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Growth Mechanism and Characterization of Single-crystalline Ga-doped SnO₂ Nanowires and Self-organized SnO₂/Ga₂O₃ Heterogeneous Microcomb Structures

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Single-crystalline Ga-doped SnO₂ nanowires and SnO₂-Ga₂O₃ heterogeneous microcomb structures were synthesized by a simple one-step thermal evaporation and condensation method. They were characterized by means of X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). FE-SEM images showed that the products consisted of nanowires and microcombs that represent a novel morphology. XRD, SAED and EDS indicated that they were single-crystalline tetragonal SnO₂. The influence of experimental conditions on the morphologies of the products is discussed. The morphology of the product showed a ribbon-like stem and nanoribbon array aligned evenly along one or both sides of the nanoribbon. It was found that many Ga₂O₃ nanoparticles deposited on the surface of the microcombs. The major core nanoribbon grew mainly along the [110] direction and the self-organized branching nanoribbons grew epitaxially along [110] or [110] orientation from the (110) plane of the stem. A growth process was proposed for interpreting the growth of these remarkable SnO₂-Ga₂O₃ heterogeneous microcombs. Due to the heavy doping of Ga, the emission peak in photoluminescence spectra has red-shifted as well as broadened significantly.

Key words: Microcomb, Nanoribbon, Photoluminescence

I. INTRODUCTION

In recent years, much effort has been made to fabricate one-dimensional semiconductor nanoscale materials for further application of nanodevices and complicated nanocircuits, due to their novel properties [1-3]. Among metal oxides, tin oxide (SnO₂) represents a functional material that can be adjusted for multiple applications by incorporation of dopant ions. Because of its large bandgap ($E_g=3.6$ eV), SnO₂ is transparent in the visible-light region of the spectrum, and is thus useful as a conductive electrode and an antireflective coating [4,5]. Stimulated by the novel properties of carbon nanotubes, quasi-one-dimensional nanostructures of SnO₂ are currently the subject of intensive research because of the potential for nanoscale electronic and optoelectronic applications [5-9]. Modification of SnO₂ properties by impurity incorporation is currently another important issue for possible applications in ultraviolet optoelectronics and spin electronics [10,11]. Doping in semiconductors with selective elements offers an effective method to adjust their electrical, optical, and magnetic properties, which is crucial for their practical application [12,13]. It is well known that for a wide-band-gap semiconductor, the addition of impurities often induces dramatic changes in its electrical and optical properties [11,13].

In our previous experiment, undoped SnO₂ asterisk-like nanostructures were successfully synthesized by the thermal evaporation method [9]. In this work, the synthesis of single-crystal Ga-doped SnO₂ nanowires and self-organized SnO₂-Ga₂O₃ heterogeneous microcombs structure is studied using a simple one-step physical process. The controlled growth of self-organized microscale comb consists of a periodic array of very uniform, perfectly aligned, evenly spaced single-crystalline straight SnO₂ nanoribbons with periods in the range of 20 µm to 80 µm. The ribbon-like stem of the microcombs is about 150 nm thick and several tens to several hundreds of microns long. Furthermore, no extra catalyst was used in our experiment, it is discovered that the formation process of the SnO₂ comb-teeth follow a faceted epitaxial growth process through atom-plane stacking parallel to the [110] or [110] directions. These branched nanostructures can potentially find diverse applications in nanoscale electronic, optoelectronic and photonic devices.

II. EXPERIMENTS

The synthesis was based on thermal evaporation of a mixture of SnO mounted horizontally inside a high-temperature tube furnace. An alumina boat filled with SnO and Ga with molar ratio of 2:1 was placed in the...
FIG. 1 Schematic illustration of the experimental setup applied to synthesize the Ga-doped SnO$_2$ nanostructures. As-prepared SnO$_2$:Ga$_2$O$_3$ microcombs and Ga-doped SnO$_2$ nanowires deposited on the Au-coated Si substrate 1 and substrate 2, respectively.

FIG. 2 XRD pattern of as-deposited products, demonstrating that products consist of SnO$_2$ and Ga$_2$O$_3$ nanowires.

FIG. 3 Morphologies of the products deposited on the Si substrates which located in the temperature region of 500-600 °C. (a) FE-SEM image of the products on a silicon substrate with a 2-nm-thick gold coating. (b) An enlarged FE-SEM image of the sample, showing a nanowire with a nanocluster catalyst at its end.

III. RESULTS AND DISCUSSION

A. Structural characteristics of Ga-doped SnO$_2$ nanowires

The XRD pattern has been measured for assessing the overall structure and phase purity (see Fig.2). The major diffraction peaks correspond to SnO$_2$ crystal faces. Some weak peaks corresponding to the Ga$_2$O$_3$ also exist in this spectrum, revealing a small amount of Ga$_2$O$_3$ also was synthesized during the experiment. Analysis from the XRD pattern reveals that SnO$_2$ has a tetragonal rutile structure with a lattice constant of $a=4.74$ Å and $c=31.9$ Å and Ga$_2$O$_3$ has a...
wurtzite (hexagonal) structure with lattice constants of $a=3.253 \text{ Å}$ and $c=5.20 \text{ Å}$, which is consistent with the standard values for bulk SnO$_2$ (JCPDS 41-1445) and Ga$_2$O$_3$ (JCPDS 43-1013).

Figure 3(a) shows the morphologies of the products deposited on the Si substrate which was located in the temperature region of 500-600 °C. Scanning electron microscopy (SEM) observations reveal that the products consist of a large quantity of wirelike nanostructures with typical lengths in the range of several tens to several hundreds of micrometers and diameters normally in the range of 100-200 nm. Figure 3(b) shows a representative enlarged FE-SEM of the as-grown products. It clearly reveals that each nanowire has a uniform diameter ranging from 100 nm to 200 nm.

Detailed microstructure and composition information of as-grown Ga-doped SnO$_2$ nanowires was further characterized by TEM. A representative TEM image shown in Fig.4(a) reveals that the each produced Ga-doped SnO$_2$ nanowire has a uniform diameter along its entire length. The HRTEM image and corresponding SAED pattern (see Fig.4(b)) reveal that nanowire is single-crystalline with a uniform structure. As shown in Fig.4(b), the spacing between adjacent lattice planes is 0.334, corresponding to the d-spacing of the (002) planes of the SnO$_2$, which indicates that the growth direction of Ga-doped SnO$_2$ nanowires is parallel to the [112] crystal direction. Further compositional analysis by EDS (see Fig. 4(c)) reveals that the Ga-doped SnO$_2$ nanowire has a Ga:Sn:O atomic ratio of 1:4.54:9.78.

According to the classical explanation, the catalyst clusters at the tip of the Ga-doped SnO$_2$ nanowires shown in TEM detection (Fig.4(a)) are considered as the evidence for the operation of the vapor-liquid-solid (VLS) mechanism. For interpreting the experimental result, a possible growth process of the Ga-doped SnO$_2$ nanowires is proposed: It is known that SnO is metastable and will decompose to Sn and SnO$_2$ at a temperature higher than 300 °C [14]. Moreover, the higher the reaction temperature, the faster the rate of the decomposition [15]. As-formed Sn may be in the form of small-sized liquid clusters (Sn: mp of 232 °C, bp of 2270 °C [14]) when reduced from SnO. The Sn clusters are then transported by the carrier gas (Ar) to
a lower temperature region, where they deposited in the form of liquid droplets on the Si substrate. Therefore, these liquid Sn droplets can serve as ideal nucleation sites for the preferential absorption of the evaporated Sn, Ga and O\textsubscript{2} vapor (The dosage of O\textsubscript{2} gas into the reactor was controlled using a leak valve). Continuous dissolution of Ga, Sn and O atoms in Ga-Sn-O eutectic alloy droplets will lead to the nucleation and growth of SnO\textsubscript{2} nanowires through the VLS process when the alloy droplets become saturated with reactant. At the same time, Ga doping was achieved through the process of Ga substitute Sn atom in SnO\textsubscript{2}. Continuous feeding of Sn and Ga atoms into the liquid droplet sustains the growth of the Ga-doped SnO\textsubscript{2} nanowires. By analyzing the EDS spectrum (Fig.4(d)) of the end particle of a single nanowire, we find that it really consists of Ga, Sn, and O, which also supports our above discussion to some extent.

**B. Structural characteristics of SnO\textsubscript{2}/Ga\textsubscript{2}O\textsubscript{3} heterogeneous microcombs structure**

Figure 5(a) shows a representative FE-SEM image of the as-prepared SnO\textsubscript{2} microcomb structure deposited on the Si substrate which was located in the temperature region of 700-800 °C. It is clearly seen that a row of nanoribbons grow along one side of a nanoribbon to form a comb-like nanostructure. It is noted that the nanoribbon branches have uniform diameters and are evenly distributed along one side of stem. High-magnification SEM images (Fig.5(b)) show that each array usually contains several tens of very straight, perfectly aligned and evenly spaced nanoribbons with almost constant width and spacing. The ribbon-like stem of the microcombs is about 150 nm thick and several tens to several hundreds of microns long. The microcombs are mainly made of periodic arrays of straight nanoribbons that have a rectangular cross section, as shown in Fig.5(b). Each nanoribbon has a uniform width and thickness, and the typical widths and thicknesses are in the range of 200-500 nm and 50-150 nm, respectively. The spacing between the nanoribbons varies in a wide range from 200 nm to 400 nm; however, for an individual comb the nanoribbons on it are evenly spaced and such uniformity can extend to up to several tens of microns wide. Further observation reveals that there are lots of nanoparticles deposited on the surface of the microcombs.

Further structural analysis indicates the growth direction of the main stem of this ribbon is parallel to the [110] crystalline orientation of SnO\textsubscript{2}. The corresponding SAED pattern (inset in Fig.6(a)) can be indexed to be the [001] zone axis of the rutile structured SnO\textsubscript{2} crystal. From the TEM image shown in Fig.6(a), it is expected that the branch grows orthogonally on the stem, resulting in comb-like structure. Furthermore, this structure can be a planar form because the SAED patterns recorded from the stem and branch have the same orientation as the sample tilted in the TEM observation. Due to the tetragonal structured SnO\textsubscript{2}, the crystalline orientation of [110] is perpendicular to the [110] (or [110]) crystalline orientation, it is apparent that the branches grow along [110] (or [110]) crystalline orientation. Figure 6(b) shows HRTEM image taken in the junction region between the stem and the branch present in (a) revealed that formed Ga\textsubscript{2}O\textsubscript{3} nanocrystals in the SnO\textsubscript{2} microcomb surface. The lattice spacing of 3.4 Å between adjacent lattice planes in this image corresponds to the distance between two (110) plane of a rutile SnO\textsubscript{2} lattice. EDS spectra were also recorded of the microcomb and the attached particles in the surface of microcomb (see Fig.7(a)), they confirmed that both the comb-stem and comb-teeth are composed of Ga, Sn and O elements with the same atomic ratios, and the particles are elemental Ga with trace of O and Sn (Fig.7(b)).

The one-step growth of the unique SnO\textsubscript{2}/Ga\textsubscript{2}O\textsubscript{3} heterogeneous microcomb structure is a spontaneous and self-organized process. Although the synthesis procedure is very simple, the formation and assembly processes are complex and precisely self-controlled since they involve: (i) the growth of the comb-stem along [110] by vapor-deposition [6]; (ii) the nucleation and epitaxial growth of evenly spaced nanoribbons arrays along [110] or [110] directions on one edge of the comb ribbon; and (iii) the
FIG. 6 (a) Typical TEM image of part of a SnO$_2$/Ga$_2$O$_3$ heterogeneous microcomb, displaying parallel, straight, uniform nanoribbons growing perpendicularly from both edges of the comb ribbon (the corresponding SAED spectra is shown in the inset, revealing the major core nanoribbon grew mainly along [110] direction and the self-organized branching nanoribbons grew epitaxially along [110] or [¯110] orientation). (b) HRTEM image of junction region of SnO$_2$ microcomb, showing the Ga$_2$O$_3$ nanocrystals formed in the SnO$_2$ microcomb surface.

FIG. 7 (a) and (b) EDS spectra of SnO$_2$ microcomb and Ga$_2$O$_3$ nano-crystal, respectively.

planar filling that makes the comb ribbon widen and thicken [16,17]. At the same time, the as-grown microcombs can also be used as templates for the adsorption or deposition of the Ga vapors in the furnace system, resulting in the formation of Ga nuclei on the growing microcomb surface. In this process, due to the residual O$_2$ insurmountable negligible leakage in the furnace system, the high temperature will cause oxidation of the Ga droplet into Ga$_2$O$_3$ nanocrystals, and thus finally form the SnO$_2$/Ga$_2$O$_3$ heterogeneous microcomb structure.

The TEM analyses suggest that the growth of the microcomb-stem is a vapor-solid (VS) process rather than a VLS process because we did not find any low melting-point phases at the growth front of the nanoribbon of comb-stem. However the exact reason for the formation of Ga$_2$O$_3$ nanocrystals was not clear at this stage, but it was most likely linked to the reaction between active Ga vapor and the formed SnO$_2$ microcombs. It was imaginable that due to the high content of Sn in the vapor, the SnO$_2$ microcombs were preferentially formed by the VS model. The content of Ga vapor around microcombs increased at the same time. The SnO$_2$ nanoparticle is provided with high surface energy, so it can absorb the Ga atom easily. Then the fresh SnO$_2$ microcomb tended to serve as a template for the adsorption or deposition of the Ga vapors, so some part of SnO$_2$ microcomb surface was eroded to form Ga$_2$O$_3$ nanocrystal. The final size of the Ga$_2$O$_3$ nanocrystal may be determined by the Ga concentration in the vapor, the ratio of Sn to Ga in the vapor may be critical to get this structure. Several repeated experiments with different ratio of Sn to Ga in the source materials have been done, and the products were quite different. If this ratio was too low to form the Ga$_2$O$_3$ nanocrystals, Ga atoms may dissolve into SnO$_2$ nanowires (surface layer) to be the impurities. If this ratio was too high, the nucleation and growth of Ga$_2$O$_3$ nanostructure will happen preferentially. A mixture of SnO$_2$ nanowires and Ga$_2$O$_3$ nanostructure (nanowire or nanocrystals) may be obtained. Therefore, we considered that the ratio of Sn to Ga in the vapor can remarkably influence the morphologies of the SnO$_2$/Ga$_2$O$_3$ composite nanostructures. Further research work should be done to measure and control the ratio of Sn to Ga in the vapor by an efficient method.

C. Luminescence properties of Ga-doped SnO$_2$ nanowires and SnO$_2$/Ga$_2$O$_3$ heterogeneous microcombs

Figure 8 displays the PL spectra recorded from the as-prepared Ga-doped SnO$_2$ nanowires and the SnO$_2$/Ga$_2$O$_3$ heterogeneous microcombs at room temperature, respectively. As shown in Fig.8, the excitation energy is 3.815 eV (325 nm) and the two nanosi
In summary, large-scale single-crystalline Ga-doped SnO$_2$ nanowires and self-assembled SnO$_2$:Ga$_2$O$_3$ heterogeneous microcombs were achieved and their composition and single-crystalline structures were confirmed using XRD, TEM, and SAED. The as-synthesized Ga-doped SnO$_2$ nanowires are single-crystalline, the typical diameter of Ga-doped SnO$_2$ nanowires is in the range of 100-200 nm, and the lengths are in the range of several tens to several hundreds of micrometers. The Ga-doped SnO$_2$ nanowires were grown by an Sn-catalyzed VLS process. The controlled growth of self-assembled microcombs consists of a periodic array of very uniform, perfectly aligned, evenly spaced single-crystalline straight SnO$_2$ nanoribbons with periods in the range of 20 µm to 80 µm. The branching mechanism discussed in this work is generic and, therefore, can be applied to other materials (e.g. In in Ga$_2$O$_3$ and Cd in SnO$_2$), thus opening a new approach in synthesizing of similarly branched structures. These branched nanostructures can potentially find diverse applications in nanoscale electronic, optoelectronic and photonic devices. Due to the heavy doping of Ga, the SnO$_2$ nanostructures yield a green emission peak in PL spectrum that has red-shifted as well as significantly broadened.

IV. CONCLUSION

In summary, large-scale single-crystalline Ga-doped SnO$_2$ nanowires and self-assembled SnO$_2$:Ga$_2$O$_3$ heterogeneous microcombs were achieved and their composition and single-crystalline structures were confirmed using XRD, TEM, and SAED. The as-synthesized Ga-doped SnO$_2$ nanowires are single-crystalline, the typical diameter of Ga-doped SnO$_2$ nanowires is in the range of 100-200 nm, and the lengths are in the range of several tens to several hundreds of micrometers. The Ga-doped SnO$_2$ nanowires were grown by an Sn-catalyzed VLS process. The controlled growth of self-assembled microcombs consists of a periodic array of very uniform, perfectly aligned, evenly spaced single-crystalline straight SnO$_2$ nanoribbons with periods in the range of 20 µm to 80 µm. The branching mechanism discussed in this work is generic and, therefore, can be applied to other materials (e.g. In in Ga$_2$O$_3$ and Cd in SnO$_2$), thus opening a new approach in synthesizing of similarly branched structures. These branched nanostructures can potentially find diverse applications in nanoscale electronic, optoelectronic and photonic devices. Due to the heavy doping of Ga, the SnO$_2$ nanostructures yield a green emission peak in PL spectrum that has red-shifted as well as significantly broadened.

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