Electron field emission properties of tetrahedral amorphous carbon films

L. K. Cheah, a) X. Shi, E. Liu, and B. K. Tay

Ion Beam Processing Lab, School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

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The electron field emission of tetrahedral amorphous carbon (ta-C) films deposited by filtered cathodic vacuum arc is reported. The ta-C films were found to have a threshold field ranging from 18 to 28 V μm⁻¹, depending on the sp³ content. The nitrogenated ta-C (ta-C:N) films show a lower threshold field of 12 V μm⁻¹ as compared to the ta-C films. The threshold field appears to be dependent on the film thickness. There is a minimum threshold field with the film thickness of around 30 nm for the ta-C:N film. Although the ta-C and ta-C:N films have relatively low threshold fields, the density of emission sites is not high for these films. The density of emission sites can be increased when the film surface is treated with H⁺, O⁻, or Ar⁺ ions after deposition. Moreover, the posttreated films show even lower threshold fields compared to the untreated films. The improvement in the emission after the ion beam treatment appears to be independent of the ions used. The surface before and after ion bombardment was analyzed using atomic force microscopy and scanning tunneling microscopy. This analysis shows the evident surface modification and more segregated cluster regions induced by the ion beam treatment. The posttreated films are analyzed using ultraviolet photospectroscopy. The photoelectrons start to emit at energies as low as about 0.6 eV. A mechanism for the electron field emission is proposed. © 1999 American Institute of Physics.

I. INTRODUCTION

Currently, there is an increasing interest in electron field emission as a potential flat panel display technology. A way to realize it is to use a geometry called Spindt tips. However, the fabrication of submicron lithographic features on a large panel is not easy. Since tip-to-tip uniformity is a problem, and the variation of emission current from the phosphor is expected. Materials having a low or negative electron affinity as flat electron field emitters may be able to overcome the instability of emission current. Diamond has been investigated for this purpose. Although diamond demonstrates the ability to emit electron easily, the emission current is not high due to less free carriers in diamond caused by its high energy band gap. The primary source of free carriers was believed to come from the graphitic phases. Diamond-like carbon (DLC) is another attractive candidate for field emission display (FED) application. DLC can be produced by a variety of techniques. It was reported that the DLC films prepared by filtered cathodic vacuum arc (FCVA) technique may have an sp³ content up to 88% and these materials were therefore termed as tetrahedral amorphous carbon (ta-C). The sp³ content can be controlled by the carbon ion energy and deposition rate during the deposition. The ta-C is interesting in the FED applications because it can be deposited on various types of substrates, such as metal, silicon, plastic, and glass, over a large area with excellent uniformity at room temperatures. The ta-C films exhibit a band gap of about 2.7 eV, a resistivity of about 10⁶ Ωcm, and a Fermi level of about 0.35 eV below the midgap. These electronic properties were reported to be adjustable by incorporation of nitrogen into the films during deposition. More efficient doping can be achieved by nitrogen ion bombardment during the growth of ta-C films (ion beam assisted FCVA).

The objective of this article is to investigate the effect of carbon ion energy, nitrogen concentration, and surface post-treatment on the field emission properties, i.e., emission current density as a function of applied electric field and emission site density projected from indium tin oxide coated glass. Atomic force microscopy (AFM), scanning tunneling microscopy (STM), current imaging tunneling microscopy (CITS), and ultraviolet photospectroscopy (UPS) techniques are employed to obtain detailed insight into the surface conditions before and after ion treatment. A possible electron field emission mechanism is proposed to explain the experimental results.

II. EXPERIMENTAL DETAILS

The FCVA technique has been discussed in detail elsewhere. Five series of films were deposited on ⟨100⟩ p⁺-type silicon wafers with a resistivity of about 0.001 Ωcm. Before deposition, all substrates were cleaned by Ar ion bombardment (400 eV, 5 mA cm⁻², 2 min) to remove the oxide layer. The first series is the ta-C films prepared under different C ion energy. The substrates in the deposition chamber were negatively biased from 0 to 480 V, which corresponds to an impinging C ion energy about 20–500 eV. The second series is the nitrogenated ta-C (ta-C:N) films deposited by a 100 eV C ion beam together with a N ion beam of 100 eV and 3 mA cm⁻². The N ions were produced by a rf ion beam source (Ion Tech, Inc.) and the N₂ flow rate was in...
The undoped ta-C films exhibit a band gap up to \( \sim 2.7 \text{ eV} \), and a Fermi level about 0.35 eV below the mid-gap derived from the thermal activation energy. In this case, the film exhibits defect-controlled \( p \)-type semiconducting properties. When \( \text{N}^+ \) is incorporated into the film, the Fermi level moves up with the doping level. For the \( \text{N}_2 \) flow rate of 1 sccm, the Fermi level is at the center of the band gap; thus the film properties become intrinsic. When the \( \text{N}_2 \) flow rate is 10 sccm, the Fermi level is 0.07 eV below the conduction band edge while the band gap reduces to 1.1 eV due to the C–N alloying effect as seen in \( a-C:H:N \). In this case, the ta-C films become heavily doped \( n \) type; thus the term \( n^+ \)-ta-C is used to denote this type of film. Details of the doping experiment will be published elsewhere.

A scanning probe microscope (Dimension 3000, Digital Instruments) was used to conduct the AFM, STM, and CITS measurements. In the CITS method, the scanning tunneling spectroscopic (STS) current–voltage (\( I-V \)) curves acquired at every pixel within the image were used to reveal the spatial localization of spectral features. The ta-C:N films before and after ion treatment were scanned by a Pt-Ir tip. UPS was measured by a VG ESCALAB system fitted with a He light source.

III. RESULTS AND DISCUSSION

The field emission measurement on the ta-C films deposited under different C ion energy shows that the threshold electric field depends on the \( sp^3 \) content in the films. The \( sp^3 \) content of the ta-C films was determined by electron energy loss spectroscopy (EELS). The threshold electric field and the \( sp^3 \) content of the ta-C films are plotted against the C ion energy, as shown in Fig. 1. The emission current density of \( 10^{-8} \text{ A mm}^{-2} \) is used as a reference from which the threshold electric field is determined. It is observed that the threshold field first decreases from 22 to 18 V \( \mu \text{m}^{-1} \) as the C ion energy increases from 20 to 100 eV and then increases to 28 V \( \mu \text{m}^{-1} \) as the C ion energy further increases to 500 eV. The minimum threshold field is observed from the film with the highest \( sp^3 \) content. The overall trend is similar to the results obtained by Satyanarayana et al. These films were also characterized in terms of density of emission sites observed from the ITO coated glass. The distance between the ITO glass anode and the ta-C field emission cathode is about 100 \( \mu \text{m} \). An electric field about 20 V \( \mu \text{m}^{-1} \) was applied across the field emission gap cell. A charge coupled device (CCD) camera was used to capture the emission sites projected from the ITO glass. Figures 2(a) and 2(b) show typical images for the emission sites projected from ITO glass for the ta-C films with different \( sp^3 \) content. Figure 2 indicates that the density of emission sites is slightly lower for the ta-C films with a higher \( sp^3 \) content.

The nitrogen content in the ta-C:N films was measured by the Rutherford backscattering technique. The variation of the nitrogen content as a function of \( \text{N}_2 \) flow rate is shown in Fig. 3. The nitrogen content in the ta-C:N films increases from 5 to 34 at % as the \( \text{N}_2 \) flow rate increases 0.5 to 10 sccm. The threshold field is plotted as a function of \( \text{N}_2 \) flow rate as shown in Fig. 3. It is observed that the ta-C film has a threshold field of 17.5 V \( \mu \text{m}^{-1} \) as compared to 19 V \( \mu \text{m}^{-1} \) for the ta-C:N films deposited under the 0.5 sccm \( \text{N}_2 \) flow rate. The threshold field decreases to 11.5 V \( \mu \text{m}^{-1} \) as the \( \text{N}_2 \) flow rate further increases to 10 sccm. A higher density of emission sites for the \( n^+ \)-ta-C films was observed compared to the as-deposited ta-C film [Fig. 2(c)].

The threshold field for the ta-C:N (34 at % N) films is plotted as a function of film thickness in Fig. 4. The minimum turning point of the threshold field at the film thickness of around 30 nm shows an optimal window for the electron field emission.

The emission current density versus applied field \( (I-V) \) of the ta-C and \( n^+ \)-ta-C films before and after H, O, and Ar ion beam treatment has been measured. The results are shown in Fig. 5. For the ta-C films, the posttreated ta-C films have a lower threshold field of about 14 V \( \mu \text{m}^{-1} \) compared to about 18 V \( \mu \text{m}^{-1} \) for the as-grown ta-C films. For the \( n^+ \)-ta-C films, the ion beam treated samples have a threshold electric field of 8 V \( \mu \text{m}^{-1} \) vs 12 V \( \mu \text{m}^{-1} \) for the as-grown \( n^+ \)-ta-C films. The saturation emission current density of the posttreated films is also improved by about an order of magnitude in both cases. As shown in Figs. 2(d), 2(e) and 2(f), a higher emission sites density is observed from the posttreated films. It is observed that the improvement on the site density appears to be independent of the type of ions used. This observation is also confirmed by the \( I-V \) curves mea-
FIG. 2. Emission sites density observed from ITO glass from (a) untreated ta-C film with a high $sp^3$ content (100 eV C$^+$), (b) untreated ta-C film with a low $sp^3$ content (500 eV C$^+$), (c) untreated $n^1$-ta-C film, (d) 100 eV H$^+$ posttreated ta-C film, (e) 100 eV O$^+$ posttreated ta-C film, (f) 100 eV Ar$^+$ posttreated ta-C film, and (g) 800 eV H$^+$ posttreated ta-C film.

FIG. 3. Variation of threshold field and N content in the ta-C:N films as a function of N flow rate.

FIG. 4. Threshold field for $n^1$-ta-C films as a function of film thickness.

FIG. 5. Current density vs applied electric field of emission from as-deposited ta-C and $n^1$-ta-C films before and after ion surface treatment.

FIG. 6. Threshold field as a function of H ion energy.
For the ta-C films treated by the H ions with ion energy ranging from 50 to 800 eV, the threshold field as a function of H ion energy is shown in Fig. 6. The threshold field increases from 14 to 22 V μm⁻¹ as the H ion energy increases from 50 to 800 eV. The emission sites densities for the ta-C films treated with the different H ion energy are quite similar, as shown in Figs. 2(d) and 2(g).

In order to understand the change of surface structure after the ion bombardment, the AFM, STM, and CITS measurements were performed on these films. The surface images (500×500 nm) measured using the AFM from the n⁺-ta-C films before and after the ion treatment are shown in Figs. 7(a) and 7(b), respectively. The sample surface roughness root mean square (rms) has increased from 0.193 nm before the ion beam treatment to 0.242 nm, with more visible nanoscale clusters after the ion treatment. The increased surface roughness caused by the ion bombardment will change the threshold field since the field amplification factor is enhanced. This observation agrees with the reduction of threshold field from the ta-C films after ion treatment (Fig. 5). The STM pictures with a scan area of 100 nm×100 nm [Figs. 8(a) and 8(b)] and 20×20 nm² [Figs. 8(c) and 8(d)] are further used to examine these nanoclusters. It can be seen from these pictures that the surfaces of the films after the ion treatment have segregated into two regions, i.e., the cluster regions and their boundaries [Figs. 8(b) and 8(d)] compared to the as-grown surfaces [Figs. 8(a) and 8(c)]. To further examine the spectral features of these nanoclusters, the CITS method was employed. Generally, a higher threshold field was observed from the untreated sample compared to the posttreated sample, as shown in Figs. 9(a) and 9(b). Figure 9(b) shows that the lower threshold electric field is normally observed from the cluster regions, for example, the I–V curves labeled from A–D in the cluster regions show a lower threshold field for electrons to emit as compared to the I–V curves labeled E–G measured from the boundaries.

UPS was used to analyze both the as-grown and the posttreated n⁺-ta-C surfaces as shown in Fig. 10. A significant number of electrons were ejected from the untreated n⁺-ta-C sample under ultraviolet irradiation at about 4 eV. The band at about 4 eV can be attributed to p-π states and the top of p-π is at about 2–3 eV. This also indicates that the work function of the untreated n⁺-ta-C sample is about 4 eV. This UPS spectrum is in good agreement with the results from Bhattacharyya et al.,¹⁹ where no significant electrons were ejected when the binding energy was less than 2 eV. However, the Ar⁺ treated n⁺-ta-C sample shows a significant number of electrons ejected at below 1 eV, which might not be contributed by the p-π states. Thus we attributed these bands to a phase more closely related to a 100% sp³ structure. A work function as low as 0.6 eV was observed from the ion bombarded sample and this observation is in good agreement with the reduction of threshold field from the ta-C films as shown in Fig. 5.

The experimental observation shows that the lower threshold electric field corresponds to a higher sp³ content, although the emission sites density in the ta-C films with high sp³ content is not high. This observation is in agreement with the emission current from diamond in which the number of free carriers is small.¹ The main source of the free carriers is believed to be the graphitic phases. The lower threshold field is observed from the n⁺-ta-C films (onset field of about 12 V μm⁻¹) compared to the ta-C films. Lowering the threshold field by nitrogen incorporation into the ta-C films was noticed by other workers.⁵,⁶,¹⁹ This phenomenon may be explained using a space charge interlayer model, which is based on the band structure diagram.⁶,⁷ It was found that the band bending is small in the ta-C heterojunction structures compared to the ta-C:N heterojunction structures. The consequence is that the probability for tunneling electrons to enter the conduction band of the ta-C:N junction structures compared to the ta-C:N heterojunction structures.
film increases. As shown in Fig. 4, the threshold field of the ta-C:N films depends on the film thickness. The \( n^+ \)-ta-C has a depletion width of about 30 nm as calculated by Cheah et al.,\textsuperscript{20} which is the optimal thickness for electron emission. Due to the amorphous nature of the ta-C films, there are a large number of scattered electrons drifting within the materials under a high electric field. As the film thickness is less than the full depletion width, the barrier height is still above the Fermi level of the \( p \)-Si substrate and the electrons are not able to gain enough energy to surmount the barrier to the vacuum. As the thickness is greater than the full depletion width, the energy of electrons may significantly be decayed by the electron scattering processes. This will reduce the probability of electron emission from the film surface. Hence, the threshold field increases. A more detailed modeling will be published elsewhere.\textsuperscript{21}

According to the AFM, STM, CITS, and UPS results, the nanofeatured texture observed on the film surface may not only give rise to enhancement in the electron field emission as shown by Silva et al.,\textsuperscript{22} but also explain the increase of density of emission sites and decrease of threshold electric field. Therefore, we believe that these nanoclusters are \( sp^3 \) rich structures and their boundaries are \( sp^2 \) rich structures. With the increase in the number of \( sp^3 \) clusters, the emission

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**FIG. 8.** STM images for ta-C:N films measured in an area of 100×100 nm² (a) before and (b) after H\(^+\) treatment, and measured in an area of 20×20 nm² (c) before and (d) after H\(^+\) treatment.
sites density increases and the threshold field decreases.

The electrons reaching the ta-C surface might reside within either the $sp^2$ rich boundaries or the $sp^3$ rich clusters. The experimental results from both the electron field emission and the CITS measurements demonstrate that the $sp^3$ rich clusters within the films are in favor to the electron field emission. Since these $sp^3$ clusters possess much lower electron affinities compared to the $sp^2$ rich regions, they will provide efficient paths for the electrons to get through and enter the vacuum. In addition to the electrons directly emitted from the $sp^3$ rich clusters, the electrons may also be accelerated by the $sp^2$ rich boundaries due to the potential difference between the clusters and the boundaries. This leads to a lower threshold electric field and a higher emission current density. A larger threshold electric field is observed from the ta-C films bombarded by the H ions with high energies. This might be due to the $sp^3$ bonding being relaxed and turned into the $sp^2$ configurations under the high energy ion bombardment. Thus, the optimal energy is necessary to produce the well-controlled $sp^3$ rich nanoclusters.

IV. CONCLUSION

A lower threshold electric field was observed from the ta-C films with a high $sp^3$ content. The nitrogen incorporation in the ta-C films further reduced the threshold field. The experimental results were interpreted in terms of a space charge interlayer model based on the band structure diagram. However, the density of emission sites was not high for these samples.

It was demonstrated that the emission sites density of films may be increased by post ion treatment. The AFM and STM images showed that the nanofeatures were created during the ion treatment. The UPS measurements demonstrated that the photoelectrons start to emit at energies as low as about 0.6 eV for the posttreated films compared to 2–3 eV for the untreated films. The emission sites density was higher and the threshold field was lower on the posttreated film surface.

We believe that the nitrogenated ta-C films composed of a controllable segregation of nanostructured two-phase materials are promising in producing cold cathodes.

![FIG. 9. CITS measurement of STS $I-V$ curves: (a) before and (b) after H$^+$ treated $n^+$-ta-C films.](image)

![FIG. 10. UPS measurements on before and after Ar$^+$ treated ta-C:N films.](image)