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Novel room tempreature grown carbon based cathodes for field emission using diamond nano-particle seeding technique

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Abstract

Low field electron emission from novel carbon based cold cathodes is reported The cathodes consisted of a layer of nanoseeded diamond and an over layer of nanocluster carbon films. The nanoseeded diamond was first coated on to thesubstrate. The nanocluster carbon films were then deposited on the nanocrystalline diamond coated substrates using the cathodic arc process at room temperature. The heterostructured microcathodes were observed to exhibit electron emission currents of 1 $\mu A/cm^2$ at fields as low as 1.5 to 2 $V/\mu m$. The effect of the nanoseeded diamond size and concentration and the properties of different nanocluster carbon films on emission characteristics is presented.

Introduction

There is an increasing interest in carbon based nanostructured materials like the nano-diamond[1-3], nanotubes[4, 5], and nanocluster or nanostructured carbon[6-10] for possible use as electron emitters. The interest stems from the feasibility of diverse applications, which include field emission displays, electron-beam lithography, electron and ion guns, sensors, electron microscopes and microprobes, image pick up tubes, low & medium power microwave sources, micro and pico satellite propulsion systems, high power devices and Tera hz communication devices. The need is for electron emitters capable of emitting high emission currents at low fields accompanied by a high emission site density. Further the materials process should be such that, it can be used for deposition on low cost substrates, easily scaled for large area growth and compatible with other materials process technologies. However most materials mentioned above are grown at high temperatures, some have poor adhesion to the substrate and also patterned growth could be a problem. Further the emission mechanism is no fully clear, even though many models have been proposed to explain the factors influencing emission in the case of the diverse nino-carbon based flat cathode materials[11-23]. The main factors influencing emission form carbon films seem to be a) field enhancement factor, b) highly conducting sp^2 bonded nanostructured carbon, in it's various manifestations c) the presence of sp^3 bonded material in the sp^2 matrix and d) the emission site density, taking into consideration factors such as shielding or overlapping of field which could inhibit or limit emission.

We had earlier studied diamond growth exten-

sively using various process including Hot filament CVD (HFCVD), Electro cyclotran resonance (ECR) Plasma CVD and Magneto active microwave Plasma CVD[3, 24-27], By using process of nano-diamond seeding[27] and magneto active microwave Plasma CVD, we had demonstrated that it is possible to grow[24-26] densely nucleated diamond films at low temperatures. We had used the magneto active plasma to essentially create a dense plasma to enhance the growth rate and the nanoseeding to increase the nucleation density and demonstrated diamond film growth at temperatures as low as 200 ℃. Some of our diamond films also exhibited emission threshold fields as low as 1 V/μm applied field for an emission current density of 1 μA/cm^2[2, 3]. However some of these nano & microcrystalline diamond films tended to show some degradation in their emission behavior over a period of time.

Further based on the present understanding of the science and technology of carbon based field emitters, it would be difficult to clearly define and tailor the emitter according toe the requirements defied earlier. The material growth process parameters seem to be the only controlling factor and the emitter site derived is random. It would be desirable to exactly tailor the emitters and also be able to do so at temperatures close to room temperature. Reported in this paper is an effort towards understanding and developing a new tailored room temperature grown, nano-carbon based, multiplayer structured, low field electron emitter. These heterostructured microcathodes exhibit very low field electron emission (1 μA/cm^2 emission current at 1.5-2 V/μm applied field). The emission behavior was observed to be dependent on the nanoseeded diamond size and concentration for a given optimized nanocluster carbon film composition. Under certain conditions the multilayered cathode consisting of nanodiamond with an overlayer of nanocluster carbon films seem to exhibit negative differential resistance behavior[10, 23].

Experimental conditions

Highly conducting n^{++} silicon substrates were first coated or pretreated with the purified nanocrystal diamond particles[10, 24-27]. The size of nanocrystalline diamond was varied from 5 nm to 1 μm. The nanocluster carbon films were then deposited on to the nano-diamond coated substrates simultaneously in a pulsed cathodic arc system, at a nitrogen partial pressure of about 10^{-1} Pascal and varying helium partial pressures ~40-120 Pascal.[7, 10] Field emission measurements have been carried out in a parallel plate configuration, where the cathode consists of the carbon films to be tested and the anode consisted of an ITO coated glass plate.[7, 28] The I-V measurements were made with an anode-cathode spacing of 100 μm and over a cathode area of 0.25 cm^2. No conditioning or forming process was required to initiate the emission. The Raman measurements were carried out using a Reinshaw micro Raman system and 515 nm, light as the incident wavelength.

Result and Discussion

Shown in Figure 1 is the measured current density against applied field plot for different nano-carbon based materials, similar to those reported earlier including nanocrystalline diamond[3], nanocluster carbon[7], nanotubes[9] and cluster

assembled nanostructured carbons[9]. It can be seen from the figure that all of the material emit electrons at relatively low fields. However the nanocrystalline diamond films were observed to degrade over a period of time. The cluster assembled carbon films studied, were very soft and could not be subject to any further processing. The nanotubes were grown at high temperatures and there could also be problem of patterned growth and scaling. The emission from nanocluster carbon films seem to saturate beyond a certain current due to possible shielding by the adjoining clusters. Hence in an effort to enhance the current density and the emission site density and also develop a room temperature process, multilayered cathodes made of nanoseeded diamond and nanocluster carbon were fabricated and studied.

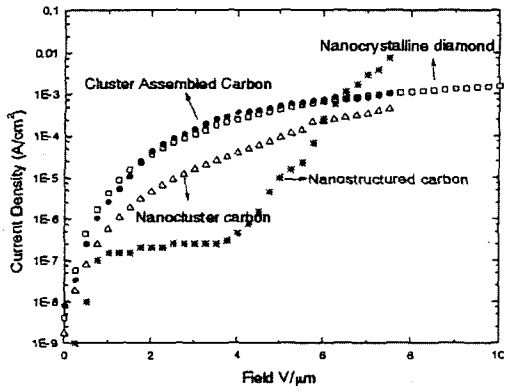

Fig. 1 Current density Vs Applied field plots of nanocarbon based low field electron emitters.

First the filed emission characteristics of the as deposited nanocseeded diamond layers were studied. Shown in Figure 2 are the emission characteristics of the nanoseeded diamond on silicon substrates. It can be seen that the threshold field for emission is very high for the as deposited nanoseeded diamond films on silicon substrates.

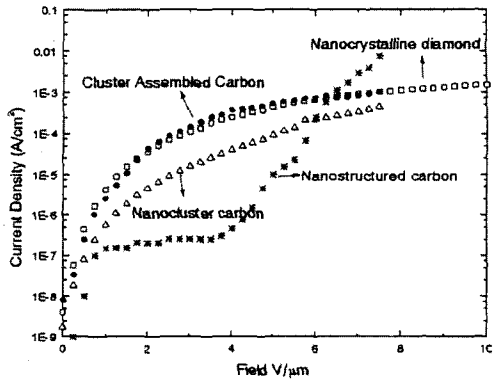

Fig. 2 Current density Vs Applied field characteristics of nanocrystalline diamond seeded Silicon substrates.

The silicon substrates coated with just the nanoseeded diamond have threhold fields in excess of 25 V/μm. Shown in Figure 3 is the emission current against the applied filed plots of heterostructured cathodes consisting of the nanoseeded diamond and nanocluster carbon. It can be seen from the Figure that initially when the nanoseeded diamond concentration is very low - 0.005 Ct/l, the emission characteristics is nearly similar to the emission characteristics of the nanocluster

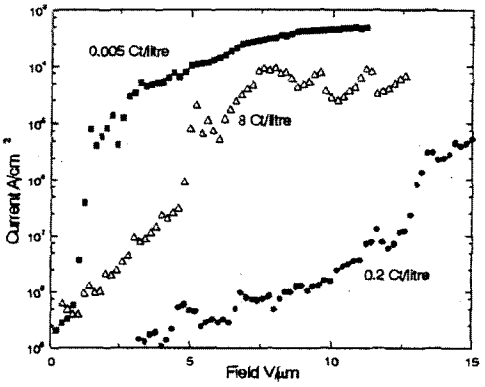

Fig. 3. Variation of emission current with applied field for varying nanoseed concentration in the case of a nanoseeded diamond and nanocluster carbon heterostructured cathodes.

carbon film in Figure 1. When the nanoseeded diamond concentration increases from 0.005 to 0.2 Ct/I, the emission current density decreases and the threshold field increases. However with further increase in nanoseeded diamond concentration, emission current again improves. Thus indicating that the emission characteristics of the multilayered cathodes depend on the nanoseeding concentration and the nanocluster layer.

In the case of field emitters, besides the sp^2 and sp^3 bonded materials of their ratio, the other factors influencing the emission are the field enhancement factor and the distribution of emission site density. In our novel multilayered field emitter cathodes, the nanoseeded diamond helps to enhance the aspect ration and thus the field enhancement factor. Further it is essential to choose the dimensions and the distribution of these nanodiamond, so that there is no shielding and we have effective utilization of the applied filed. A detailed analysis of the design would be published else were. However experimentally we have tried to identify the optimum size of nanodiamond by studying the field emission characteristics of the varying sized nano seeded diamond, coated with a thin layer of tetrahedral amorphous carbon (ta-C). Shown in Figure 4 is the variation of the emission threshold field with respect to size of the seeded nanocrsytalline diamond. It can be seen from the figure that the threshold field decreases with increase in size of the nano-diamond. However the changes in threshold field seems to be less drastic as the size increases.

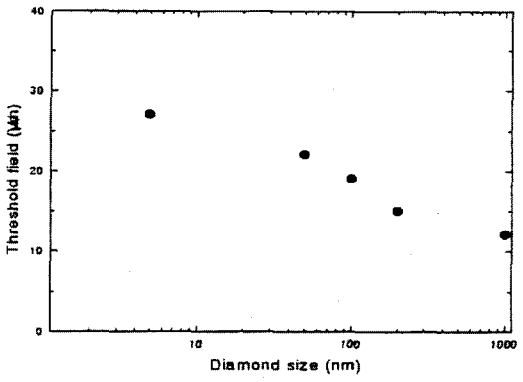

Fig. 4 Variation of the threshold field with the size of seeded nanocrystalline diamond, when coated with an over layer of tetrahedral amorphous carbon (ta -C).

Shown in Figure 5 is an SEM image of a typical silicon substrate, seeded using nanodiamond film and coated with an over layer of ta-C film. The SEM images of the typical nanocluster carbon films grown using cathodic arc process are shown in Figure 6. Further the nanoclusters in the films overlapping on each other seem to shield the emission leading toe saturation in emission currents.

Fig. 5 SEM micrograph of seeded Nanocrystalline diamond

It can be seen from Figure-1, that at an applied field of 2 V/μm, the nanocrystalline diamond emits about 3×10^{-5} A/cm^2, while the emission from nanocluster carbon film seems to less in magnitude $\sim4\times10^{-6}$ A/cm^2. The present understanding suggests that the emission from diamond films occur, predominantly from near the inter-

Fig. 6 SEM micrograph of Cathodic arc process grown Nanocluster carbon film.

face between the sp^3 bonded diamond and sp^2 bonded carbon. In the case of the sp^2 bonded nanocluster carbon, the emission is mainly due to field enhancement factor. Thus by growing a multilayer of seeded nanodiamond and nanocluster carbon, we effectively create a matrix of sp^2 bonded material and sp^3 bonded material, all at room temperature, in a very clean environment. Further the nanodiamond acts as parameter influencing the filed enhancement factor as discussed earlier. Thus leading to the possibility of better emission from the multilayered of heterostructured cathode.

Shown in Figure 7 are the current vs applied field plots of multilayered films made of 200 nm diamond layer and a layer of nanocluster carbon. The nanocluster carbon films were deposited at different pressures on the nanocrystalline diamond seeded silicon substrate. It can be seen from the figure that the emission properties vary with deposition condition. Threshold field as low as 1.5 V/μm is observed. Thus for good emission we need an optimum size and concentration of nanocrystalline diamond and an optimum nanocluster carbon film.

Fig. 7 Current Vs applied field plot of Multilayered cathodes made of nanodiamond and nanocluster carbon film grown at different helium.

Shown in Figure 8 is the Raman spectra of a typical as grown nanocluster carbon film and a nanocrystalline diamond and nanocluster carbon multilayered cathode. The presence of shoulder around 1300 cm^{-1} besides the G peak, indicates the onset of the D peak, and the possible sp^2 clustering thin the case of as grown carbon films. Details including dependence of clustering on deposition conditions and SEM micrographs of such material, grown using the cathodic arc proc-

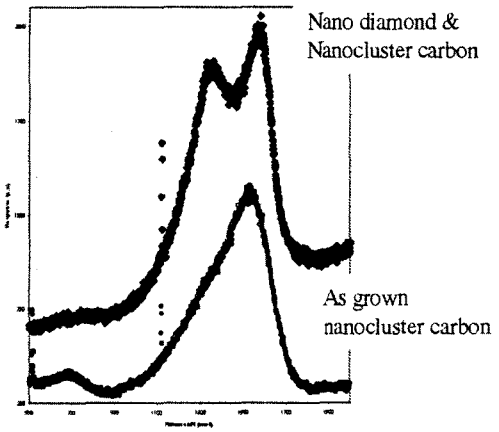

Fig. 8 Raman Spectrum of as grown nanocluster carbon and nanocrystalline diamond and nanocluster carbon multilayered cathodes

ess have been presented earlier[7, 10]. Further the absences of the small peaks around 900 cm^{-1}, usually attributed to the underlying silicon substrates, due to the optical transparency of sp^3 bonding in the film, indicates that we already have predominantly sp^2 material.

In the case of the multilayered cathode, consisting of nanocrystalline diamond and nanocluster carbon, the D ($\sim$1360 cm^{-1}) and G ($\sim$1565 cm^{-1}) peaks are clearly visible. The nanodiamond could help the growth of finer structured nanocluster carbon leading to the clear D & G peaks. The I(D)/I(G) ratio derived from Raman spectra of nanocarbon films is a good indicator of the field emission characteristics of the cathode[3]. With further optimization of the nanodiamond size and sp^2 bonded nanocluster carbon layer, the D & G peaks response may be enhanced with reduction in the width of the peak. Thus achieve a more desirable I(D)/I(G) ratio for good field assited electron emission.

From the above results it can be seen that it should be possible to tailor novel low field electron emitting cathodes using nanoseeded diamond and nanocluster carbon films grown at room temperature. By optimizing the nanoseeded diamond's size and concentration and the nanocluster carbon layer thickness and properties we can achieve enhanced emission currents at low fields, associated with high emission site density. The added advantage is that it is a clean, room temperature process and can be scaled for large area applications.

Conclusion

Low field electron emission has been reported from a novel cathode made of multilayered nanoseeded diamond and nanocluster carbon. Threshold fields as low as 1.5 V/μm have been observed. With further optimization of the nanoseeded diamond's, size and concentration and the nanocluster carbon layer thickness and properties it should be possible to achieve enhanced emission currents at low fields, associated with high emission site density. The process offers the possibility of tailioring an exact sp^2 and sp^3 bonded nanocarbon matrix and emitter site distribution, for field emission applications. The added advantage is that it is a clean, room temperature process and could be easily scaled for large area applications. These multilayered cathodes could be very useful for field emission based displays and other vacuum microelectronic applications.

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