

Field-emission enhancement of reticulated vitreous carbon (RVC) due to structural surface changes resulting from Argon Ion bombardment

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Argon-ion bombardment of Carbon has been demonstrated to result in self-assembly of surface features such as cones, nanowires and nanowhiskers. Resultant self-assembled surface features, observed by Scanning Electron Microscopy (SEM), demonstrate improved field emission both by being geometrically-attractive emission sources as well as because of induced changes bond structure at the surface. In the current study, Reticulated Vitreous Carbon (RVC) was bombarded with Argon-ions to produce a number of surface modifications resulting in the improvement of field emissive properties: namely improvement of emission uniformity from the surface, the onset of field emission at lower fields and higher current density compared to other carbon materials. Increased numbers of surface modifications associated with similar bombardment time results in a substantial lowering of the electric-field requirement. Raman and XRD are used to show changes in the bond characteristics of the RVC. X-ray diffraction from RVC irradiated under various conditions shows the beginning of peaks associated with fullerene type structures while Raman data provides evidence of nanoclustering and the potential of sp³ type bonding as well as nanowire structures.

Reticulated Vitreous Carbon is an attractive material for field emission due to Carbon's negative electron affinity. Because of the openly porous and peaked nature of RVC, shown in Figure 1, RVC has been demonstrated to be good emitter, providing a current density of 10⁻⁶ A/cm² at a relatively low applied field of 4.19 V/μm. This emission; however, is randomly dispersed throughout the RVC surface. This non-uniformity, clearly visible using a cathodoluminescent phosphor creates bright and dark spots resulting in a low total current from the surface. It is of interest create both geometrically favorable emission sites as well as modifying the surface materials bond structure to enhance field emission.

Previous study with this material demonstrated the effectiveness of Argon-Ion irradiation in isolating field emission to areas which had been subjected to ion bombardment. By doing so for as little as 7 minutes, the applied electric field for the onset of emission was reduced to 1.98 V/μm. Irradiated cathodes were also seen to better maintain their emissivity characteristics in comparison to non irradiated RVC. The turn-on field required for non-irradiated materials shifted from 4.19 V/μm to 2.69 V/μm over a 48 hour period while samples irradiated for 7 minutes shifted from 1.98 V/μm to 2.15 V/μm and samples irradiated for 60 minutes demonstrated a shift in the required turn-on field from 2.65 V/μm to 2.62 V/μm over the same period of time.

The RVC investigated was formed from the pyrolyzation of a novalac-based phenolic resin foam. Samples were solvent cleaned and subjected to ultrasonic cleaning in de-ionized water to remove debris from cutting the material into suitable sample sizes. Samples designated for field-emissivity tests were formed into 1cm² x 0.5cm sizes while materials designated for materials studies were cut into 2.54 x 10.16 x .02 cm sheets. For the overall study, samples of RVC were irradiated under various conditions of varying time, beam current and beam voltage. In this paper, only irradiations of constant time (15 min) will be discussed. Irradiation of the surface was accomplished using a Kaufman-type Argon Ion Source. Scanning Electron Microscopy (FEI XL30-SFEG) was performed to evaluate and verify restructuring of the surface. Raman measurements were taken at room temperature using a Renishaw 1000 Raman System using both HeNe (λ=632nm) and Argon (λ=514nm) lasers. Materials samples were crushed into a powder and Powder X-ray Diffraction was done using a Scintag XDS-2000 diffractometer employing Cu-Kα energy.

The changes in emissive characteristics are easily observed in current density plots such as those provided in figures 1(i-vi) which show the change in the characteristic near the turn-on emission current density of 10^{-6} A/cm² for the non-irradiated RVC sample (Figure 1(i)) as well as cathodes irradiated under conditions of the following beam voltage/beam current: 1.5kV/100mA, 1.2kV/200mA, 1.2kV/100mA, 1.2kV/50mA and 0.8kV/100mA shown as Figures 1(i-vi) respectively. Figure 1 shows the change in the turn-on response from sample to sample as well as over a 48 hour period with open symbols describing the initial current density measurements and solid symbols depicting the characteristic after being sustaining the sample at the turn-on field for 48 hours.

Increasing the number of ion impact sites by increasing the beam current (I_b) is seen to substantially lower the required turn-on field, from 2.7 V/μm to 1.41 V/μm as seen by comparison of Figures 1(iii), (iv) and (v) which describe current density plots of cathodes irradiated under varying conditions of beam current. It may also be seen by inspection of the turn-on field requirements seen over a 48 hour period that the emission from cathodes irradiated for 15 minutes is far more stable when emitting from lower numbers of emission sites: changing 1.8% at $I_b=50$ mA, 2.4% at $I_b=100$ mA and, 15.6% at $I_b=200$ mA.

The beam voltage (V_b) used to modify the surface reflects the energy imparted by the Ar-ion to the carbon surface. As each of the energies used is sufficient to promote the modification of the surface, each shows improvement in their JE characteristic (Figures 1(ii), 1(iv) and (vi)) as compared to the non-irradiated case Figure 1(i). Turn-on field requirements vary from 2.36 V/μm for a beam voltage of 0.8kV to 2.43 V/μm for a sample irradiated at 1.5kV.

Altering the beam voltage results in the increasing of the instability of the turn-on field required over time from 2.4% for $V_b=1.2$ kV to 12.6% for $V_b=0.2$ kV and 6.18% for $V_b=1.5$ kV. It is speculated this decrease is the result of the ability of the surface to form stable bonds at impact sites over the irradiation time. Surface features being formed and destroyed at higher voltages may attribute to this instability, at lower voltages, the dynamics of the time frame may be prohibitive in forming stable bonds. Optimization of the irradiation process would require balancing this creation and destruction of surface features and selecting moderate bombardment energies for any irradiation time.

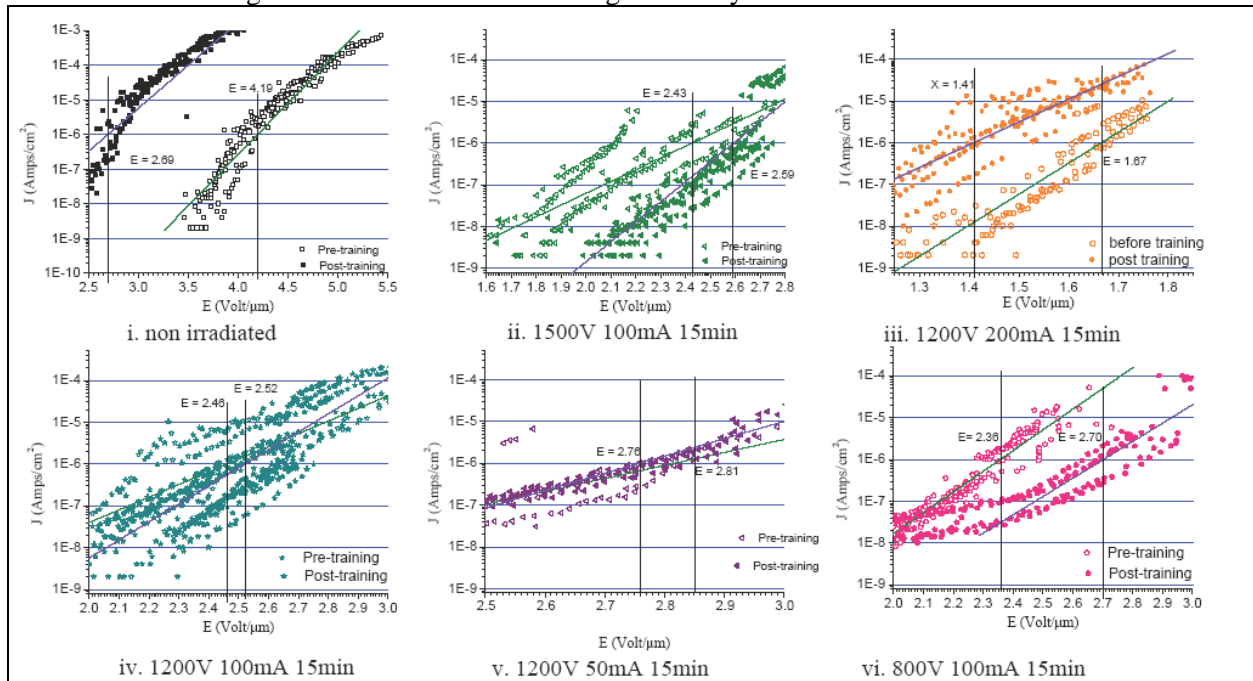


Figure 1(i-vi) Current Density measured versus the required Electric Field for RVC cathodes spaced 2mm from a mirror polished stainless steel anode.

Raman studies of the sample irradiations corresponding to irradiations with varying beam voltage are shown in Figure 2 which shows the changes in disordered D and graphitic G peaks, $\sim 1598\text{cm}^{-1}$ and $\sim 1361\text{cm}^{-1}$ respectively. Although the D peak position shifts are minor, the increase in peak width and decrease in amplitude when normalized with respect to the G peak implies an increase clustering due to the formation of nanostructures at the surface.

The shift in the observed G peak from $\sim 1598\text{ cm}^{-1}$ to $\sim 1586\text{ cm}^{-1}$ is generally thought to be due to an increase in the graphite sheet disorder due to the breaking of the graphitic bonds at the surface by the Argon ions. This shift may also signify the formation of diamond (fcc)-like materials within the glassy carbon structure as well as reflect the creation of the nanowires and nanowhiskers seen in previous SEM work. The G-peaks seen in Figure 2 are also observed to develop a sideband as well as a decrease of the trough depth between D and G peaks implying the presence of more than the obvious D and G peaks. Further study is ongoing to deconvolute the number of peaks present. It is believed,

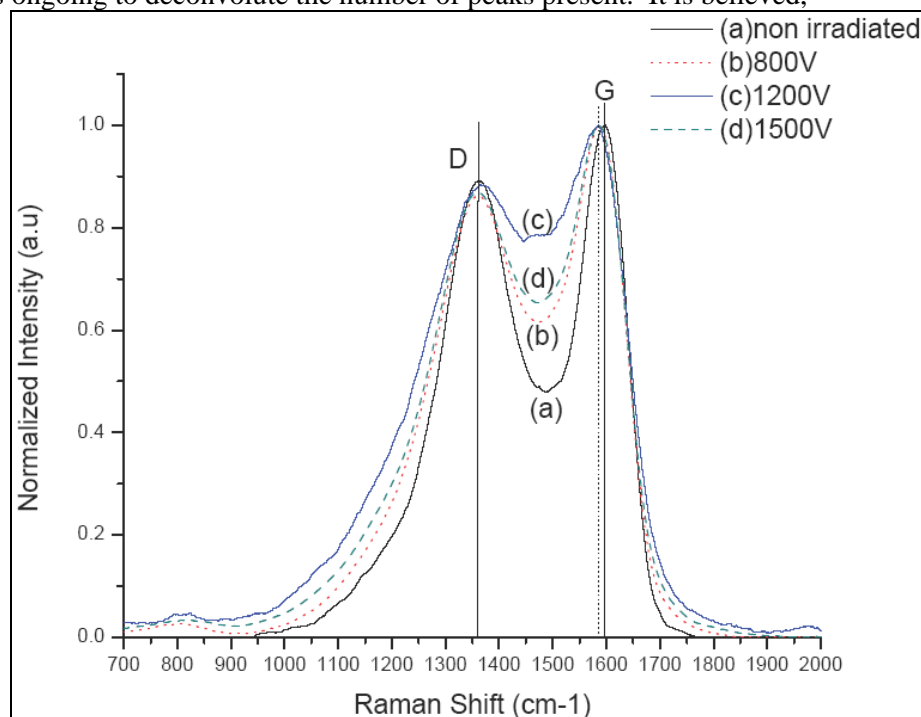


Figure 2 Raman peak shifts as seen due to impact voltage.

XRD performed shows a relatively small change in the material from the amorphous. Figures 3(i) and (ii) show XRD scans over changes in beam voltage and beam current respectively. Though peak shifts in comparison with non irradiated RVC are easily observed, trends within the irradiated set are still under investigation. It is however of interest that a slight peak is seen to form near 12 degrees suggesting the presence of C60 type fullerene materials.

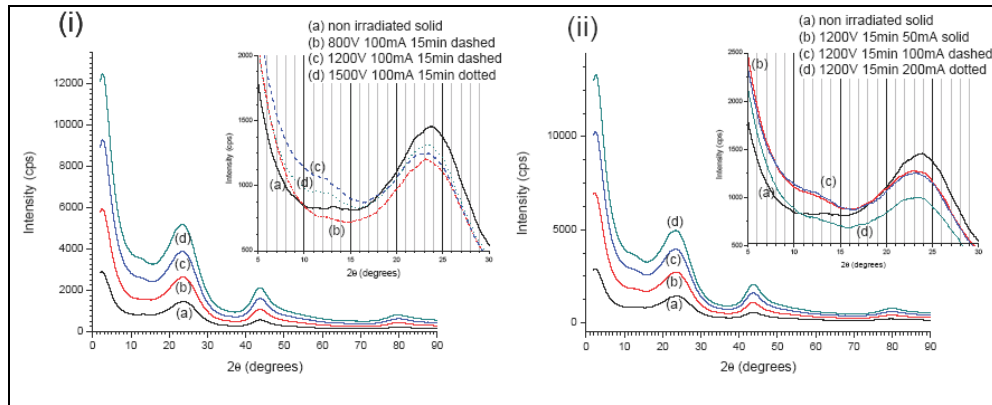


Figure 3 X-ray diffraction from samples irradiated under varying conditions of (i) beam voltage and (ii) current. Inset diagrams show an enlarged view of data of 2θ values between 5-30 degrees.

In summary, surface modifications induced by Ar^+ -ion irradiation has been correlated to known emissive properties of the material. Modification of the surface to create nanostructures requiring lower field requirements enhances emission from the argon treated areas of the cathode surface. These nanostructures may include diamond (sp^3) and fullerene type bonded materials as suggested by shifts in the Raman spectra as well as a developing peak in the X-ray diffraction from the material.

References:

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