Carbon nanotube growth for field-emission cathodes from graphite paste using Ar-ion bombardment

Charles E. Hunt[a)]
Department of Electrical and Computer Engineering, University of California, One Shields Avenue, Davis, California 95616

Orest J. Glembocki
Naval Research Laboratory, 4555 Overlook Avenue, Washington, DC 20375

Yu Wang
Department of Electrical and Computer Engineering, University of California, One Shields Avenue, Davis, California 95616

Sharka M. Prokes
Naval Research Laboratory, 4555 Overlook Avenue, Washington, DC 20375

(Received 18 August 2004; accepted 18 February 2005; published online 15 April 2005)

Multiwall carbon nanotubes (MW-CNT) have been synthesized from solid-phase graphite. The graphite is deposited as a thick-film paste and irradiated with a 1.2 keV flood Ar-ion beam, transforming the graphite surface to a composite of MW-CNT embedded in the graphite matrix. Micro-Raman measurements have verified that the nanotubes are metallic in nature. The technique was used to make printed field-emission cathodes. Emission from these cathodes demonstrates Fowler–Nordheim tunneling characteristics. The irradiated film emits at an extraction field of 5.0 V/μm, which is less than one-sixth of the minimum extraction field of the nonirradiated graphite film, and exhibit lower noise and greater emission uniformity. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1899236]

Recent interest in field-emission vacuum microelectronics has led to the use of carbon cathodes for applications where large areas of emission are required. These have typically included cathodes made from diamond,[1] ultrananocrystalline diamond,[2] diamond-like carbon,[3] reticulated vitreous carbon,[4] carbon fibers,[5] and single or multiwall carbon nanotubes (MW-CNT).[6] Bulk and paste graphite has also been explored; but it is found that the extraction field from graphite is substantially greater than that required from all other carbon forms, often exceeding 30 V/μm.[7] By comparison, field-emission from MW-CNT has been demonstrated at (parallel-plate) extraction fields below 1.0 V/μm. Typically, MW-CNT field-emission cathodes are deposited on various substrates by catalyzed CVD at temperatures exceeding 800 °C. Alternatively, CNT formed by arc discharge have been mixed into a paste and deposited by screen-printing techniques.[8] This technique has the advantage of low-cost patterning; however, the paste is expensive and difficult to produce in large quantities. We present here a method for making MW-CNT field-emission cathodes from low-cost, printed graphite paste using a flood Ar-ion beam. This technique eliminates the need for high-temperature CVD deposition, or low-throughput arc-discharge CNT synthesis.

Square glass substrates were coated on one side with commercial vacuum-compatible silver paint to give uniform conductivity. After drying, graphite paste from a commercial vendor was screen printed over the conductive layer, patterned in 1.0 cm^2 squares. The graphite paste consists of a distribution of pure, aspherical graphite particles, with mean size of ~0.5 μm, in a water-based suspension.[9] The viscosity of the paste was chosen to obtain an average graphite film thickness of 25 μm resulting from the screening process. The samples were then baked at ~450 °C for 30 min to expel the water and solidify the graphite film. The result is heavily textured, as seen in Fig. 1, with randomly oriented particles, combined with flakes and graphene sheets, and a submicron average surface roughness. The screen process results in no more than 0.5 μm film thickness variation.

The graphite paste-coated samples were brought down to a high-vacuum base pressure below 10^{-6} Torr and were then bombarded with flood Ar-ion radiation from a 0.1 mTorr thermomagnetic (Kaufmann-type) plasma source at 1.2 keV.

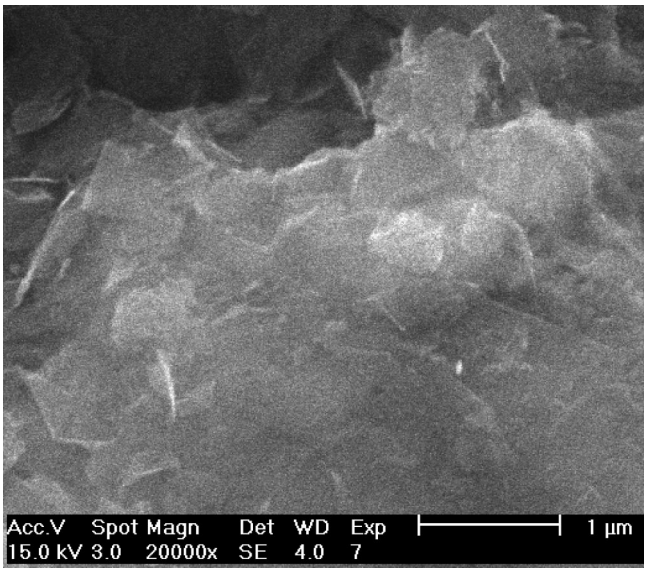

FIG. 1. Plan-view scanning electron micrograph (secondary-electron mode) of the as-deposited graphite paste film.

[a)]Electronic mail: hunt@ucdavis.edu

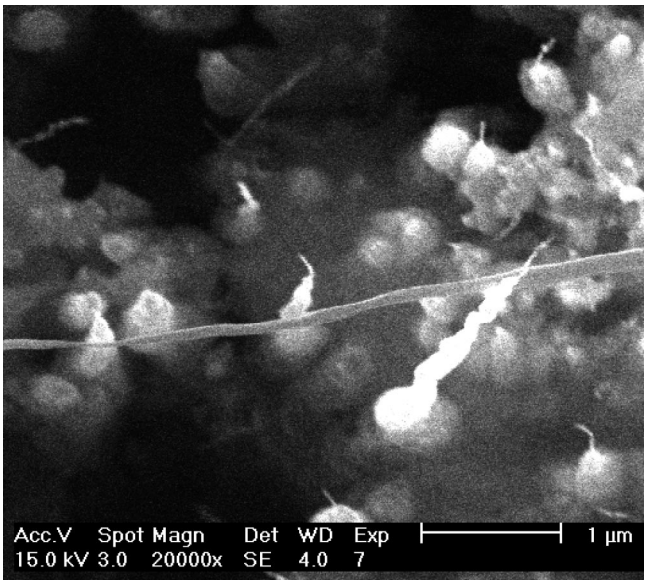

FIG. 2. Plan-view SEM of the graphite paste film after 25 min of Ar-ion irradiation. The microscope beam energy and magnification are identical to Fig. 1.

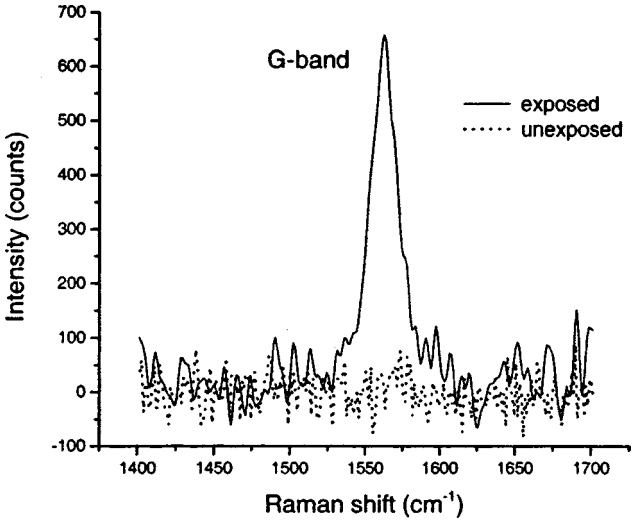

FIG. 3. The G-band region of the micro-Raman spectrum obtained from the center of an Ar-irradiated region (solid) and from an unexposed region (dotted). The data were measured using 10 mW of laser power.

No external heating or cooling was applied. At this energy, and pressure, the sputter yield of graphite is very low (<0.12).[10] The incentive for using this process was to emulate the change in surface which has been seen by irradiating reticulated vitreous carbon (RVC) with high-energy sources[11] such as lasers or electron beams. The samples presented here were given a total 25-min ion-beam exposure. It should be noted that this process has numerous degrees of freedom, including variation of the graphite particle size, variation of the Ar pressure or plasma density, control of substrate temperature, and variation of the excitation energy or exposure time. This considerable matrix of process options is being investigated and will be reported later.

The Ar-ion irradiated samples resulted in substantially altered surface morphology, as is clearly seen in Fig. 2. The topography is changed to predominantly spheroidal and rounded-cone structures. This basic morphology has long been observed in other low-sputter-yield materials under similar Ar-ion bombardment conditions.[12] A major difference from these earlier observations, as seen here, is that many of the macroscopic structures have nanofibers growing off their surfaces, caused by the stress of the ion impact, subsequent carbon migration, and eventual closure of the resultant graphene sheets. It is noted that some of the nanofibers or whiskers are straight and some are helical or horn shaped, whereas some have a random shape. The nanofibers are seen in the SEM to typically be ~19 nm in diameter and extending up to 1 μm in length. More extensive high-resolution transmission electron microscopy (TEM) is necessary to ascertain the fiber diameters and physical structure with greater precision. This study of the fiber detail is underway and will be reported later.

A second structure, which is also quite common (as seen across Fig. 2), is a graphite whisker. These are always substantially thicker and longer than the above-mentioned nanofibers. The frequency of occurrence of this secondary structure is, in these samples, substantially less than that of the nanofibers. The example seen in Fig. 2, which is typical, varies in thickness from ~30 to over 150 nm, and is slightly over 12 μm long. These larger whiskers have a nucleation site and remain attached to the substrate at one end. There appears to be no order to the whiskers, and they vary in thickness, sometimes precipitously, all along the length. This type of graphite structure has been observed by others,[13] and it was found that they are solid and amorphous; but they can have an ordered graphene surface monolayer in places.

The irradiated samples were analyzed using micro-Raman spectroscopy to ascertain if the nanofibers are single- or multiwall carbon nanotubes (SW-CNT, MW-CNT).[14] A confocal system was used, consisting of a Mitutoyo Microscope (filtered by a 514.5 nm notch filter) fiber-optic coupled to a SPEX Triplemate spectrometer equipped with a CCD imager. The 514.5 nm line of an Ar ion laser with power up to 30 mW was the excitation source. A 100× objective was used, yielding a lateral spatial resolution of 0.7 μm and a depth resolution of 15 μm. The positions of Raman lines in a given spectrum were calibrated against the 546 nm line emission from a fluorescent light source. This line was present in all of the Raman data obtained.

The sample was placed on a glass plate that is part of a computer-controlled Prior stage having 4 in. travel with submicron resolution. In addition, the focus of the microscope was electronically controlled with a resolution of less than 0.5 μm. This configuration allows for accurate spatial and depth profiling. The sample was transferred to the micro-Raman system and the features of interest were located by using the electronic stage and by viewing the wafer using a mounted digital camera. The Raman data were obtained as a function of laser power and lateral and depth position.

Figure 3 shows Raman spectrum from the central portion of an irradiated region of the sample and from a neighboring unexposed portion. The data were obtained with a laser power of 12 mW and the 100× objective. The mode that is observed at 1564 cm^{-1} is characteristic of the G-band of carbon nanotubes,[14] consistent with MW-CNTs. The lack of a second feature at 1592 cm^{-1} suggests that there are no semiconducting SW-CNTs.[15] This feature is clearly seen only in the region of the sample that was irradiated. Thus, the Raman data, coupled with the SEM images showing large-diameter

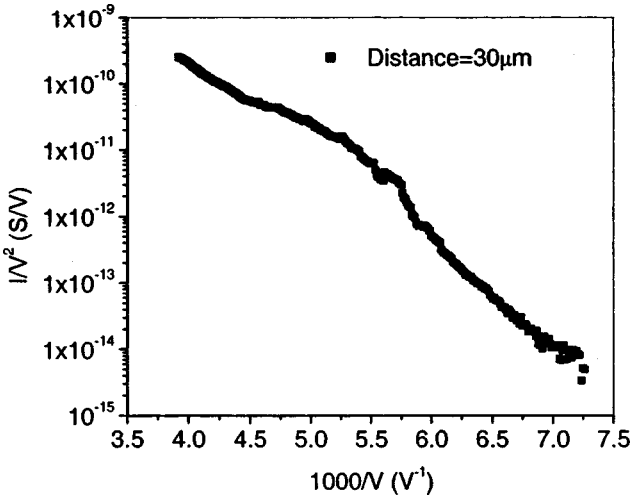

FIG. 4. Example Fowler–Nordheim plot of a diode field-emission measurement. The cathode was of an Ar-ion irradiated 0.5-mm-diameter circle.

filaments, indicate that the irradiation process produces predominantly MW-CNTs.[14,15]

In addition, we do not observe any features in the frequency range of 1250–1450 cm^{-1}, where the disorder-activated D-band is seen.[14] This suggests that the CNTs are highly ordered and do not have, in significant quantity, symmetry-breaking defects such as substitutional atoms, vacancies or grain boundaries. Others have shown,[16] using molecular-dynamic simulations, that heavy Ar-ion irradiation can lead to measurable levels of such defects. We have been able to fit the data of Fig. 3 to a single Lorentzian. This further confirms that the CNTs are crystalline, because any departure from crystallinity would result in an asymmetric non-Lorentzian line shape.[14,15]

The samples shown in Figs. 1 and 2 were utilized as cathodes in a simple parallel-plate field emission assessment. The as-deposited graphite, consistent with measurements by others, emits nonuniformly, and only at extraction fields greater than $\sim 30\ V/\mu m$. The Ar-ion irradiated samples were also measured. The circular cathode area is $\sim 0.008\ cm^2$. The measurement was undertaken at 8×10^{-7} Torr using a dc field. The anode–cathode separation was set at 30 μm and the anode voltage was swept up to 250 V. Figure 4 shows a Fowler–Nordheim plot of this measurement. The straight characteristic over greater than five decades clearly indicates field emission. The observed extraction field (for $I=0.1\ \mu A$) of $\sim 5.0\ V/\mu m$ is consistent with the results measured by others of field emission from carbon nanotubes in a graphite matrix. It is likely that refinement of the Ar-ion irradiation treatment pressure, temperature, energy, or other parameters, can lead to CNT alignment and density more optimal to field emission. Such optimization of CNTs, using Ar-ion beams, has been reported[17] to reduce the onset of field emission from 5.5 down to $2.0\ V/\mu m$. No burn-in or special treatment (such as H_2 plasma conditioning) of the cathode was performed before measurement of these cathodes; therefore, it is assumed that slight irregularities in the emission characteristics, as seen in Fig. 4, are due to ordinary multistable fluctuations in emission states on the surface, as commonly seen with untreated carbon field-emission cathodes.[18]

In conclusion, we have demonstrated the growth of carbon nanotubes from simple screen-printed graphite films which have been irradiated with a flood Ar-ion beam. The resultant films demonstrate a substantial improvement in field-emission characteristics as compared with untreated graphite films. The technique investigated represents a simple, low-cost approach to making field-emission surfaces with potential application to large-area or high-current cathodes.

[1] N. S. Xu, Y. Tzeng, and R. V. Latham, J. Phys. D **27**, 1988 (1994).
[2] A. R. Krauss, O. Auciello, M. Q. Ding, D. M. Gruen, Y. Huang, V. V. Zhirnov, E. I. Givargizov, A. Breskin, R. Chechen, E. Shefer, V. Konov, S. Pimenov, A. Karabutov, A. Rakhimov, and N. Suetin, J. Appl. Phys. **89**, 2958 (2001).
[3] B. C. Djubua and N. N. Chubun, IEEE Trans. Electron Devices **38**, 2314 (1991).
[4] A. G. Chakhovskoi, C. E. Hunt, G. Forsberg, T. Nilsson, and P. Persson, *Proceedings of the 14th International Vacuum Microelectronics Conference*, Davis, CA, August 12–16, 2001, pp. 263–264; see also: C. E. Hunt and A. G. Chakhovskoi, U.S. Patent No. 6054801 (1999).
[5] A. G. Chakhovskoi, E. P. Sheshin, A. S. Kupryashkin, and V. A. Seliverstov, J. Vac. Sci. Technol. B **11**, 511 (1993).
[6] J.-M. Bonard, H. Kind, T. Stockli, and L.-O. Nilsson, Solid-State Electron. **45**, 893 (2001).
[7] R. J. Noer, Ph. Niedermann, N. Sankarraman, and O. J. Fischer, J. Appl. Phys. **59**, 3851 (1986).
[8] N. S. Lee, D. S. Chung, I. T. Han, J. H. Kang, Y. S. Choi, H. Y. Kim, S. H. Park, Y. W. Jin, W. K. Yi, M. J. Yun, J. E. Jung, C. J. Lee, J. H. You, S. H. Jo, C. G. Lee, and J. M. Kim, Diamond Relat. Mater. **10**, 265 (2001).
[9] D. I. Amey, Jr., R. J. Bouchard, S. I. U. Shah, and J. G. Lavin, U.S. Patent, No. 6,409,567 (2002).
[10] J. L. Vossen and W. Kern, *Thin Film Processes* (Academic, Orlando, FL, 1978), p. 15.
[11] A. G. Chakhovskoi, C. E. Hunt, G. Forsberg, T. Nilsson, and P. Persson, J. Vac. Sci. Technol. B **21**, 571 (2003).
[12] J. L. Vossen and W. Kern, *Thin Film Processes* (Academic, Orlando, FL, 1978), p. 45.
[13] G. A. M. Reynolds, L.-T. Cheng, R. Bouchard, P. Moffett, H. Jones, L. F. Robinson, S. I. Shah, and D. I. Amey, J. Mater. Res. **17**, 2590 (2002).
[14] M. S. Dresselhaus and P. C. Eklund, Adv. Phys. **49**, 705 (2000).
[15] D. Chattopadhyay, I. Galeska, and F. Papadimitrakopolous, J. Am. Chem. Soc. **125**, 3370 (2003).
[16] J. A. V. Pomoell, A. V. Krasheninnikov, K. Nordlund, and J. Keinonen, J. Appl. Phys. **96**, 2864 (2004).
[17] D.-H. Kim, H.-S. Jang, C.-D. Kim, D.-S. Cho, H.-D. Kang, and H.-R. Lee, Chem. Phys. Lett. **378**, 232 (2003).
[18] A. G. Chakhovskoi and C. E. Hunt, Proceedings of the 12th International Vacuum Microelectronics Conference, Darmstadt, Germany, July 6–9, pp. 338–340 (1999).