Journal of Vacuum Science & Technology B

Selective growth of carbon nanotube on scanning probe tips by microwave plasma chemical vapor deposition

F. M. Pan, Y. B. Liu, Y. Chang, C. Y. Chen, T. G. Tsai, M. N. Chang, and J. T. Sheu

Citation: Journal of Vacuum Science & Technology B **22**, 90 (2004); doi: 10.1116/1.1640399
View online: http://dx.doi.org/10.1116/1.1640399
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvstb/22/1?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

Plasma restructuring of catalysts for chemical vapor deposition of carbon nanotubes
J. Appl. Phys. **105**, 064304 (2009); 10.1063/1.3091394

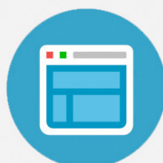
Role of thin Fe catalyst in the synthesis of double- and single-wall carbon nanotubes via microwave chemical vapor deposition
Appl. Phys. Lett. **85**, 2601 (2004); 10.1063/1.1796529

Magnetic properties of carbon nanotubes grown on Fe catalyst layer by microwave plasma enhanced chemical vapor deposition
J. Appl. Phys. **95**, 7118 (2004); 10.1063/1.1687251

Effect of Ni-surface morphology on the growth of carbon nanotubes by microwave plasma-enhanced chemical vapor deposition
AIP Conf. Proc. **590**, 39 (2001); 10.1063/1.1420052

Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition
Appl. Phys. Lett. **77**, 2767 (2000); 10.1063/1.1319529

Re-register for Table of Content Alerts

Create a profile.  Sign up today!

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. Download to IP: 140.113.38.11 On: Thu, 01 May 2014 05:08:59

Selective growth of carbon nanotube on scanning probe tips by microwave plasma chemical vapor deposition

F. M. Pan[a)]
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China and National Nano Device Laboratories, Hsinchu 30050, Taiwan, Republic of China

Y. B. Liu and Y. Chang
Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China

C. Y. Chen, T. G. Tsai, and M. N. Chang
National Nano Device Laboratories, Hsinchu 30050, Taiwan, Republic of China

J. T. Sheu
Department of Electrical Engineering, National Chi Nan University, Puli 545, Taiwan, Republic of China

(Received 29 August 2003; accepted 10 November 2003; published 14 January 2004)

We have selectively grown carbon nanotubes on the probe tip of an atomic force microscope by microwave plasma chemical vapor deposition. The catalyst domain was defined on the tip apex of an Si based scanning probe by local electric field induced oxidation of a TiN cap layer, under which the cobalt catalyst layer was predeposited on the probe surface. High resolution atomic force microscopy images of an SiO_2 trench pattern are demonstrated using the carbon nanotube tip. The nanotube tip fabrication method is simple and compatible with existing thin film process technology.
© *2004 American Vacuum Society.* [DOI: 10.1116/1.1640399]

I. INTRODUCTION

Conventional atomic force microscopes (AFM) are plagued by difficulties in obtaining surface images of high fidelity for features with a high aspect ratio or steep sidewalls due to the large end radius and sloping surface of regular pyramidal probe tips. In many imaging applications, such as nano-scaled microelectronics technology and bioscience, highly sharp tips are usually needed. Because of the extraordinary mechanical strength and a high aspect ratio with a very small tube diameter, carbon nanotubes (CNT) are widely recognized as a promising substitute for conventional pyramidal silicon and silicon nitride tips. Since the first report on using carbon nanotubes as the AFM probe tip,[1] many methods to fabricate carbon nanotube tips have been developed.[2–10] The earliest approach was to pick and adhere a multiwall nanotube bundle to the tip of commercial AFM probes.[1–3] Many other approaches that physically attach individual carbon nanotubes on AFM tips, such as electric field induced CNT probe attachment and electron beam welding, have successfully demonstrated superior imaging capability of CNT tips.[4–7] However, these processes are difficult and time consuming, and, their implementation in mass-scaled fabrication is, therefore, very questionable. Thus direct growth of carbon nanotube on an AFM tip by chemical vapor deposition (CVD) receives extensive attention.[8–10] However, for most reported works, growth of CNTs at the desired location, i.e., the tip apex, was not well controlled because of the difficulty to deposit catalyst in the tiny area around the tip apex. Here, we report an approach to selectively grow carbon nanotubes on the tip apex of a silicon based AFM probe by microwave plasma CVD (MPCVD), using local electric-field-induced oxidation (EFIO) to define the CNT growth site.

[a)]Electronic mail: fmpan@faculty.nctu.edu.tw

II. EXPERIMENT

Preparation of the carbon nanotube on the AFM tip is schematically illustrated in Fig. 1. A commercial Si based AFM probe (Nanosensors, A-NCH-100) was used and carbon nanotube growth was performed in a MPCVD system. A cobalt film was first deposited on the silicon AFM probe by electron beam evaporation as the catalyst for the CNT growth, followed by deposition of a TiN cap layer by ion-sputtering. Under the normal deposition condition for a blanket substrate, both the as-deposited Co and TiN thin films should have a film thickness of 30 nm on the probe cantilever. Before carbon nanotubes can be selectively grown at the apex of the AFM tip, TiN at the apex area needs to be removed so that the underlying cobalt layer can be exposed to the CVD ambient. This was done by oxidizing TiN at the tip apex followed by wet etch to remove the oxidized TiN layer. Local oxidation of the TiN film at the tip apex was achieved by applying a strong local electrical field at the tip in ambient. An NT-NDT scanning probe microscope (SP-47) was used to perform the local electric-field-induced oxidation. The AFM tip was biased positively with respect to a silicon wafer, and the TiN film on the tip apex was oxidized in air by the strong local electric field. The bias voltage and scan speed used for the EFIO were 10 V and 200 nm/s, respectively. After the EFIO, the AFM probe was dipped in a 1*M* NaOH solution to etch away the TiO_2 (or, possibly, TiO_xN_y)

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. Download to IP: 140.113.38.11 On: Thu, 01 May 2014 05:08:59

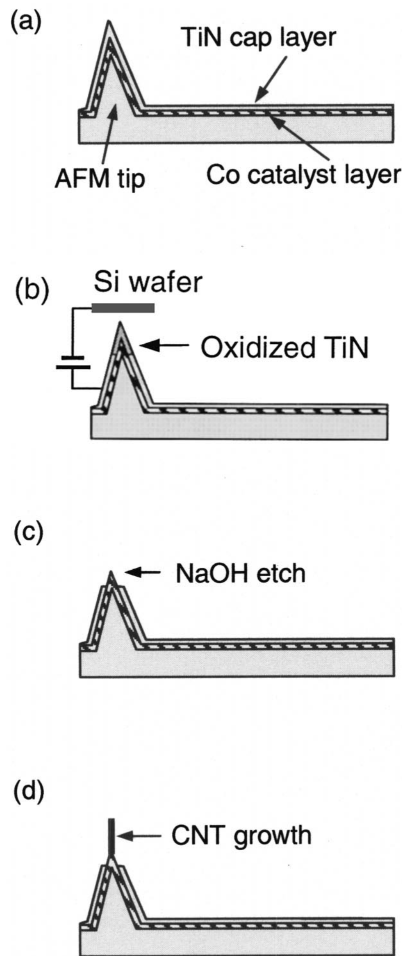


FIG. 1. Schematic diagram of the fabrication process for the selective growth of carbon nanotubes on the AFM probe tip: (a) deposition of cobalt and TiN thin films, (b) electric-field-induced oxidation of the TiN cap layer, (c) wet etch of the oxidized TiN layer at the tip apex, and (d) microwave plasma CVD growth of carbon nanotubes on the tip apex.

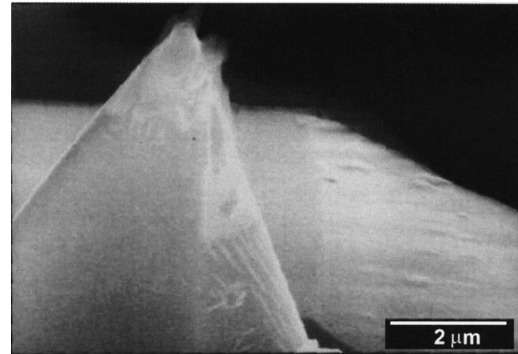


FIG. 2. SEM image of the AFM probe tip after the local electric-field-induced oxidation and the NaOH wet etch. Little residual was found on the surface area near the tip apex.

at the tip apex. After the wet etch, the AFM probe was placed on a silicon wafer with the tip facing upward and transferred into the MPCVD system for CNT growth. The chamber pressure was kept at 10 Torr throughout the CNT growth process. Prior to CNT deposition, the AFM probe was treated with hydrogen plasma at 600 W with an H_2 flow rate of 100 sccm for 3 min. The precursor gas is a mixture of methane (CH_4) and H_2 with flow rates of 10 and 100 sccm, respectively. The microwave input power was 800 W, and a dc bias of 200 V was applied to the substrate. The elemental composition on the AFM probe surface was analyzed by a VG Scientific Auger spectrometer (Microlab 310-F), and the surface morphology was studied by a field emission scanning electron microscope (Hitach S-4000).

III. RESULTS AND DISCUSSION

Oxidation of silicon or titanium nitrides on wafers in terms of local electric-field-induced oxidation (EFIO) is widely used in the nanolithography technique using a scanning probe microscope (SPM).[11–14] In most reported SPM nanolithography studies, a conductive SPM tip is biased negatively with respect to the Si substrate, which is usually capped with a TiN or Si_3N_4 thin film, and thereby patterns of titanium oxide or silicon oxide are produced by local EFIO of the cap layer. In this work, opposite to normal SPM nanolithography, the TiN/Co coated AFM tip was biased positively with respect to a silicon wafer, and the TiN film on the tip apex was oxidized in air by the strong local electric field. In order to evaluate the oxidization extent of the TiN cap layer at the tip apex under the EFIO, we have studied the oxidized volume produced beneath the surface of a TiN capped Si wafer under the same EFIO condition but with the bias polarity reversed. A titanium oxide line pattern with a height of 8 nm was thus produced on the wafer surface. According to previous studies, the depth of the buried oxide beneath the Si wafer surface after normal SPM nanolithographic operation was about 2/3 of the height of the protruding portion.[12,14] Thus the protrusion of 8 nm on the TiN layer suggests that a groove of ~5 nm in depth can be produced beneath the thin film surface under the EFIO condition. As described previously, the TiN cap layer on the AFM probe was 30 nm thick, and it would be, therefore, too thick to be completely oxidized under the EFIO condition. However, due to a lower metal deposition rate on the sloping surface of the pyramidal tip than on the flat cantilever surface, the actual film thickness on the tip should be smaller than that on the cantilever surface. Moreover, anodic oxidation is likely to be more vigorous at the tip apex than on a flat surface because the electric field is locally concentrated at the tip apex as the tip is biased negatively. As a result, it is not surprising that the TiN cap layer near the tip apex could be completely oxidized under the EFIO condition and removed by the subsequent wet etch with the 1M NaOH solution. Figure 2 shows the secondary electron microscope (SEM) image of the AFM tip after the wet etch. Some flake-like etch residual can be clearly seen to exist on the tip, but little residual is found on the surface area near the tip apex. This seems to suggest that the oxidized TiN cap layer was stripped off the tip apex, and this was confirmed by Auger electron spectroscopy (AES). Figure 3 shows the AES spectrum for the tip apex area after the wet etch. The Auger

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. Download to IP: 140.113.38.11 On: Thu, 01 May 2014 05:08:59

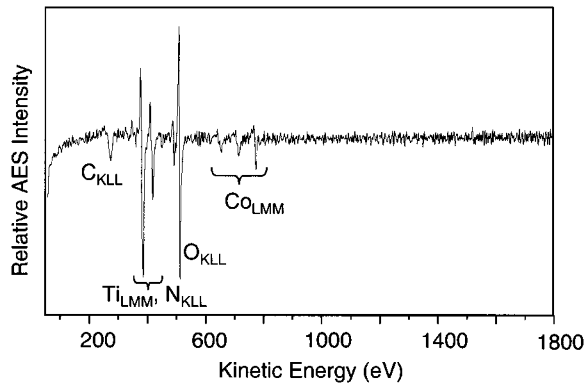


FIG. 3. Auger electron spectrum for the area around the tip apex after the local EFIO and NaOH wet etch. The Co(KLL) signal was detected at the apex area indicating that wet etch effectively removed the oxidized TiN cap layer from the tip apex.

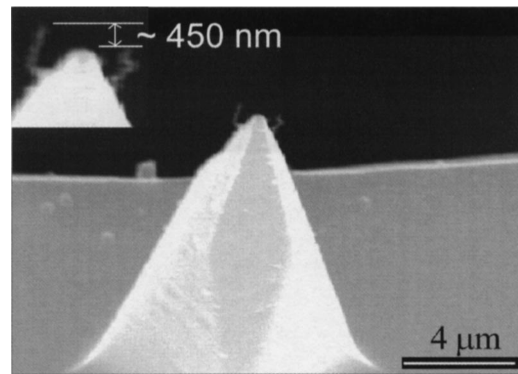


FIG. 4. SEM image of the AFM tip after the CNT growth. Two carbon nanotubes were grown in the area near the tip apex. The inset is an enlarged image for the two nanotubes. The longer carbon nanotube extends over the tip apex by ~450 nm.

analysis indicates that Co was present within the area around the tip apex, suggesting that TiN at the tip apex was effectively removed after the EFIO and wet etch. The Ti(LMM) Auger signal present in the spectrum is likely contributed from the area near the tip apex, where the TiN cap layer was not completely removed, and was subjected to unintentional illumination from the incident electron beam due to the relatively large beam size. The carbon signal found in the AES spectrum is probably due to contamination during sample preparation, such as NaOH wet etch and sample transfer in the ambient. In the region ~2 μm away from the apex, TiN was the primary surface species on the tip and no Co Auger signal was detected. The Auger analysis result suggests that the combination of the EFIO and the wet etch can effectively produce a small Co catalyst domain for latter CNT growths.

After the wet etch, the AFM probe was placed on a silicon wafer with the tip facing upward and transferred into the MPCVD system for CNT growth using CH_4 and H_2 as the plasma gas source. The microwave input power was 800 W, and a dc bias of 200 V was applied to the substrate. The dc bias set up an electric field between the tip and the plasma, which could induce electrostatic dipole moment in the growing CNT, leading to a favorable alignment of the CNT with the tip axis of the AFM probe. The substrate temperature was about 800 °C during the CNT growth. Under the same CNT growth condition, carbon nanotubes can be deposited on Si wafers via the tip-growth mode. Figure 4 shows the SEM image of the AFM tip after the CNT growth. Two whiskers, presumably carbon nanotubes, can be clearly seen to grow in the area near the tip apex. Both the nanotubes have a tail segment aligned parallel to the probe tip axis. This is particularly obvious for the longer one. The nanotube grew vertically from the sloping tip surface in the initial growth stage and bent upward as it grew to a length of ~100 nm. The segment parallel to the tip axis is about 750 nm long, and it extends over the Si tip apex by a length of ~450 nm. The two CNTs on the tip seem to start their growth on the base periphery of a small cone segment with the vertex locating at the probe tip apex and a cone height about 500 nm. No carbon nanotube could be found within the cone area, suggesting that, under the MPCVD CNT growth condition, Co in the area might be sputtered away or converted into different chemical states, which did not support CNT growth.

Figure 5 shows AFM images and the corresponding cross-sectional profiles acquired with the carbon nanotube tip and a regular pyramidal tip for an SiO_2 trench structure. The SiO_2 trench structure, 200 nm wide and 100 nm deep, was patterned by electron beam lithography and reactive ion etch. Since the longer nanotube extends over the apex of the silicon tip by ~450 nm, the extending portion of the nanotubes allows the CNT tip to scan over the trench array without any image interference caused by the silicon tip and the shorter nanotube. While the three-dimensional AFM image acquired by the regular commercial Si tip shows sloping sidewalls for the SiO_2 lines, the AFM image acquired by the CNT tip clearly illustrates the vertical sidewall and fine features in the SiO_2 pattern. The narrow trench structure prevents the pyramidal tip from approaching the trench bottom, and the average probing depth of the regular Si tip was only about 40 nm. On the contrary, the high aspect ratio of the CNT tip allows

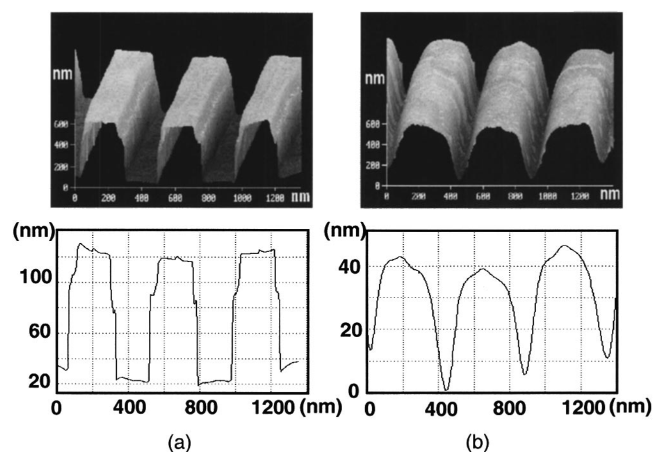


FIG. 5. AFM images and the corresponding cross-sectional profiles of an SiO_2 trench structure acquired by (a) the carbon nanotube tip and (b) a regular Si based AFM probe. The SiO_2 trench structure has a depth of 100 nm and a width of 200 nm.

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. Download to IP: 140.113.38.11 On: Thu, 01 May 2014 05:08:59

it to track the bottom surface of the trench. Slight variation in the surface contour of the vertical trench wall is obviously demonstrated in the cross-sectional profile shown in Fig. 5. Features with a height of <1 nm on the trench bottom can be clearly delineated by the cross-sectional profile.

Although two CNTs were grown on the AFM tip in this work, the high-resolution AFM image in Fig. 5 indicates that only the longer nanotube could provide the surface topographic information. However, if a sample with trench or hole structures with a depth larger than the length of the longer CNT is investigated, image interference from the shorter CNT and/or the Si tip is inevitable. Several CNT tips have been successfully made in this work, whereas most tips contain more carbon nanotubes than the one shown in Fig. 4. We are now optimizing the local EFIO parameters and the CNT growth conditions so that qualities of the CNT tips, such as the number of nanotubes on the Si tip apex and the length of the nanotube, can be well tailored. Since the CNT tip fabrication method is simple and compatible with existing thin film process technology, we believe selective growth of one single CNT on the apex of the probe tip is achievable if a nano-scaled Co catalyst domain can be defined on the apex. The approach can be used to grow CNT tips on AFM probes in the wafer scale. This can be done by growing carbon nanotubes on silicon tips of AFM probe arrays prefabricated on a Si wafer with a static anodization setup, i.e., a simple conductive plate, such as a highly doped Si wafer, is negatively biased with respect to the probe arrays.

IV. CONCLUSION

We have used a local electric-field-induced-oxidation method to define the Co catalyst domain on the tip apex of a commercial Si based AFM probe, and selectively grew carbon nanotubes on the domain by MPCVD. The Co catalyst domain was produced by removing the TiN cap layer from the tip apex of a Co coated AFM probe. This was done by oxidizing the TiN layer at the tip apex using the local electric-field-induced-oxidation method, followed by stripping the oxidized portion off the tip apex with the NaOH wet etch. Carbon nanotubes were then successfully grown on the tip apex area by MPCVD. The high-resolution AFM image of a SiO_2 trench structure acquired with the CNT AFM tip has been demonstrated.

ACKNOWLEDGMENTS

This work was supported by the National Science Council (NSC) of the Republic of China under Contract Nos. NSC90-2722-2317-200 and NSC-91-2215-E317-001. Technical support from National Nano Device Laboratories is gratefully acknowledged.

[1] H. Dai, J. H. Hafner, A. G. Rinzler, D. T. Colbert, and R. E. Smalley, Nature (London) **384**, 147 (1996).
[2] S. S. Wong, A. T. Woolley, T. W. Odom, J.-L. Huang, P. Kim, D. V. Vezenov, and C. M. Lieber, Appl. Phys. Lett. **73**, 3465 (1998).
[3] J. H. Hafner, C.-L. Cheung, T. H. Oosterkamp, and C. M. Lieber, J. Phys. Chem. B **105**, 744 (2001).
[4] S. Rozhok, S. Jung, V. Chandrasekhar, X. Lin, and V. P. Dravid, J. Vac. Sci. Technol. B **21**, 323 (2003).
[5] R. Stevens, C. Nguyen, A. M. Cassell, L. Delzeit, M. Meyyappan, and J. Han, Appl. Phys. Lett. **77**, 3453 (2000).
[6] T. Arie, H. Nishijima, S. Akita, and Y. Nakayama, J. Vac. Sci. Technol. B **18**, 104 (2000).
[7] R. Stevens, C. Nguyen, A. Cassell, L. Delzeit, M. Meyyappan, and J. Han, Appl. Phys. Lett. **77**, 3453 (2000).
[8] E. B. Cooper, S. R. Manalis, H. Fang, H. Dai, K. Matsumoto, S. C. Minne, T. Hunt, and C. F. Quate, Appl. Phys. Lett. **75**, 3566 (1999).
[9] J. H. Hafner, C.-L. Cheung, and C. M. Lieber, J. Am. Chem. Soc. **121**, 9750 (1999).
[10] P. M. Campbell, E. S. Snow, and J. P. Novak, Appl. Phys. Lett. **81**, 4586 (2002).
[11] E. S. Snow, W. H. Juan, S. W. Pang, and P. M. Campbell, Appl. Phys. Lett. **66**, 1729 (1995).
[12] B. Irmer, M. Kehrle, H. Lorenz, and J. P. Kotthaus, Appl. Phys. Lett. **71**, 1733 (1997).
[13] S. Gwo, C. L. Yeh, P. F. Chen, Y. C. Chou, T. T. Chen, T. S. Chao, S. F. Hu, and T.-Y. Huang, Appl. Phys. Lett. **74**, 1090 (1999).
[14] F. S. S. Chien, J. W. Chang, S. W. Lin, Y. C. Chou, T. T. Chen, S. Gwo, T.-S. Chao, and W.-F. Hsieh, Appl. Phys. Lett. **76**, 360 (2000).

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. Download to IP: 140.113.38.11 On: Thu, 01 May 2014 05:08:59