

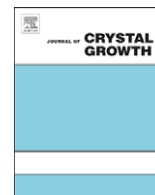


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Fabrication of SnO₂ one-dimensional nanostructures with graded diameters by chemical vapor deposition method

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ABSTRACT

Mono-dispersed SnO₂ 1D nanostructures of different diameters and SnO₂ 1D nanostructures with graded diameters have been fabricated by modulating oxygen partial pressure in chemical vapor deposition method, in which Sn powder and oxygen gas were used as the source materials. Experimental results indicate that the diameters and the band gap of SnO₂ 1D nanostructures depend much on the oxygen partial pressure in the growth chamber. When the oxygen partial pressure is increased or decreased during the growth process, the diameter of SnO₂ nanowire increases or decreases, while the band gap decreases or increases due to oxygen vacancies and tin interstitial atoms, correspondingly. Furthermore, the change of oxygen partial pressure can also induce change in growth directions of SnO₂ 1D nanostructures. The growth mechanism of SnO₂ nanowires under different growth conditions is also discussed.

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1. Introduction

SnO₂ is a typical wide band gap semiconductor ($E_g=3.6$ eV, at 300 K), which exhibits n-type conduction due to an excess of oxygen vacancies. SnO₂ has been widely used in transparent conducting electrodes [1], solid-state gas sensors [2], solar cells [3], and catalyst supports [4]. Owing to surface effect and size-confinement effect, SnO₂ one-dimensional (1D) nanostructures (such as nanowires, nanobelts and nanorods) have been shown to exhibit much more abundant physical and chemical properties than their bulk crystal, and then have even wider potential applications. Therefore, SnO₂ 1D nanostructures have attracted considerable attention and provoked extensive researches [5–9]. SnO₂ 1D nanostructures have been synthesized successfully by various methods, such as chemical vapor deposition (CVD) [10,11], hydrothermal method [12], microemulsion technology [13], laser ablation [14], etc. At the same time, various complex SnO₂ 1D nanostructures, including nanorings [15], zigzag structure [16,17], V-shaped nanorods [18], dendritic nanorods and falchion-like nanosheets [19], have also been fabricated.

In this work, we report the fabrication of mono-dispersed SnO₂ 1D nanostructures of different diameters and SnO₂ 1D nanostructures with graded diameters by CVD method, which is the most commonly used method because of its low demand in equipment, simple operation and low cost. By using Sn powder and oxygen gas as source materials, we found that the diameters and the band gap of SnO₂ 1D nanostructures depend much on the oxygen partial pressure in the growth chamber. With the oxygen partial pressure increased or decreased during the growth process, the diameter of SnO₂ 1D nanostructure increases or decreases, while the band gap decreases or increases due to oxygen vacancies and tin interstitial atoms, correspondingly. The change of oxygen partial pressure can also induce change in the growth directions of SnO₂ 1D nanostructures. The growth mechanism of SnO₂ nanowires under different growth conditions is also discussed.

2. Experimental details

The experiment apparatus for chemical vapor deposition is similar to that described in our previous work [20]. A quartz tube (1200 mm in length and 25 mm in diameter) was put in a

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horizontal tube furnace and served as sample growth chamber. One end of this quartz tube is connected to the gas supply system and the other to the vacuum system. The pressure in the growth chamber can be controlled accurately by controlling the pump velocity and the flow rate of carrier gas. The horizontal tube furnace can be heated up independently by three heaters (each heating region is about 40–60 mm long and the distance between two adjacent heating regions is about 160–200 mm), which can control the distribution of temperature in the sample growth chamber accurately. In a typical experiment source material (Sn powder, $\geq 99.9\%$) was loaded into an alumina boat and a piece of silicon substrate covered with 5 nm gold (Au) film was located 20–30 mm downstream from the Sn powder or just above the powder. The carrier gas, high-purity argon, was introduced into the quartz tube at a flow rate of 200 SCCM (Standard Cubic Centimeter per Minute) to remove the air in it. Under the protection of carrier gas, the alumina boat was then pushed into the second heating region which was preheated at a certain temperature (820 or 850 °C). And then a certain quantity of oxygen gas was introduced into the growth chamber. The pressure in the quartz tube was kept at 10130 Pa (76 Torr, the normal atmospheric pressure $P_0 = 760$ Torr = 1.013×10^5 Pa). In order to control the oxygen partial pressure more accurately, we used a mixture of oxygen (10%) and argon (90%) as oxygen source. The oxygen partial pressure can be accurately modulated by controlling the flow rate of mixture gas (measurement accuracy: 0.1 SCCM). After half an hour, samples were unloaded from the growth chamber immediately under the protection of Ar. A layer of wool-like product on the silicon substrate is the sample we have synthesized.

The as-synthesized products were characterized by scanning electron microscopy (SEM) (Hitachi S-4800 and JEOL-6360Lv), X-ray diffraction (XRD) (Aolong Y2000, Cu $K\alpha$, $\lambda = 0.15405$ nm), ultraviolet/visible/near infrared (UV/Vis/NIR) Spectrophotometer (UVS) (PE Lambda 750 UV) and energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

Fig. 1 shows the typical SEM images of SnO₂ 1D nanostructures synthesized under the oxygen partial pressure of 2.5 (a), 5 (b), 7.5 (c) and 10 Pa (d). The corresponding flow rates of the mixture gas (10% oxygen and 90% argon) in these cases are about 0.5, 1.0, 1.5 and 2.0 SCCM, respectively. As shown in Fig. 1, with the oxygen partial pressure in the growth chamber increased, the diameters of the as-synthesized 1D SnO₂ nanostructures increase, while the lengths decrease correspondingly. That is, the increase in oxygen partial pressure turns loosely entangled mono-dispersed SnO₂ nanowires (Fig. 1(a) and (b)) into short straight SnO₂ nanorods (Fig. 1(c) and (d)). The dependence of the average diameter of 1D SnO₂ nanostructures on the oxygen partial pressure in the growth chamber is shown in Fig. 2(b). Another important feature of our samples is that there are always spherical nanoparticles on the tips of nanowires or thin nanorods, which indicate that the growth of nanowires or thin nanorods is likely governed by vapor–liquid–solid (VLS) mechanism.

The optical absorption properties of SnO₂ 1D nanostructures have been characterized by UV/Vis/NIR spectrophotometer equipped with 60 mm integrating sphere. Fig. 2(a) shows the plots of $[F(R)]^{2/3}$ vs photon energy of SnO₂ 1D nanostructures synthesized under different oxygen partial pressures. $F(R) = ((1-R)^2/2R) = (\alpha/S)$ is the Kubelka–Munk function, where R , α and S are the diffuse reflection, absorption and scattering coefficient, respectively. The rising part of the $[F(R)]^{2/3}$ vs photon energy plot exhibits perfect linearity, which means that the transitions are characterized as being direct forbidden transitions. The $[F(R)]^{2/3}$ vs photon energy plots show that there is a shift for the absorption edge of SnO₂ 1D nanostructures grown in different oxygen concentrations. The band gap can be defined by extrapolating the rising part of the plots to the photon energy axis [21]. It is indicated that the band gap of SnO₂ 1D nanowires decreases from 3.77 to 3.66, 3.57 and 3.47 eV, when the oxygen partial pressure increases from 2.5 to 5, 7.5 and 10 Pa, respectively. As

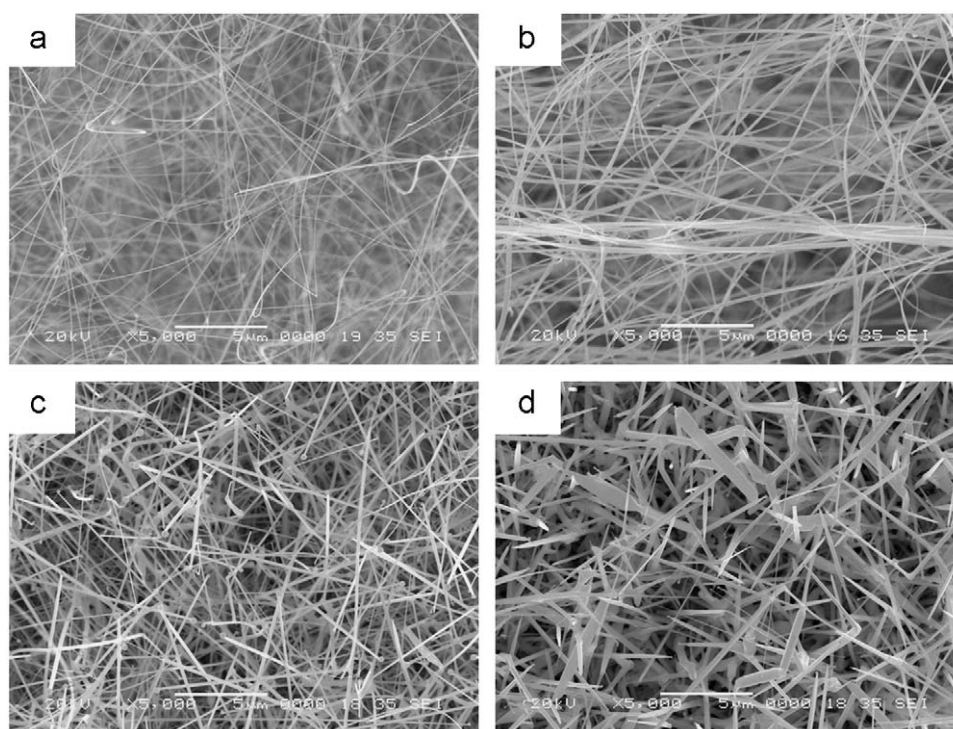


Fig. 1. SEM images of SnO₂ nanowires and nanorods synthesized under different oxygen partial pressure: (a) 2.5 Pa, (b) 5 Pa, (c) 7.5 Pa and (d) 10 Pa.

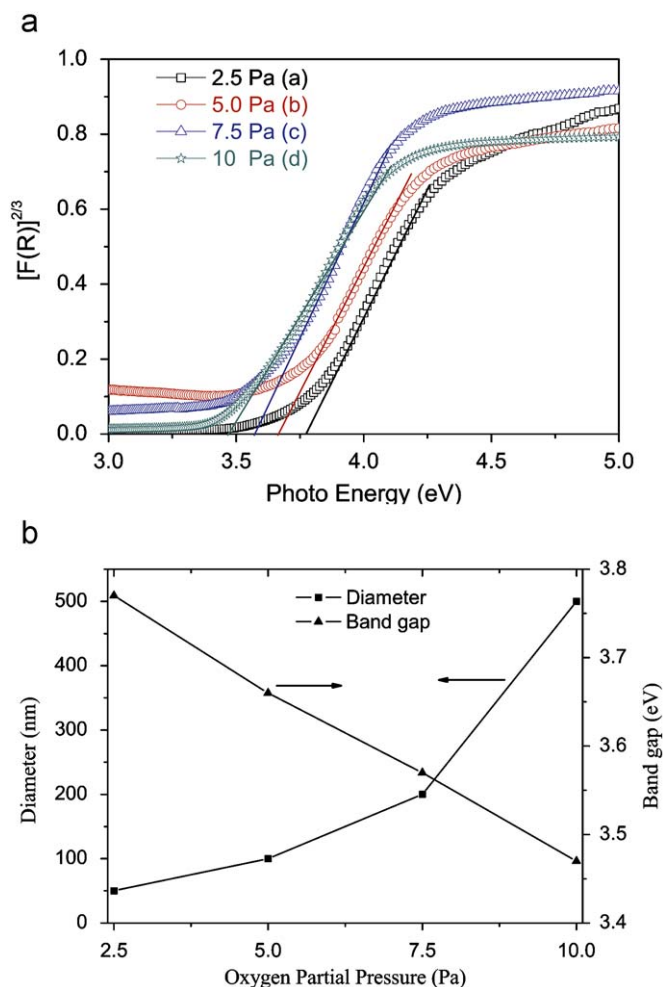


Fig. 2. (a) Plots of $[F(R)]^{2/3}$ vs photon energy of SnO₂ 1D nanostructures synthesized under different oxygen partial pressure of 2.5, 5, 7.5 and 10 Pa; (b) Dependences of the average diameter and the band gap of 1D SnO₂ nanostructures on the oxygen partial pressure in the growth chamber.

shown in Fig. 2(b), the optical band gap of SnO₂ nanowires with small diameters is slightly larger than the value of 3.6 eV for bulk SnO₂, which might be attributed to the quantum confinement effect. The optical band gap of SnO₂ nanorods with large diameters is smaller than the value of 3.6 eV, which might be attributed to oxygen vacancies or tin interstitial atoms in the SnO₂ lattice. The dependence of the band gap of 1D SnO₂ nanostructures on the oxygen partial pressure in the growth chamber is shown in Fig. 2(b). It indicates that the oxygen concentration in the growth chamber has great effect on the band gap of SnO₂ 1D nanostructures as well as their average diameters. Therefore, the nanostructures and then the electronic structures of SnO₂ 1D nanostructures can be controlled accurately by modulating the oxygen partial pressure in the growth chamber.

To further investigate the effect of oxygen partial pressure on the diameters of SnO₂ 1D nanostructures, we modulated the oxygen partial pressure in the growth chamber during the growth process. Fig. 3 shows the typical SEM image of SnO₂ nanorods with sudden change in diameters, which were synthesized under saltatory changes of oxygen partial pressure between 2.5 and 10 Pa. This process was realized by changing the flow rate of oxygen alternatively between 0.5 and 2.0 SCCM every 2 min. The segments of SnO₂ nanorod labeled by (a), (b), (c) and (d) can be assigned to the oxygen partial pressure of 2.5, 10, 2.5 and 10 Pa, respectively, which indicates that the diameters of each segment

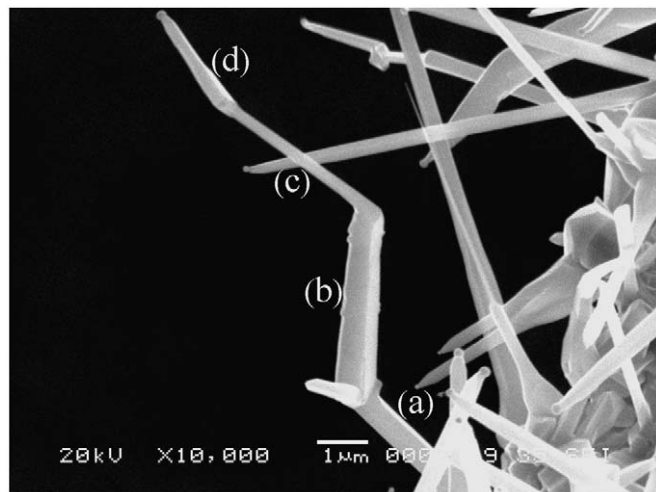


Fig. 3. SEM image of SnO₂ 1D nanostructures synthesized by changing flow rate of oxygen alternatively between 0.5 and 2.0 SCCM every 2 min. Segments labeled by (a), (b), (c) and (d) can be assigned to the oxygen partial pressure of 2.5, 10, 2.5 and 10 Pa, respectively.

of SnO₂ 1D nanostructures can be controlled accurately by the oxygen partial pressure in the growth chamber: the higher the oxygen partial pressure is, the thicker the diameters of the segments of 1D nanostructure is. This image also shows that the lengths of different segments is almost the same, which indicates that SnO₂ 1D nanostructures grow in the same velocity in different oxygen partial pressures. However, the diameters of segments (c) and (d) are obviously smaller than that of segments (a) and (b), which is most likely due to the fact that Sn vaporizing slows down as Sn powder decreases.

When the oxygen partial pressure in the growth chamber changing (between 2.5 and 10 Pa with a step size of 2.5 Pa every 2 min) continuously, the diameters of as-synthesized SnO₂ 1D nanostructures change continuously correspondingly (Fig. 4). SnO₂ 1D nanostructures synthesized under 820 °C have smooth sidewalls and nanobelt morphology in the segments with larger diameters (Fig. 4(a) and (b)), while SnO₂ 1D nanostructures synthesized under 850 °C have rough sidewalls in the segments with larger diameters and nanowire morphology (Fig. 4(c) and (d)). Furthermore, it is obvious that the diameters change more quickly at higher temperature (850 °C). Another important feature is that the growth directions of SnO₂ 1D nanostructures at 850 °C does not change, while at 820 °C there is always a bending angle about 135° at the segments with larger diameters.

When the oxygen partial pressure in the growth chamber is low, the concentration of oxygen is much smaller than double that of tin species near the grow tips of SnO₂ 1D nanostructures, and then there are superfluous tin existing as droplets on the growing tips. As shown above, there are always spherical nanoparticles on the tips of the as-synthesized nanowires, which means that the growth of SnO₂ nanowires is likely governed by vapor–liquid–solid (VLS) mechanism. The diameters of nanowires will be dominated by the diameters of the droplets. When the oxygen partial pressure is a little high and the oxygen concentration near the growing tips is very close to double that of tin species, tin species around the growing tips will react with oxygen molecules rapidly, and there will not be superfluous tin species absorbing on the growing tips. There are almost no nanoparticles found on the tips of SnO₂ nanorods, which means that the growth of SnO₂ nanobelts and nanorods is likely governed by vapor–solid (VS) mechanism. The diameters of nanorods will be in direct proportion to the concentration of oxygen. At 850 °C, the reaction

between oxygen molecules and tin species proceeds more quickly, and the as-synthesized SnO_2 1D nanostructures present nanorod morphology. The rough sidewalls of SnO_2 nanorods might be attributed to a slight fluctuation in oxygen concentration near the growing tips induced by violent reaction. When the oxygen partial pressure is high enough, the reaction between oxygen molecules and tin species proceeds so quickly that oriented growth will be suppressed, and then particles are the only product that we can obtain.

EDS spectra of segments with different diameters in a single SnO_2 1D nanostructure displayed in Fig. 5 show that tin and oxygen are the only detected elements, without any contamination. They also indicate that the atomic ratio of tin to oxygen is 1:1.65 for the thinner part (Figs. 5(a)), 1:1.85 for the thicker part (Fig. 5(b)), which manifests the natural oxygen deficiency and overall nonstoichiometry of SnO_2 1D nanostructures. It also manifests that the atomic ratio of tin to oxygen in SnO_2 1D nanostructures is inversely proportional to the oxygen partial

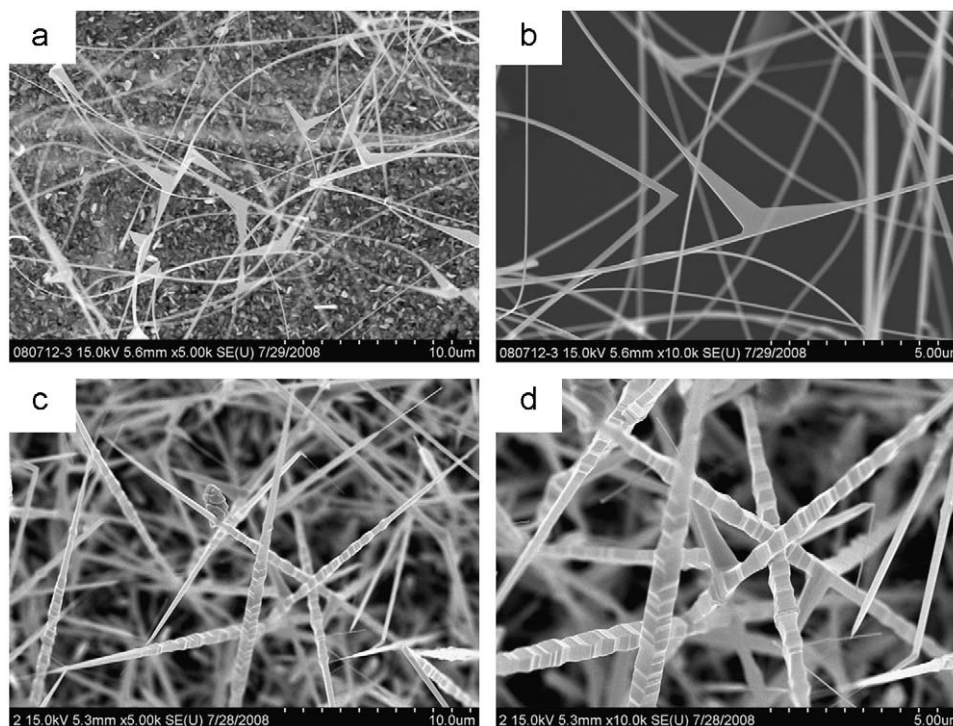


Fig. 4. SEM images of SnO_2 1D nanostructures synthesized by changing the flow rate of oxygen continuously between 0.5 and 2.0 SCCM with a step size of 0.5 SCCM every 2 min at 820 °C (a, b) and 850 °C (c, d).

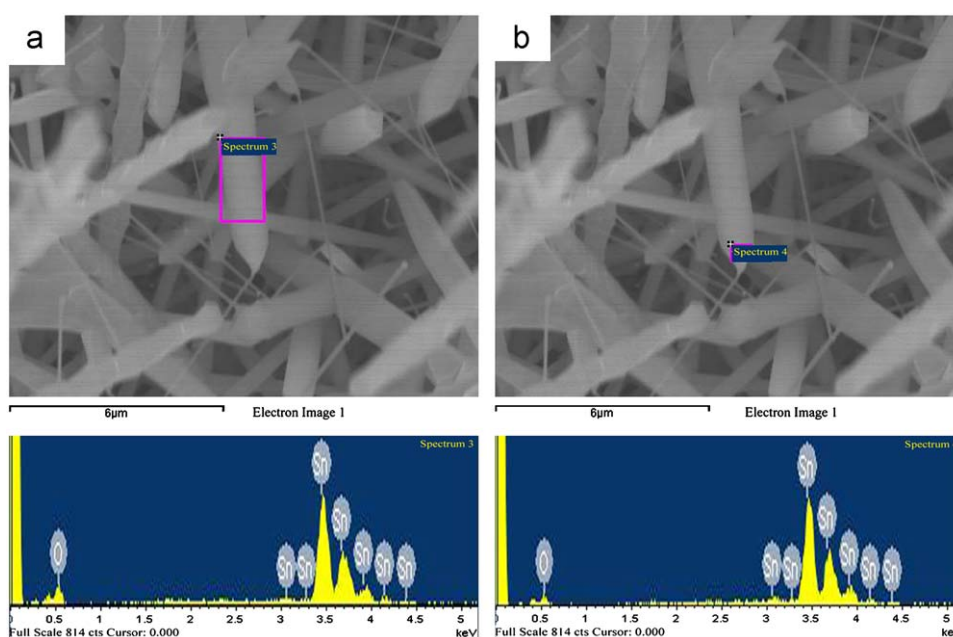


Fig. 5. EDS spectra of the thinner (a) and thicker (b) segment of a single SnO_2 1D nanostructure.

pressure where they grew and then can be controlled accurately. Therefore, the change in band gap of SnO_2 1D nanostructures can be attributed to oxygen deficiency. The band gap of SnO_2 nanowires synthesized under the oxygen partial pressure of 2.5 Pa is slightly larger than the value of 3.6 eV for bulk SnO_2 . On the other hand, tin interstitial atom has very low formation energy, and would thus exist in significant quantities. Therefore, we consider that the increase in band gap of SnO_2 nanowires can be attributed mainly to tin interstitial atoms and quantum size effect. With the oxygen partial pressure increasing, the band gap of as-synthesized SnO_2 nanowires decreases, which might be attributed mainly to oxygen vacancies.

Fig. 6 gives the typical XRD patterns of the samples shown in Fig. 4, which were synthesized under continuous change of oxygen partial pressure. All the sharp diffraction peaks can be perfectly indexed as a tetragonal rutile structure with lattice constants of $a=b=4.732 \text{ \AA}$ and $c=3.184 \text{ \AA}$, which is consistent with the standard value for bulk SnO_2 (JCPDS no. 41-1445). There are two major diffraction peaks, which are indexed to the (1 1 0) and (1 0 1) crystal lattice planes (Fig. 6(a)). As the growth temperature increased from 820 to 850 °C, the intensity of peak (1 0 1) gets suppressed (Fig. 6(b)). Fig. 4(a) and (b) indicate that the growth direction of SnO_2 1D nanostructure did change at 820 °C, while Fig. 4(c) and (d) indicate that growth direction of SnO_2 1D nanostructure did not change at 850 °C when the oxygen partial pressure and then their diameters began to decrease. The bending

angle is about 135°, which is very close to the angle between [1 1 0] and [1 0 1] directions. Therefore, it seems that SnO_2 1D nanostructures prefer to grow along the [1 1 0] direction at 850 °C, and change their growth directions between the [1 1 0] and [1 0 1] at 820 °C when the oxygen partial pressure and then their diameters began to decrease. The growth of 1D nanostructures is dependent on two factors: one is the surface energy, which determines the preferential growth surface, while the other is the growth kinetics, which determines the final structure [22,23]. The crystal morphology tends to minimize the surface energy in the growth process. As reported by Oviedo and Gillan [24], the surface energy for (1 1 0) is smaller than that for (1 0 1). In our experiment, the effective diameter of the nanobelts under 820 °C is much smaller than that of the nanorods under 850 °C, but the surface energy of the nanobelts is higher than that of nanorods. Therefore, [1 0 1] is the preferential direction during the growth process of SnO_2 nanobelts [17], while the nanowires grown under 850 °C prefer to grow along [1 1 0] direction. However, a slight fluctuation of the growth conditions, such as the oxygen partial pressure, temperature, may also cause some change in the growth direction, though the macroscopic growth conditions are kept invariable.

In addition to changing the oxygen partial pressure periodically as above described, we placed the substrate for collecting sample directly above the Sn powder 2–3 mm with the Au-coated side upwards. SEM images indicate that the as-synthesized SnO_2 1D nanostructures present periodic changes in diameters and growth directions (Fig. 7). The bending angles are very close to what we have observed in Fig. 4(a) and (b). It is worth mentioning that the periodicity of the diameter changing is shorter than that in Fig. 4(a) and (b). In fact, when the oxygen partial pressure in the growth chamber was kept unchanged, SnO_2 1D nanostructures synthesized right on top of Sn powder do exhibit changes in their diameters, which are much more indefinite than those shown in Fig. 7. This might indicate that the oxygen partial pressure or the density of Sn vapor above the Sn powder keeps changing periodically. Additionally, the temperature above the evaporating Sn powder might keep changing, which also plays an important role in the formation of different morphologies of SnO_2 1D nanostructures.

4. Conclusions

Mono-dispersed SnO_2 1D nanostructures of different diameters and SnO_2 1D nanostructures with graded diameters have been fabricated by modulating oxygen partial pressure in chemical vapor deposition method by using Sn powder and oxygen gas as source materials. Experimental results indicate that the diameters and then the band gap of SnO_2 1D nanostructures

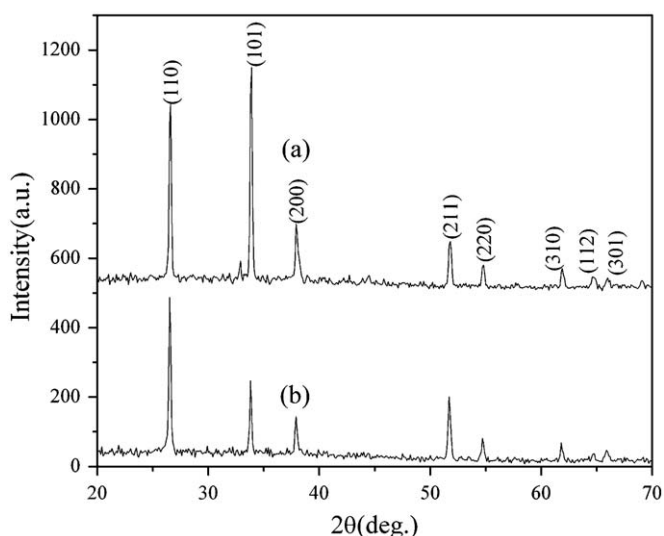


Fig. 6. XRD patterns of SnO_2 1D nanostructures synthesized by changing the flow rate of oxygen continuously between 0.5 and 2.0 SCCM with a step size of 0.5 SCCM every 2 min at 820 °C (a) and 850 °C (b).

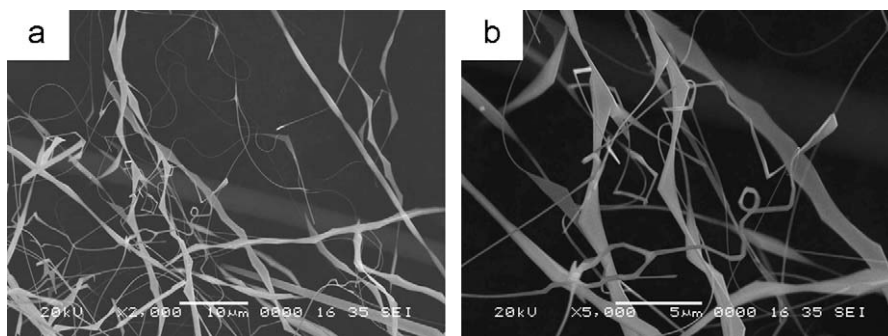


Fig. 7. Low-(a) and high-(b) magnification SEM images of SnO_2 1D nanostructures synthesized right above the Sn source by changing the flow rate of oxygen continuously between 0.5 and 2.0 SCCM with a step size of 0.5 SCCM every 2 min at 820 °C.

depend much on the oxygen partial pressure in the growth chamber. When the oxygen partial pressure is increased or decreased during the growth process, the diameter of SnO₂ 1D nanostructure increases or decreases, while the band gap decreases or increases due to oxygen vacancies and tin interstitial atoms, correspondingly. Furthermore, at relative low temperature the periodic change of oxygen partial pressure can also induce periodic change in growth directions of SnO₂ 1D nanostructures. Therefore, the electronic structures of SnO₂ 1D nanostructures can be modulated periodically and accurately along the axial direction by the most commonly used chemical vapor deposition method.

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