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# Preferential Growth of Carbon Nanotubes/Nanofibers Using Lithographically Patterned Catalysts

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## ABSTRACT

In order to utilise the full potential of carbon nanotubes/nanofibers, it is necessary to be able to synthesize well aligned nanotubes/nanofibres at desired locations on a substrate. This paper examines the preferential growth of aligned carbon nanofibres by PECVD using lithographically patterned catalysts. In the PECVD deposition process, amorphous carbon is deposited together with the nanotubes due to the plasma decomposition of the carbon feed gas, in this case, acetylene. The challenge is to uniformly nucleate nanotubes and reduce the unwanted amorphous carbon on both the patterned and unpatterned areas. An etching gas (ammonia) is thus also incorporated into the PECVD process and by appropriately balancing the acetylene to ammonia ratio, conditions are obtained where no unwanted amorphous carbon is deposited. In this paper, we demonstrate *high yield*, *uniform*, '*clean*' and *preferential* growth of vertically *aligned* nanotubes using PECVD.

## INTRODUCTION

There has been considerable interest in the application of nanotubes in nanoelectronic devices [1-4], scanning probes [5-7], field emission sources [8-10] and supercapacitors [11]. The common techniques of depositing nanotubes include high pressure arcs, laser ablation and chemical vapour deposition (CVD) [12-18]. Unlike the former two deposition methods, CVD synthesis provides controlled, in-situ growth of nanotubes on substrates.

The growth mechanism of carbon nanotubes by CVD is driven by the decomposition of a hydrocarbon gas using a suitable catalyst, the dissolution of carbon in the catalyst and the precipitation of graphitic, tubular carbon from the catalyst. Arrays of 'spaghetti-like' nanotubes and aligned carbon nanotubes have been deposited using various types of CVD [19-22]. It has also been reported recently that PECVD processes induce alignment of the nanotubes due to the electric field inherent in the plasma discharge [18,19,21,23].

Patterned growth of nanotubes is achieved by lithographically defining the catalyst areas before nanotube growth. The key requirements for the patterned growth of nanotubes are yield, uniformity and the elimination of unwanted carbonaceous by-products from the deposition process. These requirements are investigated in this paper and we demonstrate uniform preferential growth of aligned nanotubes using PECVD of acetylene and ammonia gases at 700°C.

## EXPERIMENTAL DETAILS

Due to the catalytic growth nature of carbon nanotubes, it is possible to define the growth areas of carbon nanotubes on a substrate by pre-patterning the catalyst prior to nanotube deposition. The nickel catalyst used in the synthesis of carbon nanotubes was deposited onto Si substrates by rf-magnetron sputtering and patterned lithographically using lift off. Nickel was either deposited directly on Si or on a diffusion barrier material to study if the thermal diffusion of Ni affects the yield of nanotubes. The substrates were then transferred to a PECVD chamber which was evacuated to $10^{-2}$ Torr by a rotary pump. The carbon feedstock and etching gases used for the PECVD process were acetylene and ammonia respectively. The flow rate of ammonia ($NH_3$) was fixed at 200sccm and the flow rate of acetylene ($C_2H_2$) was varied to find optimal deposition conditions.

The carbon nanotube deposition process consists of 2 main stages: (1) first, the substrates were heated to 700°C in $NH_3$ and nickel nanoparticles are formed [19,23], and (2) the $C_2H_2$ is introduced and the substrate is biased at –600V d.c. to initiate the plasma discharge for PECVD. The PECVD deposition time was fixed at 15 mins for all samples. The substrates were then observed in a Hitachi S800 Field Emission Scanning Electron Microscope. Our deposition process produces vertically aligned carbon nanotubes and further details can be found in [23]. The nanotubes produced contain structural defects and are sometimes referred to in the literature as nanofibers.

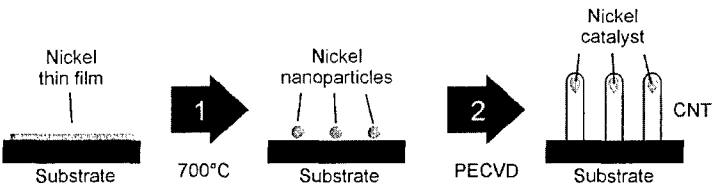


**Figure 1:** Two stage deposition process in which (1) Ni nanoparticles are formed by heating the substrate to 700°C and (2) PECVD to deposit the carbon nanotubes.

## RESULTS AND DISCUSSION

Poor yield of nanotubes, from 1μm diameter dots of Ni, is observed when the nickel catalyst is directly deposited on the Si substrates (see Figure 1(a)). This is believed to be due to the thermal diffusion of Ni into Si to form $NiSi_x$ at temperatures above 300°C. Thus, the Ni is no longer 'active' to act as catalytic nucleation centers for the growth of nanotubes. The deposition yield of carbon nanotubes is significantly improved by depositing a diffusion barrier layer between the Ni catalyst and the Si substrate. Typical diffusion barrier materials are $SiO_2$ and TiN [24]. When the substrate is heated to 700°C, the Ni film breaks up and forms nanoparticles on the diffusion barrier as shown in Figure 1(b). These Ni nanoparticles remain 'active' on the diffusion barrier for the nucleation of nanotubes and a high yield of nanotubes from 1μm dots of Ni is obtained after the PECVD process as shown in Figure 1(c).

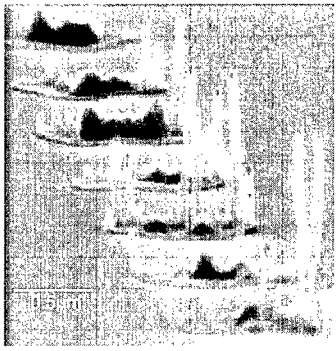

**Figure 1(a).** Poor yield of nanotubes is observed when Ni catalyst is deposited directly on Si. This is due to the thermal diffusion of Ni into Si which renders most of the Ni 'inactive'.

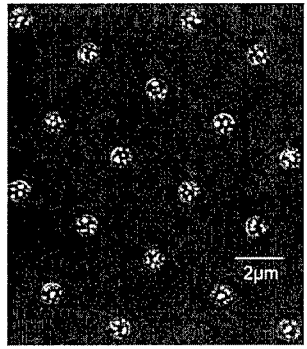


**Figure 1(b).** Ni nanoparticles are formed on a TiN diffusion barrier when the substrate is heated at 700°C. These nano-particles are 'active' for catalytic nanotube growth.

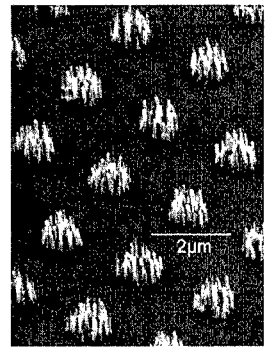


**Figure 1(c).** High yield of nanotubes is obtained from 1μm Ni dots on the diffusion barrier after PECVD of acetylene and ammonia at 700°C.

A by-product from the PECVD deposition of nanotubes is amorphous carbon (a-C). Unlike nanotube growth which occurs only at catalyst sites, a-C is formed by the plasma decomposition of the $C_2H_2$ gas and thus is deposited all over the substrate. The role of $NH_3$ in the plasma is to etch away the a-C as it is being deposited. Keeping the $NH_3$ flow rate fixed at 200sccm, the $C_2H_2$ flow rate was varied in a series of depositions to determine the optimal conditions at which no a-C remains on the substrate. The thickness of surface a-C was determined using a combination of cross sectional SEM and depth resolved Auger Electron Spectroscopy [25] and the results are plotted in Figure 2. Deposition gas ratios of 15% and 20% $C_2H_2$:$NH_3$ do not produce amorphous carbon on the substrate.

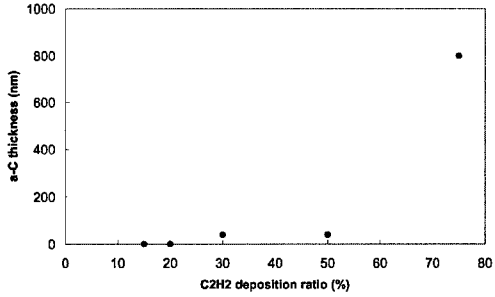


**Figure 2.** Plot of a-C thickness against $C_2H_2$:$NH_3$ ratio [25].

For depositions performed under a low concentration $C_2H_2$ (ie. high $NH_3$), anisotropic etching of the Si substrate in the unpatterned areas is observed as shown in Figure 3(a). For a high $C_2H_2$ ratio of 75%, we observe a thick a-C film covering both the nanotube and unpatterned areas as shown in Figure 3(b). The growth of the a-C proceeds in a columnar-like fashion and is 800nm in thickness as shown in Figure 3(c). Depositions performed using a 20% $C_2H_2$ ratio do not exhibit etching of the Si substrate nor have a surface a-C layer.

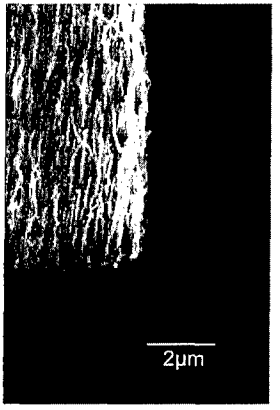


**Figure 3(a).** Using a $C_2H_2$ ratio of 15%, etching of the unpatterned Si areas is observed.

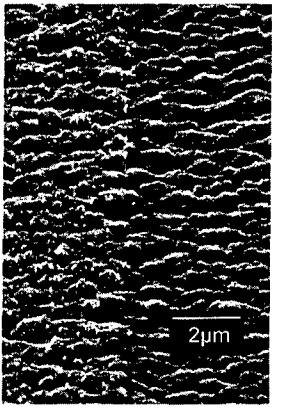


**Figure 3(b).** Using a $C_2H_2$ ratio of 75%, thick a-C covers both the nanotube (left) and unpatterned areas (right).

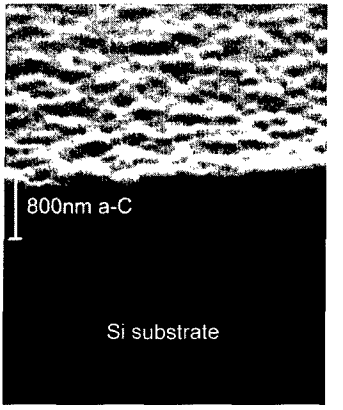


**Figure 3(c).** The thickness of the a-C layer is 800nm measured by cross-sectional SEM. The a-C grows in a columnar-like structure.

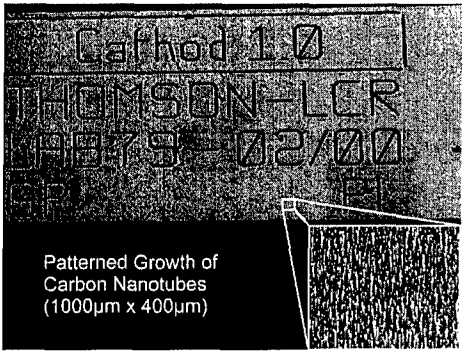


**Figure 4(a).** Uniform preferential growth of carbon nanotubes achieved by patterning the initial Ni catalyst by optical lithography.

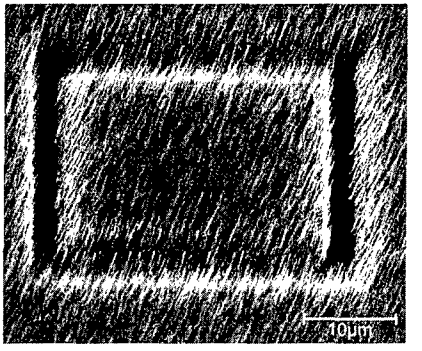


**Figure 4(b).** 25μm box of nanotubes produced using Ni catalyst patterned by optical lithography.

Uniform, patterned arrays of vertically aligned nanotubes have been deposited using the optimal deposition gas ratio of 20% $C_2H_2$:$NH_3$. The patterned Ni catalyst areas of Figure 4 were prepared using optical lithography. When the patterned Ni features are reduced to ~100nm using ebeam lithography, the nickel film forms only 1 nanoparticle when annealed at 700°C. Hence, it is possible to nucleate single nanotubes at precise locations as demonstrated in Figure 5.

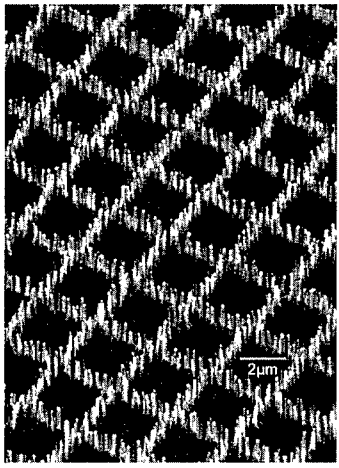


**Figure 5(a).** Grid lines of nanotubes produced using 100nm lines of Ni patterned using ebeam lithography.

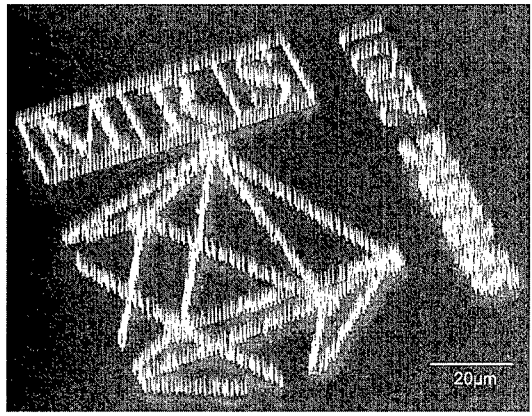


**Figure 5(b).** Precise placement of nanotubes is demonstrated using the MRS Spring 2001 logo. The logo was produced using 100nm nickel dots patterned using ebeam lithography.

## CONCLUSIONS

Preferential deposition of vertically aligned carbon nanotubes using lithographically patterned Ni catalyst has been achieved using PECVD of $C_2H_2$ and $NH_3$ at 700°C. The two step growth process consists of Ni forming nanoparticles at 700°C and then PECVD to deposit the nanotubes. Nanotube yield is significantly improved by the use of a diffusion barrier to prevent the diffusion of Ni into Si. The PECVD gas ratio of 20% $C_2H_2$:$NH_3$ elminates unwanted a-C from the deposition process. These are the conditions necessary to produce high yield, uniform, 'clean' and selective/preferential growth of vertically aligned nanotubes.

## ACKNOWLEDGEMENTS

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## REFERENCES


1. R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, Appl. Phys. Lett. **73**, 2447 (1998).
2. M. Kruger, M. R. Buitelaar, T. Nussbaumer, C. Schonenberger, and L. Forro, Appl. Phys. Lett. **78**, 1291 (2001).
3 K. Liu, M. Burghard, S. Roth, and P. Bernier, Appl. Phys. Lett. **75**, 2494 (1999).
4. W. Tombler, C. Zhou, and H. Dai, Appl. Phys. Lett. **76**, 2412 (2000).
5. H. Dai, N. Franklin, and J. Han, Appl. Phys. Lett. **73**, 1508 (1998).
6. H. Nishijima,, S. Kamo, S. Akita, Y. Nakayama, K. I. Hohmura, S. H. Yoshimura, and K. Takeyasu, Appl. Phys. Lett. **74**, 4061 (1999).
7. C. L. Cheung, J. H. Hafner, T. W. Odom, K. Kim, and C. M. Lieber, Appl. Phys. Lett. **76**, 3136 (2000).
8. W. A. de Heer, A. Chatelaine, and D. Ugarte, Science **270**, 1179 (1995).
9. J. M. Bonard, J. P. Salvetat, T. Stockli, L. Forro, and A. Chatelain, Appl. Phys. A **69**, 245 (1999).
10. P. G. Collins and A. Zettl, Appl. Phys. Lett. **69**, 1969 (1996).
11. E. Frackowiak, K Metenier, V. Bertagna, and F. Beguin, Appl. Phys. Lett. **77**, 2421 (2000).
12. S. Ijima, Nature **363**, 603 (1993).
13. S. Ijima and T. Ichihashi, Nature **363**, 603 (1993).
14. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. delaChappelle, S. Lefrant, P. Deniard, R. Lee, and J. E. Fischer, Nature **388**, 756 (1997).
15. A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzer, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, Science **273**, 483 (1996).
16. C. Journet and P. Bernier, Appl. Phys. A **67**, 1 (1998).
17. A. M. Cassell, J. A. Raymakers, J. Kong, and H. J. Dai, J. Phys. Chem. **103**, 6484 (1999).
18. Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, Science **282**, 1105 (1998).
19. V. I. Merkulov, D. H. Lowndes, Y. Y. Wei, G. Eres, and E. Voelkl, Appl. Phys. Lett. **76**, 3555 (2000).
20. H. Murakami, M. Hirakawa, C. Tanaka, and H. Yamakawa, Appl. Phys. Lett. **76**, 1776 (2000).
21. C. Bower, W. Zhu, S. Jin, and O. Zhou, Appl. Phys. Lett. **77**, 830 (2000).
22. J. I. Sohn, S. Lee, Y. H. Song, S. Y. Choi, K. I. Cho, and K. S. Nam, Appl. Phys. Lett. **78**, 901 (2001).
23. M. Chhowalla, K. B. K. Teo, C. Ducati, N. L. Rupesinghe, G. A. J. Amaratunga, A. C. Ferrari, D. Roy, J. Robertson, and W. I. Milne, J. Appl. Phys., *submitted.*
24. A. M. Rao, D. Jacques, R. C. Haddon, W. Zhu, C. Bower, and S. Jin, Appl. Phys. Lett. **76**, 3813 (2000).
25. K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I . Milne, D. G. Hasko, G. Pirio, P. Legagneux, F. Wycisk, and D. Pribat, Appl. Phys. Lett., *submitted.*