Controlled deposition of carbon nanotubes on a patterned substrate

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Abstract

We describe a new technique for the preparation of reactive templates of 1,2-aminopropyltriethoxysilane on silica surfaces, based on the chemical vapour deposition of silane molecules through a PMMA mask patterned by conventional electron-beam lithography. The template thickness and width are controlled down to the monolayer and 50 nm ranges respectively. These templates are successfully used for the selective deposition of sodium dodecylsulphate-covered single walled nanotubes at controlled locations on the surface. We demonstrate that this technique allows one to contact nanotubes with metallic electrodes deposited on top of the tubes and opens the way towards the formation of controlled crossings of nanotubes. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon nanotubes (NTs), discovered in 1991 [1], have open a promising way in nanotechnology [2–17]. For electronic applications, NTs provide insulating, semiconducting or truly conducting nanoscale wires [3–8], and components such as a junction [9–11] and a field-effect transistor [12–15] have even been demonstrated. For nanomechanics, NTs provide fibers with unprecedented mechanical properties that can be used to fabricate nanotools [16,17].

However, the fabrication of all kinds of NT-based devices is severely hindered by the lack of a simple and reliable process to deposit NTs in a controlled way. Up to now, all the demonstrated NT electrical devices have been nanofabricated either by randomly depositing NTs on a multi-electrode array or by patterning contacts onto randomly deposited NTs, after their observation [3–7,9–14]. Although alternative methods such as direct NT growth on catalytic templates [18,19] or between patterned metallic pads [15] have been demonstrated, the lack of a generic solution for the controlled deposition of NTs at given locations of a surface is a major bottleneck. Such a process was recently proposed by Liu et al. [20], relying on a local chemical functionalization of the surface of the substrate. In the present work, we

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demonstrate another method for achieving this control. This method, described in Fig. 1, is based on the electrostatic anchoring of surfactant covered NTs on amino-silane functionalized surfaces [21]: first, a reactive amino-silane template is prepared using chemical vapour deposition of silane molecules through a PMMA mask patterned by conventional electron-beam lithography. Surfactant covered NTs are then selectively deposited on the template. Finally, the PMMA mask is lifted-off, leaving the tubes on the template. In the following, we describe the method in detail, and we discuss in particular the deposition yield and the alignment quality.

2. Experimental

The SWNT raw material, produced by the arc discharge method, was purchased as AP grade from CarboLex (Lexington, USA). Surfactant stabilized tube dispersions were prepared by sonication of raw material in an aqueous 1 wt% sodium dodecylsulphate (SDS) solution. After some macroscopic particles had settled (over 10 min), the dark dispersions were loaded into the chromatographic column for purification as described in Ref. [22].

Oxidized silicon substrates (oxide thickness 300 nm) were cleaned as follows: first, they were
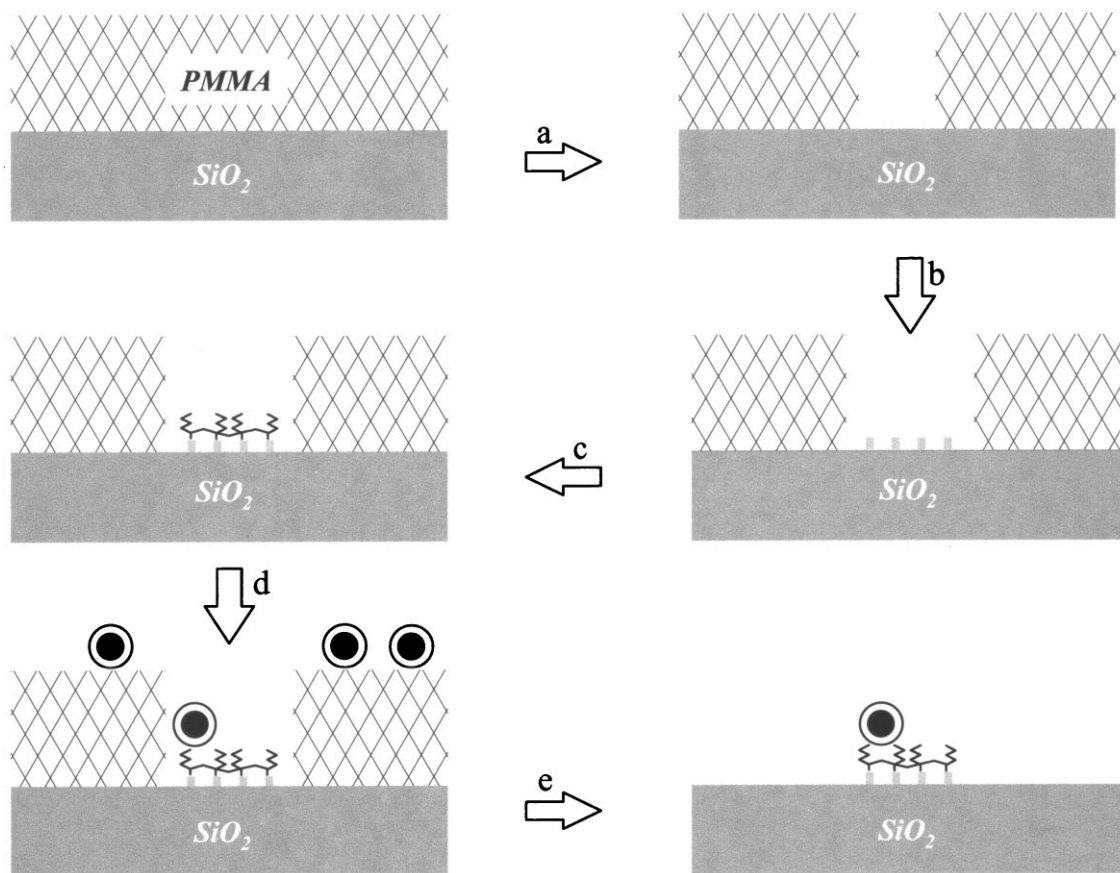

Fig.1. Principle of the nanotube controlled deposition method: starting from a PMMA covered SiO_2 surface, a PMMA mask is defined by e-beam lithography (a); silanol groups are exposed after an oxygen plasma cleaning (b); APTS is deposited from the gas phase (c); SDS covered NTs are deposited from aqueous solution (d); the PMMA mask is lifted off, leaving the NTs aligned along the pattern on the surface (e).

sonicated in acetone and ethanol for 5 min each and then immersed into a Piranha solution (H_2SO_4:H_2O_2 = 3:1) for 30 min – caution piranha solution reacts violently with organic solvents; the substrates were then exposed to UV–ozone for 30 min and finally thoroughly rinsed with DI water. A 100 nm thick PMMA resist layer was spun onto the cleaned substrate and subsequently patterned using e-beam lithography. We mainly patterned lines with widths in the range 50–200 nm. In order to improve the reactivity of the patterned surface and remove any organic contaminants from the exposed bare SiO_2 surface, the substrates were further cleaned with an oxygen plasma.

A layer of 1,2-aminopropyltriethoxysilane (APTS, Aldrich) was then formed onto the exposed SiO_2 surface by chemical vapour deposition. Typically, 1–2 ml of APTS was deposited at the bottom of a 2 l vacuum jar, with the samples held facing up 10 cm above the solution. The jar was immediately evacuated with a dry pump for 1 min. The samples were then allowed to react with the silane vapour for an additional 30 s. Immediately after removal from the reacting jar, the samples were cured for 25 min at 120°C in an oven, and subsequently exposed to HCl vapour in order to convert the NH_2 groups to NH_3^+ groups.

The samples were then allowed to react either with the NT solution or with a 10 nm gold colloid (Sigma) solution for 24 h typically. Finally, the PMMA layer was lifted off in acetone, and the attached gold colloids or NTs were observed using field emission scanning electron microscopy and atomic force microscopy in tapping mode.

3. Results and discussion

As a first step, we investigated the fabrication of a patterned self-assembled monolayer (SAM) of silane based molecules. Several techniques have been described in the literature for the patterning of a SAM of trichloro- or trialkoxy-silane on silica. Most use direct writing in the SAM with either photolithography, ion-beam, e-beam, atomic-beam or scanning probe microscopy lithography [23–28]. Some use a SAM as resist to etch the underlying substrate or insert another SAM in the holes made in the resist by one of the abovementioned techniques [20,24,25]. PMMA patterned masks have also been used to expose at specific
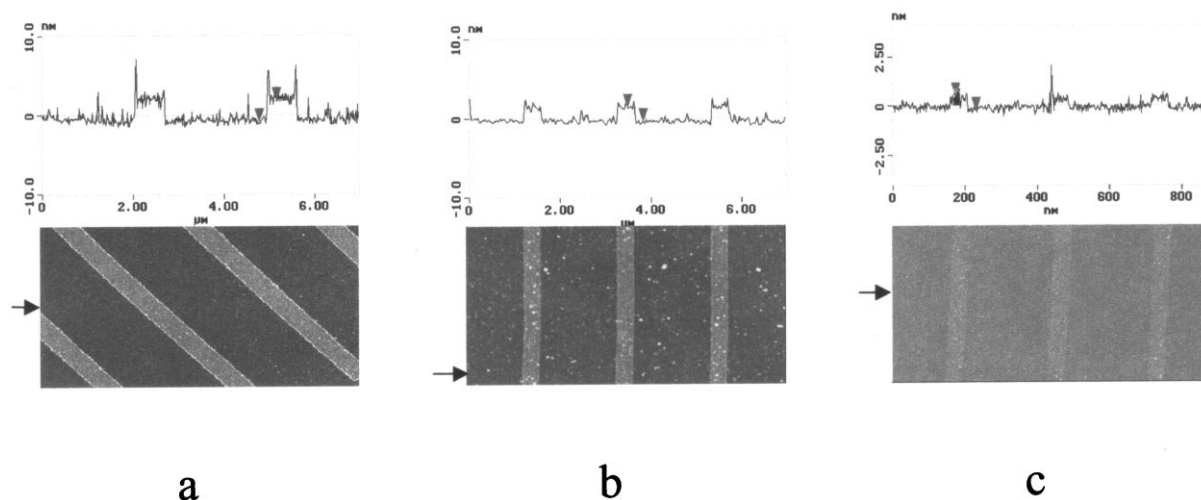

Fig. 2. Tapping mode AFM images and thickness measurements of patterned silane layers as a function of the pumping and reaction time in the APTS vapour. (a) 1 min pumping–2 min reaction–2 ml of APTS. (b) 2 min pumping–1 min reaction–2 ml of APTS. (c) 1 min pumping–30 s reaction–1 ml APTS.

locations the silica surface of a substrate to a trimethoxyalkylaminosilane aqueous solution [29]. This technique is appealing because it is simple and compatible with conventional e-beam lithography. However, using an aqueous solution of a trichloro- or trialkoxy-silane severely hinders the control of the layer thickness because these products are unstable and polymerize in the presence of water.

Various silanization techniques have been described in the literature for the APTS molecules [30]. They include the deposition of silane molecules from solution in various solvents [30,31], from the vapour of dilute solution of APTS in toluene [32], or by spin coating [33]. The measured thicknesses were found to depend upon the silanization technique used: 5, 9, 21 Å in Refs. [30–32], respectively. These deposition techniques are not applicable in our case because the solvents involved would cause swelling of the PMMA layer. To avoid this problem, we used a simple deposition method from the vapour phase of pure APTS. We found that the thickness of the silane layer varies

with the experimental conditions, such as the pumping and reaction time. However, an accurate control can be obtained down to the monolayer range, as shown by AFM profiles of silanized lines measured after lift-off of the PMMA layer. The results obtained with three different processes are gathered in Fig. 2. We found that 1 min pumping–2 min reaction times–2 ml APTS, 2 min pumping–1 min reaction times–2 ml APTS and 1 min pumping–30 s reaction times–1 ml APTS resulted in average thicknesses of 26.6, 17.8 and 7.3 Å, respectively. In the last case the layer appears rather homogeneous and its thickness corresponds to a monolayer. In what follows, we used these conditions for the silane layer preparation. As shown in Fig. 2c, 50 nm wide, monolayer stripes can be routinely and reproducibly obtained.

We first tested our technique with gold colloids in order to check that deposited particles, electrostatically bound to the silane layer, would endure the lift-off of the PMMA layer. Indeed, gold colloids are known to be negatively charged in solution and prone to bind electrostatically to an
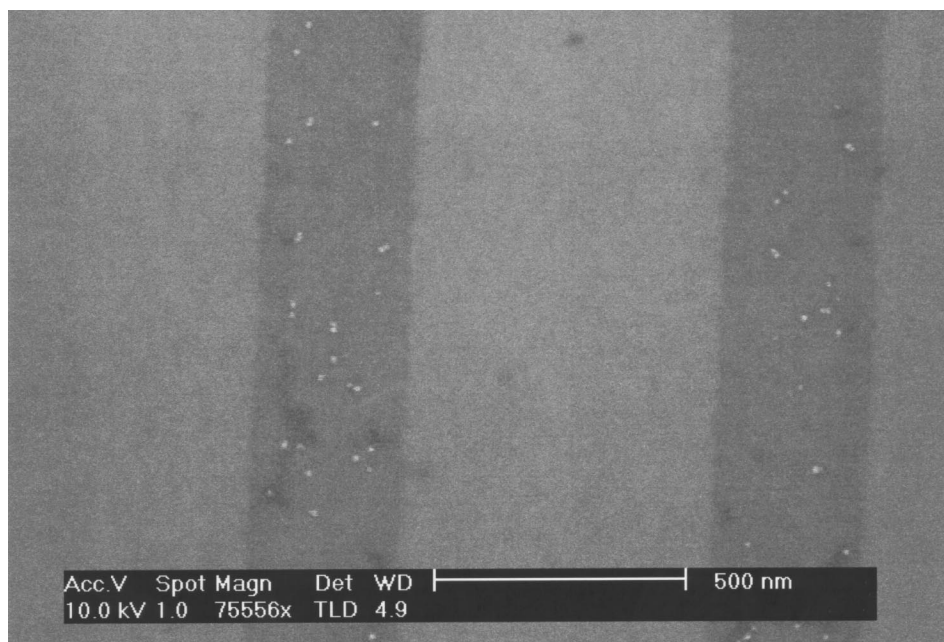

Fig. 3. SEM images of 10 nm Au colloids deposited (200 min deposition time) from a dilute solution of colloids on an APTS silane line, after PMMA lift-off. The two silane lines appear darker than the bare silica surface. The gold colloids (white spots) are visible only on the silane lines.

ammonium layer [29,34–36]. A SEM picture of gold colloids deposited along patterned lines is shown in Fig. 3. The white dots, present on the black line only, correspond to the 10 nm gold colloids deposited from a very dilute solution ($\sim 6 \times 10^{-6}$ mass fraction of gold). This demonstrates that the gold colloids resisted the lift-off process, and that the deposition technique we used is completely selective since no colloids are observed outside the silane pattern.

We have successfully deposited NTs using various patterns, as illustrated in Fig. 4a–d. Note that no NT is found outside of the silane pattern no matter how close or intricate the patterned lines are. The tubes, except for the shorter ones, are well aligned along the silane lines. The crossing lines and circle patterns show that the alignment along the patterns does not result from a dewetting effect since the tubes equally well adsorb along different directions, without any preferential direction for deposition.

Although the absolute concentration of the tubes solution is difficult to determine, the relative concentrations of two solutions can be inferred from their optical densities. As expected, we observed that the density of adsorbed NTs for a given deposition time, was higher when starting from a more concentrated solution. We also observed that the number of deposited NTs increased with the deposition time for times up to 24–48 h ours. Using longer deposition times brought no obvious improvement to the density of deposited tubes. The density of deposited NTs is also a function of the silane pattern linewidth. In particular, we found that a minimum line-width of 100 nm seems necessary to obtain a reasonable
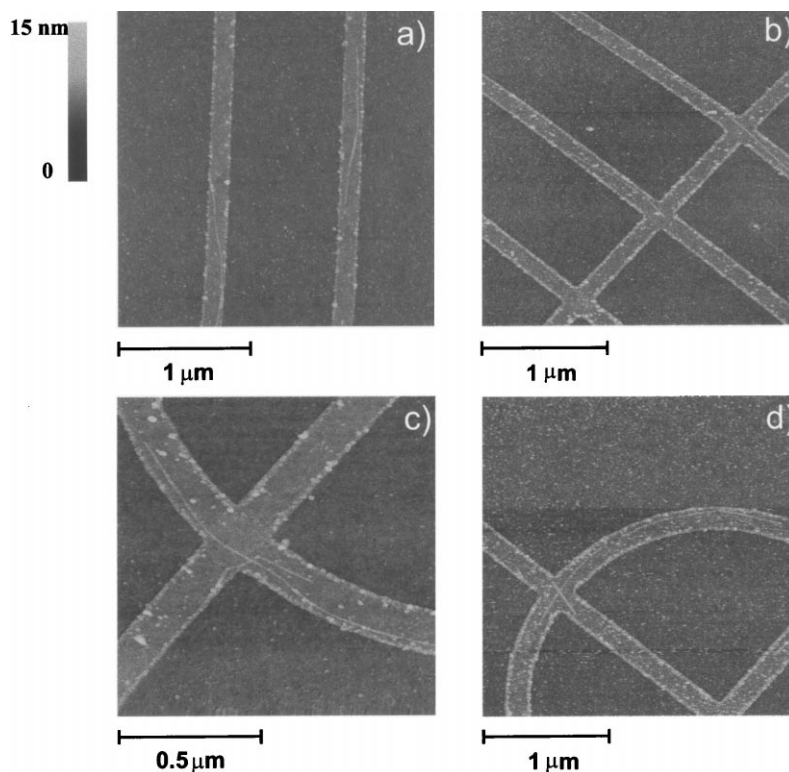

Fig. 4. AFM images of NTs onto the patterned silane monolayer (typical deposition time 24 h). The silane stripes appear brighter than the bare silica surface. The NTs appear brighter than the silane stripes onto which they are adsorbed. The typical thickness of the NTs of (a) (measured relative to the silane surface) is 1.6 ± 0.2 nm.

density. The NT density increases by a gross factor of two when the line-width is increased from 100 to 200 nm, and from 200 nm to 1 mm (not shown).

The alignment of the NTs adsorbed on the silanized lines is affected by the tube length, the type of tubes (SWNT, MWNT, ropes of SWNT) and the pattern linewidth. When considering the images of Fig. 4, it appears that long tubes (length ≫ 1 μm) are better aligned than shorter ones. Moreover, the thicker tubes (probably corresponding to ropes of SWNT) appear straighter than the thinner ones that sometimes show bending or even kinks. As expected, we observed that the quality of alignment is improved with narrower linewidths (not shown). There is thus a trade-off for the silane pattern linewidth between the density of adsorbed tubes and the quality of the alignment. For the tubes we worked with, the optimal linewidth is ca. 200 nm.

This technique is well suited for making nan-ostructures involving NT crossings, among which some have recently been shown to show diode-like behaviour [11]. As can be seen in Fig. 4c, silane patterns with crossing lines can be used to induce crossing of NTs. The results of Fig. 4c have however still to be substantially improved to allow fabrication of nanostructures with crossing tubes on a large scale. Two points in particular have to be improved: the density of adsorbed tubes and the control of the crossing. For the former point, increasing the density of tubes in the solution will probably be enough while for the second one, special designs of the crossing pattern are under investigation to avoid crossings like the one in Fig. 4c where one NT 'turns right' instead of remaining straight.

This technique is also well-suited to contact NTs with metallic electrodes in a predefined way. Fig. 5 shows a NT contacted by gold electrodes. The sample was made by first depositing the tube
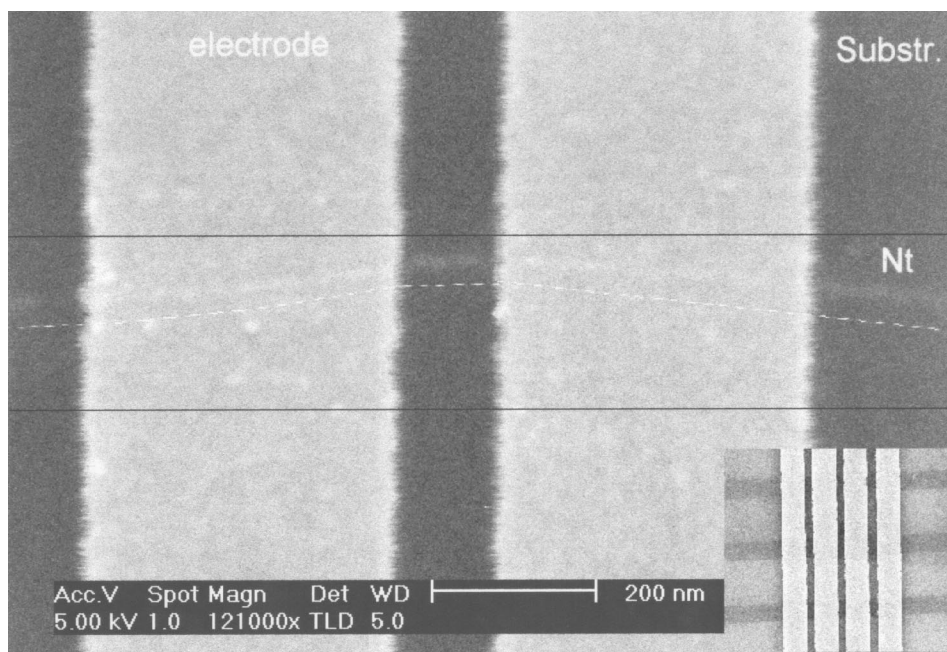

Fig. 5. SEM image of two metallic electrodes deposited on top of a NT attached to a silane line on the surface before evaporation of the metal. The NT position is marked by the Nt mark and a dotted line has been added close to the NT as a guide for the eye. The inset shows a low magnification picture of the four electrodes (vertical bright lines) and the silane stripes (horizontal darker lines) beneath. The contrast between the silane stripes and the silica surface fades at high magnification. Thus the silane line, located between the two black lines, is not apparent in the main image.

on a silane pattern prepared on a substrate fitted with position markers. After lift-off of the resist layer, a new resist bilayer (MMA/MAA copolymer first followed by PMMA) was spun on the sample and annealed (typically 165°C 15 min for each layer). Four contacts were subsequently patterned using e-beam lithography. Gold electrodes (70 nm thick) were then evaporated through the mask and the resist layer was finally lifted off. It order to assess whether such a process was not too detrimental to the attached NTs, the following control experiments was made: the NTs attached to the silane pattern were first observed by AFM, the resist layers were then spun on, annealed and lifted off and the NTs observed again. We found that the majority of the NTs remained unmodified: only occasionally was a nanotube (most of the time a 'long' one) removed by the process. Although this technique requires alignment on predefined markers, it does not require the observation of the NTs prior to evaporation of the metallic contacts. This technique is thus more powerful than previous ones relying on random adsorption of NTs on a substrate, observation of the tubes and subsequent contact patterning [7,11]. Preliminary electrical measurements using our technique gave contact resistances in the 20–200 kΩ range for SWNTs at room temperature.

We have also explored a slightly modified technique in which the PMMA layer is lifted-off prior to NT adsorption. Fig. 6 shows an AFM image of NTs deposited this way on a pattern of 200 nm wide silanized lines. As can be seen, only a fraction of the tubes is well aligned along the lines. The deposition is thus less controlled than when the deposition of NT is done prior to the lift-off of the PMMA layer. However, the density of deposited tube is higher in the former case. Clearly, NT adsorption at the bottom of PMMA channels and subsequent lift-off in acetone select well aligned tubes and avoid that NTs bridge neighbouring lines.

4. Conclusion

In this work, we designed a new simple and efficient technique to prepare patterned aminosi-
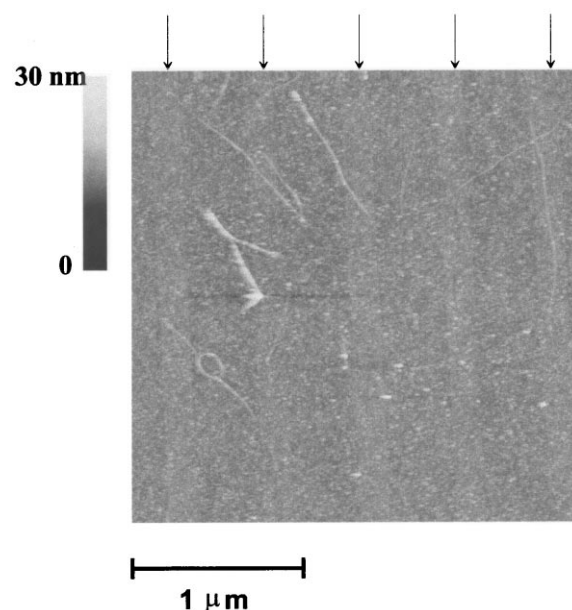

Fig. 6. AFM images of NTs deposited onto a silanized pattern after lift-off of the PMMA layer. The silane lines (marked by arrows) appear brighter than the bare silica surface.

lane monolayers forming a template suitable for the deposition of SDS-covered NTs at predefined locations. In the course of this work, we showed how gas-phase silane deposition could be controlled down to the monolayer level and a lateral extension of 50 nm, and we demonstrated a simple way for directly measuring the thickness of the silane layer. Using such silanized patterns, we deposited isolated NTs and pairs of crossed NTs, and we showed that metal contacts can be readily made on top of a NT deposited at a predefined location. This technique opens the way to multitube nanostructures.

Acknowledgements

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