Growth of Carbon Nanotubes through Selective Deposition of Nanoparticles

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Growth of CNTs on pre-patterned substrates

The metal deposition can be achieved by sputtering to the patterned substrates forming a thin catalyst layer,[1,2,3,4,5] by deposition of a catalyst on a self assembled nanoporous block copolymer template,[6] by evaporation of metallic ions,[7,8,9,10] by reduction of metallic salts,[11,12] by decomposition of a metal salt or an iron-storage protein (ferritin) coated on the surface from a solution,[13,14,15] by deposition of nanoparticles (NPs),[16] or generation of nanoparticles by laser decomposition of iron pentacarbonyl,[17] by plasma,[18] by laser activation of the catalyst,[19] by using a combination of laser ablation for particle generation and a low-pressure impactor,[20] by a hot wire generator.[21]

The necessity to prevent the deposition of nanoparticles from the walls of vias

On Fig. 1a, one can see that iron oxide nanoparticles are adsorbed on the walls of the via; a HF cleaning step permits to remove these nanoparticles. Is it really necessary to perform this cleaning step or could it be suppressed taking in account that only the connected CNTs will be used afterwards?

Without cleaning, the density of nanoparticles on the bottom and the walls of the vias is the same. In a via where the diameter is equal to the height, the surface of the walls is four times that of the bottom. It means that there will be four times more nanoparticles on the walls than on the bottom. After CNT growth, the ratio of CNTs on the walls vs connected to the bottom should also be 4. Hence only one CNT out of five will be connected to the bottom and can be used like a current conductor.

Considering the microelectronics applications, one should obtain a high density of small *connected* SWCNTs (>10^{13} CNT.cm^{-2} in order to obtain a conductivity higher than that of copper in narrow vias).[22] Supposing that this density is reached at the outlet of the vias but that only one fifth of the CNTs is connected, it will not be possible to overtake the

conductivity of the copper. We have analyzed pictures ***after the cleaning step*** and calculated that there are approximately 1% of nanoparticles located on the walls, this would lead to an acceptable amount of 1% unconnected CNTs

In this paper we are en route but have not yet reached this high density.

This cleaning step is therefore mandatory to reach a high density of connected CNTs

Moreover this process might be used for vertical deposition of nanoparticles where a CMP step is impossible to achieve on the bottom surface; e.g. on semiconductors or metallic tips: the following pictures show a titanium tip on SiO_2 layer (a) before and (b) after processing.
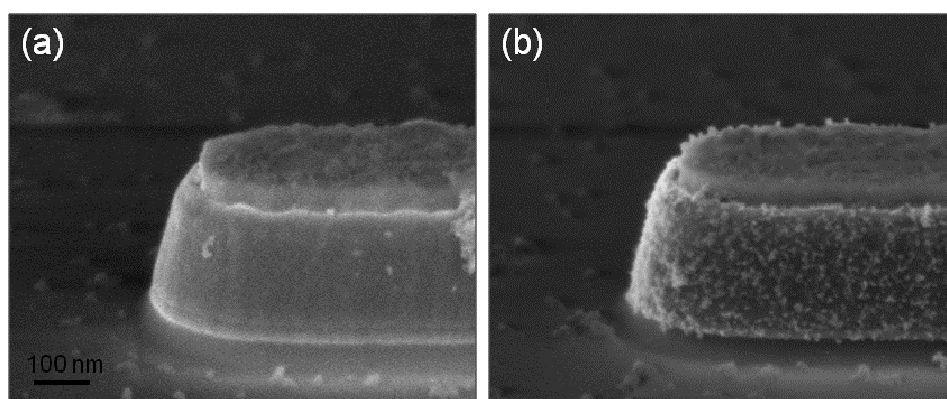
Fig. S1. SEM images of a Ti tip on SiO_2 layer (a) before and (b) after electrografting and deposition of nanoparticles.

The HF cleaning of the sample before electrografting.

Fig 1a shows DEG-capped nanoparticles adsorbed on the walls of the via, this is in line with the known adsorption properties of silica. Adsorption of alcohols on the surface of silica through H-bonding has been known for quite a time, [23] more recent publications have examined the adsorption of glycols.[24,25,26, 27]

After HF cleaning, the surface of silica $\equiv$Si-OH is changed $\equiv$Si-F[28]. In the presence of H_2O, SiH surfaces are obtained[29.] this method permits to remove thin oxides films on the surface of Si wafers to give flat hydrogen terminated surfaces, this is most likely what occurs at the bottom of the via. The mechanism has been investigated[29, 30]: "The surface resulting after this process is mainly hydrogen-terminated, containing a heterogeneous distribution of mono-,di-, tri-hydride species SiH_n (n = 1; 2; 3) and a smaller amount of terminations $SiH_{n-m}F_m (1 \leq m \leq n)$. The rinse in deionized water eventually replaces the fluorine terminations with oxo groups. The silicon surface resulting after rinsing is thus terminated with a mixture of SiH_n, andSiH_{n-}

$_m$(O–)$_m$ groups (with O bonded to silicon in a siloxo bridge or to hydrogen in a silanol). Such oxo centers are unstable when the surface is rinsed in deionized water for prolonged time or exposed to air at room temperature. The oxo-terminated surface, indeed, undergoes further oxidation in the simultaneous presence of H_2O and O_2." [30]

After treating with 0.2% HF, the sample is rinsed with water and put in contact with a DEG solution. At this point we do not know exactly the structure of the silicon dioxide surface on the walls; as our samples are P-doped we also suspect some influence of phosphorus. Whatever the surface, it is clear that it is less prone to adsorption of DEG-capped nanoparticles.

Removing the polymer at the bottom of vias before growing the CNTs

Removing the polymer is necessary so that it does not create a carbon cap around the nanooparticles during the CNT growth. The SEM images clearly show that the majority of polymer layer is burnt off. For instance, on the following pictures that present vias after deposition of nanoparticles (a), via after annealing at 250 °C for 30 minutes (b) and via after annealing at 530 °C for 30 minutes (c) we can observe that only in the latter case the polymer layer is really burnt off.
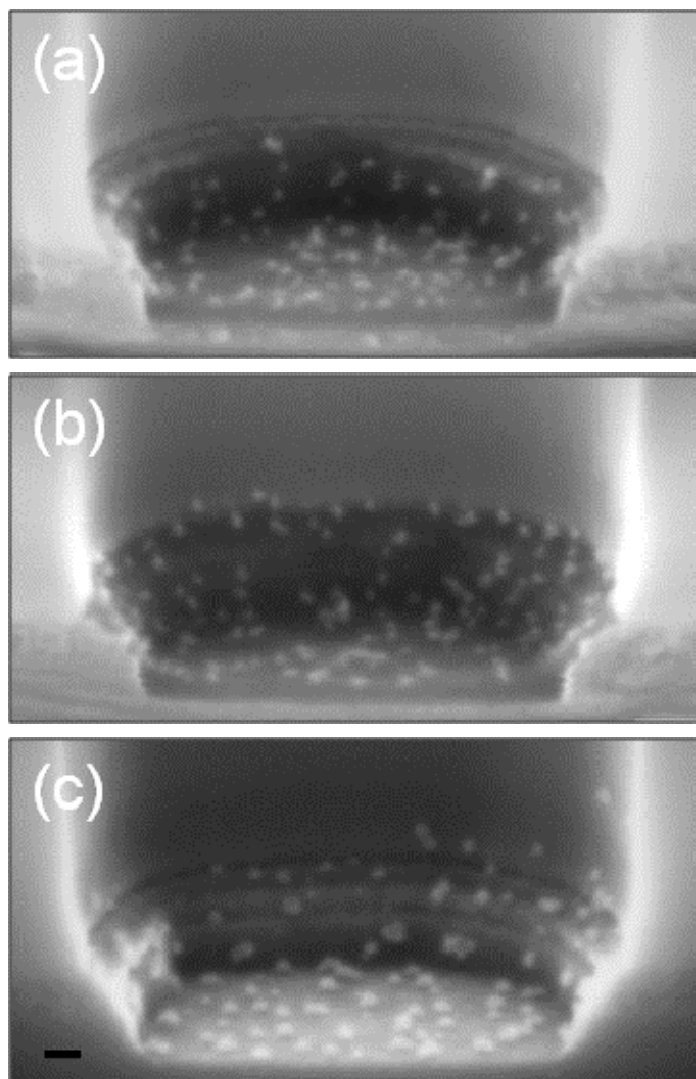
Fig. S2. SEM images of Si bottomed via after (a) electrografting and deposition of nanoparticles, (b) annealing at 250 °C for 30 minutes and (c) annealing at 530 °C for 30 minutes

The necessity to remove the polymer was indicated by the following experiments. Using a thin metallic layer deposited by PVD on a polymer layer,[31] the CVD growth of CNTs was performed under conditions similar to that used in this paper but without the previous annealing step; the results were unsatisfactory. With a previous annealing step the CNTs growth becomes efficient. The following Fig.ESI3 shows two SEM pictures of the same initial sample after growth (a) without and (b) with a previous annealing step. Hence the annealing step is absolutely necessary to obtain a proper CVD growth.
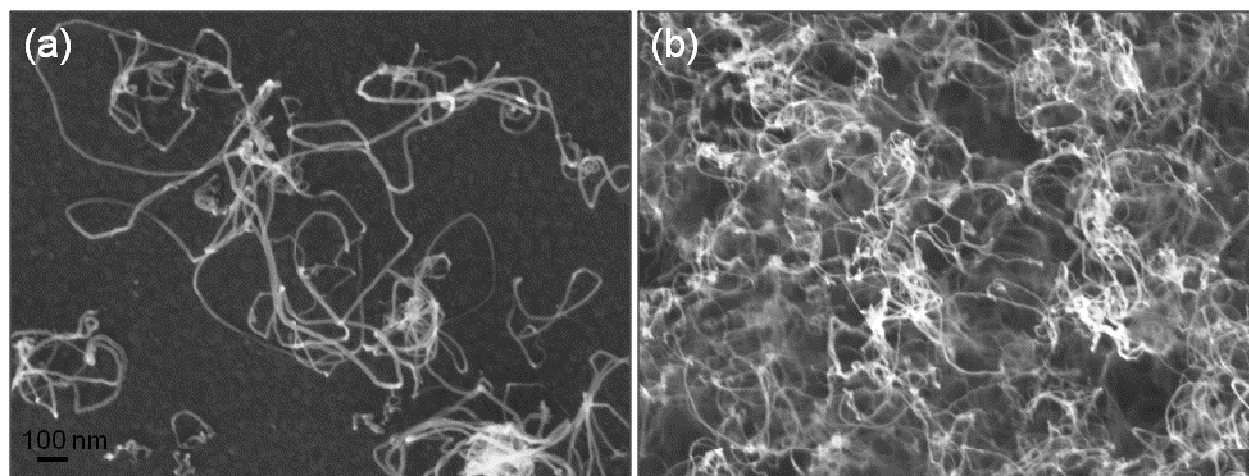
Fig. S3. SEM images of nanoparticles deposited on a Si substrate after CNT growth (a) without and (b) with pre-annealing.

Concerning the removal of DEG; in the reference 18 of this paper, the authors present investigations of polyol molecules covalently bonded to ZnCoO nanoparticles. An infrared analysis as a function of the temperature of annealing (Fig. 12) shows that the characteristic vibrations bands of PEG: $\nu(OH)$ (3382 cm^{-1}) and $\nu(CH_2)$ (2931-2971 cm^{-1}) disappear at 300-350 °C. It means that the PEG chains around the nanoparticles are burnt off during the annealing (530 °C).

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