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Field emission from zinc oxide nanowires*

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An array of random-oriented zinc oxide nanowires (ZnO NWs) was fabricated on silicon substrate by thermal evaporation. After a thermal evaporation process, the silicon substrate was covered with a large number of uniformly distributed ZnO islands, from which non-aligned NWs with a diameter of several ten nanometres were grown. During this process, the temperature around the substrate was intentionally kept below 500°C for practical consideration. From these ZnO NWs field emission was achieved. The turn-on field, under which a $10\mu A/cm^2$ current density was extracted, was measured to be $3.0V/\mu m$. Also, the emission site distribution was investigated using the transparent anode technique. The field emission was observed to have occurred from the whole sample surface. These results suggest that ZnO NWs have great potential application in flat panel displays.

Keywords: zinc oxide nanowires, field emission, thermal evaporation
PACC: 6416, 7970

1. Introduction

The field emission of zinc oxide (ZnO), a wide band gap semiconductor (WBGS), is not a new topic. For example, the electron energy distribution of the field emission from ZnO was reported as early as in the 1970s.[1] Nonetheless, the study of field emission was dwarfed by that of other important applications of ZnO as a piezoelectric material, a transparent conducting electrode or a gas sensor. While very recently, there emerged increasingly intense interest in the field emission properties of ZnO nanostructures. One-dimensional ZnO nanostructures have high aspect ratio, high mechanical strength and chemical stability. Moreover, band bending of a WBGS, which usually favours field emission by lowering the surface barrier and bringing more electrons to the bottom of conduction band, is often quite dramatic under high fields.[2] Hence, good field emission performances can be expected from ZnO nanostructures. To date, field emission has been obtained from nanowires (NWs), nanoneedles, and nanopins of ZnO.[3−6] These results have shown the perspective of employing ZnO nanostructures in the future flat panel displays (FPDs).

Up to now, various ZnO nanostructures, such as nanorods, NWs, nanobelts, nanoneedles, nanopins, and even nanotubes, have been prepared respectively by means of porous template,[7] catalyst assisted vapour-phase transport,[8] metal-organic chemical vapour deposition (MOCVD),[9] metal self-catalytic growth,[10] aqueous chemical growth,[11] vapour phase growth [12] and thermal evaporation.[13]

As will be reported in this paper, we can fabricate random-oriented ZnO NWs on silicon wafers by thermal evaporation of ZnO powders mixed with graphite, and study their field emission properties. As will be revealed in the following sections, preliminary results have shown that in many aspects our samples can meet the requirements of a field emitter to be used in future FPDs.

2. Sample preparation and characterization

An array of random-oriented ZnO NWs was fabricated in a quartz tube, 1.2m in length, 3mm in thickness, and 28mm in inner diameter. The quartz tube was inserted into a horizontal furnace. The source

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material was mixed powders of ZnO (99.0% in purity) and graphite, the molar ratio being 1:2. A quartz boat that contained these powders was pushed to the middle of the tube. The substrate, a silicon wafer, was placed in another quartz boat near the downstream outlet of the tube. The fabrication was started by introducing argon gas into the tube at a $20cm^3 \cdot min^{-1}$ flow rate. After the argon flowed through the tube for sufficiently long time, the tube was submitted to heating. During the heating, the whole tube was not at a unique temperature. The temperature of the middle was raised to 1000°C, while that near the downstream outlet was 450°C–480°C. The heating lasted 5min and then the sample was allowed to cool down to room temperature in the tube with the gas still flowing.

From practical consideration, the NW array has to be grown at a temperature lower than 500°C–600°C.[14] Our fabrication process could meet this requirement, though still very narrowly. For a more comfortable fabrication process, the deposition temperature need be further lowered. Now effort is being made to this end.

The sample fabricated using this method was first examined using a scanning electron microscope (SEM). Figures 1(a), 1(b) and 1(c) show the images of the sample with low, medium, and high magnifications, respectively. The silicon wafer was uniformly covered with islands and on these islands random-oriented NWs were grown. The islands and the NWs on them were measured to be approximately 5μm and several tens of nanometres in diameter, respectively.

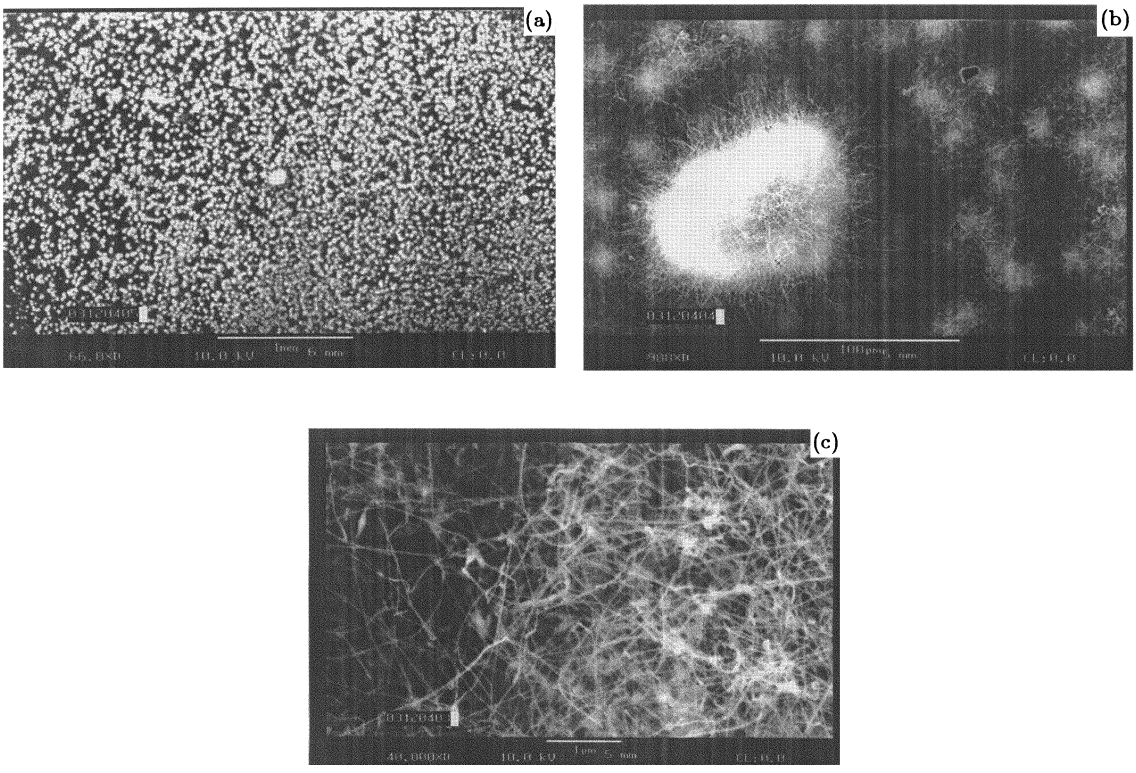


Fig.1. SEM images of an array of random-oriented ZnO NWs on a silicon wafer. (a) Low magnification, (b) medium magnification, (c) high magnification.

The sample was also submitted to transmission electron microscopy (TEM) and x-ray photoelectronic spectroscopy (XPS) analysis after the measurement of field emission. A small portion of the sample was scratched off from the substrate and dispersed ultrasonically in ethanol. Then a droplet of the ethanol was dropped onto a carbon-covered copper grid for the TEM observation. Figure 2(a) shows some individual NWs and its inset reveals the single crystallinity of these NWs. We compared the diffraction pattern in Fig.2(a) with the result obtained by other researchers[5] and arrived at the conclusion that our ZnO NWs were crystallized in a hexagonal wurtzite structure. The zone axis was identified as [100]. The energy-dispersed x-ray spectrometry (EDXS) was also acquired and the result is given in Fig.2(b). The cop-

per and carbon peaks obviously originated from the copper grid and the carbon film used as the support of the sample. No material involved in the fabrication contained phosphorus, thus we attribute the emergence of the phosphorus peak to the pollution from the anode. The EDXS alone is inadequate to determine the concrete origin of this pollution and the result of the XPS analysis has to be considered. As is known, one of the advantages of the XPS is that it can tell the chemical state of an element as long as the chemical shift between the different states is large enough. The result of our XPS analysis shows that the binding energy of the 2p electron of the phosphorus element was 134.0eV, suggesting that the phosphorus element exists in the form of phosphoric acid radical (PO_4^{3-}). Therefore, we believe that the phosphorus element in the cathode actually had its origin in the phosphoric acid (H_3PO_4), which was used to paint the fluorescent powders onto the screen and was partly vaporized during the heat treatment (see Section 3).

After excluding the peaks of copper, carbon and phosphorus in the EDXS result, one can see that the NWs we fabricated contained zinc and oxygen only.

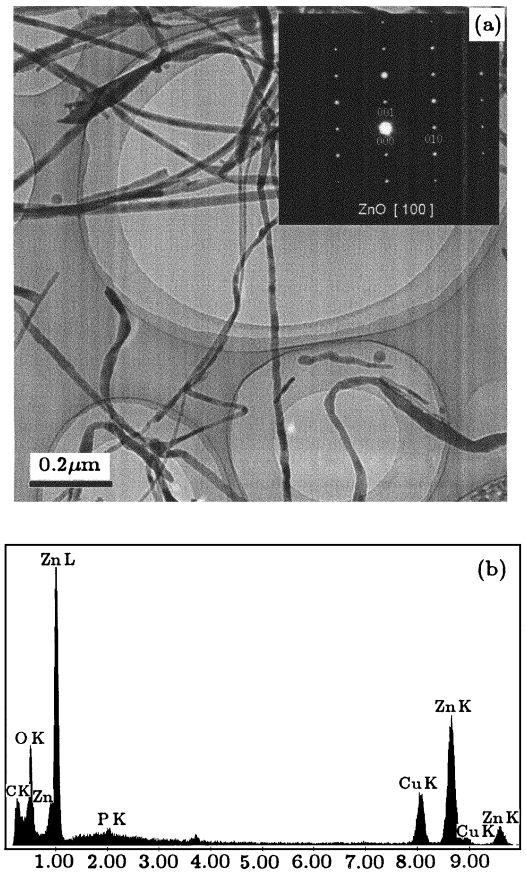


Fig.2. TEM observation of the ZnO NWs. (a) The image and the diffraction pattern, (b) the EDXS (the abscissa denotes energy in keV.)

3. Field emission from the array of random-oriented ZnO NWs

Field emission characteristics of the random-oriented ZnO NWs were studied in a lab-built ultra-high vacuum system with a base pressure of 10^{-7}Pa. The sample grown on the silicon substrate, 45mm^2 in area, was fixed on a molybdenum holder and used as the cathode. A glass screen, coated with tin oxide and fluorescent powders, served as the anode. This "transparent anode technique" allowed us to observe the two-dimensional spatial distribution of the emission sites on the cathode.[15] The field emission surface was separated from the anode by 0.8mm using spacers. External voltage up to several thousands of volts was applied between the anode and the cathode. Field emission current below and above 5μA was collected with a small-current amplifier and microammeters of different ranges, respectively. Thermal radiation from a resistively heated tungsten filament behind the cathode was used to clean the sample surface when necessary.

The curves of field emission current versus anode–cathode voltage ($I-V$ curves) of the ZnO NW array are given in Fig.3.

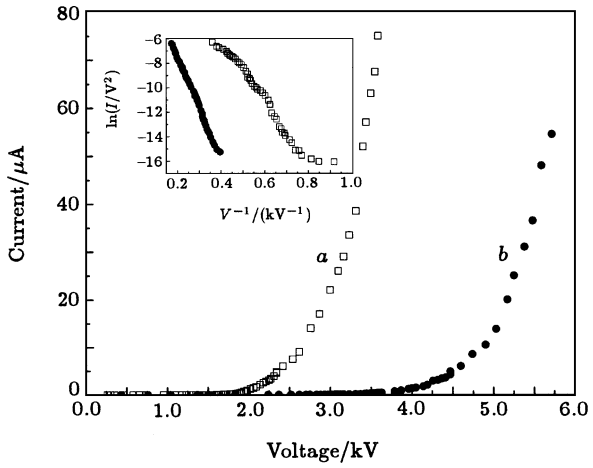


Fig.3. The field emission I–V behaviour of random-oriented ZnO NW array. The current I and the voltage V in the ordinate of the insets are in nA and V, respectively

First, before any heat treatment of the sample, the $I-V$ behaviour was measured, as shown by curve a in Fig.3. The turn-on field, at which emission current density reached 10μA/cm^2,[16] was determined to be 3.0V/μm. We failed to reach the generally defined threshold current density, 10mA/cm^2,[16] owing to the limitation of our power supply. We believe that the

adsorbates, whose removal generally requires treatment at elevated temperatures, played an important role in the field emission in this stage. Nevertheless, the above result is still very useful, because in practical cases, the surface of the field emitters is difficult to be totally cleaned owing to the relatively poor vacuum.

Curve *b* in Fig.3 was obtained after the sample was annealed at 400 °C for about 40min. This time the turn-on field rose to 5.5V/μm. As discussed in the previous section, the strong thermal radiation from the heated cathode could evaporate the H_3PO_4 on the transparent anode to the ZnO NWs. This pollution is considered to be responsible for the deterioration of the field emission performance. Thus effort remains necessary to measure the field emission from the strictly clean surface of the ZnO NWs.

Fowler–Nordheim theory (FN theory) is used to evaluate the field emission of the ZnO NWs:[17]

$$J = \frac{1.56 \times 10^{-6}\, E^2}{\phi} \exp\left(-\frac{6.83 \times 10^7\, \phi^{3/2}}{E}\right),$$

where J is the field emission current density in A/cm^2, ϕ the work function in eV, and E the local electric field at the emission sites in V/cm.

E cannot be measured directly and is usually related to the applied voltage V by setting $E = \beta V/d$, where d is the anode–cathode separation and β is the so-called field enhancement factor. In many cases β can be determined by the aspect ratio of the emitter.[18] Hereafter we call the electric field directly calculated by V/d the "apparent electric field" to differentiate it from the actual local field, $E = \beta V/d$, at the emission sites. Obviously, the two values of the turn-on field given above are both those of apparent field. In an empirical sense, the $I - V$ behaviour of our sample seemed to follow the FN formula approximately, as is suggested by the insets of Fig.3. According to the FN theory, β can be computed by the slope of FN curve if the work function of the NWs is known. If we use the generally accepted value of the work function of bulk ZnO, 5.3eV,[19] β is calculated to be on the order of 10^3. In a pure geometric consideration, such a high enhancement factor should have resulted from a very high aspect ratio, which did not seem to be available from our ZnO NWs, as indicated by Fig.1. Thus we speculate that the actual work function of our ZnO NWs might be lower than that of the bulk ZnO. What is more, the field emission mechanism of ZnO NWs could be much more involved than the scope of the FN theory. Firstly, by using the FN formula directly we ignore the disparity between the behaviour of a metal and that of an n-type semiconductor in field emission. Probably the work function in the formula should be replaced by the electron affinity, which we were unable to determine. Secondly, the contribution of possible band bending to the field emission remains to be incorporated into the theoretical treatment.

Besides low turn-on and threshold voltages, an ideal field emitter to be used in FPDs is expected to have uniformly distributed emission sites with a high density. The two-dimensional emission site distribution (ESD) on the cathode was observed with a transparent anode and the result is given in Fig.4.

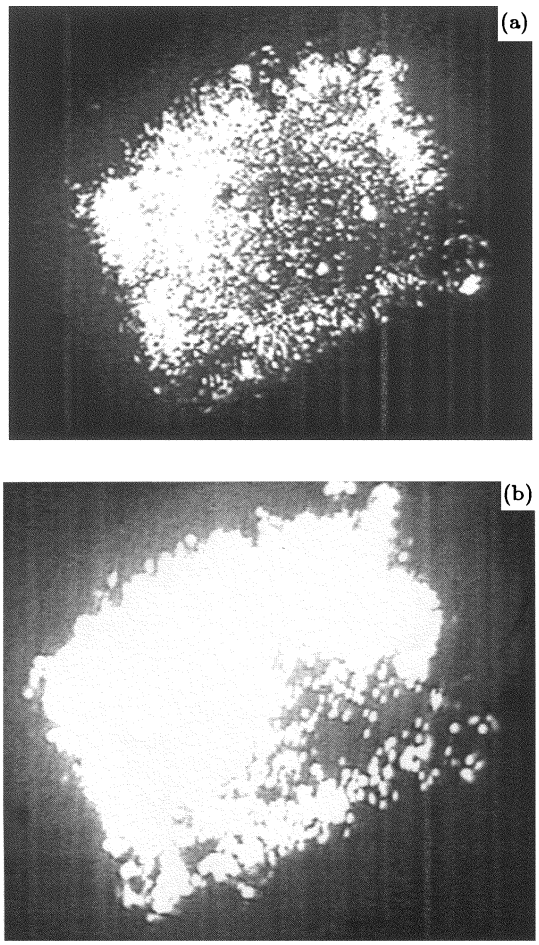


Fig.4. ESD of the ZnO NWs grown on the silicon substrate: (a) at an apparent electric field of 3.7V/μm, (b) at an apparent electric field of 4.3V/μm.

As shown in Fig.4, the field emission came from the sites located almost over the whole sample surface and the density of the emission sites was high, suggesting that the oft-encountered screening effect did not constitute a serious problem. As is well known, screening effect, which reduces the local electric field, comes

into play when the density of NWs is too high.[20] Though most researchers seemed to prefer arrays of aligned NWs than those of non-aligned NWs, it is now difficult to obtain an array of well-aligned NWs with both high aspect ratio and sufficiently large inter-NW separation. Consequently, with regard to avoiding screening effect, an array of random-oriented NWs often possesses an obvious advantage over that of well-aligned NWs.[21,22] Concerning the concrete positions of the occurrence of field emission from our ZnO NWs, we think that, besides the ends of the NWs, the flank wall can also make considerable contribution to the field emission. This argument remains to be further tested in future experiments.

The ESD of the cathode under an apparent electric field of 3.7V/μm is estimated to be larger than $4\times10^3/\mathrm{cm}^2$, as shown in Fig.4(a). The accuracy of the measured ESD value is mainly limited by the overlapping of the spots on the fluorescent screen, which is believed to arise from the charging of the screen. When the applied voltage was further raised, more spots emerged on the screen and each of them also became larger. Hence the spots appeared to be indistinguishable from each other and the ESD could not be measured any longer. Figure 4(b) is an example obtained at a 4.3V/μm apparent field.

4. Conclusion

Random-oriented ZnO NWs were fabricated on the silicon substrate by thermal evaporation. During the fabrication, the temperature of the substrate was controlled to be lower than 500°C. We obtained relatively low turn-on field and uniformly distributed emission sites with a high density. Our results show that arrays of random-oriented ZnO NWs can probably find application in future FPDs.

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