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Visible iridescence from self-assembled periodic rippling in vertically aligned carbon nanotube forests

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We observe iridescence in the form of spectrally dispersed white light reflected from the structured sidewalls of vertically aligned carbon nanotube forests. The iridescence is a result of diffraction from a self-assembled periodic rippling pattern on the forest sidewalls that acts as a reflection grating. We measure the grating spacing via white light and laser diffraction experiments and see good agreement with the spacing of the rippling pattern as measured via scanning electron microscopy. The periodic rippling pattern self-assembles during chemical vapor deposition growth of the forests. © *2010 American Institute of Physics*. [doi:10.1063/1.3485084]

Optical properties of ensembles of carbon nanotubes, such as forests of vertically aligned nanotubes, are increasingly of interest. For example, Yang *et al.*[1] report that nanotube forests are among the blackest known materials when observed along the axes of the nanotubes. However, at other angles of incidence, nanotube forests are noticeably reflective, particularly from their sidewalls. If the sidewall surface has a periodic modulation, then one would expect it to act as a diffraction grating and spectrally disperse white light. Such a periodic rippling pattern can form spontaneously during growth.[2–6] Ripples can also be obtained by compressing a forest along the axis of the nanotubes, either during growth,[7] or postgrowth.[8–10] Iridescence from periodic arrangements of individual vertically aligned multiwalled nanotubes on a substrate[11–13] and periodic arrangements forests on a substrate[14] has previously been observed. Here, it is the rippled structure of the forest itself that causes the iridescence, not their arrangement on the substrate. The periodicity of the ripples is extremely consistent and they generally have a spacing similar to the wavelength of visible light. When a large enough area of ripples is present on the sidewalls of a forest, we easily observe brilliant colors reflected from the forests as a result of optical diffraction via a reflection grating effect. Using simple optics and scanning electron microscopy (SEM), we show that the iridescence is indeed a result of the rippling pattern.

Forests were grown at 760 °C using a cold-walled chemical vapor deposition reactor operated at atmospheric pressure using C_2H_2 as the carbon source and H_2 and H_2O vapor as enhancers. Samples were approximately 5×5 mm^2 pieces of Si/SiO_2 patterned with circular Al_2O_3/Co catalyst islands (100–800 μm in diameter). Details can be found in a previous report.[15] Optical images were acquired through a long focal length microscope with a digital camera, with the color balance adjusted so the image on the monitor appeared as it does to the naked eye. A 1 mW HeNe (632.8 nm) laser, focused with a lens and passed through a variable intensity filter was used for laser illumination. The laser and white light source were parallel. All optical components, including the sample, rotated about a common axis through the sample.

Figure 1(a) shows an optical image of white light diffraction from numerous 100 μm diameter forest pillars. Forests are organized on a hexagonal grid with ~100 μm spacing at the base. The forests usually become bent and tipped over during growth. Colors are more brilliant slightly out of focus, likely because they dominate over the blackness around them. Figure 1(b) shows an SEM image of the ripples on a forest from Fig. 1(a), which appear similar to previous reports.[2–10] Here, ripples form spontaneously during growth, likely due to a growth rate difference between different nanotubes in the forest,[3,4] which in turn causes a compressive strain that bends the nanotubes. It is known that growing nanotubes exert a mechanical force,[7] which likely causes the compressive strain. The presence of strain is also suggested by the ripples generated by intentional compression of forests.[7–10] The periodic nature of the ripples is likely due to the balance between the stiffness of the nanotubes that resists bending and the van der Waals interaction between nanotubes. The van der Waals interaction is also responsible for the long range synchronization of the amplitude and the wavelength. The observed ripple spacing is similar to the average length over which nanotubes come into contact with one another in a forest.[15,16]

The angular positions of the intensity maxima of a grating are given by the grating equation: $n\lambda = d(\sin\theta_n + \sin\theta_i)$ where n is the order of the maximum (here $n=1$), λ is the wavelength observed at the maximum, d is the grating spac-

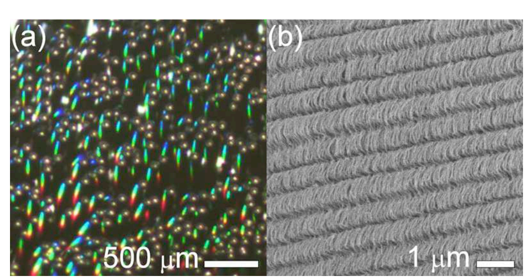

FIG. 1. (Color online) (a) Optical image of white light diffraction from numerous 100 μm diameter forest pillars. (b) SEM image of periodic rippling pattern from a forest on the same sample.

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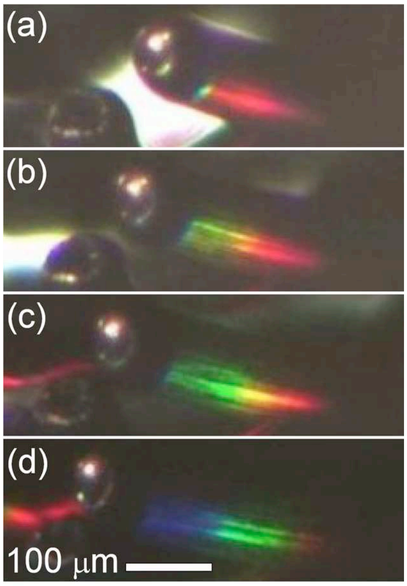

FIG. 2. (Color online) Optical images of forest (100 μm diameter) being rotated by ~5° intervals (angle of incidence and observation change simultaneously) showing a change in color from red (a) to green-red (b) and (c) to blue-green (d).

ing, θ_n is the angle of the maximum (angle of observation), and θ_i is the angle of incidence. The grating constant is $N=1/d$.

Optical images of white light diffraction from a single 100 μm forest (Fig. 2) show that tilting the forest by ~5° toward normal incidence (θ_n and θ_i decrease simultaneously) causes a change in color from red (a) to green-red (b) and (c) to blue-green (d). This change in color can be used to estimate d. For these measurements, θ_n is fixed, θ_i is scanned across the sample, and λ is estimated from the observed color. Using the grating equation, d was calculated for several (λ,θ_i) pairs for the same area of a forest and averaged. Results for three different 700 μm diameter forests (forests W1–W3) are given in Table I. To confirm that the diffraction is indeed a result of the ripples, d was measured by SEM at the same location that the diffraction was observed. These values are presented in Table I, along with corresponding values of N. We used 700 μm diameter forests because these larger forests are usually perpendicular to the substrate, which makes angular measurements easier. Larger forests are also easier to manipulate, have a smaller curvature, and larger surface area than the smaller forests.

We also measured d with HeNe laser illumination using 400 μm diameter forests (forests L1–L3). Here, $\lambda=632.8$ nm and θ_n and θ_i are varied simultaneously by rotating the sample. Angular measurements include slight corrections, obtained by SEM observation, to account for the fact that the 400 μm forests are not exactly perpendicular to the substrate. Figure 3(a) shows an optical image of forest L1 illuminated by both white light and the HeNe laser and reflecting colors. An SEM image of forest L1 from approximately the same view point is shown in Fig. 3(b). Figure 3(c) is a close up SEM image of the area indicated (approximately) in Figs. 3(a) and 3(b), where measurements were taken, showing the periodic rippling pattern that acts as the reflection grating. Compared to Fig. 1(b), these ripples have a very small amplitude, but even these small ripples are sufficient to produce a pronounced grating effect. Quantitative results for forest L1 and specific regions of two other forests measured with laser diffraction are given in Table II.

Grating efficiency was measured by diffracting the 1 mW HeNe laser (632.8 nm), of which 10% was incident on the grating area, and collecting 0.1 μW from the first order maximum, giving a grating efficiency of 0.1%. This is impressive because the forest is very sparse, and also because nanotubes are known for their strong absorption.

For all forests, both those measured by white light (Table I) and laser illumination (Table II), d is similar whether measured optically or by SEM. The discrepancy between the optical and SEM value of d is larger for the white light measurements than for the laser measurements. This is primarily a result of the uncertainty in the wavelength of the light which was simply estimated by eye from the color of the digital image, and is uncertain by as much as ±25 nm. Any further discrepancy is most likely caused by the fact that these gratings are not ideal because they are not, in general, flat. Not only are the forests round, but their sidewalls curve inward near the top, as seen in Fig. 3(b). Furthermore, there is only ever a small flat area of ripples to act as a single unified grating, making it difficult to align, particularly in

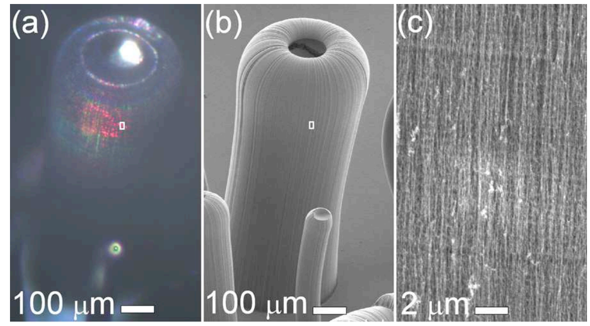

FIG. 3. (Color online) Forest L1 (400 μm diameter). (a) Optical image (black-white contrast enhanced) with white light and HeNe laser illumination showing reflected colors. (b) SEM image of the same forest. (c) Close up of area indicated (approximately) in (a) and (b) showing grating. Grating parameters given in Table II.

TABLE I. Grating spacing d for three forests (700 μm diameter), measured by white light diffraction and SEM, and grating constant $N=1/d$, determined by SEM.

Forest	d_{WL} (nm)	d_{SEM} (nm)	N_{SEM} (mm^{-1})
W1	310 ± 40	500 ± 20	2020 ± 60
W2	440 ± 100	490 ± 5	2040 ± 20
W3	330 ± 140	470 ± 10	2130 ± 50

TABLE II. Grating spacing d for three forests (400 μm diameter), measured by HeNe (632.8 nm) laser diffraction and SEM, and grating constant $N=1/d$, determined by SEM.

Forest	d_{HeNe} (nm)	d_{SEM} (nm)	N_{SEM} (mm^{-1})
L1[a]	440 ± 10	466 ± 5	2150 ± 20
L2	740 ± 30	620 ± 10	1610 ± 40
L3	1500 ± 100	1540 ± 40	650 ± 20

[a]See Fig. 3.

defining the normal direction. Even small errors in angular measurements can cause large uncertainties in d.

The grating spacing d is generally the same order of magnitude from one forest to another, but variations exist. In particular, the large d of forest L3 is the result of a stacking fault in the rippling pattern that effectively doubles the spacing of the pattern. It is somewhat remarkable that the ripples are regular enough over a large enough area to give rise to the diffraction of visible light. With proper control over the formation of the ripples it should be possible to create a variety of gratings, particularly highly dispersive gratings with narrow spacing (high grating constants). In the present report, gratings with ~2000 lines/mm are routinely obtained.

In summary, we observe brilliant iridescence of light reflected by carbon nanotubes forests. These colors are a result of a reflection grating effect generated by a periodic rippling pattern on the sidewalls of the forests. The diffracted colors were correlated with the rippling pattern by measuring the grating spacing via white light and laser diffraction, and then comparing this value to SEM measurements of the same area, with reasonably good agreement. We obtain predominantly highly dispersive gratings but also gratings of low dispersion. The periodic rippling pattern forms spontaneously during growth, providing a self-assembled method to fabricate high dispersion gratings.

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