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A simple and versatile micro contact printing method for generating carbon nanotubes patterns on various substrates

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A B S T R A C T

We present an optimized process for generating at low cost, patterns of carbon nanotubes (CNTs) on a large variety of substrates through a simple micro contact printing method. This method meets the requirements for the integration of CNTs into microdevices, for applications in microelectronics (interconnects), flexible electronics (printed conductive electrodes) and biodevices (biosensors and biosystems for regenerative medicine). We have optimized a new method for inking PolyDiMethylSiloxane (PDMS) stamps with CNTs that turned out to improve significantly the quality of the printed features over large surfaces. This inking step is performed by adapting a spray-coating process leading to a dense and homogeneous coating of the stamp with a thin layer of CNTs. The printing step is performed using a solvent mediation, allowing us to pattern this thin layer of CNTs onto various substrates by contact through a thin film of liquid. We demonstrate that this soft and rapid methodology can lead to the realization of CNTs patterns with versatile geometries onto various substrates at the micron scale. Examples of applications for CNTs interconnects and flexible electronics are rapidly shown.

Keywords:

Carbon nanotubes
Micro-patterning
Spray-coating
Soft-lithography
Flexible electronics

1. Introduction

Carbon nanotubes (CNTs) are the target of intense research since more than a decade. They show promising applications ranging from ultra-small and flexible electronic, sensing devices, functional materials to (more recently) biomedical implants and interfaces with biological components (cells). In particular, double-walled carbon nanotubes (DW-CNTs) are potential candidates for new generation of on chip interconnections due to their nearly metallic behaviour [1]. However, successful implementation of CNTs for these applications requires methods to deposit and pattern them over large areas, at high resolution, while meeting the requirements imposed by the nature/fragility of the target substrate. Previously described techniques for depositing films from aqueous solution generally yield low coverages or rely on slow procedures or repeated deposition to increase density [2]. Several other methods of nanotube film fabrication have been reported, including spray coating [3]. The most common method entails the deposition of a colloidal solution of nanotubes onto porous filtration membranes and transferring to other substrates. However, such processes do not scale up easily, require special substrates

and are not compatible with standard microfabrication processes [4]. Other CNTs patterning techniques often damage the receiving substrate, including either chemical modifications of the substrate or ablations [4,5]. Of interest from a technological point of view are processes which are cost effective, scalable to large area with high-throughput fabrication and are flexible enough to be implemented on a large class of substrates including flexible ones.

This paper is thus devoted to propose a new methodology for creating CNTs patterns onto a wide range of substrates, with high resolution and high repeatability. CNTs micropatterns were realized through a combination of spray coating and micro-contact printing (see Fig. 1). We were able to obtain patterns measuring few micro meters width and few millimeters length on various types of substrates, including flexible ones. This method is soft, rapid, compatible with optical alignment, applicable to large-area processing at high throughput.

2. Method and results

2.1. PDMS stamps

The stamps consisted in a microstructured elastomeric material, the PolyDiMethylSiloxane (PDMS), which is inert and biocompatible. The PDMS was conventionally microstructured using a simple molding process against a silicon master generated by proximity

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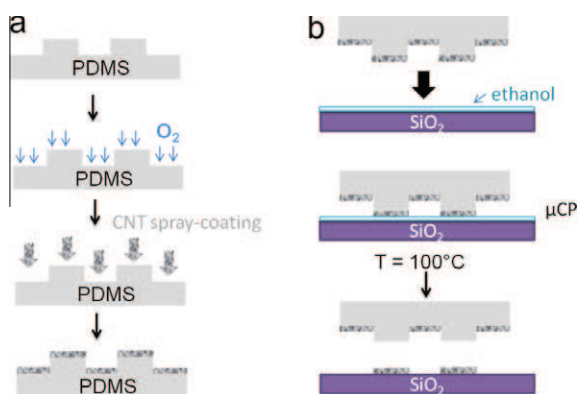


Fig. 1. Schematic of the CNTs layer patterning process. (a) Inking of a PDMS stamp by spray-coating after PDMS hydrophilization through plasma oxygen treatment. (b) Microcontact printing with solvent mediation (here ethanol). After conformal contact between stamp and receiving surface (here SiO₂ substrate), the whole is placed in an oven at 100 °C during 15 min.

UV lithography and deep Reactive Ion Etching (RIE). An anti-adhesive treatment of the master is carried out using silanisation in liquid phase with octadecyltrichlorosilane (OTS) in order to enable easy demolding of the polymer replica after thermal curing. The PDMS pre-polymer solution containing a mixture of PDMS oligomers and a reticular agent from Sylgard 184 (10:1 mass ratio, Dow Corning) was poured on the silicon master and cured at 80 °C during 3 h. Finally, the stamps were peeled from the master and cut in 4 × 4 cm pieces.

Different pattern geometries were used in this work including for example periodic arrays of lines and dots of various widths, lines exhibiting a 90° turn as well as spirals, letters, etc. The smallest feature size investigated here, was fixed by the resolution of the proximity UV lithography process used for generating the silicon masters and was around 2 μm. Prior to inking, these stamps were hydrophilized using an Oxygen Plasma process as described in a following section.

2.2. CNTs suspension

Double-walled carbon nanotubes (DW-CNTs) used in this work were prepared in-house by CCVD, by decomposition of CH₄ at 1000 °C (H₂:CH₄ atm.) [6]. After catalyst removal (HCl), the sample contained approximately 80% of double-walled carbon nanotubes, the rest being mainly single-walled carbon nanotubes (~15%) and triple-walled nanotubes. The large proportion of metallic CNTs [7] may present some advantages for applications involving electrical interconnections.

Because of their high aspect ratio, CNTs are subject to large van der Waals forces, which cause them to stick together, forming large bundles [8]. In our case, we used a surfactant to assist the dispersion of individual nanotubes inside the suspension. Purified CNTs and carboxyethylcellulose (CMC) were mixed with ultra-pure water with a mass ratio of 1:10 in mass (CNTs: 0.1%, CMC: 1%). Carboxymethylcellulose presents the advantage to be biocompatible and allow the use of such stabilized CNTs for biological investigations. Stabilization was combined with mechanical debundling. For this, the mixture was sonicated for 30 min (Sonics Vibra Cell) at a power of 150 W, under cooling in an ice bath. The mixture then appeared as a stable black suspension which was centrifuged and re-suspended in ultra-pure water (centrifugation 16,000 rpm during 30 min). The cycle “sonication–centrifugation and re-suspension” was repeated 3 times, in order to improve the purity of the CNTs suspension and to remove agglomerates.

2.3. Inking process of the stamp

Micro contact printing of suspensions of nano-objects (such as CNTs) using conventional inking methods based on simple incubation of the ink onto the stamp surface, leads to very poor results in terms of quality and reproducibility of the patterns. This well-known process is related to an inhomogeneous deposition on the stamp surface during the inking process. We have thus implemented a new methodology based on spray-coating for inking PDMS stamps which is cost effective, scalable to large area and generates a dense and homogeneous coating of the stamp. Spray-coating is a high throughput process for fabrication of various types of coatings, including CNTs [3]. In this work, the stable CNT suspension was sprayed using a manual spray coater, at room temperature (20 °C) over the PDMS stamps. Majumder et al. [3] recommended heating the receiving surface during the spray-coating process in order to avoid the formation of large droplets and induced coffee-stain rings leading to inhomogeneous films. However, in our case, instead of heating the receiving surface, we adapted the distance between the sample surface and the coater nozzle. This distance was optimized in order to obtain the smallest droplets on the sample's surface, which let a very rapid solvent evaporation and limited coffee stain effects. In this perspective, this is the reason why PDMS stamp were priorly treated with an O₂ plasma treatment.

The electrical resistance of the stamp surface was measured during the spray coating as seen in Fig. 2. This in-situ measurement enables the detection of the percolation threshold, which permits to calibrate easily the thickness of the deposited layer on the stamp. Once the set-in of the electrical conduction is detected it is possible to monitor the thickness of the CNT carpet through the measurement of the layer resistance using the calibration curve presented in Fig. 2. Indeed, we have investigated the evolution of the measured CNTs layer's electrical resistance (silver paint was deposited as contact pads) as a function of the layer thickness as measured by AFM. We observed that by increasing the spray-coating duration, the CNTs layer's thickness increased and the layer resistance decreased. The minimum thickness of a homogeneous and continuous CNTs layer we can obtain is around 15–20 nm. Resistance sheet can be varied over a wide range by controlling the amount of carbon nanotubes deposited (linked to the deposition duration and CNTs suspension's concentration). These results are in good agreement with the observations made by Zhou et al. with CNTs films created by filtration technique [9]. This in-situ control of the inking process turned out to be crucial for obtaining good reproducibility over experiments. This technique of inking through spray-coating yielded high surface coverage in a single step and allowed us to obtain dense and homogeneous CNTs layers, as shown in the Fig. 2. Typically, we can obtain 100 nm thick films in 10 min of spray coating. Fig. 2d shows a typical I(V) curve obtained for a 100 nm thick CNT layer exhibiting an ohmic behavior.

After fabrication, the coated surfaces were dipped in a water bath and heated at 60 °C for 2 h to remove residual surfactant. In comparison to other coating techniques such as solution casting [2], or dipping [10], spray-coating process developed here allowed to obtain denser CNTs layers in a single step, with a substrate surface totally covered with CNTs. Moreover, this spray coating process can be implemented several times in order to increase the film thickness in case of need.

2.4. Microcontact printing of CNTs

The spray-coating process allowed CNTs to be deposited directly onto PDMS stamps. However, as previously mentioned, it turned out to be necessary to preliminary treat the PDMS in a radio-frequency plasma cleaner (Reactive ion Etching, Tepla 300

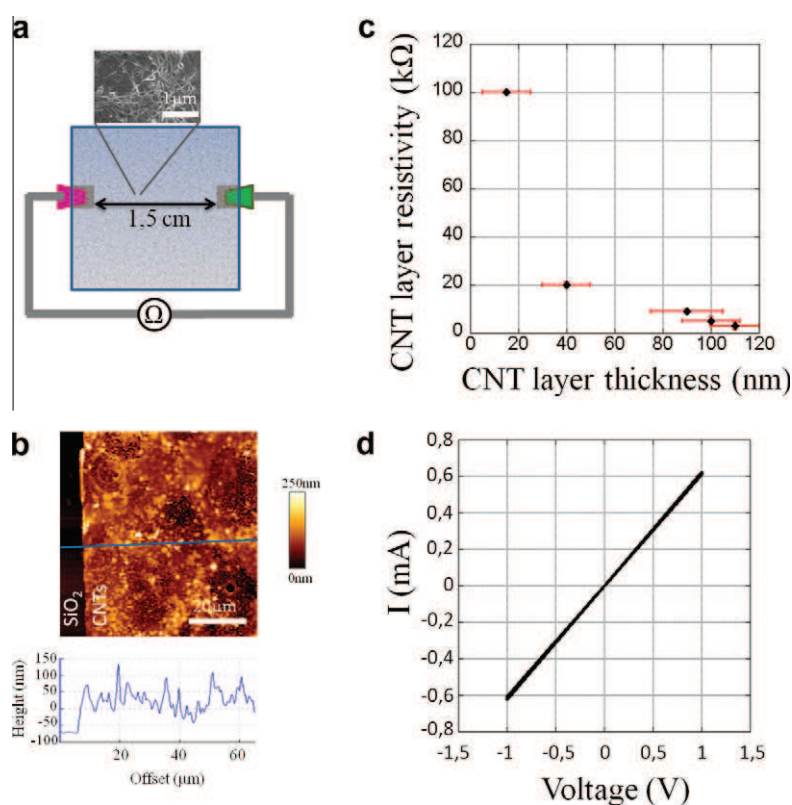


Fig. 2. In-situ monitoring of the inking step during spray-coating of a suspension of DW-CNTs. (a) Schematic representation of the layer's resistance measurement. (b) Up: AFM image of a CNTs layer deposited by spray-coating. Down: cross section analysis of the AFM image showing a CNTs carpet around 110 nm thick. (c) Calibration of the CNTs film's thickness through in-situ measurement of the electrical resistance of the film. (d) Typical result obtained by measuring the $I(V)$ response for a CNT layer (layer thickness is 100 nm).

microwave plasma processor, power = 200 W, $T = 40^\circ\text{C}$, O_2 flow = 1000 mL/min, $P = 1.65$ mbars) for 30 s. The hydrophilization of the PDMS surface enabled the maximum spreading of CNTs suspension droplets during the spray-coating step. The beneficial effect of this treatment is visible on Fig. 3. When the PDMS was not treated, the contact angle formed between the PDMS and the solution was $105 \pm 5^\circ$, leading to poor CNTs suspension droplets spreading. By increasing the spray-coating duration, and also multiplying the number of such droplets, it is possible to fully cover the PDMS surface but the resulting layer is not thin and exhibits numerous irregularities. On the contrary, in the case of a treated PDMS exhibiting a contact angle lower than 10° , the CNTs suspension droplets spread and enable the formation of a thin CNTs

homogenous layer (Fig. 3). The global film roughness was measured by AFM and reached 8 nm (root mean square roughness). Layers were considered as dense when no more substrate surface was visible.

Once the PDMS stamp has been covered by a CNT layer, the inked stamp was placed in contact with the receiving substrate (see Fig. 1). This approach has wide applicability to substrates of different types, ranging from metals, semi-conductors to polymers. To ensure the efficient CNT layer transfer from the contact regions of the stamp, it was necessary to place a droplet of ethanol on the receiving substrate. The PDMS stamp was then brought into contact with the target wet surface (Silicon, glass, Au, polymer...). The whole was placed in an oven at 100°C for 15 min. The stamp

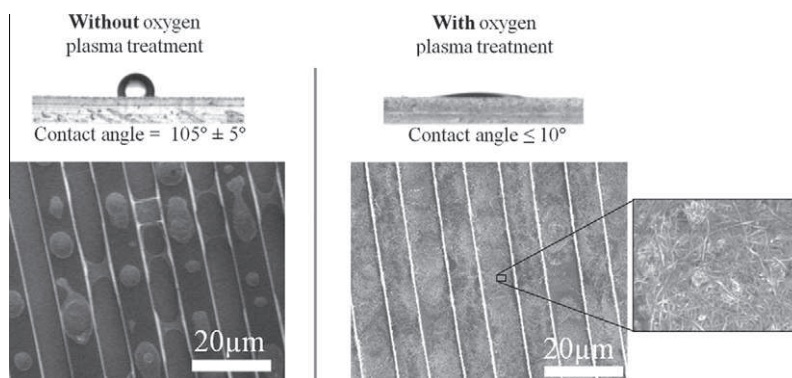


Fig. 3. Effect of the hydrophilization of the PDMS surface during the inking step performed by spray-coating. Left side: SEM image of a hydrophobic PDMS stamp after inking; right side: SEM image of a hydrophilic PDMS stamp after inking. Note the improvement of the homogeneity and density of the deposited film due to PDMS stamp hydrophilization.

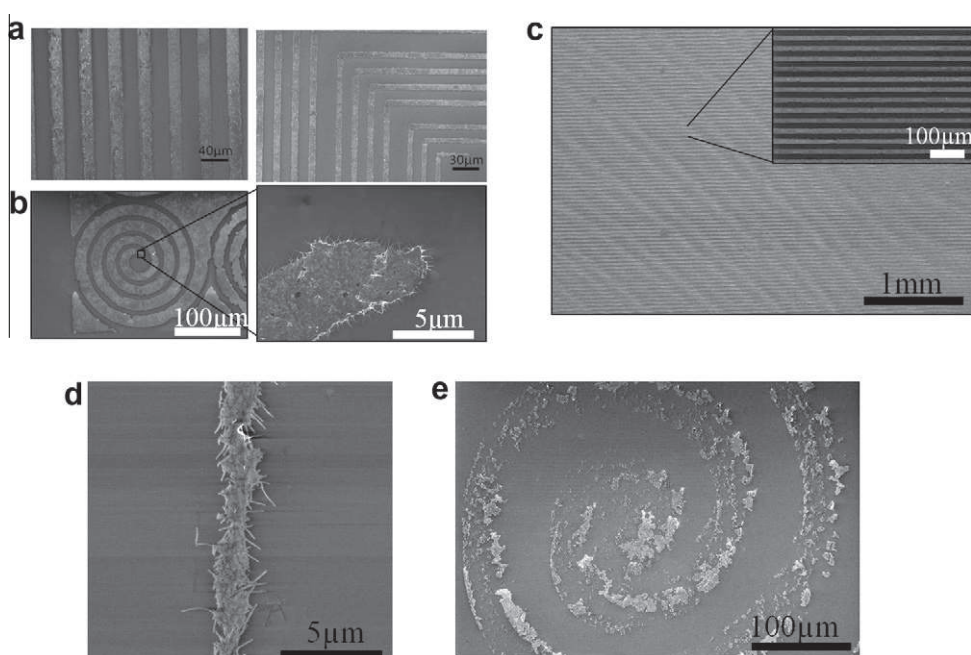


Fig. 4. SEM images of various patterns of printed CNTs on a SiO₂ substrate. (a–d) A high quality printing was performed under solvent mediation, (e) image of a spiral pattern unsuccessfully printed without solvent mediation.

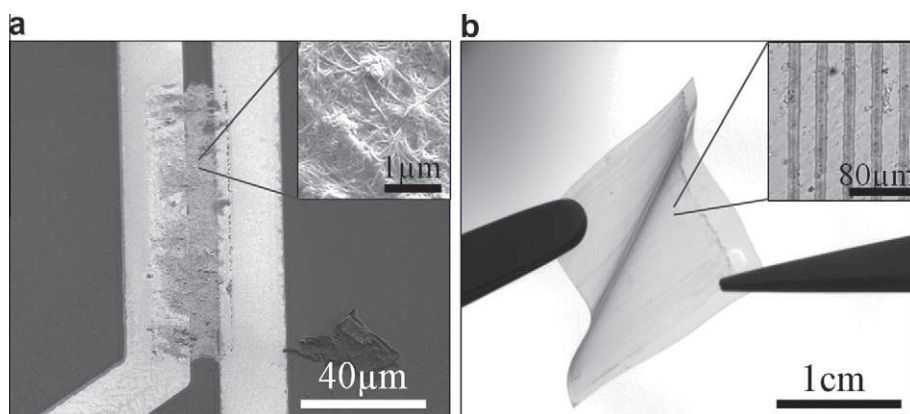


Fig. 5. Examples of applications of the printing method. (a) Realization of a conductive connection with CNTs by combining spray-coating and aligned microcontact printing over two pre-defined microelectrodes. (b) Image of a CNTs patterned flexible substrate: result obtained after spray-coating and microcontact printing of CNTs on a polyetheretherketone film. Insert: zoom on microcontact-printed lines.

was then peeled away and we finally obtained conform CNTs patterns, with variable geometries. We were able to realize patterns measuring few micrometers width and few millimeters length (see Fig. 4). Fig. 4e shows the result of a control experiment where the micro-contact printing of CNTs was implemented without any solvent mediation. We can observe from the SEM image that CNTs are almost not transferred to the substrate.

Most of receiving surfaces can be used as it and do not need a prior chemical functionalization to become compatible with this technique due to the high sticking capability of CNTs under solvent assistance. CNTs patterns were characterized by dark field optical microscopy ($\times 10$ lens) and scanning electron microscopy (SEM). By direct comparison between the stamp's surface and the substrate's surface after printing (results not shown), we have observed that the CNTs layer is entirely transferred from the PDMS to the substrate as soon as solvent mediation is used. The totality of the CNTs being transferred, the PDMS stamp is sufficiently clean to be recycled for another film transfer. We think that by entering

the CNTs layer network by capillarity, solvent molecules increase the adhesion forces between the substrate and CNTs layers. Those forces may become larger than the adsorption forces that exist between PDMS surface and CNTs, leading to the CNTs transfer from the PDMS stamp to the wet target surface. The following heating may facilitate the CNTs release by accelerating the solvent evaporation. A wide range of solvents can be used to enable the transfer from the PDMS stamp to the substrate, like deionised water or acetone. Solvents must not damage the receiving substrate and it is preferable to use solvents that evaporate rapidly in order to minimize the process duration.

Our results demonstrate that the combination of spray coating and micro-contact printing with solvent mediation is a simple solution to pattern substrates with CNTs layers with high fidelity and reproducibility. Moreover, the printing can be performed multiple times on the same substrate without additional complications (figure not shown). Through alignment during the printing we showed that the method developed in this work can be used to

realize CNTs interconnections, as shown in Fig. 5a. Furthermore, it is compatible with the use of flexible substrates, like polyetheretherketone (PEEK) for example (see fig. 5b). All those points demonstrate the high versatility of the developed method, opening the doors for various applications.

3. Conclusion

In conclusion, we have described a technological process that generates homogeneous and highly conductive carbon nanotubes micron scale patterns on various substrates (including PEEK, Au, Silicon). This process combines spray-coating for inking polymeric stamps and micro-contact printing using solvent mediation. Our process is versatile, rapid and simple thus opening the perspective of integrating CNTs into various elementary devices on a wide range of materials for applications. The same process has been successfully applied to the patterning of other nano-objects such as nanowires and nanoparticles.

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