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Etching processes of transparent carbon nanotube thin films using laser technologies

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ABSTRACT

Carbon nanotubes (CNTs) have potential as a transparent conductive material with good mechanical and electrical properties. However, carbon nanotube thin film deposition and etching processes are very difficult to pattern the electrode. In this study, transparent CNT film with a binder is coated on a PET flexible substrate. The transmittance and sheet resistance of carbon nanotube film are 84% and 1000 Ω/□, respectively. The etching process of carbon nanotube film on flexible substrates was investigated using 355 nm and 1064 nm laser sources. Experimental results show that carbon nanotube film can be ablated using laser technology. With the 355 nm UV laser, the minimum etched line width was 20 μm with a low amount of recast material of the ablated sections. The optimal conditions of laser ablation were determined for carbon nanotube film.

1. Introduction

Flexible electric devices, such as solar cells and displays, have been increasingly developed. The optical, mechanical, and electrical properties of a transparent conductive film are important for flexible electric devices. Indium tin oxide (ITO) thin films are widely used for transparent conductive film due to their high conductivity and high visible light transmittance. However, in order to reduce costs, many transparent conductive materials have been researched [1–3]. Cao et al. [4] showed that transparent carbon nanotube (CNT) electrodes with organic semiconductors form flexible TTFTs on a plastic substrate. These devices showed good electrical properties, bendability, and high transparency. Transparent conductive CNT films, which have high conductivity, high mechanical strength, and a high transmission rate, can reduce the cost of transparent conductive films. Therefore, CNT transparent conductive films have great potential to be an attractive replacement of traditional conductive indium tin oxide (ITO) film for future development [5].

Two methods are currently used to pattern CNT film. One is the transfer printing method [6], which has a resolution limitation (50 μm). The other is the direct growth of CNT films by DC plasma-enhanced chemical vapor deposition, which has a relatively high process temperature that affects plastic substrates [7]. Direct laser interference patterning of CNT films has been proposed but the process and equipment are complicated [8]. Laser patterning technology is a dry process and potentially a single step. The laser process can decrease costs and increase throughput without chemical solutions. The direct-write laser process was used to etch a large area of transparent conductive ITO thin film [9,10].

Laser patterning of CNT films on polymer substrates has yet to be researched. Since flexible electronics are becoming increasingly popular, the excellent mechanical and electrical conductivity of transparent conductive films is important. CNT films have become the promising materials because of their unique properties such as light-weight, high mechanical properties, high thermal and electric conductivity, and therefore the mechanism of laser patterning for CNT films on plastic substrates should be studied. In order to achieve the required electrode quality, the ablated section of CNT films was observed in this study at various laser wavelengths.

2. Experimental procedure

The CNTs were synthesized via fluidized catalytic-CVD (FC-CVD) process. Manufacturing CNT films was a multi-step process which included purification, sonication, CNT dispersion, bar coating and hot air drying. Multi-walled CNTs were uniformly dispersed in water, and then coated onto PET plastic substrates (MCL, ITRI). The sheet resistance was determined using a four-point-probe system supplied by NAPSON. Transmission measurements were performed with a Jasco B-570 spectrometer.

The CNT film on flexible substrates was etched using a laser direct-write method. Fig. 1 shows a schematic diagram of the workstation used in this study for laser patterning of the CNT films. The laser sources were 355 nm (AVIA 355-7000) and 1064 nm (SP-20P). CNT film patterning was carried out by laser system at 0.5–3 W; the scan rates were from 100 to 1000 mm/s. The electric property of ablated section was measured. When the resistance of ablated CNT films is over 20 MΩ, the CNT films were regarded to be completely removed.

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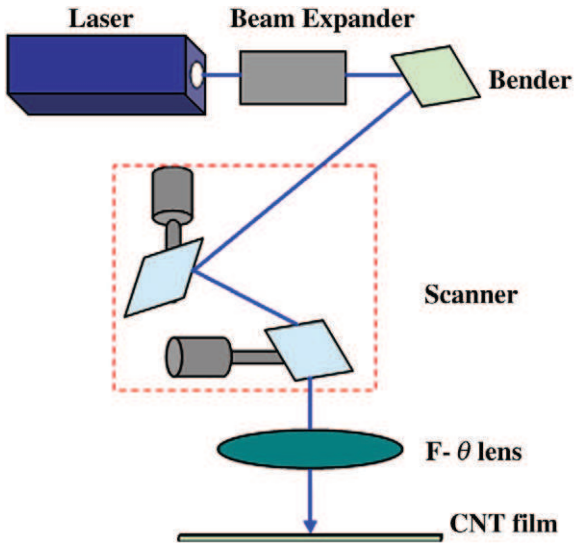

Fig. 1. Schematic diagram of the workstation used in this study for laser patterning.

The scan rate can be calculated and then used to represent the overlapping rate. The overlapping rate, which is used to control the distribution of laser pulses on the impact surface, is expressed as:

$$\text{Overlapping} = \frac{D-S}{D} \times 100\% \qquad (1)$$

where D is the laser spot diameter and S the length of two successive laser spots.

The processing speeds of 100, 400, 700, and 1000 mm/s represent overlapping rates of 92%, 67%, 42%, and 17%, respectively. The optical profile image and cross-sectional profile of the ablated sections was measured using an optical imaging profiler (PLμ2300, SENSOFAR, SPAIN).

In order to increase the resolution of the pattern, the size of the laser spot was decreased. The diameter of the laser spot, D_0, is expressed as:

$$D_0 = 1.22 \times \left(\frac{\lambda \times F}{n \times W_d}\right) \times M^2 \qquad (2)$$

where λ is the laser wavelength, F the focal length, n a refractive index, W_d the diameter of the incident laser, and M^2 the laser-quality factor. Eq. (2) indicates that the diameter of the laser beam is directly proportional to the wavelength and focal length. For our experimental systems, the 355 nm laser system consisted of 355 nm wavelength, 3.5 mm incident laser, 250 mm focal length and 1.3 M^2 and the 1064 nm laser system consisted of 1064 nm wavelength, 9.3 mm incident beam, 160 mm focal length and 1.8 M^2. When raw beam passed through our optical delivery systems, the spot size was 40 μm for both the 355 nm and 1064 nm laser systems.

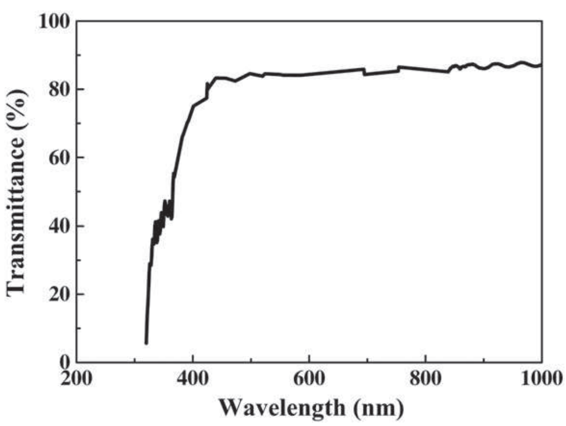

Fig. 2. Transmittance of carbon nanotube film on PET.

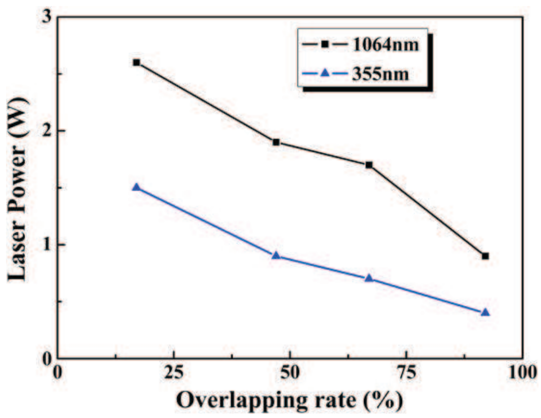

Fig. 3. Correlation of laser power and overlapping rate for completely ablated CNT film.

3. Results and discussion

Transmission of the bare substrate is 91% at 550 nm and the thickness is 188 um. The transmittance of carbon nanotube film on PET was measured in the wavelength range of 350 to 1000 nm. A transmission of 84% was achieved at 550 nm, as shown in Fig. 2. The carbon nanotube film was uniformly coated onto plastic substrates, exhibiting a sheet resistance of 1000 Ω/□.

Fig. 3 shows that for the etching process operating at either the 355 nm or 1064 nm laser wavelength, the CNT films were completely ablated within the specified ranges. Typical laser power for both systems was less than 3 W. During our experimental ranges, it is apparent that as the laser power increased, the overlapping rate decreased for both laser wavelengths to ablate the CNT films. In addition, the CNT films also could be ablated at low laser power and high overlapping rate because the local ablated section accumulated enough heat to ablate the films. The power of the 355 nm laser was two times lower than that of the 1064 nm laser at the same overlapping rate. Because the photon energy of a short wavelength is higher than that of a long wavelength at the same laser power, the 355 nm wavelength has more energy to impact the material. Furthermore, the absorption of light of CNT coated PET with the 355 nm laser was higher than that with the 1064 nm laser, providing more energy for etching the CNT film referred to Fig. 2.

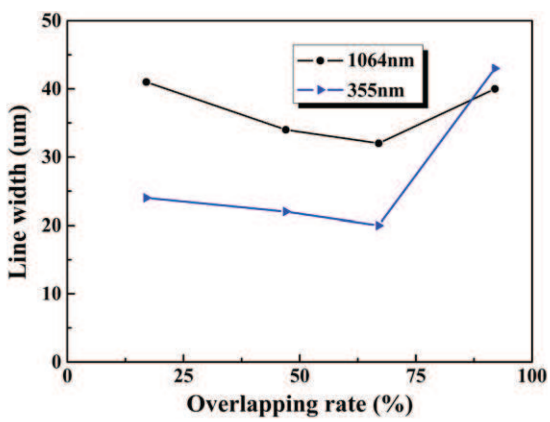

Fig. 4. Correlation of the ablated line width and overlapping rate for 355 nm and 1064 nm wavelengths.

The correlation of the laser wavelength and overlapping rate on the ablated line width is shown in Fig. 4. The results show that the laser etching process operated at a shorter wavelength resulted in a narrower ablated line at low overlapping rates. However, when the laser patterning process was operated at a 92% overlapping rate, the ablated line for both laser systems became wide. When the overlapping rate increases, the CNT films cannot completely be etched, resulting in a short circuit. In order to ablate the CNT films fully, the laser power was increased, which widened the ablated line. Fig. 5 shows that for laser etching at a 1064 nm wavelength, the overlapping rates are 92%, 42%, and 17%, respectively. When the overlapping rate was over 90%, some residual recast material became attached to the etched line, resulting in a short circuit. To completely ablate the CNT film, a higher laser power was used. The ablated line widened due to the local ablated section accumulating more heat. Therefore, the laser etching process performs at appropriate condition such as higher overlapping rate, and it effectively reduces the residue recast material on the ablated line.

Fig. 6 shows SEM micrographs of CNT films after laser etching at 355 and 1064 nm wavelengths with a 67% overlapping rate. The ablated line widths were 20 and 32 μm, respectively. The minimum etched line width was around 20 μm for the 355 nm wavelength with less residue recast material on the ablated line as compared with that for the 1064 nm wavelength.

The color flexible reflective cholesteric liquid crystal displays (Ch-LCDs) have been developed. Transparent conducting electrodes are used on color stacking structures to fabricate the devices [11]. Transparent conducting CNT films are potential to use into color stacking structures as electrode. To lower the height of the ablated section could reduce the point discharge phenomenon during driving the panel. Fig. 7 shows the optical profile image and cross-sectional

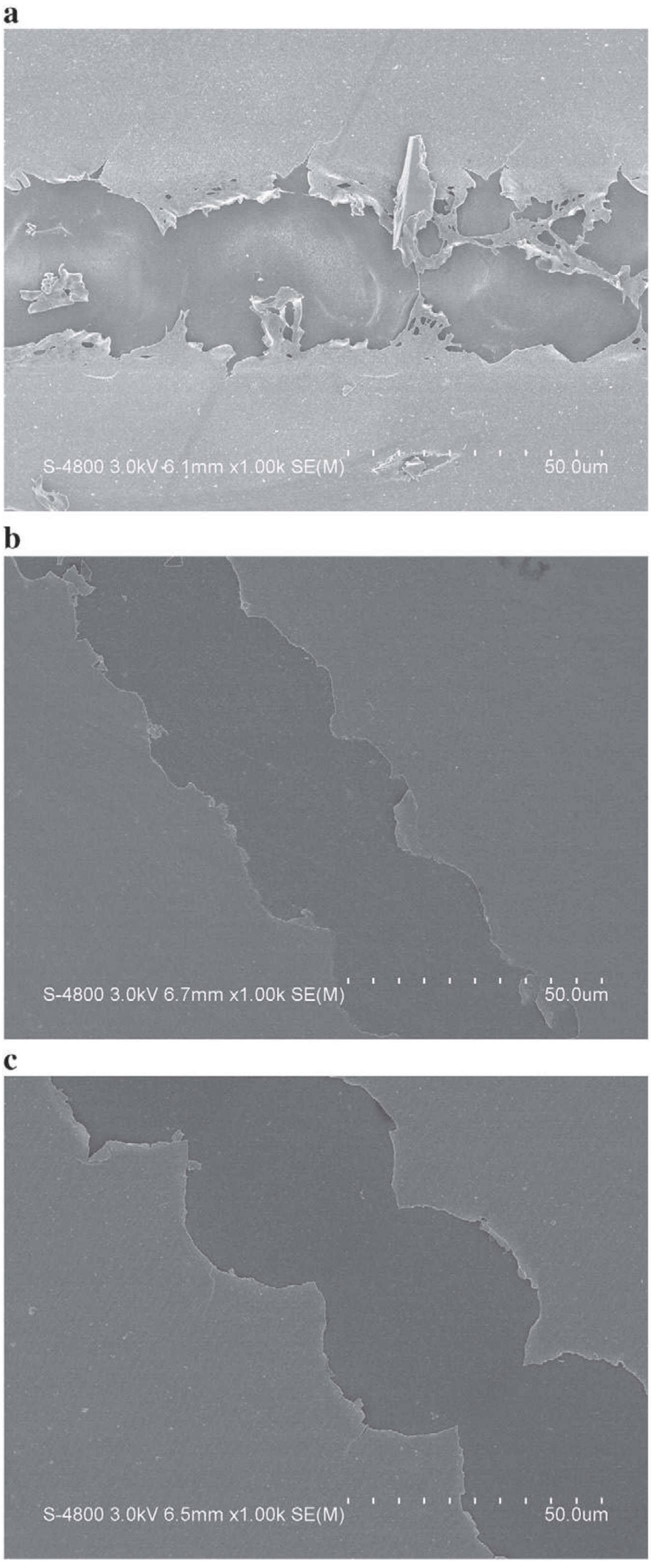

Fig. 5. SEM micrographs showing laser etching at 1064 nm wavelength at overlapping rates of (a) 92%, (b) 42%, and (c) 17%.

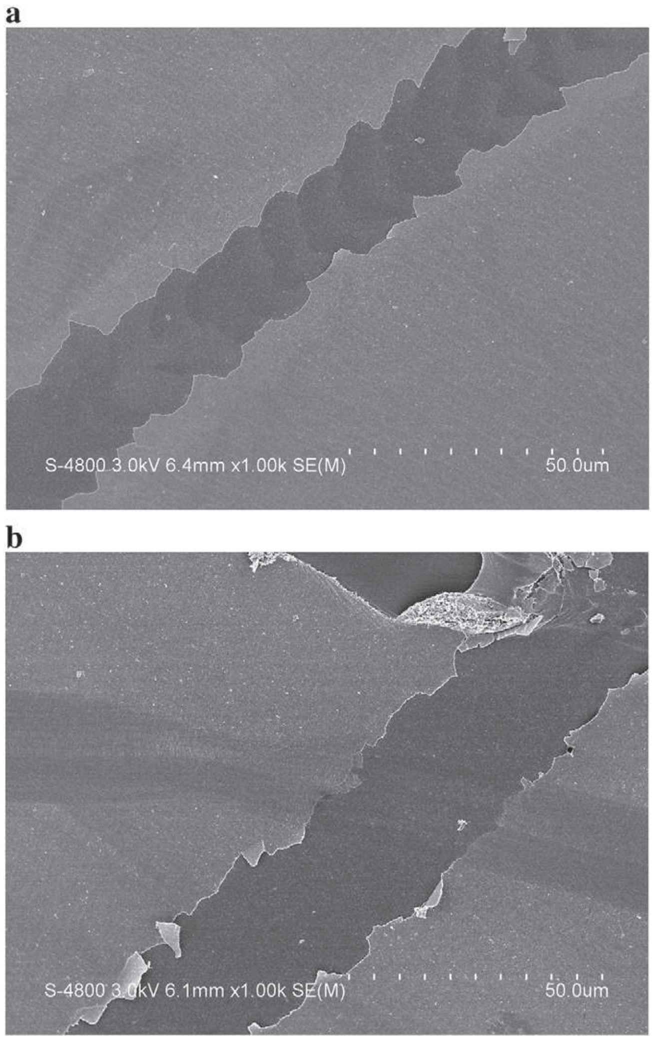

Fig. 6. SEM micrographs of CNT films after laser etching at a 67% overlapping rate for (a) 355 nm, and (b) 1064 nm laser wavelengths.

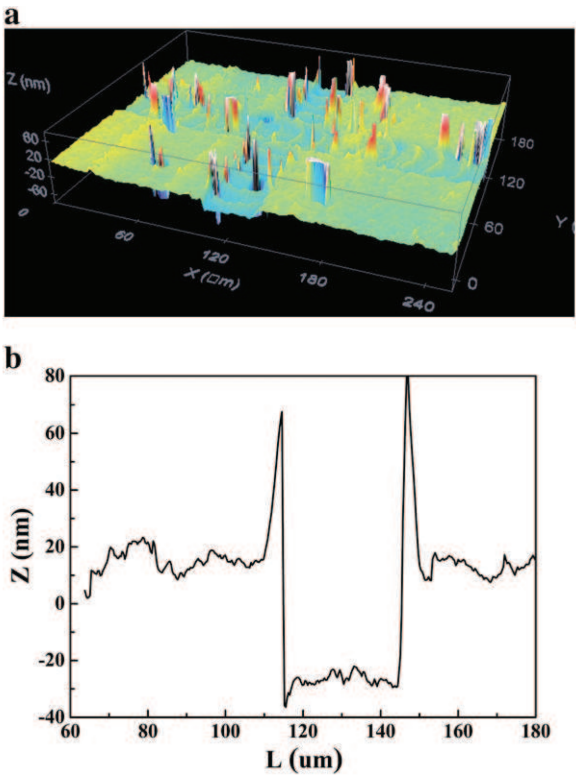

Fig. 7. Optical profile image and cross-sectional profile of CNT film on PET tested at a 17% overlapping rate with a 1064 nm wavelength.

profile of CNT film on PET tested at a 17% overlapping rate at a 1064 nm wavelength. The edges of the ablated sections had a melt ridge build-up. The height of the ablated sections was around 60 nm.

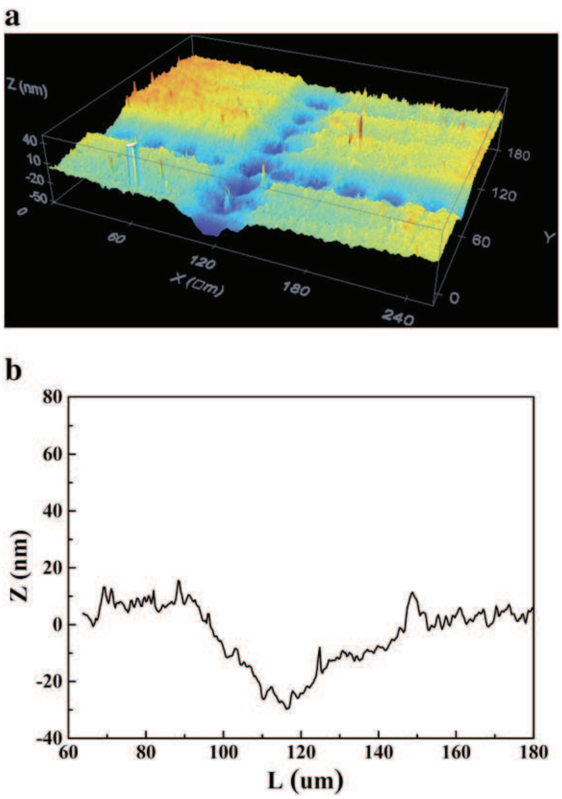

Fig. 8. Optical profile image and cross-sectional profile of CNT film on PET tested at a 17% overlapping rate with a 355 nm wavelength.

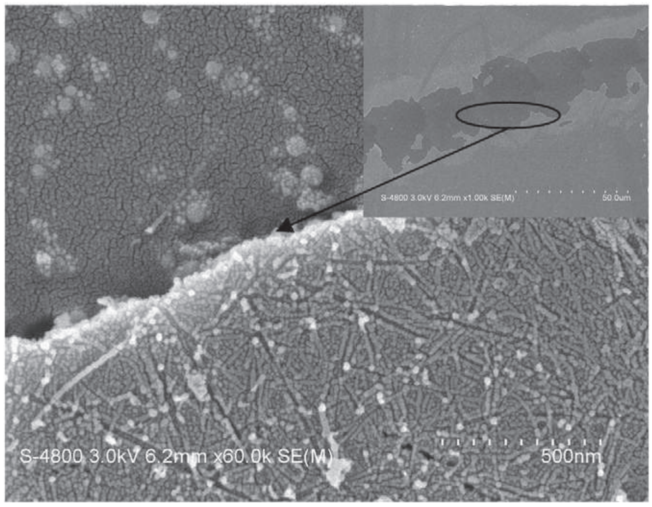

Fig. 9. Carbon nanotube film etched by a 355 nm UV laser at a 17% overlapping rate.

Additionally, some residue recast materials were observed. The ridge was produced by thermal effects during the laser etching process.

The optical profile image and cross-sectional profile of CNT film on PET tested at a 17% overlapping rate at a 355 nm wavelength are shown in Fig. 8. Although the edges of the ablated sections had a melt ridge build-up, the height of the ablated section was only 15 nm. The height of the ablated sections represents the ablation quality of an electrode. When the height of the melt ridge is high, the ablation quality of the electrode is poor. Compared with that of the 1064 nm wavelength, it significantly reduced meanwhile less residual recast materials were produced during laser patterning process. Therefore, the use of a shorter wavelength to etch CNT film can effectively reduce the melt ridge build-up and residual recast material. Further, better electrode quality can be obtained.

Fig. 9 shows a CNT film etched by a 355 nm UV laser with a 17% overlapping rate. The results show that a low amount of residue material was produced under these conditions. Therefore, operating at 1000 mm/s or at a lower overlapping rate to etch CNT films increases the output of the laser patterning and produces better electrode quality.

4. Conclusions

Carbon nanotube films have great potential as a transparent conductive material. CNT film on a flexible substrate can easily be patterned using the laser direct-write process. A minimum etched line width with 20 µm was obtained with a 355 nm UV laser, with a low amount of recast material and a low ridge height of the ablated sections. Electrodes with a high edge quality can be obtained by optimizing laser parameters such as laser power and overlapping rate.

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