

Large Scale Production of Carbon Nanotube Transistors: A Generic Platform for Chemical Sensors

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ABSTRACT

We report our work on the fabrication of nanotube-based field effect transistors (NTFET). Nanotubes were grown by chemical vapor deposition using various approaches, including a new formulation of nanotube growth catalysts that were directly patterned using UV lithography. We also report NTFETs based on randomly oriented nanotube networks that have a modulation of one. Finally, we report that a systematical and statistical characterization of millions of devices has led to the development of a robust process that may be useful in large scale production of reproducible, nanotube-based FETs, which, in turn, can be used as a generic platform for chemical sensors.

INTRODUCTION

The discovery of field effect transistors (FETs) based on single wall carbon nanotubes (SWCNT) or nanowires and the discovery of their sensing properties [2, 3], brought a totally new platform to the sensor community. This platform allows for separation of the detection and transduction functions of the sensors. A recognition layer deposited on the nanotube FET (NTFET) can play the same role as synaptic recognition membrane proteins in a nerve cell (specific binding to analytes), and the NTFET itself can play the role of an axon in a nerve cell (communication of the information to the central nerve system). Other platforms have been proposed, including membrane implantation of receptors on a semiconductor based FET [4] or functionalized based cantilevers that rely on mechanic variations induced by an analyte [5, 6]. However, the basic functional units used in these platforms are still in the micrometer range in size [7], still orders of magnitude larger than nanotube sensors. Indeed, diameters of SWCNTs are in the nanometer range, making it possible to fabricate devices sensors arrays with extremely high densities (in the thousand of sensors per square micrometer).

Nanotubes have many advantages when compared to nanowires. Carbon nanotubes have an unequalled sensitivity to minute modifications of their environment, a property reported and reproduced by many different groups [8, 9, 10]. In the case of nanowires, although their compositions are extremely varied [11], diameters are still in the range of 10 nm [12] which means that most of the conducting channels are within the core of the wires, unperturbed by small changes in their local environment.

DISCUSSION

In order to bring nanotube-based devices out of academic labs and into the market, there must be a stable process that (i) integrates fabrication requirements for both nanotubes and

semiconductors and (ii) can be scaled up for mass production. This means mainly to define: 1) A chronology for the process (when to deposit the nanotube); 2) How to deposit the nanotubes and associated processes; 3) How to control the number of nanotubes, their diameter; 4) How to reduce the number of defects ; 5) Deposition of good metal contacts.

We first investigated various sources (laser, arc or CVD – HiPCo- grown) of single wall carbon nanotubes (SWCNT) and deposited them from solution (by spin coating for example) onto substrates. We found that these nanotubes were too inhomogeneous and most had too many defects to produce devices with good electronic performance. Also, since the solubility of unfunctionalized SWCNT is fairly low, deposition of pristine nanotubes at a density high enough for high device production yields became very tedious. Therefore we decided to grow nanotubes directly on 100 mm wafers by CVD using a homebuilt setup. Synthesis parameters have been reported elsewhere.[8, 13, 14] Typically, SWNTs were grown by chemical vapor deposition (CVD) on silicon substrates coated with 200 nm silicon dioxide films. Iron catalyst nanoparticles were exposed to flowing methane and hydrogen at 900°C to grow nanotubes between 1.2 and 1.5 nm in diameter. After growth, optical lithography was used to pattern electrical leads (35 nm titanium capped with 5 nm gold) on top of the nanotubes.

Catalyst patterning by conventional lithography

To date there have been only very few reports SWCNT of growth on 100 mm wafers. The main reports use PMMA photoresist and deep UV lift off lithography. These conditions were reported to afford a very clean and favorable surface for the growth of the nanotubes [15]. Also, various compositions for the growth promoter, that worked fine with e-beam lithography, had been reported, but none were compatible with the rheology as well as the chemistry of a 100 mm wafer standard UV lithography process. We preferred a more widely-used method of lithography, which would be more cost-effective for large scale production. Photoresist was deposited onto a substrate and exposed to UV through a photomask(Figure 1). Once developed, holes were left in the photoresist, which were then filled with a nanotube growth promoter by spin coating. After the photoresist was lifted off, catalyst pads were left on the surface of the wafer. Figure2 shows examples of catalyst pad results produced by this method using various formulations and deposition parameters (Figure 2).

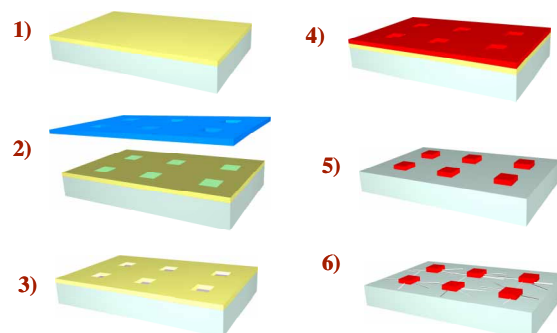


Figure 1: The various steps for deposition of the catalyst pads (1) photoresist deposition; (2) UV exposure using a mask; (3) photoresist development; (4) catalyst deposition; (5) lift-off; (6) nanotube growth by CVD.

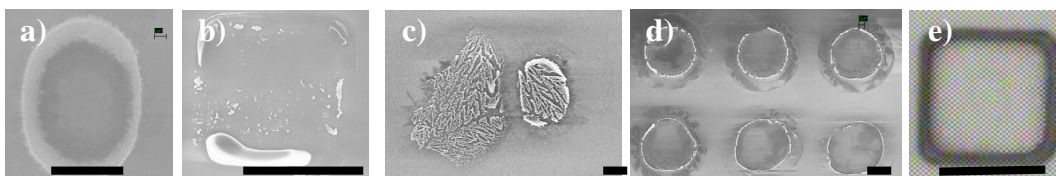


Figure 2: Various results for the catalyst pads depending upon the deposition method and catalyst formulation (scale bar is 10 μm). (failures (a-d) versus successful one (e))

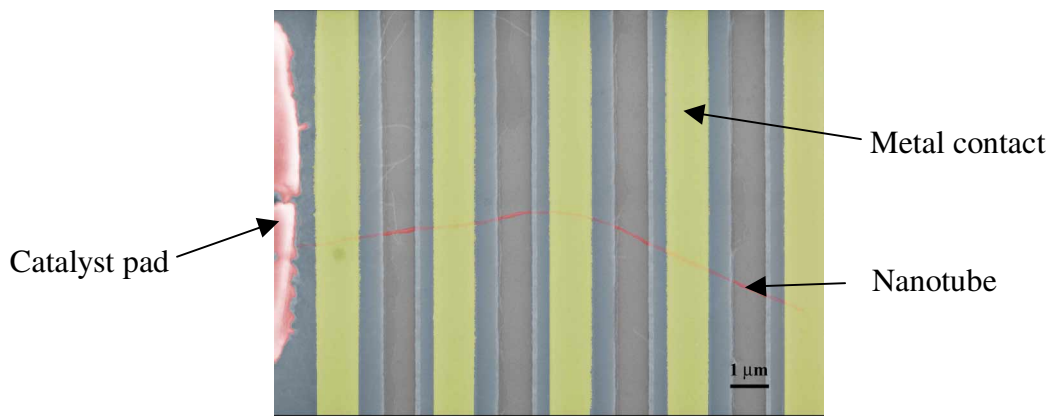


Figure 3: A SWCNT grown from the catalyst pad on the left is contacted by metal lines.

The concentration and size of the metal nanoparticles that are used to promote the nanotube growth are critical in controlling the number and diameter of nanotubes. It has been widely accepted that during the CVD process, the metal particles become super-saturated with carbon, which subsequently precipitates out of the particle in the form of a nanotube [16]. The diameter of the nanotube is correlated to the particle diameter in the first order. The number of nanotube walls depends both on the particle size and other parameters, such as temperature. Too high a temperature tends to favor multiwalls.

When all parameters are optimized, single wall carbon nanotubes can be grown at specific locations (Figure 3). Various recipes have been reported for the deposition of good metal contacts. We use titanium covered with gold.

Direct patterning of catalyst

It would be useful if catalyst patterning could be simplified to reduce the number of steps, especially for large scale production. We investigated various catalyst compositions that could be patterned directly. In this approach (Figure 4) a thin layer of specially formulated catalyst was deposited, exposed to UV and developed. Patterned catalyst pads were left on the surface, and the rest of the surface was clean [17]. Figure 4 shows an AFM image of the resulting grown nanotubes.

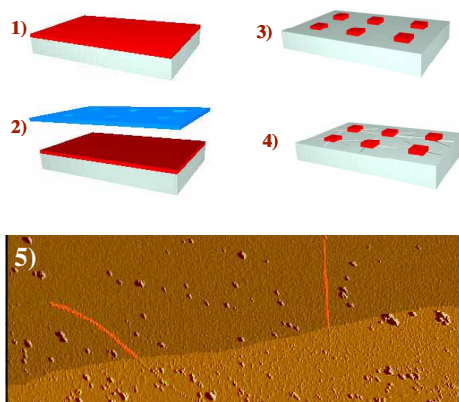


Figure 4: (1) Catalyst deposition; (2) UV exposure using a mask; (3) Development; (4) Nanotube growth by CVD; (5) AFM image of the nanotubes growth from the patterned catalyst (contrast has been modified to show the catalyst zone – brighter zone-).

Random single SWCNT network

In the processes presented above, the focus was on placing the nanotubes accurately on the surface. However, depending upon the application, one might prefer to use a network of single SWCNTs instead. Nanotube mats made by assembling SWNT bundles into a dense net, often referred to as “buckypaper” have been studied. The mats show very poor electronic properties, low reproducibility and, to our knowledge, could not be used to form FETs [18]. Also, if these mats were to be used in sensor applications, the large number of nanotubes buried deep within the bundles would tend to greatly decrease the signal/noise ratio of the devices. Indeed, the inner nanotubes would contribute to the conductance of the device but not to the sensing, since most analytes would not diffuse into the bundle.

At the time we started this program, there was no reported method to grow a loose network of randomly oriented single SWNTs directly on the surface of a wafer. The only method reported grew a SWNT network on a layer of mesoporous catalyst. In order to make devices, contacts had to be deposited directly on the rough catalyst layer, which could not be a very reproducible process. We developed processes for making thin, reproducible networks directly on the surface of a 100 mm wafer. A first method used an oxygen plasma to disperse catalyst material. In this treatment, catalyst pads were eroded, spewing catalyst nanoparticles across the wafer surface. Nanotube networks, subsequently grown by CVD, have a density that is a function of the

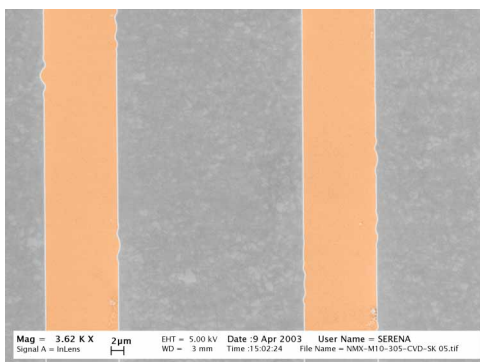


Figure 5: SEM image of a dense network of nanotubes between two electrical contacts

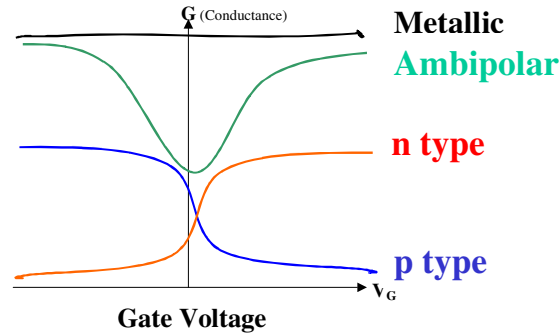


Figure 6: Various transfer characteristics (Source-drain current versus gate voltage) observed for nanotube based transistors.

intensity of the plasma. Patterning of the grown nanotube network can be done easily by protecting the desired areas with photoresist and removing the unprotected areas by etching. We have also developed other methods in which metals nanoparticles are deposited on the substrate prior to the CVD.

When devices are made with a random network of nanotubes instead of only a few nanotubes, the wide range of nanotube electronic behaviors are averaged (Figure 6). Indeed, it has been predicted and measured [19, 20] that, depending upon their chirality, nanotubes can be metallic or semiconducting with a wide range of electronic gaps. In order to get good averaging and semiconducting character, care must be taken to keep the nanotube length much shorter than the distance between the source and drain so that the all electronic pathways involve many nanotube interconnects. These interconnects have been thoroughly studied [21]. From them one can derived that, in a single nanotube network, the probability of having purely metallic electronic pathways between the source and drain can be decreased if the length of the nanotubes remains small compared to the source-drain distance (c.a. the metallic nanotube network is under the percolation threshold) [22]. Reducing the number of metallic pathway is required for a good modulation to be obtained. Thus, controlling the network density allowed us to form random network FETs having full modulation (Figure 7). Also, since one can easily adjust the distance separating the source and the drain, as well as the nanotube length, one can easily tune the conductance of the devices [23].

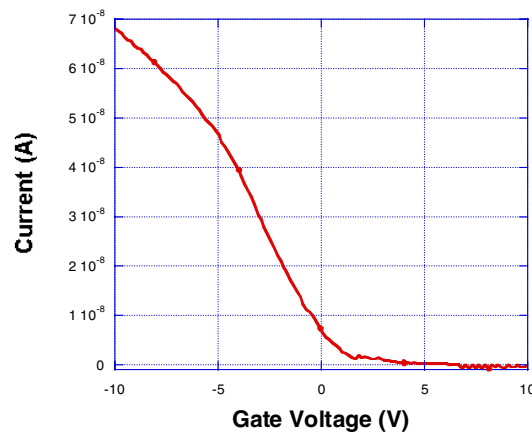


Figure 7: Transfer characteristic of a nanotube network device, typical of a p-type FET.

Large scale production of reproducible devices

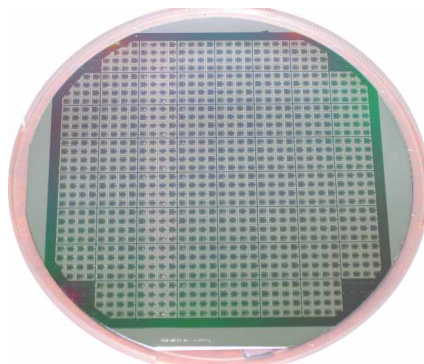


Figure 7: 100 mm silicon wafer with tens of thousands nanotube FET based sensors

In order to commercialize any product based on single nanotubes FET it will be necessary to produce a large number of devices reproducibly. This could be done by testing all devices and selecting the good one, but this is both inefficient and expensive. It would be much better to develop a process stable enough to produce highly reproducible devices directly. We have put in place automated measurement and data reduction of the electronic characteristics of our devices (including hysteresis [24]). We can measure up to 100,000 devices a week and directly correlate variations in the statistical analysis of the data to modifications in the process. This quick feedback loop has helped us to develop a process leading to high yields in high conductance and modulation devices, whether the devices are based on a few nanotubes or on a random network.

CONCLUSIONS

We have reported our findings on the fabrication of nanotube-based field effect transistors (FET). Various approaches are reported to grow the nanotubes by chemical vapor deposition, including the development of a UV lithography lift off procedure of the catalyst and a new formulation of nanotube growth catalysts allowing for direct patterning using UV light. We have also reported FETs based on randomly oriented SWCNT networks and show that reproducible transistors with a modulation of one can be obtained with these structures. Finally, systematic and statistical characterization of millions of devices has helped to increase the robustness of our processes for the large scale production of reproducible nanotube-based FETs, a generic platform for chemical sensors.

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