Application of Vitreous and Graphitic Large-Area Carbon Surfaces as Field-Emission Cathodes

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ABSTRACT

Numerous carbon bulk or thin-film materials have been used as field-emission cathodes. Most of these can be made into large-area and high-current field-emission cathodes without the use of complex IC fabrication techniques. Some of these exhibit low-extraction field, low work-function, high ruggedness, chemical stability, uniform emission, and low-cost manufacturability. A comparison of all of these materials will be presented. Two viable cathode materials, Reticulated Vitreous Carbon (RVC) and graphite paste are examined here and compared.

INTRODUCTION

Field-Emission cathodes have evolved from simple tungsten needles to metal and semiconductor "microtip" devices used in vacuum microelectronics and typically fabricated using processes employed by the IC industry [1]. Major drawbacks of the microtip technology have been the complication of a sophisticated nanofabrication process, and a limitation on the macroscopic current density which can be obtained. Many applications, such as microwave amplifiers, micro-thrusters for spacecraft, and field-emission lamps, require both large cathode areas (multiple cm^2) and large total currents (>0.5A). Microtip technology is not ideal for these requirements.

One viable option for obtaining larger-area, higher-current, and lower-cost field-emission cathodes is to use one of various forms of carbon as the emission surface. Although carbon can be employed as a coating in microtip technology [2], it also valuable as a large-area emission surface. The simplest explanation for this is that the surface morphology itself can result in random nanoscopic emission "tips", without the use of lithography or IC fab procedures. Figure 1 shows two examples of low-cost, as-deposited carbon cathodes. It is readily seen that these different materials share the attribute that the surface morphology consists of countless fractures, protrusions, edges, and other features which are readily demonstrated to emit electrons with field-enhancement, much as is found in microtip devices.

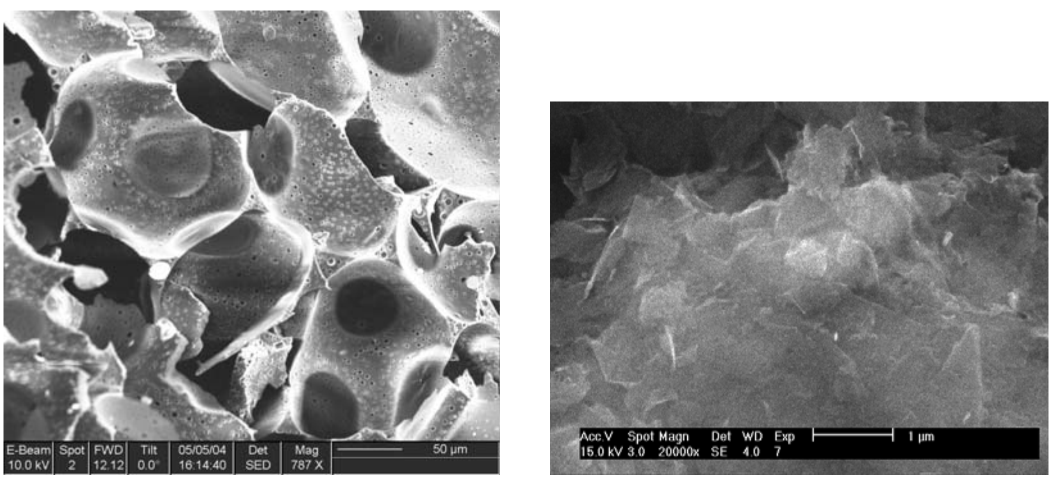

Figure 1: SEM micrographs of RVC (left) and graphite-paste (right) field-emission cathodes

Examples of carbon surfaces which have been explored for field-emission cathodes include graphite [3], PAN fibers [4], Diamond-Like Carbon (DLC) [5], Ultra-Nanocrystalline Diamond (UNCD) [6], crystalline diamond and diamond nanoparticles [7], single and multi-wall carbon nanotubes (CNT) [8], Reticulated Vitreous Carbon

(RVC) [9], and various CNT and graphite composites and pastes [10]. There are numerous variations of these material types, as well. Each of these carbon-base cathode materials have demonstrated various strengths and weaknesses; but all appear viable in some manner for large-area, high-current cathodes. Some, such as UNCD, diamond, and CNT require hot or cold-wall chemical vapor deposition techniques in manufacture. Some, such as fibers, UNCD, diamond, and RVC, demonstrate remarkable robustness in operation within compromised vacuum. Some, such as UNCD, diamond, CNT, and some carbon pastes, have exhibited remarkably-low minimum emission fields (reaching down to slightly below 0.9 V/μm.) Some, such as graphite, RVC, and certain pastes, are remarkably simple to make and use, and are very inexpensive as well. Even so, each of these types of emission surfaces have remarkably differing surface morphologies, bonding arrangements (graphene sheets, SP^2, SP^3, or combined $SP^2 + SP^3$), electronic properties (insulator, semiconducting, and semimetal,) ruggedness and chemical reactivity, as well as workfunction (ranging from 4 to 5.5 eV), despite all being the same single element. In the following, we discuss two viable options, RVC and graphite paste.

RETICULATED VITREOUS CARBON (RVC)

Reticulated vitreous carbon (RVC) has been synthesized for over 20 years as a lightweight building material, used in aircraft, brake shoes, and other mechanical applications. It is a carbon foam made either by pyrolosis of open-pore ("felted") polyurethane foam, or pyrolosis of fumed phenolic foam ("flower foam", used by florists.) The result is a material which consists of "struts" which connected the pores of the polymer precursor. The material is up to 97% void and is exceptionally light. Porosity can be extremely uniform in the 45 – 500 PPI (pores per inch) range, with emission properties optimized somewhere near the 250 PPI value. Cathodes can be fabricated either by machining the bulk RVC material or by molding the phenolic during fuming. Depending on the parameters of the pyrolosis process, the bonding of the carbon varies between predominantly SP^2 and predominantly SP^3. The balance between the two bond types not only affects the conductivity of the material, but also the field-emission efficacy as well. This result is similar to what is seen when using PAN fibers [4], but the very-sharp, natural occlusions of the RVC surface result in substantially lower extraction field (down to 2 V/μm) than what has been measured in fibers. The material is notably stable and chemically inert, The consequence is that this material can be operated in modest vacuum (0.01 mTorr), essentially under constant ion bombardment and continue to emit (albeit, with greater noise power.) This stability occurs predominantly because the bombardment exfoliates the carbon, revealing a new, equally efficient emission surface.

Like many other field-emission surfaces, RVC exhibits an initial transient when electron extraction occurs, even using pristine-clean cathodes. The cathode can be stressed, either with constant voltage or constant current, resulting in long-term, reproducible (even after breaking vacuum and restoration to vacuum), stable, low-noise emission. The low-cost and adaptable large-area nature of this cathode material makes this very attractive for high-current applications. It has been found that the surface stabilization associated with stressing of the cathode can be duplicated using thermal treatments of the surface with various sources. This makes it possible to pre-treat the cathode, during the fabrication process, before assembling the device, or putting it under vacuum [11]. From a manufacturing standpoint, this is a significant benefit. Stable 2.5 A/cm^2 current density has been observed from stressed, untreated surfaces. Higher current densities have been observed after certain surface treatments. This material is already being used in commercial, large-area field-emission applications.

GRAPHITE PASTE

Another low-cost, large-area field emission cathode surface is graphite paste. This is commercially available [12] as a simple graphitic material, but is being applied in many variations, including paste composites containing CNT embedded in a graphite matrix. There is a great deal of investigation in this class of materials, predominantly because it has been demonstrated as a low-cost, patternable, highly-efficient cathode option. These materials are already in commercial use for cathodes in field-emission flat-panel displays. Graphite paste has field-emission properties similar to those of bulk graphite. Although there are commercial field-emission applications for bulk graphite, such as cathodes for x-ray sources, this is likely the inferior carbon material for field-emission cathodes, predominantly because the extraction field is so high (on average, 20-25 V/μm.) The emission is also typically unstable, and non-uniform.

Interest in graphite, or graphite paste, as a field-emission cathode material has arisen predominantly because it can be used as a base for composites with CNT (such as for FE displays), or because it can be treated in a fashion analogous to RVC, and made stable and uniformly emitting. Recently, it has been shown that graphite paste can be treated with a flood Ar-ion beam at low energy to alter the film's surface morphology. This process emulates emission results seen with carbon-based materials, such as CNT and diamond, yet at a significantly lower cost, and with measurably greater simplicity [10]. Graphite paste is easily patterned using low-cost silk-screen techniques. This material can be printed in arbitrary shape, on various non-planar surfaces.

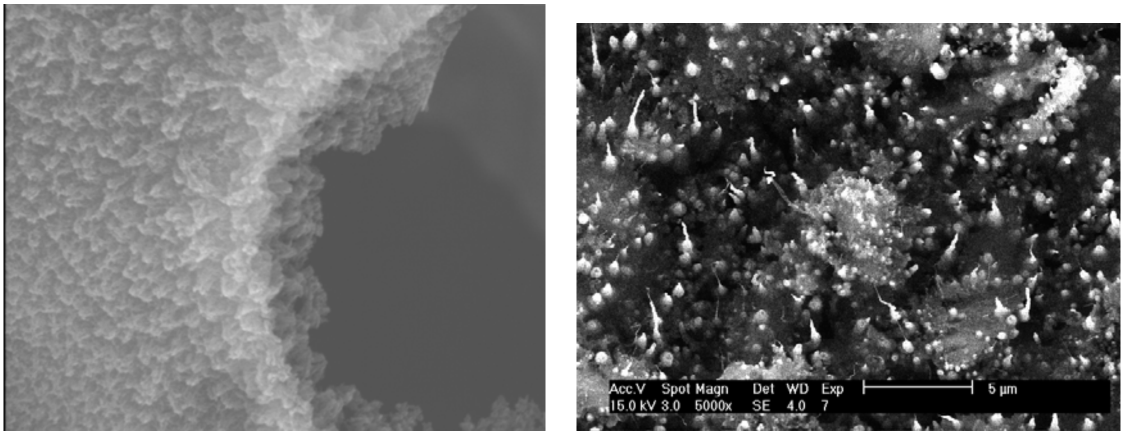

Figure 2: SEM micrographs of laser-treated RVC(left) and Flood-Ar-ion treated graphite paste (right), both shown at 5000 x magnification. Both surfaces show nano-scale emission sites and emit in similar manner.

Figure 2 shows examples (SEM micrographs at 5000x) of treated RVC and treated graphite paste. The RVC has been irradiated using pulse-laser scanning, and the graphite paste has been irradiated using flood Ar-ion exposure at 1.2 keV for 20 minutes. The emission properties of both of these cathodes has been measured to be approximately identical, having an extraction field of about 2.5 V/μm. This field-emission performance is comparable to CNT and diamond films; but the fabrication cost and complexity are both substantially lower. These materials are both also substantially more robust than CNT. The emission in both cases is uniform over the entire cathode area, and noise is comparable to, or less than, all other carbon cathodes which have been investigated.

CONCLUSIONS

Carbon materials, ranging from graphite to CVD diamond, have been demonstrated to be applicable to large-area, high-current field-emission cathode surfaces. Selection criteria of carbon cathode type is based largely on application needs; but significant advances (in many cases) have been made for high-current, large-area applications, compared with microtip technology in vacuum microelectronics. In cases where precision resolution, or fine-beam focusing are not necessary, several carbon-base cathode types may offer significant advantage.

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REFERENCES

[1] H. H. Busta, *J. Micromech. Microeng*., **2** 43 (1992) (numerous other excellent examples)
[2] M. Hajra, C. E. Hunt, et al., *J. Appl. Phys*., **94** (6) 4079 (2003)
[3] R. J. Noer, Ph. Niedermann, et al., *J. Appl. Phys*, **59** (11) 3851 (1986)
[4] A. G. Chakhovskoi, et al., *J, Vac. Sci Tech*. *B*, **11** (2) 511 (1993)
[5] B. C. Djubua. N. N. Chubun, *IEEE Trans. Elec. Dev*., **38** (10) 2314 (1991)
[6] A. R. Krauss, et al., *J. Appl. Phys*., **89** (5) 2958 (2001)
[7] N. S. Xu et al., *J. Phys. D*., **27** (9) 1988 (1994)
[8] J.-M. Bonard, et al., *Solid-State Electronics*, 45 893 (2001)
[9] A. G. Chakhovskoi. C. E. Hunt, et al., Proc. IVNC-01, 263 IEEE (2001), US Pat. #6054801
[10] C. E. Hunt et. al, (submitted to) *J. Vac Sci Tech. B*, **23**, (2) IVNC-04, Mar/Apr, (2005)
[11] A. G. Chakhovskoi, C. E. Hunt et al., *J. Vac. Sci. Tech B*, **21** (1) 571 (2003)
[12] US Patent #6,409,567