Low-temperature growth and blue luminescence of SnO$_2$ nanoblades

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Large-scale SnO$_2$ nanoblades have been synthesized on a glass substrate covered with a 100-nm-thick SnO$_2$ buffer layer in a controlled aqueous solution at temperatures below 100 °C. Typical widths of the nanoblades were about 100–300 nm and the lengths were up to 10 μm, depending on the growth temperature. The thicknesses were about a few tens of nanometers. Transmission electron microscopy data, x-ray diffraction patterns, and x-ray photoelectron spectroscopy spectral analyses confirmed that the as-grown nanoblades had the phase structure of the rutile form of SnO$_2$ growing along the [110] direction. No other impurities, such as elemental Sn and tin oxides, were detected. An intense blue luminescence centered at a wavelength of 445 nm with a full width at half maximum of 75 nm was observed in the as-grown SnO$_2$ nanoblades, which is different from the yellow-red light emission observed in SnO$_2$ nanostructures prepared by other methods. It is believed that the strong blue luminescence from the as-grown SnO$_2$ nanoblades is attributed to oxygen-related defects that have been introduced during the growth process. © 2006 American Institute of Physics. [DOI: 10.1063/1.2235925]

Transparent and semiconducting tin oxide (SnO$_2$) has been widely used for optoelectronic devices, chemical sensors, dye-based solar cells, photoconductors, and transistors because of its excellent optical and electrical properties and chemical stability. As one-dimensional (1D) and quasi-one-dimensional (quasi-1D) nanostructures are expected to dramatically improve the desired properties of materials, considerable efforts have thus been devoted to the synthesis of SnO$_2$ nanowires, nanorods, nanotubes, and nanobelts via various routes. These include vapor-liquid-solid (VLS) catalytic growth, laser ablation, and thermal evaporation. However, these methods usually require high reaction temperature (>1000 °C) or complicated processing steps so that they are highly incompatible with low-cost flexible substrates such as polymers. In addition, SnO$_2$ nanostructures prepared by those methods are frequent mixtures of several distinct morphologies and are randomly oriented due to prolonged exposure to high temperatures and the isothermal growing environment. Accordingly, a solution-based growth process at a relatively low temperature might be a better choice for the fabrication of 1D SnO$_2$ nanostructures. Recently, growth of highly ordered and crystalline SnO$_2$ nanorods of 500 nm in length and 50 nm in width has been reported by Vayssieres and Graetzel using a one-step, aqueous, low-temperature growth process. In this letter, we synthesized large-scale SnO$_2$ nanoblades with widths of 100–300 nm, thickness of a few tens of nanometers, and lengths up to 10 μm in an aqueous solution at a temperature as low as 70 °C. The photoluminescence (PL) spectra of the as-synthesized SnO$_2$ nanoblades were analyzed and exhibited an intense blue luminescence at a wavelength of 445 nm (~2.8 eV).

Large-scale SnO$_2$ nanoblades were synthesized by a hydrothermal process. An aqueous solution consisting of 0.001M of tin (IV) chloride pentahydrate (SnCl$_4$·5H$_2$O) and 0.1M of urea (NH$_2$)$_2$CO in the presence of 0.1M of NaOH was prepared and contained in a closed Pyrex bottle with an autoclavable screw cap. A 100-nm-thick crystalline SnO$_2$ buffer layer was deposited on Corning Eagle 2000 glass substrates by an ion beam assisted deposition system. Then the glass substrates were placed standing against the walls of the closed Pyrex bottle. Thereafter, the bottle was placed in a regular oven and heated at a constant temperature of 70 or 90 °C for 24 h. The as-synthesized thin films were subsequently dried in air. The microscopic morphologies of the resultant films were observed with a field-emission scanning electron microscope (FE-SEM). The structures and constituent phases of the as-synthesized films were characterized by an x-ray diffractometer (XRD) using Cu Kα radiation, a transmission electron microscope (TEM), and an x-ray photoelectron spectroscopy (XPS) using Mg radiation. The photoluminescence spectra were measured at room temperature in the spectral range of 350–800 nm using a He–Cd laser with a wavelength of 325 nm as the excitation source.

Figures 1(a) and 1(b) show typical FE-SEM images of the as-synthesized films prepared at 90 and 70 °C for 24 h, respectively. Clearly, large-scale and bladelike 1D SnO$_2$ nanostructures (nanoblades) were easily grown on glass substrates covered with a crystalline SnO$_2$ buffer layer at temperatures below 100 °C. All the SnO$_2$ nanoblades had similar thicknesses on the order of tens of nanometers, while the aspect ratios of nanoblades were found to strongly depend on the synthesis temperature. At 90 °C, SnO$_2$ nanoblades with typical lengths of ~1 μm and widths of 100–200 nm were obtained, and the aspect ratio was thus in the range of 5–10. As the synthesis temperature was reduced to 70 °C, the typical lengths and widths of SnO$_2$ nanoblades were found to increase to ~10 μm and ~300 nm, respectively, giving an aspect ratio of ~33. Apparently, SnO$_2$ nanoblades synthesized at a lower temperature exhibited a faster growth rate than those synthesized at a higher temperature. According to the energy dispersive x-ray spectra of the as-

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synthesized SnO$_2$ nanoblades measured with the same SEM system, the elemental composition was verified to be Sn and O with an approximate atomic ratio of 1:2, which confirms that the nanoblades are primarily SnO$_2$.

The structures of the as-grown SnO$_2$ nanoblades synthesized at 90 and 70 °C for 24 h were determined by XRD, as shown in Fig. 2. All the diffraction peaks for both sets of samples can be indexed to the tetragonal rutile structure of SnO$_2$ with lattice parameters of $a=0.4741$ nm and $c=0.3182$ nm, which agree well with the standard data file (ICDD-PDF card No. 41-1445). An intense diffraction peak due to the (110) plane suggests that SnO$_2$ crystal grew along the [110] direction. No characteristic peaks peculiar to impurities, such as elemental Sn and other tin oxides, were observed, which indicates that the level of impurity in the sample is lower than the resolution limit of XRD (~5 at. %). Figure 3 shows a typical TEM image of the SnO$_2$ nanoblades. A selected area electron diffraction (SAED) pattern of a nanoblade taken perpendicular to its longitudinal axis confirms the high single crystallinity. Regular diffraction spots could be indexed for the [111] zone axis of single-crystalline tetragonal rutile SnO$_2$.

The constituent phases of the as-synthesized nanoblades can be further confirmed by the core-level spectra of Sn 3$d$ and O 1$s$, as shown in Figs. 4(a) and 4(b). All peak positions were corrected by the C 1$s$ peak at 284.5 eV, which was due to contamination on the grown film. For the nanoblades prepared at 90 °C, the Sn (3$d$5/2) and O (1$s$) peaks were located at 486.6 and 531.6 eV, respectively. As the preparing temperature was reduced to 70 °C, the Sn (3$d$5/2) and O (1$s$) peaks were found to slightly shift to 486.5 and 530.6 eV, respectively. Generally, the Sn (3$d$5/2) peak in SnO$_x$ can be built up of the following three components: Sn$^{4+}$ (486.58 eV), Sn$^{2+}$ shifted with respect to Sn$^{4+}$ towards
In summary, we have synthesized large-scale SnO$_2$ nanoblades with thickness of a few tens of nanometers and aspect ratios up to 33, in an aqueous solution at temperatures as low as 70 °C. The structure of the as-grown nanoblades was confirmed to be the tetragonal rutile structure of SnO$_2$, and the SnO$_2$ nanoblades grew along the [110] direction. The Sn (3d5/2) and O (1s) peaks in the XPS spectrum for the SnO$_2$ nanoblades were built up by only the Sn$^{4+}$ and the O–Sn$^{4+}$ components, respectively. This indicates that impurities, such as elemental Sn and other tin oxides, did not exist in the as-grown nanoblades. The PL spectra of the as-synthesized SnO$_2$ nanoblades exhibited an intense blue luminescence at a wavelength of 445 nm with FWHM of 75 nm, which may be attributed to oxygen-related defects that have been introduced during the growth process.

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