Electron field emission from phase pure nanotube films grown in a methane/hydrogen plasma

Olivier M. Küttel, Oliver Groening, Christoph Emmenegger, and Louis Schlapbach

Citation: Applied Physics Letters **73**, 2113 (1998); doi: 10.1063/1.122395
View online: http://dx.doi.org/10.1063/1.122395
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/73/15?ver=pdfcov
Published by the AIP Publishing

Electron field emission from phase pure nanotube films grown in a methane/hydrogen plasma

Olivier M. Küttel,[a] Oliver Groening, Christoph Emmenegger, and Louis Schlapbach
University of Fribourg, Physics Department, Pérolles, 1700 Fribourg, Switzerland

(Received 5 May 1998; accepted for publication 10 August 1998)

Phase pure nanotube films were grown on silicon substrates by a microwave plasma under conditions which normally are used for the growth of chemical vapor deposited diamond films. However, instead of using any pretreatment leading to diamond nucleation we deposited metal clusters on the silicon substrate. The resulting films contain only nanotubes and also onion-like structures. However, no other carbon allotropes like graphite or amorphous clustered material could be found. The nanotubes adhere very well to the substrates and do not need any further purification step. Electron field emission was observed at fields above 1.5 V/μm and we observed an emission site density up to 10^4/cm^2 at 3 V/μm. Alternatively, we have grown nanotube films by the hot filament technique, which allows to uniformly cover a two inch wafer. © *1998 American Institute of Physics.* [S0003-6951(98)00141-7]

Since Iijima's original work,[1] carbon nanotubes have been recognized as fascinating materials with promising applications in carbon chemistry and physics. At present, there are several approaches to produce nanotubes. The arc discharge method[2] and the carbon vapor method use the pyrolisis of hydrocarbons (e.g., benzene at approx. 1000 °C),[3] by laser vaporization and variant or combination of these methods. A comprehensive overview is given in Ref. 4.

Catalytic methods for making nanotubes have their origin in the corresponding work on carbon fibers.[5] All methods discussed in the previous paragraph have also been used to make nanotubes by using a metallic catalyst. In the arc method such catalysts as Co, Fe, or Ni,[6,7] as well as Y and Gd[8,9] were used to grow nanotubes. Mixed catalysts such as Fe/Ni, Co/Ni, and Co/Pt are reported to give an improved nanotube yield.[10,11] Each method has its strengths and weakness. The carbon arc method remains the most useful because of its ease with which large amounts of nanotubes can be produced.

A common drawback of all the mentioned methods are a number of impurities incorporated in the nanotube material, whose type and amount depend on the deposition technique. The most common are of carbonic nature such as graphitic or amorphous nanoparticles. During the last years a number of purification processes have been developed: gas phase purification,[11] liquid phase purification,[12] and purification by intercalation.[13] Metallic impurities, used during the catalytic growth, can be removed for the most part by heating the sample up to the evaporation temperature of the impurities.[8]

In this letter we present an alternative method for the growth of nanotubes. We describe a process by which nanotubes can be deposited on a silicon substrate as a thin film. It is very phase pure (only nanotubes or onion-like structures) and adheres very well to the substrate.

The films were grown on silicon substrates via microwave plasma chemical vapor deposition in a tubular deposition system (2.45 GHz) at a gas pressure of 40 mbar and a substrate temperature of 900–1000 °C from a CH_4/H_2 (2%/98%) gas mixture, otherwise used for the growth of diamond films.[14] The growth parameters used are standard growth conditions for the deposition of chemical vapor deposition (CVD) diamond films, except for the slightly increased substrate temperature. However, instead of scratching the silicon substrate with diamond powder or biasing it with a negative dc voltage in order to get a high diamond nucleation density, we used a different pretreatment. Metal was deposited either by sputter coating a very thin film of Ni (300–400 Å) or by spraying $Fe(NO_3)_3$ dissolved in ethanol onto the silicon substrate. After introducing the sample into the growth chamber $Fe(NO_3)_3$ is chemically reduced by the high concentration of atomic hydrogen to metallic Fe and forms little clusters due to the increased mobility at 900 °C at the surface. A similar effect is observed on the sputter deposited Ni cluster. Any oxygen impurities are removed and the continuous thin layer of Ni forms little islands. These Ni or Fe clusters act as catalytic growth centers for nanotubes. A typical growth time was 15 min. Afterwards the films were analyzed either by a high resolution scanning electron microscope Zeiss DSM 982 (HRSEM) or by a transmission electron microscope (TEM).

The best deposition conditions for nanotube were found by placing the substrate in a remote position where the plasma ball, which is typical for this kind of discharge is located well above the sample. Otherwise, the high concentration of atomic hydrogen etches the growing film. Alternatively, the sample surface could be tilted by 180° in order to protect the growing nanotube film from the reactive species of the plasma. Figure 1 shows a HRSEM picture of a nanotube film. The picture at the top of Fig. 1 (a) clearly shows how the nanotubes grow from the metallic clusters in all directions like a pin holder. The image in Fig. 1(b) shows nanotubes arranged in a ''spaghetti-like'' structure. At higher resolution the diameter of the individual nanotubes can be determined to be in the range of 20–60 nm, while its length can be as long as 100 μm. Nanotubes uniformly grow over the whole substrate and adhere pretty well to it.

At the moment it is rather difficult to speculate about the growth process. It seems that nanotubes and diamond can

[a]Electronic mail: olivier.kuettel@unifr.ch

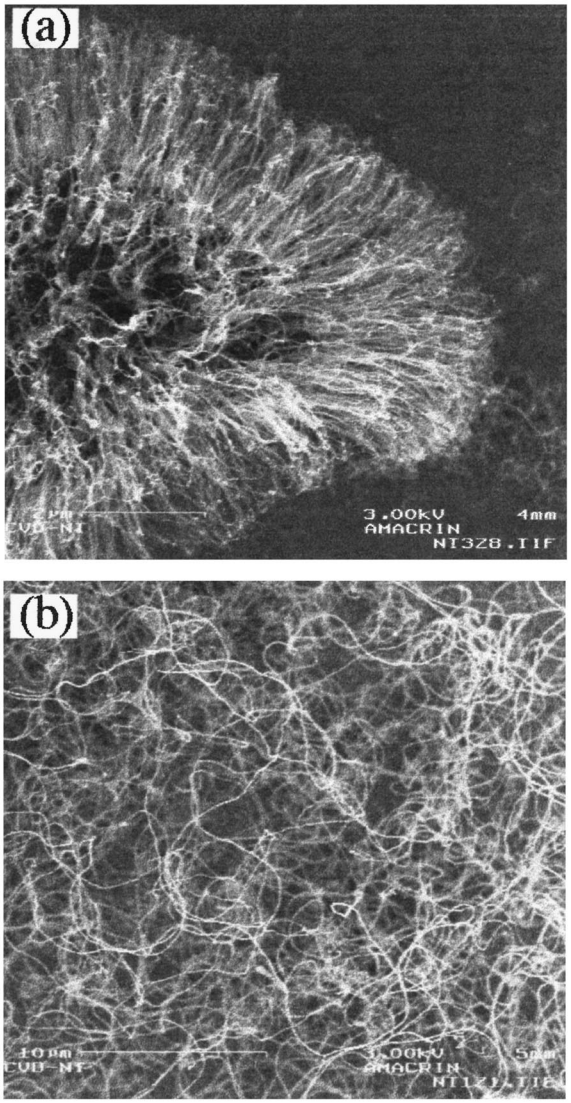

FIG. 1. HRSEM pictures of the nanotube film. Nanotubes grow from the surface of the metallic island in pin-holder manner (a) (image size 9×9 μm^2). The spaghetti-like structure is clearly shown in (b) (image size 30×30 μm^2).

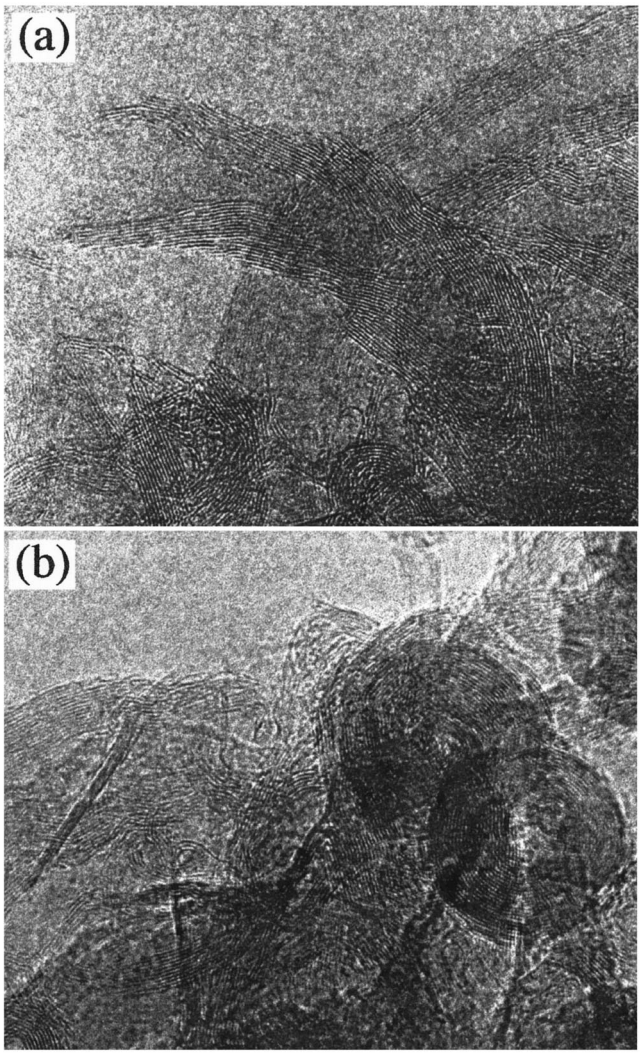

FIG. 2. TEM images of the nanotubes. Open as well as closed nanotubes can be observed (a). A closer look reveals that also onion-like structures are formed at the film surface (b).

grow side by side depending on the nature of the nucleation center. Metallic clusters give rise to the growth of nanotube films and diamonds or diamond precursors at the surface lead to CVD diamond growth. These findings were already reported by other groups.[15] It seems that the only stable carbon structure growing at typical diamond CVD conditions encountered in a microwave reactor are diamond and nanotubes. As for the growth of diamond, the high atomic hydrogen concentration is certainly a key parameter. It induces the plasma chemistry, saturates the dangling bonds during the growth process and etches nondiamond/nanotube phases. This is a rather important advantage of this growth process. The films consists of pure nanotube without any carbon nanophase impurities. Hence, these films are well suited for many applications and do not need any subsequent purification step. TEM investigations at these films revealed that open and closed nanotubes are formed [Fig. 2(a)]. This might be due to the high concentration of atomic hydrogen in the gas phase, where deposition and etching of the nanotube film are in a delicate balance. So far, we could only observe multiwall nanotubes. However, in many cases onion-like structures were found side by side with nanotubes [Fig. 2(b)].

Little is known about the role of the metal clusters. In many models the metal cluster is considered to be a seed, setting the outer radius of the filament.[16,17] However, some models assume that carbon diffuses through the metal seed and condenses at the bottom hence, pushing up the seed.[18] In contrast to results presented in Ref. 15 where metal particles were found at the top of the growing nanotubes, we could find metal cluster as seeds only. It seems that in our growth process the size of the metal cluster can be substantially larger as the diameter of the nanotube growing on its surface. This is clearly illustrated by looking at Fig. 1(a) where metal islands in the μm range can be observed.

These nanotube films are well suited for electron field emission applications. First of all they can be grown on large surfaces, are phase pure, without large clusters of carbon, and adhere well to the substrate. The electron emission is governed by the tangle of nanotubes where statistically some nanotubes protrude out of the film. Hence, it is not necessary to align the nanotube after the deposition process as it was done by other groups.[19] The field emission measurements were performed by taking current–voltage ($I-V$) curves at

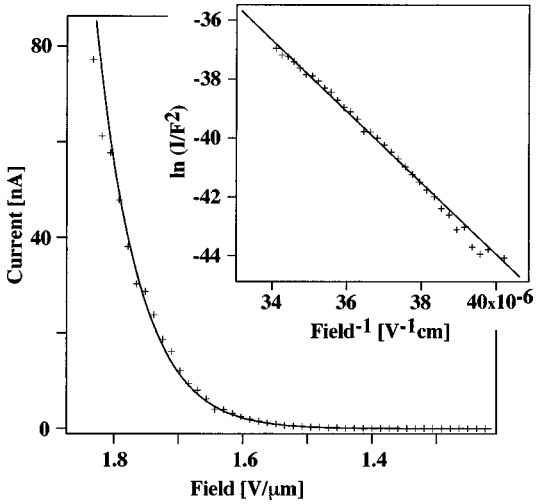

FIG. 3. $I-V$ measurements on a nanotube film with the inset being the Fowler–Nordheim representation of the data. Emission starts at 2.5 V/μm.

10^{-8} mbar with a Keithley 237 instrument. The detection limit was 1 pA at maximum voltage (± 1100 V). The emission current is collected by a highly polished steel sphere of 4 mm diameter, mounted on a linear piezo drive, with a step size of 1 μm and 10 mm travel. The anode is grounded over a 100 MΩ ballast resistor. Alternatively, the emission could be monitored with a phosphorus coated indium tin oxide (ITO) glass electrode in order to determine the emission site density. In Fig. 3 we show $I-V$ measurements with the inset being the Fowler–Nordheim representation of the data. The emission starts at a field of a 1.5 V/μm. Using a work function of 5 eV one can deduce from the slope of the straight line in the Fowler–Nordheim representation an aspect ratio of approx. 800–1000 which is further confirmed by HRSEM. The mechanism of field emission is clearly governed by the field enhancement at the apex of the nanotubes. A more rigorous investigation of the work function of nanotubes, using energy resolved field emission, gives a value of 5.3 eV.[20] In Fig. 4 the emission was monitored on a phosphorus screen. At a field of 2.5 V/μm the emission site density is approx. 10^3/cm^2 and increases to its maximum at roughly 3 V/μm when the whole screen is illuminated, making it even impossible to determine an emission site density (about 10^4/cm^2).

In this letter we presented the deposition of nanotube films onto silicon substrates by a microwave plasma from a CH_4/H_2 gas mixture under similar conditions than what is used for the growth of CVD diamond films. The film quality is excellent with regards to the purity of the film as well as the adhesion to the substrate. These films are very well suited as material for cold cathodes. They do not need any further post treatment and by masking the deposition of the metal catalyst we have succeeded in structuring the films. This is very important for technical applications.

We also have used a hot filament reactor to deposit nanotube films onto two inch silicon wafers. The advantage using a hot filament reactor lies in the fact that atomic hydrogen is less abundant and hence, we could not observe an etching of the nanotube films. Films on two inch silicon substrates are black in appearance, adhere very well to the substrate, and are very uniform.[21] These films are very suitable for applications as cold electron sources.

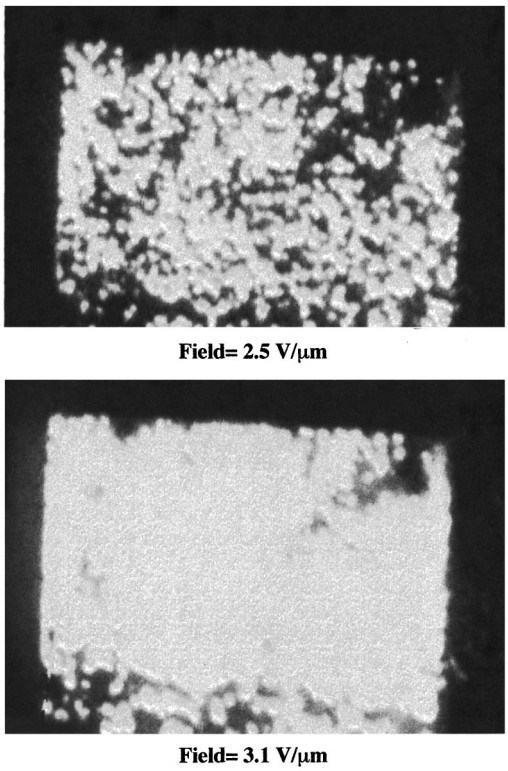

FIG. 4. Electron field emission as monitored by a phosphorous screen. (a) is taken at 2.5 V/μm, (b) at 3.1 V/μm. The size of the image is 1.5×3 cm^2.

The authors are indebted to R. Wessicken at ETH Zürich for performing the TEM investigations. Part of this work was supported by the Swiss National Science Foundation (NFP36) and the Swiss Priority Program of Materials (PPM).

[1] S. Iijima, Nature (London) **354**, 56 (1991).
[2] S. Iijima, T. W. Ebbesen, and P. M. Ajayan, Nature (London) **358**, 220 (1992).
[3] M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, and H. W. Kroto, J. Phys. Chem. Solids **54**, 1841 (1993).
[4] *Carbon Nanotubes*, edited by Th. W. Ebbesen (Chemical Rubber, Boca Raton, 1997); *Carbon Nanotubes*, edited by M. Endo, S. Iijima, and M. S. Dresselhaus (Pergamon, New York, 1996).
[5] *Graphite Fibers and Filaments*, edited by M. S. Dresselhaus, G. Dresselhaus, I. L. Spain, and H. A. Goldberg (Springer, New York, 1988).
[6] S. Iijima and T. Ichihashi, Nature (London) **363**, 603 (1993).
[7] D. S. Bethune, C. H. Kiang, M. S. de Vires, G. Gorman, R. Savoy, J. Vasquez, and R. Beyers, Nature (London) **363**, 605 (1993).
[8] J. M. Lambert, P. M. Ajayan, P. Bernier, J. M. Planeix, V. Brotons, B. Coq, and J. Castaing, Chem. Phys. Lett. **226**, 264 (1994).
[9] S. Subramoney, R. S. Ruoff, D. C. Lorents, and R. Malhotra, Nature (London) **366**, 637 (1993).
[10] S. Seraphin and D. Zhou, Appl. Phys. Lett. **65**, 1593 (1994).
[11] T. W. Ebbesen, P. M. Ajayan, H. Hiuram, and K. Tanigaki, Nature (London) **367**, 519 (1994).
[12] H. Hiura, T. W. Ebbesen, and K. Tanigaki, Adv. Mater. **7**, 275 (1995).
[13] F. Ikazaki, S. Ohsima, K. Uchida, Y. Kuriki, H. Hayakawa, M. Yumura, K. Takahashi, and K. Tojima, Carbon **32**, 1539 (1994).
[14] E. Maillard-Schaller, O. M. Küttel, P. Gröning, O. Gröning, R. Agostino, and L. Schlapbach, Phys. Rev. B **55**, 15 895 (1997).
[15] R. Stöckel, K. Janischowsky, M. Stammler, L. Ley, M. Albrecht, and H. P. Strunk, Diamond Relat. Mater. **7**, 147 (1998).
[16] S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov, and J. B. Nagy, Science **265**, 635 (1994).
[17] G. G. Tibbetts, J. Cryst. Growth **66**, 632 (1984).
[18] R. E. Smalley, Mater. Sci. Eng., B **19**, 1 (1993).
[19] W. A. de Heer, A. Châtelain, and D. Ugarte, Science **270**, 1179 (1995).
[20] O. Gröning, O. M. Küttel, Ch. Emmenegger, P. Gröning, and L. Schlapbach (unpublished).
[21] In collaboration with CSEM in Neuenburg, Switzerland, Detailed results will be published elsewhere.