



PATTERNED POLYMER-CARBON NANOTUBE COMPOSITE

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Abstract- We report on the development of processes to fabricate micro-scale dimension structures of functional nano-composite made of polyvinyl alcohol (PVA) and multi-wall carbon nanotubes (MWCNT). An elastomeric stamp of polydimethylsiloxane (PDMS) having micro-scale structures patterned on its surface is used to print complementary structures on wet layers of the polymer-carbon nanotube (CNT) composite. The liquid PVA-CNT composite conforms to the features of the PDMS mold and is cured at room temperature. The features of the PDMS mold are transferred into the nano-composite, resulting in nano-composite micro-patterns. The developed processes can be conceivably used in thin film devices and flexible microsystems for various applications. More specifically, the described processes allow for the relatively simple formation and manufacturing of structures of polymer-carbon nanotube composite materials.

Key words - carbon nanotube, nanocomposite, micro-patterning, soft lithography, flexible microsystems

1. Introduction

The development of composite materials of polymers and carbon nanotubes (CNTs) has been of considerable interest in the recent years. This has been partly driven by the quest for new materials and composites and the growth of fields such as nanotechnology. The significant interest in polymer-nanotube composites is primarily due to their enhanced mechanical and electrical properties [1-3]. Due to superior electrical conductivity and aspect ratio of CNTs, the electrical properties of composites containing carbon nanotubes are significantly improved compared to more conventional electronic composites containing fillers such as short carbon fibers or carbon flakes [4]. As a result of their unique material properties, polymer-nanotube composites offer numerous applications in wide-ranging areas. In this regard, it is essential to develop methods to pattern or structure polymer-carbon nanotube composites for certain applications including lithium batteries, energy cells, super-capacitors, biosensors, flexible transparent electrodes, among others. In particular, the successful patterning or structuring of polymer-carbon nanotube composites in the micro-scale dimensions and above is of great significance.

The present report is focused on a composite formed by polyvinyl alcohol (PVA) and carbon nanotubes. This composite is referred to in this paper as PVA-CNT composite. The PVA-CNT composite material inculcates some of the characteristic qualities of the PVA and CNT materials, in addition to some special properties

such as superior electrical and mechanical properties [5, 6]. To illustrate, PVA-CNT composite films made with high concentrations of nanotube dispersions have exhibited improved mechanical properties as compared to pure PVA films [7]. PVA is a water-soluble non-ionic polymer characterized by a relatively low toxicity and high biocompatibility [8]. The use of this material as polymer matrix dispersed with carbon nanotubes is technically relevant.

This paper reports on the development of methods that enable patterning and structuring of PVA-CNT composite either as free-standing entities or on another supporting substrate. The developed methodologies are based on combining solution casting with molding processes. These molding methods involve the use of a flexible stamp usually made of a silicone elastomer, such as PDMS [9, 10]. This elastomeric stamp has patterned structures on its surface and is employed to print complimentary structures with feature sizes ranging from nanoscale to a few hundred microns.

In our work, the PDMS elastomer stamp is used to transfer patterns onto a wet layer of PVA-CNT composite pre-polymer by replica molding or microtransfer molding. The PVA-CNT pre-polymer is prepared by a solution mixing process, wherein commercial multi-wall CNT with an aqueous solution of PVA. The PDMS stamp could be placed in contact with the wet composite layers on silicon, glass or polyethylene terephthalate (PET) substrates. The liquid PVA-CNT composite

conforms to the features of the PDMS mold and is cured at room temperature. The features of the PDMS mold are transferred into the PVA-CNT composite. The resulting patterned PVA-CNT composite layers exhibited a significant contrast in electrical conductivity between the areas with composite patterns and those with no patterns. The conductivity of PVA-CNT films can be conveniently controlled over many orders of magnitude by adjusting the CNT and PVA weight ratios. Prior research conducted by other researchers has demonstrated special mechanical and electrical properties of polymer-CNT composite thin films. For instance, the stress in the CNT film is detectable at superfine scale by Raman spectrum shift [11-13]. The described patterning methodologies have been applied to make patterns of PVA-CNT composite on different surfaces. The fabrication processes reported here can be conceivably used in thin film devices and flexible microsystems. The combination of the solution casting and molding methods can be extended to the relatively inexpensive fabrication of other polymer-carbon nanotube composite structures, in addition to the PVA-CNT composite material in the present case.

2. Materials

2.1 Polydimethylsiloxane

For the elastomeric stamp, a commercial silicone elastomer called polydimethylsiloxane (PDMS) (Sylgard® 184 from Dow Corning®) was employed. Sylgard 184 is a two part resin system containing vinyl groups (part A) and hydrosiloxane groups (part B).

2.2 Multi-walled carbon nanotube

Multi-walled carbon nanotube (MWCNT) in our research was obtained from Sigma-Aldrich Corporation (product number 677248), 3050 Spruce St., Saint Louis, Missouri, USA, 63103-2530 with the outer diameter from 10-15 nm, inner diameter from 2-6 nm and length 0.1-10 μ m.

2.3 Polyvinyl Alcohol

The poly vinyl alcohol (PVA) in this research was acquired from Sigma-Aldrich Corporation (product number 348406-500G), 3050 Spruce St., Saint Louis, Missouri, USA, 63103-2530 with Mw 13,000-23,000, 98% hydrolyzed.

3. Experiments and Results

3.1 Polyvinyl Alcohol-carbon nanotube composite formation

The PVA-CNT composite was prepared by blending MWCNT with an aqueous solution of PVA prepared by dissolving PVA in de-ionized water at 75° C. The water to PVA ratio was 6:1 by weight. For eliminating the agglomeration of MWCNT, MWCNT is mixed with acetone with vigorous magnetic stirring at 85° C until the acetone is evaporated

completely. The MWCNT was mixed thoroughly with PVA solution at different concentrations by a two hour ultrasonic bath treatment (Sonics Vibra Cell, Sonics Mandmaterials, Inc, USA). The thorough mixing was essential to ensure that the carbon nanotubes were dispersed in the PVA uniformly. The PVA-MWCNT pre-polymer blend was de-aerated by vacuum treatment for 1 hour to remove bubbles. Finally, the PVA-CNT blend was cast on a surface and cured at room temperature, to form films. Microscopic observation of the film material revealed its fibrous interconnecting characteristic, with a random orientation of the nanotubes in the polymer matrix as shown in Fig. (1).

3.2 Fabrication of master mold and PDMS mold

The master mold was fabricated on a silicon wafer by patterning it with structures complementary to those desired on the polymer soft mold. A micromachined plexiglass mold was also used as an alternative master mold. N- or P- type (100) silicon wafers with 1 μ m thick silicon dioxide (SiO₂) layer were used for fabricating master template. The wafer thicknesses ranged from 250 to 450 μ m. Before use, the silicon wafers were chemically cleaned to remove particulate matter on the surface, and any organic, ionic, and metallic impurity. A positive photoresist (AZ5214E, Clariant, Germany) was spin-coated on both sides of the wafer. In addition a cotton swab was used to apply the photoresist onto the edges of the silicon wafer. Standard optical photolithography was used to define the pattern to be transferred to the surface of the silicon wafer. The photoresist pattern was then transferred into the SiO₂ film by immersing the wafer in a buffered oxide etchant (BOE) solution (fifteen parts of ammonium fluoride and one part of hydrofluoric acid). The observed BOE etch rate ranged from 10 to 100 nm/min at 25° C. After completion of the etching, the leftover photoresist was removed by acetone.

The SiO₂ film was subsequently used as an etch mask for the anisotropic wet etching of the underlying silicon in 30% (by weight) solution of potassium hydroxide (KOH) at 80° C. Potassium hydroxide is a wet etchant which attacks silicon preferentially in the <100> plane, producing a characteristic anisotropic V-etch, with sidewalls that form a 54.7° angle with the surface (35.3° from the normal). The silicon was etched to generate structures complementary to those desired on the polymer soft mold. Fig. (2) shows the etched features on the silicon wafer, with an etch depth of 162 μ m. The photoresist protection on the edge and back side of the silicon wafer prevented its edges and backside from being chemically attacked during the extended KOH etching.

To fabricate the PDMS stamp, PDMS pre-polymer base was blended with its curing agent (base and

curing agent in 10:1 volume ratio). The mixture was subjected to a vacuum degasification process for 30 min to remove solvent and air bubbles present in the blend. The pre-polymer blend was poured over the silicon master mold and thermally cured on a hotplate at 80 °C for 3 hours. After curing, the PDMS pre-polymer turned into a solid elastomeric rubber and could be easily removed from the master mold. The thickness of the PDMS stamp was typically 1 – 2 mm. It was generally found to be more difficult to release thinner stamps.

3.3 Nano-composite structures by microtransfer molding

PVA-CNT composite structures were successfully fabricated on different type of substrates by a combination of solution casting and microtransfer molding. The PVA-CNT composite liquid was applied to the PDMS mold by solution casting and the excess liquid was removed. The filled mold was then placed in contact with a substrate such as silicon wafer, glass or polyethylene terephthalate (PET) sheet and thermally cured. Alternately, curing can also be done at room temperature which typically takes two to three days, but yields structures with much less internal stress. After the liquid PVA-CNT composite precursor cured into a solid, the PDMS mold was carefully removed to leave patterns of composite on the surface of the substrate. Fig. (3) shows patterns transferred onto a PET transparent sheet. The patterns were also inspected by scanning electron microscope (SEM) and the images are shown in Fig. (3). Prior to SEM imaging, the samples were sputtered with a very thin conductive layer of silver to prevent charge build-up by electrons.

3.4 Free-standing nano-composite microstructures by replica molding

In contrast to the preceding microtransfer molding method, replica molding involves a free-standing PDMS stamp filled with composite liquid. The side of the PDMS stamp with topological features does not contact any other surface. The features of the PDMS stamp were transferred by solidifying the liquid composite in contact with the stamp. The composite was cured at room temperature for 72 hours. Removal of the soft mold creates an inverse replica, as shown in Fig. (4).

3.5 Electrical resistivity

PVA-nanotube micro-patterns and thin films were made and studied for their electrical characteristics. It was observed that the electrical resistivity decreased considerably as the carbon nanotube content was increased in the films (Table 1). As the nanotube content increases, the average distance between the nanotubes becomes sufficiently small enough to enable physical contact to form between the nanotubes, and allow electrons to tunnel

through the polymer matrix. As a result, both the micro-patterns and thin films exhibited a significant increase in electrical conductivity as the MWCNT weight percentage was increased (Table 1).

4. Conclusion

We have successfully structured composites of PVA and MWCNT in the micro-scale dimensions. A combination of solution casting and molding procedures were developed and employed to pattern microstructures on a variety of substrates such as silicon, glass and PET. While the weight percentages of nanotube are increased from 0.99 % to 10.7 %, the electrical conductivity of the PVA-nanotube composite material is significantly increased. Scanning electron microscope observations of the surfaces of the patterned composite indicate a homogeneous dispersion of MWCNTs throughout PVA matrix and a strong interfacial adhesion, which are important for enhanced material properties, as compared to pure PVA films. The fabrication methodologies described here can be employed to make micro-miniaturized devices and systems for various applications.

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Table-1 - Measured electrical properties of PVA-CNT film with different MWCNT weight percentages:

Samples	Resistivity	Conductivity
0.99 wt% MWCNT	6.437 Ω -cm	0.15 Siemens/cm
1.96 wt% MWCNT	0.771 Ω -cm	1.29 Siemens/cm
7.4 wt% MWCNT	0.514 Ω -cm	1.945 Siemens/cm
10.7 wt% MWCNT	0.2827 Ω -cm	3.53 Siemens/cm

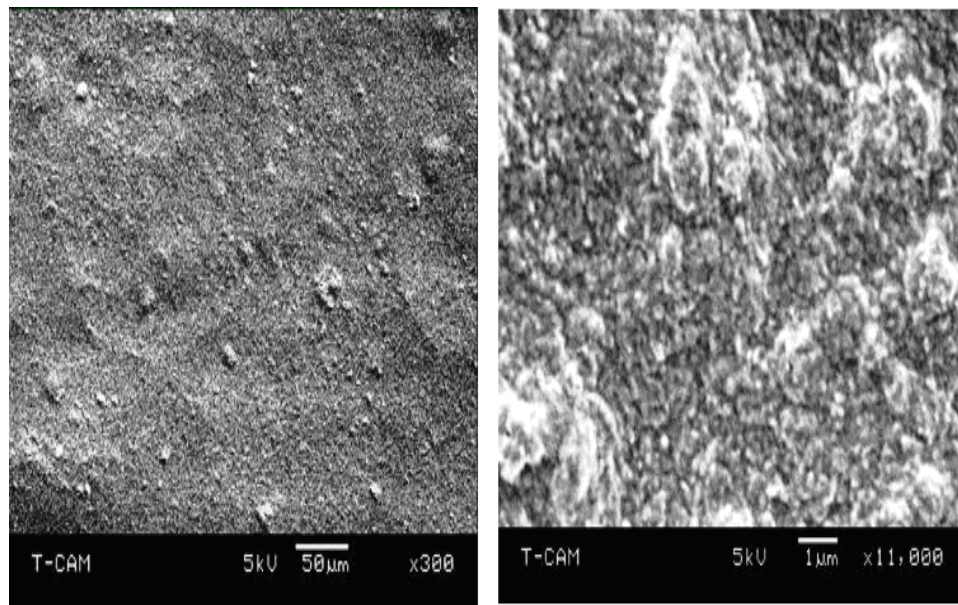


Fig. 1- Scanning Electron Microscope (SEM) micrographs of CNT dispersion in PVA on the scale of 50 μ m (left) and on the scale of 1 μ m (right)

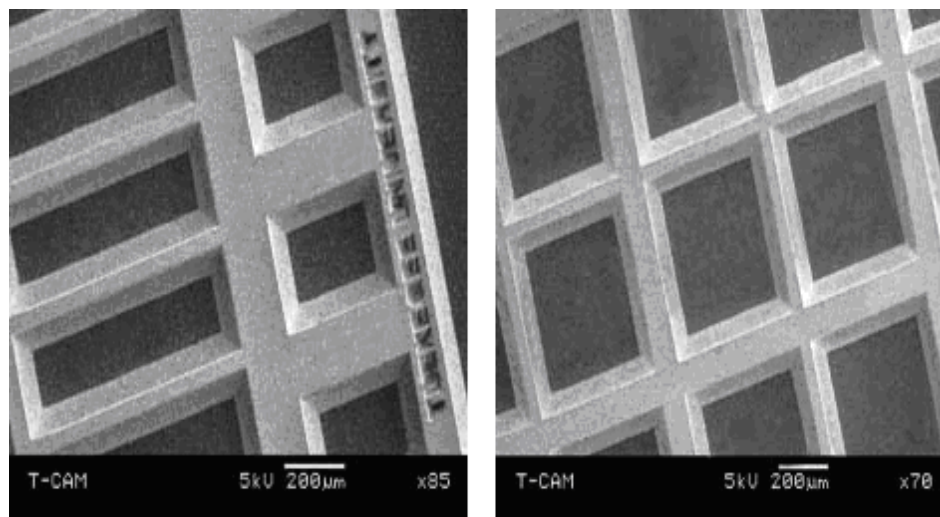


Fig. 2- SEM micrographs of Si hard mold after anisotropic etching

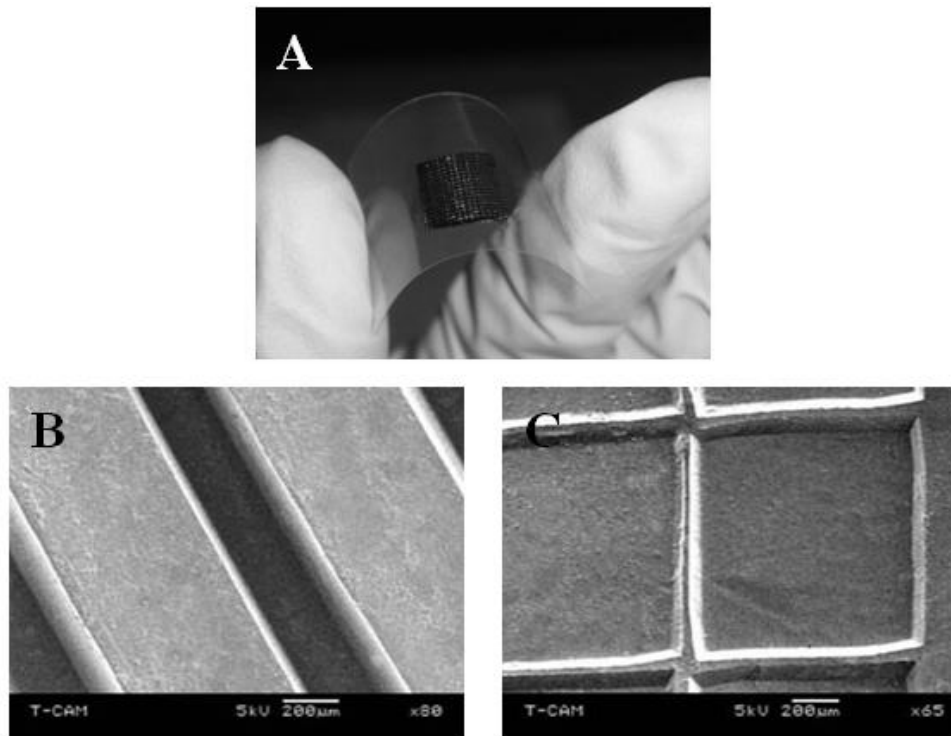


Fig. 3- (A) Optical image of PVA-CNT composite pattern by microtransfer molding on flexible PET substrate; (B, C) SEM micrographs of the composite patterns on flexible PET substrate

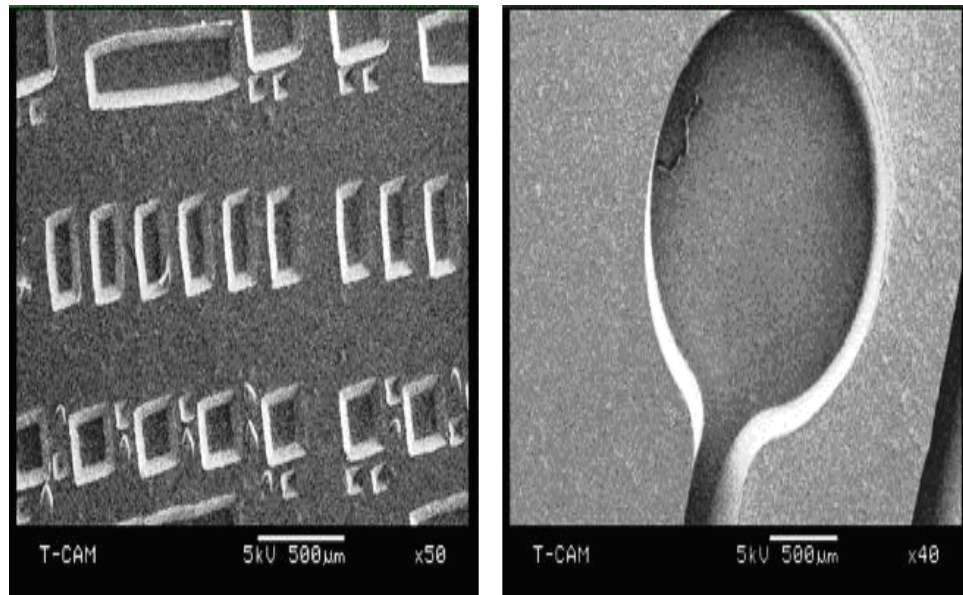


Fig. 4- SEM micrographs of nanocomposite microstructures by replica molding