Aluminum Foil Mediated Noncatalytic Growth of ZnO Nanowire Arrays on an Indium Tin Oxide Substrate

Hana Yoon,†,‡ Kwanyong Seo,†,‡ Heesung Moon,§ Kumar S. K. Varadwaj,‡ Juneho In,‡ and Bongsoo Kim*,‡

Department of Chemistry, KAIST, Daejeon 305-701, Korea and Corporate R&D Center, Samsung SDI Co. Ltd., Yong-in 449-577, Korea

Received: January 18, 2008; Revised Manuscript Received: April 11, 2008

Vertically grown ZnO nanowires are synthesized on an indium tin oxide (ITO) substrate via a vapor transport method. The arrays of ZnO nanowire are spontaneously produced from the vapor of a 1:1 mixture of ZnO and Zn powders with no metal catalyst. The key to this synthetic process lies in covering the ITO substrate with an aluminum foil that has a small hole in order to maintain an optimum level of supersaturation. Transmission electron microscopy and X-ray diffraction confirm the single crystalline nature of the wurtzite ZnO nanowires. This is the first report of vertically grown single-crystalline ZnO nanowires on an ITO substrate by gas phase synthesis. Direct growth of vertical ZnO nanowires on a conducting and transparent ITO substrate would find useful applications in field emission displays and solar cells.

Introduction

Zinc oxide nanowires (NWs) are important II–VI semiconductor NWs with a direct wide band gap of 3.37 eV, a large exciton binding energy of 60 meV, and piezoelectricity.1,2 They are considered to play an important role in optoelectronics such as field emission displays (FEDs) and solar cells.3,4 Developing convenient and reproducible synthetic methods would be an important step for practical use of the NWs. Well-controlled growth and diverse morphology of the ZnO NWs on various substrates would make their versatile applications possible. The metal catalyst mediated vapor—liquid—solid (VLS) mechanism is widely employed for heteroepitaxial growth of ZnO NWs on single crystalline sapphire and Si substrates.5,6 Catalyst-free methods based on homoepitaxial growth on Si and glass substrates from a ZnO seed layer were also explored,7–10 and NWs with a tapered or needle shape have been observed in many cases. In a recent report, it was shown that surface roughness of the substrate also plays a critical role in determining the shape of the NW arrays.11

Indium tin oxide (ITO) would be one of the best candidates as a conducting substrate for the optoelectronic applications because it has been widely used as a transparent electrode in conventional flat panel displays, including FEDs. Recently, solution-based methods have been employed as a powerful alternative synthetic tool to produce well-aligned ZnO NW arrays on conducting substrates. Yang and co-workers reported the growth of vertically grown ZnO NW arrays using a film of textured ZnO nuclei, which was prepared in a separate synthetic step on a conducting substrate.12 The solution-based method offers many advantages in terms of process scalability and production cost compared to the gas phase method. On the other hand, solution-based synthesis also presents challenges such as solvent and impurity incorporation, as well as surface defects that can substantially affect the optoelectronic properties.13

Vertically grown single-crystalline ZnO NW arrays were synthesized using a 1 in. diameter quartz tube in a horizontal hot-wall two zone furnace as shown in Scheme 1. The temperatures of both of zones were independently controlled. The 1:1 powder mixture of ZnO (99.99%, Aldrich) and Zn (99.998%, Aldrich) was used as a precursor and was placed in a small alumina boat. The precursor was vaporized in heating zone A. The NWs grew on an ITO substrate that was placed in heating zone B and tightly covered by an aluminum foil with a small hole. The carrier argon gas was supplied at the rate of 0.5 L/min.

SCHEME 1: Experimental Setup

Here we report a one-step vapor transport method for producing vertical ZnO NW arrays on a conducting ITO substrate with no catalyst. By covering the ITO substrate with an aluminum foil that has a small hole we maintain an optimum level of supersaturation, which is necessary for vertical growth of the NWs at a relatively low reaction temperature of 450 °C. This new method has several important advantages: first, the vertical ZnO NWs are grown on a conducting ITO, thus good contact between the NWs and ITO is secured for further fabrication of nano devices; second, no catalyst is used in the whole process, thereby avoiding side effects by metal catalysts that may hamper the performance of nano devices; third, the whole process of vertically growing high quality ZnO NW arrays is completed through one simple step. The thus fabricated vertical ZnO NW arrays show good field emission properties for use as electron emitters for FEDs.

Experimental Section

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140 sccm, together with 3 sccm of O₂, through a mass-flow controller (MFC). The temperatures of heating zone A and B were maintained at 770 and 450 °C, respectively, and the pressure was maintained at 19 torr for 10 min of reaction time. No catalyst was used for the NW synthesis.

X-ray diffraction (XRD) patterns of the specimen were recorded on a Rigaku D/max-rec (12 kW) diffractometer operated at 30 kV and 60 mA with filtered 0.15405 nm Cu Kα radiation. Field emission scanning electron microscope (FESEM) images of ZnO NWs were taken on a Philips XL30S. Transmission electron microscope (TEM) images, high-resolution TEM (HRTEM) images, and selected area electron diffraction (SAED) patterns were taken on a JEOL JEM-2100F transmission electron microscope operated at 200 kV. After NWs were dispersed in ethanol, a drop of the solution was put on a holey carbon coated copper grid for the preparation of TEM analysis.

Field emission (FE) measurements were carried out by twoparallel-plates, an anode and a cathode plate, in a vacuum chamber at room temperature, where the pressure was 2 × 10⁻⁶ torr. The ITO substrate on which vertical ZnO NWs were grown was used as the cathode panel. The experimental system has two-parallel-plates geometry with a separation of 570 μm between the ITO anode substrate and the cathode plate. The measured emission area was 40 mm², and emission current was recorded at intervals of 0.2 s. The bias voltage sweeps were conducted several times, and the plot shows the initiatory two sweeps. After the measurement was made several times, the current was well-stabilized due to the field annealing effect.

Results and Discussion

The morphology of the ZnO NWs was examined by SEM and TEM. Representative SEM image in Figure 1a shows vertically grown ZnO NWs on an ITO substrate. The diameters of NWs range from 80 to 100 nm, and their lengths are up to several micrometers. High magnification SEM (inset in Figure 1b) image of the ZnO NWs’ tip reveals the hexagonal cross section along the c-axis of the NW. Figure 1c shows a typical XRD pattern of the NWs grown on an ITO substrate. The observed peaks in the spectrum were successfully indexed to the wurtzite crystal structure of ZnO (JCPDS card no. 36-1451) with lattice parameters a = 3.249 Å and c = 5.206 Å of a space group P63mc. The intense and sharp diffraction peaks suggest that the as-synthesized product is highly crystalline. Although, in the bulk, the intensity of the (002) peak is about 44% of the most intense (101) peak, in this XRD pattern the (002) peak is the most dominant peak. This change in peak intensities as compared to bulk values could be due to vertical growth of the NWs along the c-axis. All other extra peaks originated from the ITO substrate (JCPDS card No. 65-3170).

To characterize the chemical composition and structure of the NWs, we carried out energy dispersive X-ray spectrometry (EDS), HRTEM, and ED studies. The TEM image in Figure 2a shows a straight and smooth NW with no secondary growth or extra structural features. The SAED study shows a regular spot pattern, which reveals the single-crystalline nature of the NW. The spots can be fully indexed to the wurtzite ZnO and demonstrate that the NW growth is along the [001] direction down the [110] zone axis. Repeated measurements for several NWs show identical results. Figure 2b shows an HRTEM image of a 80 nm diameter NW with clear lattice fringes, which again confirms the single-crystalline nature of the NWs. The lattice spacing of the planes is measured to be 0.267 nm, which agrees well with the spacing of the (002) planes of a wurtzite ZnO structure. The two-dimensional fast Fourier transform (FFT) of the lattice-resolved image obtained from the HRTEM (inset in Figure 2b) can also be indexed to a wurtzite structure. The elemental composition of the NWs was also investigated by TEM-EDS using HRTEM. Figure 2c shows a TEM-EDS spectrum of an individual ZnO NW. The analysis of a TEM-EDS spectrum confirms that the NW contains only Zn and O (the peaks for C and Cu are from the grid).

Figure 3 shows cross-sectional schematic illustrations and SEM images before and after the reaction. Before starting the synthesis, we tightly covered an ITO substrate with commercial aluminum foil and then made a small hole of about 4 mm in diameter on the foil. The volume enclosed by the aluminum foil was increased after the reaction, probably by thermal expansion, as shown in Figure 3b.¹⁴ The relative softness and large thermal expansion coefficient of aluminum easily result in deformation of the foil, leading to the formation of protrusions or hillocks. The thermal expansion coefficient of aluminum (23.2 at 300 K and 33.8 at 800 K, unit is mm/(mm °C) × 10⁶) is much larger than that of glass (9.0 at 0–727 K).¹⁵ In previous studies, aluminum thin film on the silicon also showed protrusion by thermal heating.¹² Apparently, the deformation becomes permanent when stress exceeds a certain threshold.

Figure 3d shows a cross-sectional image of the ZnO NWs grown on an ITO substrate under the aluminum foil. We suggest two possible growth mechanisms of the ZnO NWs as following; first, aluminum particles from the foil might act as a catalyst,
which induces VLS growth of ZnO NWs on the ITO substrate. In the TEM-EDS spectrum for an individual ZnO NW (Figure 2c) and the SEM-EDS spectrum for the whole substrate, however, no aluminum peak was observed.\textsuperscript{18} TEM studies also do not show the presence of any metal catalyst on the NW tips. Hence, VLS growth via aluminum particles is unlikely. Second, aluminum foil helps to maintain an optimum degree of supersaturation for the ZnO NW growth. An extra layer with thickness of few micrometers was observed on the ITO layer, as shown in Figure 3d. We confirmed that this layer is a ZnO thin film through the SEM-EDS study.\textsuperscript{18} From the observation of a ZnO layer on ITO, we hypothesized the growth process of ZnO NW. A ZnO layer was initially formed, and then ZnO NWs epitaxially grew on the surface of the layer by self-seeded growth. In conventional CVD systems, the degree of supersaturation may be high in the beginning of precursor evaporation and would get lower as the reaction proceeds.\textsuperscript{19} The crystallographic epitaxial relationship of the NWs and other initially formed structures has been previously demonstrated in the homoepitaxial growth of the ZnS NWs.\textsuperscript{20}

For further understanding of the growth behavior of the NWs, we examined as-prepared structures on both the inside and the outside surfaces of the foil as well as those formed on the ITO substrate under the foil. Figure 4 shows various morphologies of the NWs synthesized at different locations. Vertically grown ZnO NWs (Figure 4c) were also observed on the inside surface of the foil, and its morphology is similar to that of the NWs formed on the ITO substrate (Figure 4d). Randomly grown nanostructures were formed, however, on the outside surface of the foil, as shown in Figure 4b. Furthermore, microstructures were formed on the ITO substrate when the aluminum foil was not employed in the reaction as shown in Figure 4a. The dome-shaped aluminum foil inflated by thermal heating would make a different environment inside and outside of the dome as the reaction progresses. Instead of direct supply of precursor vapor by the flow of Ar, a relatively small amount of the flow is supplied into the dome through a small hole on the foil; thus, a rather undisturbed steady state would be maintained inside the dome. This might become the key factor of vertical growth of the well-aligned NWs under the foil.

We further studied the dependence of the morphology of the ZnO NWs on the hole diameter and the distance from the hole on the ITO substrate. Although no significant change was observed when the hole diameter changed from 2 to 5 mm
Figure 5. (a) Schematic illustration of a field emission experimental setup. (b) Field emission I–V curve from the ZnO NW arrays at a working distance of 570 µm. The emission current density can be as high as 114 µA/cm² at a field of 14.3 V/µm, and the turn-on field of the sample is about 3.7 V/µm. The inset depicts the F–N plot that indicates the FE satisfies the F–N model by showing linear dependence. (Supporting Information Figure S3), we could not observe any deposition of ZnO NWs on the ITO substrate when the diameter is less than 1 mm. To study the dependence on the distance from the hole, four different regions are investigated on the as-prepared sample through careful SEM measurements, which show that direct flow of the precursors could hinder vertical growth of the ZnO NWs (Supporting Information Figure S4). In the very small region just under the hole, we observed result similar to those obtained when no aluminum foil was employed in the experiment (Figure 4a). On the other hand, short nanorods grew vertically in the region most distant from the hole, whereas well-aligned vertical ZnO NWs were formed in the intermediate distance from the hole on most parts of the ITO substrate. These results again confirmed that the degree of supersaturation, and thus the morphology of the NWs grown on the ITO substrate, can be appropriately controlled by covering the substrate with aluminum foil that has a small hole. Detailed explanations with figures are provided in the Supporting Information.

Figure 5 shows the schematic illustration of a field emission (FE) experimental setup and FE I–V curve from the vertically aligned ZnO NW arrays on the ITO substrate. The turn-on voltage of the NW arrays was about 3.7 V/µm at a current density of 0.25 µA/cm². The emission current density reached 114 µA/cm² at an applied field of 14.3 V/µm (threshold field). Although the FE properties were not as good as those of carbon nanotubes (CNTs), the measured turn-on voltage for FE is lower than those reported for other ZnO nanostructures. The emission current density value from the ZnO NW arrays also could produce sufficient brightness for flat panel displays. It has been reported that 100 µA/cm² can produce enough brightness (>1000 cd/m²) under practical display operating conditions. To understand the emission behavior, the I–V data is analyzed by applying the Fowler–Nordheim (F–N) equation:

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

where \(J\) is the current density, \(A = 1.56 \times 10^{-10} \text{ (AV}^{-2}\text{eV)}\), \(B = 6.83 \times 10^9 \text{ (VeV}^{-3/2}\text{Vm}^{-1})\), \(\beta\) is a field enhancement factor, \(\Phi\) is the work function, \(E = Vd\) is the applied field, \(d\) is a distance between the anode and cathode as shown in Figure 5a, and \(V\) is the applied voltage. The field enhancement factor \(\beta\) can be calculated from the slope of the F–N plot if the work function of the emitter is known. The average \(\beta\) value of ZnO NW is related to geometry, structure, and density of NWs grown on the substrate. The inset in Figure 5b shows the F–N plot displayed for ln(I/V²) and 1/V, indicating a generally linear relation. The measured value of the work function of ZnO NW arrays was about 5.3 eV. From the inset of Figure 5b, the calculated value of \(\beta\) was about 4122, which is good enough for various applications.

Conclusion

We have successfully synthesized vertically aligned single-crystalline ZnO NWs on an ITO substrate. High quality ZnO NW arrays are produced by a catalyst-free spontaneous process using a chemical vapor transport method. The key idea for this process is covering the ITO substrate with an aluminum foil with a small hole in order to maintain an optimum level of supersaturation for the vertical growth of NWs. These well-aligned ZnO NW arrays showed very efficient FE properties with a turn-on field as low as 3.7 V/µm and an emission current density of about 114 µA/cm² at an applied field of 14.3 V/µm. This emission current density could produce sufficient brightness for flat panel displays, and the FE result followed the F–N behavior by showing linear dependence. The direct synthesis of highly ordered ZnO NW arrays on a transparent conducting ITO substrate would provide diverse application possibilities such as FED and solar cells.

Acknowledgment. This research was supported by KOSEF through NRL (ROA-2007-000-20127-0) and SRC through the center for intelligent Nanobio Materials (R11-2005-008-03001-0). SEM and TEM analysis was performed at the Korea Basic Science Institute in Daejeon.

Supporting Information Available: SEM-EDS spectrum and detailed morphology studies for as-prepared sample are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(18) See Supporting Information.
JP800515Y