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Rapid prototyping of three-dimensional microstructures from multiwalled carbon nanotubes

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The authors report a method for creating three-dimensional carbon nanotube structures, whereby a focused laser beam is used to selectively burn local regions of a dense forest of multiwalled carbon nanotubes. Raman spectroscopy and scanning electron microscopy are used to quantify the threshold for laser burnout and depth of burnout. The minimum power density for burning carbon nanotubes in air is found to be 244 μW/μm^2. We create various three-dimensional patterns using this method, illustrating its potential use for the rapid prototyping of carbon nanotube microstructures. Undercut profiles, changes in nanotube density, and nanoparticle formation are observed after laser surface treatment and provide insight into the dynamic process of the burnout mechanism. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2778292]

Carbon nanotubes have attracted a lot of attention over the past 15 years due to their exceptional properties which far exceed those of most known bulk materials. These properties include high mechanical strength, high surface area, and high thermal and electrical conductivities.[1–3] Many potential applications have been proposed that exploit these exceptional properties.[4–6] The ability to pattern carbon nanotube microstructures is an important step in realizing these applications. Conventional lithography techniques are limited to patterning two-dimensional (2D) microstructures and require a sequence of fabrication steps that introduces chemical residues that are incompatible with specialized biological applications.[7] It is therefore important to investigate alternatives to the controlled fabrication of nanotube microstructures to enable a broader set of applications. Our approach provides a nonchemical, local patterning method that leaves the patterned nanotubes unperturbed as grown. It is therefore suitable for chemically sensitive applications.

Several techniques for patterning three-dimensional (3D) carbon nanotube structures have been explored previously.[8–10] These approaches are based on bottom up growth of multiwalled carbon nanotubes (MWNTs) from a patterned catalyst, which is limited to 2D-like geometries. Complex 3D microstructures have been fabricated in systems other than nanotubes using an optical two-photon photopolymerization process.[11–13] While this technique provides high spatial resolution for creating 3D structures, it is limited to polymer-based resin materials that are electrically insulating, which severely limits their potential applications. Also, these materials do not possess the desirable surface properties of carbon nanotubes, which can be easily modified with the vast repertoire of carbon based chemistry.[14,15]

Here, we create three-dimensional microstructures using a focused laser beam to selectively burn local regions of a dense forest of multiwalled carbon nanotubes. Raman spectroscopy is used to systematically quantify this process in a controlled fashion to determine the laser power threshold for burning carbon nanotubes and, also, the depth of burnout at different laser powers.

Carbon nanotube forests are grown by CVD by passing ethylene (C_2H_4) over a predeposited iron catalyst on Si wafers. The iron catalyst is prepared by evaporating a 2.5 nm film of Fe on silicon substrates with 400 nm of thermal oxide. The nanotube growth takes place in a heated tube furnace at 650 °C.[16,17] A 532 nm 5 W Spectra Physics solid state laser is collimated and focused through a Leica DMLM microscope, and used to irradiate these samples. The samples are manipulated spatially on a PRIOR ProScan II high precision microscope stage. Raman spectra are taken with a Renishaw inVia Raman spectrometer from the scattered light collected by the same objective lens. We determine the minimum threshold laser power for burning carbon nanotubes in air by observing changes in the intensity of nanotube Raman spectra before and after laser exposure. The Raman intensity gives a measure of the density of carbon nanotubes within the focal volume. We use a 50× long working distance objective lens with NA=0.5 and spot size=1.25 μm. Nanotubes were exposed at laser powers between 50 and 9000 μW for 1 s. The results were not sensitive to exposure time, indicating that the burnout occurs on a much shorter

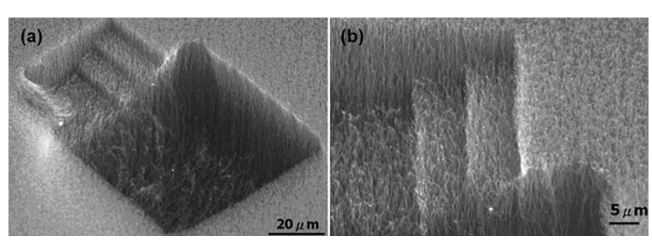

FIG. 1. 3D staircase structure fabricated in the MWNT surface.

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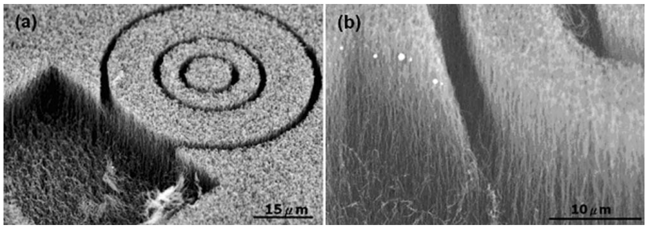

FIG. 2. (a) Concentric cylindrical structures patterned using the laser burnout method. (b) Close-up image showing a slight undercut profile.

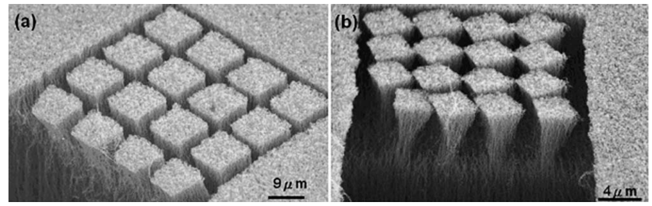

FIG. 3. Square arrays patterned with laser powers of (a) 730 μW and (b) 1900 μW.

time scale. To determine the relative change in nanotube density, Raman spectra are taken at low subthreshold laser powers (50 μW) with an accumulation time of 120 s before and after high power laser exposure. From this data,[18] we determine the threshold for laser burnout to occur at 300 μW, which corresponds to a power density of 244 $\mu W/\mu m^2$ for a 1.25 μm spot size.

Figure 1 shows a scanning electron microscope (SEM) image of a 3D staircase structure patterned using this technique. The clear depth change can be seen in the side view of this image. The dimensions of the steps are 5 μm high, 30 μm wide, and 7 μm deep. A square volume was burned adjacent to this staircase microstructure to allow for easier viewing. This technique can be used to precisely control carbon nanotube forests to create well-defined channel geometries for gas and liquid transport through carbon nanotube membranes.[19,20]

Curved surfaces can also be easily created using this technique. Figure 2 shows cylindrical structures fabricated by burning concentric rings in the MWNT forest. These images exemplify the high aspect ratios that can be achieved with this technique. Again, a square box was removed adjacent to this microstructure for better viewing. These deep trenches may be suitable for superhydrophobic microfluidic channels with complex geometries.[21]

We have also patterned square arrays using this noncontact method, as shown in Fig. 3. These arrays may be suitable for field emission applications.[22] The large undercut seen in Fig. 3(b) shows the effect of using high laser powers to pattern these microstructures. The high laser power causes the units of the matrix to twist and rotate due to their mechanical instability and the high temperatures reached during burnout. From the work of Cataldo, the burnout process in carbon nanotubes is expected to occur at 800 °C in air.[23] In fabricating these fragile structures, the sequence of write steps and laser power must be taken into consideration to avoid collapse and distortion of delicate microstructures with high aspect ratios, such as those shown in Fig. 3(b).

In this 3D patterning technique, it is important to determine the depth of burnout and, hence, resolution in the z direction. In the x-y plane, the resolution is limited by the spot size of the objective lens. It is difficult to measure the depth of burnout because of the soft surface of the MWNT forest, which prohibits the use of a profilometer or atomic force microscope. Raman spectroscopy provides a noncontact method for measuring the surface height and is therefore suitable for working with this delicate system. In order to measure the burnout depth using Raman spectroscopy, we measure spectra at various heights with respect to the sample surface. Figure 4 shows the Raman intensity versus depth profile taken before and after laser exposure at 1000 μW and exhibits a Gaussian intensity-height profile. The relative shift of these Gaussian peaks corresponds to the depth of burnout. The resulting depth-laser power data is plotted in Fig. 4(b) and exhibits a linear relation between the laser power and depth of burnout. In the limit of low laser power, the minimum burnout depth is found to be 5 μm. This is limited mainly by the relatively low numerical aperture of the objective lens (NA=0.5). Using a higher numerical aperture lens would provide more tight confinement of the laser light and allow more precise patterning of the MWNT surface. The drop in intensity from 2200 to 1450 photon counts after laser exposure reflects the change in nanotube density of the laser treated surface. This change in nanotube density has been seen in SEM images,[18] and may provide a way of varying the wetability of the hydrophobic surface of MWNT forests.[21,24,25]

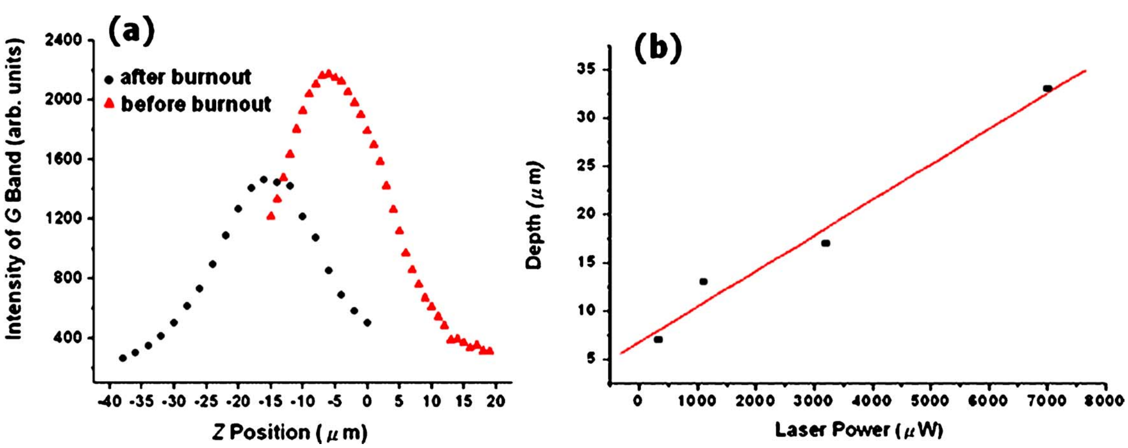

FIG. 4. (Color online) (a) Raman intensity vs height profile before and after 1000 μW laser exposure. (b) Relation between burnout depth and laser power exposure.

We observe several interesting phenomena on the surface of the MWNT forests after laser treatment. SEM images reveal white spots ranging from 100 to 200 nm on top of the burned MWNT surface.[18] At higher magnification, these white spots can be resolved as nanotube bundles that aggregate during the exothermic burnout process. This aggregation demonstrates the dynamic nature of the burnout process of these MWNTs.

In conclusion, a method for creating three-dimensional microstructures from carbon nanotubes is presented, using a focused laser beam to selectively burn local regions of a dense forest of multiwalled carbon nanotubes. Raman spectroscopy is used to quantify the threshold for laser burnout and depth of burnout. Several 3D patterns have been created with this patterning method, illustrating its potential use for the rapid prototyping of carbon nanotube microstructures. Several interesting phenomena were observed after laser surface treatment, including the formation of nanoparticles and a lowering of the nanotube surface density. This patterning method can be used widely to expand the application of MWNTs and serve as a basis for developing similar patterning methods in other material systems.

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