Electron field emission from surface treated tetrahedral amorphous carbon films

X. Shi,[a] L. K. Cheah, and B. K. Tay
School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

S. R. P. Silva
School of Electronic Engineering, University of Surrey, Guildford, GU2 5XH, United Kingdom

The electron field emission properties of tetrahedral amorphous carbon thin films deposited using a filtered cathodic vacuum arc system have improved as a result of surface treatment with H, O, and Ar ions. The limiting factor of the emission process does not appear to be only the front surface of the films. The improvement in the emission after ion beam treatment appears to be independent of the ions used. The surface which has been analyzed using ultraviolet photospectroscopy, reflected electron energy loss spectroscopy, and scanning tunneling microscopy shows evidence of the creation of segregated sp^2 and sp^3 rich regions of less than 20 nm in dimension. An extension to the space charge-induced band bending model including a multistep emission process that occurs in this mixed phase material is proposed. © *1999 American Institute of Physics.*
[S0003-6951(99)02304-9]

The field emission flat panel displays provide significant technical advantages over active matrix liquid crystal display (AMLCD) and other display technologies.[1] Much research effort has been spent on examining the emission properties of cold cathodes of flat carbon films. The carbon cathodes that can be produced with varying degrees of sp^3, sp^2, and sp^1 hybridizations means that these films can be tuned for particular applications.[2] It also means that these films can be produced with a whole gamut of different properties resulting in the difficulties to propose a single model to explain the emission mechanism. A number of models have been proposed based on the negative electron affinity,[3] defect bands in diamond,[4] space charge induced band bending,[5] surface dipole controlled emission,[6] and field enhancement due to surface features.[7] Although they can be used to fit some emission data from different types of films, none of them is universally acceptable.

In this letter, the enhancement in electron emission on ion beam surface treated *ta*-C films is analyzed and a model to explain the observed emission is proposed.

The tetrahedral amorphous carbon (*ta*-C) films were prepared using the FCVA technique.[8] n^{++}-Si was used as the substrate ($\rho \sim 0.02 \, \Omega$ cm). During deposition, the Carbon ion energy of 100 eV was used to optimize the sp^3 ratio up to ~87% in the undoped films.[8] A RF ion beam source producing 100 eV, 20 mA nitrogen ion beam was used to incorporate nitrogen in the growing *ta*-C films.[10] Undoped *ta*-C films exhibit a band gap of ~2.6 eV[11] and the Fermi level 0.35 eV below the midgap.[10] When nitrogen is incorporated, the Fermi level shifts towards conduction band corresponding to weak doping in the films (*n-ta*-C).[10]

Both doped and undoped *ta*-C films of 40 nm thickness were subjected to 1 min of ion beam surface treatment by hydrogen, oxygen, and argon ions (100 eV and 20 mA). The area for which the ion bombardment occurred is about 5 cm in diameter. After the surface treatment, we transferred the films to the field emission test chamber by breaking the vacuum. In the transfer process, the films were exposed to air for less than half an hour. The electron field emission current density versus macroscopic electric field ($J-E$) were obtained by using a typical pin to plane measurement.[11] The emission sites were observed and recorded by using a plane to plane measurement and a digital camera. The idium–tin–oxide (ITO) coated glass was used as the low efficiency cathodoluminescent material as well as the anode. Ultraviolet photospectroscopy (UPS) was made on VG ESCALAB fitted with He light source and reflected electron energy loss spectroscopy (REELS) was performed on VG MICROLAB.
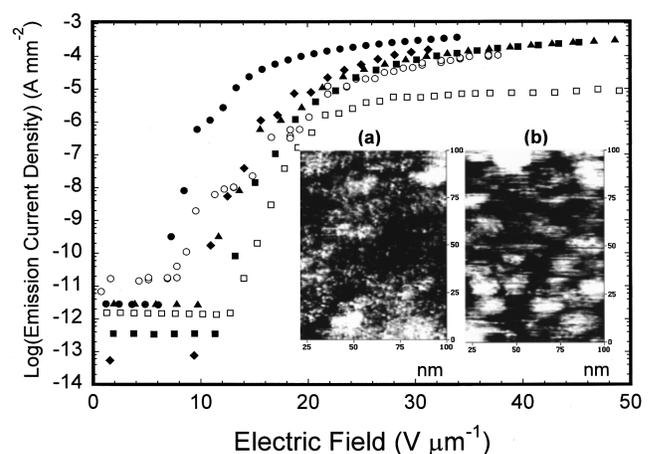
The emission $J-E$ characteristics are shown in Fig. 1.

FIG. 1. Current density vs applied electric field from as deposited *ta*-C and *n-ta*-C films. □ represents untreated *ta*-C films. ■, ♦, and ▲ represent *ta*-C films after H⁺, O⁺, and Ar⁺ treatment, respectively. ○ and ● represent *n-ta*-C films before and after H⁺ treatment, respectively. Inset shows STM images for an *n-ta*-C film (a) before treatment and (b) after treatment (Vertical scale is 2 nm).

a)Electronic mail: esxu@ntu.edu.sg

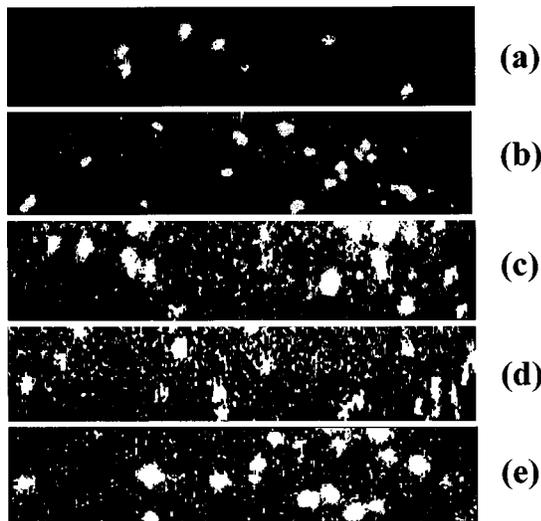FIG. 2. Emission spots projected from the ITO coated glass for (a) *ta*-C before treatment, (b) n^+-*ta*-C before treatment, (c) *ta*-C after H^+ treatment, (d) *ta*-C after O^+ treatment, and (e) *ta*-C after Ar^+ treatment.

For undoped *ta*-C films, the ion beam surface treated samples have a lower on-set electric field of about 14 V/μm for three different elemental ions (■, ♦, and ▲ representing H^+, O^+, and Ar^+ treatment, respectively) compared to about 18 V/μm for nontreated films (□) (10^{-6} A/cm^2 is used as the critical current at which the threshold electric field is obtained). For *n*-*ta*-C films, the ion beam treated samples have an on-set electric field of 8 V/μm (●) versus 12 V/μm (○) for nontreated films. The saturation current density also improves by about an order of magnitude in both cases. The emission sites over a 4 mm×1 mm surface area for undoped *ta*-C films is shown in Fig. 2(a). Higher emission site densities were observed for *n*-*ta*-C films shown in Fig. 2(b). After the surface treatment, the emission site densities were greatly improved, as shown in Figs. 2(c)–2(e). The improvement over the site density appears to be independent on the types of ions used. This observation is confirmed by the same degree of improvement in the J–E curves recorded and shown in Fig. 1 after hydrogen (■), oxygen (♦), and argon (▲) ion treatment on *ta*-C films.

The UPS spectra for the as-deposited and ion beam treated *n*-*ta*-C films are shown in Fig. 3. The as-deposited film has an apparent Fermi level, i.e., a level from which a
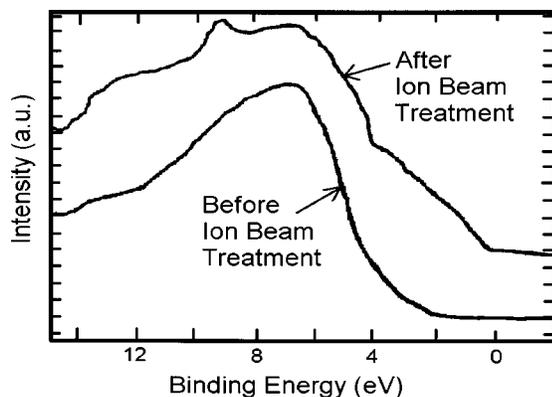

FIG. 3. UPS spectra for the untreated and Ar ion surface treated n^+-*ta*-C films.
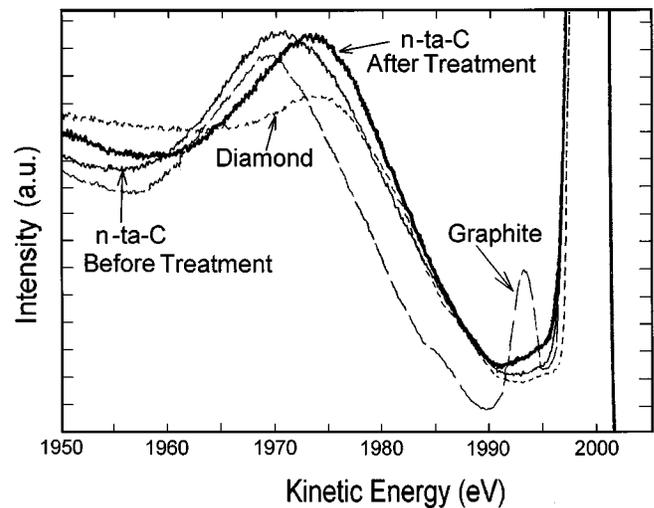

FIG. 4. REELS curves for the main forms of carbon and the untreated and treated n^+-*ta*-C film.

significant number of electrons are ejected under ultraviolet irradiation, at about 4 eV with a significantly smaller defect state appearing to supply electrons gradually from about 2 to 3 eV. This smaller feature may be due to emission from localized states within the band gap of the *ta*-C films, and indicating that the electron affinity of the material is close to 2 eV for this film, while the completely filled electronic states of the undoped material, i.e., the intrinsic Fermi level, is at 4 eV. This appears to be consistent with electron affinity calculations by Robertson[12] as well as the activation energies measured for the intrinsic *ta*-C thin films.[9] After the ion beam treatment, a large shoulder with a sharp turn-on was observed as shown in Fig. 3. Photoelectrons start to emit at energies as low as about 0.6 eV. It appears to indicate that there are surface modifications which give rise to an apparent Fermi level very close to vacuum level. UPS signals of similar value are observed for diamond surfaces. It indicates that regions of the film surface may be transformed from an sp^3 rich amorphous phase to one more closely related to a 100% sp^3 network as also observed in crystalline diamond.

To further assess the surface modifications, REELS was employed on the same samples. Reference REELS curves for the main forms of carbon together with that for the untreated and treated *n*-*ta*-C films obtained in this study are shown in Fig. 4. It is immediately apparent that in the case of graphite, a large π^* peak is observed at close to 6 eV energy loss. While in diamond, this π^* peak is absent. When the ion beam treated *ta*-C sample is compared to the untreated one, there is a slight increase in the π^* region, accompanied by a 3 eV downward shift in the low loss plasmon peak. The downshift in the plasmon peak generally indicates a reduction in the electron valence density, and in this case this could indicate a decrease in the film density of the surface layers by as much as 20%. If this was purely due to the transformation of sp^3 bonds to sp^2 hybridizations, a significantly larger than observed increase in π^* region would be expected. Therefore, the decrease in the surface layer density cannot be totally attributed to the formation of sp^2 bonds. Neither does it clarify the the formation of small regions of ''crystalline diamond,'' as indicated by UPS data.

The morphological images were then studied by STM as

shown in the inset in Fig. 1. The mirror smooth samples with a RMS roughness of 0.193 nm before ion beam treatment was transformed into films having rms roughnesses of 0.242 nm, with visible nanoscale regions or protrusions formed on the surface within the slightly receded network. This texturing explains the decrease in the volumetric measure of the surface density obtained by REELS. Combined with the UPS data it is quite plausible that some of the ''textured'' regions observed on the surface of the ion treated n-ta-C films are actually nanocrystalline diamond regions formed under intense ion bombardment.

The REELS analysis indicates an increase in the overall sp^2 content. The UPS shows evidence for the formation of surface crystalline sp^3 regions after the ion bombardment. STM observations add further visual evidence for the formation of nanoclustered regions on the film surface. The lack of dependence on the elemental ion used indicates that the surface termination of the film is less significant than previously discussed in the model proposed by Robertson,[6] where hydrogen or oxygen termination was meant to help or impede the electron emission process by creating dipoles at the surface thus changing the electron affinity of the film. The band bending hot electron model[5] was extended to polycrystalline diamond films based on a two stage emission process controlled by the grain boundaries.[13] The electron emission from ta-C films also appears to support this model, where the dependence of the threshold field on the doping of the substrate as well as its doping level was clearly shown by Cheah and Shi *et al.*[13] The current work helps extend the concept of the two stage emission process for the polycrystalline diamond films to a multiple step emission process for carbon films whose surface has both sp^3 and sp^2 rich nonclustered regions.

The electrons that are heated when traversing down the fully depleted bulk n-ta-C film come to the surface with two possible options: they may be emitted straight from the surface if they gather enough kinetic energy; or they could reside at the surface of the films in either the sp^2 or sp^3 rich clusters. The electrons in sp^2 rich clusters could then be accelerated by the fully deleted junction between sp^2 and sp^3 rich clusters due to the presence of the potential energy variations of the mixed phase and injected to sp^3 rich regions. Since these sp^3 clustered regions possess much lower electron affinities compared to the sp^2 rich regions, it will

provide an efficient route for electrons to vacuum. The implication of this research also points to the fact that there will be significantly less hysteresis, as found in this study, present in cathodes based on ion beam treated ta-C, with little or no conditioning required before emission at low electric fields. Controllable segregation of nanoclustered two phase materials may be a route to producing well behaved cold cathodes in the future.

In summary, ta-C films before and after various ion beam surface treatment have been investigated. Different ions give similar degree of reduction in the on-set electric field and similar degree of increase in saturation emission current density and emission site density. The ion beam irradiation provides an effective means to transform the ta-C film surface into well segregated sp^2 and sp^3 rich regions. According to our proposed multiple step emission mechanism the junction between sp^2 and sp^3 rich clusters provides an intermediate ladder for the electrons to climb up from the sp^2 rich clusters to sp^3 rich ones where they may have enough energy to overcome the small barrier to emit to vacuum.

[1] J. E. Jaskie, MRS Bull. **21**, 59 (1996).

[2] D. R. McKenzie, D. A. Muller, F. Kravichinskana, D. J. H. Cockayane, G. A. J. Amaratunga, and R. Silva, Thin Solid Films **206**, 198 (1992).

[3] Z.-H. Huang, P. H. Culter, N. M. Miskovsky, and T. E. Sullivan, Appl. Phys. Lett. **65**, 2562 (1994).

[4] W. Zhu, G. P. Kochanski, S. Jin, L. Seibles, D. C. Jacobson, M. McCormack, and A. E. White, Appl. Phys. Lett. **67**, 1157 (1995).

[5] G. A. J. Amaratunga and S. R. P. Silva, Appl. Phys. Lett. **68**, 2529 (1996).

[6] J. Robertson, Mater. Res. Soc. Symp. Proc. **498**, 197 (1998).

[7] A. A. Talin, T. E. Felter, T. A. Friedmann, J. P. Sullivan, and M. P. Siegal, J. Vac. Sci. Technol. A **14**, 2 (1996).

[8] X. Shi, D. Flynn, B. K. Tay, S. Prawer, K. W. Nugent, S. R. P. Silva, Y. Lifshitz, and W. I. Milne, Philos. Mag. B **76**, 351 (1997).

[9] X. Shi, L. K. Cheah, and B. K. Tay, Thin Solid Films **312**, 166 (1998).

[10] L. K. Cheah, X. Shi, and B. K. Tay, J. Non-Cryst. Solids **242**, 40 (1998).

[11] L. K. Cheah, X. Shi, B. K. Tay, S. R. P. Silva, and Z. Sun, Diamond Relat. Mater. **7**, 640 (1998).

[12] J. Robertson, Diamond Relat. Mater. **6**, 212 (1997).

[13] S. R. P. Silva, R. D. Forrest, A. P. Burden, J. Anguita, J. M. Shannon, B. J. Sealy, D. A. I. Munindradasa, G. A. J. Amaratunga, and K. Okano, 1st SMAC' 97, Cambridge, UK, 1997 (unpublished), p. 350.