Nanodevices for correlated electrical transport and structural investigation of individual carbon nanotubes

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Abstract

We report a new approach to the correlation of the structural properties and the transport properties of carbon nanotubes. Through an original combination of UV lithography, custom-made photosensitive sol–gel resist and deep reactive ion etching (RIE), we have successfully integrated membrane technology and nanodevice fabrication for the electrical connection of individual carbon nanotubes. After single wall nanotube (SWNT) deposition by molecular combing and contacting using high resolution electron beam lithography, we obtain a device that allows both the investigation of the nanotubes and the contact regions by transmission electron microscopy (TEM) and the measurement of the electronic transport properties of the same individual nano-object. The whole fabrication process is detailed and the demonstration that the micro membranes are suitable for both TEM inspection and nanoelectrode fabrication is given.

Keywords: Carbon nanotubes; Molecular combing; Nanofabrication; High resolution transmission electron microscopy; Micromembranes; Sol–gel

1. Introduction

With the discovery of carbon nanotubes (CNTs), a new topic for physics came into existence. The discovery of their atomic structure and induced mechanical and electrical properties [1,2], raised many hopes, especially in the microelectronics field. Many were envisioning new transistors and electronic components, shrunk to the size of a single molecule.

Some of those ideas were recently achieved experimentally [3]. Along with the creation of those new devices, some problems emerged. One is the impossibility to control the chirality of the CNTs during their growth process. Because of this impossibility and because of the close relationship between structure and electronic properties, the

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complete correlation between theoretical predictions and real measurements still remains difficult. Whereas many of the basic transport properties are understood, some of the most exciting ones are still toughly debated, mainly because the atomic structure of the connected nanotubes is not resolved. Indeed, most experiments rely on atomic force microscopy (AFM) and scanning electron microscopy (SEM) observations to get structural information. External diameter can be extracted from those observations but no information can be found on the inner structure of the tube.

In this paper, we propose a new experimental design, which enables one to pursue a real structural investigation of the tube electrically measured.

2. Context

Generally, transport measurements on nanotubes are carried out as a two-phase process. The first phase is the determination of the structural properties of the different CNTs found in the suspension. Because of the chiral character of CNTs and the way CNTs are produced, there are always different size and chiralities present in a suspension, necessitating a statistical study. This is done by careful TEM observation or STM inspection of a sample of CNTs. The second phase is the electrical contacting of some CNTs, by one of the many methods actually available, generally using deposition from the suspension on an oxidized silicon sample and electrodes fabrication by nanolithography techniques.

Because of the statistical approach of the first step, no direct link can be made between the CNTs observed and those used in transport experiments. Moreover, the contact zone between the molecule and the electrodes which turns out to have significant influence on the measurements is not properly characterized. In order to reach sufficient accuracy to be able to lift any doubt on the CNTs structure, we need to merge both phases so that we can get fine structural observation of the tube whose transport properties will be probed. In this perspective, we choose to use TEM inspection as a structural analysis technique. The recent progress in the analysis of TEM images and electron diffraction patterns enables to determine both the diameter and chirality of single and double walled carbon nanotubes [4].

3. Device fabrication

On a two side polished, 350 μm thick silicon wafer, we first grew a 100 nm thick SiO_2 layer by dry thermal oxidation. Then we patterned 12 contact pads and contact lines (the contact lines start with a width of 100 μm and end up at 2 μm, converging toward a 40×40 μm wide area, which will be the connection region of the CNTs). This conventional patterning was done with UV lithography (AZ5214 resist on a Karl-Süss MA150 lithography system). Those patterns were transferred by lift-off of a Ti:5 nm/Au:20 nm thin film.

On the backside, using optical back side alignment and appropriate alignment marks, we patterned the same 40×40 μm area defined on the front side by the end of the converging contact lines. This area was etched by deep reactive ion etching (RIE) using a silicon etching process that stops on the thermal oxide layer. The 40×40 μm micro-membrane which was formed was thus aligned on the zone where the carbon nanotube will be contacted and its low thickness (≈100 nm) will allow TEM inspection of the final device. The success of this process is strongly dependent on the choice of the resist which is used to pattern the membrane on the back-side. This photoresist needs to support a long etching time without inducing any stress on the structure and must exhibit very small swelling. We have obtained the best results using a custom made sol–gel resist. Deposited as a 11 μm thick layer, this sol–gel is able to withstand the processing time required to etch the 350 μm of the wafer. The deep RIE etching was done with a mixture of SF_6/C_4F_8 gases in a STS Multiplex ICP system. To ensure homogeneous etching and because of the size of the openings, the total processing time was 4 h 30 s.

Taking advantage of the differential speed between the etching of the SiO_2 and of the Si, the RIE can be stopped just on the SiO_2 layer. We also used a notching type under-etch to remove all the Si which could prove parasitic for TEM observation.

As with every deep RIE process, etching speed, heat dissipation and openings size are linked parameters. But in the case of such a thin membrane, those parameters are even more crucial to avoid membrane breakdown. For a better etching control, we have chosen a very slow etching speed and we have designed a special holder for a better heat dissipation. It enabled us to achieve membranes 100 nm thick (Fig. 1) that are very homogeneous and robust. It should be noted that the etching process was tested down to 46 nm thick membranes without any trouble.

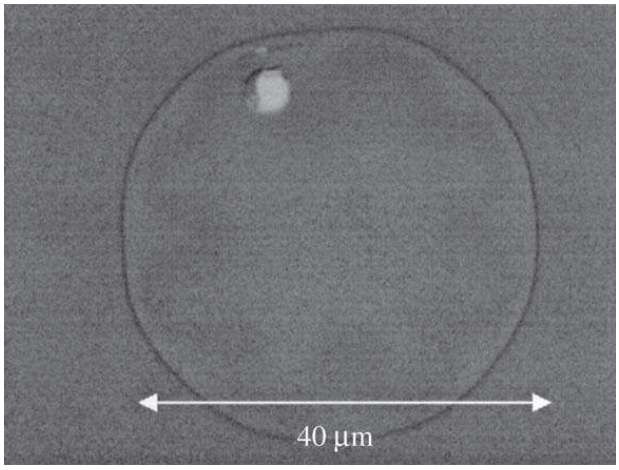

Fig. 1. Optical observation of 100 nm thick SiO_2 membrane.

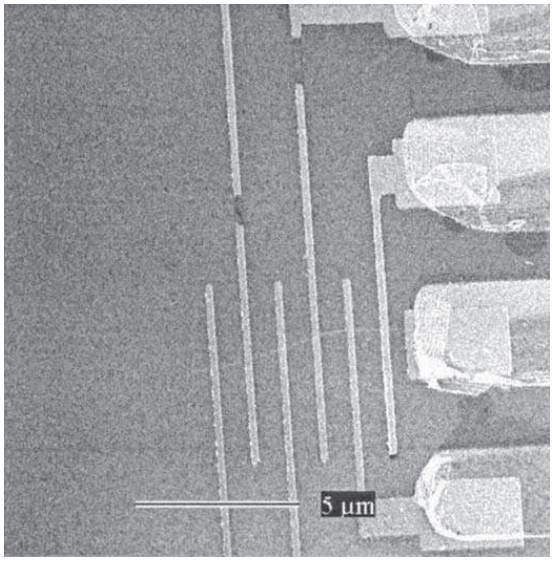

Fig. 2. MEB observation of connected nanotubes, the nanoelectrodes are fabricated after the deposition of the nanotubes by molecular combing and its registration on the surface through AFM imaging [5].

The next step is to perform the deposition of the nanotubes by molecular combing and the subsequent nanoconnection with high resolution electron beam lithography HREBL. The process which has already been described in a previous work [5,6] (Fig. 2) can be applied without any modifications on this new generation of devices equipped with the micro-membranes. It should be noted that the fact that we performed HREBL on membranes got only beneficial effects as we did not have to increase the doses and proximity effects were greatly reduced and the dose latitude of our process was significantly improved. The CNTs used in this work were prepared by a H_2/CH_4 CCVD route [7].

4. TEM observation

To validate the suitability of our micro-membrane fabrication process, TEM observations of nanotubes deposited on these thin regions have been performed. TEM observations were carried out in a Philips FEG CM 20, 200 keV field emission microscope. The originality of this work relies also in the fact that the same experimental set-up is used for making the electron beam lithography and for the TEM inspection. That means that after the connection of the nanotubes and its observation through TEM, it is also possible to perform electron irradiation of the nanotube or electron beam annealing of the contact regions [8] to observe their influence on the structure of the nanodevice and later on its electrical response. Following Kociak et al. [9], we decided to work in the high resolution mode for imaging and in the conventional selected area mode for electron diffraction. Images and diffraction patterns were recorded on conventional photographic film followed by digitalisation.

Our first step has been to check the quality of the membranes in regard to TEM requirements. On a bare sample, we checked for thickness variations, local changes in the amorphousness, silicon monocrystalline residues,..., all of those defects being able to induce either parasitic diffraction artefacts or observation artefacts detrimental for

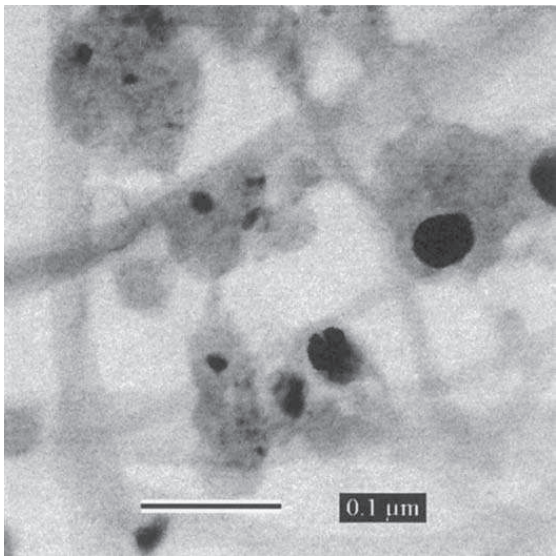

Fig. 3. STEM observation of a random deposition of bundled SWNTs. This experiment is used as a test experiment for qualifying the micro-membranes for nanotube structural investigation.

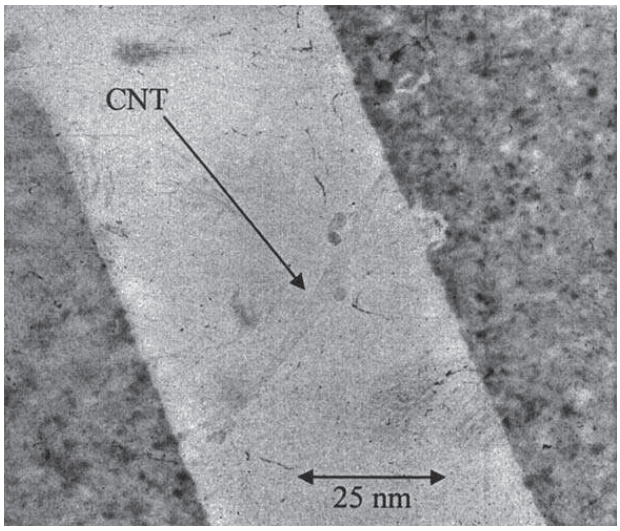

Fig. 5. TEM Bright Field observation of a nanoconnected SWNT. Inter-electrode gap is around 50 nm.

the TEM observation. On a large central zone that covers most of the active zone of the nanodevice, we did not observe any of these artefacts. The membrane also turned out to be very resistant to manipulations and specimen holder mountings. Only ultrasonic agitation for cleaning purposes destroyed the micro-membranes.

Then we checked the contrast ratio between CNTs and the membrane. Because of the difference of thickness and the close atomic weights, a very low contrast was forecasted. Yet a contrast good enough to see bundles of CNTs is achieved (Fig. 3).

Finally, we did a complete process and checked the actual viability of our process (Fig. 4(a) and (b)). We did see the CNTs and the metal nanoelectrodes (Fig. 5). In the high resolution mode, the bundles of SWNTs and their walls are clearly seen (Fig. 6). Using image processing we could confirm the single wall nature of the nanotubes present in this bundle.

Then we focused on the metal–CNT interface. In Fig. 7, one can see the bundle of CNTs and the overlapping of the bundle and the electrode. Defects and inhomogeneities in the nanoelec-

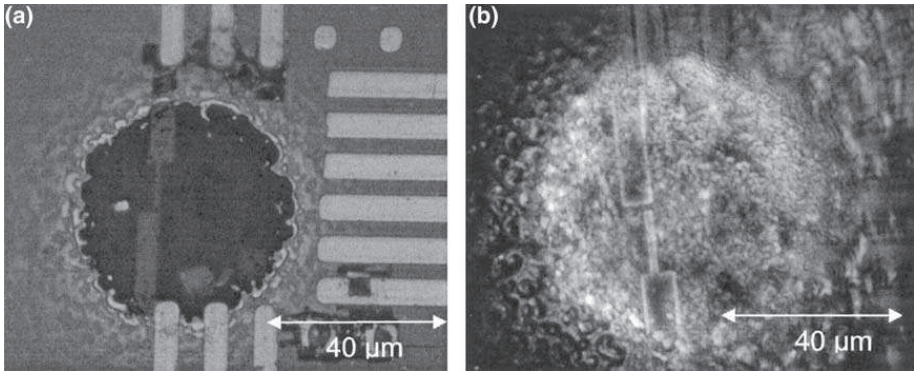

Fig. 4. (a) Optical bright field observation of a micro-membrane aligned on a nanoelectrode device. The dark circle is the circular membrane on which we can distinguish the nanoelectrodes. (b) Optical dark field observation of a micro-membrane aligned on a nanoelectrode device. The disc in the middle of the picture is the circular membrane on which we can distinguish the nanoelectrodes.

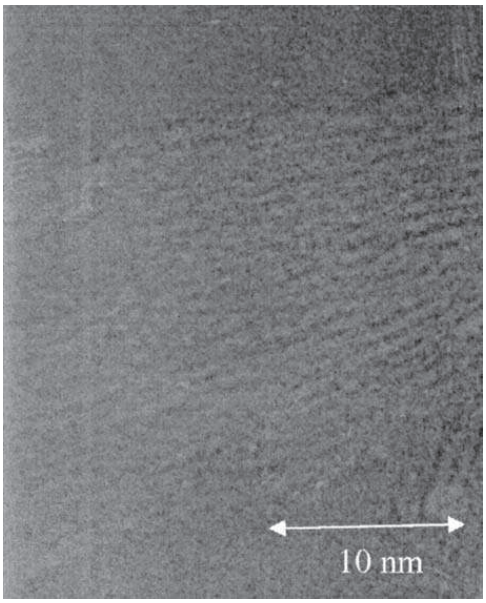

Fig. 6. TEM Bright Field observation of a bundle of SWNTs.

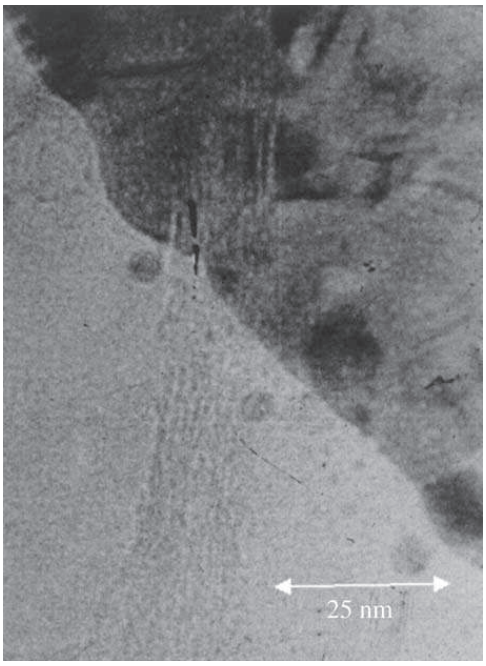

Fig. 7. TEM Bright Field observation of a bundle of SWNT deposited on a nanoelectrode. The walls can be seen both in the gap and interface region.

trodes are also visible. With a generalisation of such observations, we hope to witness the evolution of the CNT–metal junction during the experiments.

Diffraction patterns obtained on our micro-membranes are much less convincing. Fig. 8(a)) displays a typical diffraction pattern where the structure of the nanotubes is not visible due to the large diffuse diffraction rings of the amorphous SiO_2 membrane. As a comparison, we present the diffraction pattern obtained with the same TEM system on self-standing nanotubes (Fig. 8(b)), where the different spots of the tube are clearly visible leading to a possible determination of both its diameter and chirality. This shows that it should be interesting to reduce further the thickness of our micro-membrane.

5. Cross investigation and perspectives

With the process exposed here, and its validation using preliminary TEM observations, we now have a way fully to characterize a nanotube and its connection to electrodes and subsequently to measure the electrical transport properties of the same nanodevice. This achievement opens new perspectives to better correlate electrical and structural properties of nanotubes. It also allows the possible in situ modification of the nanodevice with the electron beam, for injecting intentional defects in the nanotubes or for annealing the electric contacts by e-beam irradiation. Moreover, this process has been clearly designed from the start to be completely compatible with current clean room facilities, enabling a real scaling up of sample production, compatible with a statistical study.

This process can be applied to many other kinds of experiments where the electrical addressing of individual nano-objects is the main objective. TEM characterization thus becomes compatible with nanodevice fabrication opening new routes to better characterize the ultimate nanodevices under investigation. The procedure is obviously non-destructive as the micro-membrane fabrication is already integrated in the fabrication process of the nanodevice itself. We thus avoid one of the main drawback of the TEM technique which usually is seen as a diagnostic method at the end of an experiment rather than a characterization technique available at all the steps of a fabrication process.

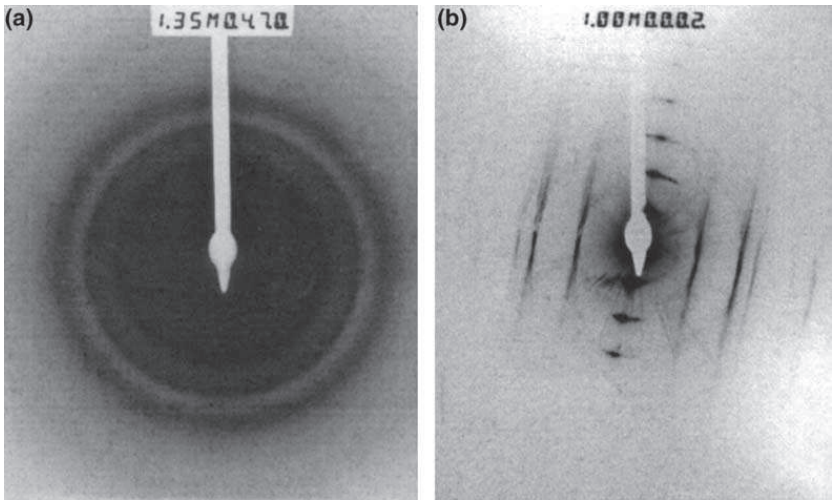

Fig. 8. (a) Electronic diffraction recorded on a NT deposited on a 100 nm thick micro-membrane. (b) Electronic diffraction of a self-standing SWNT.

6. Conclusion

In this paper, we propose a new way combine nanodevice fabrication and TEM characterization. We were able to integrate 40×40 μm micro-membranes on specific nanodevices used for connecting individual SWNTs. The regular process allows the fabrication of 100 nm thick membranes but it has been tested successfully down to 45 nm. The quality and robustness of such membranes have been investigated and showed good compatibility with TEM observation, allowing the observation of the walls of CNTS inside a bundle of SWNTs (i.e., typically some nanometers).

The resulting devices enable transport measurements while retaining the possibility of structural observation, opening the way for cross investigations between structural properties and transport properties of CNTs.

Acknowledgements

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