

UNCLASSIFIED

Defense Technical Information Center  
Compilation Part Notice

ADP014296

TITLE: Growth of Carbon Nanofibers on Electroless Ni-P Alloy Catalyst

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings Volume 740  
Held in Boston, Massachusetts on December 2-6, 2002. Nanomaterials for  
Structural Applications

To order the complete compilation report, use: ADA417952

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:

ADP014237 thru ADP014305

UNCLASSIFIED

## GROWTH OF CARBON NANOFIBERS ON ELECTROLESS Ni-P ALLOY CATALYST

T.K. Tsai, W.L. Liu, S.H. Hsieh, and W.J. Chen

Department of Materials Science and Engineering, National Huwei Institute of Technology, Huwei, Yunlin, Taiwan 632, Republic of China

### Abstract

Carbon nanotubes (CNTs) were grown by electroless Ni-P plated on silicon substrate in a microwave heating chemical vapor deposition (CVD) system with methane gas at 700 °C. The CNTs grown on Ni-P catalyst showed random orientation and small diameter around 15–30 nm. Field emission test results indicated that the Ni-P catalyzed-CNTs exhibited excellent field emission properties. The turn-on field was about 0.56 V/ $\mu\text{m}$  with an emission current density 10  $\mu\text{A}/\text{cm}^2$  and the threshold field was 4.4 V/ $\mu\text{m}$  with an emission current density 10 mA/ $\text{cm}^2$ . These excellent field emission properties may be attributed to the random orientation and small diameter of CNTs.

### 1. Introduction

Since the discovery of carbon nanotubes (CNTs) in 1991,<sup>1</sup> this kind of carbon nanostructures has attracted extensive attention and study, due to their novel properties and potential applications, such as in high-performing nano-materials, nanoelectronics, high-efficiency energy storage and cold field emitter.<sup>2-5</sup> One of the most potential applications of CNTs is as electron emitter for flat plane displays. Because CNTs have excellent field emission properties, i.e., good emission stability, long emitter lifetime and low voltage for operating. Therefore, many researchs have been done on the fabrication of field emission display (FED) and other electronic devices.

Several synthesizing methods for the fabrication of CNTs have been developed by researchers, such as arc discharge, laser evaporation, pyrolysis of hydrocarbon gases and plasma-enhanced or thermal CVD.<sup>5-16</sup> Among these methods, the CVD possessed simple process, selective growth, high purity, high yield and vertical alignment characteristics. Thus CVD was widely accepted by many investigators. In the CVD method, the transition metal, e.g., Ni, Co, Fe, plays an important and indispensable role for the growth of CNTs, because it works as a catalyst of the CNTs' growth. The chemical composition and nanoparticle size of the catalyst determine the structure, property and diameter of the CNTs. Since the catalyst nanoparticles are essential for both initial nucleation and subsequent growth of CNTs in CVD, many investigations have been developed to prepare catalyst nanoparticles. The techniques include filling metallic catalyst nanoparticle in nanoporous or mesoporous zeolite,<sup>11</sup> silicon<sup>5</sup> and anodic alumina<sup>12</sup> by evaporation or impregnation, chemically synthesized catalyst metal nanoparticle by reverse micelle method,<sup>13</sup> and etching the catalyst metal-coated substrate by laser ablation,<sup>8</sup> plasma<sup>9</sup> or NH<sub>3</sub> treatment.<sup>14</sup> Choi et al.<sup>15</sup> deposited Ni using rf magnetron sputtering on Si substrate. Sohn et al.<sup>16</sup> deposited Fe on Si (100) substrate by pulse-laser deposition. Avigal et al.<sup>17</sup> coated Co on n-type Si by e-beam, and Kim et al.<sup>14</sup> coated Ni using electroplating on soda-lime glass, etc. However, there is little literature mentioned about electroless plating Ni deposited on substrate for fabricating CNTs. Electroless plating technique has been applied for ohmic contacts with silicon in semiconductor devices and for contact filling in very large scale integrated (VLSI)<sup>18</sup> for several years. This technique is a useful process for microelectronics, because it is simple and easy to manage.

In the present study, we have deposited Ni as catalyst metal on the silicon substrate by a low cost and simple method – electroless plating technique. The CNTs with excellent field emission property grown on electroless plating Ni has fabricated

successfully by using a microwave heat CVD system. We believe the cheap and simple process of growing CNTs has potential for the fabrication of flat plane displays and other electronic devices.

## 2. Experimental

A Ni–P thin film was deposited by using electroless plating technique on p-type (100) silicon wafer (1–20 ohm cm). Prior to the electroless plating process, it is necessary to pretreat the silicon surface. This pretreatment consisted of the following four steps; (1) degrease cleaning of the surface using a weak base solution (acetone) by ultrasonic; (2) roughening the surface by etching in an acid solution of HNO<sub>3</sub>, HF and deionized (DI) water; (3) sensitizing in a solution of SnCl<sub>2</sub> and HCl; and (4) catalyzing by deposition of Pd in a solution of PdCl<sub>2</sub> and HCl. A rinse with DI water was carried out at the end of each step. The plating solution was composed of a mixture of NiSO<sub>4</sub>, NaH<sub>2</sub>PO<sub>2</sub>, Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> and Pb(NO<sub>3</sub>)<sub>2</sub>; where NiSO<sub>4</sub> as the main nickel source, NaH<sub>2</sub>PO<sub>2</sub> as the reducing agent, Na<sub>2</sub>C<sub>4</sub>H<sub>4</sub>O<sub>4</sub> and Pb(NO<sub>3</sub>)<sub>2</sub> as buffer and complexing agent for nickel. Since NaH<sub>2</sub>PO<sub>2</sub> is used as a reducer, the electroless plated nickel structures always incorporated with phosphorus. The composition of plating solution and experimental condition are list in Table I.

A microwave heating CVD system has been utilized for growth of CNTs. The electroless Ni deposited-silicon substrate was placed on a ceramic holder, which was heated to 700 °C by controlling the microwave power and CNTs were grown on the substrate using methane gas as the source of carbon with its flow rate 200 cc/min for 10 min. The CNTs were observed by field emission scanning electron microscope (FESEM). Field emission was measured by taking voltage – current (V–I) curve with Keithley 237 in a vacuum chamber.

## 3. Result and discussion

Figure 1 is a SEM micrograph showing the surface morphology of CNTs grown on the silicon substrate. The SEM image shows the CNTs are not vertically aligned but randomly tangled. The diameter of the most CNTs are 15–30 nm, only few CNTs around 60–80 nm. This result is consistent with the previous report that the size of Ni nanoparticle suitable for CNTs growth is limited to around 20–30 nm.<sup>19</sup> Figure 1 also illustrates a large amount of nanoparticles at tip of the tubes. Energy dispersive x-ray (EDX) spectra carried out during FESEM measurements showed that the nanoparticle consists of Ni, P and carbon. This phenomenon may be indicated the nucleation and growth mechanism have correlation with the process conditions and the morphology of the Ni–P nanoparticles on the surface of substrate. Although many nucleation and growth mechanisms about Ni catalyst for CNTs have been proposed,<sup>20,22</sup> the CNTs formation mechanism for catalyst by electroless plating Ni was not clear yet. Further studies are required for investigating the catalyst effect of Ni–P alloy for CNTs.

Field emission properties were measured at room temperature in a vacuum chamber with a 10<sup>-6</sup> torr by applying voltages up to 1100 V. The distance between the indium–tin oxide (ITO) film and the CNTs tips is 180 μm. Figure 2 illustrates the electron emission current density versus electric field curve of the CNTs. The turn-on field, for an emission current density of 10 μA/cm<sup>2</sup>, is 0.56 V/μm. The threshold field, for an emission current density of 10 mA/cm<sup>2</sup>, is 4.4 V/μm. Bonard et al.<sup>23</sup> has reviewed emission characteristics of carbon nanotube; the lowest turn-on field 0.75 V/μm was reported by Rao and co-workers. Our result shows the CNTs catalyzed by Ni–P alloy have very good field emission properties, especially the extremely low turn-on field, 0.56 V/μm. The Fowler–Nordheim equation was used to analyze the field emission data obtained from V–I curve. Figure 3 shows the corresponding F–N plot of Figure 2. The plot of  $\ln |I/V^2|$  versus  $|1/V|$  is approximately straight line, indicating that the emitting electrons mainly follow field emission process.

The field emission characteristics of CNTs are determined by its intrinsic structure, chemical properties, aligned density and orientation of the tubes. These excellent field emission properties of Ni–P catalyzed–CNTs may be attributed to the random orientation and small diameter of CNTs. As Davydov and co-workers<sup>24</sup> pointed out, perfectly aligned carbon nanotubes were less efficient field emitters and

had lower field enhancement than chaotic carbon nanotubes. Groning and co-workers<sup>25</sup> also suggested that some random CNTs exhibited better field emission properties than aligned CNTs. These results are good evidence to our supposition.

#### 4. Conclusion

We have grown CNTs on Ni-P catalyst electroless plated on silicon substrate in a microwave heating CVD system with methane at 700 °C. The CNTs grown on Ni-P catalyst shows random orientation and small diameter about 15–30 nm. Field emission results indicated the Ni-P catalyzed-CNTs exhibits excellent field emission properties, the turn-on field was about 0.56 V/μm with an emission current density of 10 μA/cm<sup>2</sup> and the threshold field was 4.4 V/μm with an emission current density of 10 mA/cm<sup>2</sup>. These excellent field emission properties may be attributed to the random orientation and small diameter of CNTs. The electroless plating technique not only provides a cheap and easy process for fabricating CNTs, but also promotes the field emission property of CNTs. The electroless plating technique for CNTs growth has potential for the fabrication of flat plane displays and the other electronic device industries.

#### References

- <sup>1</sup> S. Iijima, *Nature (London)* **354**, 56 (1991)
- <sup>2</sup> S. Wong, E. Joselevich, A. T. Wolley, C. L. Cheung, and C. M. Lieber, *Nature (London)* **394**, 52 (1998)
- <sup>3</sup> S. J. Tans, A. R. M. Verschueren, and C. Dekker, *Nature (London)* **393**, 49 (1998)
- <sup>4</sup> C. Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Chen, and M. S. Dresselhaus, *Science* **286**, 1127 (1999)
- <sup>5</sup> S. Fan, M. G. Chapline, N. R. Franklin, T. W. Tombler, A. M. Cassel, and H. Dai, *Science* **283**, 512 (1999)
- <sup>6</sup> S. Iijima and T. Ichihashi, *Nature (London)* **363**, 603 (1993)
- <sup>7</sup> A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, D. T. Colbert, G. Scuseria, D. Tomanek, J. E. Fisher, and R. E. Smalley, *Science* **273**, 483 (1996)
- <sup>8</sup> M. Terrines, N. Grobert, J. Olivares, J. P. Zhang, H. Terrones, K. Kordatos, W. K. Hsu, J. P. Hare, P. D. Townsend, K. Prassides, A. K. Cheetham, H. W. Kroto, and D. R. M. Walton, *Nature (London)* **388**, 52 (1997)
- <sup>9</sup> 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)
- <sup>10</sup> W. Z. Li, S. S. Xie, L. X. Qian, B. H. Chang, B. S. Zou, W. Y. Zhou, R. A. Zhao, and G. Wang, *Science* **274**, 1701 (1996)
- <sup>11</sup> K. Mukhopadhyay, A. Koshio, T. Sugai, N. Tanaka, H. Shinohara, Z. Konya, and J. B. Nagy, *Chem. Phys. Lett.* **303**, 117 (1999)
- <sup>12</sup> J. Li, C. Papadopoulos, J. M. Xu, and M. Moskovits, *Appl. Phys. Lett.* **75**, 367 (1999)
- <sup>13</sup> H. Ago, T. Komatsu, S. Ohshima, Y. Kuriki, and M. Yumura, *Appl. Phys. Lett.* **77**, 79 (2000)
- <sup>14</sup> J. Kim, K. No, and C. J. Lee, *J. Appl. Phys.* **90**, 2591 (2001)
- <sup>15</sup> Y. C. Choi, D. J. Bae, Y. H. Lee, B. S. Lee, G. S. Park, W. B. Choi, N. S. Lee, and J. M. Kim, *J. Vac. Sci. Technol. A* **18**, 1864 (2000)
- <sup>16</sup> J. I. Sohn, C. J. Choi, S. Lee, and T. Y. Seong, *Appl. Phys. Lett.* **78**, 3130 (2001)
- <sup>17</sup> Y. Avigal and R. Kalish, *Appl. Phys. Lett.* **78**, 2291 (2001)
- <sup>18</sup> C. H. Ting and H. Paunovic, *J. Electrochem. Soc.* **136**, 456 (1989)
- <sup>19</sup> M. Yudasaka, R. Kikuchi, T. Matsui, Y. Ohki, S. Yoshimura, and E. Ota, *Appl. Phys. Lett.* **67**, 2477 (1995)
- <sup>20</sup> M. Yudasaka, R. Kikuchi, Y. Ohki, E. Ota, and S. Yoshimura, *Appl. Phys. Lett.* **70**, 1817 (1997)
- <sup>21</sup> A. N. Andriotis, M. Menon, and G. Froudakis, *Phys. Rev. Lett.* **85**, 3193 (2000)
- <sup>22</sup> F. Banhart, J. -C. Charlier, and P. M. Ajayan, *Phys. Rev. Lett.* **84**, 686 (2000)
- <sup>23</sup> J. -M. Bonard, H. Kind, T. Stöckli, and L.-O. Nilsson, *Solid-State Electronics* **45**, 893 (2001)

- <sup>24</sup> D. N. Davydov, P. A. Sattari, D. AlMawlawi, A. Osika, T. L. Haslett, and M. Moskovits, *J. Appl. Phys.* **86**, 3983 (1999)
- <sup>25</sup> O. Groning, O. M. Kuttel, C. Emmenegger, P. Groning, and L. Shlapbach, *J. Vac. Sci. Technol. B* **18**, 665 (2000)

TABLE I. The composition of plating solution and experimental condition for electroless Ni-P plating.

Chemicals	concentration ( g/l )
NiSO <sub>4</sub> · 6H <sub>2</sub> O	8
NaH <sub>2</sub> PO <sub>2</sub> · H <sub>2</sub> O	27
Na <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> · 6H <sub>2</sub> O	16
Pb(NO <sub>3</sub> ) <sub>2</sub>	1 ppm
PH = 4.5	
Temperature 70°C	

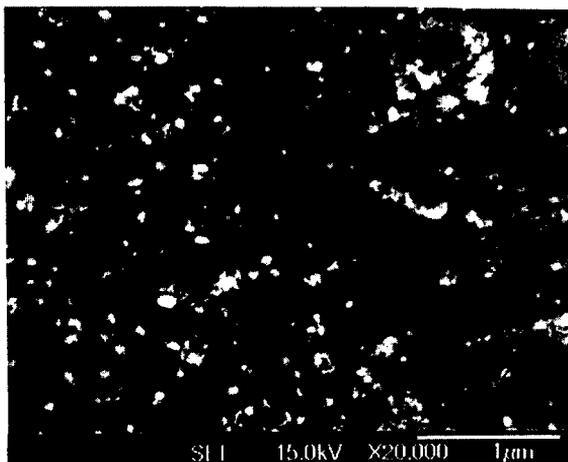


Fig. 1. FESEM image of the surface morphology of CNTs. The CNTs grown on Ni-P catalyst shows random orientation and small diameter about 15~30 nm, few CNTs' diameter is around 60~80 nm. There is a large amount of nanoparticles at tip of the tubes.

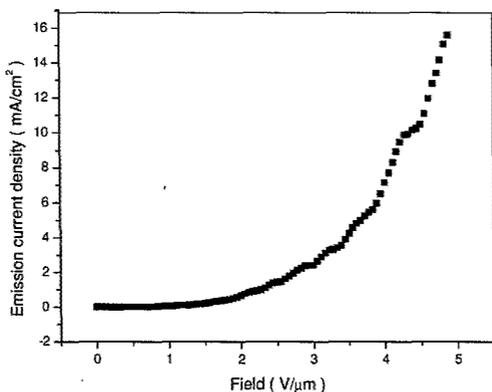


Fig. 2. Electron emission current density versus electric field ( I-V ) curve of CNTs. The turn-on field was about 0.56 V/μm with an emission current density 10 μA/cm<sup>2</sup> and the threshold field was 4.4 V/μm with an emission current density 10 mA/cm<sup>2</sup>.

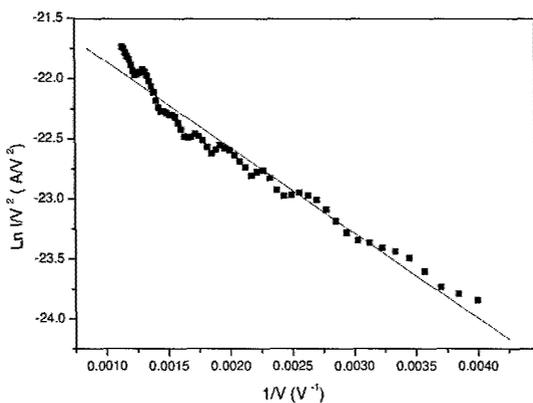


Fig. 3. The corresponding F-N plot of Figure 2. The plot of  $\ln |I/V^2|$  versus  $|1/v|$  is approximately straight line.