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Synthesis and field emission properties of well-aligned ZnO nanowires on buffer layer

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ABSTRACT

Well-aligned ZnO nanowires were grown on Si (111) substrates pre-coated with a ZnO buffer layer. The nanowires are single-crystalline wurtzite structures with a preferential growth in the [0001] direction. Room temperature photoluminescence (PL) measurements of as-grown nanowires annealed in argon and air exhibited a strong ultraviolet emission and suppressed visible emission, affirming the presence of few defects. Field emission properties of the nanowires were investigated, and the lowest turn-on field obtained was 3.8 V/μm at a current density of 0.1 μA/cm^2, with a corresponding field enhancement factor β of 1644. Current–voltage (*I–V*) and capacitance–voltage (*C–V*) measurements showed that the contact was ohmic and the ZnO nanowires were n-type, with little *C–V* hysteresis.

1. Introduction

Transparent conducting oxides (TCOs) are used in many important technological applications such as flat panel displays, solar energy devices and optoelectronic devices [1–3]. Although indium-tin-oxide (ITO) has been in practical use for most such applications, the cost and scarcity of indium, the principal material of ITO, have resulted in the research and development of other TCOs as possible substitutes to ITO [4]. Zinc oxide (ZnO) which has a wide bandgap of 3.37 eV and large exciton binding energy of 60 meV at room temperature has attracted considerable interest due to its inexpensive and non-toxic source materials. In this paper, we investigate the field emission properties of ZnO nanowires. One-dimensional (1-D) vertically-aligned nanostructures such as ZnO nanowires have been attracting much attention in recent years to be fabricated as field emission display (FED) because of their high efficiency, reduction of cost and device size compared to conventional thermionic emitters [5]. Although carbon nanotubes (CNTs) have attracted much attention due to their low turn-on fields and large emission currents [6], oxide emitters are more stable in harsh environment and controllable in electrical properties [5].

2. Experimental details

A mixture of ZnO (Sigma-Aldrich) and graphite powders (Fluka) in the weight ratio (1:1) was placed in a small quartz tube with a Si (111) substrate, and inserted into a tube furnace. A 70 nm thick ZnO buffer layer was sputtered on the substrate by RF magnetron sputtering at 450 °C. The ZnO nanowires were synthesized at 900 °C for 30 min, 2 h and 3 h at atmospheric pressure, under a constant flow of Argon (99.99%) with a flow rate of 200 sccm. For photoluminescence (PL) studies, nanowires synthesized for 30 min were annealed at 500 °C in argon and air with a flow rate of 50 sccm for 1 h at a pressure of 0.003 MPa.

Scanning electron microscopy (FESEM, Philips XL30 FEG SEM) characterized the morphology of the synthesized products, while transmission electron microscopy (TEM, Phillips FEG CM300) and X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu Kα radiation at λ = 1.541 Å) characterized the crystal structures of the ZnO nanowires. The photoluminescence (PL) of the nanowires was measured by Renishaw Micro-PL with He–Cd laser at 325 nm at room temperature. Current–voltage

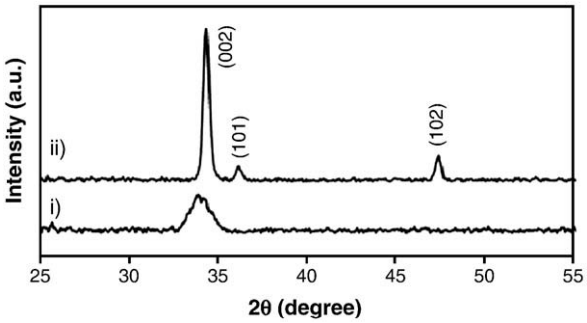

Fig. 1. XRD pattern of i) ZnO thin film (70 nm thickness) and ii) ZnO nanowire arrays.

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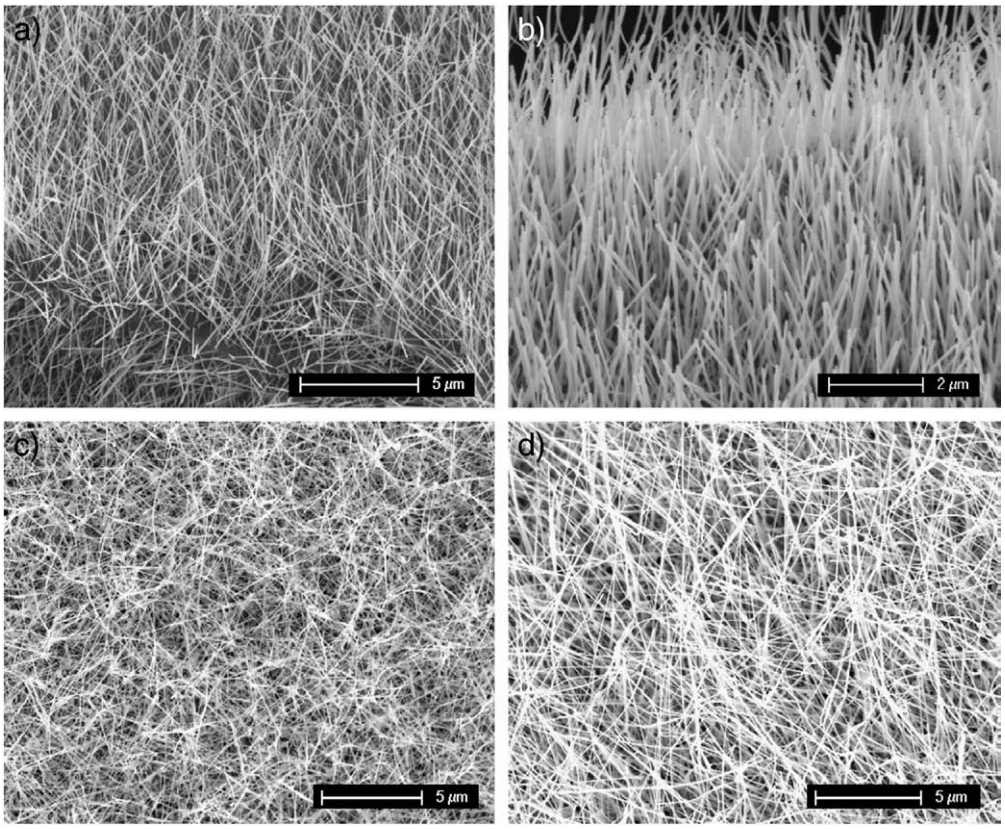

Fig. 2. SEM images show the morphologies of the as-prepared well-aligned ZnO nanowire arrays. a) Growth time of 30 min. b) Tilted view at 30°. c) Growth time of 2 h. d) Growth time of 3 h.

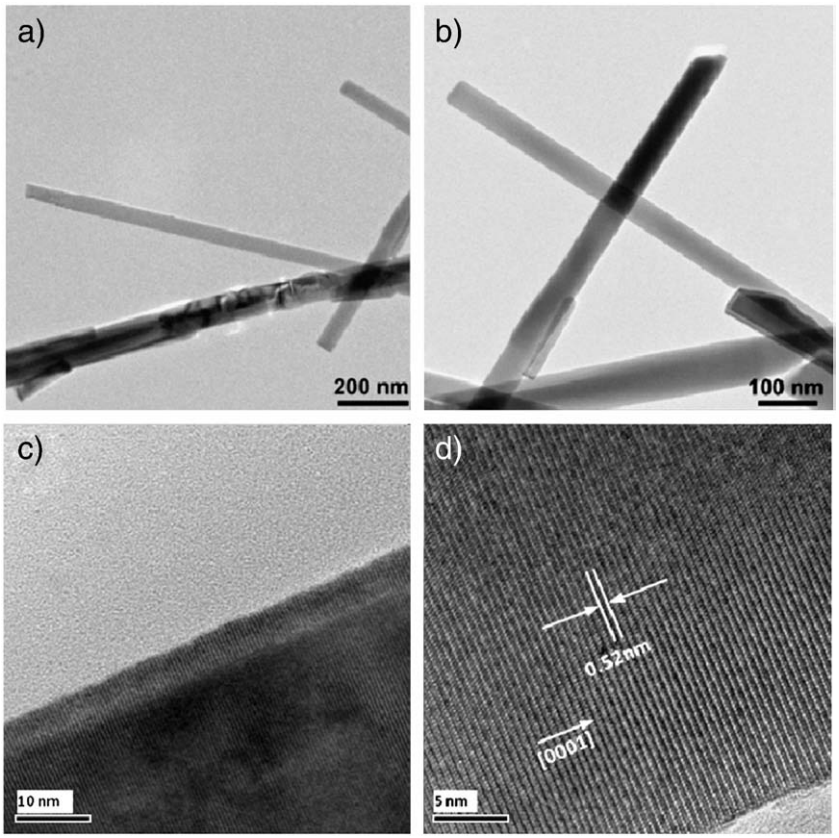

Fig. 3. TEM images. a) and b) Low magnification images of synthesized ZnO nanowires. c) and d) HRTEM images of the nanowire showing the [0001] growth direction and lattice spacing.

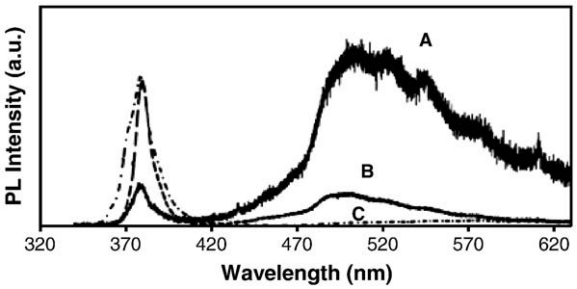

Fig. 4. PL spectra of the samples: (A) as-grown, (B) annealed in argon, (C) annealed in air.

(*I*–*V*) and capacitance–voltage (*C*–*V*) measurements were done using an Agilent 4284A LCR analyzer. Field emission from the ZnO nanowires was measured in vacuum with base pressure of 1×10^{-6} Torr at room temperature. The substrate was secured onto a Cu substrate cathode and the anode was an indium-tin oxide (ITO) glass. The distance between the anode and the tip of the nanowires was 100 μm and the emission area was 0.28 cm^2. A Keithley 237 high voltage source measurement unit (SMU) was used to apply a voltage from 0 to 1100 V and to measure the emission current at the same time.

3. Results and discussion

The XRD patterns of the ZnO buffer layer and the synthesized nanowires are seen in Fig. 1. All the peaks were indexed to the wurtzite-structure with lattice constants of $a=3.25$ Å and $c=5.21$ Å. The diffraction pattern revealed growth in the [0001] direction due to the preferential orientation of the buffer layer. The ZnO buffer layer acts as an active nucleus for the growth of ZnO nanowires, determining the growth sites of the nanowires. The SEM images in Fig. 2(a) and (b) show well-aligned ZnO nanowires synthesized for 30 min with an average diameter of 50 nm and length of 5 μm. Fig. 2(c) and (d) shows the nanowires synthesized for 2 h and 3 h, with lengths of 7 μm and 9 μm respectively. Structural characterization by TEM (Fig. 3(a) and (b)) shows that the nanowires have a uniform diameter with a smooth surface topology throughout their lengths. The clear lattice fringes with an interplanar spacing of about 0.52 nm (Fig. 3(c) and (d)) confirms that the ZnO nanowires are single crystalline with a preferential growth in the [0001] direction, supporting the XRD results.

Optical properties of the as-synthesized and annealed ZnO nanowires were studied using room temperature PL measurements, as shown in Fig. 4. Sample A (as-synthesized ZnO nanowires) has an ultraviolet emission peak at 380 nm, corresponding to the near-band-edge emission of ZnO [7], and a broad visible emission peak at 505 nm which is attributed to the single ionized oxygen vacancies in ZnO [8]. It is noted that annealing the ZnO nanowires in either argon or air atmosphere reduced the visible emission. However, the suppression of the visible emission was greatly enhanced in the case of air annealing, due to the direct combination of oxygen ions from the air with the oxygen vacancies of the ZnO nanowires [9]. On the other hand, the Ar annealed sample shows a higher visible emission due to the diffusion of oxygen interstitials into oxygen vacancies of the ZnO nanowires [10]. The suppressed visible emission affirms the presence of few defects and the good optical properties of the annealed nanowires.

Field emission properties of the nanowires were investigated and plotted in Fig. 5(a). The 3 h sample exhibits lowest turn-on field of 3.8 V/

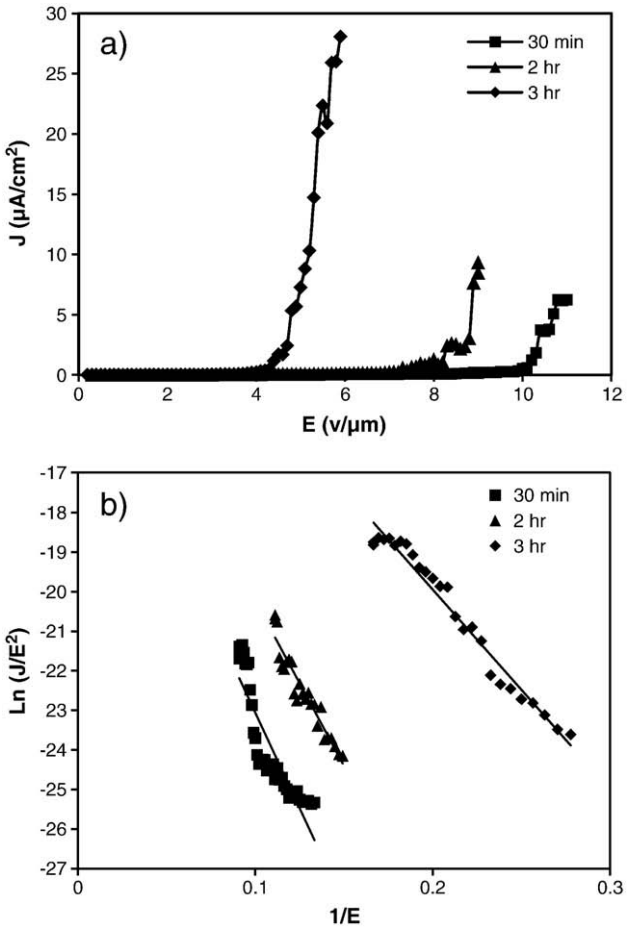

Fig. 5. Field emission properties of ZnO nanowire arrays: a) J–E plots. b) The corresponding F–N plots.

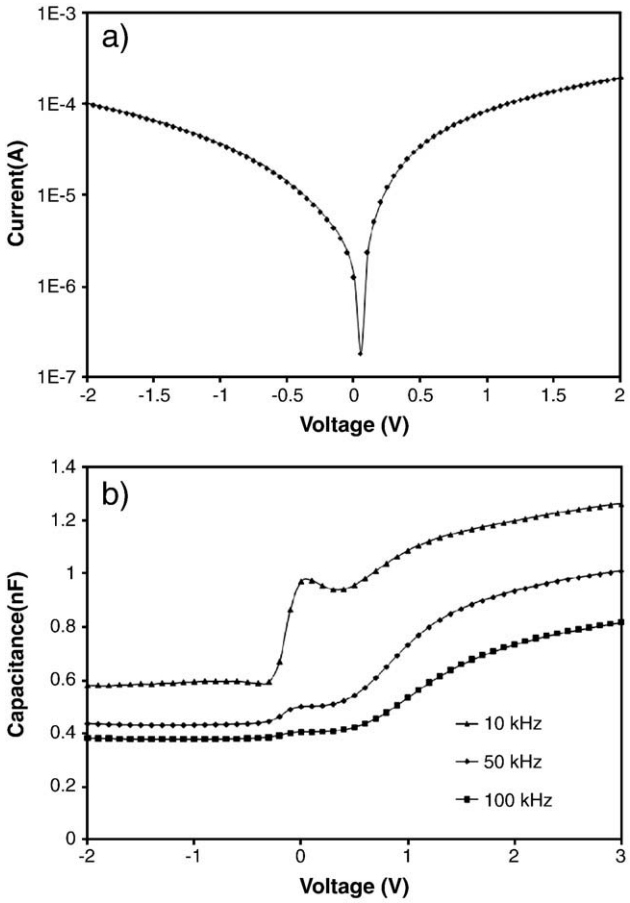

Fig. 6. Electrical measurements. a) *I*–*V* curve. b) *C*–*V* curves for 10, 50 and 100 kHz.

μm at a current density of 0.1 μA/cm^2, while the 30 min and 2 h samples had turn-on fields of 8.5 V/μm and 5.7 V/μm respectively. The low turn-on field of the 3 h sample could be attributed to its high aspect ratio [11]. During the synthesis process, diameters of the nanowires were observed to remain constant at about 50 nm while the length of the nanowires increased with the synthesis time. Hence the aspect ratio of the 3 h sample is higher than that of the 30 min and 2 h samples. The Fowler–Nordheim (F–N) plot in Fig. 5(b) shows that the field emission behavior can be well described by the F–N mechanism. The field enhancement factor β can be calculated from the slope of the Fowler–Nordheim plot, using work function of ZnO nanowires as 5.3 eV [12]. The 3 h sample has the highest enhancement factor of 1644, while the 30 min and 2 h samples exhibit enhancement factors of 863 and 998 respectively.

Electrical characterization of the ZnO nanowires was carried out via *I–V* and *C–V* measurements. The contact was Cr/Au (10/100 nm) and a layer of SiO_2 (20 nm) was sputtered to form a Metal-Oxide-Semiconductor (MOS) structure. The *I–V* curve (log scale) in Fig. 6(a) shows that the contact is ohmic. This is because the work function of Cr (4.5 eV) is less than that of ZnO (5.3 eV), hence an ohmic contact was formed. The resistance obtained at 1 V is about 11 kΩ. *C–V* measurements were carried out at frequencies of 10, 50 and 100 kHz and the *C–V* curves (Fig. 6(b)) show that the ZnO nanowires are n-type, with the curve shifting down as the frequency increases. Little *C–V* hysteresis was observed, suggesting the presence of little or no defects.

4. Conclusions

An easy method to fabricate well-aligned ZnO nanowires is presented, in which the growth process is self-catalytic using a buffer layer. This allows the nanowires to be grown on substrates other than silicon, as long as a buffer layer is pre-sputtered on the substrate. The nanowires synthesized for 3 h exhibited the lowest turn-on field of 3.8 V/μm at a current density of 0.1 μA/cm^2, with a corresponding field enhancement factor β of 1644. This could be attributed to the aspect ratio of the nanowires which is the highest compared to the 30 min and 2 h samples. The *I–V* curve shows that the contact is ohmic and a resistance of 11 kΩ was obtained at 1 V. It was observed from the *C–V* curves that the ZnO nanowires are n-type and the curve shifts down as the frequency increases. Little *C–V* hysteresis was observed, suggesting the presence of few defects.

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