A COMPARATIVE STUDY OF FIELD EMISSION FROM DIVERSE NANOCARBON BASED ELECTRON EMITTERS AND A POSSIBLE CORRELATION WITH THE RAMAN RESPONSE

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Abstract*: Various forms of carbon including nanodiamond, carbon nanotube (CNT)s, nanohorns, nanofibers, nanocluster or nanostructured carbon are being studied as materials for diverse applications. Many of these materials have been shown to be very low field electron emitters. The change in the sp^3 and sp^2 bonding ratio in these materials defines the material. Presented in this paper is a comparative study of low field electron emission from various nanocarbons. Most of these films exhibit low field electron emission of varying from 1 V/µm to 5 V/µm, for an emission current density of 1 µA /cm^2. Discussed further in this paper is the possible correlation between the field emission properties and the Raman response.*

Keywords: Field assisted electron emission; Raman response; Nano diamond; nanotubes; nanocluster carbon.

Introduction

Interest in field assisted electron emission from carbon based nano materials such as nano diamond, carbon nanotubes, Nanowalls, nanopillar, tetrahedral amorphous carbon (ta-C) and nanocluster carbon[1-10] seems to grow by the day. Carbon nanotube seems to be the material of choice. The initial motivation for interest in cold cathode based electron emitters, was to realize, having flat panel displays with a picture quality comparable to cathode ray tubes. However with the advent of many other flat panel display technologies, the interest has shifted to other vacuum Nanoelectronics. So besides field emission displays (FED), the applications being studied include flat backlights for LCD displays, lighting for bill boards, compact microwave and X-ray sources, multitude of sensors, large area E-beam lithography and a multitude of sensors.

These self aligned novel nanomaterials are being developed not only for vacuum nanoelectronics but also as the building blocks of future nanoelectronic devices[1-6]. The field assisted electron emission measurement behavior of the nanostructured carbon calls for the use of diverse sophisticated & expensive instruments, time consuming process of measurement with need for advance skills to operate the system. Further as the technology becomes more prevalent, the need for an easy characterization and analysis or quality monitoring tool, in either a lab or a factory production facility would become imminent. In the case of carbon based materials the factors influencing the field assisted emission are, nature of bonding of the carbon material namely if it is diamond like σ bonds (sp^3 type bonding) or graphite like π bonds (sp^2 type bonding) and the nano dimension of the self aligned carbon based nanomaterials. Here Raman spectroscopy could be an interesting tool. First it offers the option of an instantaneous and non destructive measurement which is also free from electromagnetic interference. Further it can give information on both the nature of bonding and bonding ratio and also the dimension of the nanostructured carbon based materials [1, 7, 8, 13, 14]. Hence if we can establish a correlation between the emission characteristics and the material parameters as estimated from Raman, it could be possible to instantaneously get an information on the field emission. Hence presented in the paper is a look at possible relation between the field assisted electron emission properties from various low field emitting nanocarbons and the Raman response.

In the case of the conventional field emitters (Spindt tips) the Fowler Nordheim (FN) plot can be used to estimate the emitter information, such as the aspect ratio and the exact emitter tip radius or even other parameters. However the same FN plot in the case of deposited nano carbon films and other similar self aligned emitters or flat emitters, cannot give much information about the emitter, except confirming that the electron emission is due to tunneling or is field assisted. As mentioned earlier, it is known that Raman could give information on bonding in carbon and also possibly on the nanostructure. Hence an effort has been made to correlate the dimensions of the nanomaterials and the Raman data to the slope of the FN plot, to see if a correlation exists between the Raman data, microstructure and FN plot slope.

Experimental details

The various nanostructured carbon films used in the study includes nanodiamond, carbon nanocluster, nanowalls, carbon nanotubes and nanopillar like material. The modes of deposition are mentioned below. The Nanodiamond films were grown using Hot Filament Chemical Vapour Deposition (HFCVD) at around 800^0C[8]. The Carbon Nanowalls films were grown using DC plasma CVD at 900^0C [9]. The Carbon Nanotubes were grown using Thermal CVD at 750^oC [10]. Nanocluster carbon films were grown using

Pulsed Laser Assisted cluster beam assembly source process[12]. Another set of nanoclusters and nanopillar like materials were grown using the the Cathodic Arc process at room temperature. The 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 consists of either an indium tin oxide (ITO) coated glass plate or a phosphor coated glass plate (for emission site density measurements). The *I –V* measurements were made with an anode–cathode spacing of 100 μm and over a cathode area of 0.24 cm^2. The Raman measurements were carried out using a Reinshaw Raman spectroscopy equipment with a 514.5nm excitation source. The samples for Raman measurements were deposited on silicon substrates. Similar samples were also used for the SEM measurements.

Result and discussion

The field assisted electron emission measurements are shown in Figure1. It was observed that, irrespective of the growth process and morphology all the nanocarbon samples exhibited low turn on fields around 1-5 V/μm for an emission current density of 1μA/cm^2. However the trend beyond the turn on voltage, is not exactly the same. The nature of the surface, the distribution, the nano dimensions and their conductivity could decide issues like, the emission current density at higher fields and the stability of the emission as can be seen from the figure 1.

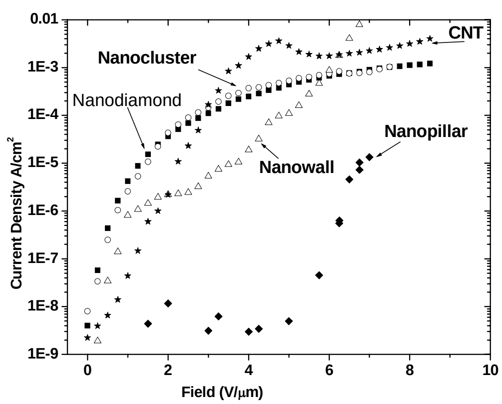

Figure1. Current density Vs applied field plots or field emission response of several nano carbons including (a) Nanodiamond films (b) Nanowalls, (c) Carbon nanotubes, (d) Nanocluster carbon and (e) nanopillar like material

Shown in figure 2 is the FN plot of the various nanocarbons being studied for their field assisted electron emission behaviour. It may be seen from the figure that the FN slope is sharper for smaller dimension nanopillars and nanowalls. Next are the carbon nanotubes, which are enveloped in an amorphous matrix. The slope is shallow for the room temperature grown nanocluster carbon and also for the nanodiamond. These clearly indicate that these films have more mixed phase or amorphous carbon material in higher ratio.

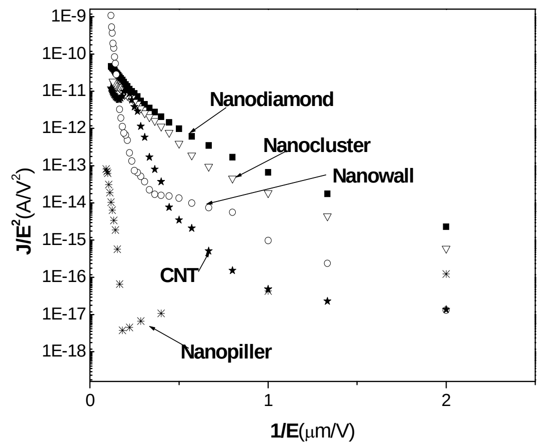

Figure 2. F-N plots for (a) Nanodiamond films,(b)nanowalls(c)CarbonNanoTubes,(d)Nano cluster carbon films and (e)nanopillar

The Raman response of nanostructured carbon thin films is shown in figure 3. It may be seen that the responses are quite different. Raman response can be used to characterize nano carbon materials varying from conductors to semiconductors and insulators as also polymeric clusters. It can be used for both qualitative and quantitative analysis of the materials. [7, 8, 14]. The presence of the G peak in figure 3 clearly indicates the existence of graphitic nanoclusters in the samples. The Nanodiamond film alone exhibits the diamond peak around 1332 cm^{-1}. Further it may be seen that the G peak width decreases as we move from nanocluster carbon to nanotubes and nanowalls.

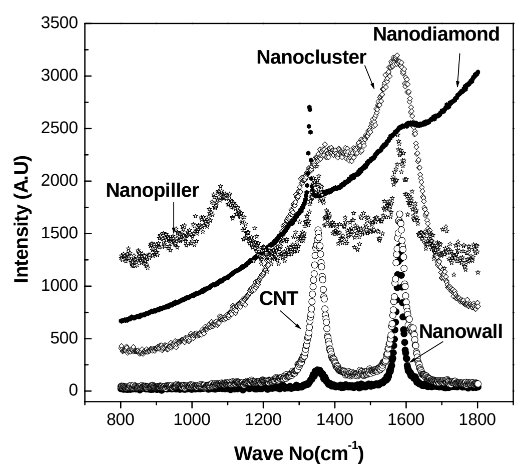

Figure 3. Raman response of the various nanocarbon films (a)Nano diamond (b)Nanowall, (c)Carbon Nantoubes (CNT), (d)Nano cluster carbon and e)nanopillar

This corresponds to the lateral dimension of the samples as observed from the SEM images. The details are published else were as it is beyond the scope of this paper to discuss the same. The nanodiamond sample has a very broad G peak. The nanopillar sample seems to be more unique with the presence of 3 peaks around 1080-90 cm^{-1}, 1350 cm^{-1} and 1580 cm^{-1} . In the case of nanostructured carbon or nanowalls, we see relatively the narrowest G peak around 1580cm^{-1} and a very short D peak, clearly showing the reduction in the amorphous phase or disorder in the sample. The I_D/I_G ratio was estimated from the deconvoluted data of Raman spectra. Other parameters estimated from the Raman data include the Full width at half maximum(FWHM) of the G and D peaks, the peak positions of the G and D peaks, the shift in the G peak position, the dimension of the nanocarbons and the deconvolution of the G peaks. The details are to be published in another communication, as it is beyond the scope of this paper.

Shown in figure 4 is the variation of the slope of the FN plot with the I_D/I_G ratio. As discussed earlier in the introduction, it was felt that it may be useful to study the correlation between the FN plot slope and the Raman response.

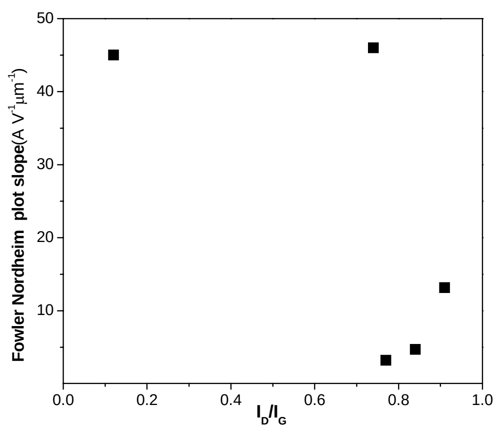

Figure 4. Relation between F-N plot Slope and I_D/I_G ratio for nanocarbon films estimated from the Raman Response.

For FN plot has a relationship with the emitter geometry in the case of conventional Spindt tips. However in the case of carbon based materials or flat cathodes, earlier it was assumed that the aspect ratio was one. The emitter was considered to emit from plane to plane, rather than point to plane. However we now know that the emission is spotty and we cannot assume uniform plane emission. The emission also seems to be dependent on the local geometry, at the point of emission. Further the emission also depends on the material's properties, including its ability to contribute electrons and at the same time, do so at low energies. As there is no relation ship to directly estimate the nanofeatures of the carbon or plane cathodes that contribute to electron emission, it was felt that the comparison with Raman data would be interesting. For Raman offers the possibility of estimating the bonding nature and structure or even dimensions of the nanocarbons. Especially so, with the view to identify if a relation exists between the nanocarbon based material's bonding nature, the dimension and the FN slope. Further, is the relation if any; is process dependent or independent of the process? It may be seen from the plot that it is difficult to predict any outcome. However most low field emitting carbon based material seem to have an I_D/I_G ratio which is above 75%. Only in the case of the nanopillars the I_D/I_G is lower.

Shown in figure 5 is the relation between the FN plot slope and the average dimension of the clusters or fibers in the case of the various nanocarbon samples.

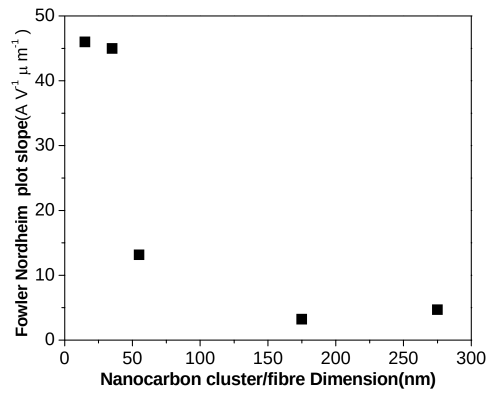

Figure 5. Relationship between nano-carbon's dimensions estimated using SEM images and F-N plot slopes.

It may be seen from the figure 5 that as the dimension of the nanocarbon material decreases the FN plot slope also decreases. Though it may be difficult from the limited data to draw too many conclusions, it may still be said that at certain optimum nano dimension up to which the slope value decreases. There after the nano dimensional non uniformity in the bigger cluster or structure become active once again in the case of relatively good emitters. Thus from figure 4 and figure 5 it may be concluded that even though the FN slope does not exhibit a significant relation ship with the I_D/I_G ratio, estimated from Raman spectra, it does show a variation with the nano dimension of the carbon films estimated from the SEM images [6-12]. The nano dimensions estimated from the Raman data do not match the actual dimensions estimated from the SEM images for all the samples. It may be due to the limitation of the current estimation methods. So effort is on to try to understand the interpretation used for nano dimension estimation and also to see if we can evolve a better method for the same. If established, than we believe it should be possible to correlate the Raman data and FN slope. From such a curve or relation, it should be even possible to use only Raman data and predict the field assisted electron emission nature of the nanocarbon samples in the future. Thus use Raman as an instantaneous characterization tool both in the lab or even in a production environment. The present work is a first step in that direction. Effort is on to work on a bigger pool of data to understand the relationship.

Conclusion

A comparative study of field assisted electron emission from diverse forms of nanocarbons including nanodiamond, carbon nanotube (CNT), nanowalls, nanocluster or nanostructured carbon at low fields are reported. The fields vary from 1 V/µm to 5 V/µm, for an emission current density of 1 µA /cm^2 . The change in the sp^3 and sp^2 bonding ratio in these materials defines the material. Raman response is a useful means to instantaneously identify the sp^3 and sp^2 bonding nature and the ratio in these nanocarbons. Conventional FN plots which give information regarding the emitter dimension and aspect ratio etc do not give much information in the case of plane to plane field assisted electron emission from flat cathodes. Hence an effort is made to understand the relation between the FN plot slopes and Raman response data (I_D / I_G) and the nano dimensions as derived from SEM data. There seems to exit some relation. In the case of (I_D / I_G) ratio it is generally high or above 75% for low field emitting nanocarbons, with in the range of samples studied in the present case. Further as the FNplot slope is clearly higher for lower nanocarbon cluster / crystal dimension. With further study it should be possible to establish a clear picture and possibly an empherical relation between Raman measurement and Field emission measurements.

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