrication of complex nanostructures of In_2O_3 have been relatively limited.

To date, the complicated nanostructures have initiated an exploding research field in which enormous efforts have been invested to ZnO and SnO_2, such as nanopropeller arrays and nanowire–nanoribbon junction arrays of ZnO,[4,5] SnO_2 nanoribbon networks, and so on.[6–8] On the basis of these complex nanostructures reported earlier, Wang, Ren, and Zhu and their respective co-workers have proposed that these novel structures could be applied in field emission, supercapacitors, sensors, and so on.[4–8] Hence, it is important to develop more researches on the complex nanostructures of In_2O_3, so that the particular nanostructures can be tailor-made towards desired functionality. Here, we report an efficient route for the fabrication of novel structures of In_2O_3: the FTIONs were prepared via a CVD process. To the best of our knowledge, In_2O_3 with such sharp tip nanowires have seldom been reported. Moreover, these peculiar crystallographically well-defined In_2O_3 nanostructures can have great potential in electronic devices,[9] such as field emission.

The FTIONs were fabricated by a CVD process. Pure In metal powders were placed at the center of an alumina tube that was inserted in a horizontal tube furnace. The evaporation was conducted at 680 °C. The fabrication was performed with heating time duration of 20 min. Ar flux was fixed at a constant flow rate of 80 sccm.

The morphologies of the as-fabricated products were examined by field emission scanning electron microscopy [(FESEM) JEOL JSM-6700F] equipped with an energy dispersive X-ray spectrometer (EDS), transmission electron microscopy (TEM) (JEM 200CX at 200 kV), high-resolution electron microscopy [(HRTEM) JEOL-2010 at 200 kV], and selected area electron diffraction (SAED).

Figure 1 shows the typical SEM images of the In_2O_3 nanostructures. The SEM image in Figure 1a shows a large quantity of nanowire structures obtained in the lower-temperature region of ca. 630 °C. These nanowires have diameters of 150–200 nm and lengths of several micrometers. The high-magnification images in set of Figure 1a give us a clear view of the tip of the nanowires and reveal that the nanowires with tetrahedral nanopyramids on the tips, which differ from the previous report on the In_2O_3 nanostructures.[10,11] All the pyramids at the top of the nanowires are well-faceted and possess extremely smooth facets. Figure 1b presents typical SEM image of the In_2O_3 nanostructures collected in the higher-temperature region of ca. 680 °C. The In_2O_3 nanowires with tetrahedral nanopyramids on the tips can be seen clearly. An SEM image of the FTIONs with different morphology is shown in Figure 1c. The wire part can appear an octagonal or a tetragonal prism shape. Figure 1d is the schematic drawing of the nanowire corresponding to Figure 1c from side view. From the geometry of the structures, it is obvious that the polyhedron (mostly partially truncated octahedron) at the top of the wire have the equivalent {111} faces. The nanowire with octagonal shape have four wide surfaces and four narrow surfaces. The wide surfaces, which face the edge of the polyhedron, are believed to be the {100} faces. While, the planes for the narrow faces are {110}, which face the (111) faces of the polyhedron. The other type of the wire has four surfaces, which are the equivalent {100} faces. It is determined that the faceted tipped nanowires grow along [001] direction.

TEM observations allow us to gain insight into further details of these structures. Figure 2a is a TEM image of a FTION, which indicates that the polyhedron shows an isosceles triangle shape with the presence of the {100} facet and the nanowire is too thick to be transparent to the electron beam. Upon detailed examination of the SAED pattern of the tip and the nanowire, it was found that they show the same SAED pattern. From Figure 2b, the SAED pattern can be indexed as the diffraction along the [100] zone axis of single-crystalline In_2O_3 with cubic structure, and indicates that the nanowire grows along the [001] direction. The HRTEM taken from the areas that are corresponding to a, b, c, and d of Figure 2a are shown in Figures 3a–3d, respectively. The HRTEM image shown in Figure 3d further confirms that (002) planes are perpendicular to the nanowires axis. It is worth noting that all the HRTEM images in the four parts are the same, which are consistent with the results of the SAED pattern, and there is no interface between the faceted tip and the stem of the nanowire; therefore, the nanowire is essentially a single crystal.

The growth of the FTIONs can be divided into two consecutive steps. In the first stage, after the indium is melted (the melting point of pure indium is 156.6 °C), the indium vapor is

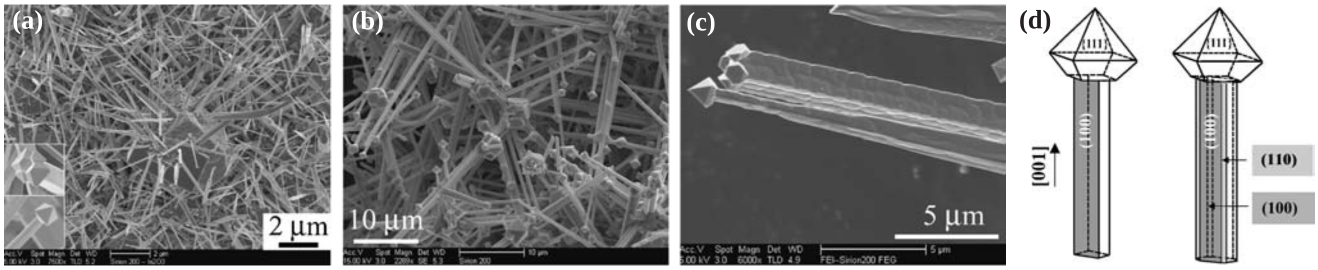

Figure 1. SEM images of The FTIONs: (a), (b) large scale of the In_2O_3 facet-tipped nanowires collected in lower-temperature region of ca. 630 °C and higher-temperature region of ca. 680 °C; (c) typical faceted tipped wires with different morphology; (d) schematic drawing of side view of a nanowire.

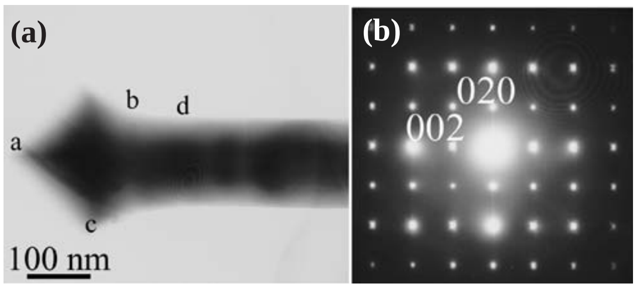

Figure 2. (a) Low-magnification TEM image of the nanowire; (b) the corresponding SAED pattern, with zone axis of [100].

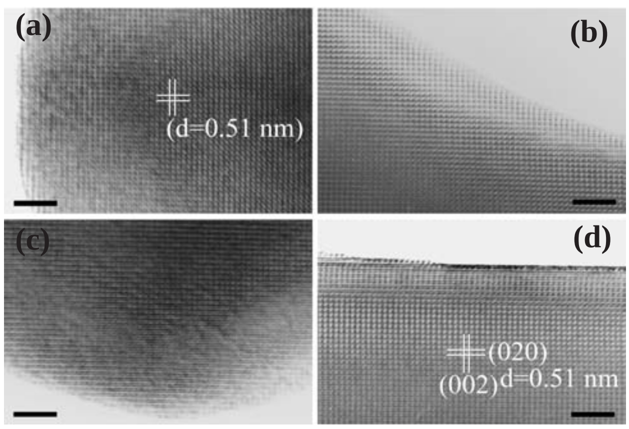

Figure 3. HRTEM images recorded from the nanowires corresponding to a, b, c, d in Figure 2a, respectively, showing that the nanowire is essentially a single crystal. Scale bar: 4 nm.

combined with the oxygen to form oxidized In clusters (the trace remnant of oxygen coming from the reaction system that was not eliminated completely by flushing with Ar and/or the leakage of the furnace). The clusters form big aggregates with the inclusion of the newly formed clusters. Upon the annealing, the aggregates act as the nucleation center for In_2O_3 octahedrons with {111} surface planes, similar to the nucleation and growth of MgO nanoflowers.[12] It has been pointed out that vapor pressure, supersaturation ratio, and surface energy are three important factors to the formation of different morphology.[13] Therefore, the pyramids with energy-stable {111} planes will be formed instead of the higher energy planes of {100} and {110}. It is essential that the big aggregates form first and act as the matrix (nucleation center) for the octahedron crystallites. Without the matrix, either nanowires or octahedrons alone will be formed.[14] In the second stage, before the complete formation of the octahedron, the supersaturation ratio of oxidized In vapor is still larger than what can feed the growth of octahedrons completely. Thus, the growth of the octahedrons was interrupted and the growth was forced to progress as In_2O_3 nanowires along ⟨001⟩. We have indeed observed the formation of the FTIONs in different stages (see Supporting Information for detail). From the SEM images, octahedrons at the nucleation stage (without the wire trunk) from the matrix particle can be clearly observed. Further evidence is that almost all the FTIONs end with the octahedron tip. This observation could not be possible for nanowires at rather different stages if the growth of the nanowires precedes that of the octahedrons.

In conclusion, facet-tipped nanowires have been fabricated successfully, which increase the versatility of the family of In_2O_3 products. The nanowires grow by a two-step process. We believe that the In_2O_3 nanostructures with special morphology here can be potentially used in a variety of fields such as nanoelectronic devices and in building high-sensitivity gas sensors.

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