One-Step Growth and Field Emission Properties of SnO₂-Capped Silicon Nanowires: A Sn-Catalyzed Approach

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SnO₂-capped Si nanowires have been reproducibly fabricated via a simple one-step chemical vapor deposition (CVD) method, in a high yield and uniform distribution. The Sn-catalyzed reaction is determined by a process of combined vapor−liquid−solid (VLS) and oxide-assisted growth (OAG) mechanism. Detailed microstructures of the nanowires have been investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), together with X-ray diffraction (XRD) analysis and Raman spectroscopy. Field emission (FE) measurements revealed that the SnO₂-capped nanowire structure can significantly reduce the turn-on field value of silicon nanostructures to ∼3.7 V/µm and even lower. A dual-component model for the motion of electrons in the unique heterojunction architecture has been proposed, in comparison with the classical Fowler−Nordheim (FN) theory. Furthermore, adsorption effects have also been confirmed in the actual course of field emission, which can play an important role in the realization of field emission devices.

1. Introduction

Ever since their emergence1,2 1 decade ago, silicon nanowires have always been the hot topics of materials research, driven by their natural compatibility with the modern semiconductor technology and low cost for production. Possibilities of fascinating applications such as biological sensors3 and logical circuits4 have been demonstrated. Up to now, several self-consistent growth mechanisms concerning silicon nanowires have been proposed. The vapor−liquid−solid (VLS),5−7 solid−liquid−solid (SLS),8−11 and oxide-assisted growth (OAG),12−14 etc. are among the best-known ones. Our work has emphasized the application of silicon nanowires, dedicating in an easier way for large-scale fabrication. Meanwhile, the heterojunction architecture has been introduced to tailor the behavior of electron transport in the nanostructures under high external electric field, whose applicability indicates that the efforts in tunable control of the chemistry composition and physical property of nanowires15 do have a fundamental influence on the potential applications.

In the present work, we demonstrate that a representative low melting temperature metal, Sn (melting point, ∼232 °C), is effective to achieve an optimization and simplification for the synthesis procedure of silicon-based nanowires. A successful combination of advantages in established mechanisms has been demonstrated. The new designed approach is uniform-distributed, high-yield, time-saving, and almost substrate-independent. Detailed morphology and composition characterization have verified the successful production of SnO₂-capped Si nanowires. Significantly low turn-on field of vacuum tunneling field emission has been achieved, due to the unique heterojunction architecture. The motion of electrons in the nanowires under extensive external field and the effects of adsorption on emission current density are discussed.

2. Experimental Section

SnO₂-capped Si nanowires were synthesized in a horizontal tube furnace via chemical vapor deposition (CVD), described elsewhere.16 SiO powder is used as the source of the silicon element according to the OAG mechanism, and Sn powder is utilized directly in the reaction zone. An alumina boat loaded with SiO and Sn powder (weight ratio ∼2:3) was placed in the center of a quartz tube. Silicon (100) substrates and TEM copper grids (hydrochloric acid treated) were cleaned ultrasonically in pure acetone and ethanol in turns for ∼5 min, leached in distilled water, and then dried. The substrates were positioned on a clean ceramic slab about tens of centimeters downstream of the source. The quartz tube was then transferred into the furnace and evacuated to vacuum via a mechanical pump. During the whole growth process, the ambient pressure inside the tube was kept at the limit of the pump, about 10 Pa. The furnace was heated up at a rate of 20 °C/min to 1100 °C from the room temperature and kept at that temperature for 30 min, under a continuous argon flow of 100 sccm (standard cubic centimeter per minute). After the growth, the furnace was cooled down naturally to the circumstance temperature, and substrates were picked out of the fabrication system and found covered with a yellowish layer, regardless of the selection of substrates.

A scanning electron microscope (SEM) accelerated at 15 kV in a high-vacuum mode was employed to investigate the general morphology of the as-synthesized sample. A Tecnai F30 transmission electron microscope (TEM) operating at 300 kV was used to analyze the detailed microstructure of the as-grown product. The chemical composition analysis was conducted using energy-dispersive spectroscopy (EDS). X-ray diffraction (XRD) patterns of the as-prepared specimen were recorded with a Rigaku Dmax/2400 device. Raman spectra of the as-fabricated material were measured by a Renishaw Raman microscope system with an excitation wavelength of 514 nm. Field emission (FE) properties of the silicon-based nanostructures were studied in a homemade system under ultrahigh vacuum (UHV) condition better than ∼6 × 10⁻¹⁰ Pa. The sample was adhered with commercial conductive glue to one of the two stainless steel...
plates as cathode, and another parallel plate was biased as the anode. The emission current was recorded using a Keithley 485 picoammeter.

3. Results and Discussion

3.1. Morphology Characterization. Generally, the wire-shaped high-yield products cover the whole substrate uniformly, with tens of micrometers in length and tens of nanometers to \( \sim 100 \text{ nm} \) in diameter. SEM images of SnO\(_2\)-capped Si nanowires grown on a copper TEM grid are shown in Figure 1, parts a and b. An obvious heterojunction composed of a spherical tip and long wirelike stem structure is clearly identified. To determine the chemical composition of these nanowires, the EDS analysis was carried on the nanowires. As shown in Figure 1c, despite the inevitable signal of Cu arising from the copper grid, the nanowires are mainly composed of Si and O, with an atomic ratio \( \sim 1:1 \). Meanwhile, the percentage of Sn composition is found to be rather small.

A typical SEM image of the silicon nanostructures grown on the silicon (100) substrate is shown in Figure 2a. It is safe to point out the existence of ball-like tip structure on the top of every individual stem nanostructure, which is consistent with the previous observed results in Figure 1. The microwhisker has further revealed a neck substructure, which may result from the unique catalyzing mechanism of Sn. Corresponding EDS analysis results confirmed the silicon composition in the structures, shown in Figure 2b-d for labeled regions 1, 2, and 3 on the microwhisker, respectively. Still, the silicon to oxygen ratio is approximately 1:1 in the main region of the stem. The tip has a much higher Sn concentration than the neck and stem structure. In addition, the core of the stem has a bright contrast, indicating that there may be a different phase type from the outer layer in the inner core.

To understand the phase structure of the detected chemical composition, XRD experiments were conducted for the nanowires grown on silicon (100) substrates. A typical XRD pattern is shown in Figure 3a. The main peaks were indexed to the face-centered cubic Si, body-centered tetragonal Sn, and tetragonal SnO\(_2\). Clearly established Si(111) and Si(220) peaks confirm the existence of silicon element in the nanowires and further give evidence of the crystalline nature of the Si nanowire. The Sn- and SnO\(_2\)-related peaks also approve the EDS studies and show the detailed information of tip structure. Furthermore, the well-established Raman signals in Figure 3b suggest the good crystalline nature of the as-grown sample. As described by corresponding theory,\(^\text{17}\) the left-shifted and extended silicon TO peak reveals the low-dimension nature of the silicon composition in our sample.
The microstructures of the silicon nanowires were further analyzed by TEM in scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM) mode. Figure 4a has shown the general morphology of as-grown nanowires ultrasonically removed from the substrates. In Figure 4b, the linear scanning EDS analysis was conducted both transversely and longitudinally on an individual wire shown in the STEM image. Patterns 1 and 2 are the element mapping of the transverse and longitudinal scans, with scanning directions indicated by the arrows. In pattern 1, the peak of Sn indicates a core–shell structure (for simplicity, Si in the scanning results is not shown here). The sharp steps of Si and Sn shown in pattern 2 come from an atomic interface of Sn and Si in the core structure, which is consistent with the different contrast in the STEM image. As shown in Figure 4c, the crystalline core region of the nanowire is around ~100 nm with an amorphous layer tens of nanometers. There is a sharp atomic boundary along the growth direction between the crystalline core and the oxide amorphous sheathing layer. From the diffraction pattern in the inset, we can index the growth direction to be (111), which is the energy favorite growth direction for diamond silicon structures. According to Figure 4c, the planar spacing is \( d_{111} = 0.32 \) nm, and the lattice constant measured is \( a = 0.55 \) nm, which is 1.29% larger than that of the bulk silicon, \( a_0 = 0.543 \) nm. This may come from the expansion and distortion induced during the growth. The corresponding EDS analysis shows that the chemical composition of the amorphous layer is SiO\(_x\), without Sn.

### 3.2. Synthesis Mechanism

First of all, considering the morphology characteristic and the chemical composition of the nanostructures, especially the existence of the ball-like tip structure on each nanowire, the VLS mechanism should have played an important role underlying the maintenance of tips and formation of nanowires. Sn composition in the tip region catalyzes the growth, which is similar to the effect of other catalysts such as gold and nickel, etc., used in the VLS mechanism for nanowire growth. Second, the unique core–shell morphology is an analog to what the OAG mechanism favors. Thus, a combined VLS–OAG mechanism should be determinate in the whole synthesis process.

We propose that, there are three important sections of the whole growth process dependent with the temperature of the reaction system. (1) Initially, after the temperature exceeds the melting point, Sn powder begins to evaporate. When gathered on the substrates, transported by the carrier gas downstream, Sn vapor forms nanosized liquid droplets. (2) Further elevation of temperature causes the sublimation of SiO, and the existence of remaining Sn powder in the source catalyzes such physical transition into a relatively low-temperature region which makes our approach applicable around just 1100 °C. When delivered to the substrates, SiO will be adsorbed into Sn droplets and then react with Sn there. That is why there is oxygen in the tip region. Then VLS-related saturation and precipitation subsequently come into work, followed by the formation of nanowires composed of silicon and oxygen. Meanwhile silicon and oxygen in the wires will further change into crystalline silicon inner core and outer oxide amorphous layer. In this period, liquid Sn catalyst of larger scale may tend to support multiwire growth, which constructs the neck structure and finally contributes to one common main wire as shown in Figure 2. (3) After the furnace is shut down, SiO vapor diminishes quickly as the temperature falls beyond its evaporation region, and the growth of silicon core is terminated. However, the evaporation of Sn in the source will continue until the temperature drops below the melting point. Then the liquid Sn may be forced into the nanostructures due to continuous adsorption and finally solidifies in the stem regions as shown in Figure 4b. In the tips, Sn may combine with the oxygen into SnO\(_2\) crystalline form.

### 3.3. Field Emission Properties

To study the field emission effect of the as-grown sample, we investigated the dependence of emission current density \( J \) on the apparent electric field \( E \), which is defined as the applied voltage divided by the vacuum gap, \( D \). The voltage is limited in a range of 0–5 kV. We characterized the FE properties under circumstance of different \( D \) values of 200, 300, and 500 \( \mu \)m, respectively. The results are shown in Figure 5a. It is clear that a larger \( D \) value corresponds to a higher current density in the experiment. According to an adsorption–desorption model,\(^{19}\) when the \( D \) value increases, the probability for the remaining molecule in the chamber to be adhered on the sample will increase, which lowers the effective work function of the sample and then increases the current in the emission performance. The turn-on field (defined as the electric field to a current density of \( 10^{-9} \) A/cm\(^2\)) is estimated to be 5.57, 4.43, and 3.67 V/\( \mu \)m for a \( D \) value of 200, 300, and 500 \( \mu \)m, respectively. These newly
achieved values are significantly lower than that of the previous obtained results on silicon nanostructures.\textsuperscript{20–22}

In the low electric field region, our sample exhibits quite a good vacuum tunneling mode field emission property as predicted by Fowler and Nordheim’s formula:\textsuperscript{23–25}\n
\[ J \propto (\beta E^2/\phi) \exp(-B\phi^{3/2}/\beta E), \]

where \[ B = 6.83 \times 10^9 \text{ (V \cdot eV}^{-3/2} \cdot \text{m}^{-1}) \]

Nevertheless, in the relative strong electric field region, experiments deviate from the theoretical estimation systematically to larger current site. We maintain that this deviation is one intrinsic property of our sample, which should be related to the unique SnO\textsubscript{2}-capped configuration. A possible mechanism underlying this phenomenon is that (1) when the electric field is in the relatively low region, electrons from the substrate tend to transport along the stem directly into the SnO\textsubscript{2} sphere and tunnel into vacuum from there. The work function electrons face there is that of SnO\textsubscript{2}. (2) When the electric field increased, more electrons can be dragged up into the nanostructures from the substrate and start to tunnel into the vacuum from the sides along the wires, which increase the current and result in the deviation in the FN plot. In this point of view, taking the local work function of SnO\textsubscript{2} to be 4.5 eV, the field enhancement factor \( \beta \) is estimated to be 2331, 2983, and 4710, respectively, for a \( D \) value of 200, 300, and 500 \( \mu \text{m} \). As mentioned by this two-step model, modifications in structures can have a great influence on the field emission of silicon-based nanomaterials and may help to accelerate the application course.

4. Conclusions

High-yield fabrication of SnO\textsubscript{2}-capped Si nanowires has been easily and reproducibly achieved in a uniform-distributed and time-economic way. The relatively simple setup is in favor of further scaling production. Low turn-on field, \( \sim 3.7 \text{ V/}\mu\text{m} \), of such nanostructures is achieved and may be utilized in considering the natural compatibility with contemporary silicon-based modern technology.

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References and Notes


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Figure 5. Field emission properties of the SnO\textsubscript{2}-capped Si nanowires: (a) field emission properties of the as-grown sample under different anode–cathode distance, \( D \), values: 200, 300, and 500 \( \mu\text{m} \); (b) the corresponding Fowler–Nordheim plot.