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Selective Positioning and Density Control of Nanotubes within a Polymer Thin Film

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ABSTRACT

We introduce a completely new and innovative method of producing polymer/nanotube composites where the density and position of the nanotubes within the composite can be controlled. Carbon nanotubes are grown from organometallic micropatterns. These periodic nanotube arrays are then incorporated into a polymer matrix by depositing a curable polymer film on the as-grown tubes. This controlled method of producing free-standing nanotube/polymer composite films represents a more efficient method of combining these materials for potential flexible electronic applications in an inexpensive and scalable manner.

Carbon nanotubes have captured the imagination of scientists and industrialists for the past decade. They appeared during initial investigations into fullerene research[1] and now stand on the brink of applicability in a number of noted directions. Both multiwalled and single-walled nanotubes have been studied for possible use in areas that would utilize their electrical,[2,3] mechanical,[4] and optical[5] properties. Potential applications encompass a diverse range of devices including: flat panel displays,[6] sensors,[7] electronic devices,[8,9] polymer composites,[10,11] quantum wires,[12] and actuators.[13] Before realizing their full potential, the issue of economic production of controlled nanotube arrays, either free-standing or in composites, must be overcome.

Popular and successful methods of nanotube growth include chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD). Large quantities of nanotubes can be produced on a substrate simultaneously, with a high degree of morphological control. In fact, in the past twelve months inventive methods have illustrated the possibility of control over growth, position, and directionality of nanotubes.[14−18] The next step is to find a direct method of incorporating them into polymer composite systems. Various other groups have addressed this issue.[19]

We report in this paper a controlled, efficient and cost-effective method of producing carbon nanotube arrays within a poly(dimethylsiloxane) polymer (PDMS) matrix. Carbon nanotubes were grown by chemical vapor deposition (CVD) on a pre-patterned template. From this, a mixture of base/curing agent (weight ratio of 10:1) from a Sylgard 184 elastomer kit is deposited onto the patterned arrays of as-grown tubes. The mixture migrates into vacant areas on the nanotube film. The resultant cured (for 24 h at room temperature) PDMS composite is then simply peeled off the substrate giving a free-standing flexible film containing a controlled nanotube morphology.

Our template for carbon nanotube growth is first prepared by soft lithography patterning, similar to previous reports.[20,21] Soft lithography can be used to rapidly pattern large areas under atmospheric conditions. The shape and dimensions of the molded elastomer, used to create the patterns, can be modified to create a variety of templates for CNT growth. Using an elastomer stamp, the organometallic polymer catalyst is patterned onto a silicon oxide substrate (Figure 1a−c). The micropattern feature sizes are dictated by the dimensions of the stamp. The height of the catalyst features can be controlled by varying the concentration of the polymer solution used to create the patterns. The organometallic polymer used was a poly(styrene−vinylferrocene) copolymer blend (PS−PVF). This PS−PVF was anionically synthesized in our lab. A combination of gel permeation chromatography and nuclear magnetic resonance revealed that the PS−PVF

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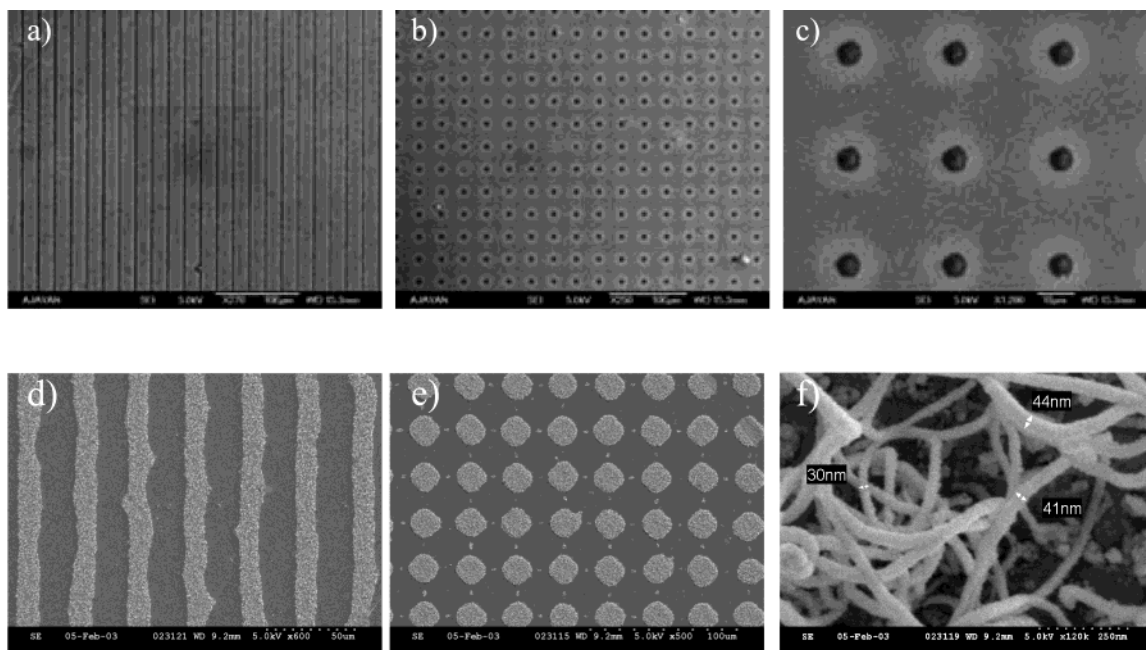§ Materials and Engineering Department, RPI.
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Figure 1. Polymer micropatterned substrates for NT growth. Darker areas correspond to regions of high organometallic polymer concentration and paler areas represent the silicon oxide substrate [a−c]. After CVD (using acetylene), it was observed that carbon nanotube growth occurred only on the micropatterned areas of the substrate [d−e]. A close-up image of one of the micropatterned areas [e] appears in [f].

copolymer blend contained 8% vinylferrocene (results not shown). The vinylferrocene contains an iron core and is the part of the polymer that is active as a catalyst for carbon nanotube growth during CVD. A PS−PVF copolymer rather than a polyvinylferrocene (PVF) homopolymer was used for reasons of dispersion. Nanotubes grown on patterned PVF homopolymer grow in clusters of islands (FESEM images not shown). Growth is more homogeneous when the PVF homopolymer is co-polymerized with polystyrene, thus diluting it's concentration.

CVD growth of the nanotubes is performed at elevated temperatures, usually between 550 °C and 1100 °C.[22] Most polymers decompose in the region of 400 °C. It was therefore necessary to investigate the thermal stability of the synthesized polymer PS−PVF to ensure that it was suitable as a catalyst for CVD. A combination of thermal gravimetric analysis and energy dispersive X-ray spectroscopy confirmed the presence of iron particles at temperatures in the region of 800 °C. This is therefore the temperature subsequently used for CVD growth. Carbon nanotubes were grown successfully using both acetylene as xylene as the carbon source.

Observation of the CVD samples using a field emission scanning electron microscope (FESEM) revealed that nanotube growth was selective to the PS−PVF polymer patterned areas of the silicon oxide substrate (Figure 1d−f). This is due to the presence of catalyst (Fe) particles within the confines of the micropattern and the absence of the catalyst particles elsewhere on the substrate. Alignment of the tubes was not as good as reported elsewhere.[23,24] This is perhaps due to imperfect dispersion of the iron catalyst, since straight and aligned tubes have been previously reported using ferrocene.[23,24] Improved quality and alignment of tubes grown

under the conditions used here should improve as a function of better control over both the growth and patterning processes and is the focus of ongoing research.

The density of carbon nanotubes produced on the substrate was shown to be dependent on the thickness of the micropattern features (Figure 2). The height of these features is easily controlled by altering the concentration of the PS−PVF polymer solution used to pattern the substrates. For lower concentrations (1 wt %) the nanotube growth is quite sparse, and for higher concentrations (2 wt %) increased tube growth occurs. For concentrations 5 wt % and above, complete coverage of the substrate between catalyst patterns was observed. Control over density of tube growth is critical for applications such as field emission.[28] If the nanotube density is too high, screening by neighboring emitter tips occurs. If the density is too low, amplification of the applied electric field is not sufficient.

The presence of nanotubes (rather than fibers) was verified by transmission electron microscopy and Raman spectroscopy. Raman spectra (see Supporting Information, Figure S1) show two main characteristic first-order peaks for multiwalled carbon nanotubes. First-order peaks are dominated by the E_{2g} optical phonon at 1580 cm^{-1} (G mode) and a peak at 1350 cm^{-1} (D mode). The relationship of these two modes has been resolved elsewhere using double resonant theory.[25,26] Peaks at higher wavenumbers are second-order combinations of first-order modes, as reported elsewhere.[27] Spectral resolution increases for intermediate CVD times. This indicates the formation of more graphitic tubular structures and less amorphous carbon deposition during this growth phase.

The as-grown nanotubes can then easily be incorporated into a polymer matrix. A thin film of PDMS was spin coated
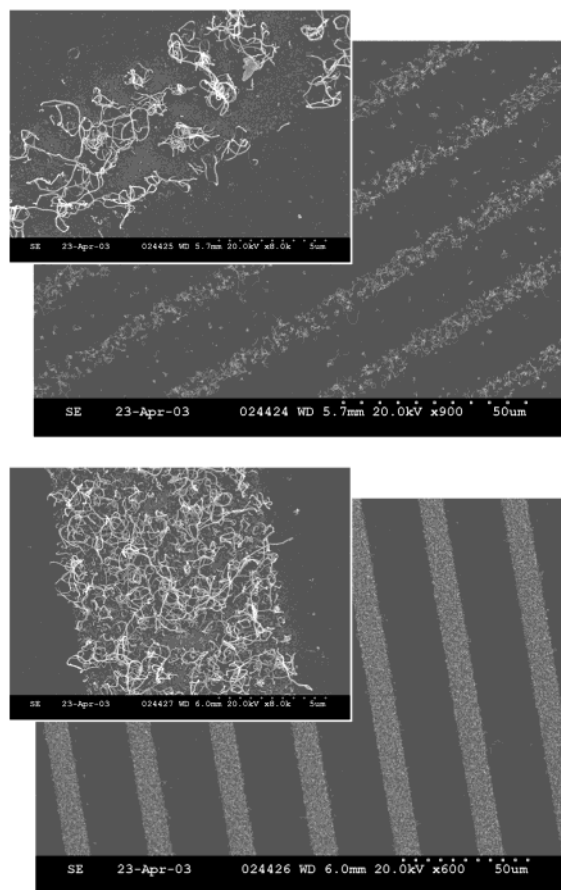
Figure 2. FESEM images illustrate the dependence of growth density on feature height of the polymer micropatterns. Patterns (from the top) were made using 1 wt % and 2 wt % solution of an iron-containing polymer. CVD conditions were identical for both samples. Magnification is of the same order for all larger FESEM images. The smaller insets show a portion of the image at higher resolution.

Figure 3. Nanotube patterns incorporated into a PDMS matrix (a) show controlled tube growth on a SiO_2 substrate and (b) show the tubes integrated into a polymer composite.

onto the nanotube film (Figure 3). The polymer disperses into vacant areas on the nanotube film. The nanotube/polymer matrix is then cured for 24 h at room temperature and under atmospheric conditions. The composite can then be easily peeled away from the substrate. Pre-patterning of the substrate on which the tubes are grown controls the position of the nanotubes within the composite. The density of tubes within the composite depends on the density of the as-grown tubes, which as discussed, is easily controlled by varying the feature height of the polymer micropatterns used as a template for tube growth. Cross-sectional scanning electron microscopy (Figure S2 a and b) show that there is good wetting between the carbon nanotubes and the PDMS polymer, indicating that the polymer should fill any vacant voids within the nanotube arrays.

Bright areas in Figure 3b correspond to conductive channels within the PDMS polymer, which, is represented by the darker regions in the FESEM image. It is well-known that nanotubes enhance the transport properties of a polymer.[29] The presence of these conducting channels was verified by a combination of atomic and electron force microscopy (AFM/EFM). AFM images (Figure 4a,b) show
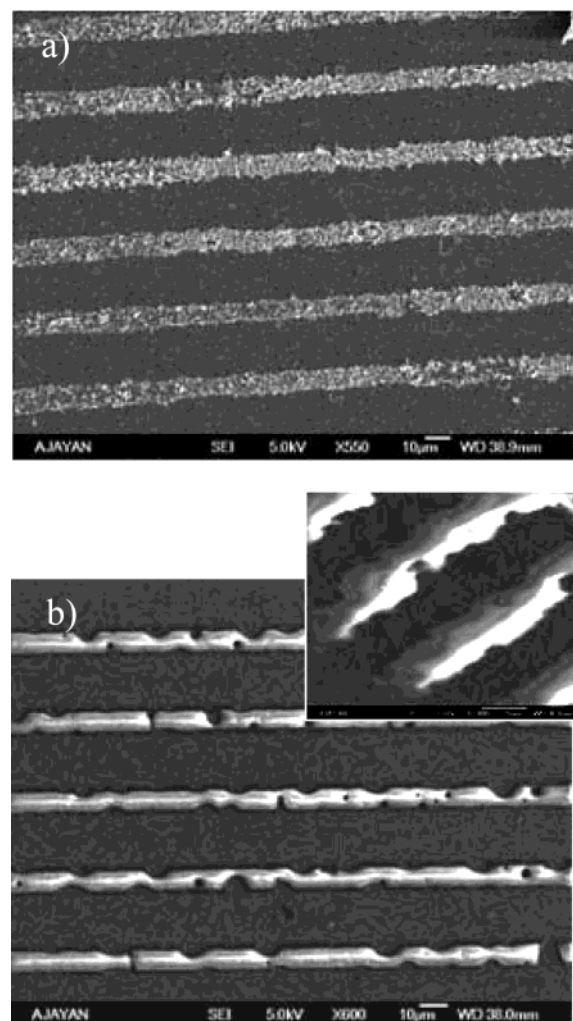
height image data on a scale of 0−10 nm, and the corresponding EFM images (Figure 4c,d) show amplitude image data on a scale of 0−300 mV. Results shown in Figure 4 were recorded in tapping mode at a scan rate of 0.500 Hz. It is clear from these images that the height profile of the composite correlates with the position of the conduction channels. The uneven height of the composite surface is due to the nanotubes protruding from the PDMS surface (dark areas in Figure 4a,b). The 'dots' in the AFM images, which correspond to the nanotube positions, are in the region of 20 nm in diameter. The position of the nanotubes observed in (a) and (b) matches the location of the conduction paths through the composite in (c) and (d). These conduction paths were also observed as 'dots' in the EFM images. The diameter of the EFM dots was found to be 10 nm. The decrease in diameter is due to an increase in the resolution of the system using a sharper diamond tip cantilever for the EFM measurements. The diameter of the nanotubes used to make the composite was measured by FESEM to be in the region of 20−50 nm, which indicates that it is possibly only the very tips of the tubes that project from the PDMS surface.
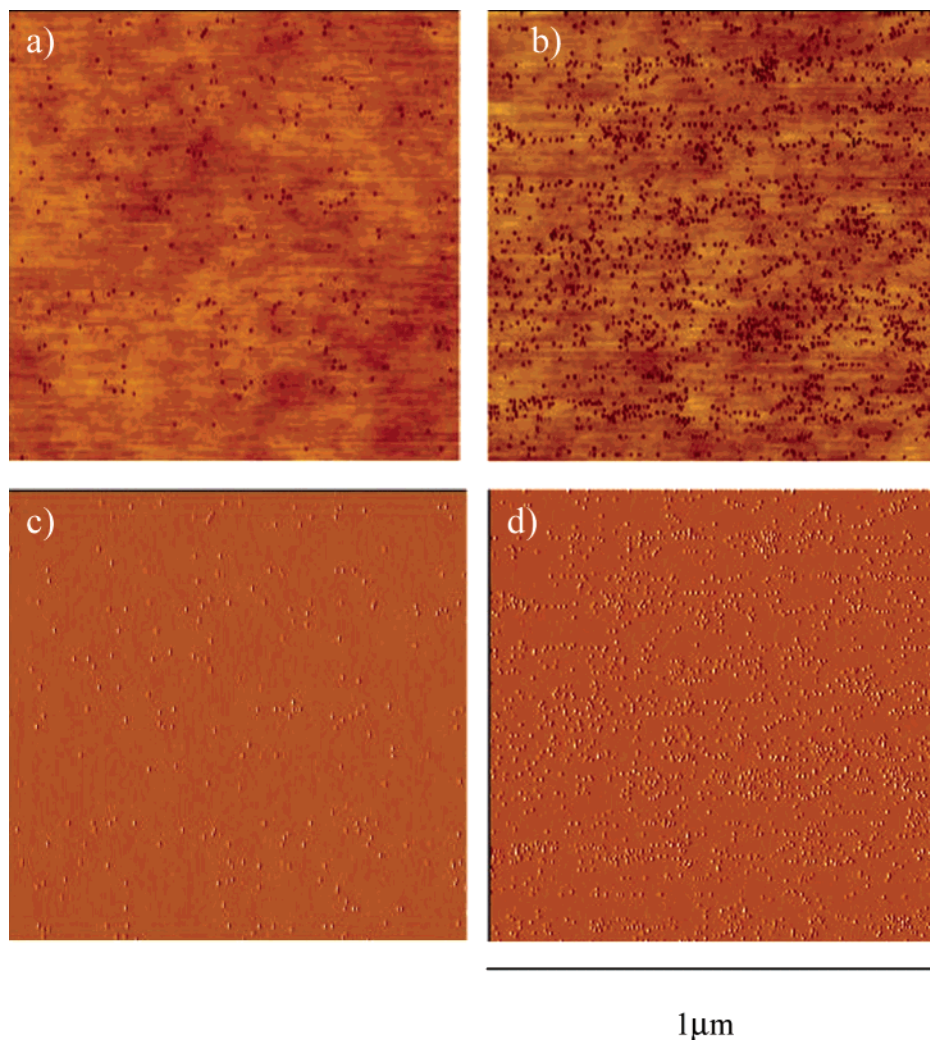
Figure 4. AFM images of both the PDMS area of the composite (a) and the nanotube channels within the polymer composite (b). EFM images were taken on corresponding areas on the PDMS (c) and the nanotube channels (d). Features are $0-10$ nm for (a) and (b) and $0-300$ mV for (c) and (d). Scale bars for all images are 1 μm^2.

In conclusion, we report a scalable inexpensive technique to fabricate flexible carbon nanotube composites. The location and density of conducting channels within the composite can be easily controlled by soft lithography patterning. The composite can then be used for applications that require conductive channels within a flexible matrix. Control over the position and density of nanotubes within the composite is of the utmost importance for commercial nanotechnological devices. That we can control this parameter in such a simple manner should be of great interest for industrial applications.

Supporting Information Available: Raman spectra showing two main characteristic first-order peaks for mul-tiwalled carbon nanotubes and SEM image of DMS-CNT composite. This material is available free of charge via the Internet at http://pubs.acs.org.

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