Formation of Super Arrays of Periodic Nanoparticles and Aligned ZnO Nanorods – Simulation and Experiments

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ABSTRACT

It had been demonstrated that large-scale honeycomb-like nanoparticle arrays could be fabricated inexpensively by the process of monolayer nanosphere self-assembly. Here we report that a double-layer masking procedure can be effectively used to overcome the restriction of honeycomb order in an array resulted from a monolayer mask. By varying the relative angle between the two layers, different arrangement of nanoparticles could be obtained. The relative angle can be directly controlled with the aid of diffraction patterns from illuminating the layers by a laser beam. Experimental results were fully confirmed by computer simulations. Using these nanoparticles as catalysts, we have grown arrays of aligned ZnO nanorods with various orders.

There is an increasing interest in fabrication of various two- and three-dimensional periodic nanostructures. A precise control of their geometry has a great importance for future applications in numerous electronic and optoelectronic devices. This involves controlling positions, spacing, and shape of nanoparticles or nanorods arranged in an array. Originally, these lattices have been manufactured using electron beam lithography, photolithography, or X-ray lithography techniques. These methods give highly reproducible results and allow fabrication of nanostructures. However, they are mostly not scalable to large area and are limited by a multistage, time-consuming, and expensive preparation procedure. Therefore, there have been efforts to find alternative methods such as scanning probe lithography, interferometric lithography,1 soft lithography,2,3 nanosphere lithography,4–6 etc., which is particularly interesting with regard to preparation time and costs. Nanosphere lithography has been proven to be a very simple and cost-effective technique for preparation of large-scale particle arrays with long-range periodicity.7–9

It utilizes submicron latex beads hexagonally arranged into a monolayer as a lithographic mask for further evaporation of various materials. Deposited nanoparticles have a quasi-triangular shape, which is determined by the aperture between the spheres in the mask, and their size is tunable by the use of different diameters of the beads. To overcome the restriction of triangular shape and the honeycomb lattice order, a double-layer masking can be used. Here we report a double-layer mask preparation technique that allows control over the relative angle between the two layers, and a detailed study of the obtained structures by computer simulations. Moreover, we present the fabrication of periodic arrays of ZnO nanorods with various symmetries on large-scale substrates using the nanoparticles prepared from the double-layer mask. The main practical purpose of the trian- gularly arranged ZnO nanorods is for achieving super strong nanolasers when the relative angle is 0°. It may also have potential applications in optical limiting.

As an example, 590 nm polystyrene spheres (PSs), with chloromethyl surfactant coating, purchased from Interfacial Dynamics Corp. (USA) as a 4% aqueous suspension and mixed in 1:1 ratio with methanol, were used. These PSs were deposited onto a surface of deionized water as a monolayer and consolidated into a stable mask by addition of dodecyl-sodiumsulfate solution. Subsequently, masks were put on a-plane sapphire substrates and dried in air. Completely dried substrates were immersed in deionized water again, and their mask orientation was determined using green laser pointer with wavelength of 537 nm. Because all the used substrates were transparent, the diffraction patterns were clearly visible on the bottom of the preparation dish. Then, a second monolayer of PSs was prepared on the water and the orientation of this second mask was also examined by a laser. While the substrate with the first deposited mask was fixed underwater, a floating monolayer was moved right above the first masking layer and rotated using tweezers or a steel rod frame to the angle needed. One may expect that the
spheres in the second layer will acquire the lowest energy packing with respect to the first one. However, the surfactant added during the microspheres compression made the whole second layer very rigid. Therefore, the second layer could be easily manipulated relative to the first one. Because of the distance between the first monolayer on Si substrate and the second floating monolayer on water, the diffraction spots of both layers were arranged as two concentric rings (Figure 1). The outer one belongs to the floating PSs layer and could be aligned at various angles, in the range of 0° to 30°, relative to the first layer. In such a way, miscellaneous nanostructures could be created. The relative angle can be controlled at a very high precision in simulation (±0.1°). However, the current experimental setup only allows us to have a rough control within 2° to 3°. In the future we expect to have a much higher precision with an automated system. After the required relative angle is obtained, the water is drained to let the second layer deposit on the top of the first one. Because both layers forming the double-layer mask were selected to be single-grain only, many structural defects, such as grain boundaries, were eliminated at this point.

Metal catalysts were prepared by e-beam evaporation. During this process metal vapor can go through apertures in hexagonally packed PSs leading to a honeycomb lattice of quasi-triangular particles (when a single mask is used) or a triangular array of nearly spherical particles (in case of a double-layer mask). All the PSs were then removed by either THF or toluene. Details regarding the fabrication of periodic nanoparticle arrays using such technique were reported elsewhere.8

Periodically patterned nickel (Ni) particles on a-plane sapphire substrates were used to grow aligned ZnO nanorods via carbothermal reduction10–12 of a mixture of ZnO and graphite powder at 850–900°C. To grow ZnO nanorods, a constant flow (50 sccm) of argon gas mixed with 2% of oxygen was introduced to maintain a pressure of 1.5 Torr. It was extensively reported that ZnO nanorods can be grown catalytically on gold (Au) nanoparticles.13,15 However, due to a high mobility at higher processing temperature of VLS (vapor–liquid–solid)13 growth, Au particles tend to diffuse and migrate away from their original locations and lose their periodicity. At the same time according to the previous studies13 on an Au–sapphire system in an oxygen-rich atmosphere, the thermodynamic work of adhesion of the interface increases significantly at an elevated temperature.

High interfacial adhesion causes fracture in the thin film leading to formation of several spherical droplets on each original Au island.15 Therefore, it is difficult to selectively grow individual ZnO nanorods with high periodicity using Au as a catalyst.15,16 On the other hand, Ni, having higher melting point, has been demonstrated to be a stable catalyst for aligned carbon nanotube growth at similar temperature range.7,8,17 In this report Ni has been proven to be a better catalyst for selectively growing periodically patterned individual ZnO nanorods in nanoscale pitch. Details of Ni-assisted growth of ZnO nanorods will be reported separately.

Periodic nanoparticle arrangement in the arrays depends on the relative alignment angle between the two layers of PSs. If this angle is equal to zero, a perfect hexagonal order of PSs is achieved. In this case, after evaporation of metal and removal of PSs, a triangular lattice of nearly spherical periodic nanoparticles can be observed (Figures 2d and 3). Because of local defects in one of the monolayers or alignment mismatch, some of these nanoparticles have a shape other than round (Figure 3). When the relative angle is different from zero, the nanoparticles in the array remain mostly quasi-spherical, but their arrangement changes and is strongly dependent on the relative alignment angle. For a small relative angle between 0.1° to about 3°, six large triangular-shaped groups of nanoparticles surround a round

Figure 1. Arrangement of the immersed first monolayer and the floating second monolayer with the schematic diffraction spots from relative angles of 0° and 30°.

Figure 2. Computer simulations compared with experimental AFM images of particles resulted from a double-layer mask with relative alignment angles of 0° (a,d), 10° (b,e), and 30° (c,f). Images (a), (b), and (c) are simulations, (d), (e), and (f) are experiments. All experimental images have the same scale.
central group (Figure 4b), which is confirmed by the simulation (Figure 4a). (Computer simulations were done using a graphics software that allows overlapping of two hexagonally arranged layers of spheres with the same diameter at any relative angle.) The nanoparticle arrangement within all triangular-shaped groups is triangular, while the central round one has a honeycomb order. Although group size changes, the shape remains constant when the relative angle is varied in relatively narrow range (0° to about 5°), thus this kind of structure can be considered as a fractal-like pattern. However, the number of nanoparticles in each group decreases when the relative angle is increased. Figure 4b presents the nanoparticle pattern where the relative angle is close to 4°. When the relative angle increases further, the groups of nanoparticles shrink (Figure 4a compared to Figure 2b). This also fully corresponds with the experimental data (Figure 2e). Due to the 6-fold symmetry of hexagonally packed PSs, the maximum relative angle is 30°. In this case the structure consists of concentric rings of nanoparticles (Figure 2f), which is also in agreement with the simulation (Figure 2c). One of these rings in each group consists of bigger nanoparticles and is particularly visible.

Results of the ZnO nanorod growth are presented in Figures 5 and 6. It is evident that positions of nanorods in the array exhibit a very good correlation with arrays of catalytic Ni nanoparticles described above. Therefore, each ZnO nanorod corresponds with a single Ni nanoparticle in
an array. The structure resulted from small relative angle (\(\sim 2^\circ\)) is shown in Figure 5a, while that from the higher relative angle (of about \(7^\circ\)) is shown in Figure 5b. Because Ni was used as the growth catalyst, it resulted in only one ZnO nanorod from each Ni particle. Another advantage of using Ni is that, due to its higher melting point, it has a lower evaporation rate during the ZnO growth process, which resulted in smaller number of missing sites of nanorods. When the relative angle increases further to about \(10^\circ - 12^\circ\), groups of nanorods shrink to 3-6 rods (Figure 2b). This does not perfectly correspond with the nanostructure shown in Figure 5c where groups of only 2-4 rods can be observed. It might be caused by a partial evaporation of Ni nanoparticles during the growth process. Figures 6a and 6b present a top- and side-view of the triangular pattern of ZnO nanorods, respectively. Among the perfectly vertically aligned nanorods, some longer ones growing in other directions are visible. This is probably caused by the use of Ni as catalytic material since this effect is not so distinct on Au-patterned substrates. \(15,16\) Moreover, it can be noticed that when nanorods have been grown too long they have a tendency to collapse and join into one.

In summary, we have demonstrated an effective and low-cost method to fabricate various configurations of periodic nanoparticles by nanosphere self-assembly and aligned ZnO nanorods in large-scale periodic arrays on transparent substrates by vapor transport and condensation technique. To obtain triangular instead of honeycomb arrangement, double-layer masking procedure was used. Both mask layers were aligned according to the diffraction patterns obtained with the aid of a green laser. The experimental results are in good agreement with computer simulations. It is proved that self-assembly process of PSs can be used for fabrication of a great variety of nanostructures, which differ in arrangement, separation, and nanoparticles shape. Moreover, this method can be further improved by combining with angle-resolved techniques. \(18\)

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