

Polymer/carbon nanotube composite patterns via laser induced forward transfer

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Direct and high spatial resolution printing of polymer/carbon nanotube (CNT) composite layers has been demonstrated by means of laser induced forward transfer (LIFT). Laser irradiation of composite target materials, such as poly(acrylic acid)/CNT and polyvinylpyrrolidone/CNT, enabled dry deposition of well resolved composite pixels onto glass substrates. The dispersion of the CNT into the deposited composite pixels was investigated by transmission electron microscopy. The LIFT technique was also employed for the accurate deposition of polymer/CNT composite pixels onto aluminum microelectrodes for the fabrication of chemical sensors based on polymer/CNT compounds. © 2010 American Institute of Physics. [doi:10.1063/1.3299004]

Carbon nanotubes (CNT) are attractive materials for nanotechnology applications due to their unique electrical and mechanical properties.¹ The incorporation of CNT into nonconductive polymer matrices can form conductive polymer composites, which are being used as sensing materials for biosensors and chemical sensors.^{2,3} One of the most important challenges for the fabrication of these sensing devices is the deposition of the polymer/CNT composites onto the sensing elements. In particular, the fabrication of microsensors demands accurate deposition and/or patterning of polymer/CNT composite layers with micrometric size. Since the common microelectronic techniques, such as photolithography, are difficult to implement on these complex materials, conventional ink-jet printing became a useful technology for the deposition of polymer/CNT composites for the fabrication of transparent conducting electroactive layers⁴ and chemical sensors.^{5,6} However, ink-jet printing technology presents several limitations regarding the spatial resolution of the deposited patterns and the rheological properties of the complex solutions, which should be compatible with conventional nozzles.

During the last two decades, laser induced forward transfer (LIFT) has become important for high resolution direct printing of a wide range of materials.^{7,8} The dry printing of polymer materials by means of laser induced forward transfer (LIFT) has been demonstrated using ns pulses, for the fabrication of organic light-emitting diodes^{9,10} and organic thin-film transistors,¹¹ while liquid phase laser printing of polymers has been applied for the fabrication of chemical sensors.¹² It has also been shown that using femtosecond (Ref. 13) or nanosecond (Ref. 14) laser pulses the technique can achieve submicron resolution for printing of metals. Recently, in a variant of the technique, laser printing of pure CNT onto indium tin oxide substrates covered by a metallic prepatterned mask has been demonstrated for the fabrication of field emission cathodes.¹⁵

Here, we present the direct dry printing of polymer/CNT composite patterns via the LIFT technique. We focus on the optimization of the printing process and the electrical characterization of the deposited layers. Additionally, the dispersion of CNT in the deposited composite layers has been investigated by transmission electron microscopy (TEM). The LIFT technique is direct, contactless, offers high spatial resolution, and overcomes the main drawback of the ink-jet printing technology because it is not restricted by the complex solution rheological properties. LIFT is employed in a two-step process: the preparation of the target material and the selective deposition of a region of the target material through laser irradiation. Thus, the technique is applicable to a wide range of polymer/CNT composites, which may form uniform targets by spin coating or drop casting, regardless of the polymer and CNT concentration.

In this work, we have studied the printing process of different target materials based on poly(acrylic acid) (PAA)/CNT and polyvinylpyrrolidone (PVP)/CNT composites, which have been reported to find applications to amperometric biosensors and chemical sensors.^{16,17} Two types of CNT, multiwall carbon nanotubes (MWCNT) and carboxyl (COOH) functionalized multiwall carbon nanotubes (f-MWCNT) were used in order to study the effect of the MWCNT dispersion on the electrical properties of the LIFT deposited layers. Initially, two different concentrations of MWCNT and f-MWCNT, 5% and 10% w/w each, were first added in 2% w/w polymer solutions in H₂O. The polymer/MWCNT composite solutions were then sonicated for 10 min. Afterwards, each target was prepared by spin coating the composite solution onto a quartz plate to attain a uniform layer thickness. A drying step of 80 °C for 10 min was applied to the target in order to remove the residual water solvent, and the resulting film thickness obtained on the quartz plates was about 1.5 μm.

During the LIFT process the target was placed in close proximity ($d < 1 \mu\text{m}$) to the substrate under vacuum conditions. The transfer of a region of the target material was achieved by single laser pulses produced by a Nd:YAG

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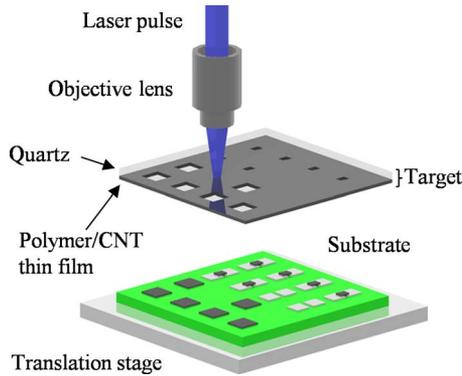


FIG. 1. (Color online) Schematic illustration of the LIFT process.

(yttrium aluminum garnet) laser ($\tau=4$ ns, $\lambda=266$ nm). The laser beam was expanded to irradiate a variable rectangular mask and the resulting homogenous part of the beam was imaged on the target through a system of lenses (Fig. 1). An in-house program was used to synchronize a x-y motorized translation stage with the laser repetition rate at 2 Hz. The whole process was monitored through a customized microscope system, equipped with a camera, which enabled accurate alignment of the target and substrate materials. Standard glass microscope slides were used as substrates for the initial study of the LIFT process and aluminum microelectrodes on SiO_2/Si substrates for the electrical characterization of the deposited layers. PAA/CNT and PVP/CNT composites present a strong and broad absorption peak around 250 nm,^{18,19} which enabled laser printing at relatively low laser fluences without the use of any intermediate sacrificial layer²⁰ between the quartz plate and the composite film.

The targets prepared by PVP/f-MWCNT and PAA/f-MWCNT composites present a high degree of homogeneity due to the chemical functionalization which provides better dispersion of MWCNT into the polymer matrices. Thus, the laser printing of PVP/f-MWCNT and PAA/f-MWCNT composites was performed efficiently due to the uniform absorption of the laser energy across the irradiated area. Figure 2 shows an optical microscopy picture of $70\ \mu\text{m} \times 70\ \mu\text{m}$ PVP/5% f-MWCNT composite pixels deposited on a glass substrate at $250\ \text{mJ}/\text{cm}^2$. The deposited pixels present sharp edges and their thickness was measured by a profilometer to be about $1.5\ \mu\text{m}$, which is approximately equal to the depth of the corresponding etching in the target. This results, in combination with the smooth surface of the deposited pixels, indicates that there was negligible ablation of the composite

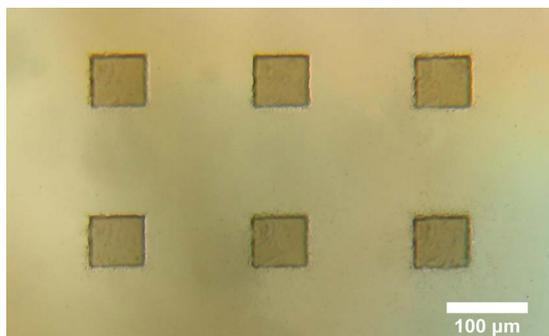


FIG. 2. (Color online) Optical microscopy image of PVP/5% f-MWCNT layers deposited by single laser pulses on a glass substrate.

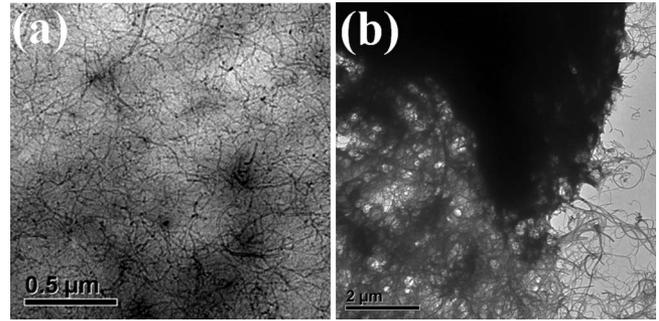


FIG. 3. TEM images of polymer/MWCNT composite layers deposited on TEM grids by LIFT. (a) Uniform network of f-MWCNT in a PVP/5% f-MWCNT composite layer. (b) Bundle of nonfunctionalized MWCNT in a PVP/5% MWCNT composite layer.

material during the transfer. Optimal transfer conditions for the deposition of PVP/5% f-MWCNT composite layers were obtained for a laser fluence of $250\ \text{mJ}/\text{cm}^2$. For lower laser fluences, below $200\ \text{mJ}/\text{cm}^2$, there was no transfer of the composite material. For significant higher laser fluences, above $400\ \text{mJ}/\text{cm}^2$, the transferred composite layers presented nonuniform thickness, characteristic cracks, and dispersion of the deposited material out of the pixel edges.

Furthermore it was observed that the homogeneity of the targets, in terms of the CNT dispersion, affects the quality and homogeneity of the deposited patterns. The targets prepared by PVP/MWCNT and PAA/MWCNT composites presented a low degree of homogeneity. In particular, targets prepared by PVP/MWCNT and PAA/MWCNT composites presented microscopic bundles of MWCNT that strongly absorb the laser beam and regions of higher transparency with a low concentration of MWCNT. Thus, laser irradiation of PVP/MWCNT and PAA/MWCNT composites resulted in the deposition of discontinuous layers with lack of reproducibility. However, the printed PVP/MWCNT and PAA/MWCNT composites on the aluminum microelectrodes have achieved good electrical measurements.

In order to evaluate the degree of dispersion of the MWCNT and f-MWCNT into the deposited layers, TEM was used. Laser printing of composite layers was performed onto ultrathin carbon membranes of copper TEM grids. Figure 3(a) shows a TEM image of a uniform network of f-MWCNT in a PVP/5% f-MWCNT composite layer deposited by LIFT. The laser irradiation has not affected the network of the f-MWCNT during the laser process. Figure 3(b) shows a TEM image of nonfunctionalized MWCNT bundle in a PVP/5% MWCNT composite layer. These findings indicate that the deposited polymer/MWCNT and polymer/f-MWCNT layers reproduce the homogeneity of the MWCNT network of the target material on the substrate without any changes or damage induced by the laser irradiation.

Polymer/CNT composites have been reported to exhibit significant electrical response toward a wide range of chemical compounds. Therefore, we have investigated potential applications of the laser printed composite layers in the fabrication of amperometric sensors. Electrical characterization of the composite layers was achieved by depositing pixels from all the prepared targets onto aluminum microelectrodes separated by a $10\ \mu\text{m}$ gap. Figure 4(a) shows a well defined $30\ \mu\text{m} \times 40\ \mu\text{m}$ PVP/5% f-MWCNT pixel deposited onto aluminum microelectrodes at $220\ \text{mJ}/\text{cm}^2$. All the deposited polymer/CNT layers were characterized by a Hewlett Pack-

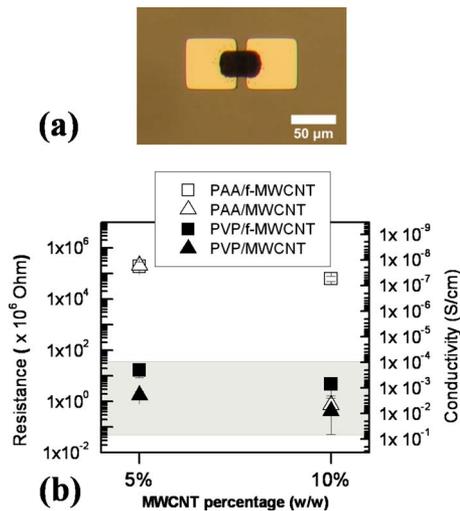


FIG. 4. (Color online) (a) Optical microscopy image of a $30\ \mu\text{m} \times 40\ \mu\text{m}$ PVP/5% f-MWCNT pixel deposited by LIFT on aluminum microelectrodes. (b) Electrical properties of the LIFT-deposited polymer/CNT composite layers as a function of the MWCNT percentage in the polymer matrix.

ard 4140B picoammeter. Figure 4(b) shows the resistance and dc electrical conductivity properties of the deposited composite layers, which were calculated by current-voltage (I - V) measurements. As expected, layers with higher concentration of MWCNT and f-MWCNT presented higher electrical conductivity, which in the case of PVP/10% MWCNT reaches 8×10^{-3} S/cm. It can also be observed that for a given concentration of carbon nanotubes into the polymer matrices, composite layers with f-MWCNT systematically present lower conductivity compared to those prepared by nonfunctionalized MWCNT. This is attributed to the initially weaker electrical properties of the functionalized CNT compared to nonfunctionalized CNT. Although chemical functionalization results in better CNT dispersion, several mechanisms have been proposed to explain the reduced electrical conductivity.²¹ In the case of the PAA/10% CNT layers, the conductivity of the PAA/10% MWCNT layers is five orders of magnitude greater than the conductivity of the PAA/10% f-MWCNT layers, which has an average value of 5.3×10^{-8} S/cm. This result indicates that the microscopic bundles of the non-functionalized MWCNT which appeared in the composite layers, in combination with the narrow $10\ \mu\text{m}$ gap, enhanced the percolation of the electrical current between the electrodes. Finally, as can be seen in Fig. 4(b), the electrical conductivity of five different types of the deposited polymer/CNT layers has a value between 1.9×10^{-3} and 2×10^{-4} S/cm. These values correspond to composite pixels with CNT content clearly above the electrical percolation threshold, making them good candidates for sen-

sitive and low noise chemical sensing through amperometric measurements.

In conclusion this work presents the use of laser induced forward transfer as an alternative and very promising technique for dry printing of polymer/CNT composite layers. TEM analysis revealed that the LIFT deposited PVP/f-MWCNT and PAA/f-MWCNT composite layers exhibit a high degree of dispersion of the carbon nanotubes into the polymer matrices. Polymer/MWCNT composite pixels were also deposited onto aluminum microelectrodes for electrical characterization. The PAA/10% MWCNT, PVP/10% MWCNT, PVP/5% MWCNT, PVP/10% f-MWCNT, and PVP/5% f-MWCNT composite pixels presented high electrical conductivity that makes these layers candidates for chemical sensing through amperometric measurements. This simple and direct printing process can be applied for the deposition of a wide range of polymer/CNT composite materials and will help scientists to produce multianalyte chemical and biological sensors and organic electronics based on the fascinating properties of the CNT.

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