

Patterned boron nanowires and field emission properties

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Patterns of assembled Fe_3O_4 nanoparticles on Si(111) wafer were formed by the self-assembly technique. Three factors, concentration of the Fe_3O_4 nanoparticles solution, dosage of the solution, and temperature of the Si wafer, were found to affect the quality of the Fe_3O_4 nanoparticle patterns. The prepared Si(111) wafer was used as the substrate to grow the patterned boron nanowires by thermoreduction method. Furthermore, a notable field emission property with moderate turn on field was obtained on the patterned boron nanowires. Our results indicate that the patterned boron nanowires have a great potential of applications in flat plane display and electron emission nanodevices. © 2009 American Institute of Physics. [DOI: 10.1063/1.3080211]

There has been a great deal of interest in the fabrication of patterned nanostructures for applications ranging from nanoelectronics through display units, information storage devices, micro-optical components, to miniaturized sensors.¹⁻³ To date, much effort has been focused on the synthesis and patterning of nanoparticles by lithography, using either photon, electron/ion-beams, or other high energy particles.⁴⁻⁷ Although these direct patterning methods have reduced the number of process steps, the vacuum required for exposure is still costly and could potentially limit throughput. Patterned nanostructures can also be realized by using an electrical or magnetic field,⁸⁻¹⁰ or through localized addition of materials such as a liquidlike ink from an external source, or local heating by laser.¹¹⁻¹⁴ While these techniques are easier than lithography, they still need to be assisted by other expensive tools. Therefore, a simple and more convenient way to directly pattern large-scale nanoparticles on a certain substrate is still desirable. In this letter, we present a very simple and direct methodology to pattern Fe_3O_4 nanoparticles on Si (111) surface by the self-assembly technique. Furthermore, we realize patterned growth of boron nanowires on these prepared substrates and investigate their field emission properties for potential applications in electron emission nanodevices.

Fe_3O_4 nanoparticles were synthesized by high temperature solution phase reaction.^{15,16} Figure 1(a) shows a typical transmission electron microscopy (TEM) image of the product. It can be seen that the diameters and shape of nanoparticles are very uniform. Figures 1(b)–1(d) show the images of the prepared solutions with different concentrations. The original concentration of Fe_3O_4 nanoparticles solution with Fig. 1(b) is 30.8 mg/ml. The concentrations of the solutions diluted with heptane shown in Figs. 1(c) and 1(d) are 7.7 and 1.54 mg/ml, respectively.

The Si (111) wafer was cleaned ultrasonically in acetone for 10 min, followed by washing it in alcohol for 10 min. Then the wafer was cleaned in de-ionized water for 10 min under the same condition. Finally it was dried by N_2 gas. The route to assemble the as-prepared Fe_3O_4 nanoparticles on a

Si (111) wafer can be divided into three steps. The first step is to drop some of the nanoparticle solution with a certain concentration onto the Si surface. The second step is the evaporation of the heptane at a proper rate according to the temperature of the wafer. The last step is annealing the Si wafer under flowing H_2/Ar at 250 °C to get rid of the organic ligands for further growth of nanowires.

In order to obtain large-scale and uniform patterns on the Si wafer, three factors have to be considered. First, the concentration of the nanoparticle solution plays an important role in the formation of patterns. If one droplet (~ 0.1 ml) of the 30.8 or 7.7 mg/ml solutions is used [shown in Figs. 1(b) and 1(c)], a thin film with the thickness of 100 nm–1 μm can be easily formed. Because of the high concentration of Fe_3O_4 nanoparticles, they have no chance to reassemble themselves with the evaporation of heptane. In our experiment, the 1.54 mg/ml Fe_3O_4 nanoparticles solution in Fig. 1(d) was used. Second, the most important factor is the dosage of the solution. Figure 2 gives the different morphologies of the patterns by tuning the dosage. When one droplet (~ 0.1 ml) of the solution was put onto 1×2 cm^2 Si (111) surface, patterns of microcircles were formed on the surface. It can be seen that the large-scale microcircles were uniformly distributed on the Si wafer [Fig. 2(a)]. From the higher magnification scanning electron microscopy (SEM) image [Figs. 2(b) and 2(c)], it can be seen that the circles have uniform diameters of 20 μm and most of the nanoparticles are aligned at the edges of the circles. If two droplets

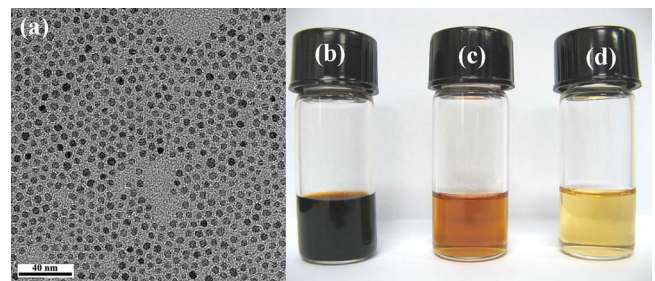


FIG. 1. (Color online) (a) The TEM image of Fe_3O_4 nanoparticles. The digital camera images of Fe_3O_4 nanoparticles solution with different concentrations: (b) 30.8 mg/ml, (c) 7.7 mg/ml, and (d) 1.54 mg/ml.

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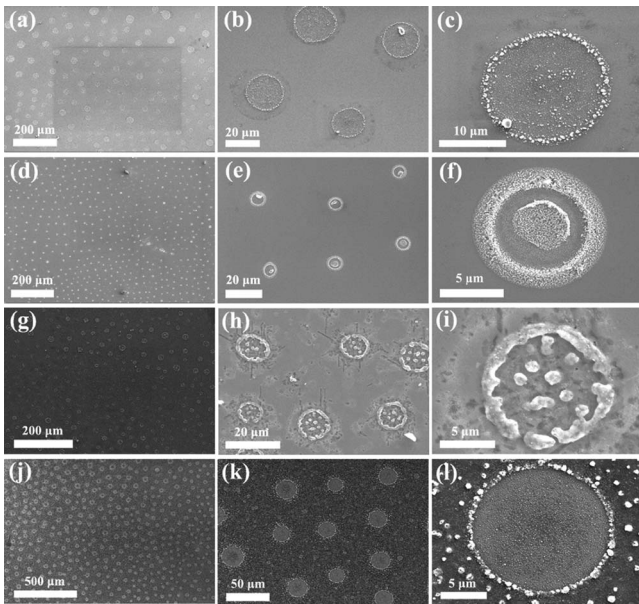


FIG. 2. The SEM images of assembled Fe_3O_4 nanoparticles. [(a)–(c)] One droplet of the solution. [(d)–(f)] Two droplets of the solution. [(g)–(i)] Two droplets of the solution with rotation of the wafer. [(j)–(l)] Five droplets of the solution. The concentration of the used Fe_3O_4 nanoparticles solutions is 1.54 mg/ml shown in Fig. 1(d).

of the solution were used, large-scale uniform microdisks are formed, as shown in Fig. 2(d). The distance between two disks is about 20–30 μm and the microdisks are composed of an outside circle and an inside small disk with a diameter of 10 μm [Figs. 2(e) and 2(f)]. For comparison, after putting two droplets of the solution, the Si wafer was rotated at a rate of 2 rps during the evaporation of heptane. A different morphology of the pattern was formed and the typical configurations are shown in Figs. 2(g)–2(i). It can be seen that the patterns were changed to comprise circles containing several 1–2 μm particles in their centers. This may be due to the centrifugal force which makes the small disk in Fig. 2(f) separate into microparticles [Fig. 2(i)]. When five droplets of the solution were put on the substrate, there was only a thin film with a few microdisks in it. The diameter of the disks, which have lower height than that of the film, is about 20 μm and the distances between each disk are almost the same [Figs. 2(j)–2(l)]. If more droplets were dispersed, a flat film would be formed on the Si wafer. Third, the last important factor is the temperature of the wafer. If the temperature is low, the rate of evaporation of heptanes is low, and the surface tension will be too weak to assemble the nanoparticles. At higher temperature, the surface tension becomes stronger and the patterns would be irregular. In our case, the uniform patterns of assembled Fe_3O_4 nanoparticles were formed around 30 $^\circ\text{C}$ by a moderate surface tension. In the droplet, there are two kinds of forces in the system. One is the surface tension. The other is the electromagnetic force between the magnetic nanoparticles. The self-assembly of nanoparticles involves a competition between the two kinds of forces. When a solution with proper concentration is evaporated at a moderate rate, the competition reaches a balance and the patterns can be formed.

Fe_3O_4 nanoparticles with uniform sizes have been used as a catalyst to synthesize one-dimensional (1D) nanostructures.^{17,18} Our Si (111) surface covered with patterned Fe_3O_4 nanoparticles provides a good substrate to re-

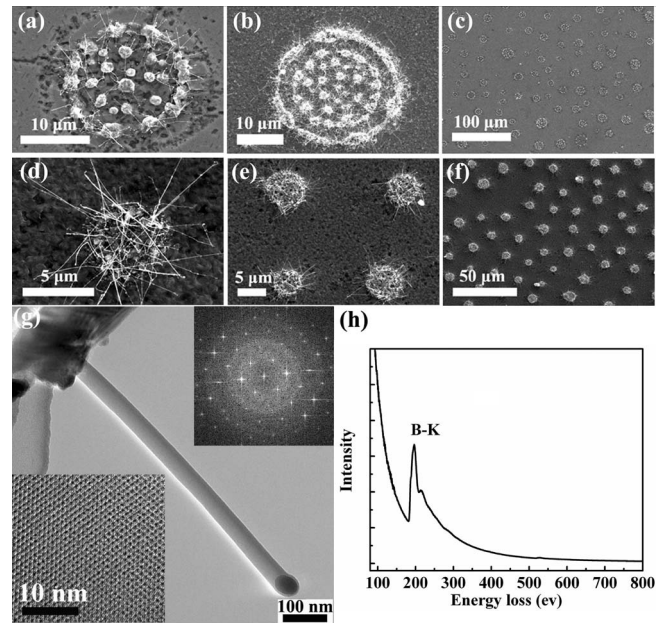


FIG. 3. [(a)–(c)] The SEM images of patterned boron nanowires grown on the substrate shown in Figs. 3(j) and 3(k). [(d)–(f)] The product from the substrate shown in Figs. 2(d)–2(f). (g) The TEM image of a single boron nanowire, the inset is its HRTEM image, and FFT pattern. (h) The EELS core electron *K*-shell spectra from the individual boron nanowire showing characteristic B *K*-edges at 188 eV.

alize the patterning growth of 1D nanostructures for field emission applications. We use the substrates shown in Figs. 2(d)–2(i) to synthesize nanowires via a simple chemical vapor deposition^{19,20} method reported for boron nanowires.¹⁸ Typical SEM images of the patterned boron nanowires are shown in Fig. 3. It can be seen that the boron nanowires have been fabricated on the patterned microparticles [Figs. 3(a) and 3(b)] or disks [Figs. 3(d) and 3(e)] and there are no nanowires at any other site. The diameter of the prepared boron nanowires is about 50–100 nm with a length up to several micrometers. Figure 3(g) gives a typical TEM image of the synthesized boron nanowires. There is a catalyst cluster at the top of the boron nanowire indicating its vapor-liquid-solid (VLS) growth mechanism. The insets in Fig. 3(g) are the high-resolution transmission electron microscopy (HRTEM) images taken from the central part of the nanowire and its corresponding fast Fourier transform (FFT) pattern. Both the results indicated that the nanowire is single-crystalline. The chemical compositions of the wires were analyzed by electron energy loss spectroscopy (EELS). Figure 3(h) depicts a representative of the EELS core electron *K*-shell spectrum from a single boron nanowire. The characteristic B *K*-edge at 188 eV demonstrates that the as-prepared nanowire is predominantly boron. A small O *K*-edge signal is visible at 532 eV indicating the possibility of a thin oxide shell.

Excellent field emission properties have been reported for nanostructured boron.¹⁵ Here we also observed good field emission from the patterned boron nanowires. For these measurements the vacuum gap between the boron nanowires and Mo tip was 300 μm at a pressure of 2×10^{-6} Pa. Figure 4 shows the relationship between current density *J* and applied field *E*. It can be seen that the turn on field (defined as the applied field of 10 $\mu\text{m}/\text{cm}^2$) is 15 V/ μm , and the apparent threshold field (defined as the applied field of 1 mA/ cm^2) is

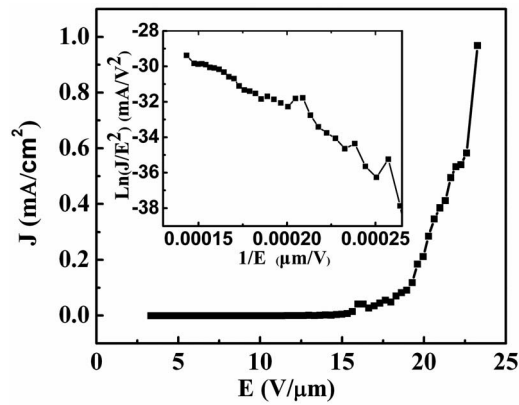


FIG. 4. Typical field emission characteristics of the patterned boron nanowires, where inset is the F-N plot, indicating field emission current originated from barrier-tunneling electrons extracted by the electric field.

24 V/ μm . Although its turn on field is higher than that of boron nanocones,¹⁷ it is better than that of AlN nanocones²¹ and other 1D nanoemitters.^{22–24} The moderate turn on field might be due to the fact that the distance between each pattern is much larger than the distance for the most effective electron emission. It is well known that for the most effective nanowire emitters the ratio of their separation to length should be close to 1. In our case, the distance between each pattern is about 20–30 μm , and the length of the boron nanowires is about 5 μm , giving a ratio of 4:6. Furthermore, the density of the as-grown boron nanowires is high for a single pattern, which has obviously the screening effect. Another possible explanation is that the random growth angles of the nanowires are responsible for the moderate turn on field. Another possibility is poor conductivity of the Si wafer. A silicon oxide film on the Si wafer surface was unavoidably formed during the experiment due to some oxygen impurity.^{21,25} The J - E relationship was analyzed by the Fowler–Nordheim (FN) theory.²⁶ The inset of Fig. 4 shows the corresponding FN plot for the patterned boron nanowires. The linearity of the curve implies that the current originates from electron tunneling through the barriers as a result of the electric field.

In summary, a simple technique has been developed to realize self-assembled Fe_3O_4 nanoparticles on Si (111) wafer by control of the concentration, dosage of the solution, and temperature of the substrate. The patterned Si wafers were subsequently used as substrates to grow patterned boron nanowires. The field emission properties of the patterned boron nanowires appear suitable for potential applications in flat plane displays and electron emitting devices.

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