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Self-organized carbon nanotips

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We have developed a carbon nanostructure, which is comprised of high-density carbon nanotips on a graphite layer. These carbon nanotips, with tip diameters of ~10 nm, are grown by high-density plasma chemical vapor deposition onto Ni-coated Si using an inductively coupled plasma. The Ni on Si changes into $NiSi_2$ by substrate heating. First, a carbon buffer layer and then a graphene sheet are formed on the $NiSi_2$. Then, the carbon nanotips are grown by a C_2H_2/H_2 plasma on the graphene sheet. The carbon nanotips show good adhesion to the substrate and are almost aligned, with an average length of 110 nm. They exhibit a turn-on field of 0.1 V/μm, a field amplification factor of ~13 000, a current density of 2 mA/cm^2 at a field of 2 V/μm, and uniform electron emission. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1401777]

Carbon materials are found in various forms such as graphite, diamond, carbon fiber, graphite whiskers,[1] fullerenes, carbon nanotubes (CNTs), amorphous carbon, diamond-like carbon (DLC), and polymer-like carbon. Graphite is a hexagonal plate-like crystal with a very weak bond between graphene sheets. On the other hand, CNTs, carbon fibers and carbon whiskers have an unusual coaxial tubular structure consisting of rolled graphene sheets. Since Iijima first found carbon nanotubes in 1991,[2] carbon composites of nanometer size have become of increasing interest due to their unique structural and electrical properties. CNTs especially have been considered the most promising material for field emission display (FED) field emitters[3] due to their low turn-on field and high emission current. In order to have CNTs as field emitters on a substrate, purifying and aligning of the CNTs have generally been carried out.[3] An advanced method to make CNT field emitters is to directly deposit them on the substrate by chemical vapor deposition (CVD), plasma CVD[4] or other deposition methods.[5] However, CNTs directly deposited on the substrate show poor adhesion to the substrate and the substrate temperature must be as high as ~800 °C to exhibit good field emission properties.[6]

In this work, we have developed self-organized carbon nanotips, a form of carbon nanostructure on Si. The carbon nanotips show good adhesion to the substrate and exhibit a turn-on field of 0.1 V/μm and uniform light emission from an anode phosphor screen above the tips. The self-organized carbon nanotips exhibit the lowest turn-on field among all electron-emitting materials reported so far.

To grow carbon nanotips, we used high-density plasma CVD using an inductively coupled plasma. The rf power and gas pressure for the plasma were fixed at 1.1 kW and 1 Torr, respectively. A C_2H_2/H_2 mixture was introduced into a reaction chamber for formation of the tips. The C_2H_2 and H_2 flow rates were fixed at 25 and 50 sccm, respectively. The deposition temperature was ~700 °C. A Ni layer of 70 nm was deposited onto the Si using a sputtering system. The Ni was used to form the catalyst for growth of the carbon nanotips. The Ni was exposed to a NH_3 plasma to modify its surface morphology prior to growth of the nanotips. $NiSi_2$ formed during substrate heating. Note that the Ni can be also used as a catalyst for the growth of CNTs.[5,6] However, in this work, the Ni silicide acts as a catalyst for growth of graphite sheets and subsequently the carbon nanotips on them. The growth conditions for carbon nanotips are similar to those for the CNTs except for the formation of the Ni silicide. However, we have produced carbon nanotips, a form of carbon nanocomposite, instead of CNTs. This may be due to the formation of Ni silicide before growth of the carbon nanotips.

Figure 1 shows field emission scanning electron microscopy (SEM) images of the carbon nanotips deposited by high-density plasma CVD for 25 min. The carbon nanotips were uniformly grown on the substrate with a tip density of ~400 ea/μm^2. The carbon nanotips have an average length

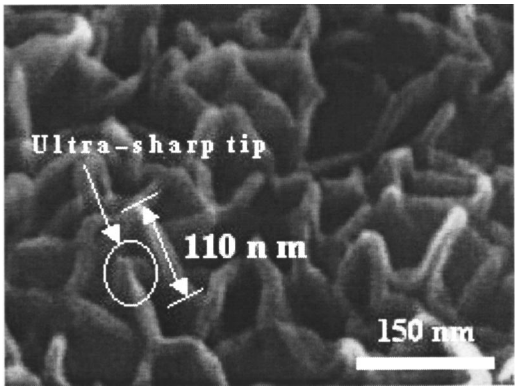

FIG. 1. Plane SEM image of the carbon nanotips.

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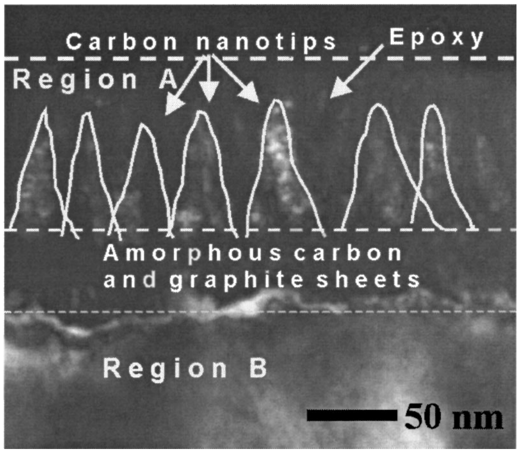

FIG. 2. Cross-sectional TEM dark-field image of the carbon nanotips.

of 110 nm and are roughly aligned to the substrate. The diameters of nanotips, the full width at half maximum (FWHM) of the perimeter for the tips, are not uniform. They are distributed mostly in the range of 10–20 nm. But the minimum diameter of the tip end is smaller than 5 nm.

Figure 2 shows a cross-sectional transmission electron microscopy (TEM) dark-field image of carbon nanotips nearly aligned to the substrate. Region A is composed of the carbon nanotips and epoxy. Note that epoxy was used for the TEM measurement and this does not exist in the real samples. The electron diffraction pattern of region B was measured together with TEM and we found its structure is the same as that of the bulk Si and this means the silicide is $NiSi_2$.[7]

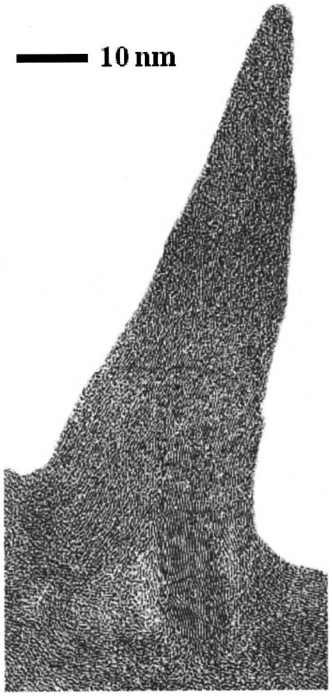

FIG. 3. HRTEM images of a carbon nanotip.

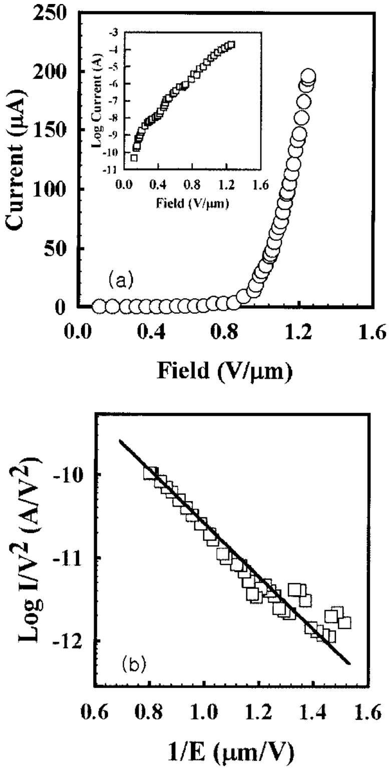

FIG. 4. (a) Current–voltage characteristics plotted on linear and log (in the box) scales of the carbon nanotips deposited for 10 min at a temperature of 700 °C and (b) FN plot of the emission currents for the carbon nanotips.

Figure 3 shows high-resolution transmission electron microscopy (HRTEM) images of a carbon nanotip. Note that the carbon nanotip consists of carbon atoms with threefold covalent bonding-like graphite. The number of sheets decreases with the growth of the carbon nanotip and this results in the formation of a sharp tip. The spacing between the carbon sheets is 0.34 nm which corresponds to the spacing between carbon layers in graphite. The tips are mostly composed of graphene sheets, but some amorphous phase may be included.

For growth of CNTs, the Ni layer turns into small grains during substrate heating and pre-plasma treatment on Ni and these Ni grains play important roles as catalysts and nucleation sites for the growth of CNTs. The structure of the CNTs depends on the Ni seeds. The graphene grains were nucleated around the Ni seeds and became the walls of the CNTs. These Ni grains can remain at the bottom for a bottom based growth model of CNTs[8–10] or rise to the top for a top based growth model.[8,11,12] In both cases, Ni seeds can be catalysts by themselves and are encapsulated by the tube walls. Carbon atoms or molecules are absorbed onto these Ni seeds and form the walls of CNTs.

For growth of the carbon nanotips, on the other hand, the Ni was changed into $NiSi_2$ by a rise in temperature and NH_3 plasma treatment. For this, the thickness of Ni must be thin enough not to remain on the silicide surface after silicide formation. When the Ni remained on the silicide, multiwalled CNTs grew. Carbon atoms or molecules were added to the Ni silicide surface and nucleated, so the carbon layers form on the whole Ni silicide layer, parallel to the silicide surface. This is the main reason for the growth of carbon nanotips instead of carbon nanotubes despite using similar deposition conditions. Between the Ni silicide and graphene sheets, an amorphous carbon layer of ~10 nm is formed as a buffer layer due to the difference in crystal structure between graphite and $NiSi_2$. The graphite has a hexagonal structure with a lattice constant of 0.34 nm to the *c* axis, normal to the

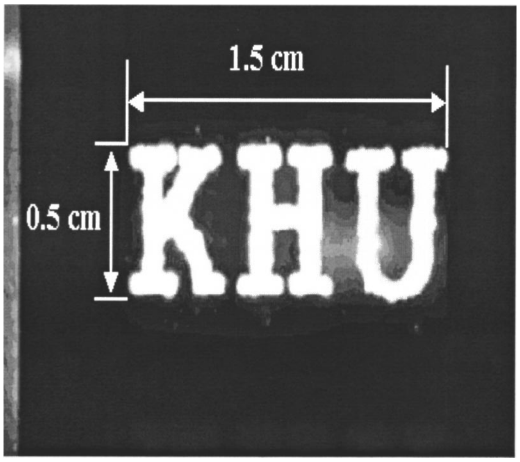

FIG. 5. Photoimage of light emission from a phosphor screen using the carbon nanotips.

graphene sheet, and $NiSi_2$ has a diamond structure with a lattice constant of 0.54 nm. After growth of about tens of graphene sheets, carbon nanotips were grown on these sheets. During growth of the graphene sheets, amorphous carbon or defective graphite nanoparticles can form on the sheets.

Figure 4(a) shows current–voltage characteristics plotted on linear and log (in the box) scales for carbon nanotips deposited for 10 min at a temperature of 700 °C. The electron emission performance for carbon nanotips was investigated using a diode structure. The gap between the anode and the carbon nanotips was 1 mm and the anode area was 2 cm^2. The turn-on field of the carbon nanotips is $\sim 0.1\ \mathrm{V}/\mu\mathrm{m}$. This, we believe, is the lowest value reported so far. Note that the CNTs show turn-on field of $>0.5\ \mathrm{V}/\mu\mathrm{m}$.[13] The emission current of the carbon nanotips at a field of 1.25 $\mathrm{V}/\mu\mathrm{m}$ is about 186 $\mu\mathrm{A/cm}^2$. This current density at a field of 1.25 $\mathrm{V}/\mu\mathrm{m}$ is much higher than the values of film-type CNTs emitters reported so far.[9,14–17] These low turn-on fields and high emission currents are mainly due to the sharp tip structure and high tip density of 400 $\mathrm{tips}/\mu\mathrm{m}^2$. Figure 4(b) shows a Fowler–Nordheim (FN) plot of the emission currents for the carbon nanotips. From Fowler–Nordheim theory,[18] the field emission current I can be expressed as

$$I \propto A(\beta^2/\phi)E^2 \exp[-B\phi^{3/2}/(\beta E)],$$

where ϕ is the work function of the nanotips, A and B are constants and E is external macroscopic electric field. In the Fowler–Nordheim plot, a plot of $\log I/E^2$ vs $1/E$, the slope of the straight line is $B\phi^{3/2}/\beta$ with $B = 6.87 \times 10^9\ (\mathrm{V\,eV}^{-3/2}\,\mathrm{m}^{-1})$.[14,19] The field amplification factor β can be obtained from the slope of the FN plot and it was $\sim$13 000 assuming 5 eV for ϕ.[20] The β reported here is smaller than those (30 000–50 000)[14] of a single free standing CNTs emitter, but much higher than that of film-type CNT emitter.[14–17] Note that the film-type CNT emitters show β of 1000–10 000 regardless of the fact that single walled or multiwalled CNTs are mostly lower than 8000.[15–17,21] This also confirms that the carbon nanotips developed in this work are better than CNTs as field emitters.

Figure 5 shows a light emission pattern using the carbon nanotips at a field of 2.3 $\mathrm{V}/\mu\mathrm{m}$. The gap between the cathode and the anode was 1 mm and was maintained by glass spacers. ITO glass with a printed ZnO:Mn blue phosphor was used as an anode plate. Uniform bright light emission can be seen. The adhesion of nanotips to the substrate is very firm so they could not be peeled off even by scratching.

In summary, we have developed carbon nanotips on Si with a diameter of less than 10 nm. Ni silicide formation has an important role in allowing the growth of carbon nanotips. The carbon nanotips show good adhesion to the substrate and good field emission properties because they formed on a graphene sheet grown on Ni silicide with an amorphous carbon buffer layer between the graphite and Ni silicide. The carbon nanotips exhibited a turn-on field of 0.1 $\mathrm{V}/\mu\mathrm{m}$, a field amplification factor of 13 000 and uniform light emission from a phosphor screen. These nanotips are promising for use in electron sources.

[1] R. Bacon, J. Appl. Phys. **31**, 283 (1960).
[2] S. Iijima, Nature (London) **354**, 56 (1991).
[3] W. B. Choi, D. S. Chung, S. H. Park, and J. M. Kim, SID'99 Dig., 1135 (1999).
[4] Q. Zhang, S. F. Yoon, J. Ahn, B. Gan, Rusli, M. B. Yu, L. K. Chean, and X. Shi, Int. J. Mod. Phys. B **14**, 289 (2000).
[5] 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).
[6] Y. C. Choi, Y. M. Shin, S. C. Lim, D. J. Bae, Y. H. Lee, B. S. Lee, and D. C. Chung, J. Appl. Phys. **88**, 4898 (2000).
[7] T. Hempel, O. Schoenfeld, and F. Syrowatka, Solid State Commun. **85**, 921 (1993).
[8] J. Kong, H. T. Soh, A. M. Cassell, and C. F. Quate, Nature (London) **395**, 878 (1998).
[9] S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassell, and H. Dai, Science **283**, 512 (1999).
[10] C. Bower, O. Zhou, W. Zhu, D. J. Werder, and S. Jin, Appl. Phys. Lett. **77**, 2767 (2000).
[11] S. H. Tsai, C. W. Chao, C. L. Lee, and H. C. Shih, Appl. Phys. Lett. **74**, 3462 (1999).
[12] M. H. Kuang, Z. L. Wang, X. D. Bai, J. D. Guo, and E. G. Wang, Appl. Phys. Lett. **76**, 1255 (2000).
[13] S. Uemura, T. Nagasako, J. Yotani, T. Shimojo, and Y. Saito, SID'98 Dig., 1052 (1998).
[14] J.-M. Bonard, F. Maier, T. Stockli, A. Chatelain, W. A. de Heer, J.-P. Salvetat, and L. Forro, Ultramicroscopy **73**, 7 (1998).
[15] Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang, and A. R. Krauss, Appl. Phys. Lett. **70**, 3308 (1997).
[16] W. A. de Heer, A. Châtelain, and D. Ugarte, Science **270**, 1179 (1995).
[17] J.-M. Bonard, J.-P. Salvetat, T. Stöckli, and W. A. de Heer, Appl. Phys. Lett. **73**, 918 (1998).
[18] R. H. Fowler and L. W. Nordheim, Proc. R. Soc. London, Ser. A **119**, 173 (1928).
[19] J. W. Gadzuk and E. W. Plummer, Rev. Mod. Phys. **45**, 487 (1973).
[20] B. Robrieux, C. R. Seances Acad. Sci., Ser. B **278**, 659 (1974).
[21] Alexandrou, M. Baxendale, N. L. Rupesinghe, G. A. J. Amaratunga, and C. J. Kiely, J. Vac. Sci. Technol. B **18**, 2698 (2000).