Field-emission studies on thin films of zinc oxide nanowires

S. H. Jo, J. Y. Lao, and Z. F. Rena)
Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467

R. A. Farrer, T. Baldacchini, and J. T. Fourkas
Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467

(Received 20 May 2003; accepted 15 October 2003)

Studies on field emission (FE) from thin films of zinc oxide (ZnO) nanowires found that both the turn-on voltage and emission current density depend on the areal density of nanowires. The density of ZnO nanowires is controlled by the gold (Au) nanoparticle density deposited on the silicon substrates. The growth of ZnO nanowires was achieved by the thermal evaporation/condensation method. It is shown that the same screening effect observed on carbon nanotube field emitters also affects the FE from thin films of ZnO nanowires. Thin films with the lowest areal density of ZnO nanowires showed much better FE characteristics, comparable to that of carbon nanotubes. More importantly, the FE characteristics of ZnO nanowire thin film were further improved with annealing in hydrogen. © 2003 American Institute of Physics. [DOI: 10.1063/1.1631735]

Thin films of nanostructures with high aspect ratio, such as nanotubes, nanowires, and nanorods are considered to be ideal field-emission (FE) electron sources that can emit electrons at low electric field. Among these materials, carbon nanotube (CNT) thin films have received much attention.1,2 However, relatively few studies have been carried out on the field emission from nanostructured thin films made of other materials such as zinc oxide (ZnO) nanowires.

Recently, ZnO nanowires have been synthesized by various processes, such as metalorganic vapor-phase epitaxy,3 infrared irradiation,4 thermal evaporation,5–7 thermal decomposition,8 and electrochemical deposition.9 Optical10 and electronic11 devices based on ZnO nanostructures have been fabricated. Due to the chemical stability and structural rigidity of ZnO nanowires as compared to CNTs, it is also expected that a stable FE electron source from ZnO nanowire thin films could be achieved. However, few results on FE from ZnO nanowires have been reported.12,13

Lee et al. reported FE current density of 1 mA/cm² at about 11 V/µm from well-aligned ZnO nanowire thin film with high density, although their ZnO nanowires had a high aspect ratio.12 The need for such a high electric field may have resulted from the screening effect due to the high density, an effect that has also been observed from CNT field emitters.14,15 Therefore, it is interesting to see whether improved FE properties can be achieved on low-density ZnO nanowire thin films. In this letter, we report a significant improvement of FE from the randomly oriented ZnO nanowire thin films with low areal density, which are obtained by controlling the density of Au nanoparticle seeds dispersed on the substrate from solution.16

The ZnO nanowire thin films were synthesized by the same thermal evaporation/condensation method as reported before,6,17,18 except that gold (Au) nanoparticles were used as a catalyst. Very little nanowire growth was observed on the catalyst-free silicon (Si) substrate surface. Two methods were used to prepare the Au catalysts on (100) silicon substrate. One method was thermal evaporation of a 1–3 nm Au film, and the other was dispersion of a suspension of 3 nm Au nanoparticles in toluene solution on Si surface. Au nanoparticles were synthesized following the procedure of Leff et al.,19 in which tetraoctylammonium bromide was employed as a transfer agent to move Au ions from an aqueous environment to toluene, and dodecylamine was used as a capping molecule for the crystalline nanoparticles. The suspension was diluted in toluene to different concentrations for different areal densities of Au nanoparticles on Si surface. A mixture of ZnO and graphite powders was placed in the sealed end of a small quartz tube, and the Si substrate was put at the open end of the tube for the ZnO nanowire thin-film growth. The source temperature was raised to about 950–1000 °C and held for 15–30 min at pressure of 0.5–1.5 Torr air. After cooling, a thin layer of ZnO nanowires on the Si substrate was observed.

Eight samples with different Au catalyst densities, as described in Table I, were prepared in this study. Among them, two samples were prepared using a continuous Au catalyst thin film, and the remaining six samples were prepared with four different concentrations of the Au catalyst nanoparticle suspension. Some of the scanning electron microscope (SEM) micrographs of these samples are shown in Fig. 1. Figure 1(a) shows the ZnO nanowire thin film on the silicon

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Areal density (µm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Continuous</td>
</tr>
<tr>
<td>B</td>
<td>Continuous</td>
</tr>
<tr>
<td>C</td>
<td>5.6×10⁶</td>
</tr>
<tr>
<td>D</td>
<td>5.6×10⁶</td>
</tr>
<tr>
<td>E</td>
<td>1.2×10⁶</td>
</tr>
<tr>
<td>F</td>
<td>1.2×10⁶</td>
</tr>
<tr>
<td>G</td>
<td>0.7×10⁶</td>
</tr>
<tr>
<td>H</td>
<td>0.4×10⁶</td>
</tr>
</tbody>
</table>

a)Author to whom correspondence should be addressed; electronic mail: renzh@bc.edu

1. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
2. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
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4. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
5. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
6. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
7. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
8. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
9. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
10. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
11. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
12. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
13. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
14. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
15. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
16. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
17. R. A. Farrer, T. Baldacchini, and J. T. Fourkas, Department of Chemistry, Boston College, Chestnut Hill, Massachusetts 02467.
18. S. H. Jo, J. Y. Lao, and Z. F. Ren, Department of Physics, Boston College, Chestnut Hill, Massachusetts 02467.
substrate from the continuous Au film, and Figs. 1–1 show the corresponding ZnO nanowire thin films generated from the Au nanoparticles with areal densities on the Si substrate of $5.6 \times 10^6$, $1.2 \times 10^6$, and $0.4 \times 10^6$ cm$^2$, respectively. The ZnO nanowires from the continuous Au film have a diameter of about 100 nm on average, and tend to grow perpendicularly to the Si substrate surface as was confirmed by the strong x-ray diffraction (XRD) (002) peak, as shown in Fig. 1(e). On the other hand, the ZnO nanowires grown from the 3 nm Au nanoparticles have an average diameter of about 60 nm and a length of 5–20 μm. The XRD pattern for the ZnO nanowires, shown in Fig. 1(f) for sample D, shows that the ZnO nanowires have the wurzite structure and are randomly aligned on the Si substrate surface.

The FE current of all these samples was measured using a simple diode configuration. The anode was a molybdenum disk with a diameter of 5 mm, and the gap between the Si substrate and the anode was 130 μm. The vacuum level was kept at about $2 \times 10^{-6}$ Torr during measurements. The measured current densities as a function of the macroscopic electric field are shown in Fig. 2. The horizontal line corresponds to the current density of 1 mA/cm$^2$, and the values of electric field required to obtain this current density are 18.77, 18.50, 15.57, 14.96, 12.92, 11.43, 10.16, and 6.46 V/μm for samples A to H, respectively. It is worth noting that higher vacuum of $2 \times 10^{-7}$ Torr had been used in another report. Therefore, it is expected that a much lower macroscopic electric field could have been achieved if the same vacuum level had been used.

Figure 3 shows the values of electric field required to obtain the current density of 1 mA/cm$^2$ as a function of the areal density of the Au catalyst nanoparticles on the Si substrate surface. This graph clearly shows that screening affects FE of the ZnO nanowire thin films. The FE characteristics of the ZnO nanowire thin films are much improved as the Au catalyst nanoparticle solution is diluted, and the FE from the ZnO nanoparticle thin film with very low density is comparable to the FE from the CNT thin film. Based on these results, we would expect much better FE properties if the diameter of the ZnO nanowires could be reduced down to the range of 10 nm.

After FE current measurement, sample G was annealed in hydrogen in a quartz tube in order to investigate the effect of hydrogen annealing on the FE. The annealing was carried out at 420 °C for 1 h at a pressure of 1 Torr flowing H$_2$ gas. Figure 4 shows that the FE current is increased after hydrogen annealing. The value of electric field required to obtain 1 mA/cm$^2$ is reduced from 10.16 to 8.38 V/μm after hydrogen annealing. Further work is in progress to systematically study the effect of hydrogen annealing on the FE from ZnO nanowire thin films.

In summary, it is clearly shown that the field emission from the randomly oriented ZnO nanowire thin films grown by the thermal evaporation/condensation method can be significantly improved by reducing the nanowires’ areal density, which is controlled by the areal density of Au catalyst nanoparticles deposited on the Si substrates from solution. The electric field required to obtain the FE current density of 1 mA/cm$^2$ from a ZnO nanowire thin film with very low areal density was 6.46 V/μm, which is comparable to the result from CNT field emitters. It is also shown the FE cur-
rent can be further improved with annealing in hydrogen gas. Even better field emitters could be realized on ZnO nanowires with diameter smaller than 10 nm, together with annealing in hydrogen gas.

The work performed by one of the authors (S.H.J.) is supported by DOE under grant DE-FG02-00ER45805, and the work done by another (J.Y.L.) is supported by the U.S. Army Natick Soldier Systems Center under grants DAAD16-02-C-0037 and DAAD16-00-C-9227. Another author (Z.F.R.) thanks support from DOE and the Army. The work done by the remaining authors was supported by the NSF (ECS-0088438). Another author (J.T.F.) is a Camille Dreyfus Teacher-Scholar.

FIG. 4. The measured current densities as a function of the macroscopic electric field before and after hydrogen annealing for sample G.