# Self Aligned Multi-Layer Electrodes with Nano-Gap for Fluidic and Magnetic Assembly of Carbon Nanotubes

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## ABSTRACT

A self aligned nano scale gap between multiple metal layers has been fabricated using a newly developed technique of controlled undercut and metallization (CUM), and applied for the assembly of an individual carbon nanotube (CNT). The new method enables conventional optical lithography to fabricate nano-gap electrodes and self aligned patterns with nano scale precision. Individual CNTs were assembled over the fabricated nano-gap electrodes by the fluidic assembly using magnetic attraction on a residual catalyst. This work may allow the mass production of self-assembled carbon nanotubes for nano electronic devices or biosensors.

***Keywords***: controlled undercut and metallization, nano gap, self assembly, carbon nanotube, self align

## 1 INTRODUCTION

Nano-scale components such as nanoparticle, nanowire and CNT have shown tremendous potentials for applications in electronics, biosensors, and optical devices. [1] In particular, CNT has its own advantages compared with the other nano-materials in the sense of strong mechanical property, fast electron mobility and high sensitivity from large surface ratio to volume. [2] However, the integration of nanotubes with electrical architectures has remained as a major obstacle to utilize the superior properties of CNT for practical devices. [3, 4]

For the assembly of nanotubes, there have been various trials such as dielectrophoretic (DEP) capturing [5], direct growing on the electrode [6] and patterning through the use of chemically functional groups [7]. However, DEP capturing requires a power connection to electrodes for the assembly and cannot selectively assemble semiconducting CNT which is useful component for transistors and biosensors. Also, the growth of nanotubes on patterned electrodes requires a high temperature process, and it is difficult to control the number of nanotubes grown on the electrodes. Functionalizing nanotube to chemically bind at a target position is suitable for a mass producible technique, but chemical groups can change the electrical property of CNT.

In addition to the manipulation of nanotubes, the fabrication of nano-gap between electrodes is also a challenging issue for implementing nanotube-assembled devices. Because the sonication process for dispersing nanotubes in solution results in mechanical breaking of nanotubes, the length of individual nanotubes could be reduced to the sub-micron scale. In order to ensure successful contact of the sub-micron length nanotubes over the electrodes, the nano-scale gap between the electrodes is desirable for the CNT assembled devices.

During the development of microfabrication technology, optical lithography has played a key role because of its advantages in rapid, reproducible, uniform, cost-effective and precise processes. For the nano-scale fabrication, an advanced optical lithography with alternative light sources such as deep UV and X-ray has achieved the patterning of sub-micron features. In spite of these advances, nano-scale patterning is still difficult to fabricate with such lithography due to the high cost of equipment set-up, mask fabrication, light source and photoresist for X-ray or deep UV lithography. Moreover, the alignment of multiple metal layers with nano scale precision is considered as one of the most difficult tasks in optical lithography. Recently, nano imprint lithography (NIL) has been extensively explored and successfully achieved sub-100 nm patterns. [8] However, NIL has suffered from a low yield in large area fabrication, a lack of long lasting stamp, and a difficulty in alignment for multi-layer processes.

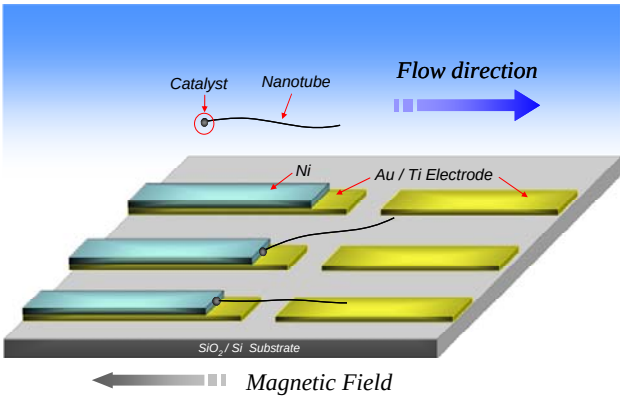


*Figure 1. Illustration of fluidic self-assembly of carbon nanotubes between nano-gap electrodes by magnetic attraction on a residual iron catalyst.*

Previously, we demonstrated precise fluidic assembly of individual CNTs by magnetic attraction on a residual catalyst as depicted in Figure 1. [9] In this technique, while the solution containing CNTs flows over a nickel (Ni) patterned electrode, a residual iron catalyst at one end of a nanotube is magnetically attracted to the Ni pattern which induces magnetic force from the external magnetic field. Then, a fluidic shear force aligns the nanotube along the flow direction. This technique does not require pretreatment on the nanotube for the assembly, thereby exploiting the full functionality of pristine nanotubes. Additionally, an electrical connection to the electrodes and a restricted design of the electrode-shape for concentrating electric field is not necessary. Also, this technique does not have the selectivity between metallic nanotube and semiconducting nanotube, and thus it is possible to integrate multiple transistors only with semiconducting CNTs.

However, our previous method requires the use of expensive fabrication equipment such as the e-beam lithography to achieve a small gap between electrodes and a precise alignment between Ni and Au/Ti electrodes. In this work, we have explored and realized a new approach to fabricate self-aligned electrodes using optical lithography for precise assembly of CNT. The technique developed in this work is fully processed with i-line optical lithography (365 nm wavelength of UV light source) with Shipley 1818 photoresist, which is usually available from most clean room facilities. Accordingly, this approach enables inexpensive and fast process to fabricate nano-gap electrodes, suitable for mass production of nano-scale features. Furthermore, this method allows alignment between Ni and Au/Ti electrode with sub-micron precision by the self-aligning method. As a result, our newly developed technique successfully fabricates individual CNT assembled devices through a simple and inexpensive process.

## 2 FABRICATION

During an isotropic wet-etching process, an undercut is inevitably generated under the lithographically patterned photoresist. Utilizing this undercut, directional metal-deposition by e-beam evaporation was performed to generate the gap between the first etched patterns and second deposited pattern. [10] The gap between the two electrodes can be controlled by increasing the etching time for the first deposited metal-layer. Also, the contact length of nanotube on the electrode was controlled by the second etching of the Ni layer which increases the undercut between the Ni and the electrode gap.

The detailed procedure for the suggested fabrication is described in Figure 2. First, Au/Ti layer (50 nm / 10 nm) was deposited on a $SiO_2$/Si substrate, followed by Ni (100 nm) deposition. Conventional optical lithography with a mask, which has a minimum feature size of 10 μm, was processed. The Ni layer was etched at room temperature with the etchant which is the mixture of nitric acid ($HNO_3$), acetic acid ($CH_3COOH$) and DI water with the ratio of 3:1:1. After first etching of Ni layer, gold etching was performed at 50°C with a mixed solution of iodine (40 g), potassium iodine (10 g) and DI water (400 ml). Additional Ni etching was completed for the fabrication of Au/Ti contact area with nanotube by increasing Ni undercut at Ni/Au/Ti electrode. Followed by the formation of the controlled undercut, a second metal deposition of Au/Ti (50 nm/ 10 nm) was performed by e-beam evaporation. Finally, an array of 10 μm wide electrode was patterned by the

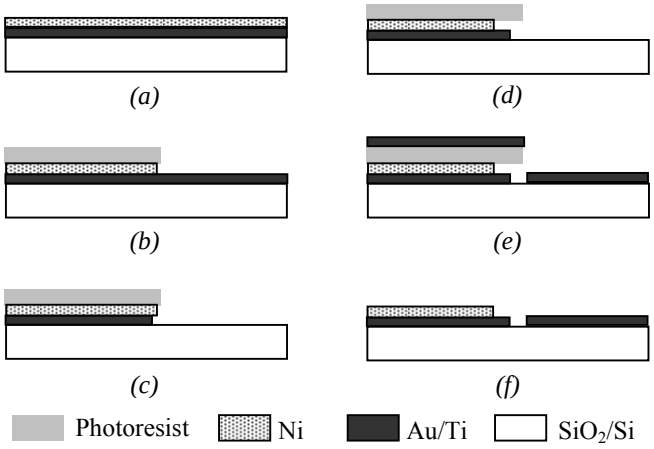


*Figure 2. Fabrication procedures. (a) Ni/Au/Ti deposition on Si/$SiO_2$, (b) PR patterning & Ni Etching, (c) Au/Ti Etching with undercut, (d) 2nd Ni Etching generating contact area for CNT assembly, (e) 2nd Au/Ti deposition, (f) Lift off.*

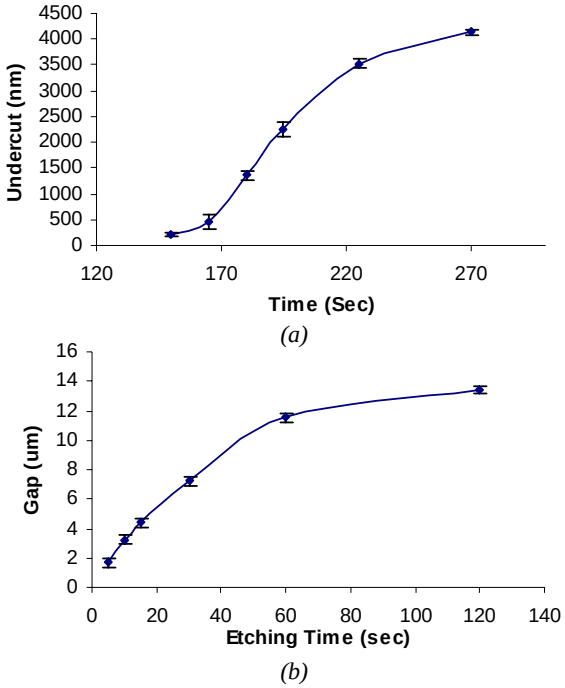


*Figure 3. Gap generation of (a) Ni with respect to etching time and (b) gold under Ni layer as a function of etching time.*


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additional photolithography, crossing the fabricated nano-scale gap.

For the synthesis of CNT, the previous reported CVD process was performed. [11] The synthesized CNT was characterized with high resolution transmission electron microscopy (HRTEM) and proved to be a multi wall nanotube (MWNT) with 20 nm diameter. By reducing the size of iron catalyst, double walled nanotubes (DWNT) were also synthesized. HRTEM detection showed the synthesized nanotube had two carbon shells with outer diameter of 10 nm.

The grown nanotubes were dispersed in a surfactant solution which is a mixture of 1 wt% sodium-dodecylbenzenesulfonate (SDBS, Sigma-Aldrich Co.) in DI water. A microchannel with 20 μm thickness and 2 mm width was fabricated by soft lithography using PDMS. While the solution containing dispersed CNT was flown in the microchannel, external magnetic field of 0.7 T was applied to the Ni patterns. The flow rate of 10 μl/min is selected for magnetically capturing iron catalyst with the fluidic alignment of nanotube. After this assembly of CNT on the electrode, the PDMS microchannel was detached from the substrate for SEM detection and electrical characterization. The substrate was dried at room temperature under the external magnetic field, which prevented a possible detachment of nanotube while drying.

## 3 RESULTS AND DISCUSSION

The time-dependent generation of the undercut during etching the metal layer of Au and Ni is plotted in Figure 3. There are three phases of the etching rate as increasing the etching time. For first period, etching molecules in the etchant are consumed while contacting the open area of metal, leading to a slow undercut generation. During second phase, the undercut rapidly increases because the active etching molecules massively diffuse under the photoresist. Finally, mass-transport of etching molecules is limited by the consumed etchant, so that the undercut is slowly generated and finally saturated.

Figure 4 shows a SEM image of the fabricated electrodes, where the bright upper electrodes have the Ni layers on the Au/Ti electrode with nano-gap and the lower electrodes are the Au/Ti electrodes only. In order to assemble the shortened nanotubes during the dispersion in solution, the Ni patterns were designed to have a sub-micron distance with the gap of Au/Ti electrodes. The distance between Ni and Au/Ti gap determines one of the contact lengths for the assembled nanotubes. The dimensions of each electrode are 10 μm width, 1 μm gap and 600 nm contact distance.

Figure 5 shows the enlarged SEM image of square box in Figure 4 to clarify an image of assembled nanotube. As the flowing volume of CNT solution was increased, the more nanotubes were assembled on the electrode. Also, small volume of CNT flowing reduced the probability of the CNT assembly on each electrode. Ensuring the success

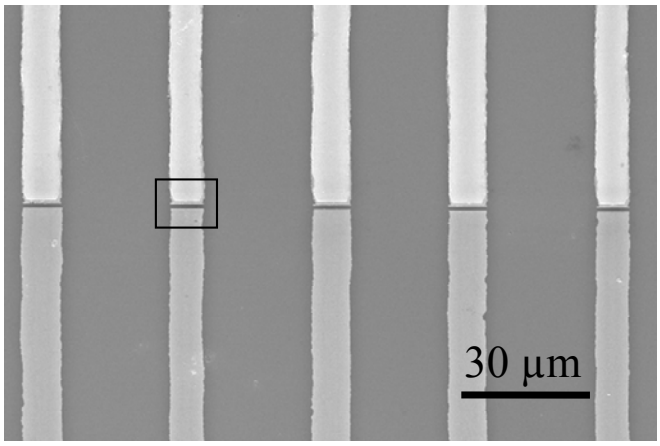


*Figure 4. SEM photograph of fabricated nano-gap electrodes by developed CUM technique.*

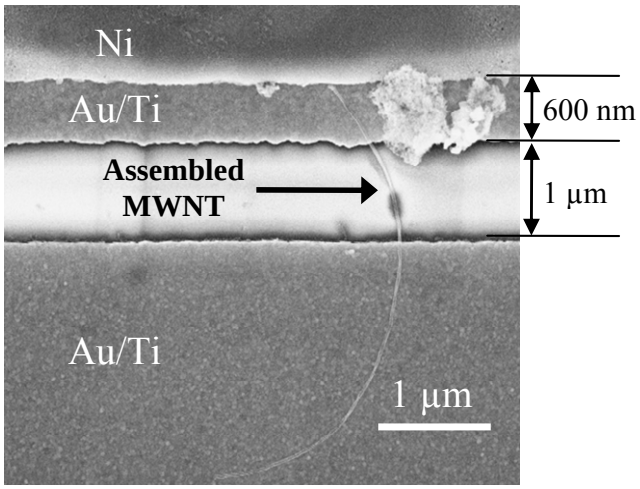


*Figure 5. SEM photograph for the enlarged picture of square in figure 4 showing magnetically assembled CNT at Ni pattern on the Au/Ti electrode.*

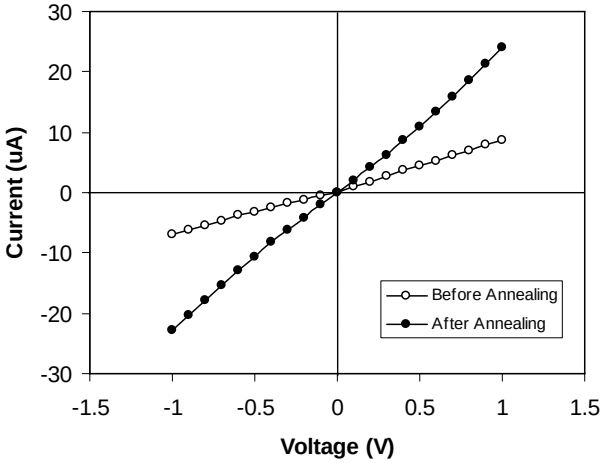


*Figure 6. Measured I-V curve for the aligned MWNT.*

of the assembly to be more than 80 %, the flowing volume of CNT solution was optimized to 10 μl. With this

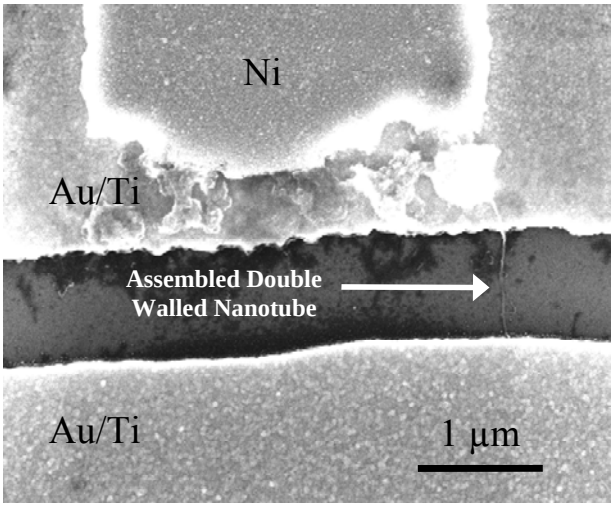


*Figure 7. SEM picture of the assembled DWNT.*

condition, the number of assembled nanotubes ranged between one and five.

Both the synthesized MWNT and DWNT were successfully assembled on the fabricated electrodes. After the assembly of nanotubes, V-I measurements were performed for electrical characterization of the assembled nanotubes. As MWNTs reported with a metallic property in previous experiments [12], the measured electrical result shows stable ohmic behavior as shown in Figure 6. Annealing the CNT assembled device at 120 °C for 2 hours was performed to reduce the contact resistance between nanotube and electrode. After annealing, the resistance of MWNT assembled electrode was lowered from 126 kΩ to 42 kΩ.

Figure 7 shows the assembled DWNT on the nano-gap electrode, which had a narrower width of Ni pattern to localize the assembled nanotubes at the middle of Au/Ti electrode and to reduce the assembly of multiple nanotubes at one Ni pattern. As shown in Figure 8, the electrical measurement shows a schottky contact between nanotube and metal electrode, demonstrating the assembled DWNT has a semiconducting property. The asymmetry of current response in positive voltage and negative voltage would come from a different contact condition of electrodes such as contact length and oxidation.

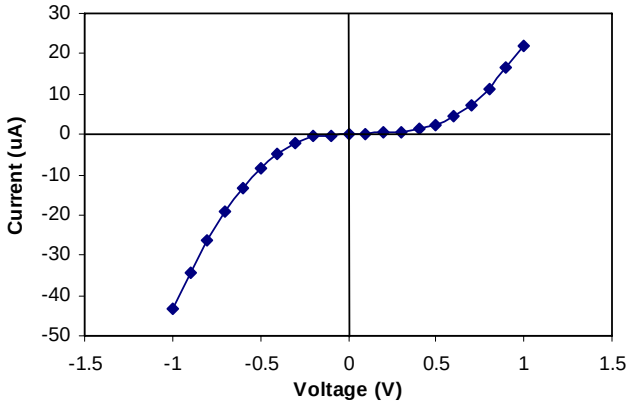


*Figure 8. Measured I-V curve for the assembled DWNT.*

## 4 CONCLUSION

Nano-gap electrodes assembled with DWNT and MWNT were successfully fabricated in this work. The fabrication for nano-gap electrodes and the assembly of nanotubes consist of simple, inexpensive and mass-producible processes. Also, the individual pristine CNTs were reliably assembled on the nano-gap electrodes with the high yield of 80 %. These assembled nanotubes could be readily applied to various functional nano electronic or biosensing devices utilizing the superior capability of CNTs.

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