Triangular lattice of carbon nanotube arrays for negative index of refraction and subwavelength lensing effect

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Self-assembly of polystyrene microspheres has been utilized in a two-step masking technique to prepare triangular lattices of catalytic nanodots at low cost. Subsequent triangular lattices of aligned carbon nanotubes on a silicon substrate are achieved by plasma-enhanced chemical vapor deposition. Nickel is used both in the nanodots and in the secondary mask. The triangular lattices of carbon nanotube arrays as two-dimensional photonic crystals show higher geometrical symmetry than the hexagonal lattices previously reported, enabling broader applications including negative index of refraction and subwavelength lensing effect. © 2005 American Institute of Physics. [DOI: 10.1063/1.1900941]

Since the discovery of carbon nanotubes, tremendous progress has been made, not only in controlling the growth yields and atomic structures of carbon nanotubes, but also in aligning their orientations, varying site densities, etc., for various potential applications. Driven by the very recent accelerating development of nanoscale devices, most of which utilize carbon nanotubes not in a large quantity at a time but one by one, and the importance to efficiently integrate these devices as functional units at high density, more specific preparation techniques dealing with individual nanotubes over a relatively large area are seriously demanded. One of the most important research areas is to make ordered configurations in which single nanotubes can be grown at selective locations on substrates without using expensive patterning techniques, such as electron-beam lithography or any elaborate microscopic maneuvers. Self-assembly of polystyrene microspheres was utilized by Kempa et al. and perfected soon after to pattern hexagonal nickel dots and subsequently grow aligned carbon nanotube arrays in large-scale hexagonal lattices at low cost. Those arrays have been used as photonic crystals and many other applications due to the periodic structures composed of single carbon nanotubes with three-fold symmetry. However, other geometries with higher degrees of ordering and symmetry will be even more useful if they can be produced inexpensively. This letter presents a low-cost technique to prepare triangular lattices of aligned carbon nanotube arrays by further exploring the self-assembly of polystyrene microspheres, and the potential applications of these arrays in negative index of refraction and subwavelength lensing effect.

The challenge to arrange individual carbon nanotubes in a certain periodicity is to form the catalytic dots at periodic locations. This is again accomplished herein by forming the periodic structure from self-assembled polystyrene microspheres to avoid the costly lithographic methods. It was found out that in order to have only a single nanotube with uniform morphology grown from each catalytic dot (single growth), the catalyst must have a moderate volume and a proper shape. In order to form triangular lattices, a second-order masking procedure, one step further from the previous single-layer masking technique in the fabrication of hexagonal lattice structures, is adopted.

Figure 1 shows the scheme of fabricating a triangular lattice pattern of catalyst dots on a silicon (Si) substrate from which individual aligned carbon nanotubes are grown. A thin layer of photoresist (MicroPosit S1818) is first spin coated onto a Si substrate (~0.5 mm thick), and a monolayer of polystyrene microspheres (980 nm in diameter is reported here, but other diameters were often used in experiments) self-assembled on an aqueous surface is then transferred onto the photoresist layer. The photoresist thickness is 1–2 μm at a spin rate of 4000 rpm. The assembly is then
The periodic Ni dots are then used as catalysts to grow aligned carbon nanotubes by plasma-enhanced chemical vapor deposition. The growth is carried out for 10 min at 550 °C, using a 0.4 A plasma current and 1 min pregrowth plasma etching.\(^7\) \(\text{C}_2\text{H}_2\) and \(\text{NH}_3\) are used as reaction gases at a ratio of 1:2, while the system pressure is kept within 5–10 Torr during growth. Triangular lattice arrays of aligned carbon nanotubes of diameters about 200–300 nm are therefore obtained and characterized by top and inclined views, respectively, as shown in Figs. 3(a) and 3(b). At most of the periodic spots, only single nanotubes are grown with excellent alignment, but some double growth also occurs at a few spots due to the irregular shape of some catalysts. The irregularity could be caused by the defects in the original monolayer of polystyrene microspheres, nonuniform thickness of the sputtered Ni layers, leftover photoresist scum, and excessive plasma etching. Better qualities can be expected by improving the handling in each patterning step and optimizing the growth parameters. Nevertheless, the idea is clearly demonstrated. The well-defined round shape of the catalyst dots are more suitable to yield single growth compared to the quasi-triangular shape of catalysit islands before. The fabrication technique can also be applied to obtain triangular lattice arrays of aligned nanowires, such as \(\text{ZnO}\), etc.

One of the potential applications of the periodic nanotube arrays is that they can act as two-dimensional photonic crystals. Compared to our previous honeycomb arrays of carbon nanotubes, this triangular photonic crystal has higher rotational symmetry and planar uniformity (each nanotube is two dimensionally equivalent in position), which enables more applications, such as negative index of refraction and subwavelength lensing effects.\(^8-19\) Here, we present the calculated photonic band structure of these triangular arrays of nanotubes for transverse magnetic modes (electric field parallel to the nanotubes), as shown in Fig. 4(a), where the lattice constant \(a=1\ \mu\text{m}\), the nanotube diameter \(D=0.3\ \mu\text{m}\), and the nanotubes (multiwalled and bamboo-like) are treated as perfect metallic rods at optical frequencies.\(^20\) There is an absolute band gap below the first band due to the metallic properties of the nanotubes. A frequency range exists around \(2.76 \times 10^{14}\ \text{Hz} (a/\lambda=0.92)\), where the band is almost isotropic. The equifrequency contours, centered at the \(\Gamma\) point, are essentially circular in that region, and their radii decrease with increasing frequency. Therefore, an effective isotropic negative refractive index can be defined, which is \(n_{\text{eff}}=-1\) for \(2.76 \times 10^{14}\ \text{Hz}\), meaning negative refraction could occur in a simple slab of the triangular arrays of carbon nanotubes. To demonstrate the subwavelength lensing effect, one needs to work at the frequency range where \(a/\lambda < 0.5\) (Ref. 21) to avoid high reflection at the slab surface. This can be easily achieved by filling the internanotube space with dielectric materials, so that all the bands move downward without changing their pattern. For example, if we choose the dielectric material with \(\varepsilon = 12\) (i.e., \(\text{Si}\) at 1.55 \(\mu\text{m}\) wavelength), the negative index \(n_{\text{eff}}=-1\) then occurs at \(0.75 \times 10^{14}\ \text{Hz} (a/\lambda=0.25)\). Figure 4(b) demonstrates the simulated subwavelength lensing effect. More importantly, the fabrication technique...
The proposed pattern-assembly of polystyrene microspheres. Periodic arrays of inexpensively by a two-step masking approach based on self-ranges.

By adopting polystyrene microspheres of different diameters, would result in larger nanotube diameters and larger filling factor to further open the photonic band gap drastically. And, catalytic nanodots by increasing the evaporation thickness of Ni or reducing pregrowth plasma etching, both of which technique has the flexibility to increase the volume of individual catalytic Ni dots in a suitable shape for the single growth of carbon nanotubes. The geometry—composed of isolated carbon nanotubes—is shown to be suitable for broader application purposes including negative index of refraction and subwavelength lensing effect. The patterning technique can be generally applied to fabricate triangular lattice arrays of other materials.

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FIG. 4. (Color online) Negative index of refraction and subwavelength lensing effect. (a) Band diagram (transverse magnetic mode) of a triangular lattice of carbon nanotube arrays calculated by the plane wave expansion method. (b) Subwavelength lensing effect of a slab of triangular lattice of carbon nanotube arrays (nine layers) in dielectric matrix (ε=12). Here, we show a simulated snapshot of the electric-field intensities produced by a point source of frequency 0.75×10^{14} Hz placed on the left side of the slab at a distance of 4 μm using the finite-different time-domain method. There is a point image on the right side of the slab. The transverse size of the image is Δ=0.86λ (resolution R=Δ/2), which is clearly subwavelength. The color gradient bar quantifies the relative electric-field intensity.

In conclusion, triangular lattices of Ni dots are prepared inexpensively by a two-step masking approach based on self-assembly of polystyrene microspheres. Periodic arrays of aligned carbon nanotubes are also grown by plasma-enhanced chemical vapor deposition. The proposed pattern-