Carbon-assisted Fabrication of Novel ATO Structures

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Novel antimony-doped tin oxide (ATO) structures, such as microships and quadrilateral microframes have been prepared by a carbon-assisted method in level tube furnace. Possible growth mechanisms of the as-prepared ATO microstructures are briefly discussed.

Novel morphology is one of the focuses of the nanomaterial researches owing to its special properties. In recent years, dozens of novel nanostructures have been fabricated,[1] such as ZnO nanocastles, nanohelices, and nanoflowers, zigzag-shaped Al_2O_3 nanobelts, MgO nanoflowers, nanowire arrays, and so on, but people will not stop their steps, and now, some of research teams turn their interests from the single matters to the multimatters or the doped matters (such as indium-doped tin oxide, antimony-doped tin oxide, fluorine-doped tin oxide, etc.). Antimony-doped tin oxide (ATO) is a famous multifunctional material which can be used as catalyst for the oxidation of phenol,[2] conductive transparent optical thin film,[3] electrochromic materials for printed displays,[4] radioactive waste management,[5] heat shields,[6] and so on. People have spent more vigor on the fabrication of ATO nanostructures and have explored several methods[7] including hydrothermal, coprecipitation, combustion, sol–gel and microemulsions, and so on. But it is very regretful that only nanoparticles and film were produced by these methods. So it is significative to search for new way to fabricate some new morphology.

In this paper, two novel ship- and quadrilateral frame-like ATO microstructures which have not been reported so far were produced by a chemical vapor deposition method using ATO nanoparticles and high-pure graphite as the source materials.

In a typical experiment, 0.3 g of mixtures of ATO nanoparticles and graphite (6:1 in weight) was located in an alumina boat which was put at the central of an alumina tube with 100 cm in length and 3 cm in inside diameter. Si wafers as the deposit substrates were located 12 cm away from the source materials. Then, the alumina tube was inset in the tube furnace and flushed by flowing Ar gas with the rate of 100 sccm (standard cubic centimeters per minute) for 2 h. After that, the system was quickly heated to 1150 °C in 10 min and kept at this temperature for 2 h; meanwhile, high-pure Ar gas as the carry and protect gas was introduced into the system at the rate of 100 sccm. When the system was gradually cooled to the room temperature, Si wafer with blue deposition was collected for testing.

The as-prepared samples were examined by energy dispersed spectroscopy (EDS), X-ray diffraction (XRD, Philips PW 1710 with Cu Kα radiation) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F).

Figure 1 shows EDS pattern of the sample in which five elements are found, C and Si come from the residual graphite carried by Ar gas from the source materials and silica wafer, respectively, Sn, Sb, and O with the atomic ratio of Sn and Sb of 4.27:7.87 come from the as-prepared sample. XRD spectrum (not shown here) can be indexed to the standard card of cassiterite (JCPDS 05-0469). So the ATO composition of the sample can be affirmed according to the EDS and XRD analysis.

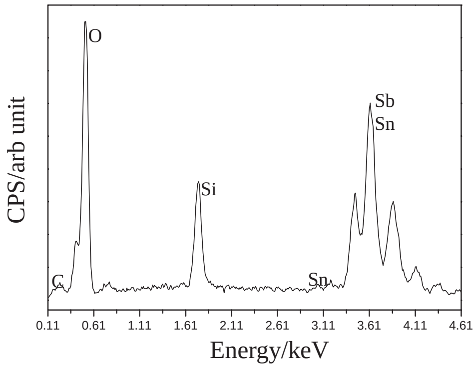

Figure 1. EDS spectra of the as-prepared sample.

Figure 2 shows SEM images of the sample. Figure 2a is a low-magnification image showing the scattered distribution of the ship- and quadrilateral frame-like ATO microstructures. Statistics from counting tens of these microstructures (see Supporting Information[10]) shows that the quantity ratio of the ship and quadrilateral frame is about 3:1. Figure 2b is the magnified image of the quadrilateral frame structure which is achiral and symmetrical in configuration and composed of four rims with the length, width, and thickness of 1 µm, 500 nm, and 60 nm, respectively. According to Figures 2c–2e, we find that each ship structure is composed of four side faces, two crossbeams and a hexagonal particle, and the sizes of the side faces and crossbeams are the same to the frames' rims. Figures 2c and 2d show a ship standing on a side face and two ships sharing one side face, respectively. Figure 2e is a planform of the ship which demonstrated that the profile of the ship is a rhombus with a couple of obtuse angles (111 degree) and acute angles (69 degree), and the ceiling of the ship which is composed of two crossbeams linking at the bisector of the acute angles is on the bisector of the obtuse angles and plumb to the base.

The following equations summarized the reactions involved in the growth process:

$$SnO_2 + C \rightarrow SnO + CO \quad (1)$$

$$2SnO \rightarrow SnO_2 + Sn \quad (2)$$

$$Sb_2O_4 + C \rightarrow 2SbO_x + CO \quad (3)$$

$$2SbO_x + O_2 \rightarrow Sb_2O_3 \quad (4)$$

$$Sb_2O_3 + O_2 \rightarrow Sb_2O_5 \quad (5)$$

When the system is heated to a relatively high temperature, SnO_2

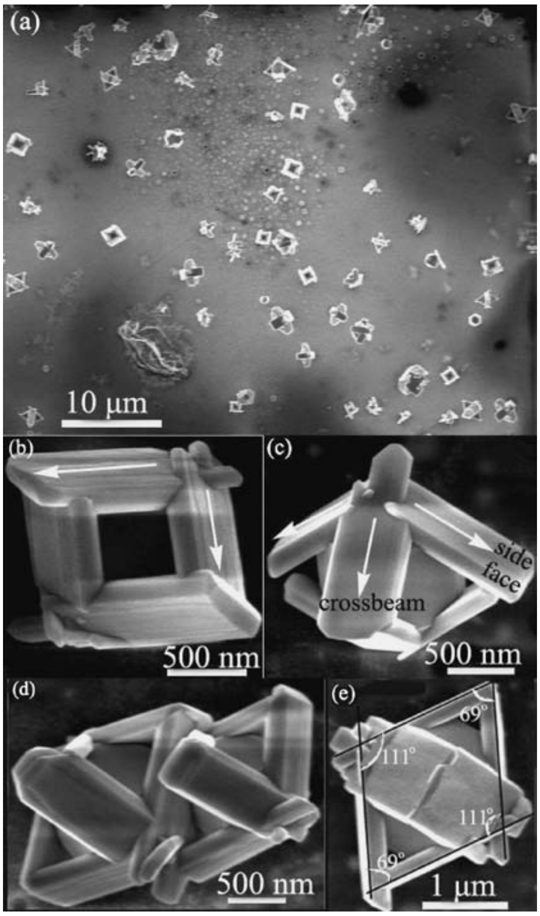

Figure 2. Low-magnification SEM image of the novel ATO microstructures (a), high-magnification SEM images of quadrilateral microframe (b), and microships (c), (d), (e).

and Sb_2O_4 (composed of Sb_2O_3 and Sb_2O_5) are reduced to SnO and SbO_x, respectively. SnO will disproportionate to SnO_2 and Sn owing to the metastable property.[8] SbO_x will be oxidized to Sb_2O_3 by the oxygen remained inside the system or leaked from the outside, and part of newly formed Sb_2O_3 will be further oxidized to Sb_2O_5. When the mixted vapor of SnO_2, Sb_2O_3, and Sb_2O_5 is carried to the deposition zone by the carry gas, Sb^{3+}, and Sb^{5+} from Sb_2O_3 and Sb_2O_5, respectively, will dope into SnO_2 molecules and form ATO structures duo to the impact of the molecules.[7]

The growth process of the microships can be separated into two steps: 1) the growth of the hexagonal cores, 2) the growth of the side faces and crossbeams. At the beginning of the thermal retardation course, owing to the high temperature and sufficient source materials, the supersaturation ratio of ATO vapor at the deposition zone was very high, so hexagonal particles in large size were formed;[9b] with the reactions going on, the source materials were depleted gradually, and the temperature began to decrease, so the concentration of ATO vapor decreased, but it still over supersaturation level. As we know, low supersaturation is propitious to the growth of 1D structures,[9] so the side faces and crossbeams of the ships grew along three preferred orientations (signed by three arrows in Figure 2c) in exactly fixed angles from the two most active opposite sides of the hexagonal cores and formed the so-called ships. The frame structures started their growth at the second growth step of the ship structures. When the side faces and crossbeams of the ships were growing, two rims of frames grew from an active nucleating point on the Si wafer along two preferred orientations (signed by two arrows in Figure 2b), owing to the polarity of the rims and in order to decrease the energy, these two rims will combine with other two rims grew from the nearby active nucleating point and formed the frame structure.

In summary, novel ship-like and quadrilateral frame-like ATO microstructures were produced by a carbothermal reduction route in a level tube furnace under the temperature of 1150 °C for the first time. The possible growth mechanisms were discussed.

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