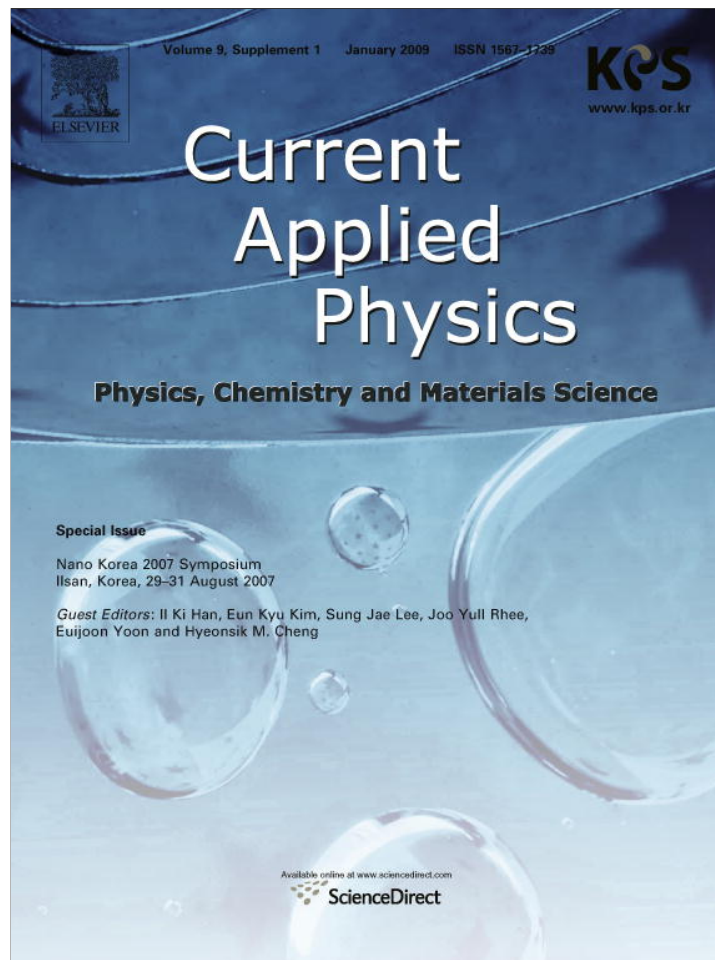


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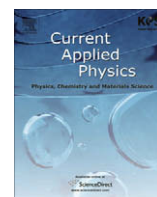
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## Selective placement of single-walled carbon nanotubes on pre-defined micro-patterns on SiO<sub>2</sub> surface based on a dry lift-off technique

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### ABSTRACT

We reported a new technique for self-assembly of selective placement of carbon nanotubes (CNT) on pre-defined micro-patterns. Our work based on the use of a poly-para-xylylene C passivation layer on silicon dioxide (SiO<sub>2</sub>) surface which was micro-patterned by reactive ion etching (RIE) process and follow by the CNT deposition step. The lift-off of poly-para-xylylene layer then was carried out relying on a dry lift-off method in order to remove the nanotubes adsorbed on the poly-para-xylylene layer leaving the CNT on the desirable areas. CNT located at specific micro-areas with pre-defined patterns from 50 μm down to less than 10 μm line width and variable shapes. This approach provides a simple and useful means allow controlled placement of CNT which is necessary for the large-scale fabrication of electronic devices.

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### 1. Introduction

CNT has immersed as a promising materials in nanometer science for the past decade since the discovery. Due to its properties, CNT meets the requirement of many fields and has been made toward many applications, including, chemical and physical sensing devices and etc. [1]. The advantages of these applications have been demonstrated small size, low power, low weight, and high performance. To utilize CNT in nanodevices, it is necessary to develop efficient strategies for their assembling into hierarchical nanostructures, which could be achieved by controlling the shape, location, and orientation of large NT arrays. In order to fabricate micro-CNT based devices, exact placement of CNT on desire locations where it is needed is necessary and this ensures the homogeneity in performances of same kind of devices. Moreover, the mass fabrication of CNT based micro-devices requires a method for self-assembly of selective placement of CNT. Therefore it is essential to have a method enable us to make simple microstructures with CNT and to connect these to other structures for fabrication of all kinds of CNT based devices.

However, up to date, the lack of a mass-production method due to the lack of a simple and reliable process to deposit CNT in a controlled way is holding back CNT based gas sensors for practical

applications. Several approaches have been developed for high-yield controlled deposition of CNT on desirable positions [2–10]. Heretofore there has been no controlled and reliable technique for fabrication of CNT based devices, and NT devices have been made by randomly depositing NT on an electrode array. This technique does not promise to make large numbers of NT devices in a reliable way.

Previous techniques often rely on external forces to precisely align nanowires, it can be a time-consuming task to produce a large number of nano circuits with arbitrary orientation. In addition, the surface functionalization of nanomaterials in some techniques may even change and/or destroy the properties of the materials.

Recently, Choi et al. reported the deposition of CNT on the nanolithographically defined region of aminopropylsiloxane (APTES) in a controlled way [9]. This method required silanization technique for the formation of the reactive polar APTES templates and the selective deposition depended strongly on the quality of APTES self-assembly monolayer (SAM). It was found that the thickness of the APTES layer is important because CNT do not seem to adhere to the surface if there is more than one monolayer of APTES [8]. Later, Lewenstein et al. [10] reported the similar method with selective placement CNT on patterns of APTES monolayer. In order to avoid the swelling of PMMA resist and increase the effectiveness of the selective placement, in this method the surfactant used to suspend the SWCNTs needed to be considered. The removal of PMMA resist then was carried out with some complexity via Soxhlet extraction with acetone or methylene chloride for 24 h. Valentin et al. [8] reported the same way with the PMMA was dissolved

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during the CNT adsorption phase and it induced a decrease in the selectivity. Also, Choi et al. reported the deposition is less controlled than when the deposition of CNT is done prior to the lift-off of the PMMA layer.

In this paper, we reported a new method by using poly-paraxylylene C (Parylene C) material instead of using photoresist PMMA layer. A conformal Parylene layer, which is a pinhole-free

vapor phase deposited inert polymers is the key to this approach. This method allows us need not care about the swelling of photoresist and without using APTES monolayer induced the selective property of procedure does not rely on the quality of monolayer-the silanization technique. First, Parylene C was deposited using chemical vapor deposition and patterned by Reactive ion etching (RIE) through an AZ7220 mask. The suspension of SWCNT was

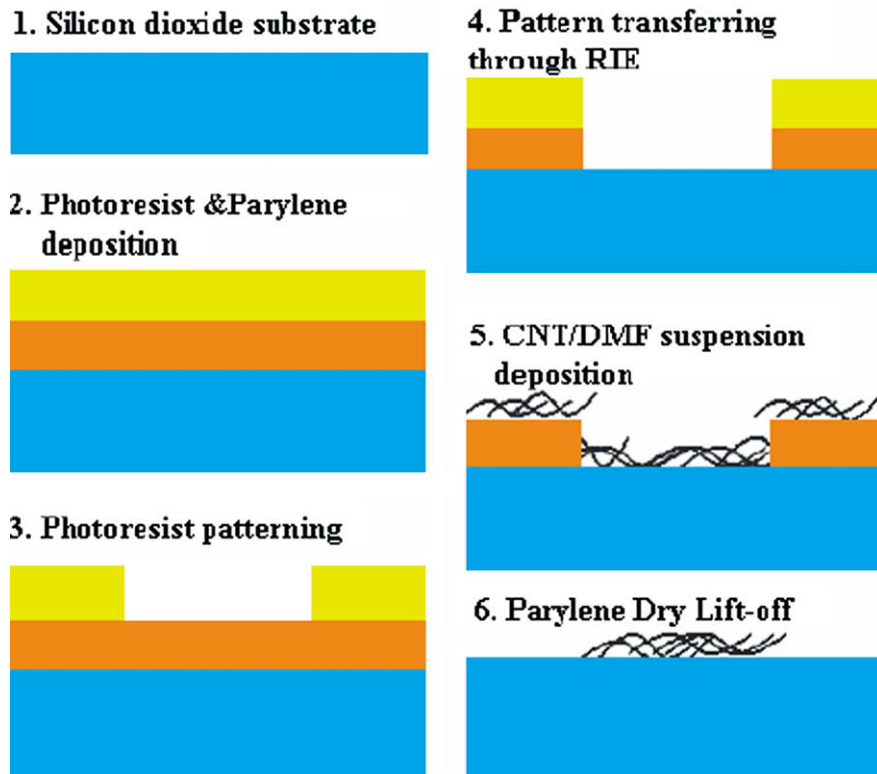


Fig. 1. Process of selective deposition of CNT using a Parylene dry lift-off method.

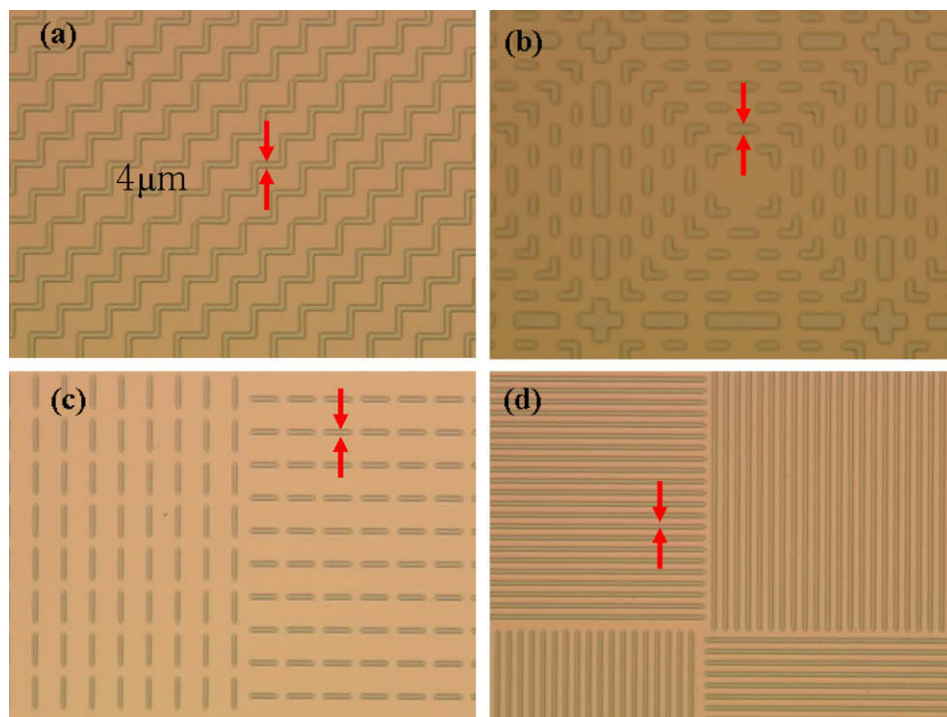


Fig. 2. Photograph of the Parylene C layer lifted off to remove any NT that adsorbed on the Parylene C layer using sharp tweezers.

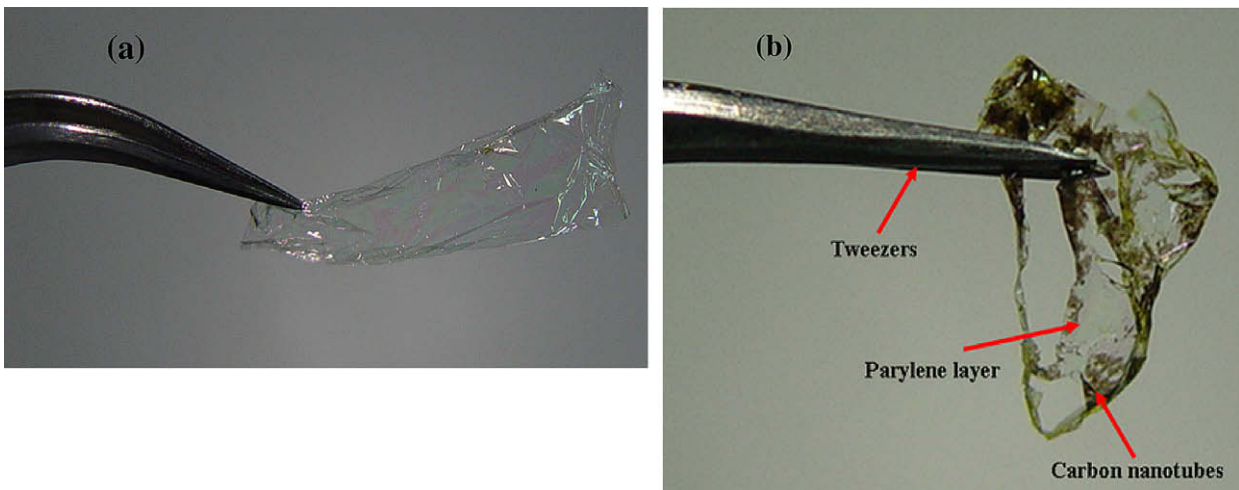


Fig. 3. Optical images of micro-patterns shows the pre-designed areas for CNT adhesions.

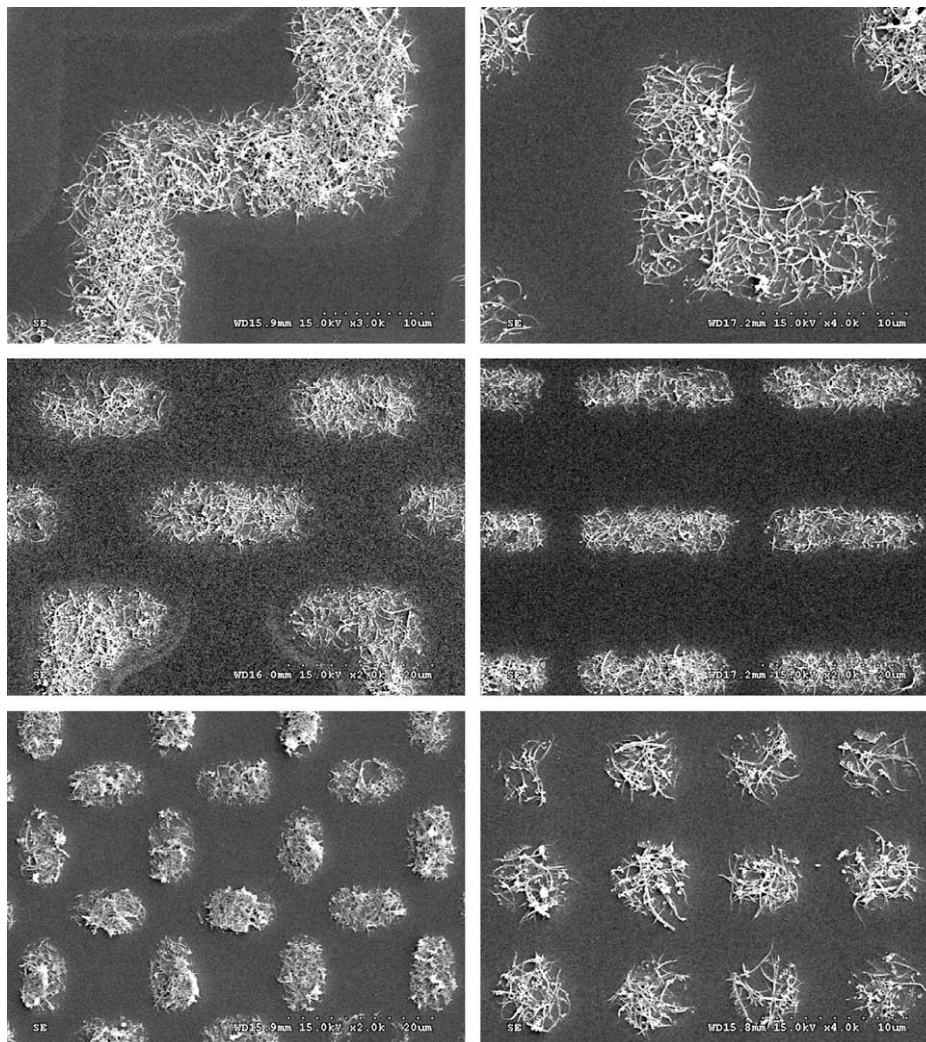


Fig. 4. SEM images of CNT patterns selectively located in the zigzag areas, dot areas and the separate lines in a rectangle.

deposited on the samples. Then, Parylene C layer was removed leaving the SWCNT on the specific areas. This simple method using the passivation and available commercial Parylene C allows for rapid mass fabrication of SWCNT nanoscale devices.

## 2. Experiments

The SWCNT powder purchased from Iljin Nanotech Co., Ltd. have properties of 1–1.2 nm in average diameter, 5–20 μm length,

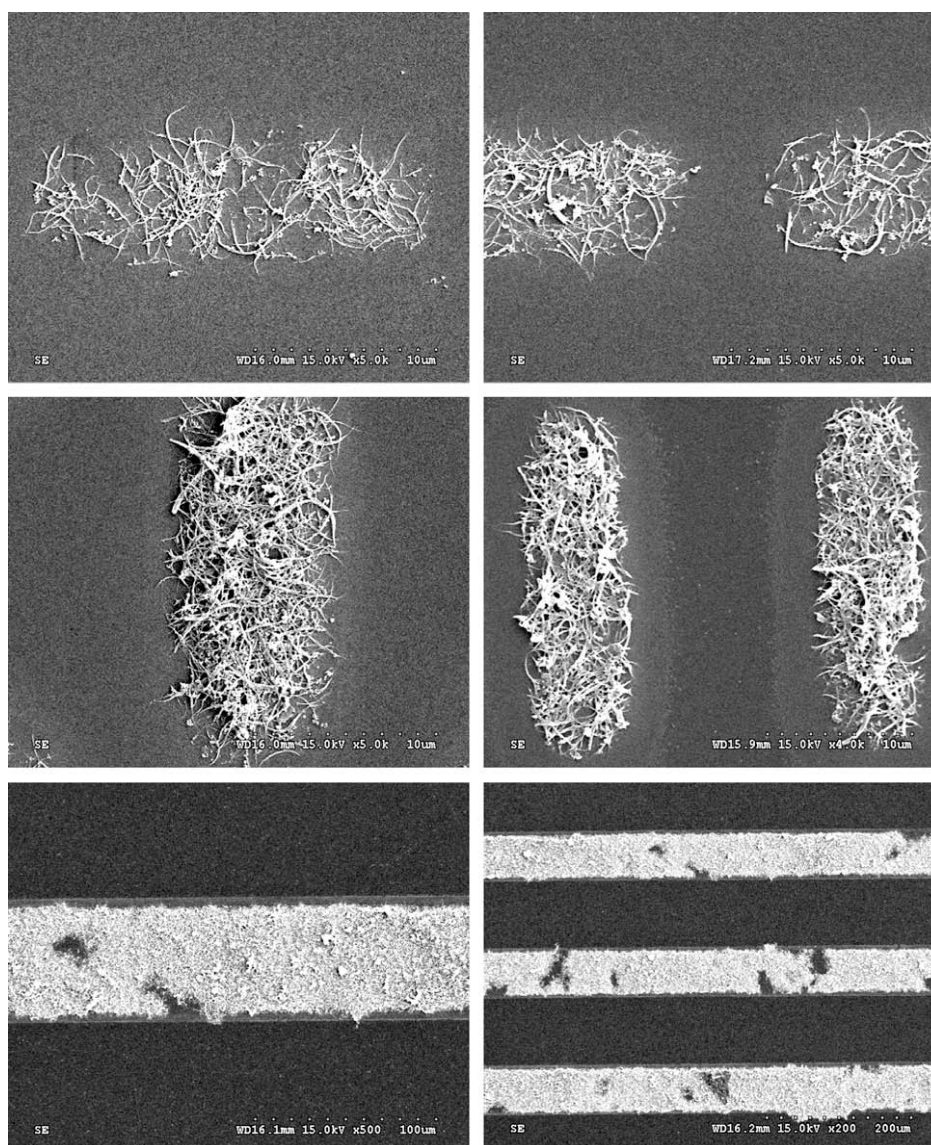


Fig. 5. SEM images of CNT patterns selectively located in separate and parallel lines.

and ~90% purity (prepared by an arc discharge process). The SWCNTs were used without further purification. Prior to the SWCNTs' manipulation, 8 mg of the sample was ultrasonically dispersed in 40 ml dimethylformamide (DMF) solution for 4 h (at a pulse cycle: 1 sec on, 1 sec off and at 200 W). The resulting solution was diluted to 20 mg/L.

Our templates for CNT deposition were prepared by the combination of soft lithography patterning and RIE. The shape and dimensions of mask patterns can be modified to create a variety of templates for CNT growth. To demonstrate the efficiency of this method, we fabricated a variety of topologies, such as isolated dots, zigzag lines and parallel lines. Typical dimensions of microfabricated lines were in the range of 4–10  $\mu\text{m}$ , 50  $\mu\text{m}$  wide and 5  $\mu\text{m}$  to few hundreds  $\mu\text{m}$  long. Our process as described in Fig. 1 with the use of inert Parylene C layer and the conventional photolithography carried out on top of these films.

First, a 2  $\mu\text{m}$  thick conformal Parylene C layer, which is pinhole-free, was deposited in the vapor phase on cleaned silicon dioxide surface. Once deposited, Parylene C film are nearly inert, they resist solvent, strong acids and bases. Another layer of photoresist (AZ7220) served as mask for a dry etch step to transfer the patterns

to the Parylene C layer was developed. The AZ7220 was double deposited with 4500 rpm firstly, 2500 rpm secondly and the soft baking time was 4 min in 95  $^{\circ}\text{C}$ . The patterns formed in the photoresist during the photolithographic process were transferred to the Parylene layer through an anisotropic oxygen plasma etch using Plasma Thermal 790 series. After patterning, the residual photoresist was stripped off with an acetone/methanol bath before the deposition of CNT suspension.

The samples then were soaked in an aqueous suspension of SWCNT-DMF 20 mg/L for 2 h, rinsed in DI water and dried by  $\text{N}_2$  blow. During all processes, we must take care of mechanical contacts in order not to destroy the Parylene layer. For selective deposition of CNT, the Parylene C layer was lifted off to remove any NT that adsorbed on the Parylene C layer. Due to the tensile property, peeling the Parylene films was accomplished carefully by using a sharp tweezers then pulling the Parylene layer away from the substrate. The actual peeling process used a combination of Scotch tape and tweezers to peel the entire film from the substrate, starting from an edge. Once the edge is lifted, the film separates easily [11]. After removing, the samples were cleaned in DI water and dried in  $\text{N}_2$  blow thoroughly in order to move out particles or the

redundant Parylene attached on the CNT patterns. Finally, field emission scanning electron microscopy (FESEM Hitachi S-4300 unit) was carried out to observe how well the SWCNT selective deposited on the substrate. The selective placement of SWCNT with high density on the micrometer sized patterns was readily achieved.

### 3. Results and discussion

The patterning approach shown in Fig. 1 leads to Parylene C patterns in reserve for CNT deposition directly to on the SiO<sub>2</sub> surface inside these patterns. Examples of patterns using this approach are shown in Fig. 2.

Parylene with the CNT deposited on the top was peeled off the substrate by pulling and lifting using micrometer sharp tweezers. Photograph of Parylene peeled easily from a substrate is shown in Fig. 3a and photograph of the Parylene peeled from the substrate after deposition the samples with CNT/DMF suspensions is shown in Fig. 3b. The CNT patterns on specific areas of different shapes using this method were imaged by FESEM to confirm SWCNTs controlled placements.

Observation of the CNT patterns using FESEM revealed that CNT micro-patterns with clear boundary were achieved as shown in Figs. 4 and 5. After the Parylene patterning, the residual photoresist was stripped off with an acetone/isopropanol bath before the deposition of CNT/DMF suspension. The density of CNT produced on the substrate was shown to be dependent on the size of the micro-pattern features and the time of CNT deposition process. The concentration of CNT suspension during deposition process also affected to the density of CNT on the patterns.

The use of Parylene C in the place of PMMA photoresist is the most important in this method. First, passivation property of Parylene allow us avoid the swelling of photoresist which affects significantly to the selective deposition of CNT. Second, this method without using APTES monolayer induced the selective property of procedure does not rely on the quality of monolayer and the silanization technique. Finally, Parylene can be selective etched away using RIE and can be readily peeled off the surface due to its low adhesion to many kinds of material. Parylene can be lifted-off using a dry lift-off method which was reported by DeFranco et al. [11] and Ilic and Craighead [12] recently for patterning of organic electronic and biological materials. This method relies on the poor adhesion of Parylene films on a variety of substances. However, the way carried out for the peeling of the Parylene films need to be improved in order to get better control and ease. In some cases the films would not peel at all which can affect to the behaviors of devices. The peeling of the Parylene films, which was carried out manually in this work, can be achieved with better control by a commercial delaminator reported by DeFranco et al. [11].

### 4. Conclusion

We have reported on the high efficiency selective placement of CNT by self-assembly. Using Parylene C as a sacrificial layer, we greatly developed a simple and fast method which is useful for the fabrication of CNT electronic devices. Available commercial Parylene C is selected as the structural material has desirable properties such as high flexibility, chemical inertness and biocompatibility. Moreover, Parylene is compatible with microfabrication technology and can be deposited as a pinhole-free conformal coating at room temperature. Parylene can be etched away using RIE and can be readily peeled off the surface due to its low adhesion to many kinds of material. This approach is based on a dry lift-off method and avoids the potential problem of introducing defects and contaminants that could arise in electrode patterning after SWCNT placement. This method without using an external chemical material does not affect to the SWCNT structures and therefore does not change SWCNT properties. This approach takes use of advantages of the dry lift-off method and avoids the potential problem of introducing defects and contaminants that could arise in patterning electrodes after SWCNT placement. The applications of this method with device design are ongoing.

### Acknowledgements

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