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Synthesis and Field Emission Characterizations of Ag-Catalyzed ZnO Nanostructures

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1. Introduction

Carbon nanotubes were first fabricated in 1991 [1]. Since then, nanotip technology has revolutionized the development of FEDs. For the field emitter materials, carbon is used in the preparation of nanotubes, and zinc oxide (ZnO) is another alternative for developing nanostructures. ZnO is a wide-band-gap (3.37 eV) semiconductor with an exciton binding energy of approximately 60 meV, which offers the possibility to fabricate nanostructures by self-organization with a high degree of c-axis orientation. One-dimensional ZnO nanostructures have been synthesized successfully [2]. The structure and properties of ZnO nanostructures, such as crystallite orientation, grain size, luminescence, and electron emission intensities, are influenced by fabrication techniques.

2. Experimental

A p-type (100) silicon wafer was used as a substrate for the growth of ZnO nanostructures. The high-temperature vapor-phase (VS) method was used for synthesizing the ZnO nanostructures. First an Ag thin film was evaporated on Si under 10^{-7} Torr. Subsequently, the ZnO and graphite powders were put in an alumina boat and then placed at the center of a tube furnace. The Ag-catalyzed Si substrate was placed downstream of the source powders. N_2 and O_2 were reaction gases. The source powders were set at 1050–1150°C and the substrate was set at 620–680°C. The growth time were fixed at 10–60 minutes.

The surface morphologies of the ZnO nanostructures were observed by scanning electron microscopy (SEM). The crystal structure of the nanostructure was investigated by X-ray diffraction (XRD). The photoluminescence (PL) spectrum of the nanostructures was measured using a Hitachi F-4500 fluorescence spectrophotometer. The field emission characteristics of the nanostructures were evaluated in a vacuum chamber under a pressure of 5×10^{-6} Torr. The field-emission current-voltage characteristics were evaluated with a Keithley 2410 programmable power source.

3. Results and discussion

The ZnO nanostructures were grown by the VS mechanism. Diffraction peaks of the Al catalyst were not observed in XRD patterns, and the ZnO had a wurtzite structure. The ZnO nanostructures grown at a substrate temperature of 680°C showed a sharp (002) diffraction

peak, indicating that the ZnO nanostructures were grown with c-axis orientation in a direction perpendicular to the substrate surface. The values of full width at half maximum of the (002) peak were 0.26° , 0.21° and 0.16° for nanostructures grown at 620, 650 and 680°C, respectively. The relative intensity of the (002) peak in XRD patterns showed that the c-axis orientation of the nanostructures grown at 680°C was superior to the ones grown at 620 and 650°C, consequently, better field emission characteristics were expected when the ZnO nanostructures were deposited at 680°C.

The morphology of the ZnO nanostructure was related to the source and substrate temperatures which affected the flow of the Zn and ZnO_x vapors and influenced both the nucleus density and stoichiometry of the ZnO nanostructures. The nanostructures of whisker nanorods, protruding film and well-aligned nanorods were grown at substrate temperatures of 620, 650 and 680°C, respectively, as shown in Fig. 1. The diameters of the emitter tips were approximately 40–150 nm for the nanostructures and their length was approximately 2 μm . Energy dispersive X-ray fluorescence (EDX) analysis showed that the nanostructures consisted of only Zn and O.

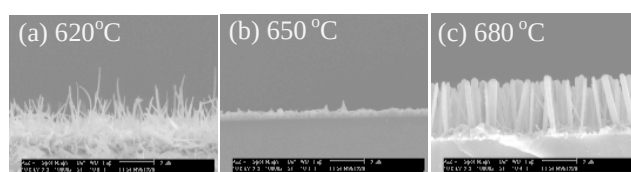


Fig. 1 SEM photographs for the ZnO nanostructures grown at different substrate temperatures.

The PL property of the ZnO nanostructures exhibited that not only a relatively weak UV-band peak centered at 376 nm (3.29 eV) but also a strong broad green–yellow band (visible emission) with a peak at 493 nm (2.52 eV) were measured, which were correspondingly referred to the near-band-edge emission and the radial recombination of a photogenerated hole with an electron belonged to a singly ionized oxygen vacancy. It revealed that the ZnO nanostructures contained many surface defects related to oxygen vacancies.

Figure 2 shows the current density-electric field (J-E) curves of the ZnO nanostructures. The turn-on fields of the ZnO nanostructures of whisker nanorods, protruding film, and well-aligned nanorods were 4.5, 5.8, and 6.1 V/ μm ,

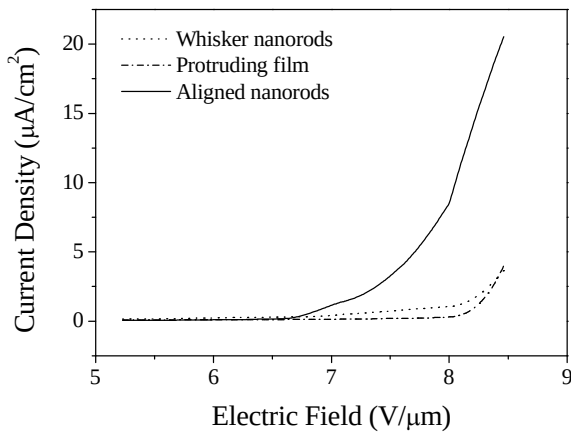


Fig. 2 J-E plots of the ZnO nanostructures of whisker nanorods, protruding film, and well-aligned nanorods.

respectively. The high emitter density and high aspect-ratio of the nanostructures with well-aligned nanorods resulted in an enhancement in the current density; the current densities of nanostructures of whisker nanorods, protruding film and well-aligned nanorods were 3.7, 4.0 and 20.5 $\mu\text{A}/\text{cm}^2$, respectively, at an electric field of 8.46 V/ μm .

The FN plots of the ZnO nanostructures are shown in Fig. 3. From the averaged slope of the FN plot, the estimated field enhancement factor β , assuming the work function $\phi_{\text{ZnO}} = 5.3 \text{ eV}$, was 1115, 1149 and 1167 cm^{-1} for the nanostructures of whisker nanorods, protruding film and well-aligned nanorods, respectively. The nanostructure of well-aligned nanorods exhibited high crystalline quality together with an appropriate emitter density and a preferable aspect ratio, resulting in a high β value and superior field emission characteristics.

The emission stability of ZnO nanostructures is shown in Fig. 4, where the anode voltage was set at 1100 V. The maximum and minimum emission current densities of nanostructures were correspondingly 3 and 1.1 $\mu\text{A}/\text{cm}^2$ for the whisker nanorods (63% variation), 9 and 0.36 $\mu\text{A}/\text{cm}^2$ for the protruding film (96% variation), and 25 and

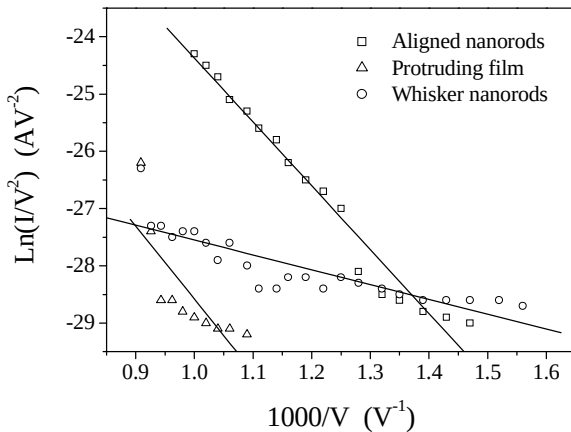


Fig. 3 F-N plots for the ZnO nanostructures of whisker nanorods, protruding film, and well-aligned nanorods.

15 $\mu\text{A}/\text{cm}^2$ for the well-aligned nanorods (40% variation). It revealed that the nanostructure with well-aligned nanorods exhibited considerably higher stability during field emission than the ones with whisker nanorods and protruding film. The emission current densities of the ZnO nanostructures with whisker nanorods, protruding film, and well-aligned nanorods measured after 6 h of continuous operation were approximately 2.05, 4.68 and 20.5 $\mu\text{A}/\text{cm}^2$, respectively.

4. Conclusions

The ZnO nanostructures were grown on an Ag-catalyzed Si substrate by the VS mechanism using ZnO and graphite powders as source materials at different temperatures. The morphology of the ZnO nanostructure was related to the source and substrate temperatures that affected the flow of Zn vapor and influenced both the nucleus density and stoichiometry of the ZnO nanostructures. A relatively weak UV band and a strong broad green-yellow band were observed in the PL spectrum, indicating that the as-prepared ZnO nanoparticles had many surface defects related to oxygen vacancies. The turn-on fields of the ZnO nanostructures of whisker nanorods, protruding film, and well-aligned nanorods were 4.5, 5.8 and 6.1 V/ μm , respectively. A stable field emission property was observed from the well-aligned ZnO nanostructures, which achieved a current density of 20.5 $\mu\text{A}/\text{cm}^2$ at an electric field of 8.46 V/ μm after 6 h of continuous operation.

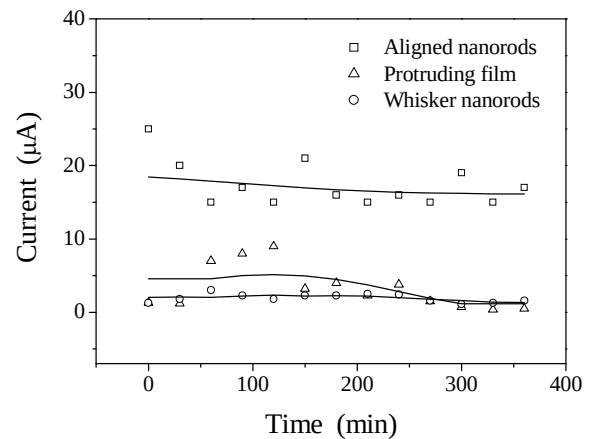


Fig. 4 Emission stability of nanostructures for the whisker nanorods, protruding film, and well-aligned nanorods.

Acknowledgements

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References

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