Effect of nanostructured morphologies of SnO$_2$ on field emission properties

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Abstract. SnO$_2$ nanoneedles, nanorods and nanowires were synthesized at different temperatures, and their field emission properties were investigated in detail. On comparing the three nanostructures of SnO$_2$, we find that the synthesis temperature has a prominent influence on the morphology, consequently affecting the field emission properties, especially the turn-on field and the emission current density. Among them, the SnO$_2$ nanoneedle possesses the lowest turn-on field of 1.23 V/$\mu$m and the highest current density 2.19 mA/cm$^2$ at 3.06 V/$\mu$m. The mechanism behind the influence of the synthesis temperature on the morphology and field emission properties of SnO$_2$ nanostructures is discussed in detail. These results can be valuable for the application of SnO$_2$ nanomaterial in the cathodes of field emission based devices.

1 Introduction

Field emission has received much attention because of its numerous applications in luminescent tubes [1,2], field emission displays [3,4], backlight units [5], X-ray sources [6] and other vacuum devices [7]. The key factor behind the development of the field emission based devices is the selection of proper materials, the so-called “cold cathodes”. Recently, one-dimensional nanomaterials such as carbon nanotubes (CNTs) and oxide semiconductors [8–13], which have been used as electron emitters, have been widely investigated due to their special nanostructures. Although CNT has the lowest turn-on field, the lack of emission stability under an oxygen atmosphere limits its application [14]. Among the various oxide semiconductors, SnO$_2$ is one of the important oxides because it is an n-type semiconductor with a wide band gap (3.6 eV) and has an advantage over other oxides in terms of thermal stability and oxidation resistance in harsh environments. Various SnO$_2$ nanostructures including nanowires [15], nanotubes [16], nanoneedles [17] and nanosheets [18] have been reported for their field emission properties with potential applications in the near future. However, it is still necessary to investigate the key factors that influence their field emission properties.

In this work, SnO$_2$ nanostructures with different morphologies were synthesized by thermal evaporation at various temperatures. The influence of the morphologies on the field emission properties is discussed in detail.

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2 Experiment

The experimental apparatus consists of a horizontal tube furnace, an alumina tube, a vacuum pump and a gas control system. Commercial Sn (99.9%) powder was used as the source material and was dispersed on a ceramic boat. The boat was placed in the center of the furnace. A stainless steel mesh was placed 5 cm far downstream from the source and was used as a substrate to collect the product. The furnace was quickly heated to the desired temperatures (850 °C, 900 °C and 950 °C) under the environment of argon (Ar) gas, which was flown at a rate of 100 sccm (standard cubic centimeter per minute). This was followed by the introduction of the oxygen at a rate of 30 sccm for 30 min. Finally the system was cooled down to the room temperature. Some white products were found on both the boat and the substrate. For convenience, the samples fabricated at temperatures of 850 °C, 900 °C and 950 °C are referred to as Samples A, B and C, respectively.

The morphologies of the as-grown SnO$_2$ samples were investigated by scanning electron microscopy (SEM, Hitachi-S3000 N), X-ray diffraction (XRD, D/Max-γA, CuKα radiation) and high-resolution transmission electron microscopy (HRTEM, JOEL JEM-2010F). The as-prepared SnO$_2$ samples on stainless steel mesh operated as a cathode, and an indium tin oxide (ITO) coated glass with green phosphor powder printed on it as an anode. They were separated by a spacer with a height of 1000 μm. The field mission properties of the samples were measured in a vacuum chamber under a pressure of 1 × 10$^{-5}$ Pa at the room temperature.
Fig. 1. Top view SEM image of SnO$_2$ nanostructures synthesized at different temperatures. (a) Sample A: 850 °C, nanoneedles. (b) Sample B: 900 °C, comb-like. (c) Sample C: 950 °C, nanorods. (d)–(f) The magnified SEM images of the scatter samples in (a), (b) and (c), respectively.

3 Results and discussion

Figures 1a–1f show the SEM images of SnO$_2$ samples synthesized at 850 °C, 900 °C and 950 °C. It is clear that the morphology of SnO$_2$ is very sensitive to the synthesis temperature. Sample A (obtained at 850 °C) shown in Figures 1a and 1d is full of nanorods together with a few nanowires. The diameter of the nanorods ranges from 100 nm to 400 nm, whereas the length extends to more than 10 μm. There are some remains on the surface of Sample A, which may be due to the growth temperature not being high enough. SnO$_2$ nanoneedles (obtained at 900 °C) in Sample B, shown in Figures 1b and 1e, are 160 nm in diameter and several micrometers in length. The SnO$_2$ nanoneedles are dimensionally uniform and vertical to the substrates. Figures 1c and 1f show nanowire structures in Sample C (synthesized at 950 °C). The densely tangled SnO$_2$ nanowires have a diameter of approximately 100 nm and a length of several tens of micrometers.

The XRD patterns of Sample B in Figure 2a indicate that the SnO$_2$ nanowires have a tetragonal rutile structure with lattice constants of $a = b = 0.4742$ nm and $c = 0.319$ nm, consistent with the data reported in the powder diffraction file compiled by the JCPDS (Joint Committee on Powder Diffraction Standards, 1985, Card No. 77-0449). No other diffraction peaks for impurities are found. The atomic structure of SnO$_2$ nanowire is
demonstrated by the HRTEM, shown in Figure 2b. The HRTEM images indicate that the SnO$_2$ is structurally uniform and contains no defects such as dislocations and stacking faults in the examined area.

The growth of SnO$_2$ nanostructures can be explained by the theory of vapor-solid (VS) mechanism. If the temperature is higher than the melting point of Sn (231.9 °C), there will be some Sn vapor in the atmosphere. On introducing O$_2$ (at temperature >850 °C), the Sn vapor combines with O$_2$ forming SnO$_2$ nuclei, which deposits on the substrate [19]. More Sn vapor exists at a higher temperature resulting in the formation of more SnO$_2$ nuclei to promote further growth of grains. According to the nuclei theory, the size of the grains is inversely proportional to the number of nuclei. Therefore, the mean width of SnO$_2$ nanostructures decreases with the increase in temperature. Moreover, at higher temperatures, Sn and O will have more energy to combine into SnO$_2$ crystals leading to an increase in the length of the SnO$_2$ nanostructures.

The curves of emitting current density versus the electric field ($J$-$E$) are shown in Figure 3. The turn-on electric field is defined as the electric field required for attaining 10 $\mu$A/cm$^2$ current density, whereas the threshold field is defined as the electric field required for attaining 1 mA/cm$^2$ current density. The SnO$_2$ nanoneedles have the best field emission properties having the lowest turn-on field of 1.23 V/μm and the lowest threshold field of 2.85 V/μm. The turn-on field for nanowires and nanorods is 1.44 V/μm and 3.62 V/μm, respectively. The threshold field for nanowires is 3.12 V/μm; however, the threshold field for the nanorods could not be obtained due to its very small current density (far below 1 mA/cm$^2$) at the voltage range in our facility.

According to Fowler-Nordheim ($F$-$N$) law, the relationship between the current density ($J$) and the applied field ($E$) can be described in the following equation:

$$J = \left( \frac{AE^2}{\varphi} \right) \exp \left( -\frac{B\varphi^2}{\beta E} \right). \quad (1)$$

Here, $\varphi$ is the work function of the emitting material with $\varphi = 4.3$ eV for SnO$_2$. $A$ and $B$ are constants with values $1.56 \times 10^{-10}$ AV$^{-2}$ eV and $6.83 \times 10^9$ VeV$^{-3/2}$ m$^{-1}$, respectively. The $F$-$N$ plot in the inset of Figure 3 exhibits straight lines approximately, indicating that the emission electrons are the barrier tunneling electrons extracted by electric field.
The field enhancement factor $\beta$ can be estimated by using the following formula:

$$\beta = -\frac{6.83 \times 10^3 \varphi^2}{\text{slope}} \text{ cm}^{-1}.$$ 

The slope can be calculated from the $F-N$ plot. In the case of the nanoneedles, the slope is lower than the slope of the nanorods and the nanowires. The estimated value $\beta$ for the nanoneedles is 4042, which is higher than the value for the nanorods (1376) and the nanowires (2165). By using the simplified form of $F-N$ equation for the local field of the emitter, it can be seen that the nanoneedles enhance electric field to a larger degree. Hence, the current density of the nanoneedles is higher than those of the nanorods and the nanowires in the same applied electric field:

$$E_{\text{local}} = \beta E = \beta \frac{V}{d}.$$ 

The various field emission properties of SnO$_2$ samples may result from the difference between their morphologies influenced by the temperature. Firstly, it is generally regarded that a high length-diameter ratio helps to enhance the field; consequently, the nanorods have the weakest field enhancement and the highest turn-on field. Secondly, the density of emitters also affects the field emission ability. More emitters will contribute to a larger emission current, but a very high density of emitters will produce a screening effect. Hence, the nanowires have a little higher turn-on field than nanoneedles, despite having a larger length-diameter ratio. Thirdly, the orientation of the emitter is also an important factor that influences the field emission. If the emission tips are vertical toward the anode, they will strengthen the electric field to the maximum and make the anode easier to capture electrons. As it can be seen from Figure 1b, most of the nanoneedles are placed upright on the substrate indicating that most of the tips contribute to efficient emission. However, the nanowires are too long to be upright. All of them lie horizontally on the substrate entangled with each other suggesting that a part of emitters may be constricted or buried locally by the nanowires which may result in some invalid emission. The small emitter radius, upright placement and less screening effect of nanoneedles cause the greatest enhancement effect, the lowest turn-on field and the highest emission current density.

4 Conclusions

In summary, three different morphologies of SnO$_2$ were obtained at different temperatures. The investigations demonstrated that the field emission properties of SnO$_2$ are greatly influenced by their morphologies. The SnO$_2$ nanoneedles displayed the lowest turn-on field of 1.23 V/$\mu$m and the highest emission current density of 2.19 mA/cm$^2$, because they have small emitter radius, an upright placement toward the anode and a reduced screening effect. The results show that the SnO$_2$ nanomaterials can have potential applications in field emission and other photoelectric devices.

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References

2. T. Guo et al., SID 99 (2010)
5. Y.C. Kim et al., Nanotechnology 20, 095204 (2009)
7. S. Thongpang, Dissertations [Master Engineering], University of Canterbury, 2007
15. L. Li et al., Mater. Lett. 61, 4152 (2007)