Controlled Deposition and Applied Field Alignment of Single Walled Carbon Nanotubes for CNT Device Fabrication.

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ABSTRACT

Carbon nanotubes (CNTs) offer great potential for advanced sensing devices due to their unique electronic transport properties. However, a significant obstacle to the realization of practical CNT devices is the formation of controlled, reliable and reproducible CNT to metallic contacts. In this work, a procedure for the deposition and alignment of CNTs onto metallic electrodes using chemically functionalized lithographic patterns is reported. This method uses photo and electron beam lithography to pattern simple Cr/Au thin film circuits on oxidized Si substrates. The circuits are then re-patterned with a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTES) to specify desired CNT locations between electrodes. The application of an electric field to the metallic contacts during the deposition of solution suspended single walled CNTs causes alignment of the CNTs in the field direction. This method consistently produces aligned CNTs in the defined locations.

INTRODUCTION

Over the past several years, carbon nanotubes have been in the spotlight of materials research due to their remarkable strength and conductive properties [1]. The single walled carbon nanotube (SWNT) is the strongest known material with a Young's modulus of approximately 1TPa making it an excellent candidate to be the mainstay of next generation structural materials. Also, the SWNT can be either a semiconductor or a metal based on the chirality of the tube while ballistically transporting electrons and maintaining their spin state down the length of the tube [1]. By exploiting these unique electronic transport properties, CNTs offer great potential for use in advanced sensing devices. However, a significant obstacle to the realization of practical CNT devices is reproducible, controlled formation of reliable CNT-to-metallic contacts.

CNTs can be immobilized on a surface via electrostatic interactions between the nanotubes and surface-bound moieties. The strength of this interaction greatly depends on the nature of the terminal groups on the substrate. CNTs have previously been shown to adhere strongly to amino-terminated surfaces and weakly to methyl-terminated surfaces [2, 3, 4].

In this work, we report a procedure for the deposition and alignment of CNTs onto metallic electrodes using standard lithographic techniques and chemical surface functionalization as depicted in Figure 1. Photo and electron beam lithography first are used to pattern simple Cr/Au thin film circuits on oxidized Si substrates. The samples are then re-patterned with a self-assembled monolayer (SAM) of 3-aminopropyltriethoxysilane (APTES) to delineate the desired

CNT locations between electrodes. During the deposition of solution-suspended single walled CNTs, the application of an electric field to the metallic contacts causes alignment of the CNTs along the field direction. This method consistently produces aligned CNTs in the defined locations.

EXPERIMENTAL

The substrates used in all experiments were silicon wafers upon which a 500 nm SiO_2 layer had been thermally grown. Prior to modification, the wafers were cleaned in "piranha" solution (70:30 H_2SO_4:H_2O_2) for 30 minutes at 100 ^oC to remove any organic contaminants present. After cleaning, the wafers were rinsed with de-ionized water four times, ethanol four times, and finally dried with a nitrogen stream.

Depositing gold electrodes on the surface was accomplished by conventional photo and electron beam lithographic techniques. First, a layer of photoresist [5] was deposited on the surface by spin coating at 3000 rpm for 30 sec. Square windows were defined on the photoresist layer by UV exposure of the resist through a 100-mesh TEM grid. Following development of the photoresist, an adhesion layer of Cr (10nm) and a thin layer of Au (20 nm) were evaporated onto the surface, resulting in an array 205 μm^2 contact pads separated by 50 μm. To create the thin parallel electrodes, a layer of PMMA was deposited onto the array by spin-coating at 3500 rpm for 30 sec [6]. An electron beam was then used to define pairs of electrodes connected to neighboring pads. The electrodes were designed so that they were 300 nm wide and had a spacing of 1 μm. Following development, the sample was cleaned with an oxygen plasma to remove any residual PMMA in the defined locations. Cr (10 nm) and Au (20 nm) were then evaporated onto the surface, followed by lift-off of the remaining photoresist.

To define the areas for CNT deposition, another thin layer of photoresist, was deposited onto the electrode surface by spin-coating. Using the previously deposited electrodes for alignment, an electron beam was used to expose small areas of the photoresist such that portions of each electrode were exposed. After development, the sample was again cleaned with an oxygen plasma, and then immersed in an aqueous 1 mM APTES solution for 20 minutes to deposit a self-assembled monolayer of amine-terminated moieties. After immersion, the sample was rinsed four times with water and then dried in a nitrogen stream, followed by lifting-off of the undeveloped photoresist. A diagram of the resulting device is shown in Figure 2.

Purified SWCNTs synthesized by the HiPCO process were purchased from Carbon Nanotechnologies, Inc., and used as received [7]. A small amount of the CNTs were dispersed in toluene by ultrasonication for 24 hours. Because the concentration of CNTs in the toluene was very small, only a slight discoloration of the solution could be observed.

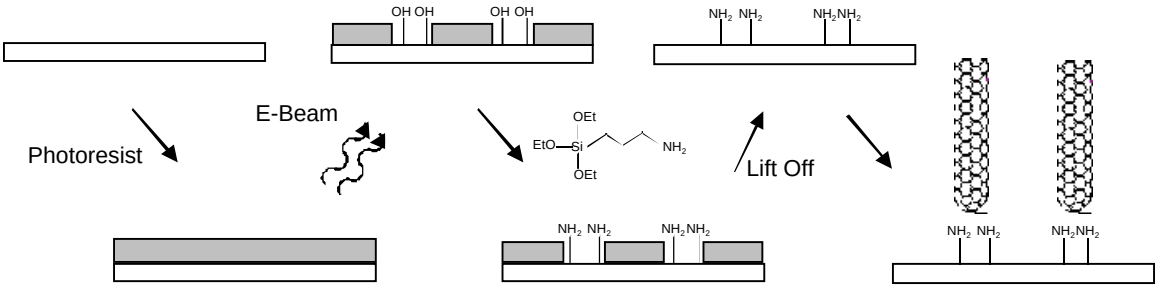

Figure 1. Lithographic patterns are created in e-beam photoresist. Amino terminated groups are then deposited into nanotube attracting patterns. The remaining photoresist is removed, nanotubes are deposited with the applied field present and the excess nanotubes are lifted off.

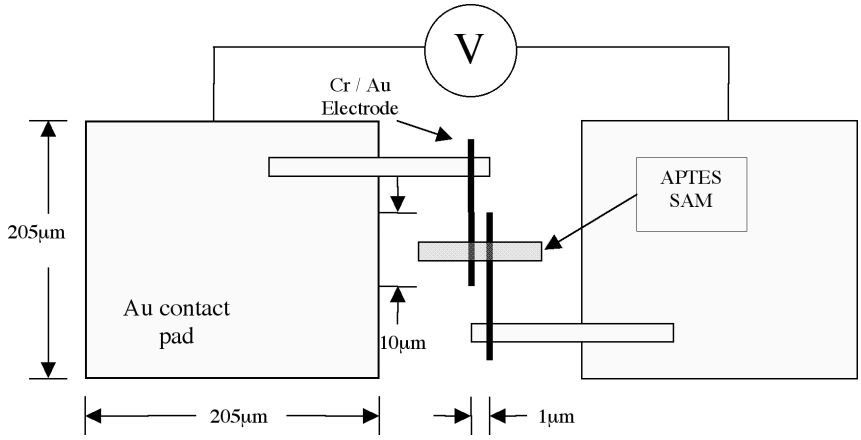

Figure 2. Diagram of simple CNT circuit with Cr / Au contact pads and electrodes fabricated by basic photo and e-beam lithography methods.

Deposition and alignment of the CNTs on the APTES-modified areas was performed using a procedure similar to that described by Chen et al [8]. Several drops of the nanotube dispersion were placed on the sample, covering the surface. Two spring-loaded pins were then used to make contact with the pads and a $10V_{pp}$ sine-wave at 5 MHz was applied to the pads for 6 minutes to generate an electric field. After applying the electric field, the sample was immersed in N-methylpyrrolidone, sonicated for 10 seconds, and blown dry with a nitrogen stream [9]. Immersion in N-methylpyrrolidone was found to remove CNTs from all parts of the silicon surface that had not been modified with APTES. The dispersion and alignment of the SWCNTs was verified by imaging with an atomic force microscope [10].

RESULTS AND DISCUSSION

To verify the effectiveness of this deposition method, various lithographic patterns have been designed, fabricated, and tested. Two different patterns are displayed below in Figures 3 and 4. Figure 3 shows an AFM image of a 4 x 13mm rectangular section of APTES positioned over the Au / Cr electrodes illustrated in Figure 2, after depositing the CNTs and lifting off the excess. Here we can see how the application of the electric field has aligned the CNT bundles to the field lines and how the CNTs are localized to the APTES modified surface. AFM topography measurements of the aligned nanotubes indicate relatively large bundles of SWCNTs, with bundle diameters measuring 10-30nm.

Resistively measurements performed on various aligned and unaligned samples show a large drop in the contact resistance in the aligned junctions. Generally, resistance values in the tens of kΩ's are measured in the aligned junctions while similarly processed unaligned junctions show resistances in excess of 10MΩ. In a similar attempt to align Au nanowires, Smith et al [11] noticed that when a nanowire bridges adjacent electrodes, the electric field between them is eliminated since the nanowire shorts out the electrodes. This then greatly impedes further alignment of additional nanowires. With CNTs, the large contact resistance of the nanotubes prevents the shorting out of the electrodes and a large potential difference is still seen instead of being eliminated while the field is applied.

The electric field alignment not only aligns the CNTs but also concentrates them between the electrodes. This effect can be observed in both Figures 3 and 4 where large populations of CNTs are located between the electrodes. Similar results have been reported by X.Q. Chen et al [8] in their CNT alignment work. Away from the electrodes, there is less alignment and more even dispersion due to a weaker field in those locations.

The circuit used in Figure 4 is identical to Figure 3 but the pattern used for the electron beam lithography is different. In this case, we produced aligned CNTs in three locations between the electrodes by patterning the APTES in three parallel lines, which intersect the electrodes.

This process could be used to consistently deposit single SWCNTs or small bundles of SWCNTs between electrodes. One method for realizing this is to achieve better dispersion of the CNTs in solution. Here we report bundles approximately 10-30nm in diameter between the electrodes, for many applications single tubes are most desirable [12]. Our testing has also shown the quantity of CNTs found in the CNT - electrode junctions can be controlled by adjusting the density of CNT suspended in solution. Diluting the solution results in fewer CNTs found between the conductive traces.

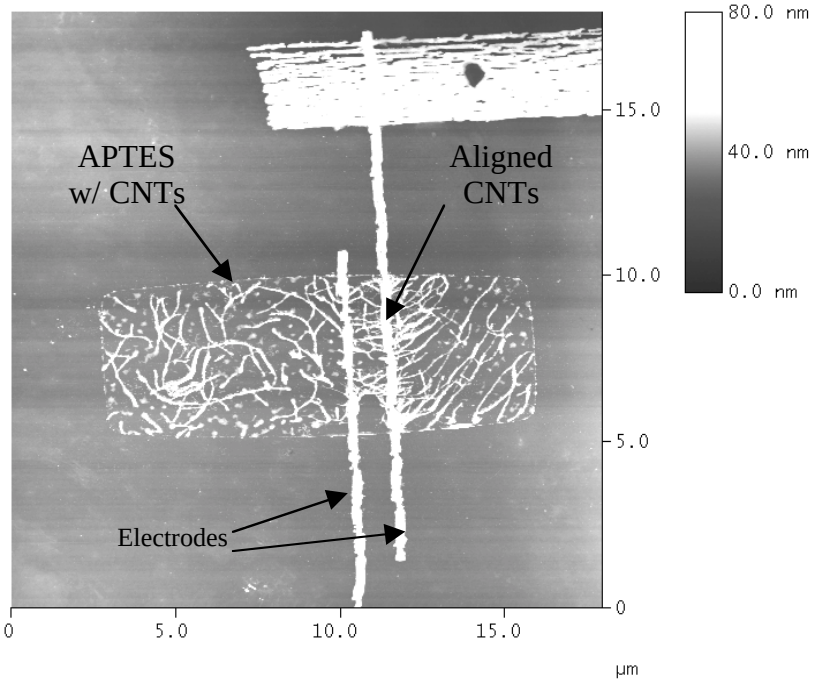

Figure 3. Applied field alignment of SWCNTs on a patterned APTES monolayer, 4x13 mm.

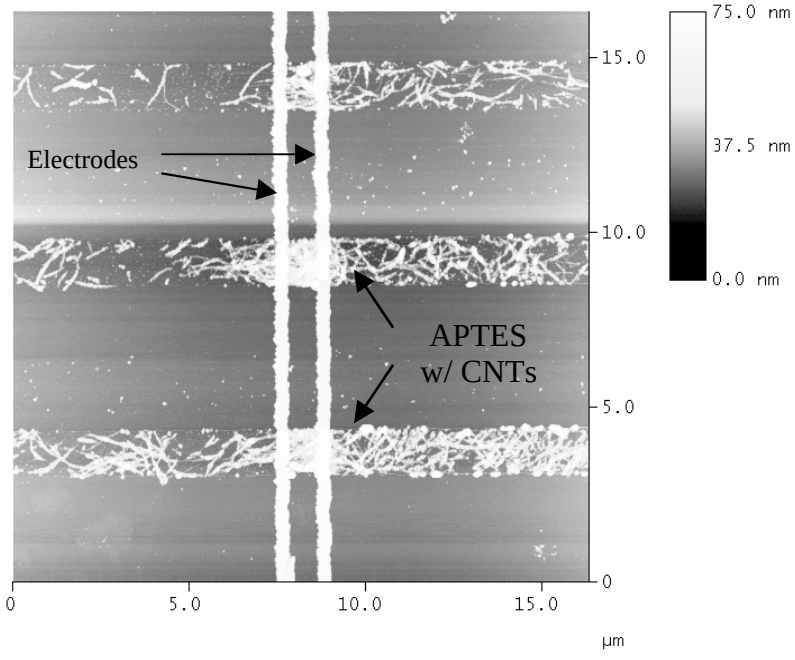

Figure 4. Applied field alignment of SWCNTs between electrodes and located only with in the patterned locations.

CONCLUSION

A method of controlled CNT deposition and electric field alignment has been presented which enables reproducible, controlled, formation of CNT-to-metallic contacts. The ability to deposit nanotubes in precise locations while controlling their orientation using e-beam lithographic patterning, self-assembled surface functionalization, and applied field alignment techniques has been demonstrated. Further refinement of the technique is currently underway to extend this process to the deposition of single SWCNTs between electrodes. The application of this process, which has been shown to consistently produce aligned CNTs in the defined locations, should help to overcome some of the obstacles in the path towards practical CNT device development.

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