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Influence of sp^2 clusters on the field emission properties of amorphous carbon thin films

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The influence of the concentration and size of sp^2 carbon clusters on the field emission properties of hydrogenated amorphous carbon thin films is investigated. In combination with electron paramagnetic resonance and optical measurements, it is shown that the trend in the threshold field for emission for films deposited under certain conditions can be explained in terms of improvements in the connectivity between sp^2 clusters. These clusters are believed to be located near the Fermi level, and the connectivity is primarily determined by the cluster size and concentration which in turn is determined by the choice of deposition conditions.

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Amorphous carbon (*a*-C) and hydrogenated amorphous carbon (*a*-C:H) have attracted considerable attention due to possible applications as semiconductor materials [1] and as a potential field emission (FE) cathode material. [2] There has been a great deal of interest in determining whether the most important factors which govern emission are "front surface" based such as negative electron affinity and surface termination. [3] An alternative mechanism in which the presence of a large internal electric field at the film/substrate interface resulting in hot-electron transport – the "back contact" model – has also been proposed. [4] The reduction of the threshold field with N content [4], the dependence of the threshold field with film thickness [5], and the non-uniformity of emission across a film surface have also been reported. [6, 7] The relative proportion of the different hybridised C states influences the electronic structure with the optical properties being largely controlled by the size of sp^2 clusters. [8, 9].

The sp^2 content is also important in the understanding of electron paramagnetic resonance (EPR) measurements made on *a*-C:H films [10]. EPR is sensitive to centers with a net unpaired election spin, for example such centers can result from odd numbered clusters. The location in the energy gap of sp^2 clusters depends on whether they are even or odd numbered and whether they are distorted or not [8]. Undistorted even numbered clusters give rise to states near the Fermi level (E_F) only if they are large enough, whereas odd clusters will give rise to states even if composed of a small number of clusters. Distorted clusters will give rise to states that are closer to the E_F than undistorted clusters [8]. In this way EPR can give a measure of the density of sp^2 states at the Fermi level provided that a majority of these states have a net unpaired electron present though the paramagnetically active sp^2 states are likely to be only a small fraction of the total density of sp^2 clusters. [8] There is some evidence that the properties of the sp^2 clusters may have a significant role in determining the FE properties of amorphous carbon films [11]. In this letter we report the results of field emission, EPR and optical measurements on *a*-C:H thin films deposited using r.f. plasma-enhanced chemical vapor deposition at different self-biases and varying nitrogen content.

Films of *a*-C:H(:N) were deposited on the driven and earthed electrode of a Plasma Technology DP800 capacitively coupled radio frequency (13.56 MHz) plasma enhanced chemical vapour deposition system. Films were grown on *n*-type 1-2 Ω cm (100) Si substrates for FE measurements, onto Corning 7059 glass for optical measurements and high resistivity (>100 Ω cm) Si (100) substrates for EPR measurements. During deposition feed gases of methane (30 sccm) with He (75 sccm) were used. The total deposition pressure was 200 mTorr. Film thicknesses were measured using ellipsometry. Nitrogenation of films deposited on the earth electrode was accomplished by addition of N_2 into the deposition chamber with flow rates between 0-15 sccm. [12]

The FE characteristics of these films were examined using a sphere-to-plane geometry in which a 5 mm stainless-steel ball bearing is suspended 40 μm above the surface at a high positive potential in a vacuum better than 4 x 10^{-6} mbar. In a majority of the samples examined a large (> 40 V/μm) field was required to initiate emission on the first voltage cycle, this reduced after subsequent cycles and is evidence of conditioning of the film. [5] The threshold field (E_{th}) is defined as the macroscopic electric field which gives an emission current of 1 nA for a conditioned film. Room-temperature EPR measurements were made in a modified Bruker EPR spectrometer using 100 kHz field modulation and a microwave frequency of about 9.9 GHz. Spin concentrations were determined by comparing with a standard Varian sample of pitch in KCl. The absolute spin populations are estimated to be correct to within a factor of 2; however, their relative values are correct to within ± 20%.

The variation of E_{th} for films deposited under different self-biases is shown in Fig. 1(a). At a dc self bias of –50 V, E_{th} is 18 V/μm, which initially increases to 26 V/μm for films deposited at –90 V and then decreases at high biases to remain approximately constant at about 12 V/μm. The measured spin densities, N_s, of these films are shown in Fig. 1(b). From the lowest bias N_s rises rapidly from 3 x 10^{17} cm^{-3} to 1.1 x 10^{20} cm^{-3} at –125 V. At higher biases N_s increases only very gradually, finally reaching 1.6 x 10^{20} cm^{-3}. The Tauc gap and peak-to-peak linewidth ΔB_{pp} of the EPR signal are shown in Fig. 2. The Tauc gap falls rapidly from 2.6 eV (-50 V bias) to 1.3 eV (-125 V) and then falls gradually to about 1.1 eV at the highest bias voltages. In the case of ΔB_{pp} there is an initial increase in the linewidth reaching a maximum of 1.4 mT at –125 V bias and then followed by a rapid decrease to 0.7 mT, which continues to decrease to 0.56 mT at –265 V bias. At these higher biases the line shape is Lorentzian and the *g* value is 2.0027(2). At lower biases the line shape is composed of the C related centers at 2.0027 as well as defects originating from the Si substrate as described elsewhere. [13]

For the sample deposited at –125 V bias the measured spin density is 1.1 x 10^{20} cm^{-3} and observed linewidth is 1.4 mT. This line has a Lorentzian line shape and one of the sources of line broadening which would produce such a line shape is dipolar broadening between like spins. Abragam has shown that the linewidth $\Delta B_{pp}^{dipolar}$ (mT), is related to the spin density (cm^{-3}) via [14]

$$\Delta B_{pp}^{\ \ dipolar} = \frac{4\pi^2}{9} g\mu_B N_s = 8.1\times 10^{-21} N_s \ . \qquad (1)$$

Using the measured value of N_s determined for this film, Eq. (1) gives a predicted linewidth of 0.9 mT. This is slightly lower than the measured value of 1.4 mT but indicates that the principal source of broadening in this film is most likely to be dipolar broadening. At higher biases the spin density gradually *increases* but there is a significant *reduction* in the observed linewidth. This is clearly in contrast to what would be predicted from Eq. (1) and indicates that another mechanism is also present, which is narrowing the linewidth. The decrease in linewidth with increase in self-bias, for voltages above –100 V bias, has been reported previously [10] and was attributed to motional effects. We believe that motional effects arising from exchange or rapid electron hopping between sp^2 clusters of increasing size are also occurring in these films. This is consistent with the narrowing of the Tauc gap since the size of the gap is related to the size of the cluster. [8,15] The presence of these motional effects can also be used to explain the similarity of the threshold fields measured for the samples deposited at the higher biases. All these films will have a high sp^2 content, and the consequent overlap of the clusters will result in electron delocalisation and/or enhanced hopping between the clusters. We regard this as an effective improvement in the connectivity between the clusters. Application of an external electric field results in extraction of electrons from the film surface. Replenishment of the emitted electrons to the surface layer is easily accomplished due to the good connectivity between the clusters. Emission from these high sp^2 rich films would be characterized as a "front surface" type emission and since the sp^2 clusters are located at or about E_F they would be expected to yield a peak in the field electron energy distribution (FEED) at E_F with a low energy cut off tail. Such a FEED characteristic has been observed in the high N (approximately 17 at. %) containing *a*-C:H:N films examined by Gröning *et al*. [16].

Reducing the self bias to –90 V results in a reduction in the spin density by about two orders of magnitude and a rapid rise in the Tauc gap and shows that major structural changes in the film are occurring. At low self biases a low concentration of small isolated sp^2 clusters form. Initially, the number of C atoms in each cluster is small (as inferred from the large Tauc gap) but the greater energy available at higher biases allows the formation of a greater number of larger, but still isolated, clusters. This results in a reduction of the Tauc gap and an increase in N_s, though the electron delocalisation in the cluster and/or hopping between clusters is kept to a minimum. This leads to poor connectivity between the clusters and results in films which needs a higher applied electric field for the onset of emission and explains why E_{th} is higher at –90 V bias when compared with the films deposited the higher biases. The subsequent drop in E_{th} for the film at the lowest bias voltages indicates that another emission mechanism is also present. This additional mechanism is brought about by the presence of the high internal electric field (up to 20 V/μm) at the *a*-C:H/Si interface which produces 'hot' electrons from the Si conduction band. [4,5] The low concentration of the more conductive sp^2 clusters is unable to screen the field at the front surface. In this way emission, from these low bias deposited films would be more correctly described as being determined by "the back contact" rather than the "front surface".

In order to demonstrate that it is the size of the cluster that is still important in determining the emission mechanism rather than the absolute concentration of the clusters we have made measurements of the threshold field and spin density as a function of N content in the low defect polymeric films. Addition of N has been shown previously to reduce the threshold field in diamond-like carbon (DLC) films [4] and also in ta-C films [17]. However, in both of these types of films there has been a reduction in the spin density and this was partly attributed to passivation of defects. [4,17] It can be seen from Fig. 3 (a) that E_{th} drops with addition of N similar to that reported elsewhere [4,16] but in contrast to the DLC films of Silva *et al*., [18] no reduction in N_s is observed (Fig 3 (b)). The reduction in N_s in the DLC films was attributed to the passivation of defects as evidenced by the initial increase in the Tauc gap followed by a subsequent decrease. [17] In the polymeric films the continued decrease in the Tauc gap without an increase in the spin density indicates that the number of sp^2 clusters remains the same but that the cluster size in increasing. Therefore, we attribute the lowering of the threshold field with addition of N to an increase in the cluster size.

We believe that the field emission from *a*-C:H film can be explained in terms of the number and size of sp^2 clusters lying at or near the Fermi level and that it is important that the cluster be large enough for efficient connectivity between clusters. In this way the *a*-C:H films deposited under different conditions will consist of a matrix of sp^3 C with regions of varying sp^2 cluster concentration and size. Since these clusters will have dielectric constants, the application of the external field will result in local field enhancement around the clusters and will aid in the emission of electrons. A similar conclusion concerning the importance of the size of the sp^2 cluster has also been reached by Ilie *et al*. [11] based upon a correlation between the measured values of threshold fields for various type of amorphous carbon films with the behaviour of the intensity of the I_D to I_G peaks measured using Raman spectroscopy [11]. They determined that the optimal size of the clusters for emission to be 1.5-2 nm depending on the specific type of film investigated.