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# Microcontact printing process for the patterned growth of individual CNTs

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## Abstract

We report an original approach to pattern a substrate with isolated carbon nanotubes. Through the improvement of the microcontact printing technique by the use of a new composite stamp, we were able to produce on flat substrates micrometric features of a catalyst suitable for the localised growth of single-walled carbon nanotubes by catalytic chemical vapour deposition. This catalyst material is for the first time prepared via an original sol-gel process. The growth of straight carbon nanotubes between the patterns was observed and a method to promote the controlled growth of such isolated nanoobjects is thus conceivable.

*Keywords:* Carbon nanotube; Microcontact printing; Composite stamp; Catalytic chemical vapour deposition; Sol-gel

## 1. Introduction

Since their discovery by Iijima [1] in 1991, carbon nanotubes have been the object of many works. Because single-walled carbon nanotubes (SWNTs) are nanoscale structures with interesting mechanical, electrical, and chemical properties, they appear useful for a variety of applications.

Developing controlled-synthesis methods to obtain well-ordered carbon nanotube architectures is an important and viable route to nanotube-based

devices. Self-directed growth of suspended SWNT networks by means of catalytic chemical vapour deposition (CCVD) was first demonstrated by Cassell et al. [2,3]. The catalysts were prepared by printing a liquid-phase catalyst precursor selectively on the top of Si towers with a flat polydimethylsiloxane (PDMS) stamp [2]. The patterning of flat substrates by microcontact printing ( $\mu$ CP) has proved to be valuable for the growth of patterned multiwalled carbon nanotubes (MWNTs) films [4] or the growth of entangled SWNTs [5]. Compared to standard electron-beam lithographic and photolithographic patterning techniques, soft lithography [6–8] appears more suitable for patterning large areas ( $>1\text{ cm}^2$ ) in one single-step process.

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Here, we propose to grow isolated SWNTs and double-walled CNTs (DWNTs), by means of a new catalyst precursor which is patterned using an original  $\mu$ CP process. To achieve our goal, the standard approach of  $\mu$ CP was improved by making a composite stamp because the specific nature of our catalyst precursor turned out to be incompatible with conventional PDMS stamps. The key elements in our overall approach include understanding the chemistry of catalyst materials and synthesizing nanotubes on rationally designed substrates having patterned catalyst.

## 2. Microcontact printing of catalyst precursor

The first step of our process is the patterning of the substrate with a  $\text{Mg}_{1-x}\text{Co}_x\text{O}$  catalyst developed in our group, which is known to promote efficiently the growth of SWNTs and DWNTs [9]. In order to make this catalyst compatible with patterning techniques, we prepared a new precursor of the  $\text{Mg}_{1-x}\text{Co}_x\text{O}$  oxide solid solution, which could be used as an ink for the  $\mu$ CP process. For a reason of non-compatibility between this precursor and the conventional stamp material, we developed an original composite stamp that combines affinity with the precursor and conformal contact.

### 2.1. Development of the catalyst precursor

Flahaut et al. [9] have developed the synthesis of CNT samples mainly composed of SWNTs and DWNTs, by selective reduction in  $\text{H}_2\text{-CH}_4$  of  $\text{Mg}_{1-x}\text{Co}_x\text{O}$  oxide solid solution powders. The solid solution was prepared by combustion synthesis [10] from a stoichiometric mixture of the metal nitrates and urea, dissolved in water. In our work, we aimed at patterning a substrate with a homogeneous catalyst precursor thin film, as opposed to using a suspension of the oxide powder. Thus, we developed a sol-gel route, inspired from the work of Gaudon et al. [11], in order to prepare a  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  material in both powder and thin-film forms, for the first time by this method. The first step is the preparation of a sol, a polymeric precursor solution. This sol is mainly composed of  $\text{Co}(\text{NO}_3)_2$ ,  $6\text{H}_2\text{O}$  and  $\text{Mg}(\text{NO}_3)_2$ ,  $6\text{H}_2\text{O}$  reagent

grade salts, a polyimine resin used as organic carrier and acetic acid as main solvent. The total concentration of metal salts in the starting solution is  $0.2 \text{ mol l}^{-1}$  and the viscosity of the deposited sol ranges from 80 to 140 mPa s. The sol is then used for the preparation of  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  thin films or powders as required. To obtain the  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  oxide solid solution phase, the sol was heated at  $550 \text{ }^\circ\text{C}$  in air. The X-ray diffraction patterns of powders made from sol were found to be similar to those obtained with the powders made by combustion, revealing only the desired  $\text{Mg}_{0.95}\text{-Co}_{0.05}\text{O}$  phase.

### 2.2. Preparation of the composite stamp

The microcontact printing is a technique based upon pattern-replication methods, which uses stamps that are replicas of a micro- or nano-structured masters generated initially by conventional optical or electron-beam lithography. Most of the work on  $\mu$ CP has been done using PDMS Sylgard 184 (Dow Corning, Midland), a thermocured siloxane elastomer. The main disadvantage is that PDMS nanostructures tend to merge or collapse during inking and printing [12,13]. Both the stability of the small structures and the lateral long-range accuracy require a stiff system, still tolerant of topographical irregularities of the substrate. In order to meet these requirements, a composite stamp is often used: a hard backplane which is directly hybridised to the stamp polymer [13,14].

A drawback of using a PDMS stamp is that, for the compatibility of the stamp with hydrophilic inks or molecules, one often has to change the surface properties of the material, by physical or chemical treatments. Aiming at depositing patterns of our sol by  $\mu$ CP for the first time obliged us to modify the stamp: we made a composite stamp based on PDMS and PMMA materials. Indeed, we observed that the sol has affinity for PMMA, probably due to the polar nature of the polymer. The idea of a composite stamp was exploited by Donzel et al. [15] who demonstrated that PEG-derivatised PDMS stamps are significantly more useful than stamps hydrophilised using  $\text{O}_2$  plasma for printing a polar ink such as a solution of polar  $\text{Pd}^{2+}$  complexes in ethanol.

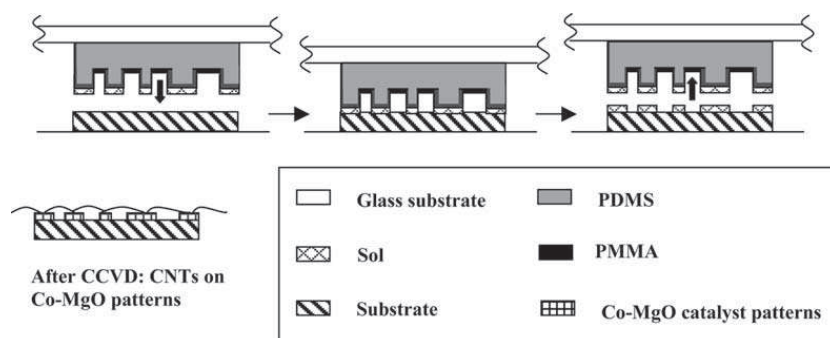


Fig. 1. Scheme of the microcontact printing process for patterned growth of CNTs by CCVD.

A PDMS stamp with a surface layer made of PMMA was made as follows. All the masters used for the stamp were fabricated by transferring resist patterns defined by electron-beam lithography or by UV lithography into silicon wafers through reactive ion etching. Then, an anti-adhesive silane (octadecyltrichlorosilane) layer was deposited on the master by liquid impregnation. A PDMS stamp was first made by pouring the liquid PDMS prepolymer into the master. A 300  $\mu\text{m}$  glass blade was used as a substrate for the stamp. After curing 90 min at 100  $^{\circ}\text{C}$ , we obtained a PDMS stamp. A PMMA ( $\text{MW} = 996,000 \text{ g mol}^{-1}$ ) layer was spin-coated (solution in methylisobutylketone) at 3000 rpm on the PDMS stamp in order to obtain a composite stamp. We used the  $\mu\text{CP}$  technique as described in Fig. 1: after impregnating the stamp with the sol, we put the stamp in contact with a substrate (Si wafer covered with a 100 nm thermal oxide layer) and, after removal, the substrate was submitted to a heat treatment at 550  $^{\circ}\text{C}$ .

### 3. Patterning of CNTs by localised CCVD

The next step after deposition of the catalyst patterns is the localised growth of the CNTs. The reaction was carried out in a CCVD system consisting of a tubular furnace and a gas flow control unit. Once the patterned substrates were introduced into the furnace, the temperature was raised to 850  $^{\circ}\text{C}$  in  $\text{N}_2$  atmosphere at a flow rate of 500 sccm, before  $\text{CH}_4$  was introduced into the system at 250 sccm for 30 min.  $\text{CH}_4$  was then turned off and the furnace was cooled to room temperature

in an  $\text{N}_2$  flow. The gas flows were dried with  $\text{P}_2\text{O}_5$ . The surface cobalt particles are produced in situ by selective reduction of the  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  oxide solid solution phase and they catalyse the decomposition of  $\text{CH}_4$ . These particles are small enough in CCVD conditions to produce CNTs, as described in earlier reports [9,16]. CNT growth is then selectively made on catalyst patterns (cf. scheme in Fig. 1).

## 4. Results and discussion

We investigated different catalyst patterns for CNT growth by CCVD. More than just performing a selective growth of CNTs, we intended to promote the formation of CNT bridges between catalyst patterns, by varying the dimensions of the individual patterns and the spacing between them.

### 4.1. Microcontact printing

We chose the thickness of the PMMA layer according to the dimensions of the patterns of the master, in order to avoid modifying significantly both width and height of the original PDMS patterns.

For a master with 25  $\mu\text{m}$  deep micrometric patterns, a PMMA layer of  $\sim 125 \text{ nm}$  was spin-coated. We were able to deposit micrometric structures of catalyst precursor which reproduce the micrometric patterns of the composite stamp: the feature size ranges from 100 down to 10  $\mu\text{m}$  (Fig. 2) and the thickness varies from 200 to 300 nm. For the sake of comparison, it is worth noting

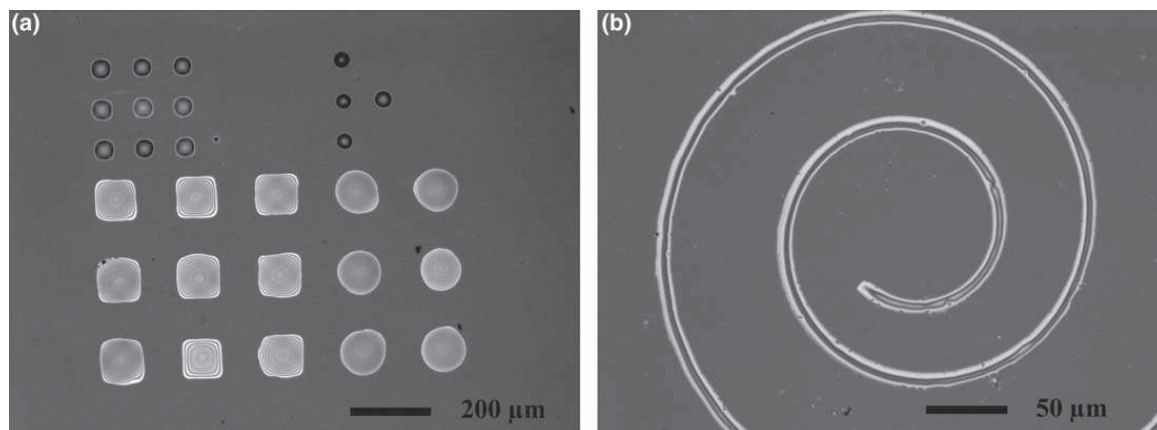


Fig. 2. Examples of micrometric features of catalyst precursor made by  $\mu\text{CP}$ : (a) 105 and 55  $\mu\text{m}$  large patterns (squares or dots); (b) 10  $\mu\text{m}$  wide spiral.

that Gu et al. [5] fabricated SWNTs on micro-contacted catalyst patterns (networks of  $\sim 3 \mu\text{m}$  large islands with a 10  $\mu\text{m}$  spacing), using a suspension of catalytic powder.

In the micron and submicrometric range, the stamp patterns consisted of series of adjacent features of different sizes ranging from 5 down to 200 nm, with spacing ranging from 1  $\mu\text{m}$  to less than 400 nm. We used a master with 600 nm deep patterns and a composite stamp was made with a  $\sim 20 \text{ nm}$  PMMA layer. However, we were not able to replicate the patterns of the stamp, because of the distortions of the stamp during the contact. The performances of our technique are, however, comparable with those of Micromolding in Capillaries (MIMIC) [7,17] which proved to be a soft lithography technique usable to make 500 nm wide catalyst lines prepared by sol-gel route, for the growth of SWNTs. Our  $\mu\text{CP}$  process remains perfectible, but one should note that this kind of stamp allows making catalyst patterns with a width of approximately 1  $\mu\text{m}$  and spacing down to  $< 400 \text{ nm}$  (Fig. 3): indeed, this range of spacing dimension suits our goal of making CNT bridges. The thickness of the smallest features is evaluated to be  $\sim 100 \text{ nm}$  through optical profilometry.

One has to note that this type of stamp cannot be used many times because the PMMA layer is damaged through several depositions. However, the fact that the stamp can be kept operational without any treatment for a long time represents its main advantage.

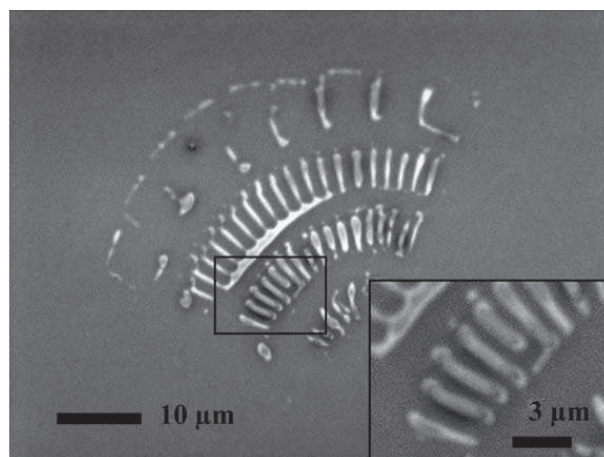


Fig. 3. Catalyst precursor features deposited by  $\mu\text{CP}$ . The softness of our stamp limits the fidelity of the printed features to those of the stamp.

#### 4.2. Patterned growth of CNTs

The growth of CNTs from  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  thin films was studied first (unpublished results), in order to find the suitable CCVD conditions, which are used in our present work.

The localised growth of CNTs on micrometric patterns which are depicted on Fig. 2 was successful: the selective growth of CNTs on the catalyst patterns was observed by scanning electron microscopy (Fig. 4). We identified straight bundles of CNTs with an apparent diameter of 10 nm: an example of a bundle bridging the opposite side-walls of a  $\sim 1 \mu\text{m}$  wide gap in the catalyst layer is

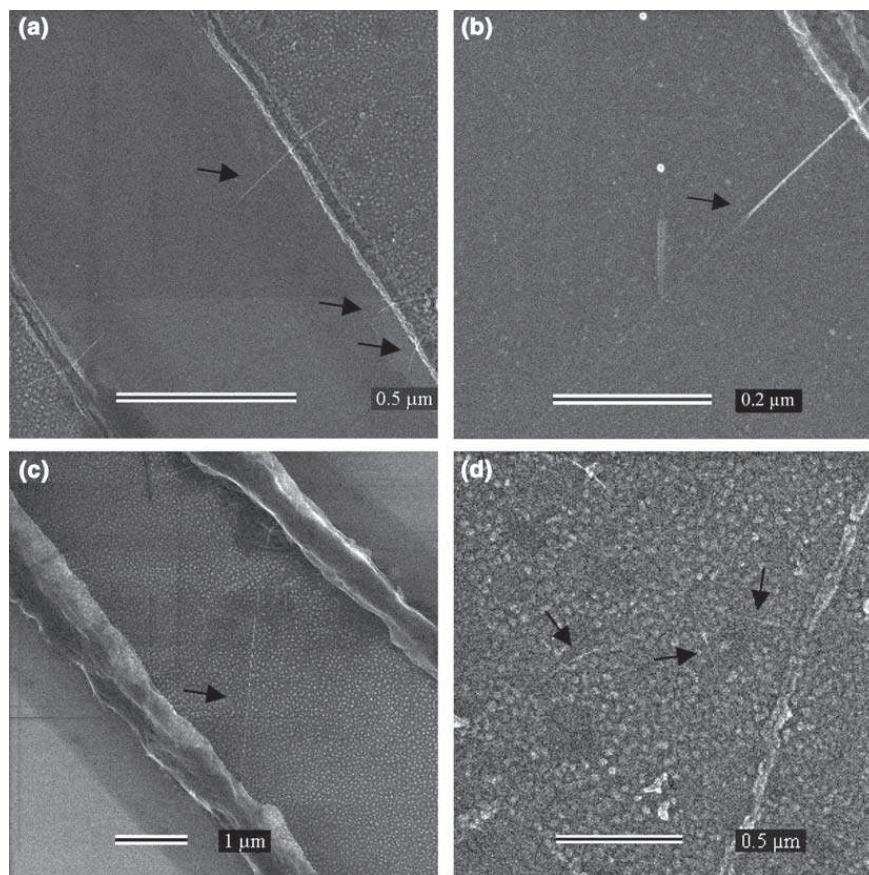


Fig. 4. Scanning electron microscopy images of CNTs grown by CCVD (black arrows point out some CNTs). (a) CNTs (probably bundles) bridging opposite sidewalls of a gap over a zone depleted in catalyst material. (b) Zoom of figure (a) (the large trail near the CNTs is an example of contamination due to the e-beam). (c) CNTs bridging opposite sidewalls of a gap over a large domain containing catalyst particles. (d) Representative view of particle morphology and CNT density.

shown in Fig. 4(a). The catalyst used in this work is known to promote the formation of SWNTs and DWNTs [9], so we assume that this bundle mainly includes these types of CNT. Fig. 4(b) is a higher magnification image of the area depicted in Fig. 4(a) and shows that the CNT bundle is only partially suspended, since it contacts the bottom of the gap over part of its length. The presence of a few gaps and zones of catalyst depletion in some areas of the deposited film is attributed to the effect of successive air and  $\text{CH}_4$  heat treatments. A  $\sim 10$  nm large straight bundle of CNTs forming a  $\sim 5$   $\mu\text{m}$  long bridge above a catalyst layer is shown in Fig. 4(c).

In the field of patterned growth, several approaches have been explored by researchers to produce SWNTs on substrates with directionality: rationally designing the substrates [2], controlling

the growth orientation and the CNT diameter by the use of an ordered mesoporous catalyst film [17] or realizing an electric-field-directed growth [18]. Here, the CNT directionality is attributed to the first cited approach: only the pattern configuration promotes the formation of CNT bridges in our CCVD conditions. A carbon nanotube grows freely from a catalyst pattern, it can then emerge from the pattern and reach an adjacent one. This method has proved to be valid for pattern spacing up to  $\sim 10$   $\mu\text{m}$ , as reported by Dai and co-workers [2].

Fig. 4(d) is representative of the granularity of the catalyst material ( $\sim 50$  nm diameter grains) and of the low CNT density. The latter point is of importance in our approach, regarding the formation of isolated CNTs, because a too high CNT density tends to favour the bundling of CNTs. The

exact nature of the CNTs (bundles or not, number of walls) will be soon further investigated by realising the same process on a membrane [19].

Regarding near-micron and submicrometric patterns, the CCVD treatment caused the alteration of the catalyst patterns, resulting in the absence of CNT growth, although the CCVD conditions were identical. It seems that some chemical reaction (formation of a  $\text{MgSiO}_x$  compound for example) or diffusion process occurs between the catalyst and the  $\text{SiO}_2$  layer of the substrates, the consequence of which appears to be especially detrimental for submicrometric catalyst patterns. It is expected that the control of pattern thickness will provide a way to keep patterns catalytically active even for nanoscale features (work in progress).

## 5. Conclusion

We have developed a new approach aimed at the patterned growth of individual SWNTs. First, by using a sol-gel process, we have proposed a new way for the preparation of the catalyst material previously developed by our group, and demonstrated its suitability for localised growth of CNTs. The use of a polymeric precursor as ink for  $\mu\text{CP}$  allows performing micrometric patterning of  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  precursor, using an original multi-layered stamp. After heat treatment, the obtained  $\text{Mg}_{0.95}\text{Co}_{0.05}\text{O}$  patterns have proved to be suitable for the localised growth of CNTs by CCVD. We demonstrated that our method can be used to grow straight bundled CNTs bridging catalyst features over a distance larger than one micron. The control of CNT networks should then be conceivable through a good choice of pattern geometry.

This preliminary work demonstrates that the combination of  $\mu\text{CP}$  and CNT growth by CCVD is a powerful tool in the area of nanoaddressing carbon nanotubes, although we have not investigated yet all the potentialities of this approach. The next step of our work will consist in: (1) optimising the nature of the composite stamp in order to obtain high quality submicrometric patterns; (2) promoting the growth of individual

SWNTs with a better efficiency and control of the CNT density. Then, it should be possible for us to realise more complex connection layouts and to bridge a large number of SWNTs per sample, all at once.

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