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

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ABSTRACT

Well-aligned ZnO nanorod arrays with uniform diameters and lengths have been fabricated on Si substrate by simply thermal evaporation of Cu-Zn alloy powders in the presence of oxygen. The ZnO nanorods are characterized by X-ray diffraction, electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron energy. The nanorods have a single-crystal hexagonal structure and grow along the <0002> direction with diameters of 200-400 nm and lengths up to several micrometers. The well-aligned ZnO nanowire arrays exhibit good field emission properties with a low turn-on field of 6.1 V/\mu m. 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 nanowire arrays. The simple synthesis methodology in conjunction with the good field emission and optical properties make the study both scientifically and technologically interesting.

1. INTRODUCTION

Zinc oxide is an important semiconductor having a direct wide 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, nanocomb and their three-dimensional assembly have attracted increasing attention due to their potential applications in nanolasers, field effect transistor vacuum cathode field emitters, nanoresonator, and high-efficiency photonic devices [3-10]. It is generally believed that the performance and device applications can be enhanced and broadened if the 1D ZnO nanostructures can be synthesized controllably with good alignment and uniform morphology. For example, the field emission properties of 1D ZnO nanostructures can be greatly improved if they are aligned perpendicularly to the substrates [11]. Recent research works also suggest that the light-emitting properties of ZnO depend on the alignment of the nanostructures [12]. Consequently, the synthesis of well-aligned 1D ZnO nanowire or nanorod arrays is of great interest. Aligned ZnO nanowire or nanorod arrays are usually synthesized by a wet chemical method with the precoated ZnO nanoparticles as the seed layer or by a vapor-phase transport process with the assistance of metal catalysts or a template-assisted growth [5,13-16]. However, the use of templates or predeposition of a catalyst or ZnO seed layer may increase 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. Therefore, it is desirable to develop a simple catalyst-free and template-free procedure to synthesize aligned ZnO nanowire or nanorod arrays.

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 simply thermal evaporation of Cu-Zn alloy powders (30 at% Zn) in Ar/O\textsubscript{2}. The well-aligned ZnO nanowire arrays show good field emission properties with a low turn-on field of 6.1 V/\mu m and good field emission stability. Raman and photoluminescence measurements reveal intensive near-band ultraviolet emission at 378 nm and indicate that the nanowire arrays have good optical properties. The simple synthesis methodology together with the...
resulting good FE and optical properties make the procedure scientifically and technologically important.

2. EXPERIMENTAL PROCEDURES

Well-aligned ZnO nanowire arrays were prepared by direct thermal evaporation and oxidation of Cu-Zn precursors under Ar/O₂ at 700-900°C. The Cu-Zn alloy powders (70/30 atm%, 60 mesh, Aldrich) were loaded into a ceramic boat in a quartz tube 3 cm in diameter centered inside a horizontal tube furnace. A Si(100) wafer (0.5x0.5 cm²) was ultrasonically cleaned in acetone and distilled water sequentially, and then dried in nitrogen. The Si substrate was placed 0.5 cm from the surface of the Cu-Zn alloy. This system was 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/O₂ (4% O₂) mixture with 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 homogeneous white 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 T6400 and JY HR800 laser Raman spectrometers at room temperature. The field emission measurements were carried out using a parallel-plate diode configuration in a test chamber maintained at 1.5 x 10⁻⁶ Torr.

3. RESULTS AND DISCUSSION

Figures 1(a) and (b) which show the SEM images of the product synthesized at 750 and 850 °C, respectively suggest that large amounts of well-aligned nanowires with a uniform height are formed 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 become wider from 200-300 to 300-400 nm when the reaction temperature is raised from 750 to 850°C and the nanorods coalesce at high reaction temperature. A typical EDS spectrum is shown in FIG 1(c), and only Zn and O signals are observed, suggesting that the nanorods are ZnO.

Considering that the nanorods produced at 750 °C have smaller diameters, the nanorod arrays synthesized at this temperature are selected for further investigation.
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Figure 2(a) depicts the typical XRD patterns of the ZnO nanowire 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 those of the other peaks, implying that the as-prepared ZnO nanowires grow preferentially along the (001) direction. The XPS results in FIG 2(b) suggest that the products are composed of Zn and O with the atomic ratio close to 1:1, further confirming the high purity of the ZnO nanorods.

![XRD patterns of ZnO nanowire arrays](image)

**FIG. 2:** (a) XRD patterns and (b) XPS spectrum of ZnO nanowire arrays produced at 750°C

Room temperature micro-Raman scattering and photoluminescence (PL) are employed to evaluate the optical properties of the ZnO nanowires and the results are displayed in FIG. 3 and 4, respectively. It is well known that the wurtzite structure of ZnO belongs to the C\textsuperscript{6\_v} (P6\textsubscript{3}mc) space group. The primitive cell includes two units with all atoms occupying the 2b sites of the symmetry group C\textsubscript{3v} [1,17]. Group theories predict that the Raman active modes of ZnO are A\textsubscript{1}+E\textsubscript{1}+2E\textsubscript{2}, in which the A\textsubscript{1} and E\textsubscript{1} modes are polar and split into two transverse optical (TO) and longitudinal optical (LO) components [1,17]. The peaks at 381, 438, and 582 cm\textsuperscript{-1} in the Raman spectrum (Fig. 3) can be assigned to the A\textsubscript{1}(TO), E\textsubscript{2}(high) and E\textsubscript{1}(LO) modes of wurtzite hexagonal ZnO, respectively [1]. The second order Raman scattering is observed to be at 332 cm\textsuperscript{-1} [18-19]. The Si Raman signals are also observed at 520 cm\textsuperscript{-1} [8]. The intense, sharp, and dominant E\textsubscript{2} mode at 439 cm\textsuperscript{-1} indicates that the ZnO nanowires are highly crystalline with a wurtzite hexagonal phase, in agreement with the XRD results. The PL spectrum in FIG 4 discloses intense near-band-edge ultraviolet (UV) emission at 378 nm which matches the band gap of bulk ZnO and is commonly attributed to the radioactive recombination of free exciton via the exciton-exciton collision process [8]. No visible green band emission is observed, indicating that the ZnO nanowires are highly crystalline with few oxygen vacancies.

![Raman spectrum of ZnO nanowire arrays produced at 750°C](image)

**FIG. 3:** Raman spectrum of ZnO nanowire arrays produced at 750°C

These results indicate that well-aligned ZnO nanorod arrays have been successfully produced on the Si substrate by simple thermal evaporation of Cu-Zn alloy powders. At high temperatures of 700-900°C, Cu\textsubscript{0.7}Zn\textsubscript{0.3} alloys and Cu are in the solid state. Solid Cu has negligibly low vapor pressure, whereas Zn is in the liquid state and its vapor pressure which is very high
increases rapidly with temperature. When the Cu-Zn alloy is heated, the Zn species segregate and diffuse towards the surface of the Cu-Zn alloy and are vaporized to form Zn vapor. Upon exposure to oxygen, the Zn vapor reacts with O₂ to form ZnO species which subsequently deposit on the Si substrate to form a thin ZnO nanoparticle film. As the reaction proceeds with continuous supply of Zn and O species, aligned ZnO nanorods gradually grow epitaxially on the preformed ZnO seeds. This is similar to the synthesis of 1D ZnO nanowires or nanorods using ZnO seeds or buffer layers as reported in the literature [20-21]. 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 grown 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 grown at higher temperature have larger diameters due to faster growth rate, as suggested in FIG. 1.

In recent years, the FE properties of 1D vertically aligned nanostructures have attracted a great deal of attention because of their high electron emission efficiency [22]. It is well known that FE properties depend largely on the work-function (φ) of the emitter materials and emitter geometry which determines the field enhancement factor (β) [22]. 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 [23-25]. 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 [26], enabling the materials to tolerate a higher oxygen partial pressure and poorer vacuum in FE applications [27]. Therefore, 1D ZnO nanostructures are promising cathode 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 [11]. 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 nanowires at a sample to cathode distance of 200 μm. J is calculated by dividing the measured emission current by the area of the ZnO nanowires assuming homogeneous electron emission from the sample. It is found that the turn-on field (E_on) which is usually defined as the electric field that produces a current density of 10 μA/cm², is 6.1 V/μm. This value is lower than or comparable to the E_on reported for 1D ZnO nanostructures in the literature [8, 26, 28-29].

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**FIG. 4: PL spectrum of ZnO nanowire arrays produced at 750°C**

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**FIG. 5: Field emission current density (J) as a function of applied electric field (E) measured from the nanowire arrays together with the corresponding F-N plot (inset)**

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

\[ J = (A \beta^2 E^2/\phi) \exp (-B \phi^{3/2}/\beta E) \]  

(1)
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where \( J \) is the current density, \( E \) is the applied field, \( \phi \) is the work function of the emitting materials, \( \beta \) is field enhancement factor, and \( A \) and \( B \) are constants with values of \( 1.56 \times 10^{-10} \) (A eV \(^{-2}\)) and \( 6.83 \times 10^{5} \) (V eV\(^{-3}\) \( \mu \)m\(^{-1}\)), respectively. The F-N plots of the ln(\( J/E^{2} \)) vs \( 1/E \) are shown in the inset of Fig 5(a). The good linearity within the measurement range suggests that electron emission from the ZnO nanowires follows the F-N behavior. Taking the work function of ZnO as 5.3 eV, the \( \beta \) value of the nanowires is estimated to be about 2183. 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, which can be further enhanced if they have smaller diameters and are grown on a more electrically conductive substrate.

4. CONCLUSION

Vertically aligned ZnO nanorod arrays have been synthesized on silicon substrates by simple thermal evaporation of Cu-Zn alloy powders in \( \text{ArO} \), without any catalyst 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 nanowire arrays exhibit good electron emission properties. The turn-on field is about 6.1 V/\( \mu \)m and field enhancement factor is 2183. Raman and photoluminescence spectra suggest that the ZnO nanorod arrays are highly crystalline with fewer oxygen vacancies and have an excellent optical quality. The good field emission and optical properties suggest promising applications for the ZnO nanowires in light- and electron-emitting nanodevices.

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