

Conditioning of hydrogenated amorphous carbon thin films for field emission via current stressing

J.D. Carey ^{a)} and S.R.P. Silva

School of Electronic Engineering, Information Technology and Mathematics,

University of Surrey, Guildford, GU2 7XH, United Kingdom

The effects of electrical current stressing on the field emission characteristics of hydrogenated amorphous carbon (*a*-C:H) thin films are reported. In these *a*-C:H films an initial conditioning treatment of the film is often required before the onset of stable emission and only after several voltage cycles do the values of the threshold field tend to converge. By stressing of the film by applying a pre-determined current through the film, the initial conditioning treatment can be removed and stable and reproducible emission observed. Retesting of the current stressed films shows that the films remain fully conditioned provided a sufficiently high stress current was initially used.

a) Electronic mail: David.Carey@surrey.ac.uk

Amorphous carbon (*a*-C) and its hydrogenated alloy (*a*-C:H) have been shown to emit electrons at relatively low electric fields and thus have potential applications as cold cathode materials. [1, 2] *A*-C:H films deposited by r.f. plasma enhanced chemical vapour deposition (PECVD) also have the advantage of being able to be produced over large areas at low temperatures and often exhibit rms roughnesses of less than 1 nm. However, in these ‘mirror smooth’ films it has often been noted that a conditioning or initiation of the film is required before the onset of reproducible field emission (FE). [3, 4] This often involves the cycling of the voltage upward and downward over 1-2 cycles and is sometimes accompanied by surface damage due to microarcing. [3] Similar conditioning treatments have also been reported necessary in tetrahedral amorphous carbon (*ta*-C) [5, 6] and in diamond films grown by chemical vapour deposition. [7] The exact nature of this conditioning step and the role of the damage-induced surface microprotrusions is not fully understood though conditioning may involve an increase in the concentration of threefold coordinated carbon atoms at the expense of fourfold coordinated atoms [8]. For a practical *a*-C(:H) based display the values of the threshold field (E_{th}) should be as reproducible as possible. Furthermore, to limit the spread in the drive voltages, the hysteresis in the current-voltage (*I*-*V*) characteristics should be kept to a minimum. In this Letter we report on the results of current stressing treatments on *a*-C:H films. By varying the stressing current not only can the need for the initial conditioning treatment be removed but the width of the hysteresis present in the *I*-*V* characteristic kept to a minimum.

Films were deposited on the water-cooled earthed electrode of a Plasma Technology DP800 capacitively coupled r.f. PECVD system onto *n*-type 1-2 Ω cm Si substrates. Feed gases of CH₄ (30 sccm) and He (75 sccm) were used. The deposition pressure was 200 mTorr and an r.f. power of 200 W was used which resulted in negative dc self bias of about 10 V. These films are polymeric in nature with a H content of up to 50 % [9] and a low paramagnetic spin density of about $3 \times 10^{17} \text{ cm}^{-3}$. [10] The film thickness was measured using ellipsometry.

The FE characteristics of the films were examined using a sphere-to-plane geometry with a 5 mm stainless steel ball bearing suspended 30 μm above the film with a high positive potential applied in a vacuum better than 4×10^{-6} mbar. The anode is attached to a Vacuum Generators high precision translator possessing a 2.5 μm step resolution. Although a spherical anode is used it is assumed that the electric field between the anode and the surface of the film can be modelled as a parallel plate. The high voltage is stepped up and down four times and the macroscopic electric field is defined as the applied voltage divided by the vacuum separation; E_{th} is defined as the macroscopic electric field which gives an emission current of 1 nA. It should be noted that in improperly conditioned films there may be significant differences in values of E_{th} depending on whether the current is read on the upward voltage cycle or on the downward cycle. As a measure of this 'hysteresis effect' the difference in the applied fields between the upward and downward voltage cycles at a current of 1 nA is used. Current stressing of the films was performed by contacting the anode to the film and passing a current through the film up to a pre-determined level. Each film was tested before stressing by applying a field of up to 100 V/ μm and only those samples which *did not* emit after this preliminary test were subject to current stressing. Atomic force microscopy (AFM) imaging was carried out using a Digital Instruments Nanoscope IIIa system. Atomic force micrographs, not presented here, show that the rms surface roughness of the as-deposited films to be less than 0.4 nm on a 5 μm square scan area. No evidence of surface protrusions was visible and the as-deposited films can be considered as 'mirror smooth'.

For the current stressing measurements several identical films from the same deposition run were examined. In order to minimise any possible dependence on the film thickness [11], the same film thickness, in this case 57 nm, was used. For reference the typical value of E_{th} for films which did emit after conventional conditioning is about 30 V/ μm . The three current stress levels chosen were 10^{-8} , 5.2×10^{-8} and 2×10^{-7} A. The FE characteristics of the film stressed to 10^{-8} A (not shown) exhibited emission but with an E_{th} of over 85 V/ μm and a width of the first cycle hysteresis loop of over 20 V/ μm . Subsequent voltage cycles resulted in a reduction of E_{th} ,

though the average threshold field obtained from the latter three cycles was 66 ± 4 V/ μm . Stressing to a higher current of 5.2×10^{-8} A results in an initial emission at a field of 48 V/ μm though a hysteresis width of 20 V/ μm , as shown in Fig. 1. The I-V characteristics of the film before stressing is also presented and shows that no emission had occurred from this film even up to fields of 90 V/ μm . The threshold field continues to decrease after subsequent voltage cycles and finally reached 40 V/ μm after the 4th cycle. The average value of E_{th} obtained from this film is 38 ± 10 V/ μm , higher than that obtained from a film which underwent the conventional conditioning treatment. It is evident from Fig.1 that since the width of the first cycle is 20 V/ μm the film is not fully conditioned.

The I-V characteristic of the film stressed to 2×10^{-7} A is shown in Fig. 2 on the same scale as used in Fig. 1. In this case the value of E_{th} for the 1st cycle was only 34 V/ μm , which subsequently decreased to 30, 26 and 27 V/ μm in the remaining three cycles. The average E_{th} of 28 ± 2 V/ μm is comparable to the values of E_{th} for films which have undergone an conventional conditioning treatment. The width of the I-V hysteresis loop was about 2 V/ μm in each run and Fig. 2 shows no evidence of a conditioning cycle after current stressing. Since the FE characteristics are different and are observed to improve with higher stress currents, we can eliminate the mechanical effects of contacting between the anode and film as the primary reason for the improvements.

An AFM study of the edge of the stressed area of film stressed to 2×10^{-7} A shows that the surface morphology has altered. An AFM image of the edge of the stressed area of film stressed to 2×10^{-7} A is shown in Fig. 3 (a) where three distinct regions, labelled 1, 2 and 3, have been identified. Region 1 consists of surface protrusions the majority of which are less than 80 nm in height and the film possesses an rms roughness of about 44 nm. The surface protrusions of region 3 are less than 120 nm in height and the rms roughness is 105 nm. By contrast the protrusions of region 2 are over 800 nm in height and the roughness is 170 nm. To examine

whether the protrusions are the source of the emitted electrons we have used the simplified Fowler-Nordheim (FN) equation to relate the emission current I to the local field βF via

$$I = \frac{aA\beta^2 F^2}{\phi} \exp\left(\frac{-b\phi^{3/2}}{\beta F}\right), \quad (1)$$

where $a = 1.54 \times 10^{-6} \text{ A eV V}^{-2}$, $b = 6.83 \times 10^7 \text{ eV}^{-3/2} \text{ V cm}^{-1}$, A is the emission area, ϕ is the front surface barrier height (in eV) and β is the field enhancement factor for a field F . Figure 3 (b) shows the best fits using Eq. 1 to one of the I-V characteristics of the film stressed to $2 \times 10^{-7} \text{ A}$ and one of the characteristics of an unstressed but conditioned film. The slopes of the two lines are -4.98×10^6 and -3.2×10^6 , which for barriers of 4 eV result in values of β of 110 and 170 respectively. If a lower effective barrier of 2.5 eV is used, β values of the 54 and 84, respectively result. Since the value of β from the stressed film is *less* than that from the unstressed film and the values of the E_{th} are similar, we believe that that the surface protrusions do not play a significant role in the emission process. Values of $\beta \sim 250$, attributed to surface protrusions, were reported in the study by Talin *et al.* of FE from *ta*-C and were proposed as the source of the emission. [5]

In order to examine whether the current induced conditioning is permanent the films were retested some hours after the initial stressing had been performed. In order to prevent any possible atmospheric contamination the samples remained held under vacuum during this period. Figure 4 (a) shows that even after just 15 h in the sample that was stressed to $5.2 \times 10^{-8} \text{ A}$, E_{th} had risen to about $50 \text{ V}/\mu\text{m}$, similar to the value obtained in the first cycle after this sample had just been stressed, indicating some form of ‘healing’ process had occurred. By contrast Fig. 4 (b) shows that in the film stressed to $2 \times 10^{-7} \text{ A}$ shows no evidence of a conditioning cycle is required 23 hours after the original current stressing had occurred. Only the first two I-V characteristics are presented in Fig. 4 (b) and values of E_{th} obtained after 23 hours are 30 and 32 $\text{V}/\mu\text{m}$ with a hysteresis width of 2-3 $\text{V}/\mu\text{m}$. Testing after 87 h revealed similar results to those

