Metal Oxide Nano-Honeycombs Prepared by Solution-Based Nanosphere Lithography and the Field Emission Properties

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Periodic nanostructures have attracted great interest because of their potential applications in catalysts,[1,2] data storage,[3] photonic crystals,[4] and biosensors.[5] Nanostructures with a tip-like geometry have been regarded as a promising electron field emitter for X-ray sources, flat panel displays, and vacuum microelectronic deveices as a result of their good electrical, chemical, and mechanical properties and high field enhancement effect.[6−10] Extensive research on the field emission properties of one-dimensional metal oxide nanostructures has also been completed as a result of excellent chemical inertness and thermal stability.[11−15] The nanosphere lithography (NSL) technique is a low cost and simple technique for growing two-dimensional (2D) periodic nanoparticle arrays.[16] NSL is based on self-assembly of polystyrene (PS) or silica nanospheres onto a substrate to form a closely packed monolayer or bilayer, which is employed as a deposition mask. Combining the capillary and dewetting process, 2D poly(vinyl alcohol) (PVA) periodic nanorings and nanopores were prepared by infiltrating a PVA-containing solution into interspaces among nanospheres.[17] Besides, nanospheres were also a good template to fabricate three-dimensional (3D) periodic porous materials by using electrochemical deposition.[4] Other 2D or 3D nanostructures, such as zeptoliter beakers,[18] triangular nanopores,[19] and nanorod arrays,[2] have also been prepared by NSL-based methods.

Nickel oxide (NiO) is a transparent conducting oxide and has a work function of 5 eV and low resistivity of about 0.14 Ω cm.[20,21] Nickel oxide film is often used as an insertion layer between the indium tin oxide anode and hole transport layer of organic light emitting diodes to improve hole injection efficiency. In this study, we present a novel solution-based NSL (s-NSL) technique to prepare nickel oxide and iron oxide nano-honeycombs by using a metal-containing organic or inorganic solution to fill in the interspaces of the self-assembled PS nanosphere mask. The organic or inorganic solution is transformed to metal oxide after heating at elevated temperatures in air.[22,23] The nano-honeycombs, having tips at corners of every hexagon, can be formed by vibrating the samples in an ultrasonic bath. In addition, field emission properties of nickel oxide nano-honeycombs are presented, and the field enhancement factor scales with tip height and concentration of the Ni organic solution.

Silicon and B270 optical crown glass (Schott, Inc.) substrates were cleaned by immersing in piranha solution (H_2SO_4/30%H_2O_2 = 3:1) at 80 °C for 5 min. A buffer oxide etch was then applied to the silicon wafer to remove native oxide. Both substrates were further cleaned in RCA-1 solution (H_2O/30% H_2O_2/NH_4OH = 10:2:1) at 60 °C for 5 min and then rinsed in deionized water. The 200 and 400 nm PS nanospheres (10% by volume, Bangs Laboratories, Inc.) were received as suspensions in water and then further diluted in a solution of surfactant Triton X-100 (Aldrich)/methanol (1:400 by volume) with a volume ratio of 1:4. The PS nanospheres were uniformly spin-coated on the substrate at a speed of 2000 rpm for 10 s. An organic or inorganic solution in a volume of 200 μL was dropped into the nanosphere template. The sample was dried and then heated in air at 350 °C for 30 min to evaporate the nanospheres and solvent to form a nano-honeycomb and an upper layer. After sonication in a deionized water bath for 30 s, the upper layer was removed, leaving behind the nano-honeycomb.

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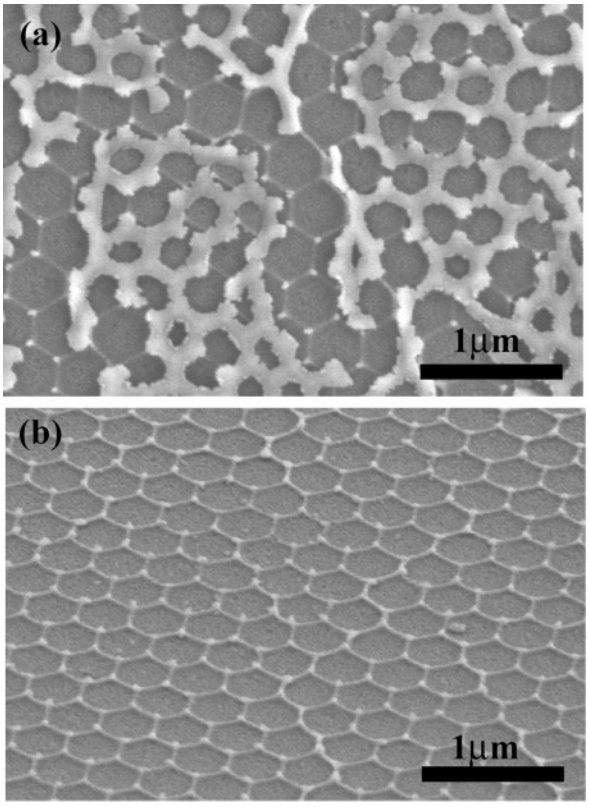

Figure 1. SEM images of a nano-honeycomb formed on the B270 substrate after heating at 350 °C for 30 min (a) before and (b) after removal of the upper layer. The 400 nm PS nanospheres and 0.1 M Ni organic solution were used. The image in part b is a 60° tilted view.

Unlike NSL, the mask for s-NSL can be composed of multilayers of nanospheres so that the mask could be easily made.

Atomic force microscopy (AFM; Nanoscope IIIa, Digital Instruments) and scanning electron microscopy (SEM; FE4300, Hitachi) were used to obtain the surface topography and morphology, respectively, of the nano-honeycombs. Small-angle X-ray diffraction was conducted using a Simens D 5000 X-ray diffractometer. The field emission experiment was carried out in a high vacuum chamber with a base pressure of 1×10^{-6} Torr, in which a sphere-anode to plate-cathode configuration was used. A power source, Keithley 237, was used to provide a voltage of 1100 V with an accuracy of 10^{-13} A. The distance between the anode and the cathode was fixed to give an effective area of 1.6×10^{-3} cm^2 and a distance of 52.67 μm.

To prepare a NiO nano-honeycomb, for example, a Ni organic solution, nickel 2-ethylhexanoate, was selected as a precursor. As shown in Figure 1a, the upper layer left on the nano-honeycomb was also honeycomb-like and was consistent with the shape of interspaces among the 400 nm PS nanospheres. Some of the connections in the upper layer were broken due to the volume shrinkage during the organic removal process. The upper layer could be easily removed in an ultrasonic bath, leaving behind a uniform nano-honeycomb, as shown in Figure 1b. Small-angle X-ray diffraction analysis confirmed that the nano-honeycomb was made of NiO. AFM imaging shows that the nano-honeycombs prepared by using 200 and 400 nm PS nanospheres have tips at the corners of every hexagon, as shown

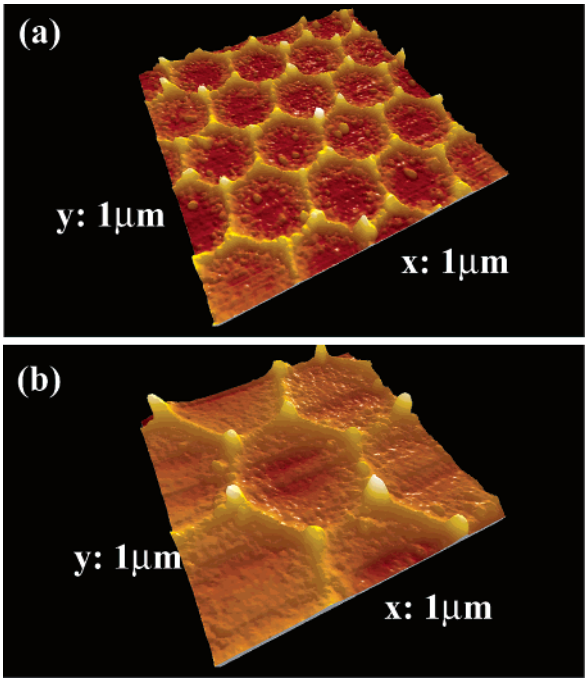

Figure 2. AFM images of nano-honeycombs on the Si substrate prepared by using 0.1 M Ni organic solution and (a) 200 nm and (b) 400 nm PS nanospheres.

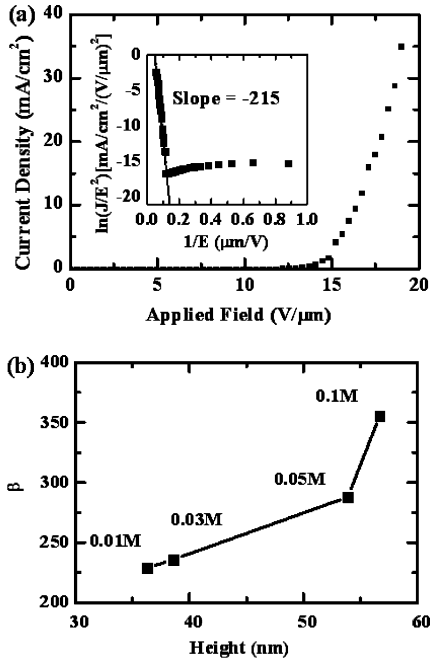

Figure 3. (a) Field emission $J-E$ curve and F-N plot (inset) of a nano-honeycomb prepared by using 400 nm PS nanospheres and 0.1 M Ni MO solution. (b) Dependence of field enhancement factor β on the tip height of nano-honeycombs prepared by using different concentrations of the Ni MO solution.

in Figure 2. When a higher concentration of Ni organic solution was used, the tip height in the NiO nano-honeycomb became larger.

The field emission measurement was carried out for the NiO nano-honeycombs prepared from 400 nm PS nanospheres and different concentrations of Ni organic solution. Figure 3a shows a plot of emission current density versus applied electric field for the NiO nano-honeycomb prepared by using a 0.1 M Ni organic solution. The field emission

characteristics can be described by the Fowler−Nordheim (F-N) equation,[24]

$$J = (1.54 \times 10^2 E/\phi) \exp(-6.83 \times 10^3 \phi^{1.5}/\beta E)$$

where J is the emission current density in A/cm^2, E is the external field in V/μm, ϕ is the work function in eV, and β is the field enhancement factor. The turn-on field is 10.3 V/μm when the current density reaches 10 μA/cm^2. The inset in Figure 3a is the corresponding F-N plot, $\ln(J/E^2)$ versus $1/E$, showing a typical linear relation for field emission behavior in the high-field region. The slope of the F-N plot is equal to $6.83 \times 10^3 \phi^{1.5} \beta^{-1}$ and can be used to determine the work function of the emitter if the field enhancement factor at the emission site is known and vice versa. The work function of NiO is about 5 eV, and the slope of the F-N plot is −215 as shown in Figure 3a, leading to a field enhancement factor of 356. The field enhancement factor of the NiO nano-honeycomb was found to increase with the tip height and concentration of the Ni organic solution, as shown in Figure 3b.

In addition to the Ni organic solution, we have also used iron 2-ethylhexanoate and nickel nitrate solution to prepare nano-honeycombs, as shown in Figure 4. It was found that the nano-honeycombs prepared by using iron and nickel organic solutions were very similar. Interestingly, the nano-honeycomb prepared by using the nickel nitrate solution has triangular holes rather than tips at the corners of every hexagon, as seen in Figure 4b. This might be due to lower concentration or lower surface tension of this solution. More tests are required to understand the reason for this difference.

In summary, we have developed a low cost and versatile process to produce metal oxide nano-honeycombs by using organic or inorganic solutions. Different from NSL, the formation of nano-honeycombs using s-NSL is based on solution filling between the nanospheres and the substrate. Therefore, a large area of uniform single layers or bilayers of nanospheres is not necessary in s-NSL. The straight line in the F-N plot reveals that the NiO nano-honeycomb has a typical field emission behavior. The field enhancement factor of the nano-honeycomb increases with the tip height and concentration of the Ni organic solution. Because it is easy to tune the composition of organic and inorganic solutions, s-NSL is a promising method to form alloyed and doped oxide nano-honeycombs.

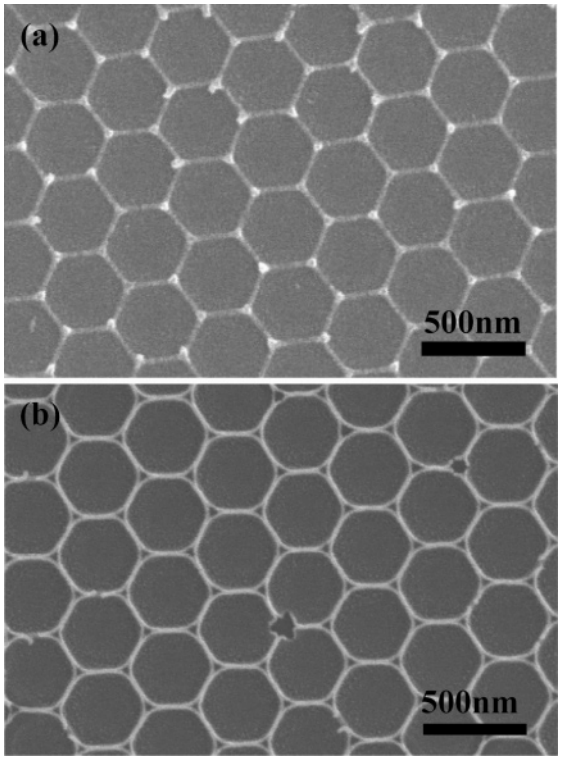

Figure 4. SEM images of nano-honeycombs on the Si substrate prepared by using 400 nm PS nanospheres and 0.03 M (a) iron organic solution and (b) nickel nitrate solution.

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