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2000 Jpn. J. Appl. Phys. 39 L925

(http://iopscience.iop.org/1347-4065/39/9A/L925)

Jpn. J. Appl. Phys. Vol. 39 (2000) pp. L 925–L 928
Part 2, No. 9A/B, 15 September 2000

Field-Emission Properties of Aligned Carbon Nanotubes

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(Received April 24, 2000; accepted for publication July 3, 2000)

Dense, well-separated, and aligned carbon nanotubes have been prepared via bias-enhanced microwave plasma chemical vapor deposition. The turn-on fields defined at the emission current density of 10 μA/cm^2 are about 3.35 V/μm, 2.54 V/μm, and 3.54 V/μm, for the immersion times in $PdCl_2$ of 1 min, 20 min, and 40 min, respectively. The corresponding emission current densities are about 0.97 mA/cm^2, 4.5 mA/cm^2, and 0.44 mA/cm^2 at the electric field of 5 V/μm. The higher emission current obtained from the aligned carbon nanotubes for the immersion time of 20 min is ascribed to the denser and sharper nanotubes formed in this condition.

KEYWORDS: field-emission, aligned carbon nanotubes, bias-enhanced microwave plasma chemical vapor deposition

1. Introduction

Recently, carbon nanotubes have attracted considerable attention because of their unique structural and electronic properties[1,2] that can be used in a broad range of potential applications.[3–6] One potential application of carbon nanotubes is as field emitters in vacuum microelectronics, owing to their high aspect ratios, high chemical stability, and small tip radii of curvature that can easily emit electrons at a very low electric field.[7] Good field-emission properties from multiwalled nanotubes and single-walled nanotubes grown by arc discharge have been reported.[8,9] For display applications, it is necessary to produce high-density and vertically aligned nanotube arrays. However, carbon nanotubes produced by arc discharge have disordered orientation and it is difficult to align the nanotubes after growth. However, vertically aligned carbon nanotubes have recently been synthesized by thermal decomposition[10,11] and plasma-enhanced chemical vapor deposition of hydrocarbon gas.[12,13] In this letter, a method using microwave plasma chemical vapor deposition (MPCVD) with a DC bias was performed to align the carbon nanotubes. Typically, catalytic metals used for the growth of carbon nanotubes are Fe, Co, and Ni. On the other hand, Pd has also been found to have good catalytic ability and can be easily deposited on a porous silicon substrate by electrodeless plating.[13] These aligned carbon nanotubes catalyzed by Pd show good field-emission properties and superior emission stability compared to the nonaligned carbon nanotubes.

2. Experimental Procedures

The aligned carbon nanotubes were synthesized using a MPCVD system with a negative DC bias. The preparation procedure is briefly described as follows. The porous silicon layers were first formed on p-type silicon substrates by anodization. A reductive deposition of nanoparticles of Pd on the porous silicon surface was carried out by immersing the porous silicon specimen into an aqueous solution of $PdCl_2$. Then, carbon nanotubes were grown on Pd-catalyzed substrates by MPCVD. The microwave input power was 1100 W and the substrate was heated directly by plasma without other heating sources. A mixture of methane and hydrogen gases was introduced into the chamber. The total pressure was kept at 30 Torr and the flow rates were maintained at 0.5 sccm and 100 sccm for methane and hydrogen, respectively. In this experiment, various times of immersion in $PdCl_2$ including 1 min, 20 min and 40 min were adopted to produce different shapes of carbon nanotubes. The experimental conditions are listed in Table I.

3. Results and Discussion

Scanning electron microscopy (SEM) was used to determine the morphology of aligned carbon nanotubes. Figure 1(a) shows a SEM micrograph of aligned carbon nanotubes for the immersion time of 1 min. It can be seen that most nanotubes are approximately perpendicular to the substrate and are well separated from each other. These aligned carbon nanotubes are 100 nm to 151 nm in diameter and 3 μm to 4 μm in length. Most of the aligned carbon nanotubes have closed ends at the tips. Figure 1(b) shows a SEM micrograph of aligned carbon nanotubes for the immersion time of 20 min. From the SEM micrograph, it can be seen that more densely aligned carbon nanotubes can be obtained by increasing the time of immersion in $PdCl_2$. This is attributable to the greater number of catalytic nanoparticles of Pd deposited on

Table I. Experimental conditions for aligned carbon nanotubes.

No.	Immersion times in $PdCl_2$	CH_4/H_2	Microwave power	Temperature	Pressure	Deposition time	DC bias
A1	1 min	0.5/100 (sccm)	1100 W	600°C–700°C	30 Torr	11 min	−350 V
A2	20 min						
A3	40 min						

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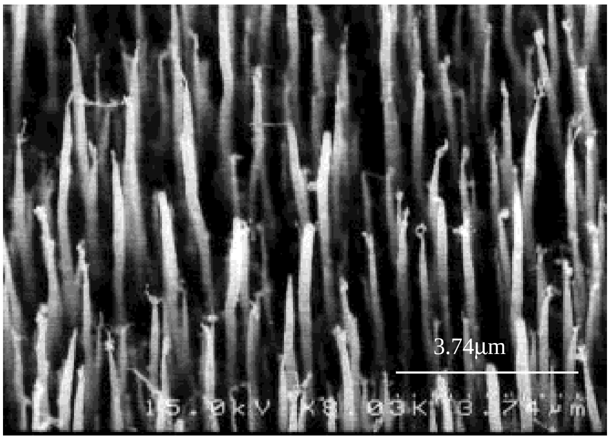
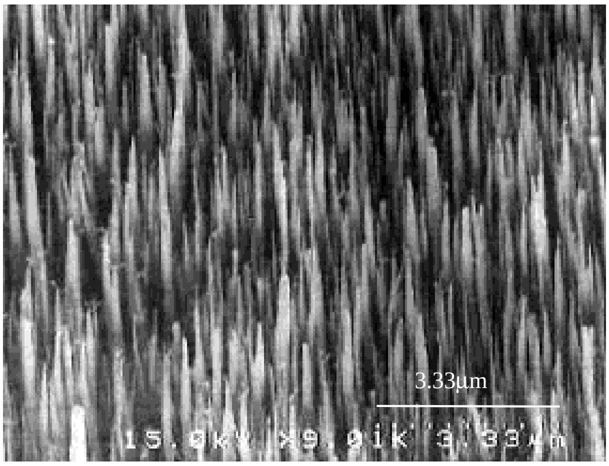
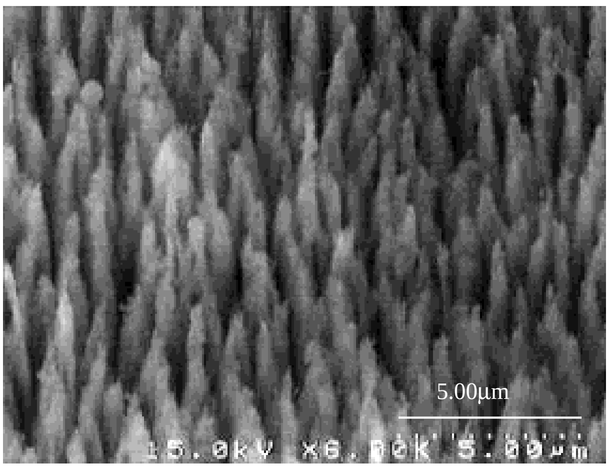
the porous silicon surface. Figure 1(c) shows a SEM micrograph of aligned carbon nanotubes for the immersion time of 40 min. This SEM micrograph shows carbon nanotubes of a different shape than the prior ones. Figures 2(a), 2(b), and 2(c) show the SEM micrographs of Pd nanoparticles after immersion in $PdCl_2$ for 1 min, 20 min, and 40 min, respectively. For the immersion time of 1 min, catalytic nanoparticles of Pd can be dispersed with a low density. The immersion time of 20 min can achieve a higher density and more uniform distribution of Pd catalytic nanoparticles. However, the excessive immersion time of 40 min causes the aggregation of the Pd



(a)

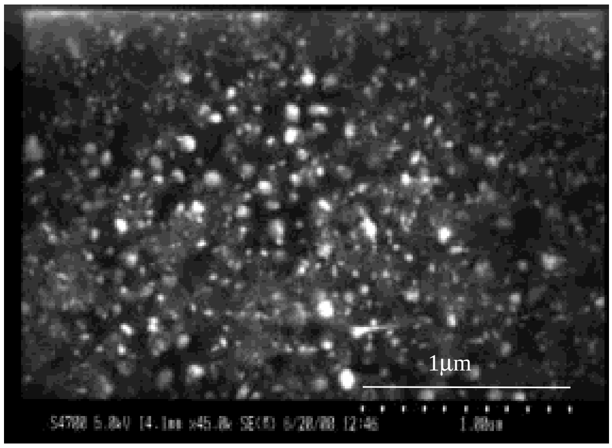


(b)

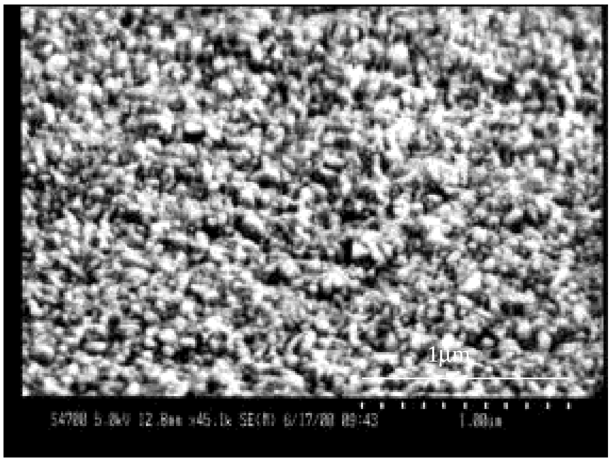


(c)

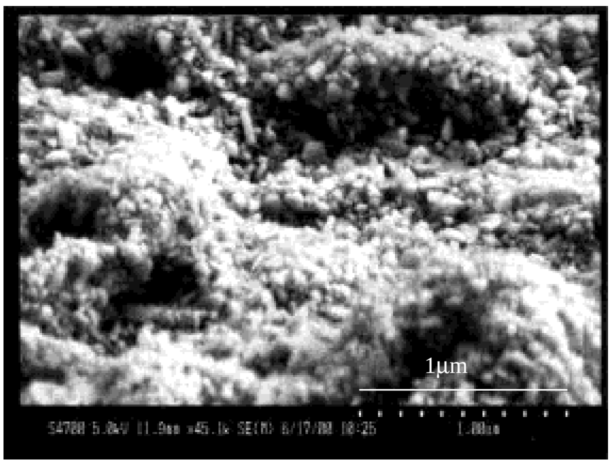
Fig. 1. SEM micrographs of aligned carbon nanotubes for different immersion times in $PdCl_2$: (a) 1 min, (b) 20 min, and (c) 40 min.



(a)



(b)



(c)

Fig. 2. SEM micrographs of Pd nanoparticles for different immersion times in $PdCl_2$: (a) 1 min, (b) 20 min, and (c) 40 min.

catalytic nanoparticles. This aggregation results in a cluster of carbon nanotubes which causes the blunt morphology of the carbon nanotubes formed in Fig. 1(c).

The field-emission properties of these aligned carbon nanotubes were characterized in a high vacuum environment with a base pressure of about 1×10^{-7} Torr. The measurement system is based on Keithley 237 high voltage source units with a IEEE 488 interface. The anode was a graphite plate and the spacing between the emitter and the anode was controlled at 220 μm. Prior to the electrical measurement, a high constant voltage of 1100 V was applied to the emitters to exhaust the adsorbed molecules and impurities. Figure 3 shows the field-emission properties of the aligned carbon nanotubes for different immersion times in $PdCl_2$. It can be seen that the aligned carbon nanotubes exhibit high emission current at low electric field. The turn-on fields E_{on} defined at the emission current density of 10 μA/cm^2 are about 3.35 V/μm, 2.54 V/μm, and 3.54 V/μm, for immersion times in $PdCl_2$ of 1 min, 20 min, and 40 min, respectively. The corresponding emission current densities are about 0.97 mA/cm^2, 4.5 mA/cm^2, and 0.44 mA/cm^2 at the electric field of 5 V/μm. The aligned carbon nanotubes for the immersion time of 20 min show superior field-emission properties compared to others. This is due to the much more densely aligned carbon nanotubes formed under this condition. On the other hand, the immersion time of 40 min results in relatively poor emission properties. This may be ascribed to the blunt tip of nanotube emitters obtained under this condition. According to Fowler-Nordheim (FN) theory, the emission current density J can be expressed as a function of the applied electric field E, the local work function of the tip ϕ, and the field-enhancement factor β. That is, $J \propto (\beta^2 E^2/\phi) \times \exp(-6.83 \times 10^7 \times \phi^{3/2}/\beta E)$. With proper arrangement, a linear relationship between $\ln(J/E^2)$ and E^{-1} can be obtained from the above equation. A typical FN plot, $\ln(J/E^2)$ vs (E^{-1}), is used to verify the field-emission characteristics. Figure 4 shows the corresponding FN plots of the aligned carbon nanotubes. Nearly straight lines are observed for all of the samples exhibiting the field-emission phenomena. The field-enhancement factor β can be derived from the slope of the FN plot by assuming a work function of carbon nanotubes of 5 eV. The β values for the immersion times in $PdCl_2$ of 1 min, 20 min, and 40 min are about 3436, 3674, and 2920, respectively. The first two values are close due to the similarly aligned carbon nanotubes formed under the first two preparation conditions. The last value is smaller than the others, which is ascribed to the larger tip radius of emitters. Figure 5 demonstrates the emission current stability of the aligned carbon nanotubes over a period of 2 h. An emission current density of 4.5 mA/cm^2 was established at the electric field of 5 V/μm. No obvious degradation of the emission current density was observed in the stability test. The emission current fluctuation was found to be from −25% to +15%. This is relatively more stable than that of the nonaligned carbon nanotubes previously reported.[14)]

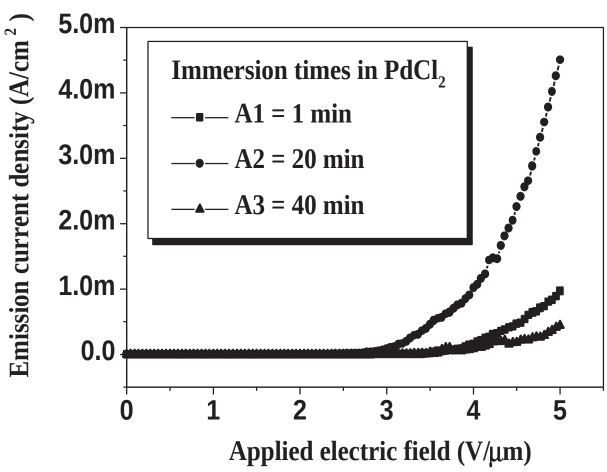


Fig. 3. Field-emission properties of aligned carbon nanotubes for different immersion times in $PdCl_2$.

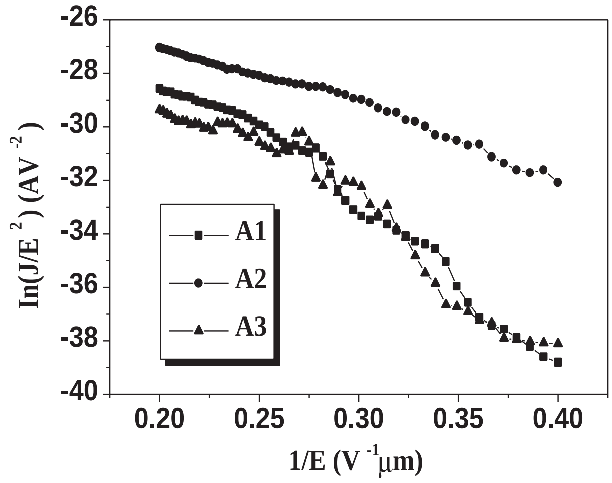


Fig. 4. FN plots of aligned carbon nanotubes for different immersion times in $PdCl_2$.

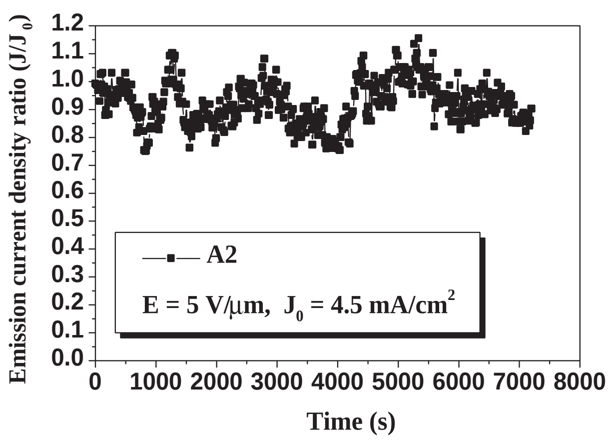


Fig. 5. Emission current stability of aligned carbon nanotubes over a period of 2 h.

4. Conclusions

In summary, the bias-enhanced microwave plasma chemical vapor deposition technique was adopted to synthesize aligned carbon nanotubes on Pd-catalyzed porous silicon substrates. The turn-on fields E_{on} defined at the emission current density of 10 μA/cm^2 are dependent on the immersion times in $PdCl_2$. The emission current densities are about 0.97 mA/cm^2, 4.5 mA/cm^2, and 0.44 mA/cm^2 at the electric field of 5 V/μm for the immersion times in $PdCl_2$ of 1 min, 20 min, and 40 min, respectively. The lower turn-on field and higher emission current density obtained from the aligned carbon nanotubes for the $PdCl_2$ immersion time of 20 min are attributed to the denser and sharper nanotubes. Moreover, these aligned carbon nanotubes indicate no obvious degradation of the emission current density over a period of 2 h.

Acknowledgements

This research was supported in part by the National Science Council (NSC) of the Republic of China under Contract NSC-89-2215-E-009-069 and NSC-89-2215-E-009-068. Technical support from the Semiconductor Research Center of National Chiao Tung University and the National Nano Device Laboratory of NSC are also acknowledged.

1) C. T. White, D. H. Robertson and J. W. Mintmire: Phys. Rev. B **47** (1993) 5485.
2) J. W. G. Wildoer, L. C. Venema, A. Rinzler, R. E. Smalley and C. Dekker: Nature **391** (1998) 59.
3) A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune and M. J. Heben: Nature **386** (1997) 377.
4) M. Freemantle: Chem. Eng. News **74** (1996) 62.
5) C. Niu, E. K. Sichel, R. Hoch, D. Moy and H. Tennent: Appl. Phys. Lett. **70** (1997) 1480.
6) G. Che, B. B. Lakshmi, E. R. Fisher and C. R. Martin: Nature **393** (1998) 346.
7) T. W. Ebbesen: *Carbon Nanotubes* (CRC Press, Boca Raton, 1997).
8) Y. Saito, K. Hamaguchi, T. Nishino, K. Uchida, Y. Tasaka, F. Ikazaki, M. Yumura, A. Kasuya and Y. Nishina: Nature **389** (1997) 554.
9) J. Bonard, J. Salvetat, T. Stockli, W. A. de Heer, L. Forro and A. Chatelain: Appl. Phys. Lett. **73** (1998) 918.
10) S. Fan, M. G. Chapline, N. R. Frankin, T. W. Tombler, A. M. Cassell and H. Dai: Science **283** (1999) 512.
11) W. Li, H. Zhang, C. Wang, Y. Zhang, L. Xu, K. Zhu and S. Xie: Appl. Phys. Lett. **70** (1997) 2684.
12) Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal and P. N. Provencio: Science **282** (1998) 1105.
13) S. H. Tsai, C. W. Chao, C. L. Lee and H. C. Shih: Appl. Phys. Lett. **74** (1999) 3462.
14) F. G. Tarntair, L. C. Chen, S. L. Wei, W. K. Hong, K. H. Chen and H. C. Cheng: to be published in J. Vac. Sci. & Technol. B.