Structural and Electronic Characterization of Nanocrystalline Diamond-Like Carbon Thin Films

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ABSTRACT

The origin of low threshold field emission (threshold field 1.25 V/\mu m) in nanocrystalline diamond-like carbon (nc-DLC) thin films is examined. The introduction of nitrogen and thermal annealing are both observed to change the threshold field and these changes are correlated with changes to the film microstructure. A range of different techniques including micro-Raman and infrared spectroscopy, X-ray diffraction, electron microscopy, energy dispersive X-ray analysis and time of flight-secondary ion mass spectroscopy are used to examine the properties of the films. A comparison of the field emission properties of nc-DLC films with atomically smooth amorphous DLC (a-DLC) films reveals that nc-DLC films have lower threshold fields. Our results show that nc-DLC can be a good candidate for large area field emission display panels and cold cathode emission devices.

Keywords: diamond-like carbon, carbon nanostructures, field emission, threshold field, Raman spectroscopy, electron microscopy

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1. INTRODUCTION

Carbon based materials have a number of properties that are attractive for large area electronic applications.\textsuperscript{1-6} For example, diamond-like carbon can be deposited over large areas and at low substrate temperatures.\textsuperscript{5} An important electronic property of such carbon based materials, which includes diamond, carbon nanotubes (CNT) and CNT-composites, is their ready ability to emit electrons into vacuum which make them suitable for applications in field emission display technology.\textsuperscript{2,7,8} Diamond-like carbon (DLC) thin films are well known for their exceptional mechanical properties\textsuperscript{9-14} and recently, we have explored the mechanical, optical and electrical properties of DLC and modified DLC thin films.\textsuperscript{15-19} DLC thin films are known to emit electrons\textsuperscript{20,21}, however, compared with diamond and CNTs, their threshold field ($E_T$) tends to be higher and emission current ($I_E$) is lower. As a consequence for the past few years research has been focused on nanocrystalline DLC (nc-DLC) films in order to reduce $E_T$ and enhance $I_E$. If the value of $E_T$ found in DLC and nc-DLC thin films could be engineered to be comparable to that of CNTs this will be a major breakthrough for field emission based devices as the deposition of DLC and nc-DLC thin films over large area is a relatively simple and inexpensive process.

At present the values of $E_T$ reported from CNT cathodes vary from 1 V/μm to 5 V/μm.\textsuperscript{2,6,7} whereas $E_T$ normally starts beyond 5 V/μm and can reach above 20 V/μm for DLC, tetrahedral amorphous carbon and nano-diamond thin films.\textsuperscript{20-22} Ikeda and Teii\textsuperscript{23} have demonstrated a low value of $E_T$ of 3 V/μm in a nanocrystalline diamond field emitter. However, further reductions in $E_T$ below 3 V/μm in DLC, modified DLC and nano-diamond films will be a great achievement towards the realization of simple, cheap and efficient field emission devices. In this paper, low threshold field emission ($E_T \sim$1.25 V/μm) of electrons in simply fabricated nanocrystalline DLC (nc-DLC) films is demonstrated. In addition, the influence of nitrogen and vacuum annealing on the properties of modified nc-DLC thin films is also studied. The field
emission characteristics of comparatively higher self-bias grown amorphous DLC (a-DLC) and nitrogen incorporated amorphous DLC (a-DLC:N) films are also studied and compared with the as grown and modified nc-DLC thin films.

2. MATERIALS AND METHODS

2.1 Samples Preparation. Radio frequency (13.56 MHz) plasma enhanced chemical vapor deposition (RF-PECVD) is used for depositing the nanocrystalline diamond-like carbon (nc-DLC) and nitrogen incorporated nanocrystalline diamond-like carbon (nc-DLC:N) thin films over cleaned n-type silicon (Si) substrates at a base pressure of $10^{-5}$ Torr. The nc-DLC film is grown at a self-bias of -100 V (sample EA-1) by maintaining a working pressure of $2.4 \times 10^{-3}$ Torr. This working pressure is obtained by first incorporating acetylene ($C_2H_2$) gas that changes the pressure from $10^{-5}$ Torr to 7.5 x $10^{-4}$ Torr and then argon (Ar) gas that changes the pressure from 7.5 x $10^{-4}$ Torr to $2.4 \times 10^{-3}$ Torr. The nc-DLC:N thin film is deposited at a self-bias of -100 V (sample EA-2) with at a working pressure of $2.4 \times 10^{-3}$ Torr, obtained by incorporating $C_2H_2$ and nitrogen (N$_2$) gases. Samples EA-3 and EA-5 are obtained when sample EA-1 is annealed in a vacuum better than $10^{-5}$ Torr at 150°C and 250°C, respectively, for 90 min. Samples EA-4 and EA-6 are obtained when sample EA-2 is annealed at 150°C and 250°C, respectively, for 90 min. Besides nc-DLC films, amorphous DLC (a-DLC) and nitrogen incorporated a-DLC (a-DLC:N) films are also fabricated at comparatively higher self-bias of -180 V at a working pressure of $2.4 \times 10^{-3}$ Torr. The a-DLC and a-DLC:N films grown at -180 V are labeled as samples EA-9 and EA-10, respectively.

2.2 Characterization of Samples. All of the films are characterized for their morphological, structural and field emission properties by field emission-scanning electron microscopy (FE-SEM) (FEI QUANTA 200 F), Raman spectroscopy (Reinshaw inVia Reflex
micron Raman spectrometer attached with air cooled argon ion laser), X-ray diffraction (XRD) (Rigaku Miniflex II), Fourier transform infrared (FTIR) spectroscopy (Perkin Elmer Spectrum BX), time of flight secondary ion mass spectroscopy (ToF-SIMS) (TOF-SIMS 5 of ION-TOF GmBH, Germany), Energy dispersive X-ray analysis (EDAX) and a Keithley software controlled I-V measurement unit (Keithley 2410), respectively. In addition, the optical and mechanical properties of the deposited films are investigated using ultra-violet spectroscopy (Shimadzu spectrophotometer) and nanoindentation (IBIS nanoindentation, M/S Fisher-Cripps laboratory, Australia), respectively. The field emission measurements are carried out at base pressure of 3 x 10^{-7} Torr. The threshold field is defined as the applied field at which an emission current of ~ 5 x 10^{-7} A is obtained. The micro-Raman measurements are performed using excitation wavelength of visible range (514.5 nm). ToF-SIMS measurements are conducted at ultrahigh vacuum condition with 5 x 10^{-10} mbar pressure, where pulsed primary ions from a 25 keV Bi liquid-metal ion gun (LMIG) are used to bombard the sample surface to create secondary ions. The sputtering is done using a 500 eV O₂ source to remove the first few layers from the sample surface. The sputtering and analysis area is 200 × 200 μm² and 70 × 70 μm², respectively for all the samples. The overall resolution for ToF-SIMS is 1 nm.

3. RESULTS AND DISCUSSION

Figures 1(a)-1(c) show the FE-SEM images of samples EA-1, EA-2 and EA-5, respectively. The microscope images reveal nanostructured morphology with a uniform distribution of nanostructured carbon throughout the surface. A highly dense tightly-packed structure is found in sample EA-1. However, when nitrogen introduction and annealing at 250°C for 90 min of sample EA-1 are performed, slight changes into the structure of samples EA-2 and EA-5, respectively. FE-SEM images of samples EA-2 and EA-5 clearly reveal the formation of
nanocrystalline but images show no significant changes in the structure. The FESEM image of the a-DLC film (sample EA-9, Fig. 1(d)), clearly confirms the amorphous morphology in that sample grown at higher self-bias.

The structural analysis of these samples is conducted using XRD with the recorded XRD patterns of samples EA-1 and EA-2 shown in Figs. 2(a) and 2(b), respectively. The XRD spectra clearly reveal a mixture of nanocrystalline and amorphous carbon due to the presence of several sharp peaks as well as a broad band in the range of 10° - 60°. The peaks which appear in the range from 40° to 60° in sample EA-1 correspond to various reflections of the sp³ diamond phase. Generally, nanodiamond films show a sharp and high intense diamond <111> peak at 43.9°. In contrast, sample EA-1 exhibits three peaks at 42.2°, 45° and 46.6°, which are close to peak 43.9°. We expect that sample may have significant strain and these peaks are appeared as a consequence of strain induced splitting of <111> peak. The peak obtained at 53.6° also correspond to a diamond reflection. The sharp peaks at 28.4°, 31.1°, 34.9°, 47.6° and 56.4° are attributed to the silicon substrate. The sharp peak generated at 38.4° may arise from SiC <102>, which comes from a contribution of Si and C both at the interface. Between 20° - 30° the peaks are attributed to various reflections of sp² bonded graphitic material. A very sharp peak appeared at 26.6° corresponds to graphite <111>. A broad band is seen centered around 22°, which shows the amorphous structure of the carbon bonding. In sample EA-2, all these peaks are slightly shifted to higher 2θ side due to nitrogen induced modification. This sample show sharp peaks at 27°, 28.7°, 31.4°, 35.2°, 38.6°, 41.4°, 42.4°, 45.4°, 46.7°, 47.7° and 53.7°. Looking at the extra peak 41.4°; the peak at 42.4° in EA-1 splits into two peaks at 41.4° and 42.4° in EA-2 attributed to nitrogen induced modification. It is to be noted that the intensity of the sp² bonded band generated in the range 20°-30° is found to be comparatively less intense and sp³ bonded diamond peaks originated in the range 40°-60° are found to be comparatively more intense in sample EA-1.
than in sample EA-2. This suggests that sample EA-2 may have more sp$^2$ phase owing to nitrogen introduction. Furthermore, an XRD spectrum of sample EA-9 is also recorded (not given here) that clearly confirms the creation of amorphous structure in this sample.

ToF-SIMS is a high resolution destructive technique by which not only the constituents of films can be investigated but also atomic diffusion at the film/substrate interface can be visualized. Figures 3(a)-3(d) show the ToF-SIMS depth profiling of samples EA-1, EA-2, EA-5 and EA-6. It can be seen that C and H are found to be main constituents of samples EA-1 and EA-5, whereas C, H and N are found to be main constituents of samples EA-2 and EA-6, which agrees with our deposition parameters. An intense peak corresponding to the Si substrate is evident in all four spectra. It is important to note that no oxygen appears in the film region, as the presence of oxygen is recorded only when depth profiling of substrate region begins. The presence of oxygen in the Si substrate is attributed to the fact that Czochralski (Cz)-Si wafer possesses oxygen as an impurity. The depth profile gives clear elemental demarcation between C, H and Si in case of samples EA-1 and EA-5 whereas C, H, N and Si in case of samples EA-2 and EA-6. This can be seen in sample EA-1 where C and H diffuse slightly into the Si substrate but that H diffuses deeper owing to its lower atomic weight. It is worth noting that the diffusion of C in sample EA-1 is found to be significantly lower than in unhydrogenated DLC and tetrahedral amorphous carbon (ta-C) films owing to presence of H. Furthermore, when sample EA-1 is annealed at 250°C for 90 min, the diffusion of C and H is enhanced. Similarly based on analysis of samples EA-2 and EA-6, it is inferred that annealing at 250°C for 90 min enhances the diffusion of C, H and N into the substrate. By taking the average intensity ratios, the approximate percentage of nitrogen in a sample EA-2 has been estimated to be about 6 at.%. This agrees well with the nitrogen content as estimated by EDAX which is about 7 at.%.
The micro-Raman spectra of nanocrystalline (samples EA-1, EA-2, EA-5 and EA-6) and amorphous (samples EA-9 and EA-10) DLC films are shown in Fig. 4(a). The visible (514.5 nm) Raman spectra of DLC films exhibit two bands, D (disorder) band near 1350 cm\(^{-1}\) and G (graphite) band near 1540 cm\(^{-1}\). Visible Raman spectra are predominantly sensitive to sp\(^2\) bonding due to the low energy separation. However, changes in G peak position and \(I_D/I_G\) ratios imply changes in carbon bonding and sp\(^2\) carbon clustering. It is well understood that an increase in G peak position from 1520 cm\(^{-1}\) to 1600 cm\(^{-1}\) and an increase in \(I_D/I_G\) ratio correspond to enhanced sp\(^2\) bonding.\(^{25}\) From figure 4(a), it is evident that the as-deposited samples EA-1 and EA-2 have not only a low D peak intensity (lower disorder) but also had G peak towards lower wavenumber. Among the two samples, sample EA-1 (nc-DLC film) has a lower disorder and G peak shifted towards lower wavenumber side than sample EA-2 (nc-DLC:N film). By contrast, annealing of the films leads to increased disorder with a shifting of the G peak towards higher wavenumber side in annealed samples EA-5 and EA-6. In order to get exact D and G peak position and their \(I_D/I_G\) ratios, the Raman spectra are fitted by considering two Gaussian components. The variations of G peak position and \(I_D/I_G\) ratio for different samples are given in Figs. 4(b), respectively. The position of G peak and \(I_D/I_G\) ratio in sample EA-1 is found to be 1547 cm\(^{-1}\) and 0.391, respectively, and 1560 cm\(^{-1}\) and 0.665, respectively, in sample EA-2. For the annealed samples, the position of the G peak and \(I_D/I_G\) ratio in sample EA-5 are found to be 1550 cm\(^{-1}\) and 0.424, respectively, whereas they are changed to 1570 cm\(^{-1}\) and 1.19, respectively, in sample EA-6. The nitrogen incorporation and annealing significantly affects the microstructure of these films by increasing the sp\(^2\) phase. Ilie et al.\(^{12}\) have also observed increased disorder and hence, enhanced \(I_D/I_G\) ratio in a-C:H, tetrahedral hydrogenated carbon (ta-C:H) and tetrahedral nitrogenated carbon (ta-C:N) thin films. Ferrari et al.\(^{25,26}\) and Rodil et al.\(^{27}\)
have also suggested that the shifting of G peak towards higher wavenumber and increased $I_D/I_G$ ratio in amorphous carbon films are accompanied by enhanced sp$^2$ bonding.

Our analysis also infers that thermal annealing had more pronounced behaviour in nitrogen included nc-DLC:N films than pure nc-DLC films. This can be confirmed by analyzing the data of the as-deposited and annealed nc-DLC:N films with respect to the as-deposited and annealed nc-DLC film. The as-deposited nc-DLC:N film (sample EA-2) has a G peak at 1560 cm$^{-1}$ but it is shifted by ~10 cm$^{-1}$ towards higher wavenumber side in 250°C annealed nc-DLC:N film (sample EA-6) and found to be at 1570 cm$^{-1}$. Similarly, the $I_D/I_G$ ratio in sample EA-2 is found to be 0.665, which is larger than the value of 0.12 in sample EA-6. By contrast, the as-deposited nc-DLC film (sample EA-1) had a G peak at 1547 cm$^{-1}$ which is shifted by only 3 cm$^{-1}$ towards higher wavenumber side in 250°C annealed nc-DLC film (sample EA-5) and found to be at 1550 cm$^{-1}$. The $I_D/I_G$ ratio in sample EA-1 is found to be 0.39, which is increased to 0.42 in sample EA-5.

Temperature induced structural transformation are more pronounced in nc-DLC:N film and give rise to the creation of more sp$^2$ bonding in annealed nc-DLC:N film (sample EA-6). The G peak position and $I_D/I_G$ ratio in comparatively higher self-bias deposited a-DLC film (sample EA-9) are found at 1551 cm$^{-1}$ and 0.453, respectively. These are increased to 1563 cm$^{-1}$ and 0.7, respectively, in a-DLC:N film (sample EA-10) due to nitrogen driven enhanced sp$^2$ bonding. The difference in the G peak position and $I_D/I_G$ ratio between -100 V and -180 V self-bias grown nc-DLC and a-DLC; nc-DLC:N and a-DLC:N films are found to be small which suggests that at a higher self-bias of -180 V an increase in sp$^2$ bonding takes place. FTIR is found to be an important tool for investigating the bonding environment of DLC and modified DLC thin films. Figures 5(a)-5(b) shows the FTIR spectra of sample EA-1 and EA-2 in the range 1200 – 2200 cm$^{-1}$ and 2700 – 3500 cm$^{-1}$, respectively. Sample EA-1, which is a pure nc-DLC film, shows
various vibrating modes such as the C-H\textsubscript{n} stretching mode in the range 2700 - 3150 cm\textsuperscript{-1}, C-H\textsubscript{n} bending mode (or olefinic mode) in the range 1300 - 1550 cm\textsuperscript{-1}. The FTIR spectra also shows an important peak corresponding to C=C vibrations in the band 1560 - 1660 cm\textsuperscript{-1} and OH bonding above 3200 cm\textsuperscript{-1}. When nitrogen is introduced in nc-DLC film, two changes are realized in the nc-DLC:N film (sample EA-2). First, the intensity of the peak in the range 1560 - 1660 cm\textsuperscript{-1} is significant increased, which is attributed to nitrogen introduction promoting the formation of C=N bonding (enhanced sp\textsuperscript{2} bonding). Second, the intensity of the C-H\textsubscript{n} stretching vibrations is reduced, which is due to the fact that nitrogen inclusion may replace some of the C atoms in C-H\textsubscript{n} stretching vibrations and generate N-H based bonding above 3150 cm\textsuperscript{-1}. The optical and nano-mechanical properties of these EA samples are examined and discussed in brief here. Sample EA-1 with an optical band gap of 1.7 eV shows highest hardness as 35.8 GPa. However, introduction of nitrogen, annealing and increase in self bias leads to reduction of hardness owing enhanced sp\textsuperscript{2} bonding. The optical property also supports the increase in sp\textsuperscript{2} bonding due to introduction of nitrogen because optical band gap in sample EA-2 reduces to 1.1 eV. Thus, optical and nano-mechanical properties infer that sample EA-1 possesses more sp\textsuperscript{3} bonding due to its higher hardness and large band gap.

The field emission current (I) versus field (E) curves of sample EA-1 recorded over various successive cycles are shown in Fig. 6(a). Moving from run 1 to run 4, the threshold field is found to reduce from \(~2.1\) V/\textmu m to 1.25 V/\textmu m. Not only this, the emission current (I\textsubscript{E}) is also found to be highest in run 4. The recorded I-E characteristics of sample EA-1 in various runs are fitted with a Fowler-Nordheim (F-N) model in Fig. 6(b), where a plot of ln (J/E\textsuperscript{2}) versus 1/E is shown. The F-N theory is related to the emission of electrons from the front surface via tunneling\textsuperscript{5, 28} through an approximately triangular barrier. The Fowler-Nordheim equation takes the form
\[ J = \frac{a(\beta E)^2}{\phi} \exp\left(\frac{-b\phi^{3/2}}{\beta E}\right), \]

where \( J \) is the current density, \( \Phi \) is the potential barrier height (taken as the work function), \( E \) is the applied (or macroscopic) electric field, \( \beta \) is the field enhancement factor and \( a \) and \( b \) are constants and have the values of \( 1.56 \times 10^{-6} \text{ A eV}^{-2} \) and \( 6.83 \times 10^7 \text{ VeV}^{-3/2} \text{ cm}^{-1} \), respectively. It can be seen that these emission curves are well fitted in their F-N plots, confirming that the electrons are emitted by the cold cathode emission process. With the help of such F-N plots the field enhancement factor (\( \beta \)) can be estimated for a given value of \( \Phi \), taken as 5 eV. The parameter \( \beta \) is associated with the generation of the local field rather than the applied field and is normally expressed in terms of ratio of local (\( E_{\text{local}} \)) to applied (\( E \)) field. If \( \beta \) is large then lower applied fields can generate the high local fields necessary for good field emission. The value of \( \beta \) is found to vary from 7620 to 8962 for sample EA-1 from run 1 to run 4 which explains the reduction in the threshold applied field.

Depending upon film structure, two types of field emission mechanisms are possible in amorphous and nanostructured carbon films. Generally low bias grown polymer-like amorphous carbon (PAC) films with fewer defects and low conductivity show back contact controlled field emission due to the formation of leaky barrier at the film/back contact interface. In contrast, comparatively higher self-bias grown DLC and nc-DLC films having high defect density and higher the conductivity exhibit front surface based emission. Various models have been suggested with regard to the explanation of field emission from DLC thin films, but a complete interpretation remains unresolved. The situation becomes difficult when \( E_T \) reaches below 5 V/\( \mu \text{m} \); Ikeda and Teii have observed a low value of \( E_T \sim 3 \text{ V/} \mu \text{m} \) in nanodiamond films and suggested a possible reason based on defect-induced conduction that becomes stronger under nitrogen inclusion. Previously Carey et al. had suggested that defect and localized states near
the Fermi level in the form of sp\textsuperscript{2} clusters in the sp\textsuperscript{3} matrix help to obtain efficient field emission with E\textsubscript{T} below 10 V/\mu m. Normally, sp\textsuperscript{2} clusters in DLC films are distributed in the sp\textsuperscript{3} matrix; in diamond and polycrystalline diamond films the conducting sp\textsuperscript{2} bonded grain boundaries surround the sp\textsuperscript{3} bonded grains. The same explanation used for diamond and polycrystalline diamond is also applicable for the present nc-DLC film (or nanodiamond film sample EA-1), where sp\textsuperscript{3} bonded nanodiamond grains are bordered with sp\textsuperscript{2} bonded grain boundaries. However, in contrast to diamond and polycrystalline diamond films, nc-DLC or nanodiamond film possesses more grain boundaries. Since diamond grains with sp\textsuperscript{3} bonding exhibit low and even negative electron affinity (NEA), the electrons see a negligible potential barrier for emission and are emitted at lower E\textsubscript{T}. Under the action of an external field, a large local field will be generated around the sp\textsuperscript{2} bonded grain boundaries due to termination of the field lines. As a result both sp\textsuperscript{2} bonding and sp\textsuperscript{3} bonding play an important role for field emission from nc-DLC films.

Optimum values of sp\textsuperscript{3} and sp\textsuperscript{2} bonding are needed for optimum field emission from nc-DLC films. It is important to mention that in contrast to unhydrogenated counterpart, hydrogenated DLC and nc-DLC film (with certain amount of hydrogen) exhibit high sp\textsuperscript{3} bonding as well as low electron affinity. Since a low value of E\textsubscript{T} is realized in sample EA-1, a possible model pertaining to explain the field emission behaviour is schematically depicted in Fig. 7. In present model, we refer sp\textsuperscript{2} bonded conducting grain boundaries as a ‘conducting pathway’ and the surrounding sp\textsuperscript{3} bonded nanodiamond grains are treated as dielectric (insulator/semiconductor) regions. These sp\textsuperscript{2} bonded conducting pathways may have a high aspect ratio forming an effective percolating network pathway in the film. Recently, Varshney et al.\textsuperscript{30} have fabricated a diamond and CNT composite structure and observed low E\textsubscript{T} and high I\textsubscript{E} characteristics during field emission measurement. They have suggested that CNTs have a high aspect ratio and during field emission heat is produced in CNTs. The sp\textsuperscript{3} diamond grains act as a
heat sink and help to maintain the efficient field emission property of overall structure. Similarly in sample EA-1, under the action of an external field the sp² bonded conducting pathways may be heated due to predominant emission of electrons through this region. Among the four runs, run 4 exhibit lowest $E_T$ and highest $I_{El}$ attributed to current induced transformation of sp³ bonding into sp² bonding.³¹

In order to explore the influence of nitrogen incorporation and annealing on the field emission characteristics of nc-DLC and modified nc-DLC films, the field emission I-E curves of different nc-DLC based devices are recorded (samples EA-1 to EA-6), as shown in Fig. 8(a). Here, it is found that among all samples, the sample EA-1 shows lowest $E_T$ at 1.25 V/µm. However, when sample EA-1 is annealed at 150°C for 90 min, the value of $E_T$ in sample EA-3 is slightly increased to 1.76 V/µm. Nevertheless, when the temperature for annealing of sample EA-1 is increased to 250°C (for 90 min), the value of $E_T$ in sample EA-5 is drastically enhanced to 9.8 V/µm, which is found to be the highest $E_T$ among all the nc-DLC samples. This infers that annealing of these nc-DLC films modifies the film structure and affects the electron emission. Based on a change of 0.51 V/µm in $E_T$ between samples EA-1 and EA-3, it is realized that annealing at low temperature (150°C) has a less pronounced effect on field emission properties of nc-DLC films. When annealing temperature is raised to 250°C, the structure of the film gets changed considerably (e.g. the generation of more sp² clustering as confirmed by Raman analysis and the enhanced diffusion of atoms as measured by ToF-SIMS) that causes the largest shift of $E_T$ of 8.6 V/µm between samples EA-1 and EA-5. When nitrogen is introduced, the value of $E_T$ in sample EA-2 is significantly increased to 8.3 V/µm. This is due to the fact that introduction of nitrogen significantly modifies the structure of resulting sample EA-2 and increases the sp² bonding, as confirmed by Raman and FTIR analyses. Furthermore, when sample EA-2 is
annealed at 150°C and 250°C for 90 min, the value of $E_T$ in samples EA-4 and EA-6 is increased to 8.4 V/μm and 9.2 V/μm, respectively.

Not only is the value of $E_T$ but also the magnitude of maximum $I_E$ varied significantly with the changing annealing temperature and the introduction of nitrogen. We believe that the annealing and nitrogen inclusion disturbs the optimum ratio of sp³ bonded dielectric regions (nano-grains) and sp² bonded conducting pathways (grains boundaries) and hence, enhanced the $E_T$ and lower $I_E$. The increased value of $E_T$ in samples EA-5 and EA-6 are also correlated with interdiffusion of C, H and N into Si as studied by ToF-SIMS. As annealing of sample EA-1 at 250°C leads to enhanced diffusion of C and H elements into Si, which results in large mismatches at the interface and hence, contribute enhancing the value of $E_T$ of sample EA-5. Similarly, annealing of sample EA-2 at 250°C enhanced the diffusion of C, H and N species into Si that further enhances the interfacial mismatch and therefore, helps increasing the $E_T$ of resultant sample EA-6. The interdiffusion of these elements may also disturb the electrical characteristics of the back contact making the back contact more resistive explaining the large values of $E_T$ obtained in annealed samples than that of as-deposited samples.

The influence of morphology and self-bias on field emission property of carbon films are also explored. The I-E characteristics of a-DLC (sample EA-9) and a-DLC:N films (sample EA-10) are recorded is shown in Fig. 8(a). The value of $E_T$ and the maximum value of $I_E$ in a-DLC film (sample EA-9) are found to be 7.6 V/μm and 2.7x10⁻⁵ A, respectively. On the other hand, a-DLC:N film exhibits a comparatively higher value of $E_T$ and lower current. In sample EA-10 initial emission begins at 9.77 V/μm which is higher than the value of $E_T$ of sample EA-9 due to nitrogen induced structural changes as confirmed by micro-Raman analysis. When compared the values of $E_T$ of sample EA-9 with EA-1, the value of $E_T$ is found to be significantly larger in EA-9, which is due to fact that EA-1 possess nanostructure (some geometrical structure that helps
enhancing local field) whereas EA-9 shows an amorphous structure (no geometrical enhancement). Similarly, the value of $E_T$ of EA-10 is found to be larger than that of EA-2 due to the amorphous structure and higher self-bias growth of former sample.

Examining the current research on carbon based materials for field emission applications; Talapatra et al. have demonstrated the lowest $E_T$ as 3.22 V/μm in his MWCNT sample. On the other hand, Varshney et al. have obtained a low value of $E_T$ as 2.4 V/μm in a complex graphene-diamond hybrid film. They have also reduced $E_T$ to 1.1 V/μm (at a current ~ $10^{-8}$ A) in complex and expensive nanotube/diamond composite but the value of $E_T$ in this sample is found to be 4 V/μm at current ~ $10^{-5}$ A. They have also observed $E_T$ of 5 - 6 V/μm in complex rod-shaped DLC nanostructures. Shimada et al. have also observed low $E_T$ as ~ 3 V/μm in their complex and unconventional carbon nanowalls structure. Moreover Ikeda and Tei have realized $E_T$ as 3 V/μm in nanocrystalline diamond. In our case of nc-DLC film (sample EA-1) the value of $E_T$ of 1.25 V/μm must be seem to be very encouraging. All the I-E characteristics of the samples are fitted to F-N plots. Since, F-N plots of samples EA-2, EA-4, EA-5, EA-6, EA-9 and EA-10 overlap each other, hence we have sketched F-N plots of samples EA-1 and EA-3 seperately, which as shown in Fig. 8(b) and F-N plots of samples EA-2, EA-4, EA-5, EA-6, EA-9 and EA-10 are given in Fig. 8(c). Here all emission curves properly fitted for F-N plots confirming electrons are emitted from the front surface. It is to be noted that sample EA-10 possesses two slopes; one in low field and other in comparatively higher field; as represented by S1 and S2, respectively which usually signifies the presence of current saturation at the higher field values.
4. CONCLUSIONS

In conclusion, we have demonstrated low threshold field emission in a simple and inexpensive nanocrystalline DLC thin film. We have explained the data in terms of model based upon conducting pathways of $sp^2$ bonded carbon surrounded by dielectric regions of $sp^3$ bonded carbon. We believe that this lowest threshold field could be obtained from an optimum amount of $sp^3$ and $sp^2$ bonding. The addition of nitrogen and thermal annealing both results in increased value of threshold field, which was attributed to the introduction of increased disorder and enhanced interdiffusion of C and H species into the substrate Si. The effects of self-bias and surface morphology have also been examined. Compared with -100 V deposited nanocrystalline counterpart, the threshold field is found to be higher in higher self-bias deposited amorphous DLC and nitrogenated amorphous DLC thin films. Owing to excellent field emission characteristic with low threshold field, nc-DLC films have great potential for large area electronic devices.

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(24) Standard data, JCPDS Card numbers 791473, 791471, 791470, 731664, 752078 and 791715.
FIGURE CAPTIONS

**Figure 1:** Scanning electron microscope images of (a) sample EA-1, (b) sample EA-2, (c) sample EA-5 and (d) sample EA-9.

**Figure 2:** X-ray diffraction spectra of (a) sample EA-1 and (b) sample EA-2.

**Figure 3:** ToF-SIMS profiles of (a) sample EA-1, (b) sample EA-5, (c) sample EA-2 and (d) sample EA-6.

**Figure 4:** (a) Micro-Raman spectra of EA samples and (b) variation of G peak and $I_D/I_G$ ratio for different samples.

**Figure 5:** FTIR spectra of samples EA-1 and EA-2 in the ranges (a) 1200 – 2200 cm$^{-1}$ and (b) 2700 - 3500 cm$^{-1}$.

**Figure 6:** (a) Field emission I-E curves of sample EA-1 taken at different runs and (b) Fowler-Nordheim plots of sample EA-1 for different runs.

**Figure 7:** Proposed model where diamond grains are considered as dielectric regions and graphite grain boundaries are considered as conducting pathways.

**Figure 8:** (a) Field emission I-E curves of different EA samples and (b) F-N plots of EA samples and (c) F-N plots of samples EA-2, EA-4, EA-5, EA-6, EA-9 and EA-10.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Array of sp³ bonded diamond grains

Figure 7
Figure 8