

Clustering in Nanostructured Carbon: Evidence of Electron Delocalization

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Abstract

The electronic properties of disordered carbon based materials can be discussed in terms of the clustering of the sp\textsuperscript{2} carbon phase and delocalization of the electron wavefunction. In smooth amorphous carbon thin films this results in a mixed phase material of conductive sp\textsuperscript{2} clusters embedded in an electrically insulating sp\textsuperscript{3} matrix. The delocalization of the electron wavefunction associated with the sp\textsuperscript{2} clusters is shown to play an important role in understanding many of the electronic and optical properties of the films. It is demonstrated that the extent of the electron delocalization and clustering can be estimated using magnetic resonance methods. Evidence for delocalization in a range of carbon based materials such as diamond-like carbon thin films produced by chemical vapour deposition, nanostructured carbon produced by pulsed laser ablation and ultrananocrystalline diamond is presented.

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I Introduction

Carbon based electronic materials span a wide range of functional materials with the crystalline forms of diamond and graphite representing the extremes of sp\(^3\) and sp\(^2\) content, respectively. \[1\] The isotropic, high hardness and high thermal conductivity of diamond has spurred considerable interest in its use in high power electronics. The differences between the strong intra-layer and weaker interlayer bonding in graphite results in an anisotropic material which is used as a lubricant as well as in composites \[1\]. The strong sp\(^2\) bonding in the graphene layer is, of course, important for understanding many of the properties of carbon nanotubes with extensive research being carried out in the characterisation and potential applications of both single wall and multiwall carbon nanotubes. \[2\] In recent times graphene itself has emerged as an interesting electronic material with unexpected quantum Hall effect behaviour \[3\] observed. Hard diamond-like carbon (DLC) thin films, with a high concentration of sp\(^3\) C-C bonding have tended to be used mainly as coatings such as on razor blades, hydraulic pumps and as well as other applications in the automotive industry including car door locks and injector pumps \[1, 4\]. Other successful applications of amorphous carbon (a-C) films have included their use in hard disks and optical storage and the excellent haemo-compatibility of carbon films has seen the emergence of carbon thin films for biomedical applications such as cardiac stents \[5\].

As an electronic material a-C films have, in principle, a number of intrinsic advantageous properties. Their electronic properties can be controlled by varying the deposition conditions and films can be deposited over large areas with good uniformity \[1\]. In addition, films can be deposited at low substrate temperatures which is an important consideration in the case of temperature sensitive substrates. Less success has been forthcoming in the development of active electronic applications of a-C and the hydrogenated form of a-C (a-C:H) films \[6\]. It is generally agreed that the sp\(^2\) hybridised carbon atoms tend to exist as nm-sized clusters in the form of graphitic rings and give rise to occupied \(\pi\) and unoccupied \(\pi^*\) bands \[7\]. The optoelectronic properties of these films, such as the Tauc gap and the Urbach energy, are usually discussed in terms of transitions between occupied \(\pi\) states and unoccupied \(\pi^*\) states. In general, the larger the sp\(^2\) cluster in size, the smaller
the Tauc gap [7]. The sp³ component tends to be found as aliphatic chains. Transport in disordered carbon films can be discussed in terms of transport in extended states, band tails or localised states near the Fermi level [8]. In a-C, localised state transport is usually interpreted in terms of hopping between sp² clusters [9]. In the case of a-Si, it is possible to discuss transport in the localised states being separated by a mobility edge from the extended states, in which there is a strong correlation between the mobility edge and the Tauc gap [10]. In the case of a-C this strong correlation breaks down to such an extent that in a recent study by Cherkashinin and colleagues [11], it was reported that the photoconductivity did not appear to correlate with the Tauc optical gap. Furthermore, the measured photoconductivity associated with σ-σ* states of hydrogen containing DLC films was reported to be up to two orders of magnitude larger than from π – π* states. Whilst the usually methods are employed for the extraction of the Tauc gap and the Urbach energy, there is a growing realisation that the interpretation of the Urbach energy as a measure of disorder in a-C may be more complicated [12, 13].

Figure 1 shows the variation of Urbach energy, $E_U$, with Tauc gap for a range of a-C:H films. It is apparent that the values of $E_U$ are largest for samples with the largest Tauc gap. Since the size of the sp² cluster scales inversely with the Tauc gap, it would be expected that the films with the highest Tauc gaps are those with the smallest average cluster size as discussed in ref 9. Since there are only a limited number of configurations or conformations of atoms possible in a small cluster, a small Urbach energy would be predicted – a conclusion that is in disagreement with the experimental evidence of Fig. 1. This disparity between prediction and experiment lead Fanchini and Tagliaferro to conclude that the Urbach energy in amorphous carbon is a complicated measure of disorder [12]. They furthermore went onto propose two types of disorder:

(i) a structural disorder associated with clusters of the same size but with different amounts of distortion and

(ii) a topological disorder arising from undistorted clusters but of different sizes.

The interplay between Tauc gap, Urbach energy and topological and structural disorder has also been examined using multi-wavelength Raman spectroscopy [14]. Here it was shown that the G peak
width is a measure of structural disorder and can be related to the structural and mechanical properties of the film. Topological disorder was inferred from the variation of the G peak position with wavelength. However this study was unable to quantify the relationship between the different types of disorder, the density of electron centres and the clustering of the sp$^2$ phase.

The location of the sp$^2$ clusters in the energy gap depends on two factors; whether the clusters consist of an odd or even number of carbon atoms and whether they are distorted [15]. Undistorted even numbered clusters will give rise to states near the Fermi level ($E_F$) only if they are sufficiently large. This differs from the case of odd numbered clusters which can give rise to gap states even if composed of a small number of atoms. In general, distorted clusters will give rise to a state that is closer to $E_F$ than undistorted clusters. Carrier transport due to localized states will therefore be influenced by the concentration of clusters near to the Fermi level.

One way to probe the singly occupied electron states near the Fermi level is to use electron spin resonance (ESR). In doing so there are, in general, four pieces of information that can be obtained from such a measurement. The first of these is the $g$ value, which is the related to the resonant Zeeman magnetic field at a particular microwave frequency, and is characteristic of the electron centre with the $g$ value in carbon based materials tending [15, 16] to be in the range 2.0025 - 2.0030. The free electron $g$ value, associated with complete wavefunction delocalization with no orbital contribution to the total magnetic moment, would be 2.0023. The second piece of information that can be obtained is the volume spin density, $N_s$, determined by integrating the microwave absorption profile and comparing it with a known standard. As shall be shown later typical values of $N_s$, are around $10^{20}$ cm$^{-3}$ for DLC films. It is important to note that spin densities do not themselves measure the sp$^2$ content since not all sp$^2$ centres will be measured in an ESR experiment [17]. For example, electron energy loss spectroscopy measurements made on plasma enhanced chemical vapour deposition (PECVD) grown films showed that the sp$^2$ content of these films varied from 63% to 72% for a change of negative self bias from 100 V to 265 V. This was accompanied by an increase in the spin density from $4.9 \times 10^{19}$ cm$^{-3}$ to $1.5 \times 10^{20}$ cm$^{-3}$. However, whilst increasing the negative self bias to 460 V, the spin density hardly changed ($2-3 \times 10^{20}$ cm$^{-3}$).
the sp² content increased above 80%. The third and four pieces of information are the peak-to-peak linewidth, ΔBpp, and the resonance line shape. Indeed whilst a number of reports have commented on the variation of Ns with growth conditions [1, 15, 18], less discussion exists about the line width and shape. The latter is important since it provides information about the broadening mechanisms present and a Lorentzian line shape suggests a form of homogeneous broadening between the spins. As shall be shown later, the variation of the line width can provide information about the delocalization of the electron wavefunction. It is one of the main aims of this paper to examine the delocalization in a-C films and to show how the results of magnetic resonance measurements can be related to size of the sp² cluster. A number of different examples of disordered carbon film are examined.

II Quantifying Clustering and delocalization

Figure 2 shows the variation of the spin density, Ns, and peak-to-peak linewidth, ΔBpp, with negative self-bias for a series of a-C:H films deposited from CH₄ as a hydrocarbon source gas. Two other sets of data reported in the literature are also presented [11, 19]. It is evident that the spin density rises from a low value of ~10¹⁷ cm⁻³ and saturates at ~10²⁰ cm⁻³. The ESR linewidth initially increases, often as the spin density increases, but at higher biases the linewidth decreases. At the higher biases the line shape of the resonance is Lorentzian. At lower biases (<100 V) the spin density is lower and the line shape is Gaussian, suggesting an inhomogeneous broadening due to unresolved hyperfine interaction with hydrogen [17]. In this paper we shall concentrate on films grown at high bias where the spin densities are typically ~10²⁰ cm⁻³, corresponding to 1 at. % of the material present, we may reasonably assume that the ESR signal can be considered as originating from a dilute paramagnetic material. It is therefore possible to apply the theory of Abragam to calculate the contribution to ΔBpp from the dipole-dipole interaction between like spins [20]. Assuming a spin concentration Ns, measured in cm⁻³, the contribution to the dipolar interaction ΔBpp, measured in mT, can be given as

\[ \Delta B_{pp} = \frac{4\pi^2}{9} g\mu_B N_s \]

(1)
This equation has been previously [17] applied to C related centres with a $g$ value of 2.0025 to obtain the expression $\Delta B_{pp} = 8.12 \times 10^{-7} N_s$. Figure 3 shows the variation of $\Delta B_{pp}$ against $N_s$ directly for the three data sets reported in Fig. 2, together with the predicted line width based on dipolar broadening. It is apparent that there is a poor correlation between $\Delta B_{pp}$ predicted and measured for the different spin densities indicating that the line width is not determined by the dipolar broadening.

This reduction in the line width is due to the motional averaging of the electron wavefunction within the sp$^2$ cluster. As the sp$^2$ cluster increases in size, the probability of the electron being associated with a particular atom decreases. This spread out or delocalization of the wavefunction as the cluster size increases is accompanied by a general reduction in the Tauc gap. Further evidence for delocalization comes from measurements of the spin-lattice, $T_1$, and spin-spin relaxation times, $T_2$. Both relaxation times reflect how the magnetization of the magnetic moment relaxes in time. In the case of a $T_1$ process, the relaxation often involves lattice interactions, such as phonon scattering, and often possess a strong temperature dependence [20, 21]. In the case of a $T_2$ process, the spin-spin interaction reflects a loss of coherence, and is often more rapid than the $T_1$ process. Relaxation, in general terms, can be thought of as the spin system interacting with a fluctuating magnetic field of magnitude $\left( B^2 \right)^{1/2}$. These fluctuations may arise from the motion of the spins from hopping between clusters (an intercluster interaction), the dipolar interaction or the exchange interaction due to an effective motion of the spin within the cluster. In the absence of exchange effects $\left( B^2 \right)^{1/2}$, can be related to the half width of the microwave absorption signal $\frac{1}{2} \Delta B_{1/2}$, which in turn is related [21] to the Lorentzian line width $3^{1/2}\Delta B_{pp}$. In such a situation it is possible to re-write Eq. 1 to show the relationship between $\left( B^2 \right)^{1/2}$ and the spin density to give

$$\left( B^2 \right)^{1/2} = 7 \times 10^{-21} N_s.$$  

(2)

Note that this expression is only valid if the fluctuating field is associated with the dipolar interaction. It can be shown [17] that relaxation times can be related to the Lamour frequency $\omega_0$,.
exchange frequency $\omega_c$ and the perturbing frequency $\omega_p = \gamma^2 \left( B^2 \right)^{1/2}$ where $\gamma$ is the gyromagnetic ratio. In the limit when $\omega_p < \omega_c < \omega_0$, it can be shown that

$$\frac{1}{T_1} = \frac{2\omega_p \omega_c^2}{\omega_c^2} \quad \text{and} \quad \frac{1}{T_2} \approx \frac{\omega_c^2}{\omega_p}$$

which leads to

$$\omega_c \approx \omega_0 \left( \frac{T_2}{2T_1} \right)^{1/2} \quad (4)$$

This approach has been successfully employed to examine the delocalization of films grown at different biases. In one case, values of $T_1$ and $T_2$ were reported [17] for a film deposited at a self bias of 540 V, which possessed a spin density of $3.5 \times 10^{19}$ cm$^{-3}$, a Lorentzian line shape and a line width of 0.3 mT. Measurements were performed at X-band microwave frequencies, so $\omega_0$ was about $6.2 \times 10^{10}$ rad s$^{-1}$. Using the relaxation times measured above and equations 3 and 4, provides estimates of $\omega_c = 1.14 \times 10^{10}$ rad s$^{-1}$ and $\omega_p = 1.79 \times 10^{10}$ rad s$^{-1}$. The corresponding value of $\left( B^2 \right)^{1/2}$ is estimated to be 4.3 mT. In the absence of any exchange effects, to obtain a fluctuating magnetic field of magnitude of 4.3 mT from the dipolar interaction would require, via Eq. 2, a spin density in excess of $6 \times 10^{20}$ cm$^{-3}$. Since the measured value of spin density is only $3.5 \times 10^{19}$ cm$^{-3}$, this clearly demonstrates that the spins have clustered for this sample. Correlating the variation of spin density with line width has also been reported in a-CN thin films produced by laser ablation [22]. At low laser power densities the spin density increased form $4.5 \times 10^{20}$ cm$^{-3}$ to $9 \times 10^{20}$ cm$^{-3}$ and that the room temperature linewidth increased from 0.25 mT to 0.38 mT. These experimentally measured linewidth are an order of magnitude smaller that predicted by Eq. (1) suggesting that clustering is taking place in these films as well.

From the discussion above it is clear that understanding the relationship between the line width, relaxation times and spin density is a powerful method in examining delocalisation within a carbon film. It is possible to extend this approach to other material systems such as ultrananocrystalline diamond (UNCD) prepared by microwave plasma enhanced CVD (MWCVD). In a recent study Rovere et al., have measured the relaxation times of nitrogen containing UNCD
films [23]. They reported line widths and relaxation times for a range of temperatures between 10 K and room temperature for films containing zero, 7% and 9% nitrogen in the gas phase. It is important to note that this is not the same as the amount of nitrogen in the sample. Spin densities for all three samples investigated were in the range of \((1.5 \pm 1.0) \times 10^{20}\) cm\(^{-3}\) and application of Eq. 1 would suggest line widths to be in the range of 0.4 – 2.0 mT. At 10 K the experimentally measured values of \(\Delta B_{pp}\) are 0.34, 0.22 and 0.23 mT for each of the three samples. How are these line widths to be interpreted? The spin-lattice relaxation times for the three samples are 1.2, 0.46 and 0.56 \(\mu\)s, respectively, and the spin-spin relaxation times are 3.9, 6.0 and 5.7 ns, respectively. With the aid of Eqs. 3 and 4, it is possible to extract values for the \(\omega_c, \omega_p\) and \(\left(\frac{B^2}{12}\right)^{1/2}\). For the case of the sample with 0% N in the gas phase, \(\omega_c < \omega_p\) with values of \(\omega_c \approx 2.5 \times 10^9\) rad s\(^{-1}\) and \(\omega_p \approx 4 \times 10^9\) rad s\(^{-1}\), respectively suggesting that little or no exchange is occurring in this sample. Here the exchange frequency is not fast enough to average out the dipolar interaction. In the other two samples, \(\omega_c > \omega_p\) with values of 5 \(\times\) \(10^9\) rad s\(^{-1}\) and 3.2 \(\times\) \(10^9\) rad s\(^{-1}\) respectively for the 7% sample and 4.4 \(\times\) \(10^9\) rad s\(^{-1}\) and 3.3 \(\times\) \(10^9\) rad s\(^{-1}\) for the sample with 9% N in the gas phase. The value of \(\left(\frac{B^2}{12}\right)^{1/2}\) for the three samples is 4.6, 5.2 and 5.1 mT, respectively and certainly in the case of the latter two samples, is responsible for the narrowing of the line width below that predicted due to the dipolar interaction. It is believed the ESR active centres may be associated with the grain boundaries rather than the sp\(^3\) grains.

In the case of the UNCD films, there was no strong variation of the spin density with N content in the gas phase. Varying the growth parameters is often a way to vary the spin density and line width – as previously shown in Fig. 2. Figure 4 shows the spin density as a function of argon back pressure for nanostructured amorphous carbon thin films produced by ns pulsed laser ablation from a graphite target in different background pressures of inert gas. At the lowest pressure the areal spin density is 1.82 \(\times\) \(10^{15}\) cm\(^{-2}\) for films deposited under vacuum conditions and this reduces to 0.26 \(\times\) \(10^{15}\) cm\(^{-2}\) for films produced at a pressure of 340 mTorr. The surface morphology of these films has been discussed elsewhere [24] but briefly; films deposited under vacuum or low pressure conditions...
are hard and flat with mirror smooth finishes. Increasing the background pressure a transition from nodular-like, cluster assembled films occurs and at the highest pressures, the films are filamentary with a high surface area. It is worth noting that spin densities quoted are areal spin density and a conversion to a volume spin density is suitable for flat films where the film thickness is known.

For all the films investigated the line shape is Lorentzian and the line width is narrow in the range of 0.18 mT to 0.28 mT. For films deposited at the lowest pressure a film thickness of 35 nm has been measured and this corresponds to a volume spin density of $5.2 \times 10^{20}$ cm$^{-3}$. As such at these high spin densities, estimates of the line width due to the dipolar interacting suggest that the line width should be 4 mT. This is again well in excess of the measured line width (0.22 mT) for this film suggesting that delocalization of the sp$^2$ clustered wave function has occurred in these films as well. An obvious question arises is whether it is possible to know if this delocalization is associated with sp$^2$ sixfold rings or other sp$^2$ cluster configurations. One way to address this issue is through the use of visible Raman spectroscopy, in which the ratio of the intensities of the D band to the G band provides qualitative information about clustering within the sp$^2$ phase. The G band is associated with the $E_{2g}$ vibration found in all sp$^2$ materials, whereas the D band is limited to the breathing mode of six fold rings [25]. As a result any change in the clustering with the sp$^2$ phase will appear as an increase in the $I_D/I_G$ ratio. Figure 5 shows the variation of both the $I_D/I_G$ ratio and the room temperature photoluminescence (PL) intensity for PLA grown films as a function of background argon pressure. At low pressure $I_D/I_G$ approaches zero but steadily rises before levelling off above around 100 mTorr pressure [26]. A similar behaviour is seen in the room temperature PL; an initial increase followed by a levelling off. These two results immediately suggests a strong correlation between PL and Raman and the importance of clustering. However the absence of a strong variation of the spin density or line width with pressure suggests that while delocalisation sp$^2$ clusters exist in these films, they may not be strongly related to sixfold rings.
Conclusions

In conclusion, we have shown that an understanding of electron delocalization within an $sp^2$ cluster is important in understanding some of the electronic properties that disordered carbon films possess. Probing the $sp^2$ phase optically and with magnetic resonance confirms and quantifies the extent of the delocalization and in this paper we have reviewed the evidence for delocalization for three important types of disordered carbon film; namely flat amorphous carbon thin films produced by PECVD, UNCD films produced by MWCVD and nanostructured carbon thin films produced by pulsed laser ablation. In each of the three cases we have described how the ESR spin density, line width and shape and relaxation times provide strong evidence for delocalization of the $sp^2$ cluster wave function.

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References


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Figure captions

Figure 1 Variation of the Urbach energy with Tauc gap for three different $a$-C:H films. Adapted from Ref. 13 and 19.

Figure 2 Variation of (a) spin density and (b) peak-to-peak linewidth for three series of $a$-C:H films with negative self-bias. Adapted from Ref. 13 and 19.

Figure 3 Variation of peak-to-peak linewidth with spin density for the data presented in Figure 2. The dashed line represents the predicted dipolar contribution to the linewidth based on Eq. (1).

Figure 4 Variation of spin density for a series of a-C films produced by pulsed laser ablation in different background pressure of argon.

Figure 5 Variation of Raman $I_D/I_G$ ratio (□) and relative room temperature photoluminescence intensity (●) as a function of background pressure of argon. Adapted from Ref. 26.
Figure 1

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Figure 2

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Figure 3  
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Figure 4

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Figure 5: 

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- $I_D/I_G$ vs. Pressure (mTorr)
- Raman intensity (arb. units)
- PL intensity (arb. units)