Patterning of single walled carbon nanotubes using a low-fluence excimer laser photoablation process

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(Received 24 January 2008; accepted 11 April 2008; published online 1 May 2008)

Carbon nanotube films were patterned by an excimer laser projection photoablation process at low incident energy conditions. The carbon nanotubes were deposited on a quartz substrate and then a conventional photoresist was coated on it as a photoablation assistor. The photoresist and the carbon nanotubes were simultaneously patterned by the projection photoablation process, and then the photoresist was removed. It was possible to make clean patterns of carbon nanotubes even though the incident fluence on the carbon nanotubes was significantly lower than the threshold energy otherwise needed for their direct ablation. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2919093]

In this letter, we describe a patterning method that can be used in the fabrication of devices and other applications,[1–6] which use carbon nanotubes as a component material. The process is compatible with conventional microelectronic fabrication processes and it is high speed compared with previous reports.[7–9] Figures 1(a)–1(d) illustrate the concept of this method. Before the patterning of the target material, i.e., the carbon nanotube layer, it is deposited on the substrate, as illustrated in Fig. 1(a).

Single walled carbon nanotubes were grown on quartz. Ferritin catalyst (Aldrich) diluted 1:20 by volume with deionized water was cast onto the substrate. A high concentration of catalyst on a double sided polished, unannealled quartz substrate was used to obtain a random network of tubes.[10] The transparency of the quartz ensures that it is not ablated in the process and does not interfere with the ablation of the carbon nanotubes. The catalyst was oxidized in air by heating it up to 800 °C and cooling it back to room temperature. Heating to 925 °C in hydrogen in a 20 SCCM (SCCM denotes cubic centimeter per minute at STP) flow of hydrogen and 20 SCCM flow of argon bubbled through ethanol for 15 min yielded random networks of individual single walled tubes. After the growth, the samples were slowly cooled back to room temperature to prevent the quartz substrate from cracking.

After the deposition of the target material, a photoablation assistor layer was coated on it. We used a conventional photoresist, MicroChem AZ4620 or MicroChem S1818, as the ablation assistor and it was coated on the carbon nanotube layer, as shown in Fig. 1(b). The photoresist deposition process causes the resist to be placed *under* the carbon nanotubes as well as on top of the carbon nanotubes because liquid phase photoresist was coated and baked. After the coating of the photoablation assistor, it was ablated using pulsed excimer laser radiation, as shown in Fig. 1(c). We used deep ultraviolet radiation from a KrF excimer laser at 248 nm wavelength and the exposures were carried out using a projection imaging configuration for the photoablation process. The laser had a pulse repetition rate of 5 Hz, and provided an energy fluence of 100–600 mJ/cm^2 at the substrate. When the photoresist under the carbon nanotubes gets ablated during the laser photoablation process, the physical force of dissociated fragments of the photoresist also removes the carbon nanotubes above it. Although, as previously reported, the carbon nanotubes can be directly ablated by the convention ablation process, the exposure fluence required is very high (several J/cm^2). In comparison, with the process we report, the carbon nanotubes can be patterned with a much lower fluence of illumination by using a photoablation assistor layer. After the photoablation of the photoresist, we used oxygen plasma ashing to remove the remaining debris and residue layer. After the oxygen plasma cleaning process, patterned photoresist on the sample was

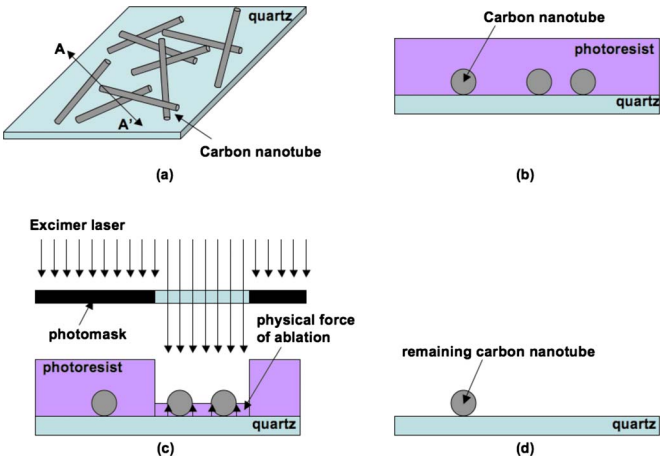

FIG. 1. (Color online) The concept of material assisted excimer laser photoablation. (a) A layer of a porous material or carbon nanotubes is deposited on a substrate. (b) The photoablation assistor layer is coated on the target material to be patterned. The cross sectional view of AA′ in (a) is illustrated. (c) Ablation of the ablation assistor layer and removal of the target material. (d) After ablation of the ablation assistor material, it was removed and the final material patterns of the carbon nanotube film or other porous material remained.

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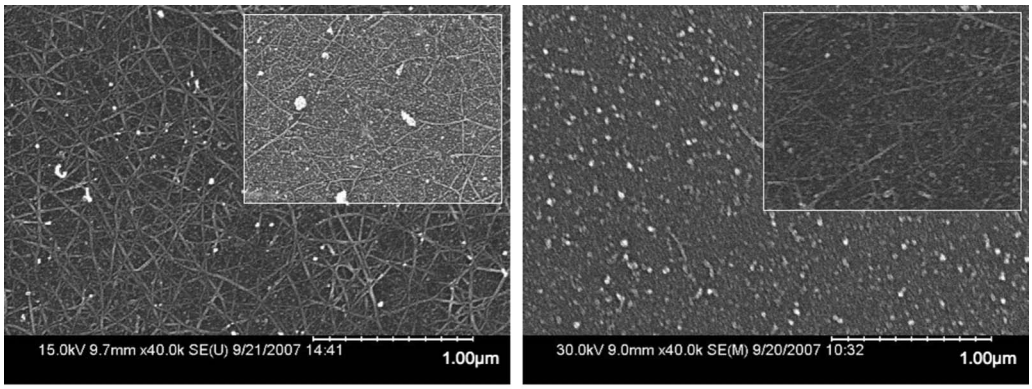

FIG. 2. SEM photographs of carbon nanotube films. (a) Carbon nanotubes after exposure by excimer laser radiation. The initial carbon nanotubes on a quartz substrate are shown in the inset. The exposure fluence was 590 mJ/cm^2 and the number of pulses was 500. (b) The carbon nanotubes were removed during the ablation process at an incident fluence of 270 mJ/cm^2. Inset in (b): the carbon nanotubes in the nonilluminated region.

removed in an acetone rinse, leaving behind patterned carbon nanotubes, as illustrated in Fig. 1(d).

Before carrying out the proposed method, we investigated the direct ablation characteristics of the carbon nanotubes using our excimer laser ablation system. Figure 2(a) shows the carbon nanotubes after excimer laser exposure, and the inset picture in Fig. 2(a) shows a scanning electron microscope (SEM) image of the initial carbon nanotubes before processing. The incident fluence of the laser illumination was 590 mJ/cm^2 and the number of pulses was 500. It is clear that the carbon nanotubes were neither damaged nor ablated at the fluence of 590 mJ/cm^2. The threshold for direct ablation of carbon nanotubes is therefore higher than 590 mJ/cm^2.

In order to demonstrate the method of our concept, we coated a photoresist, MicroChem AZ4620, on the carbon nanotube layer, with a thickness of 3.5 μm. After coating the photoresist, we illuminated the sample with the excimer laser imaging system at a fluence of 270 mJ/cm^2. The number of incident laser pulses was 100. We used a metal hardmask between the illumination source and the sample to make a square pattern on the substrate. After the photoablation of the sample, the photoresist was removed in an acetone rinse and a SEM picture was taken, as shown in Fig. 2(b). All the carbon nanotubes were removed after the photoablation process even though the fluence of illumination was less than the conditions in Fig. 2(a). The white dots in the SEM image are attributed to a catalyst material which is used in the deposition process of the carbon nanotubes. The inset in Fig. 2(b) is an SEM image of the same sample which was taken in the nonilluminated region. As seen, the initial carbon nanotubes remain intact after the process. Thus, from the results shown in Fig. 2, it is clear that the carbon nanotube film can be patterned by the low-fluence photoablation process when a photoablation assistor is used, even though the fluence of illumination is lower than the threshold value for direct photoablation.

We used an excimer laser projection imaging configuration to produce patterns of carbon nanotubes using the proposed method. Flowing nitrogen gas was used to remove the debris which is generated during the photoablation of the photoresist. We used MicroChem S1818 photoresist as the photoablation assistor; it had a thickness of 2.2 μm. The fluence of illumination was 100 mJ/cm^2 at the substrate. After the photoablation process, the carbon nanotubes in some regions are cleanly patterned with photoresist. However, some residue layer remains in other regions. Figures 3(a) shows the formation of the residue layer in case of high-density carbon nanotubes, and Fig. 3(b) for low-density carbon nanotubes. We believe that the residue layer is formed due to thermally dissociated carbon nanotubes, because the photoresist can hinder the heat dissipation of the carbon nanotubes. However, the reason is not fully clear at present, and we are investigating the mechanism of the formation of

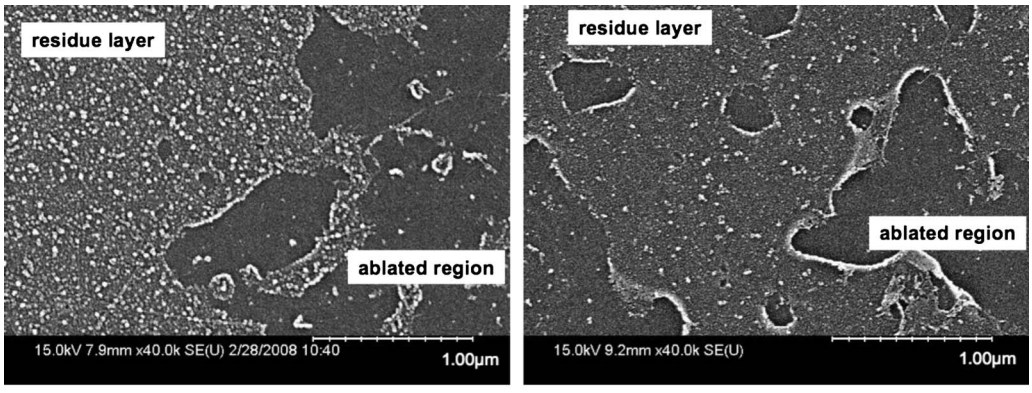

FIG. 3. SEM photographs of residue layer in excimer laser illuminated region. (a) High-density carbon nanotube films. (b) Low-density carbon nanotube films. The incident fluence was 100 mJ/cm^2.

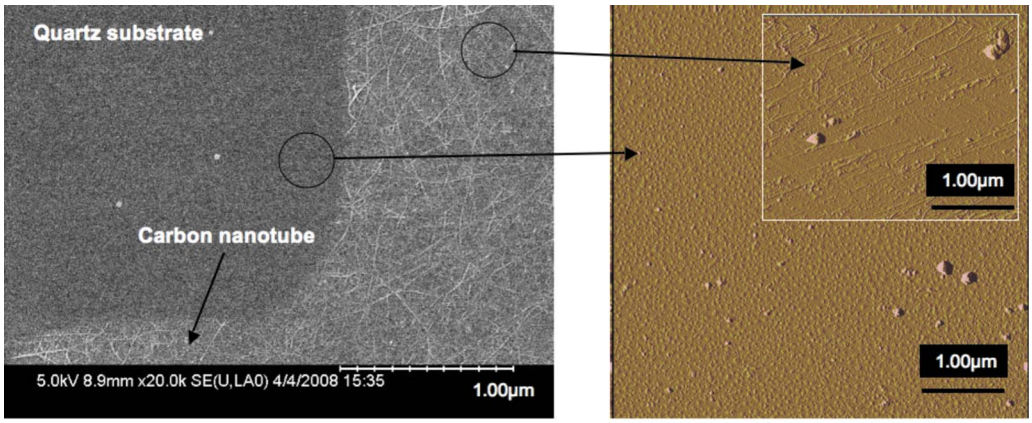

FIG. 4. (Color online) SEM photographs of patterned carbon nanotubes which were fabricated using an excimer laser projection imaging system. The exposure fluence was 100 mJ/cm^2 and the number of pulses was 25. (a) Pattern of carbon nanotubes around a corner shape. (b) AFM images of patterns in ablated region and nonablated region (inset).

the residue layer during the photoablation process. Although the residue layer was not completely removed by further excimer laser illumination, it was readily removed by addition of the oxygen plasma ashing step. After the oxygen plasma cleaning of the photoablated patterns, we removed the remaining photoresist using an acetone rinse and patterns of carbon nanotubes were fabricated, as shown in Fig. 4(a). The patterns of carbon nanotubes were clean and sharp. The number of incident illumination pulses was 25. Figure 4(b) is an atomic force microscope (AFM) image of the ablated and nonablated regions, and no carbon nanotubes remain in the exposed regions after the patterning process.

As shown by the results in Fig. 4, it is clear that the carbon nanotubes can be patterned under low-fluence conditions when a photoablation assistor is used. When the carbon nanotubes are embedded in a polymer, such as a photoresist, and illuminated by excimer laser radiation, they can be removed by the physical force of the dissociated fragments of the photoresist, as illustrated in Fig. 1. Also, some carbon nanotubes are thermally dissociated due to the heat confinement effect of the photoresist and the residue layer is formed. The debris and residue layer are readily removed by the oxygen plasma cleaning process. This method can be used in the patterning of various porous materials as well as carbon nanotubes if the materials have sufficient porosity to enable incorporation of a photoablation assistor in their voids. There are some required characteristics for a photoablation assistor to be suitable for this process concept. It should have a low threshold fluence of photoablation and one should be able to place it under or in the main (i.e., target) material to be ablated. Also, the photoablation assistor should be easily removable without damaging the main material after the photoablation process. There are many materials that can be used as the photoablation assistor, but a suitable photoresist would be the best choice. Some photoresists have all the required properties mentioned above. Most importantly, the photoresist is a common material in the microelectronic fabrication process.

This carbon nanotube patterning method has several merits compared with conventional patterning methods previously described. The fluence of illumination required for the process is low so that the damage on the devices or substrate can be minimized. Many photoresists can be ablated at fluences well below 200 mJ/cm^2.[11–13] In addition, this patterning process is economical because it does not require the steps of resist development and material etching.

In conclusion, we have developed a patterning method using excimer laser photoablation for patterning of carbon nanotubes and other porous materials. With a fluence of illumination that is significantly lower than the threshold value for direct photoablation, the materials can be patterned when a photoablation assistor layer is used. We fabricated patterns of carbon nanotubes on a quartz substrate using a photoresist as a photoablation assistor under low-fluence photoablation conditions, and demonstrated patterns of carbon nanotube films that are clean and sharp.

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