Local and Global Effects on the Growth of Carbon Nanotube Micropillar Arrays

Yuki Matsuoka
Department of Future Industry-Oriented Basic Science and Materials, Toyota Technological Institute, Japan

NNIN iREG Site: Lurie Nanofabrication Facility, University of Michigan, Ann Arbor, MI
NNIN iREG Principal Investigator: Professor Anastasios John Hart, Mechanical Engineering, University of Michigan
NNIN iREG Mentor: Sameh Tawfick, Mechanical Engineering, University of Michigan
Contact: sd11503@toyota-ti.ac.jp, ajohnh@umich.edu, stawfick@umich.edu

Abstract and Introduction:

The mechanism of carbon nanotubes (CNTs) isn't unveiled in detail despite the efforts of many researchers. Therefore, non-uniform CNT films are synthesized frequently. Generally speaking, a CNT film thickness was increased or decreased around the substrate edge. Jeong, et al., reported whole CNTs film thicknesses changed depending on the total catalyst area [1]. Here, these effects affecting whole CNTs film structures are called "global effect." Moreover, Hart has observed partial CNT growth enhancing [2]. Here, this effect is called "local effect." It is vital to understand these effects to control precise CNTs structure—for example, homogeneous film thickness, straight pillar with small diameter.

In this study, we investigated the effect of pattern density on the growth rate and straightness of high aspect ratio cylindrical CNT micropillars. To this end, we designed catalyst circle patterns having different diameters and spacings keeping a constant total catalyst area per substrate to study the global effect. We also designed patterns having sinusoidal spacings between circles to investigate local and non-symmetric pattern density effects.

Our experiments show that the pillars can deflect towards (attractive) or away from (repulsive) one another and these two deflection regimes can occur on the same substrate on identical patterns. We hypothesize that the non-uniform growth rates among the patterns can be responsible for the pillars deflection. A simple theoretical model was formulated to quantitatively capture the effect of non-uniform growth rate on bending of individual pillars.

	Fe thickness [nm]	Flow rate of C_2H_4 gas [sccm]	Growth time [min]	Average Pillar length [µm]
A	1	100	4	424
B	1	25	4	130
C	1	100	20	1057
D	1.5	25	4	127

Table 1: Experimental conditions.

Experimental:

We employed photolithography methods to prepare for patterns having diameters of 10, 30 and 90 µm, and different spacings—keeping a constant total catalyst area, 0.16, 0.77 and 1.84 mm^2 per substrate for global effect—and having sinusoidal spacings between circles under a total catalyst area of 0.77 mm^2 for local effect. Iron (Fe) and Alumina (Al_2O_3) were deposited on the pattern with thicknesses of 1 and 10 nm, respectively, followed by development using sonication in acetone solution. After reduction of patterned substrate by heating (775°C) in H_2 atmosphere for 10 min, CNT micropillars were synthesized by a hot wall chemical vapor deposition (CVD) tube furnace with C_2H_4 precursor gas under constant temperature (775°C). Table 1 shows the experimental conditions used in this study. The length and deflection of grown CNT micropillars were measured by scanning electron microscopy (SEM).

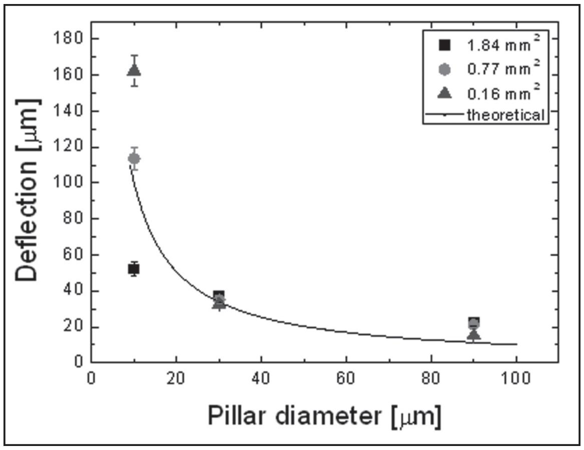

Figure 1: Relationship between deflection of CNT micropillars and pillar diameter.

Results:

Figure 1 shows the result of CNT micropillars grown from standard condition A. In Figure 1, deflection was inversely decreased with increasing pillar diameter. Deflection was larger than higher pillar density. This indicates the grown pillars were supporting one another at high pillar density. To explain these results, we made a simple theoretical model based on the theory of thermal bending of bimetal [3].

In the model, the pillar was divided into two equal parts in a longitudinal direction. Then, we hypothesized the misfit strain generated from the difference of growth rate in catalyst area, $\Delta\varepsilon = \Delta gt$. Using the equation of misfit strain and the moment, deflection was deduced (Equation 1),

$$\delta = \frac{d\,L}{2\,\Delta g\,t}\left(1 - \cos\left(\frac{2\,\Delta g\,t}{d}\right)\right)$$

where d is pillar diameter and L is the length of the CNT micropillars. The theoretical curve was well accorded with the trend of deflection. The result of short CNT micropillars grown from condition B also showed the same trend and fitted well Equation 1.

However, one of the long CNT micropillars grown from condition C showed differently. The deflection of a diameter of 10 μm was decreased, compared to 30 μm of each total catalyst area. From a cross-sectional SEM image (not shown here), it was evident the difference was also caused by high pillar density. This indicates Equation 1 is only effective at low pillar density. We could not see the effect of total catalyst area to pillar length in every condition.

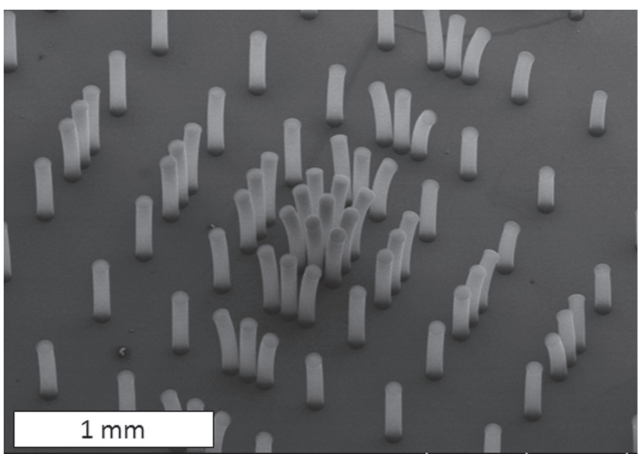

Figure 2: SEM image of the observed attractive bending effects.

In this study, two kinds of local bending effects were observed, i.e. deflection away from (Figure 2) and towards (not shown here) one another on the density-modified pattern. To explain the repulsive effect, we hypothesize a CNT-growth enhancing field around the catalyst circle.

When the space between catalyst circles is close, the fields are overlapped, and the growth rates are more enhanced. From cross-sectional SEM images, the growth rate enhancing was verified, because about 7% of the longer pillars were grown in a dense catalyst area than a sparse area. Therefore, the CNT growth on the side near other catalyst circles increased, resulting in repulsive deflection. This repulsive effect was not influenced by gas flow direction.

The attractive effect seemed to be affected by the substrate size or the distance from the substrate edge to the patterned catalyst. However, this is still under investigation.

Conclusions:

The relationship between deflections of CNT micropillars and pillar diameter was clearly identified. The simple bending theory based on the growth rate difference was in good accordance with the obtained results. It suggests the origin of bending is the growth rate difference.

When the pillar length and catalyst density increased, bending theory departed from the results, because of the pillars supporting one another.

From the density modified pattern, two types of local effects were observed, i.e. attractive and repulsive effects. The repulsive effect was explained by the CNT-growth enhancing field.

Future Works:

We need to improve the theoretical model using the misfit strain generated from feasible growth rate distribution.

Acknowledgements:

I would like to thank my mentor, Sameh Tawfick, and principal investigator, Dr. Anastasios John Hart, for their kind support of my experimental work, and their valuable discussions. I would also like to acknowledge the staff at the University of Michigan: Brandon Lucas, Sandrine Martin, and Trasa Burkhardt, and the Japanese staff: Keijiro Hirahara and Kayoko Tomisawa. Finally, I thank the Lurie Nanofabrication Facility and the National Nanotechnology Infrastructure Network International Research Experience for Graduates (NNIN iREG) Program.

References:

[1] G. H. Jeong et al., Carbon 47 (2009) 696.

[2] A. J. Hart et al., J. Phys. Chem. B,110 (2006) 8250.

[3] Y. Clyne, Key Engineering Materials, 116 (1996) 307.