ELECTRON EMISSION FROM A NOVEL MULTILAYERED, LOW TEMPERATURE PROCESS GROWN NANOCARBON BASED COLD CATHODES AND IT'S POSSIBLE EMISSION MECHANISM

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Abstract:*Field assisted electron emission from nanostructured carbon materials is becoming increasingly attractive. The need is for an inexpensive, low temperature processed scalable process technology. Presented in this paper is a concept and proof of a novel nano carbon based multilayered electron emitter which matches the criteria. The nanocarbon films used in the device were grown using the Cathodic arc process, without heating the substrates. The emitters typically exhibit an emission current density of 1μA/cm^2 at an applied field of around 1 - 2 V/ μm. Some of the multilayered films under certain conditions also exhibit negative differential resistance type behaviour.*

Keywords: Multilayered electron emitter; nanoclustered carbon; nanodiamond; tetrahedral amorphous carbon; cathodic arc and low temperature process technology.

Introduction

Field assisted electron emission based on relatively flat, as deposited, self aligned nanostructured materials, as compared to Spindt tips is being increasingly studied by many groups. The interest stems from the feasibility diverse applications, which include field emission displays, electron-beam lithography, electron and ion guns, multitude of sensors, electron microscopes and microprobes, low & medium power microwave sources, micro and pico satellite propulsion systems, high power devices and Tera hz sources & communication devices. and lighting systems[1-4]. The intense study finally seems to be leading to possible products in the market. Companies including Canon-Toshiba (SED), Samsung (Printed CNT) and Motorola (deposited CNT on glass) have all reported that their respective technologies are nearly ready for launching flat panel displays. However there is still a need for a relatively low temperature process based technology, compatible with semiconductor technology, inexpensive and scalable to larger dimensions.

Among the many materials that are being studied as flat and self aligned cathodes (field assisted electron emitters) carbon based materials varying nano-diamond, nanotubes, nanowalls, nanofibers, nanocluster carbon and tetrahedral amorphous carbon (ta-C) [1-9] have drawn the maximum interest. Carbon based emitters came to be noticed, with the interest in diamond as a candidate for flat cathodes. The motivation to use diamond came from its physical properties such as low electron affinity, high mechanical strength, chemical inertness and high break down voltage. Further the termination of a diamond surface with hydrogen led to negative electron affinity. However the work on diamond based field assisted electron emitters showed that, good quality diamond were not suitable for field emission application. There were very few free electrons available in them. The emission if any came from near the interface between the defective grain boundaries and crystalline diamond.

The study of defective diamond led to the study of nanocrystalline diamond. The study showed that the electrons conducted through the sp^2 bonded grain boundaries and amorphous matrix. Emission occurred preferentially through sp^3 bonded small diamond region or protrusions in the films. The study of diamond led to the interest in other manifestations of carbon including nanotubes, nanocrystalline graphite, nanohorns and nanocluster or nanostructured carbon [2-9] as possible materials suitable for flat cathode. All the nanomaterials emit electrons at relatively low fields. However most of them are grown at relatively high temperatures. Further the nanocrystalline diamond films were observed to degrade over a period of time [8]. The cluster assembled carbon films studied, were very soft and could not be subject to any further processing [7]. The nanotubes were grown at high temperatures [9] and there could also be problems 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 [4, 6].

Thus in general the problems associated with the nano carbons include the high process temperature, adhesion, scaling, current saturation, incompatibility with existing process technology and conditioning of the emitters. The need is for electron emitters capable of emitting high emission currents at low fields accompanied by a high emission site density. Further the material process should be such that, it can be used for deposition on inexpensive substrates, easily scaled for large area growth and compatible with other material process technologies as discussed earlier. Further the progress to date clearly shows that, no carbon based material is immediately suitable for all vacuum nanoelectronic applications. Each material has some limitations. Coming to the physics of electron emitters, the standard Fowler-Nordheim expression cannot exactly predict or lead to estimation of factors such as the emitter dimension or the aspect ratio, as in the case of the metal tips. Many alternate models have been proposed to

explain the factors influencing field assisted electron emission in the case of the diverse nano-carbon based flat cathode materials. However the models do not seem to be universal for all materials.

Proposed emitter model;
Based on the present understanding of the carbon based field emitters, the key factors influencing field assisted electron emission may be broadly defined as

a) Field enhancement factor,
b) Highly conducting sp^2 bonded (π bond) nanostructured carbon, in it's various manifestations
c) The presence of sp^3 bonded (σ bond) material in the sp^2 matrix and
d) Optimum emission site density distribution, taking into consideration factors such as shielding or overlapping of field, which could inhibit or limit emission.

All this factors cannot be easily controlled or implemented using single deposition process. This calls for multiple processes, which also means cost and time and complexity. Taking into consideration the above, we have tried to develop a novel, room temperature grown, carbon based multilayered electron emitter, suitable for most vacuum micro/nano electronic applications. The heterostructured cathode consists of layers or features to ensure the following factors

i. A Field enhancement provider – A layer of nano particles distributed uniformly on the back contact. This could be nay material; in the present case the material used is Nano diamond. The nanodiamond are very stable, do not degrade or melt easily under influence of high fields and currents.
ii. Electron source / supplier: An over layer of conducting nanostructured material. In the case of carbon sp^2 bonded Nanocluster / nanostructured Carbon
iii. Electron Escape Valve: A wide band gap material with a relatively lower electron affinity. - sp^3 bonded tetrahedral amorphous carbon islands on nanocluster carbon in the present case.
iv. Emission site density Distribution: Optimized dispersion of nano diamond during the seeding process and the distribution of sp^3 Islands. Thus ensuring minimum of field over lapping and efficient distribution of emission sites.

Shown in figure 1 is the schematic of the proposed multilayered electron emitter. The image is not to scale.

Experimental Conditions

First purified nanodiamond mixed in an desired concentration in a liquid medium (water or alcohol base) was coated / dispersed on to the substrate with appropriate back contacts (glass or n++silicon) using dip or spin or spray coating[4]. Then the nanocluster carbon and tetrahedral amorphous carbon films with the desired properties of sp^3 and sp^2 bonding ratio were then deposited simultaneously using the same Cathodic arc process[6], under varying deposition conditions. The samples were deposited on to the substrate, without any means of external heating. Field emission measurement was carried out using a coplanar configuration, with an anode -cathode spacing of 100 μm. The anode probe used was a 1mm diameter metal disc. The measurement was carried out under a vacuum of $\sim 10^{-5}$ Pascal. The SEM images were taken using a JEOL SEM system and the Raman measurements were carried out using Renishaw Raman spectroscopy system, with an incident wavelength of 514.5nm.

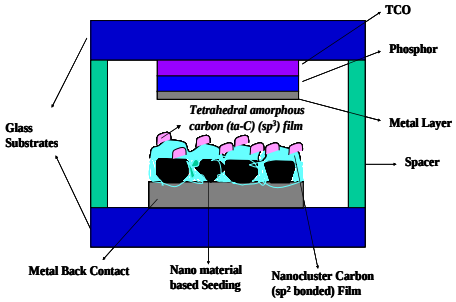

Figure 1. Image of the concept of the multilayered electron emitter. (not to scale)

Result and Discussion

As dispersed 5 nm nanocrystalline diamond layers proposed for the seeding process, were studied first. The 5nm nanodiamond on silicon substrates were observed to emit electrons at threshold fields in excess of 25 V/μm. The threshold field is defined as the field at which an emission current density of $1\mu A/cm^2$ is emitted. Next multilayered cathodes consisting of nanoseeded diamond and nanocluster carbon, with varying 5nm nanoseeded diamond concentration were studied. Shown in figure 2 is the emission current against the applied field plots of these 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 carbon film used as the electron emitter. When the nanoseeded diamond concentration increases from 0.005 to 0.2 Ct/l, 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. Further the samples seem to exhibit a behaviour similar to negative differential resistance devices or resonant tunnelling. This seems to be dependent on the nanoseeded diamond

size and concentration and the nanocluster carbon film.

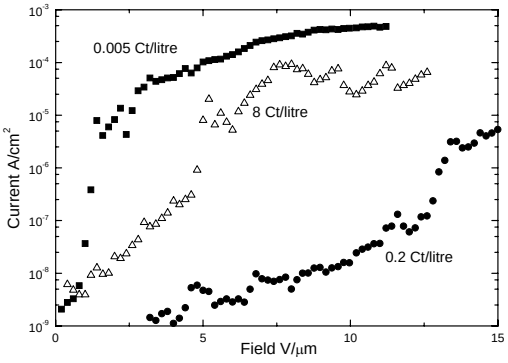

Figure 2. Variation of emission current with applied field for varying nanoseed concentration in the case of a nanoseeded diamond and nanocluster carbon

Next in order to identify the optimum size of nanodiamond to influence the field enhancement factor, the effect of the size of the seeded nanocrystalline diamond was studied. The study showed that threshold field decreases with increase in size of the nano-diamond. However the changes in threshold field were less drastic, as the size of nanodiamond was increased. Suggesting an optimum seeding size between 100 to 200nm for efficient field enhancement and also prevent shielding of adjacent emitters. Further as the initial adhesion of the nanodiamond is just through Vander waal forces, bigger dimension also leads to problems of adhesion and pin holes.

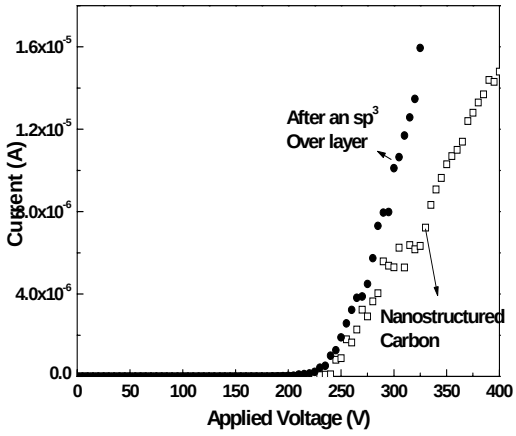

Figure 3 The Influence of a thin sp^3 layer (tetrahedral amorphous carbon) on field emission form nanostructured carbon films

The earlier studies on field emission from various nano carbons have shown that, very narrow regions of sp3 assist in electron emission. The sp3 region lowers the energy for tunneling of electrons, as compared to the energy needed to escape from sp^2 bonded graphitic material . However the sp^3 region in the above experiments were not tailored. The growth was incidental or inherent to the growth process. In an effort to test the possibility of exactly tailoring the sp^3 regions on the nanocluster carbon layer, optimum thickness of tetrahedral amorphous carbon films were grown on the nanocluster carbon[10]. Figure 3 shows the influence of the sp3 regions on emission. It can be seen from the figure that there is a marked lowering of threshold for emission and also enhancement in emission current [13]

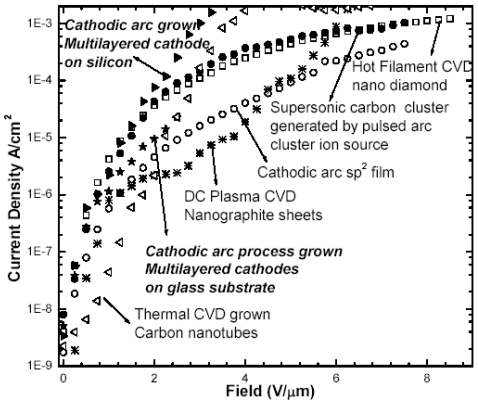

Figure 4. Comparison of the Applied field Vs emitted current density plots of multilayered electron emitters performance with other various Nano carbon based electron emitters along with .

Combining the above observation, novel multilayered cathodes consisting of nanosseded diamond, nanocluster carbon and tetrahedral amorphous carbon were fabricated. Threshold fields as low as 1-3 V/μm was observed in $1cm^2$ samples grown on silicon and glass substrates. Shown in figure 4 is a comparison of the field assisted electron emission from various carbon based electron emitters along with the novel multilayred electron emitter. It may be seen that they are comparable. Shown in figure 5 are the current Vs applied field plots of these nano carbon based multilayered cathodes, fabricated over an area of 40mm x 30mm on glass substrates before and after sealing. It may be seen from the figure that even an unpatterned emitter grown over a large area shows an emitter threshold field of around 5 V/μm. Further on sealing the panel the emission threshold field decreases to 2V/μm . this could be due to possible condensation of the nanocluster carbon films under the sealing temperature of 400 ^oC. Thus clearly showing that even if the films were deposited at near room temperature, the sealing process essentially enhances the performance of the device. An AFM based current mapping of the emitter surface clearly shows that the proposed model for electron emission is working. Without any conditioning process the emitters over an area of 30mm x 40mm, exhibit about 50-60 % emission site density. With further conditioning and optimization it is expected that this technology could be of interest for vacuum nanoelectronics and especially low cost displays and lighting. The detailed report on the same is to be published else were.

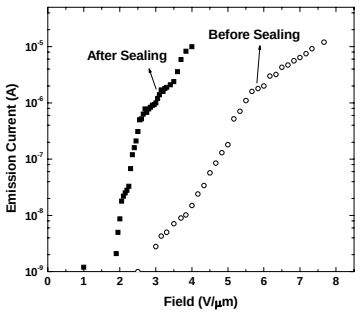

Figure 5 Field emission from a sealed panel of size 40 mm x 30mm (before and after sealing) were the cathode is based on the concept of the novel multilayered emitter.

Conclusion

Presented in this paper is a concept of a novel multilayered electron emitter and the proof of working of the model based electron emitter. The novel multilayered electron emitter consists of a layer of nanodiamond, nanolcuster carbon and tetrahedral amorphous carbon. All the processing is done at room temperature. The nanocarbon films used in the device were grown using the cathodic arc process, without heating the substrates. The emitters typically exhibit an emission current density of 1μA/cm^2 at an applied field of around 1 - 2 V/ μm. Some of the multilayered films under certain conditions also exhibit negative differential resistance type behaviour.

Acknowledgement; The author would like to acknowledge his colleagues from Cambridge University –UK, Kochi University of Technology and Rodel Nitta for their support and possible discussions.

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