Effect of substrates and underlayer on CNT synthesis by plasma enhanced CVD

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Abstract Due to their unique thermal, electronic and mechanical properties, carbon nanotubes (CNTs) have aroused various attentions of many researchers. Among all the techniques to fabricate CNTs, plasma enhanced chemical vapor deposition (PECVD) has been extensively developed as one growth technique to produce vertically-aligned carbon nanotubes (VACNTs). Though CNTs show a trend to be integrated into nanoelectromechanical system (NEMS), CNT growth still remains a mysterious technology. This paper attempts to reveal the effects of substrates and underlayers to CNT synthesis. We tried five different substrates by substituting intrinsic Si with high resistivity ones and by

increasing the thickness of SiO₂ insulativity layer. And also, we demonstrated an innovative way of adjusting CNT density by changing the thickness of Cu underlayer.

Keywords Carbon nanotube (CNT) · Substrate · Underlayer · Effect

1 Introduction

Since the remarkable discovery work on CNTs in 1990s, this novel structure has stimulated extensive researches. CNTs have shown many promising characters, such as excellent thermal conductivity [1, 2], exceeding mechanical strength [3, 4], and unique electrical properties [5]. Due to these extraordinary properties, various related applications of CNTs have been boosted, such as composite materials [6, 7], logic and memory devices [8], switched capacitors [9], and membranes [10]. NEMS is one of the areas where CNTs are considered as a superior material for building various mechanical structures [11, 12].

Dipping into CNT research, substrates with different various kinds of catalysts have been tried to achieve better quality of CNTs. Despite the differences in preparations of substrates, Fe, Ni, Co [13] and Cu are the most frequently used catalysts for CNT growth. Different trials of various metal and oxide underlayers [14, 15] have been tested to find better growth results. In order to meet the requirement of future NEMS, it is inevitable to take well control of the CNT growth on different substrates and underlayers.

However, current researches of CNT growth on various substrates and underlayers are not very summarized. In this paper, several experiments were implemented to find out the effect of substrate type and underlayer thickness on CNT growth.

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2 CNT growth on different substrates

2.1 Experiment details

We designed a structure with Ni catalyst dots on TiN barrier pads, on various substrates, as shown in Fig. 1a. The diameter of Ni dots is around 800 nm, while the TiN pads have a slightly larger diameter of 1.2 μm , in order to prevent potential diffusion of Ni into substrates. Magnified details are shown in Fig. 1b.

Preparation of patterns on substrates was done by e-beam lithography. All the tested samples were all chip sized as 8 mm $\times$ 8 mm. All the growths were carried out by PECVD mode with the CNT CVD equipment—Black Magic, by Axitron. NH_3 (300 sccm) and C_2H_2 (65 sccm) were chosen to be the feeding gases. After 15 min of growth at 650 $^\circ\text{C}$ with 650 V plasma voltage, samples were taken out for SEM observation.

2.2 Results and discussion

Silicon with native oxide of 2 nm thick is reported as the most commonly used growth substrate. Figure 2 shows the well grown CNT bumps on Si/2 nm SiO_2 substrate with the TiN/Ni pattern structure shown in Fig. 1. On each

Fig. 1 Patterned structure design: **a** arrays of Ni catalyst dots with TiN barrier pads; **b** magnified view on one dot of Ni catalyst and TiN barrier pad

patterned dot, CNTs are vertically aligned with similar length, reaching the height around 3 μm .

Among all the applications of CNTs, applying CNTs into NEMS switches for radio frequency (RF) field is a hot topic [16]. Due to the conducting property and parasitic capacitance of common Si, which may lead to large signal losses and leakage especially in RF region [17], high resistivity Si (HR Si) was chosen to improve the system performance [18].

Therefore, we tried substrates of HR Si/300 nm SiO_2 and doped Si/500 nm SiO_2 . While undergoing the same growth period, what we got was totally different from the previous good result in Fig. 2. As Fig. 3 shown, CNT growths resulted poorly on both substrates. It's obvious that both substrates are totally damaged whose surfaces are no longer flat and continuous. What is more, if we take a closer look at the CNT morphology, the outlook of CNTs in Fig. 3 is hardly tube like, but actually like mountain shape. We suspected that this was caused by the damage of substrate surface decomposition and redeposition onto the protrusive CNTs' surface under high temperature and high plasma voltage.

To prevent the damage caused by plasma during growth, we tried another substrate of HR Si/2 μm SiO_2 , with a thicker surface layer of SiO_2 compared with that shown in Fig. 3a. As shown in Fig. 4a, although the surface of the substrate remained intact, the CNT growth is however not straight and falling down. We speculated that it was because of the low conductivity caused by the 2 μm thick SiO_2 surface. So we added another conductive layer of TiW on the substrate, which indicated the best CNT growth among all the substrates we tried in Fig. 4b. Though the lengths of CNTs are shorter compared with Fig. 2, it verifies the possibilities and feasibilities of integrating CNTs into NEMS in RF field.

3 Effect of thickness of Cu underlayer on CNT growth density

3.1 Experiment details

In this part, a set of experiments was carried out to study the effect of thickness of Cu underlayer. As shown in

Fig. 2 CNT growth results on Si/2 nm SiO_2 substrate

Fig. 3 **a** CNT growth results on HR Si/300 nm SiO₂ substrate; **b** CNT growth results on doped Si/500 nm SiO₂ substrate

Fig. 4 **a** CNT growth results on HR Si/2 μm SiO₂ substrate; **b** CNT growth results on HR Si/2 μm SiO₂/50 nm TiW substrate

Fig. 5, we used Cu as underlayer, Al₂O₃ as barrier layer and Ni as catalyst. The only controlled parameter was the thickness of Cu, ranging from 5 nm, 20 nm to 150 nm. Ni catalyst layer and Al₂O₃ barrier layer were all controlled to be a fixed thickness of 7 nm and 10 nm respectively.

Depositions of different layers were done by electron beam evaporation. All the tested samples were of 10 mm × 10 mm in size. All the growths are carried in PECVD mode with the CNT CVD equipment, Black Magic, by Axitron. NH₃ and C₂H₂ were chosen to be the feeding gases. After 15 min of growth at 700 °C with 600 V plasma voltage, SEM was then used to study the morphologies of CNTs on samples' surfaces. Based on the CNT growth results, two important things would be investigated in this work: (i) the compatibility of Al₂O₃ barrier layers with Cu underlayer, (ii) the influence of Cu's thickness to CNT growth.

Fig. 5 Schematic diagram of experimental samples

3.2 Results and discussion

Figure 6 shows the CNT growth result with different thickness of Cu underlayer. As we expected, the growth of CNTs with Al₂O₃ barrier layer was acceptable. But here is an unexpected finding, with the increasing of the thickness of Cu underlayer, the quality and quantity of CNTs changes. In Fig. 6a, with 5 nm thick Cu underlayer, we can clearly see the root of each CNT indicating a low density of CNTs. At the same time, the CNTs are not so straight. In

Fig. 6 SEM images of 3 samples with different Cu thickness: **a** 5 nm thick Cu underlayer; **b** 20 nm thick Cu underlayer; **c** 150 nm thick Cu underlayer

Fig. 7 Statistics of CNT number per meter square according to the average density of tested samples

Fig. 6b, with 20 nm thick Cu underlayer, the density of CNTs is larger than that in Fig. 6a, and the CNTs are straighter. Compared with Fig. 6b, Fig. 6c shows CNTs are less with curly tips. By watching carefully into the gaps between CNT roots, we can tell that the surface of substrate become really coarse and rough.

To get a clearer picture of the density of these three samples, we calculated the number of CNTs from various parts of chips in different runs of CNT growth, and get three average CNT densities with three Cu underlayer thicknesses, which are shown in the Fig. 7. This figure gives a clear view that the CNT density reaches the highest to $6.89 \times 10^{12}/\text{m}^2$ with 20 nm thick Cu underlayer. While in the cases of 5 nm and 150 nm thick Cu underlayer, the density is almost the same to be around $4 \times 10^{12}/\text{m}^2$.

We suspected that it's because the thickness of Cu underlayer alters the surface roughness, and finally leads to different CNT density. Diffusions between contiguous metal layers during CNT growth at high temperature are inevitable as reported before. Diffusions between different layers in CNT growth were also reported before [19]. We suspect that this phenomenon is caused by the diffusion of Cu into Al_2O_3 barrier layer. When there is only limited amount of 5 nm thick Cu underlayer, the effect of diffusion

is not so obvious. Whereas, increasing Cu underlayer to 150 nm may lead to too much diffusion which may poison the Ni catalyst thus less dense CNT growth. As our set of experiment shows, Cu underlayer of 20 nm thick may be most suitable and favorable for dense CNT growth.

4 Conclusions

In order to integrate CNTs into NEMS applications, we still need to research into more detailed fundamental studies on CNT growth, such as the effects of substrates and underlayers. The first part of this paper showed the effects of substrates on CNT growth, by changing the substrate from Si to HR Si and increasing the thickness of SiO_2 on the surface. In addition, we obtained a reasonable result by adding a TiW layer on HR Si/thick SiO_2 substrate. Then we also verified the thickness of Cu underlayer does affect CNT growth density.

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References

- Che J, Çagin T, Goddard WA (2000) Thermal conductivity of carbon nanotubes. *Nanotechnology* 11(2):65–69
- Huxtable ST, Cahill DG, Shenogin S, Xue L, Ozisik R, Barone P, Usrey M, Strano MS, Siddons G, Shim M, Koblinski P (2003) Interfacial heat flow in carbon nanotube suspensions. *Nat Mater* 2(11):731–734

3. Allaoui A, Bai S, Cheng H, Bai J (2002) Mechanical and electrical properties of a MWNT/epoxy composite. *Compos Sci Technol* 62(15):1993–1998
4. Salvetat JP, Bonard JM, Thomson NH, Kulik AJ, Forró L, Benoit W, Zuppiroli L (1999) Mechanical properties of carbon nanotubes. *Appl Phys A* 69(3):255–260
5. McEuen PL, Fuhrer MS, Park H (2002) Single-walled carbon nanotube electronics. *IEEE Trans Nanotechnol* 1(1):78–85
6. Lau AKT, Hui D (2002) The revolutionary creation of new advanced materials—carbon nanotube composites. *Compos Part B: Eng* 33(4):263–277
7. Thostenson ET, Ren Z, Chou TW (2001) Advances in the science and technology of carbon nanotubes and their composites: a review. *Compos Sci Technol* 61(13):1899–1912
8. Bohr MT (2002) Nanotechnology goals and challenges for electronic applications. *IEEE Trans Nanotechnol* 1(1):56–62
9. Jang JE, Cha SN, Choi YJ, Kang DJ, Butler TP, Hasko DG, Jung JE, Kim JM, Amaratunga GAJ (2008) Nanoscale memory cell based on a nanoelectromechanical switched capacitor. *Nat Nanotechnol* 3(1):26–30
10. Huczko A (2000) Template-based synthesis of nanomaterials. *Appl Phys A* 70(4):365–376
11. Jiang D, Wang T, Chen S, Ye L, Liu J (2013) Paper-mediated controlled densification and low temperature transfer of carbon nanotube forests for electronic interconnect application. *Microelectron Eng* 103:177–180
12. Fu Y, Nabiollahi N, Wang T, Wang S, Hu Z, Carlberg B, Zhang Y, Wang X, Liu J (2012) A complete carbon-nanotube-based on-chip cooling solution with very high heat dissipation capacity. *Nanotechnology* 23(4):045304
13. Huang ZP, Wang DZ, Wen JG, Sennett M, Gibson H, Ren ZF (2002) Effect of nickel, iron and cobalt on growth of aligned carbon nanotubes. *Appl Phys A* 74(3):387–391
14. Kim SM, Gangloff L (2011) Thermal chemical vapor deposition (T-CVD) growth of carbon nanotubes on different metallic underlayers. *Phys E: Low-Dimens Syst Nanostruct* 43(8):1481–1485
15. Hu JL, Yang CC, Huang JH (2008) Vertically-aligned carbon nanotubes prepared by water-assisted chemical vapor deposition. *Diam Relat Mater* 17(12):2084–2088
16. Ziaei A, Charles M, Le Baillif M, Xavier S, Caillard A, Cojocar Cs (2010) Capacitive and ohmic RF NEMS switches based on vertical carbon nanotubes. *Int J Microw Wirel Technol* 2(5):433–440
17. Feng Z, Lueck MR, Temple DS, Steer MB (2012) High-performance solenoidal RF transformers on high-resistivity silicon substrates for 3D integrated circuits. *IEEE Trans Microw Theory Tech* 60(7):2066–2072
18. Zhang F, Shi L, Li C (2005) Cpw transmission insertion loss on Si and SoI substrates. *Microw J* 48(11):138–142
19. Teo KBK, Chhowalla M, Amaratunga GAJ, Milne WI, Legagneux P, Pirio G, Gangloff L, Pribat D, Semet V, Binh VT, Brunger WH, Eichholz J, Hanssen H, Friedrich D, Lee SB, Hasko DG, Ahmed H (2003) Fabrication and electrical characteristics of carbon nanotube-based microcathodes for use in a parallel electron-beam lithography system. *J Vac Sci Technol B: Microelectron Nanometer Struct* 21(2):693–697