Ion-beam morphological conditioning of carbon field emission cathode surfaces

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Samples of reticulated vitreous carbon (RVC) and paste graphite film have been evaluated for field-emission properties both before and after surface modification. The RVC has been treated using an open-air laser method. The graphite has been treated using an Ar-ion flood bombardment method. Both methods result in a change in surface morphology of the emission cathode which physically resembles results obtained using current or voltage stress treatment methods. Emission properties become more uniform, exhibit less noise, and, in the best cases, match results seen from carbon nanotubes or ultra-nanocrystalline diamond cathodes. The results demonstrate a method for obtaining large total currents at optimal extraction voltages, from large-area, low-cost cathodes. This method is useful for applications, such as field-emission lamps and x-ray tubes, which do not require nanofabricated, lithographically-patterned cathode structures. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1880052]

BACKGROUND

Various forms of graphitic and diamondlike surfaces have been investigated for some time as potential field-emission cathode materials for vacuum microelectronics. Some of these, such as carbon nanotubes[1] and ultra-nanocrystalline diamond,[2] have demonstrated substantial emission at comparatively low extraction fields. Other materials, which may be lower cost, or more readily manufacturable, such as bulk[3] and paste[4] graphite, reticulated vitreous carbon (RVC),[5] and PAN fibers,[6] although perceived as having great potential for robust, large-area, high-current cathodes, do not demonstrate comparably low-field operation without undergoing substantial "training,"[7] either through voltage or current stressing, or surface-morphology conditioning with high-energy sources, such as pulse-mode lasers. These treatments have proven to be either time consuming, unwieldy, or damaging to the cathode. We report and compare here two low-cost surface conditioning methods for use with inexpensive bulk or paste graphite, RVC, or other glassy carbon forms, which overcome the deficiencies of field training. The results are comparable with the electron extraction performance seen with carbon nanotubes and ultra-nanocrystalline diamond.[8] We also report the use of flood Ar^+ ion irradiation applicable to several carbon cathode types, including bulk and paste graphite, molded or machined RVC, and bulk vitreous carbon. The choice of exploring RVC and paste graphite is motivated by the (comparatively) greater ease in use, and lower cost in application than the other carbon field-emission cathode materials currently being explored. For some applications, such as field-emission lamps, the greater complexity, or greater cost, associated with materials such as arc-discharge carbon nanotubes, or ultra-nanocrystalline diamond would be cost prohibitive.

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EXPERIMENT

The method is demonstrated using graphite thick films as starting material. The technique is also compatible with RVC samples, fabricated by pyrolizing either molded, fumed phenolic, or machined felted, open-pore polyurethane. Details of the application to RVC are still being investigated and will be fully reported later. The paste samples, which represent one of the most cost-effective approaches, utilize a commercial graphite suspension in an expellable binder.[9] The film samples used were deposited at room temperature, by screening methods, onto flat glass substrates which had been coated on one side with vacuum-compatible silver paint to assure uniform conductivity in the films. The samples were then baked at 150 °C for 30 min, in air, to expel the binders and solidify the films. The final average graphite layer thickness was 50 μm, with approximately $+/-1$ μm tolerance. Graphite paste surface morphology, and field-emission characteristics, of untreated (as-deposited) samples, is consistent with results found from untreated bulk graphite.[3] Field-emission measurements from the cathode samples were initially made before any ion treatment. Typically, graphite field emission initiates at (equivalent parallel-plate) fields in excess of 30 V/μm, with an erratic and nonuniform electron stream.

The samples were then exposed to flood Ar^+ ion radiation at 1.2 keV acceleration energy, for 25 min. The total pressure during irradiation was held to 0.1 m Torr, and the plasma concentration was estimated to be $<10^{-5}$. The specimens were not subjected to either heating, nor cooling, externally. The energy maintained is in a range which modifies the cathode surface to emulate the morphology resultant from voltage or current stressing,[7] but does not significantly sputter or reshape the cathode on a macroscopic scale (such as seen using laser treatment[10]). The irradiated regions are an array of 92 circular areas, delimited by shadow masking during the Ar^+ ion irradiation process. Each circular area is 1/32 in. in diameter, such that the total area emission is $S=4.55$

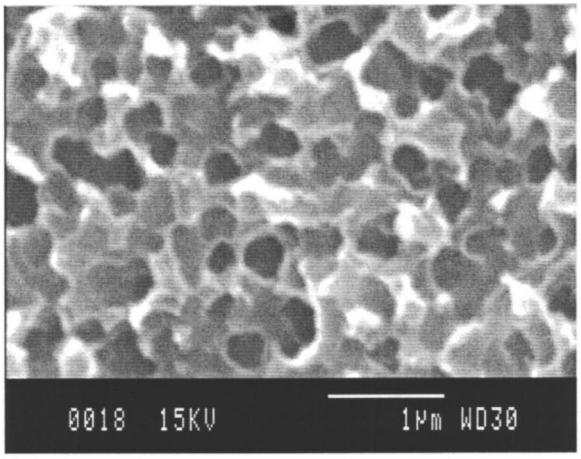
$\times 10^{-5}$ m^2. A typical radiated sample was observed under a XL FEG/SFEG scanning electron microscope (sem), operated in secondary electron mode under the accelerating voltage of 15 kV.

Field emission properties were measured using a custom-built vacuum system. The pressure of the chamber, without baking, was maintained at 2×10^{-7} Torr by a turbo-pump. The measurement was conducted in the diode mode. The chamber is equipped with Model LMM-275-2 manipulator by MDC MFG Inc., which holds the anode. While the sample cathode was fixed, the position of the moveable anode (a 2 cm diameter 304 stainless circular disk) was controlled by the manipulator. Great care was taken to align the centers of the anode and cathode and to ensure the anode and cathode were fixtured parallel. The zero distance between the anode and the cathode is defined as the setting at which the resistance between the anode and the cathode sample is 10 MΩ. The tolerance of the anode-cathode spacing is estimated to be approximately 2 μm. A standard HP 4142B Modular DC Source/Monitor was used to apply the stimulating voltage, and to measure the emission current. The stimulating voltage was increased linearly from 0 V by uniform steps of 1.0 V. The whole process was controlled using INTERACTIVE CHARACTERIZATION SOFTWARE by Metrics Technology Inc., At anode–cathode spacings of $d=100$, 200, 400, and 600 μm, the measurement was conducted ten times and averaged.

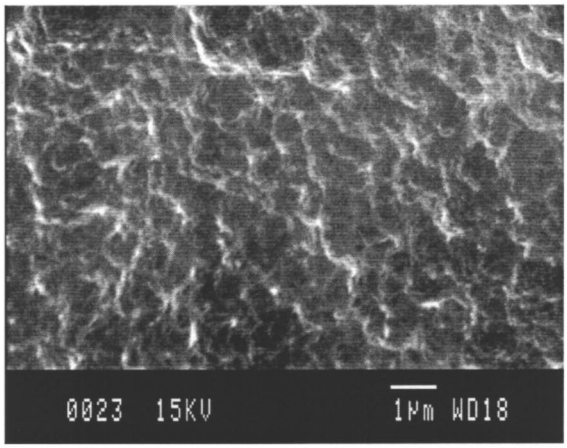
RESULTS

The flood Ar^+ ion irradiation method was implemented in order to duplicate results obtained by laser training or by field stressing; but in a more manufacturable manner. To verify this result, Fig. 1(a) shows untreated, molded RVC and Fig. 1(b) shows an example of laser-treated RVC. The result of this treatment is the formation of a statistically stable, self-regenerating ensemble of countless nanoscopic individual emission sites which distribute the field emission more uniformly over the entire cathode surface. The result has been shown to reduce the noise, and to make a more uniform and longer lasting emission,[10] immediately from the initial use of the cathode. It has also been found, however, that the laser treatment (in this case, performed in air) results in significant macroscopic reshaping of the cathode surface, in large measure through consumption of the carbon. This macroscopic reshaping, accompanied with redeposition of some (SP^2) bonded soft graphite material is somewhat similar to the effects of laser treatment recently observed for nanocarbon CVD grown films.[11]

The untreated carbon paste surface is seen in Fig. 2(a). The results of the Ar^+ irradiation of carbon paste films is seen in Fig. 2(b). The appearance is similar to that found by laser treating or by current (or voltage) stressing; however, it is found by micro-Raman analysis that these surfaces are covered with (predominantly) multiwall carbon nanotubes (MW-CNT) which nucleated during the irradiation process.[12] The Raman analysis also verified the anticipated increase in SP^2 bonding which was suspected as a consequence of the



(a)



(b)

FIG. 1. Samples of RVC cathode, before (a) and after (b) surface treatment.

measured emission improvement. There were also resulting solid, larger dimension graphite whiskers as had been noted (using TEM) in the work of others investigating graphite films.[4] Considerable speculation exists in the literature concerning the physical mechanism for deformation, subsequent reforming, and nucleation of the whiskers and nanotubes (including our own discussion, cf. Ref 12.) We believe the thermal excitation from the beam causes mobility of available graphene sheets (predominantly in the graphite flakes) and restructuring into the energetically more-favorable tubes, which nucleate on graphene sheets within the amorphous matrix. Ascertaining the details of the kinetics of such a restructuring requires molecular-dynamics modeling beyond the scope of our project; but we hope to undertake this study in the future. Figure 3 is a micrograph which shows both a MW-CNT, and its nucleation site, over which is a single, nonfullerene graphite whisker. The whiskers contribute little to the emission characteristics, compared to the MW-CNT because the initial extraction voltage is measurably greater.[4] Treated graphite paste samples were briefly used to illuminate a ZnO phosphor screen and found to (qualitatively) emit with notable uniformity in brightness, and without visible flickering.

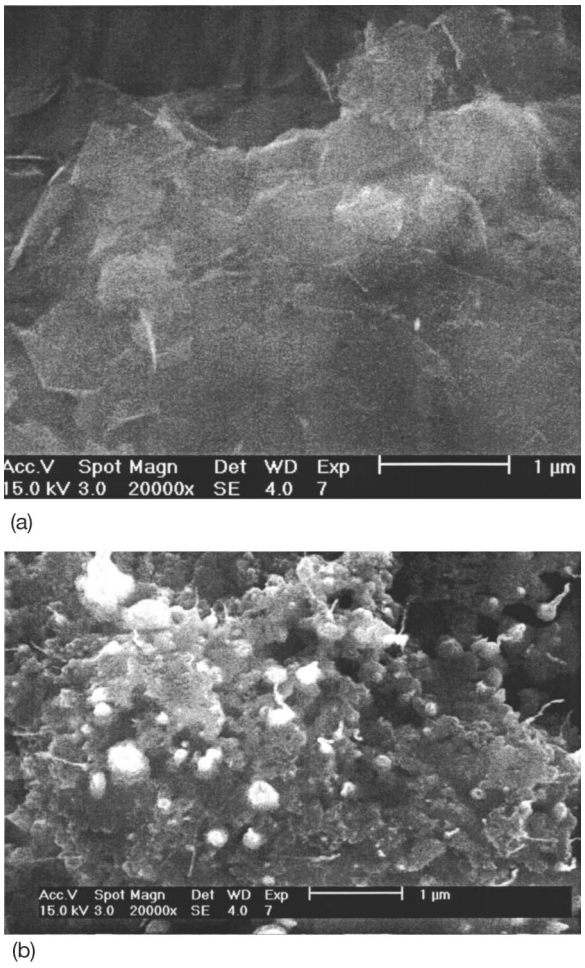


FIG. 2. Samples of graphite film, before (a) and after (b) surface treatmen.t

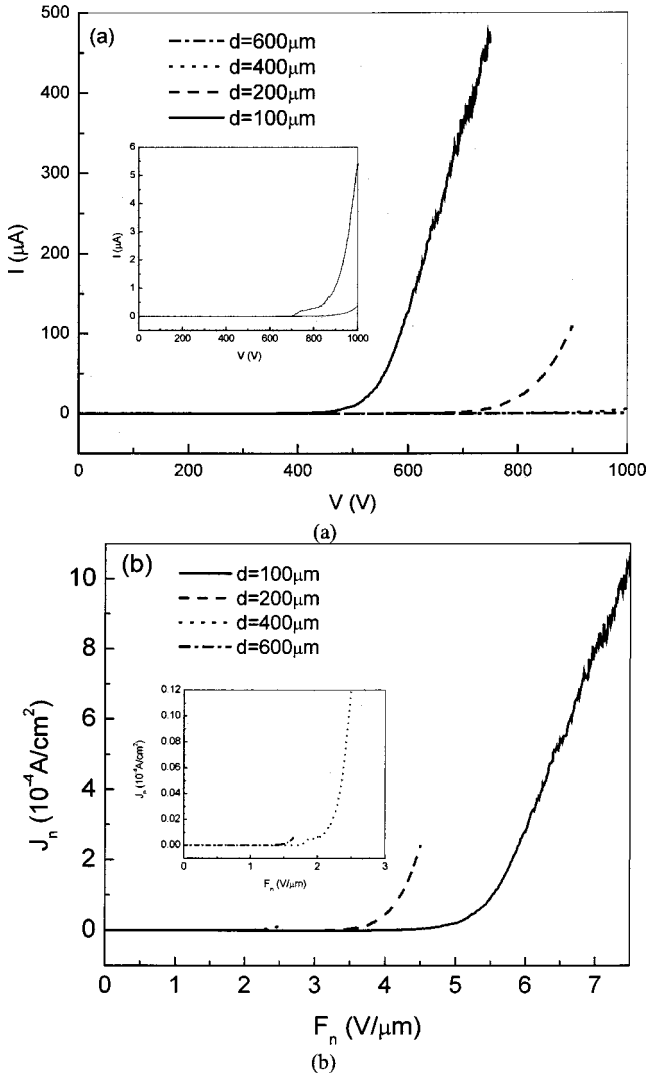


FIG. 4. For various anode-cathode spacings, (a) *I–V* characteristics and (b) nominal current density versus field curve. All measurements were made using an Ar^+ ion irradiated cathode.

Figure 4 shows the *I–V* characteristics and nominal current density J_n versus nominal parallel-plate field (F_n) for various anode–cathode spacings. J_n and F_n are defined as I/S and V/d, where $S=4.55\times10^{-5}$ m^2, is the total area of the sample that was treated by Ar^+ ion radiation. It has been previously verified that untreated cathode material will not significantly emit electrons at these fields, as so we have assumed that all current is coming from the irradiated portions of the cathode. The linear Fowler–Nordheim plots shown in Fig. 5 verify that the characteristic is due to field emission (FE). The turn-on voltage V_{on}, defined as the voltage at which the FE current is $I=0.1$ μA, or current density $J_n=2.20\times10^{-7}$ A/m^2, is 380, 610, 727, and 935 V, for $d=100$, 200, 400, and 600 μm, respectively. These values correspond to turn-on fields, $F_{on}=3.80$, 3.05, 3.21, and 1.56 V/μm, respectively. We believe the variation in turn-on field values is predominantly due to variations in the fringing field within our measurement system, since the anode and cathode areas are quite comparable in physical dimension.

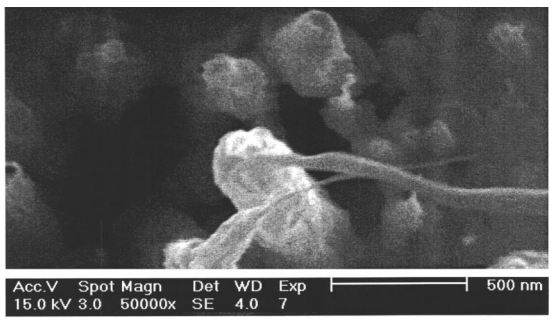


FIG. 3. SEM micrograph showing graphite whisker, at nucleation site, and underlying multi-wall carbon nanotube.

We have estimated the work function and the "average" emission-point radius of curvature, using the geometric factor used by others in analyzing MW-CNT.[13] The values (4 eV), as derived from the measured data, are consistent with those found in MW-CNT.

CONCLUSION

We have investigated methods for treating vitreous or graphite paste carbon surfaces in order to change the surface morphology to include nanoscopic structure which makes a

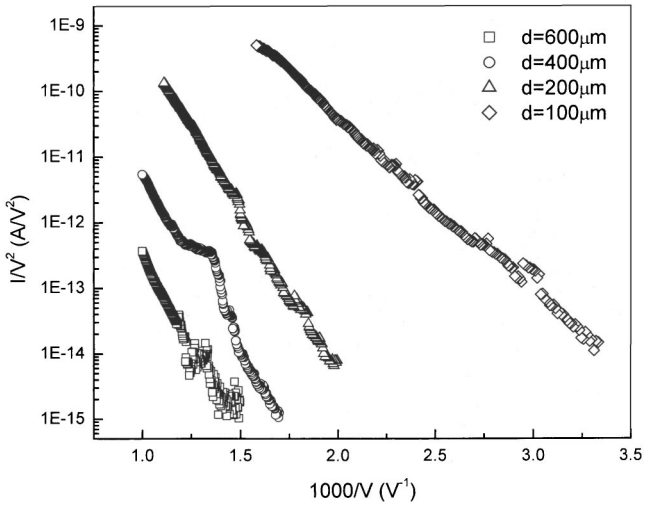


FIG. 5. Fowler–Nordheim plots of the measurements in Fig. 4, for differing anode-cathode spacings.

uniform field-emission cathode. One method uses laser radiation; which achieves the desired result; but at the expense of deformation of the macroscopic cathode shape. A method, which we demonstrate in use on printed graphite paste thick films, uses flood Ar^+ ion radiation. This latter method results in a similar morphological change in the cathode surface, with a corresponding improvement in field-emission characteristics, but without the resultant deformation of the cathode shape. We believe either of these methods represent a viable approach to carbon-cathode treatment which eliminates the need for voltage or current stressing (long-term "burn in"). Because the carbon cathodes are not patterned with lithography, these materials, once treated, can be used in applications which require emission large-areas, such as field-emission lamps.

[1]J.-M. Bonard, H. Kind, T. Stockli, and L.-O. Nilsson, Solid-State Electron. **45**, 893 (2001).
[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]R. J. Noer, Ph. Niedermann, N. Sankarraman, and O. J. Fischer, J. Appl. Phys. **59**, 3851 (1986).
[4]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).
[5]A. G. Chakhovskoi, C. E. Hunt, G. Forsberg, T. Nilsson, and P. Persson, *Proceedings of the 14th International Vacuum Microelectronics Conference*, Davis, California, 12–16 August 2001, pp. 263–264; U.S. Patent No. 6,054,801.
[6]E. P. Sheshin, Ultramicroscopy **79**, 101 (1999).
[7]A. S. Baturin, R. G. Tchesov, K. N. Nikolski, and E. P. Sheshin, *Proceedings of the 4th IEEE International Vacuum Electronics Conference*, pp. 240–241. (IEEE Cat. No. 03EX640). (IEEE, Piscataway, NJ, 2003).
[8]M. Hajra, C. E. Hunt, M. Ding, O. Auciello, J. Carlisle, and D. M. Gruen, J. Appl. Phys. **94**, 4079 (2003).
[9]U.S. Patent No. 6,409,567.
[10]A. G. Chakhovskoi, C. E. Hunt, G. Forsberg, T. Nilsson, and P. Persson, J. Vac. Sci. Technol. B **21**, 571 (2003).
[11]A. Obraztsov, G. Mikheev, and A. G. Chakhovskoi, *Proceedings of the 17th International Vacuum Nanoelectronics Conference*, Cambridge, MA, 11–16 July 2004, pp. 252–253.
[12]C. E. Hunt, O. Glembocki, Y. Wang, and S. M. Prokes, Appl. Phys. Lett. (submitted).
[13]V. Semet, V. T. Binh, P. Vincent, D. Guillot, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga. W. I. Milne, P. Legagneux, and D. Pribat, Appl. Phys. Lett. **81**, 343 (2002).