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ZnO nanowires formed on tungsten substrates and their electron field emission properties

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Using a vapor transport method, ZnO nanowires were selectively synthesized both on tungsten tips as electron field emitters and on tungsten plates with designed patterns. Control of the growth locations of the nanowires was accomplished by selectively positioning a thin film of Au catalyst. The angular intensity and fluctuation of the field emission current from the ZnO nanowires synthesized on tungsten tips have been demonstrated to be similar to those of carbon nanotubes. A self-destruction limit of ~ 0.1 mA/sr for angular intensity was observed, and the power spectra showed a $1/f^{3/2}$ characteristic from 1 Hz to 6 kHz. © *2003 American Institute of Physics.*
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Nanowires with various compositions, such as Si, Ge, GaN, GaP, and InP, have attracted great attention due to their potential applications in both nanoscale electronic and optoelectronic devices.[1] The study of the physical and chemical properties of these one-dimensional nanowires will result in further understanding of some basic issues about dimensionality and space-confined transport phenomena. ZnO, a semiconductor with a large exciton binding energy (60 meV) and wide band gap (3.37 eV), has been considered a promising material for short-wavelength, light-emitting, and gas-sensing applications.[2] At room temperature, ultraviolet lasing has been observed in ZnO nanowires.[3] With structural properties similar to carbon nanotubes, such as a high aspect ratio and stability in various vacuum environments,[4,5] it is possible that ZnO nanowires could have excellent electron emission properties. Several methods for synthesizing ZnO nanowires on different substrates have been investigated for various potential applications. For example, polycrystalline ZnO nanowires have been fabricated by oxidizing the metal Zn electrodeposited on a porous alumina template.[6] Aligned ZnO nanowires have been grown epitaxially on silicon or silica substrates via a metal–organic vapor-phase method.[7] Using a Au thin film as the catalyst in a vapor-transfer process, ZnO nanowires have been synthesized randomly on silicon substrates[8] while aligned ZnO nanowires have been grown on sapphire substrates.[3] These experimental results suggest that the substrates could affect the formation of ZnO nanowires. The focus of the work reported here is the study of the electron field emission properties of ZnO nanowire electron emitters, synthesized on a tungsten tip using a simple vapor-transport method. The angular intensity and fluctuation of field emission current, which are critical parameters for high-resolution electron sources, were studied in a field emission microscope (FEM).

Tungsten, a refractory metal with good conductivity and stability at high temperature, is often used as an electron emitter and a heating filament. Controlling the growth area of ZnO nanowires is an important step in obtaining single nanowires for field emission study. To study the effectiveness of using Au thin films to achieve controlled growth of ZnO nanowires in selected areas, patterned ZnO nanowires were synthesized on tungsten plate substrates. In this experiment, flat tungsten plates (Alfa Aesar, 99.95%) were polished, ultrasonicated in acetone for 5 min, and rinsed with deionized water. Using a 500 mesh copper grid as a mask during sputter coating, a thin layer of Au was directly sputter coated onto the tungsten plates. A 1:1 mixture of ZnO and graphite powder was dispersed in ethanol and ultrasonicated for 20 min. The resulting suspension solution was heated at 80 °C for 4 h to evaporate the ethanol. The residual powder mixture was then ground and put in an alumina boat. This boat was then placed in a quartz tube that was inserted into a horizontal tube furnace, and the tungsten plates were put downstream 2–10 cm from the ZnO/graphite powder. The quartz

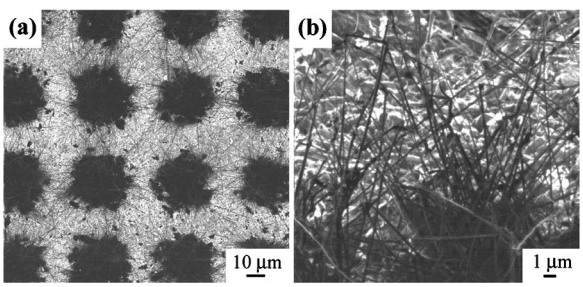

FIG. 1. (a) Low magnification and (b) higher magnification of SEM images of patterned ZnO nanowires formed on the tungsten plate. Growth of patterned nanowires depends on the location of the coated Au catalyst.

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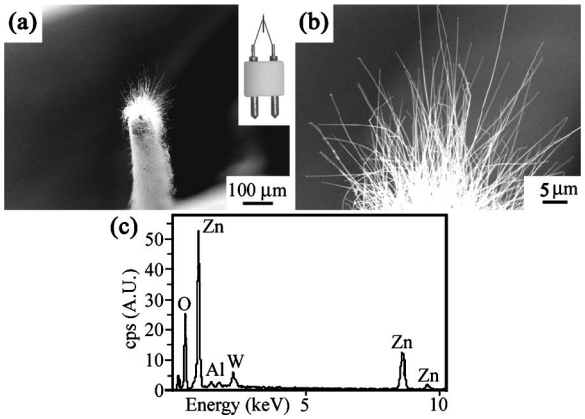

FIG. 2. (a) SEM image of ZnO nanowires grown on a tungsten tip (inset: geometric structure of nanowire emitter). (b) High-resolution SEM image of ZnO nanowires in (a). (c) EDX spectrum of ZnO nanowires formed on the tungsten tip (Al signal comes from SEM sample holder).

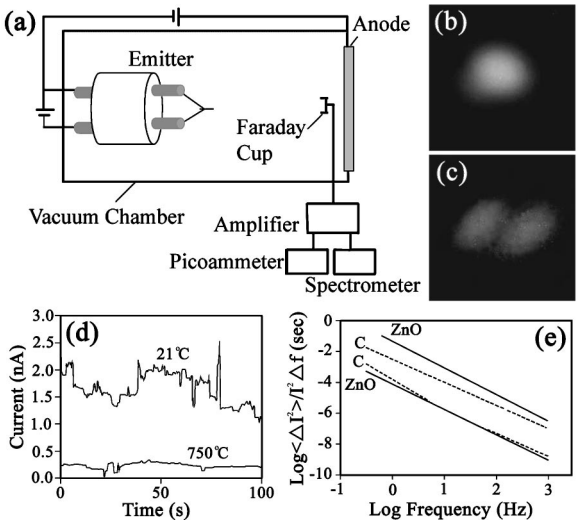

FIG. 3. (a) Schematic illustration of a field emission microscope system. (b) and (c) typical electron emission patterns of ZnO nanowires with one and two lobes, respectively. (d) Current fluctuations of ZnO nanowires measured at room temperature and 750 °C. (e) Power spectra of ZnO nanowires and carbon nanotubes acquired in a frequency range from 1 Hz to 6 kHz at room temperature.

tube was then heated at 915 °C for 30 min with a constant flow of argon. The argon flow rate was 150 sccm. The scanning electron microscope (SEM) images in Figs. 1(a)–1(b) are of the ZnO nanowires formed on these tungsten plates. These images clearly show the nanowires originating from the Au-coated regions of tungsten, while no growth originates where the Au catalyst is absent. Note in Fig. 1(a) that some nanowires form bridges across catalyst-free regions to regions with a catalyst, resulting in an intricate network with a defined origination pattern. The length of the nanowires is in several tens of micrometers, and their diameters range from 25 to 200 nm. Some Au particles were observed on the tips of ZnO nanowires, which is an indication of the vapor–liquid–solid (VLS) growth mechanism.[9] Based on the VLS growth mechanism, Si, Ge, and other types of nanowires have been synthesized on substrates other than tungsten.[10] Using the method reported here, it is expected that nanowires with various elemental compositions could be directly synthesized on tungsten substrates, such as tungsten tips and plates, and offer opportunities for further research.

In high-resolution electron microscopes, including the SEM and transmission electron microscope (TEM), an electron emission source of low angular intensity is desirable in order to avoid the anomalous energy spread and virtual source size broadening that result from Coulomb interactions in the electron beam. However, at angular intensities <0.2 mA/sr, the tips of well-known Schottky emitter cathodes tend to collapse.[11] In the search for a type of emitter with low angular intensity and low current fluctuation, we directly synthesized ZnO nanowires on a tungsten tip as an electron field emitter to study the field emission properties of an isolated ZnO nanowire. In this experiment, the tungsten tips were prepared as follows. A 100-μm-diam tungsten wire was spot welded onto a tungsten loop filament, which was located on a standard electron source ceramic base. To limit the number of nanowires grown on the tungsten wire, and to study the electron emission of a single ZnO nanowire, one end of the tungsten wire was electrochemically etched to a sharp tip using 2.5 M KOH solution. A thin layer of Au was then directly sputter coated onto the tungsten tip. The tungsten loop filament provides a means to heat the emitter for thermal cleaning. The geometric structure of a ZnO nanowire emitter is shown in the inset of Fig. 2(a). The preparation parameters for growing the nanowires were kept the same as for growth on the tungsten plates. After the furnace system containing the samples cooled down to room temperature, white wool-like products appeared to have formed on the tungsten tips. An ISI SS-40 SEM equipped with an energy dispersive x-ray (EDX) spectrometer was used to characterize the morphologies and elemental compositions of these products. A set of SEM images of ZnO nanowires and an EDX spectrum are shown in Figs. 2(a)–2(c). The results show that nanowires grew only on the area of the tungsten tip coated with the Au catalyst. The average diameter of the ZnO nanowires is about 150 nm, and typical lengths of nanowires are in the range of several tens to several hundreds of micrometers. A small number of nanowires, having lengths in millimeters, were also observed. Qualitative and quantitative EDX analysis suggests that these nanowires are composed of ZnO.

Although there are numbers of ZnO nanowires on a tungsten tip, we were able to study the electron field emission behavior of individual ZnO nanowires. Field emission experiments were performed in a field emission microscope equipped with a movable Faraday cup. The Faraday cup with a standard SEM aperture (600 μm in diameter) was connected to a Keithley 485 picoammeter for the emission current measurement and to an Ametek 181 current preamplifier followed by a Stanford Research Systems 785 digital signal analyzer for the spectrum measurement. The test system, as shown in Fig. 3(a), had a point-to-plane electrode geometry with a separation of ~ 12 cm between the phosphor-coated planar anode and the tungsten tip. The field emission microscope base pressure was $\sim 5\times 10^{-8}$ Torr. Emitter temperatures greater than 700 °C were measured with an optical micropyrometer.

With this equipment, the field emission behavior of individual ZnO nanowires was studied. The results show that at an applied voltage higher than 2 kV, but without external

heating of the tungsten tip, some individual field emission patterns from ZnO nanowires start to appear on the viewing screen of the FEM. This occurs because some nanowires have more exposure to the applied electric field and start their electron field emission more readily along the tungsten tip axis, while other nanowires are partially shielded from the electric field or are not aligned with the tip axis. The typical electron emission patterns of a ZnO nanowire, with one and two lobes, are shown in Figs. 3(b) and 3(c), respectively. Since an individual field emission pattern corresponds to a single ZnO nanowire, the movable Faraday cup can be adjusted to measure field emission current from a single nanowire. In our experiments, the Faraday cup aperture subtends a solid angle $\Omega = 57.7\ \mu$sr with respect to the tip. A limit of approximately 0.1 mA/sr in current density was measured from the ZnO nanowires, and the emission current decreased with increasing temperature. It was suspected that the occurrence of the 0.1 mA/sr limit was caused by self-destruction of the emitter, either due to field evaporation of the tip or field-induced removal of the entire nanowire from the tungsten substrate. As shown in Fig. 3(d), emission currents fluctuate as a function of time at both room temperature and 750 °C. As the temperature increased from 25 to 750 °C, the emission current rapidly decreased. A plausible explanation for this phenomenon is that at room temperature ZnO nanowires emit through adsorbate states from residual gases such as H_2O and O_2. After adsorbate removal at 750 °C, the apparently clean nanowire state shows lower emission current. To further investigate the current fluctuation at room temperature, noise power spectra were acquired from ZnO nanowire emitters in a frequency range from 1 Hz to 6 kHz. Noise power spectra are often used to study the current fluctuation mechanisms of an electron emitter. For example, in the study of noise in the tungsten field emitter, Timm and v. d. Ziel found that the noise spectra were of the $1/f^{\alpha}$ characteristic due to the presence of impurity atoms of low work function from residual gases diffusing over the emitter point.[12] In most cases, α was close to 3/2. In our experiment, the relationship between noise spectral power and the frequency of ZnO nanowires is demonstrated in Fig. 3(e). The slopes of two straight lines marked as ZnO in Fig. 3(e) were calculated to be about $-3/2$. Therefore, the power spectra of ZnO nanowires show a $1/f^{3/2}$ characteristic. These noise spectra suggest that current fluctuations of ZnO nanowires may also have resulted from diffusion of adsorbates on the surface of the ZnO nanowire. As we know, carbon nanotubes are considered important candidates for use as electron emitters. The comparative noise power spectra from carbon nanotube emitters[13] are also shown in Fig. 3(e). The spectra of both ZnO nanowires and carbon nanotubes reveal the similar $1/f^{3/2}$ characteristic. It is worth noting that electron emissions from carbon nanotubes also exhibit a current density limit of approximately 0.1 mA/sr with emission currents decreasing with increasing temperature.[13–15] A systematic investigation of the effect of different adsorbates on the field emission properties of ZnO nanowires and carbon nanotubes is in progress.

In summary, a simple and effective vapor-transport method was used to directly synthesize ZnO nanowires on a sharp tungsten tip as a field emission electron source. The electron field emission properties of ZnO nanowires were studied by a field emission microscope. A limit of 0.1 mA/sr angular intensity and $1/f^{3/2}$ characteristic of the noise spectrum has been demonstrated from ZnO nanowires, which is similar to that of carbon nanotubes. In addition, patterned, controlled area growth of ZnO nanowires was achieved on tungsten plates with a Au catalyst thin film. Using the method reported here, nanowires with different compositions could be synthesized on tungsten tips to study electron field emission properties of single nanowires.

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