Reticulated vitreous carbon field emission cathodes for light source applications

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Reticulated vitreous carbon (RVC) is demonstrated as a viable field emission electron source for cathodoluminescent lamps. The high void volume and porous structure of RVC help create a large number of natural emission sites on the surface. Emission centers are formed by the sharp edges of the carbon struts, which result from simple machining of the macroscopic open-pore material. Additional surface treatment of the emitters in vacuum or in open air helps to increase the extracted current and reduce the current fluctuations. Electron emission has been evaluated in the 10 to 500 μA range, in 10^{-6} to 10^{-8} Torr vacuum ambient. Extended lifetime tests were carried out for over 5000 h in sealed glass prototype devices utilizing commercial cathodoluminescent phosphors. Brightness levels exceeding 10 000 cd/m^2 were achieved for diode and triode configurations. The low cost of manufacturing, along with chemical and mechanical robustness, make RVC a viable material for electron-beam vacuum device applications such as mercury-free cathodoluminescent light sources. [DOI: 10.1116/1.1527956]

I. INTRODUCTION

Field emission cathodes fabricated from carbon materials are known as electron sources capable of producing significant emission currents in relatively modest vacuum conditions. Carbon fibers and fabrics, natural bulk graphite, single- and multiwall nanotubes, fullerenes, thin films of pyrolitic and diamondlike carbon, and other forms of carbon materials, as well as carbon coatings of metal and semiconductor field emitters and arrays have been reported recently by numerous authors as viable electron sources for field emission flat panel displays and other electron-beam vacuum devices.[1] One of the most attractive features for all the carbon materials compared to field emitter arrays composed of metal or semiconductor microtips is that the products of chemical interaction between carbon and most common residual gases (oxygen and hydrogen) are in turn noncondensable gases such as carbon monoxide, carbon dioxide, and methane, which leave no contamination on the emission surface. Another property of most carbon materials is a microrough surface with a statistically large number of micro- and nanoprotrusions acting as emission sites; this ensures the robustness of the emitters under bombardment by the ions of residual gases. These two factors combine to enable a significantly higher operating pressure range for carbon cathodes (about 10^{-6} Torr) compared to metal microtips (usually 10^{-8} Torr and better).

At the present time, however, carbon-based field emission devices remain mostly in the laboratory stage of development. A major reason for this is that the known carbon field emitter materials do not conform to manufacturing requirements readily. Some cathodes, such as arrays or brushes of carbon fibers, require manual handling and positioning. Others, such as matrix cathodes made of bulk graphite, rely on surface micromachining or chemical etching to create an array of field emission sites. Selective carbon coating of metal or semiconductor field emission arrays or manufacturing of patterned field emitters based on carbon nanotubes usually requires a costly manufacturing process using expensive equipment.

In this work, we introduce an alternative carbon material, which is viable for low-cost field emission cathode manufacturing and suitable for numerous applications. Among the primary applications, we consider here a mercury-free, high-efficiency cathodoluminescent light source using a reticulated vitreous carbon (RVC) emitter as a field emission electron source, and a layer of industrial cathode-ray tube (CRT) type phosphor as a source of light of a desirable color.

II. RETICULATED VITREOUS CARBON

In this research, we present an investigation of electron field emission from reticulated vitreous carbon.[2] RVC is manufactured as an open-pore material from a raw polymer, such as polyurethane foam, or by molding a phenolic resin. The vitreous (glassy) porous carbon is obtained by subsequent pyrolysis in the temperature range of 600–3000 °C under a controlled nonoxidizing atmosphere to convert the plastic foam to diamond-bonded carbon. The most important distinctions of the glassy carbon material compared to natural forms of graphite are (1) greater chemical inertness and (2) more uniform nanostructure. Ordinary vitreous carbon, however, is homogeneous, and would require a special surface treatment or micromachining to generate emission sites. Recent developments in materials fabrication technologies have enabled the formation of a reticulated (inherently po-

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rous) form of vitreous carbon. First used for electrochemical and electroanalytical applications as a large-area flowthrough electrode with substantial chemical inertness, RVC has also been utilized as a building material for aerospace applications, a high-temperature thermal insulator, a filter medium, and an acoustic control material. We believe RVC material is ideal as a field emission cathode for vacuum microelectronics applications.

A unique combination of properties of RVC makes it a viable candidate for usage as a field emission material. Vitreous carbon possesses the mechanical properties of amorphous glass along with the chemical and electrical properties of industrial graphite. The three-dimensional porous structure, with a high void volume (up to 97%), greatly increases the surface area compared to that of bulk graphite.[3] Numerous sharp edges result from simple machining of the RVC foam, creating innumerable emission sites on the sharp edges of the carbon ''struts'' once an electrical field is applied to the cathode. RVC is nearly inert and oxidation resistant. As a consequence, it operates well in a modest vacuum ambient where most other cathode materials are subject to surface contamination due to surface chemical reactions with ions or molecules of residual gases. RVC also possesses a greater inherent resistivity compared to solid carbon materials, which is helpful for field emission applications due to the resultant localized current limiting. This phenomenon, in turn, reduces the probability of surface arcs and can thereby increase the lifetime of the cathode.

Some characteristics of RVC include (1) porosity of commercially available RVC material ranges from 10 to 100 ppi (pores per inch); material with additional compression factors of up to 10× can also be manufactured; (2) surface area of up to 66 cm^2 for 1 cm^3 of the 100 ppi RVC; (3) void volume of 90%–97% for different porosity grades; (4) compressive strengths of 40–70 psi; tensile strengths of 25–50 psi; and, (5) specific resistivity of 0.47–0.69 Ω cm (solid vitreous carbon is typically $\sim$0.001 Ω cm).

III. EXPERIMENT

A. Cathode manufacturing

We have examined a wide variety of commercially available RVC samples with different porosities ranging from 10 to 100 ppi, as well as specially fabricated samples with directional compression along one direction or two orthogonal directions. Samples with compression factors of 2×, 3×, 5×, and 10× were prepared and tested. The geometry of the samples also varied. The simplest geometry used included cubes or rectangular blocks with sides of 3–5 mm machined or even manually cut from the bulk RVC material using a simple knife or razor blade. Cylinders with diameters of up to 20 mm and pyramid configurations were also tested. However, more sophisticated shapes of the emitters such as three-dimensional arrays, disks, cones, and hollow tubes of various sizes can be easily machined depending on the desired configuration of the electron beam. A number of RVC samples was fabricated by molding a raw polymer resin into a desired shape mold, usually cylindrical with flat or semispherical ends; thus making the cathode manufacturing process even simpler.

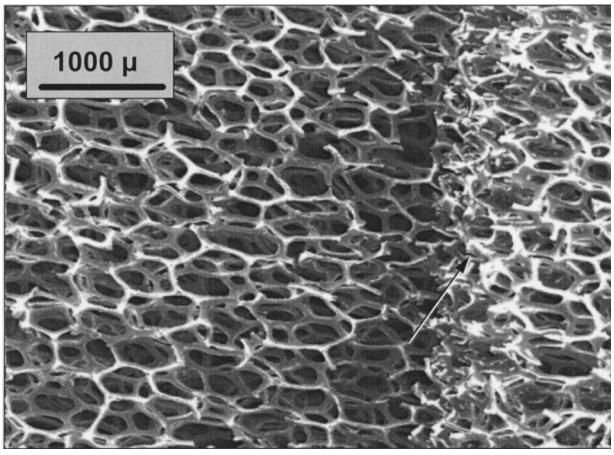

FIG. 1. SEM micrograph showing the open-pore honeycomb structure of the RVC cathode. The arrow points to the vertical wall formed during mechanical cutting.

We studied cathodes with planar emission surface as well as cathodes with three-dimensional surface structure made by cutting parallel grooves on the surface. A scanning electron microscope (SEM) image in Fig. 1 shows a surface of the RVC cathode prepared by a manual cut; the arrow is pointing to the vertical wall formed during cutting. As a result of machining operations, sharp and hard edges of the RVC three-dimensional structure are usually formed. These sharp edges resulting from cuts across carbon struts have characteristic radii of curvature from 0.2 to 2 μm, as can be seen from the SEM image fragment in Fig. 2. The sharp edges and corners of the carbon struts are acting as field emission sites due to local enhancement of the applied electrical field during the device operation.

During the measurements the RVC cathodes were mounted on a flexible stainless steel or molybdenum wire embedded 2–4 mm deep into the bulk on the back side of the

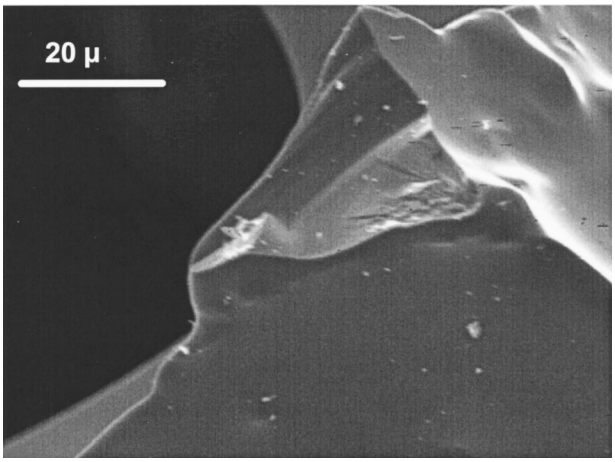

FIG. 2. SEM micrograph showing the fragment of RVC strut with sharp edges resulting from mechanical machining.

RVC block. An electrical contact was provided using a few drops of the colloidal graphite with isopropanol alcohol dried in air for 3–4 h without additional heating. This attachment provided sufficient mechanical and electrical contact for our measurements.

B. Experimental setup and surface treatment

We tested the cathodes in high-vacuum and ultrahigh-vacuum ambient in stainless steel chambers equipped with an ion or turbo pump. Although the pumps could provide an ultimate pressure down to 10^{-9} Torr, some experiments were carried out only after a brief period of pumping to the level of 10^{-6}–10^{-7} Torr. A few samples were also tested in a miniature sealed stainless steel chamber with a volume of 0.2 l and an appendage 2 l/s ion pump.

During the operation, the cathodes were kept at either a ground or high negative potential, while phosphor screens made of high-voltage P-22 commercial television phosphors deposited over an indium tin oxide-coated glass or a metal disk were used as anodes kept at high positive or ground voltage, respectively.

The cathodes positioned 2–5 mm from the phosphor screens were tested in dc mode at low to medium voltages—from 500 to 8000 V. The behavior of the RVC emitters is quite similar to the behavior of the carbon fiber or bulk graphite cathodes: during the very first turn-on, the increase of extracting voltage results in a very slow increase of the emission current; then one can often observe a sudden arcing in the chamber resulting in a series of ''spikes'' in the I/V characteristics. This arcing is followed by an abrupt increase or decrease in the emission current and corresponding changes of the I/V characteristics and field emission pattern on the phosphor screen. After a period of fairly unstable operation, the emission behavior becomes significantly more stable, usually at higher voltages than during the initial turn-on. This process of the stabilization of the cathode characteristics may last anywhere from a few minutes to a few hours.[4] Typical I/V characteristics showing the performance of the cathode during the first turn-on and after 2 h of operation under dc load at the extracting voltage of 1700 V are shown in Fig. 3. The arrows indicate the arcs occurring during the initial increase of the voltage. Figure 4 shows the short-term emission current stability of the same cathode immediately following the first turn-on, and after 2 h of operation. This natural stabilization of the emission current under continuous dc load, often referred to as ''training'' or ''conditioning'' of carbon emitters,[5] may be explained by desorption of the initial contaminants left on the surface of the emitter, and by destruction of the sharpest emission sites. After the sharpest sites are destroyed during the initial period of operation, the current gets distributed more uniformly among a large amount of emission sites, related to fine structures developed on the surface, as seen from Fig. 5. Obviously, the performance of RVC cathodes made of material with different porosity grades is different due to different densities of sharp carbon ''tips'' at the surface, and it takes a different amount of time for each RVC sample to achieve the same level of emission stability.

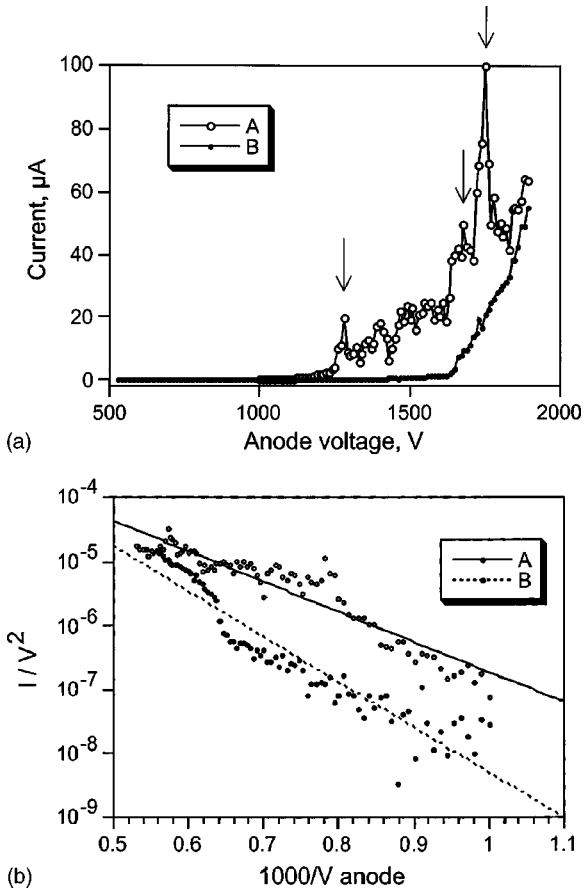

FIG. 3. (a) Typical I/V characteristics of a RVC emitter in dc mode. (b) Corresponding Fowler–Nordheim characteristics of a RVC emitter. A—an untreated surface; B—after 30 min treatment with dc current.

During activation of the cathodes it was found that the desired natural stabilization of RVC emission can be achieved faster by providing a gradual increase of the dc

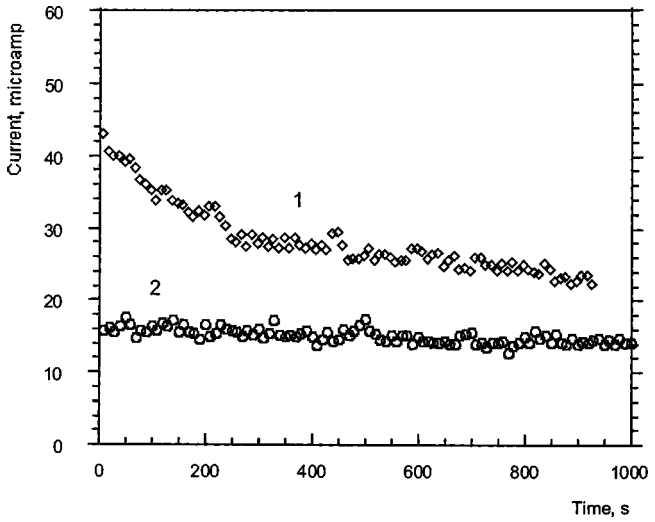

FIG. 4. Short-term stability of emission current during first turn-on (1) and after two hours of dc operation (2).

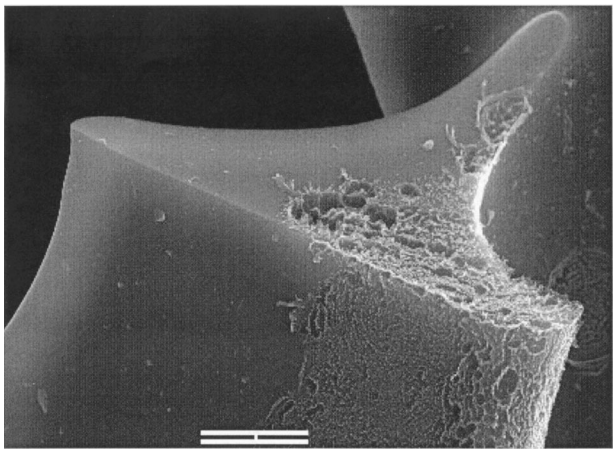

FIG. 5. Emission surface after conditioning by dc current for 1 h (right). SEM, magnification 1000×, scale bar corresponds to 10 μm.

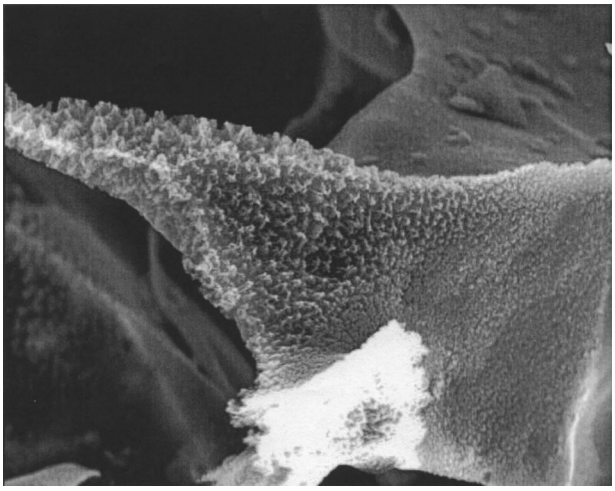

FIG. 6. Emission surface after thermal treatment in open air, SEM, magnification 2000×.

current level in several steps from 10%–15% to about 150% of the desired emission level while holding the current for 10–15 min at each step.[6] It should be pointed that even after a long period of ''training'' the emission current can never achieve an absolutely stable state. The fluctuations of current within 10%–20% of the average value are generally present during the lifetime of the cathode, being accompanied by slight changes in the field emission pattern. On the other hand, this behavior may be an indication of a statistical equilibrium of the destructive and recuperative processes on the emission surface involving a constant redistribution of the net emission current over a large number of the emission sites. The magnitude of the fluctuations can be reduced by including a series ballast resistor of 10–500 MΩ.

While a multistep training with dc current provides a good improvement of emission properties, it still requires a significant time. It has been found that the identical surface morphology as obtained by current or voltage training can be duplicated by applying localized high-energy radiation (electron beam, optical, or perhaps other sources). This has been demonstrated using optical energy in air,[7] as can be seen in Fig. 6. The same result has been reported using a laser or electron beam for punching rivet holes in carbon composites,[8] or using a high-energy pulse laser in treating doped silicon to make a field emission surface.[9] Cathodes thus treated emit identically to samples trained by dc current.

C. Long-term tests in sealed glass devices

Sample emitters made of 100 ppi RVC were tested at currents ranging from 10 to 200 μA in triode mode for a period of 5000+ h in a specially designed test rack using sealed vacuum glass ''test tubes,'' as shown in Fig. 7—capsules built using industrial CRT technology.[7] The test devices were intended to serve as proof of principle prototypes for mercury-free cathodoluminescent light sources using colored and warm-white television type phosphors such as P-22. The aluminized phosphor coated front end plate used as an anode was kept at high voltage, up to 8 kV, the RVC cylinder (cathode) was negatively biased up to 4 kV, and a grounded metal (nickel or stainless steel) grid was used as an extraction electrode. The vacuum in the tubes was maintained using a barium evaporative getter. External 10–100 MΩ ballast resistors were connected to the cathodes to limit arcing. We have routinely achieved brightness levels of 10 000+ cd/cm^2 at emission currents below 200 μA for diode and triode configurations. Although a gradual decrease of the average current value and of the corresponding phosphor screen brightness was observed during the lifetime of some devices, in many cases the emission current remained within 20% of its initial value.

D. High-voltage tests and beam focusing

Operation of the RVC cathodes with different porosities ranging from 50 to 100 ppi was also observed in a vacuum of 10^{-6} Torr at much higher acceleration voltages—up to 55 kV in pulsed and dc diode mode. For this experiment, the field emission cathode was placed in a high-voltage chamber with a base pressure of 5×10^{-8} Torr at a distance of 12 cm away from a 15 cm round metal plate coated with P-22 phosphor.

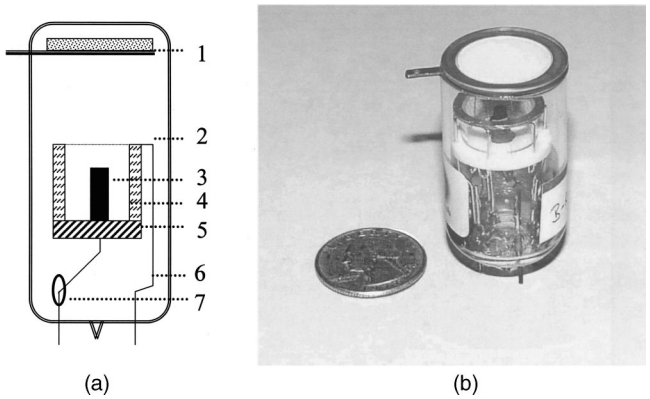

FIG. 7. Sealed test CL light source prototypes: (1) aluminized phosphor screen and high voltage contact, (2) grid (at ground potential), (3) RVC emitter (negatively biased), (4) glass insulator, (5) ceramics base, (6) emitter and grid contacts, and (7) getter.

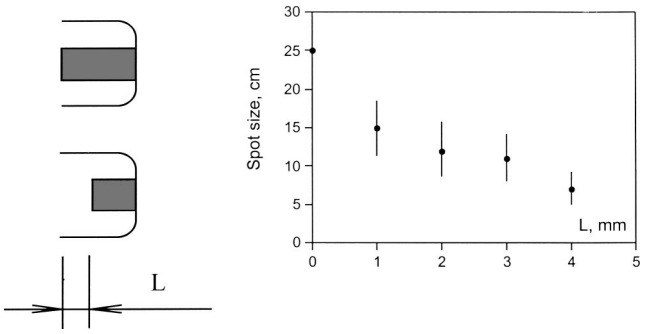

FIG. 8. Focusing of electron beam. RVC cathode (1) is recessed in a nickel cup (2): electron-beam size on the screen is measured versus the RVC recession depth L below the cup edge.

High voltage was applied to the RVC cathode; the metal plate was kept at the ground potential. Because of the risk of x-ray generation, the stainless chamber was surrounded by lead plates, and the viewport was covered by lead glass. The x-ray level outside the lead box was continuously monitored using a portable x-ray sensor.

During the high-voltage tests, stable emission at a current level up to 10 mA has been observed over 2–4 h for a total of six samples. It should be noted that the operation of the field emitters was accompanied by a significant outgassing from the phosphor screen, resulting in a chamber pressure increase up to the level of 10^{-6} Torr.

The significant distance between the cathode and the phosphor screen resulted in a large beam spread on the phosphor screen, resulting in a beam spot exceeding the diameter of the screen, with part of the beam captured by the walls of the chamber. To reduce the beam spread, the RVC emitter was positioned in an 8-mm-diam nickel cap. A recession of the top surface of the RVC block below the edge of the cup, as shown in Fig. 8, helped to reduce the beam size. At the same time, the voltage necessary to maintain the current level had to be increased for a maximum of 50% (55 kV versus 37 kV) for a recession of the cathode at the level of 4 mm below the cup edge.

IV. CONCLUSIONS

Field emitters made from reticulated vitreous carbon were examined. The high void volume and porous structure of this material naturally help to create a large number of emission sites on the surface. Emission centers are formed by sharp edges of carbon struts resulting from simple mechanical machining. The low cost of manufacturing along with chemical inertness and mechanical robustness make this material a good prospect for vacuum electron-beam applications. The emission properties of the RVC are characterized by the porosity grade, which is responsible for the total surface area. Field emission was studied in modest vacuum ambient in diode and triode mode at low to medium voltages (500–8000 V) resulting in currents up to 120 μA, and at high voltages (up to 55 kV) resulting in currents up to 10 mA. Sealed glass prototype devices demonstrated the concept of cathodoluminescent mercury-free light source with brightness of 10 000+ cd/m^2. Field emission cathodes made of RVC can be viable low cost field emitters for various vacuum electron-beam applications.

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