Field emission enhancement and microstructural changes of carbon films by single pulse laser irradiation

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ABSTRACT
The effect of single nanosecond laser pulse irradiation on the microstructure and field emission (FE) properties of carbon films is studied. Amorphous carbon films were exposed to a single pulse of a 248 nm Excimer laser with pulse width of 23 ns. Microstructural changes of the films were investigated by Raman spectroscopy, transmission electron microscopy and electron energy loss spectroscopy. FE study was conducted in a parallel plate configuration. It was found that the landscape of the FE properties is not directly correlated to the laser energy in a simple way, whereas low energy laser irradiation (<117 mJ/cm²) leads to a lower emission threshold field due to the formation of sub-nanometer conductive sp2 clusters within the insulating sp3 matrix. A medium energy range (117–362.5 mJ/cm²) would actually reduce field enhancement and increase the threshold field because of the increased size of the same sp2 clusters. Interestingly, a much higher laser energy (>362.5 mJ/cm²) would reverse this effect by forming multiple continuous conductive sp2 channels and thereby reduce the threshold field sharply again.

1. Introduction
Electron field emission (FE) from amorphous carbon (a-C) films [1,2] is widely investigated in the past few years due to its outstanding emission properties such as low macroscopic emission field [3,4]. Much effort has been concentrated to reduce the threshold field (Fth) at which the electron emission occurs [5]. In addition, the mechanisms responsible for easy emission of a-C films as well as all other carboneous materials are of great interest [6–8].

a-C film is formed from carbon atoms with mainly sp2 and sp3 bonding. Electronic properties of a-C films strongly depend on the sp2 content of the film as well as the presence, size and distribution of sp2 bonded clusters within the sp3 matrix [1]. For instance, electrical conductivity of a-C films is governed through the hopping of electrons between the conductive sp2 clusters and hence depends on the microstructure and orientation of sp2 bonded atoms [9]. These unique sp2 clusters will also provide a local field enhancement mechanism which results in electron emission at very low macroscopic fields.

It is believed that the sp2 bonded atoms are the emission sites in a-C films [7] as it is also the case in chemical vapor deposition (CVD) grown nanocrystalline diamond films where the emission is found to be from sp2 bonded atoms at the grain boundaries [10]. It was found that the change in sp3 content does not affect the work function of the film which remains in the range of 4–5 eV [11].
Carey et al. [9] proposed a mechanism for large field enhancement in carbon film which is responsible for emission at low macroscopic fields. The presence of a conductive sphere embedded in an insulating matrix leads to small field enhancement. However, the presence of two or more such spheres can further increase the enhancement; for instance, the field enhancement of two conductive spheres in the bispherical coordination system was studied and it was found that the presence of two gold spheres which are placed five nanometers apart from each other results in enhancements of 56 which can be increased to 400 for a 1 nm separation [12]. Carey et al. show that in the case of a-C films, the presence of conductive sp$^2$ clusters within the sp$^3$ matrix plays a very important role in local field enhancement near the sp$^2$ sites which leads to FE at low macroscopic fields. This phenomenon is schematically shown in Fig. 1.

Based on this model, different methods such as thermal annealing [6], nitrogen doping [4] and incorporation of metallic nanoparticles in the microstructure of the film [13] have been used to improve FE properties of carbon films.

Besides the above methods, laser irradiation has been widely used to modify the structure and hence electrical properties of carbon films. For example Miyajima et al. [14] found that UV laser irradiation increases the conductivity of carbon films through formation of sp$^2$ bonded nanocrystals. Besides a-C, laser irradiation has been widely used to control the microstructure and field emission properties of CNTs as well. Li et al. [15] found that laser irradiation of CNTs results in decrease in threshold field and significant increase in the emission current density. It is believed that photon bombardment induced degeneration of graphite structure is the key mechanism in emission enhancement in laser treated CNTs.

Laser irradiation has also been used to modify the microstructure and hence the emission properties of amorphous silicon (a-Si) film [16]. It was shown that beside morphological changes laser irradiation leads to formation of columnar nanocrystals which are thought to be the enhancement factor for easy emission of a-Si films.

In this work, single pulse laser irradiation is used to control the microstructure of sp$^2$ bonded atoms in the structure of the film and hence to increase the field enhancement factor which in turn reduces the emission Fth. Low energy laser irradiation can be used to control the size of the sp$^3$ nanoclusters which results in local field enhancement. Moreover, single pulse high laser energy leads to formation of conductive sp$^2$ channels throughout the film thickness which works as another field enhancement mechanism and reduces the Fth significantly.

2. Experimental details

A “Double bend filtered cathodic vacuum arc” (FCVA) which is discussed elsewhere [17], was used to deposit a-C films while antimony doped (100) silicon wafers with resistivity of 0.01 Ω cm was used as the substrate. The cathode used was a 99.999% pure graphite rod. The deposition base pressure was kept lower than 2 × 10$^{-6}$ Torr. Negative DC substrate bias of 300 V was applied to the substrate during the deposition to control the initial microstructure of the film. To eliminate possible effect of film thickness on FE properties, all the samples which were used in this study were deposited in one deposition and then were cut into smaller square pieces of 3 mm in length. The thickness of the films was measured to be 150 nm using a surface profiler.

248 nm KrF Excimer-laser with pulse width of 23 ns was used to irradiate the samples in ambient conditions. The laser spot was a square of 3 mm in length. In order to achieve large area processing laser can be scanned throughout the sample surface. The spatial energy distribution of the laser pulse was studied and it was shown that the laser has a uniform near-flat-top energy profile [18]. The samples were irradiated by just one single pulse.

The Raman spectra were recorded by a Renishaw Raman spectrometer (50 mW 514.5 nm Ar$^+$ laser) to study the bonding structure of the as deposited and laser irradiated samples. The spectra were fitted using a Breit–Wigner–Fano (BWF) line shape to the G band and a Lorentzian curve for the D band.

JEM 2010 transmission electron microscopy (TEM) operated at an accelerating voltage of 200 kV was used to investigate the microstructure of the samples before and after the laser irradiation. Electron energy loss spectroscopy (EELS) was done on 30 × 30 nm areas using an FEI Titan, operated at 80 kV in scanning-TEM mode. TEM specimens were prepared by mechanical polishing followed by dimpling and Ar$^+$ ion milling.

FE was tested in a parallel plate configuration with an indium tin oxide (ITO) coated glass as the cathode with anode–cathode spacing of 100 μm in a pressure lower than 5 × 10$^{-6}$ Torr. In order to check the repeatability of the data, two samples were annealed at each laser energy. FE tests have been done on two different positions of every individual sample. More than ten measurements have been done on each test spot.

Fig. 1 – Schematic representation of FE from carbon film. The film is formed from sp$^2$ nanoclusters (yellow spheres) embedded in insulating sp$^3$ bonded matrix. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)
3. Results and discussion

Fig. 2 shows the Raman spectra of the as deposited and laser irradiated carbon films. The as deposited spectrum can be fitted by a single BWF curve located at 1537 cm\(^{-1}\). The fact that the spectrum can be fitted by only a single G peak reveals that the film is purely amorphous in structure with no short range order in the microstructure [19]. This is further proved by Figs. 3 and 4 which show the high resolution transmission electron microscopy (HRTEM) image and the high-loss and low-loss EEL spectra of the film respectively.

The low-loss EEL spectrum shows a bulk Plasmon peak at 28.1 eV. The mass density can be derived from the valance electron density \(n_e\) by assuming that the film is hydrogen and nitrogen free and also each carbon atom contributes four valance electrons:

\[
\rho = \frac{3\epsilon_0\mu_0 m_e E_0^2}{12\hbar^2 N_a e^2}
\]

The mass density will then be estimated at 2.49 g/cm\(^3\). It should be noted that no \(\pi\) Plasmon peak (4.5–5.5 eV) can be observed in the low-loss spectrum which confirms that there is no ordering of \(\pi\) bonds in the microstructure [20]. The high-loss spectrum on the other hand, shows a sharp \(\pi-\pi^*\) transition at 285 and a broad \(\sigma-\sigma^*\) transition at 285–315 eV intervals. The sp\(^2\) content of the film can then be determined using [21]:

\[
\text{Sp}^2 = \frac{\frac{\text{area}(\pi^*)}{\text{area}(\pi+\sigma^*)} \text{sample}}{\frac{\text{area}(\pi^*)}{\text{area}(\pi+\sigma^*)} \text{100% sp}^2 \text{ reference}}
\]

281–289 and 281–311 eV was used as the \(\pi^*\) and \(\pi^* + \sigma^*\) transition windows respectively. Glassy carbon which is 100% sp\(^2\) bonded amorphous carbon was used as the reference sample. The sp\(^2\) content of the film was then calculated to be 56%, which is in agreement with the Raman results.

Fig. 5 shows the FE spectra of the as deposited and laser irradiated carbon films. The field at which the respective current density is 20 \(\mu\text{A/cm}^2\) is taken to be the \(F_{\text{th}}\) in this study. As it is also shown in Fig. 5B, the \(F_{\text{th}}\) for the as deposited film is 11 V/\(\mu\text{m}\). Fig. 5B shows the variation of \(F_{\text{th}}\) as a function of laser energy. Three distinct regions can be observed in this figure. At the first region where the film is irradiated by low laser energy, (up to 117 mJ/cm\(^2\)) the \(F_{\text{th}}\) decreases from 11 to 6 V/\(\mu\text{m}\). In the second region, (117–362.5 mJ/cm\(^2\)) \(F_{\text{th}}\) increases from 6 to 9.4 mJ/cm\(^2\). Irradiating the film by a single pulse of 472.5 and 510 mJ/cm\(^2\) however, leads to a very sharp decrease in the \(F_{\text{th}}\). The \(F_{\text{th}}\) in this region is decreased to 4.4 V/\(\mu\text{m}\).

The Raman spectra (Fig. 2) show that, the decrease in \(F_{\text{th}}\) in the first region is due to the formation and growth of sp\(^2\) clusters in the amorphous sp\(^3\) matrix. The curve cannot be fitted by a single G peak and a second D peak is needed to fit the original spectrum. The \(I_D/I_G\) increase indicates that the sp\(^2\) cluster size is increasing. The sp\(^2\) cluster size in this region can be determined by [19]:

\[
I_D/I_G = C_{sp^2} k_a^2
\]

Where \(C_{sp^2} = 0.0055\) and \(L_a\) is the sp\(^2\) cluster size. Our curve fitting shows that the sp\(^2\) cluster size in this region increases to about 4 Å. As the laser energy increases, the cluster size will also increase.
In the second region, the cluster size increases from about 4 to 14 Å. Fig. 6 shows the HRTEM image and the diffraction pattern (inlet) of the carbon film irradiated at 362.5 mJ/cm². As it can be seen, very small sp² clusters in the range of 1 nm (shown by the ellipses) can be observed in the image which is in agreement with the Raman spectrum. On the other hand, the diffraction pattern shows a unique feature. Beside the presence of diffused ring which is due to the presence of amorphous matrix phase, two dim arcs (shown by the arrows) can also be observed. The arcs are indexed to be due to the diffraction of (002) graphitic basal planes as it is also observed in the HRTEM image. However the more important point is that the (002) ring is not continuous and just two distinct arcs are observed indicating the presence of a preferred orientation in the sp² clusters. Fig. 7A shows the low-loss EEL spectrum of the carbon film irradiated at 362.5 mJ/cm². Beside the bulk Plasmon peak located at 25.1, a shoulder at 5 eV can also be observed which is related to π Plasmon excitation [20].

The presence of this shoulder shows the nucleation of short range order in the sp² bonded atoms which is in agreement with TEM and Raman results.

The larger cluster size increases the ability to carry emission current but on the other hand decreases the field enhancement. Hence, the critical diameter of the cluster for easy FE is a tradeoff between these two parameters. Therefore, in the second region although the film conductivity...
increases, the \( F_{th} \) will also increase which is due to the lower structural field enhancement. It should be noted that the \( F_{th} \) experiment has been repeated for two times as it is mentioned in the experimental part. Although the exact \( F_{th} \) value was different but the same trend in the variation of \( F_{th} \) as a function of laser energy was observed.

The samples irradiated using 462.5 and 510 mJ/cm\(^2\) on the other hand show a significant decrease in \( F_{th} \). As it is shown in Fig. 2, according to Raman spectra the in-plane \( sp^2 \) cluster size increases to about 15 Å but the \( F_{th} \) has sharply decreased from 9 to 5.1 V/\( \mu \)m which suggest that there should be another mechanism activated by high energy laser irradiation. Fig. 8 shows the Fowler–Nordheim plot of the emitted current using simplified F–N equation [22]:

\[
J = aV^2 \exp \left( -\frac{b \times V^{3/2}}{\beta E} \right)
\]

Where \( \Theta \) is the barrier height, \( E \) is the field, \( \beta \) is the dimensionless field enhancement factor and \( b \) is a constant (\( b = 6.8 \times 10^9 \) eV\(^{-3/2}\) Vm\(^{-1}\)). All F–N plots show a linear relation which confirms that the emission obeys F–N equation. Moreover, the slope of the F–N curve (which is proportional to \( \Theta^{3/2} \beta \)) decreased from 91.2 for the sample irradiated at 44.5 mJ/cm\(^2\) to 70.9 for the samples irradiated at 160 mJ/cm\(^2\) which as discussed above shows an increase in field enhancement factor (\( \beta \)) due to formation of sub-nano \( sp^2 \) clusters in the first region (assuming that \( sp^2 \) bonded phase is the emission site and hence the work function is the same for all the samples). The slope has increased to 99.7 for the sample irradiated at 362.5 mJ/cm\(^2\) which shows a decrease in \( \beta \) due to further increase in the cluster size. However, the slope of the F–N plot for the sample irradiated at 462.5 mJ/cm\(^2\) has decreased to 39.7 which shows a significant increase in the field enhancement factor which will be discussed in detail here.

Fig. 9 shows the HRTEM image of the carbon film irradiated by 462.5 mJ/cm\(^2\) Excimer laser. As it is shown in the diffraction pattern, the arcs related to (002) reflections are enhanced as compared to the 362.5 mJ/cm\(^2\) irradiated which shows that the crystallinity has increased in this film. More importantly the radial distribution of the arcs is smaller compare to the 362.5 mJ/cm\(^2\) irradiated diffraction pattern, which shows that the degree of preferred orientation is enhanced by higher energy irradiation. As it is shown in the higher magnification image, the preferred orientation in this case is distributed uniformly throughout the whole thickness of the film. The formation and propagation of preferred orientation in the film leads to formation of \( sp^2 \) bonded filaments throughout the film as one of them is shown by the broken line in Fig. 9B.

The formation and propagation of preferred orientation in the microstructure of the film is due to the high internal stress and anisotropic nature of graphite crystal structure. High intrinsic stress leads to formation of high strain energy in the system. \( sp^2 \) clusters with preferred orientation will form to relieve the strain energy and hence reduce the total energy of the system. Graphite has anisotropic hexagonal structure. The spacing between carbon atoms in the (002) basal planes is 1.421 Å while the interplanar spacing is 3.354 Å. Application of any internal or external deviatoric stress field to the structure, results in reorientation of the structure in such a way that the basal planes lie perpendicular to the direction of the highest stress component [23].
In the case of a-C film, the intrinsic biaxial stress is in the growth plane (perpendicular to the substrate) [23]. Therefore, if sufficient energy is transferred to the system, the (002) planes will reorient in the direction perpendicular to the surface. This formation of preferred orientation was observed before in conventional thermal annealed carbon films [24] and here, it was observed in laser treatments of a-C films as well.

Fig. 7B shows the low-loss EEL spectra of the film irradiated at 462.5 mJ/cm². As it is shown, the $\pi$ Plasmon peak at 5 eV is obviously enhanced which is an evidence of formation of $\pi$ bonds in the microstructure of the film.

Formation of preferred orientation in the microstructure of the film, leads to formation of conductive sp² channels in the entire cross section of the film. In this case, two different field enhancement mechanisms will be activated. As it is schematically shown in Fig. 10, preferred orientation in this case leads to formation of emitting sp² filaments perpendicular to the substrate and hence in the emitting direction. Therefore, beside the presence of a conductive phase embedded in an insulating matrix which enhances the field, the formation of sp² filaments with large aspect ratio activates a new field enhancement mechanism. Field enhancement due to a filament of length $h$ and diameter $r$ can be approximated as $h/r$ [25]. Assuming $h$ to be the thickness of the film and $r$ the average diameter of the channels which can be estimated from the Raman spectrum, another field enhancement factor with an enhancement factor of 100 is activated which results in sharp decrease in the $F_{th}$ as it is shown in Fig. 5. Field emission enhancement in this case, depends on the average diameter of the channels and also the length of the channels which can be assumed as the thickness of the film. Further increase in laser energy leads to further promotion of preferred orientation and hence the average diameter of the channels. Therefore, field enhancement is reduced from its optimum amounts as it is the case in the sample irradiated at 510 mJ/cm² which then leads to a slight increase in $F_{th}$.

Besides the threshold field, emission site density is another crucial factor which needs to be studied in detail should these films be used for applications such as flat panel displays.

4. Conclusions

Single pulse laser irradiation can be used to increase the field enhancement factor in carbon films through two distinct mechanisms. Low energy laser irradiation results in formation of very small sp² nanoclusters embedded in an insulating matrix. Such a structure leads to the formation of a large local field enhancement near the sp² clusters which are the emitting sites and hence a reduction of the electron emission $F_{th}$. Large clusters on the other hand increase the threshold field by lowering the field enhancement factor. High energy laser irradiation and intrinsic biaxial stress of the film leads to formation of a preferred orientation in the microstructure of the film in such a way that (002) graphitic planes are reoriented in a direction perpendicular to the substrate. Such a texture forms conductive channels in the amorphous matrix which increases the local field enhancement and hence reduces the $F_{th}$ significantly.
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