Growth of Well-Aligned ZnO Nanorod Arrays on Si Substrates by Thermal Evaporation of Cu–Zn Alloy Powders

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Well-aligned ZnO nanorod arrays with uniform diameters and lengths have been fabricated on a Si substrate by simple thermal evaporation of Cu–Zn alloy powders in the presence of oxygen without using a template, catalyst, or pre-deposited ZnO seed layer. The ZnO nanorods are characterized by X-ray diffraction, electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy and the growth mechanism is suggested. The nanorods have a single-crystal hexagonal structure and grow along the (0001) direction. Their diameters range from 200 to 400 nm and the lengths are up to several micrometers. The photoluminescence (PL) and Raman spectra disclose the optical properties of the products. The PL spectra show intense near-band ultraviolet emission at 378 nm from the nanorod arrays. The well-aligned ZnO nanorod arrays have a low turn-on field of 6.1 V/μm, suggesting good field emission properties. The simple synthesis methodology in conjunction with the good field emission and optical properties make the study both scientifically and technologically interesting.

Keywords: ZnO Nanorod Arrays, Cu–Zn Alloy, Raman Spectroscopy, Photoluminescence, Field Emission.

1. INTRODUCTION

Zinc oxide is an important semiconductor having a wide direct band gap (3.37 eV), large exciton binding energy (60 meV), as well as good piezoelectrical properties.1,2 In the past several years, one-dimensional (1D) ZnO nanostructures such as nanowires, nanotubes, nanobelts, nanocombs, and their three-dimensional assembly have attracted increasing attention due to their potential applications in nanolasers, field effect transistors, field emitters, nanoresonators, and high-efficiency photonic devices.3–10 It has been experimentally confirmed that the performance and device applications of 1D ZnO nanostructures can be enhanced and broadened if they are synthesized controllably on suitable substrates with good alignment and uniform morphology.11 Hence, synthesis of aligned 1D ZnO nanowire or nanorod arrays attracts increasing attention. Preparation of aligned ZnO nanowires or nanorods has been demonstrated by template-confined growth,12 catalyst-assisted vapor–liquid–solid (VLS) growth,13–15 and ZnO seed layers-assisted solution-phase growth.4,16–17 However, the use of a template, metal catalyst, or ZnO seed layer increases the complexity of the synthesis procedures and introduce adventitious impurities, consequently degrading the performance of the products and limiting their applications in some electronic and optoelectronic devices. Thermal evaporation and condensation of Zn or ZnO vapor species can be used to fabricate heteroepitaxially ZnO nanostructures on suitable substrates,18 in which exotic metals catalysts or ZnO seed particles are not necessary. This vapor–solid growth method, albeit technologically simple, often yields mixtures of ZnO nanostructures with different morphologies due to sporadic supply and variable vapor pressure of Zn at the product zone.19 It has been disclosed that the Zn/O2 vapor pressure ratio is the major factor determining the morphology of ZnO nanostructures.19–22 Though the importance of the Zn vapor pressure has been indicated, it is actually hard
to design a simple and effective method to control the vapor generation. Very recently, a convenient method has been developed by our group to achieve direct and large-area growth of 1-D ZnO nanostructures on a conductive brass substrate. This process consists of thermal oxidation of a Cu_{50}Zn_{34} alloy foil in the presence of oxygen. Various 1-D nanostructures such as nanowires, nanobelts, nanocombs, and nanosheets have been in situ grown on the Cu–Zn alloy substrate under different reaction temperatures. Since the Zn species in the ZnO product comes from the brass substrate, the reaction temperature has an important influence on the segregation and diffusion rates of the Zn atoms as well as the Zn vapor pressure. Thus, this provides a simple way to control the release of Zn vapor and adjust the morphology of the final products by varying the reaction temperature.

In this work, we demonstrate that well-aligned ZnO nanorod arrays with uniform diameters and lengths can be fabricated on a Si substrate by a simple thermal evaporation of Cu–Zn alloy powders (30 at% Zn) in Ar/O_2. The synthesis of ZnO nanorods presented here is not the same as conventional thermal evaporation and oxidation of Zn powders. Addition of Cu increases the boiling point of the Cu–Zn alloy slowly and continuously at the reaction temperature. In addition, the CuO coming from the oxidation of Cu on the surface can be reduced to pure Cu by the Zn vapor before re-oxidation, thereby absorbing a portion of the Zn vapor and mitigating the release of Zn vapor. The added Cu effectively controls the Zn vapor instead of a catalyst finally yielding uniform and aligned ZnO nanorod arrays on a large-area Si substrate. These well-aligned ZnO nanorod arrays possess good and stable field emission properties with a low turn-on field of 6.1 V/μm. Raman and photoluminescence measurements reveal that the nanorod arrays have good crystallinity and optical properties.

2. EXPERIMENTAL PROCEDURES

The well-aligned ZnO nanorod arrays were prepared by direct thermal evaporation and oxidation of Cu–Zn precursors under Ar/O_2 at 700–900 °C. The Cu–Zn alloy powders (70/30 atm%, 60 mesh, Aldrich) were loaded on a ceramic boat in a quartz tube 3 cm in diameter which was located in the center of a horizontal tube furnace. A Si (100) wafer (1 × 2 cm²) was ultrasonically cleaned in acetone, ethanol, and distilled water sequentially, and then dried under flowing nitrogen. The Si substrate was placed 1 cm above the surface of the Cu–Zn alloy powders. The system was first flushed with Ar several times to remove oxygen and moisture and then heated to the desired temperature (700–900 °C). Afterwards, argon was replaced by an Ar/O_2 (4% O_2) mixture at a flow rate of 50 sccm and the system was kept at this temperature for 60 min. The reactor was then cooled down to room temperature in argon and a white homogeneous layer was formed on the substrate.

Field emission scanning electron microscopy (FE-SEM, FEI, NOVA NANOSEM 400), X-ray diffraction (XRD, Philips X’ Pert Pro), energy-dispersive X-ray spectrometry (EDS, Oxford INCA 200), as well as X-ray photoelectron spectroscopy (XPS, ESCALB MK-II) were employed to characterize the products. Room temperature photoluminescence (PL) was conducted on an Amino Bowman Series-2 spectrometer equipped with a 325 nm He–Cd laser. The Raman spectra were acquired on a Renishaw micro-Raman system 2000 at room temperature. The field emission measurements were carried out using a parallel-plate diode configuration in a test chamber maintained at 1.5 × 10⁻⁶ Torr. The aligned ZnO nanowire arrays on the Si substrate were directly used as the FE cathode. Another plate-shaped stainless steel electrode was used as an anode with a sample-anode distance of 200 μm. The high voltage was supplied by a power source (Keithley 248), and the emission currents at different applied voltages were measured using a Keithley 6514 electrometer with an accuracy of 10⁻¹¹ A.

3. RESULTS AND DISCUSSION

Figures 1(a) and (b) which show the SEM images of the product synthesized at 750 and 850 °C, respectively indicate large amounts of well-aligned nanorods with a uniform length grown on the entire Si substrate. The hexagonal facet can be obviously observed from the large magnification images in the inset. The nanorods have lengths of several micrometers. Their diameters increase from 200–300 to 300–400 nm when the reaction temperature is raised from 750 to 850 °C and the nanorods coalesce at their tips at a high reaction temperature. A typical EDS spectrum is shown in Figure 1(c). Only Zn and O signals can be observed, suggesting that the nanorods are ZnO. In contrast, if the Cu–Zn powders are replaced by pure Zn while keeping other experimental parameters the same, nanorods cannot be found, implying that the Cu–Zn alloy is crucial to the growth of uniform and aligned ZnO nanorod arrays on the Si substrate. The detailed growth mechanism will be discussed later in this section. Because the nanorods produced at 750 °C have smaller diameters, the nanorod arrays synthesized at this temperature are selected for further investigation.

Figure 2(a) depicts the typical XRD patterns of the ZnO nanorod arrays. All the strong peaks in these patterns can be readily indexed to hexagonal wurtzite ZnO with cell constants comparable to the reported data (JCPDS Card No. 75-1526). No copper and copper oxide peaks can be observed. In the XRD patterns, the ZnO (002) peak is the dominant one and its intensity is much higher than...
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Fig. 1. SEM images of the products synthesized at (a) 750 °C and (b) 850 °C; (c) Typical EDS spectrum of the product. The insets in (a) and (b) are the corresponding large magnification SEM images.

Fig. 2. (a) XRD patterns and (b) XPS spectrum of ZnO nanorod arrays produced at 750 °C.

those of the other peaks, implying that the as-prepared ZnO nanorods grow preferentially along the (001) direction. The XPS results in Figure 2(b) suggest that the products are composed of Zn and O with the atomic ratio close to 1:1, further corroborating the high purity of the ZnO nanorods.

Room temperature micro-Raman scattering and photoluminescence (PL) are employed to evaluate the optical properties of the ZnO nanorods and the results are displayed in Figures 3 and 4, respectively. It is well known that the wurtzite structure of ZnO belongs to the \( \Gamma_{6v} \) \((P6_{3}mc)\) space group. The primitive cell includes two units...
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The large lattice mismatch and the difference in the crystal structure between ZnO and Si, aligned ZnO nanorod arrays can be fabricated directly on the Si substrate by heating and oxidation of Cu–Zn alloy powders without using a template or catalyst because the ZnO nanoparticle seed layers is formed in situ on the Si substrate when the Cu–Zn powders are heated. When most of the Zn species in the Cu–Zn alloy are consumed, growth of the ZnO nanorods ceases. As a result, well-aligned 1D ZnO nanorod arrays are produced on the Si substrate. Because the Zn species in the ZnO comes from the Cu–Zn alloy only, the reaction temperature has a large influence on the segregation and diffusion rate of the Zn atoms in the Cu–Zn alloy as well as the Zn vapor pressure. The higher the reaction temperature, the faster the Zn atoms segregate and diffuse, and the higher is the Zn vapor pressure. Therefore, the ZnO nanorods produced at higher temperatures have larger diameters due to the faster growth rates, as suggested by Figure 1.

In recent years, the electron field emission (FE) properties of 1D vertically aligned nanostructures have attracted a great deal of attention because of their high electron emission efficiency. It is well known that the FE properties depend largely on the work function (φ) of the emitter materials and emitter geometry which determines the field enhancement factor (β). Research on FE in the past ten years has mainly focused on carbon nanotubes (CNTs) because of their high aspect ratio, small curvature radius, i.e., high β, as well as high mechanical stability and conductivity. Similar to CNTs, ZnO nanowires or nanorods have small curvature radii, high aspect ratios, and high β. Furthermore, 1D ZnO nanostructures have better thermal stability and oxidation resistance compared to CNTs, enabling the materials to tolerate a higher oxygen partial pressure and poorer vacuum in FE applications. Therefore, 1D ZnO nanostructures are promising cathodic

**Fig. 4.** PL spectrum of ZnO nanorod arrays produced at 750 °C.

**Fig. 5.** Field emission current density (J) as a function of applied electric field (E) measured from the nanorod arrays together with the corresponding F-N plot (inset).
materials in FE devices. Here, we investigate the FE properties of the aligned ZnO nanorod arrays produced at 750 °C. The experimental procedures to measure the FE properties can be found elsewhere. Figure 5 shows the measured field emission current density \( J \) as a function of the applied electric field \( E \) measured from the quasi-aligned ZnO nanorods at a sample to cathode distance of 200 \( \mu \text{m} \). \( J \) is calculated by dividing the measured emission current by the area of the ZnO nanorods assuming homogeneous electron emission from the sample. It is found that the turn-on field \( E_{\text{to}} \), which is usually defined as the electric field that produces a current density of 10 \( \mu \text{A/cm}^2 \), is 6.1 V/\( \mu \text{m} \). This value is lower than or comparable to the \( E_{\text{to}} \) reported for 1D ZnO nanostructures in the literature.\(^3,4,36-37\)

The field emission current–voltage characteristics are further analyzed by using the Fowler-Nordheim (F-N) equation:\(^1\)

\[
J = \left( \frac{\lambda e^2}{\phi} \right) \exp\left( -\frac{B\phi^{3/2}}{E} \right)
\]

where \( J \) is the current density, \( E \) is the applied field, \( \phi \) is the work function of the emitting materials, \( B \) is field enhancement factor, and \( A \) and \( B \) are constants with values of 1.56 \times 10^{-10} \text{ (A eV V}^{-2}) \text{ and 6.83} \times 10^{3} \text{ (V eV}^{-3/2}) \text{ \( \mu \text{m}^{-1}) \text{, respectively. The F-N plots of the } \ln(J/E^2) \text{ versus } 1/E \text{ are shown in the inset of Figure 5(a). The good linearity within the measurement range suggests that electron emission from the ZnO nanorods exhibits the F-N behavior. Taking the work function of ZnO as } 5.3 \text{ eV, the } \beta \text{ value of the nanorods is estimated to be about } 2183. \text{ The good FE properties observed from the ZnO nanorods are believed to stem from the sharp tips, high aspect ratio, good crystallinity, as well as quasi-aligned configuration.}

4. CONCLUSION
Vertically aligned ZnO nanorod arrays have been synthesized on silicon substrates by simple thermal evaporation of Cu–Zn alloy powders in Ar/O\(_2\) without any catalysts or predeposited buffer layers. The diameters of the nanorods are in the range of 200 to 400 nm and their lengths are up to micrometers. The ZnO nanorod arrays possess good electron emission properties. The turn-on field is about 6.1 V/\( \mu \text{m} \) and field enhancement factor is 2183. Raman and photoluminescence spectra suggest that the ZnO nanorod arrays with high crystallinity and few oxygen vacancies have an excellent optical quality. The good field emission and optical properties bode well for their use in light- and electron-emitting nanodevices.

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References and Notes


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