Deposition and properties of amorphous carbon phosphide films

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Abstract

Radio frequency plasma deposition has been used to deposit phosphorus doped diamond-like carbon (DLC) films on Si and quartz substrates, using a gas mixture consisting of CH_4 with additions of 0–90% PH_3. XPS studies reveal that the films contain P/C ratios as high as 3:1, although they also contain ~10% H. The degree of P incorporation in the films and the deposition rate is proportional to the PH_3 concentration in the gas phase. SIMS depth profiling shows the films to be homogeneous in composition, although the surfaces are oxidised due to reaction with air. The optical band gap of the films is inversely proportional to the P/C ratio, with values ranging from 2.1 to 2.6 eV. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently there has been much interest in doped diamond-like carbon (DLC) for use in electronic devices. Most previous studies have concentrated on N as a dopant [1,2], and films with <40% N content have been reported [3]. A possible alternative dopant to nitrogen is phosphorus. Additions of PH_3 into the traditional CH_4/H_2 gas mixture have been used to produce n-type chemical vapour deposited (CVD) diamond films [4] but, to date, there have been relatively few reports of P doping of DLC films [5–11]. Veersamy et al. [6] incorporated up to 1% P into DLC (or tetrahedral amorphous carbon) films produced by a filtered cathodic arc method using a red phosphorus-doped carbon cathode. They found that P addition reduced the resistivity of the films by 6–7 orders of magnitude, with no apparent change to the amorphous nature of the carbon films. Capacitively-coupled radio frequency (r.f.) plasma deposition has been used to produce P-doped DLC films [5,7] using PH_3 as a dopant gas producing films with P contents estimated to be ~11 at.%. These films also showed increases in room temperature conductivity of nearly five orders of magnitude. Golzan et al. [8] showed that when films were doped with ~3% P, the dopant destabilised the tetrahedral network in favour of an sp^2 bonded network.

Recently, Kuo et al. [11] studied the effect of doping DLC with larger amounts of phosphorus. The films were produced using r.f. plasma deposition using CH_4 and PH_3 mixtures as the process gases, with PH_3 concentrations up to 21% by volume. This resulted in films which had P/C ratios of up to 0.9, and with such high P content that it was no longer valid to call these films 'doped DLC' — instead, they were termed 'amorphous carbon phosphide'. Micro-combustion analysis showed that the films still contained ~10% H, and secondary ion mass spectrometry (SIMS) indicated that this H was distributed throughout the bulk of the film. Auger electron spectroscopy showed that the surface contained a high proportion of oxygen, suggesting that these films were air sensitive. Laser Raman spectroscopy (LRS) established that the long-range order of the films decreased with increasing P incorporation. The optical band gap (measured by the Tauc plot method [12]) was found to be a complicated function of the P content of the film.

We now extend the range of Kuo et al.'s work. The proportion of PH_3 in the gas phase was increased to ≤90% PH_3, enabling a set of films to be deposited with much higher P/C ratios than has previously been report-

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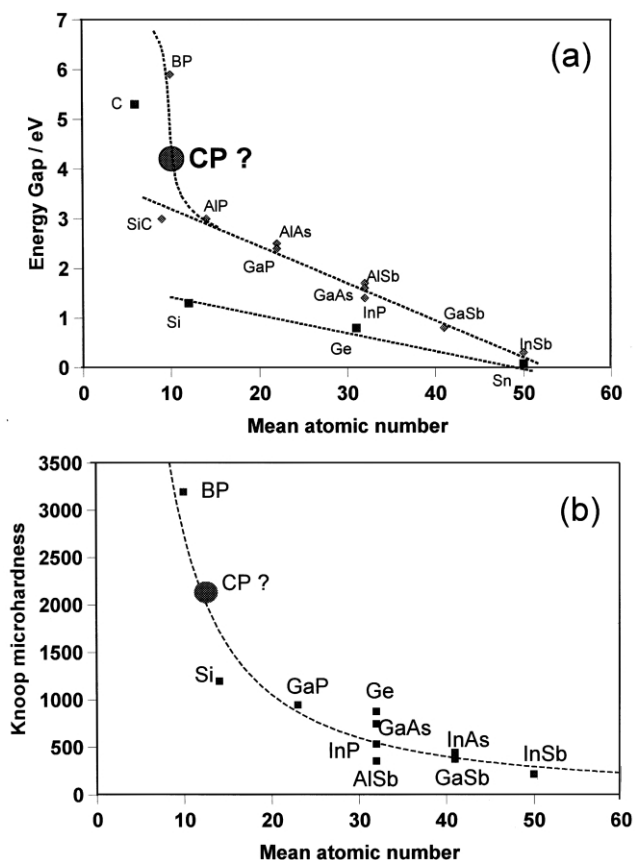E-mail address:* paul.may@bris.ac.uk (P.W. May).

Fig. 1. The properties of various semiconductor materials and binary compounds as a function of their mean atomic number. The estimated position of a hypothetical crystalline compound of carbon phosphide (C_xP_y, with $x=y=1$) is indicated by interpolation between the data points for other known binary phosphides, but this position has a degree of uncertainty depending upon the exact stoichiometry (x, y) of the material. (a) The predicted band gap for the material is between 3 and 5 eV; and (b) the Knoop hardness is predicted to be ~ 2000 GPa.

ed. The aim of this work was ultimately to produce a stable form of carbon phosphide with potentially useful electronic properties. Fig. 1 shows the predicted electronic band gap and Knoop microhardness for a crystalline form of carbon phosphide. Although the exact stoichiometry of the material is not known, the figures show that such a material (if it is stable) should be a mechanically hard wide band gap semiconductor ($E_g \sim 3$ eV), and thus have many potentially lucrative applications in both optoelectronics and engineering.

2. Experimental

Film deposition was carried out in a 13.56 MHz capacitively-coupled radio frequency (r.f.) parallel plate plasma reactor. This reactor is the same as used by Kuo et al. and a full description can be found in reference [11]. The process gases were a mixture of CH_4 and PH_3, with each gas metered independently by mass flow controllers. The total gas flow was 25 sccm, and the

gas pressure was maintained at 25 mtorr. The r.f. power was 40–60 W, adjusted to maintain a constant d.c. self-bias on the lower powered electrode (supporting the substrate) of -150 V. The duration of all depositions was 30 min giving film thicknesses of 0.5–1 μm. The chamber was vented with dry nitrogen to minimise exposure of the films to air.

The substrates were mirror-polished 1 cm^2 B-doped single-crystal Si (100), or for optical absorption experiments, 1 cm^2 mirror-polished quartz. Prior to deposition the substrates were cleaned with propan-2-ol, then acetone, and then dried with dry nitrogen gas. Subsequent surface analysis of the films was performed as soon as possible after the deposition, typically within a few hours, in order to minimise unwanted oxidation or hydrolysis reactions with air. Samples were stored and transported in an evacuated desiccator containing silica gel drying crystals.

The thickness of the films was measured using cross-sectional scanning electron microscopy (SEM). The film composition was analysed with X-ray photoelectron spectroscopy (XPS), which allowed detection (detection limit of $\sim 0.1\%$) and quantification of all elements present with the exception of H. A typical XPS spectrum from one of these films is shown in Fig. 2a. The areas beneath the main elemental peaks for C, O, P, Si, and N were measured and multiplied by the appropriate element sensitivity factor [13] to yield the relative fraction of each element present in the area scanned (Si and N were measured as they would be likely contaminants, but were not observed in the spectra). XPS calibration was confirmed by comparison with results from Auger electron spectroscopy analysis, which gave film compositions to within 5% of those measured by XPS. SIMS was employed in combination with Ga ion etching for depth profiling (see Fig. 2b). SIMS allowed detection (detection limit 1 ppm) of all elements present (including H), but accurate quantification of SIMS data was not possible as the sensitivity to different species can vary over orders of magnitude.

UV/visible absorption spectra were recorded over the range 200–600 nm. The optical band gap was estimated using the Tauc plot method [12]. Further structural information was obtained from LRS using an excitation laser wavelength of 488 nm. The sharpness and contrast of the G-band at approximately 1500 cm^{-1} was taken as a measure of the degree and ordering of C–C bonding within the film.

3. Results and discussion

The films exhibited a range of colours depending upon film thickness and composition. In general, the C-rich films appeared dull, but the P-rich films looked shinier and more silvery. Electron microscopy showed all the films to be smooth on a nm scale. Some of the films showed a tendency to crack and flake, especially
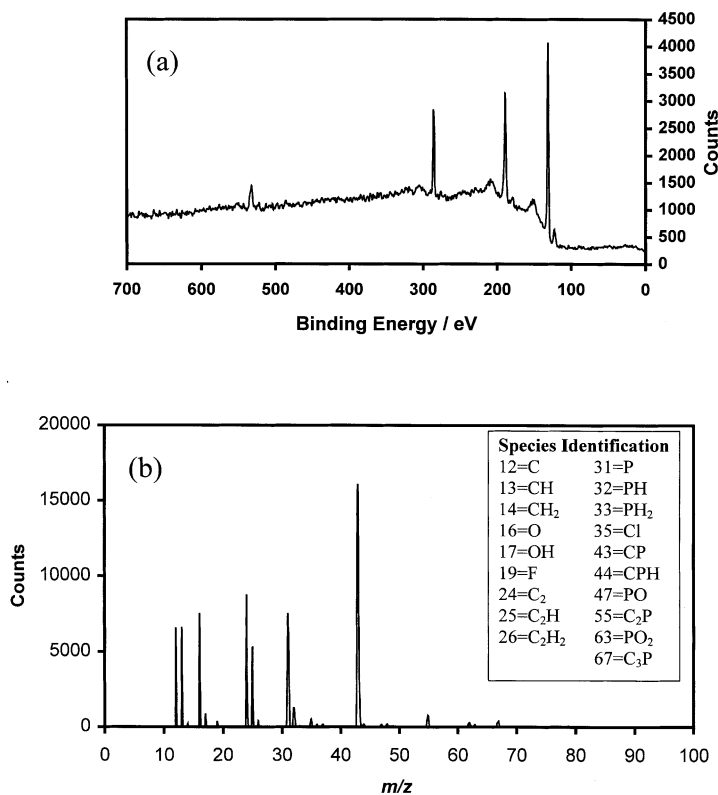
Fig. 2. (a) An XPS spectrum from a 1-μm-thick film having a P/C ratio of 0.97. The four largest peaks are identified as: 133 eV phosphorus 2p, 189 eV phosphorus 2s, 286 eV carbon 2s, and 532 eV oxygen 1s. No Si or N peaks are observed. (b) A SIMS spectrum (m/z is the mass/charge ratio of the secondary ions) from the same film, showing prominent C_xP ($x = 1–3$) peaks, suggesting the presence of direct C–P bonds within the film. Small peaks from PO_x species arise from surface oxidation, and are greatly reduced after the surface layer has been etched away during depth profiling. (Peaks due to Cl and F are observed since SIMS is several orders of magnitude more sensitive to these elements than it is to C and P, so that even ppm level contamination would be detected).

those containing a low concentration of P. As-deposited P-containing films that were left for more than a few hours in air often cracked and delaminated. This could be prevented by either (a) keeping the samples under high vacuum; (b) in an evacuated desiccator; or (c) by thermal annealing in vacuum. This suggests that the as-deposited films are highly reactive to components within air, and are being either oxidised or hydrolysed by O_2 or water vapour, respectively. SIMS analysis of films exposed to air showed the presence of many PO_x and CP_xO_y species at or near the film surface. The results of annealing these films will form the basis of a future publication, but we believe that annealing serves to (a) restructure the film, allowing reactive species to cross-link with neighbouring species, so reducing their reactivity; and (b) allow reactive trapped species, such as PH_3, to diffuse out of the bulk and desorb/evaporate, so preventing them from reacting with O_2 or water vapour from the air.

Fig. 3 shows that there is a linear relationship between the P/C ratio in the as-deposited films (measured by XPS) and the PH_3 concentration in the process gases. The inset in Fig. 3 shows that at low PH_3 concentrations, P is incorporated into the films more readily than C, but

above a P/C ratio of ~2:1 (equivalent to ~67% PH_3 in the gas mixture) this trend for the apparent preferential deposition of P is reversed. Fig. 4 shows the growth rate of the films against the measured P/C concentration in the film. The general trend is for the growth rate to increase with increasing P content, i.e. with increasing PH_3 content in the input gas. Both the above observations can be explained by recalling that deposition in such r.f. plasma systems is a balance between the impacting species adhering to the film and the removal of surface atoms by physical sputtering or even chemical etching [14]. The increased deposition rate may simply be due to the fact that P is heavier than C, and so sputters less easily, or it may be a more complicated function of the actual structure of the surface bonding for the two types of atom and the nature of the impacting species. Nevertheless, from Fig. 3 it is apparent that films grown with the highest PH_3/CH_4 ratio contain P/C ratios of 3:1, i.e. the film composition is CP_3H_x (where $x \sim 0.5$). This is the highest P/C ratio we are aware of in a thin film.

Fig. 5 shows a SIMS depth profile for a film containing a P/C ratio of 0.86 (as quantified previously by XPS). Although the relative magnitudes of the signals
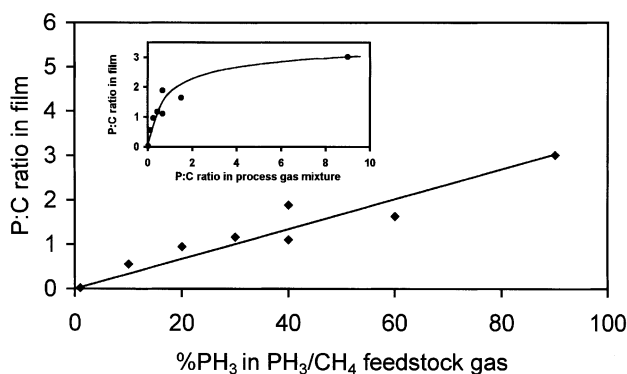
Fig. 3. P/C content of the as-deposited film against the percentage of PH$_3$ in the PH$_3$/CH$_4$ process gas mixture, with a general trend line to guide the eye. The inset shows the same data plotted as a function of P/C ratio in the process gas mixture, again, with a trend curve to guide the eye.

from each species are not quantitative and so cannot be taken as a guide to absolute concentrations within the film, the variation with depth can be used to assess the film homogeneity. Fig. 5 shows that for the entire thickness of the film, the ratio of C/P/H remains roughly constant, showing that the film has a uniform composition throughout. Only at the very surface is there a slight deviation from this composition: there is a slight increase in O concentration and a decrease in H, indicating possible surface oxidation. We note that in all P containing films SIMS reveals the presence of O at low levels (estimated to be $\sim <1\%$ of the film composition), throughout the bulk of the film. This could be due to (a) trace oxygen impurities in the PH$_3$ gas supply; (b) residual oxygen being present in the deposition chamber due to the relatively high base pressure (0.1 mtorr compared to a process pressure of 25 mtorr); or alternatively (c) despite our precautions, the film still undergoing oxidation/hydrolysis during its

brief contact with air, with the porous nature of the films allowing the oxidation to propagate throughout the bulk. Another explanation might be that since the levels of O are only just above the background detection limit for SIMS and XPS, they may result simply from reaction of the film with O-containing diffusion pump oil vapours present in the analysis chambers — and thus be an artefact of the analysis rather than the deposition.

Fig. 6 shows the LRS spectra from various films containing different P/C ratios. As found by Kuo et al., the general trend is for the ordered graphite band (G-band) to become less prominent with a higher concentration of P in the gas phase, and hence in the film. This is consistent with a decrease in the number of C–C bonds as P is added. This could be due to the formation of more C–P bonds in place of the C–C bonds. Evidence for this has been obtained from SIMS analysis of these films which gives a plethora of peaks due to C$_x$P$_y$ species (see Fig. 2b), suggesting that there are definite C–P bonds within the film. Alternatively the decrease in size and increase in width of the G-band might suggest that the effect of P incorporation is simply to amorphise the film and reduce the long range order — in other words the P is simply 'diluting' the carbon network preventing the formation of extensive C–C structures.

The inset in Fig. 7 shows an example of a UV/visible absorption spectrum for a film containing a P/C ratio of 0.55, along with the Tauc extrapolation used to obtain the optical band gap. The curved nature of the absorption profile leads to a fair degree of subjectivity in the position of the extrapolation line, and hence uncertainty in the estimation of the band gap. Also, absorption at wavelengths smaller than the estimated Tauc band gap suggest that these films have a great many mid-band gap states, which again emphasises their amorphous, defective nature. The main part of Fig. 7 shows the
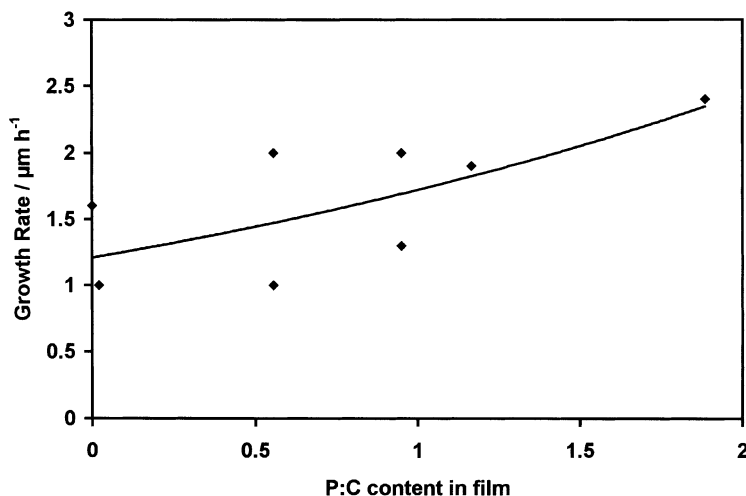

Fig. 4. Growth rate of the as-deposited films plotted against P/C ratio in film.
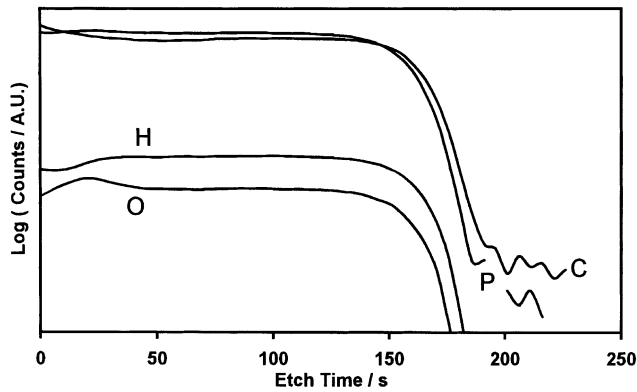
Fig. 5. SIMS depth profile for a film containing a P/C ratio of 0.86. The intensities of each species are not quantitative, and are plotted on an arbitrary logarithmic vertical scale with an offset for clarity. During depth profiling, the ~ 0.75-μm-thick film took approximately 160 s to etch down to the Si substrate.

estimated Tauc band gap for films containing various P/C ratios, and show values similar to those for the P-doped films of Veerasamy et al. [6]. The trend is for the optical band gap to decrease with increasing P/C ratio in the film. This appears to contradict the findings of Kuo et al. [11] who found that for P/C ratios of 0.1–0.9 the optical band gap increased to ~ 3.2 eV. The difference in the two observed trends may be due to the highly air sensitive nature of these high P-content films. Unless extreme care is taken to prevent oxidation/hydrolysis of the films following deposition (as in the present work), the films change in composition and the measured properties become unrepresentative of the original as-deposited film.

Alternatively, we note that the present films were almost certainly deposited at significantly higher ion impact energy than in the previous work. Calculations

based on the model of Field et al. [15] for r.f. reactors similar to the one used here, lead to an estimate of the plasma sheath thickness of ~ 5 mm, which is similar to the ion mean free path at the process pressure of 25 mtorr. Thus, ions will suffer few collisions on their path through the sheath, so the average energy of ions impacting the substrate surface for these conditions can be calculated [15] as ~ 100 eV. Comparing this with the values from Kuo et al.'s work, where a higher pressure (60 mtorr) was used, the ion mean free path is calculated at ~ 1.5 mm which is approximately 3.5 times less than the estimated sheath thickness at this pressure. In the earlier work therefore, collisions within the sheath will have significantly reduced the energy of the impacting ions. Using an estimate for the spread of energies due to sheath collisions based on the model of May et al. [16], we calculate that for Kuo's process conditions the average ion impact energy on the substrate was only ~ 40 eV. Thus, it would not be surprising if the two types of film have different structures and compositions, and therefore exhibit different trends. Fig. 7 illustrates that the band gap of the present films can be tuned in a systematic manner from 2.1 to 2.7 eV — which may have implications if these films are to find application in electronics or optoelectronics.

4. Conclusions

Although we have demonstrated that films can be deposited with P/C ratios of 3:1, these films are still amorphous and contain up to 10% H. Furthermore, these films show considerable air sensitivity and have to be handled with care to avoid contact with air otherwise they rapidly oxidise/hydrolyse and delaminate. In order for such films to have commercial potential, therefore, a method needs to be found to eliminate this air sensitivity. One possible solution may be to anneal the
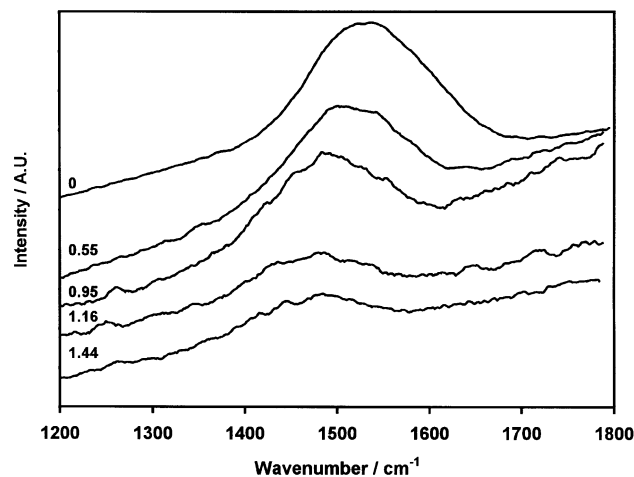

Fig. 6. Laser Raman spectra (488 nm excitation) of films with a range of P/C ratios, as indicated. The spectra have been offset vertically for clarity.
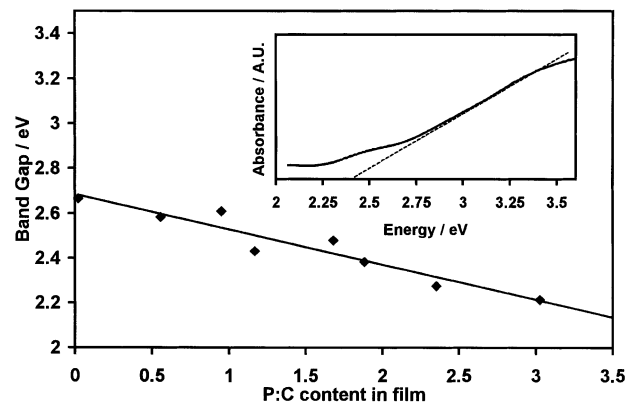

Fig. 7. The optical band gap vs. P/C ratio in film, with a best fit trend line. Inset is an example of a UV/visible absorption spectrum for a film containing a P/C ratio of 0.55, along with the Tauc extrapolation (dashed line) used to obtain the optical band gap.

films in vacuum or in an inert atmosphere, since this may allow the reactive components of the film (presumably isolated P-containing species) to bond with neighbouring species, thereby stabilising the structure. Annealing in this way may also lead to a loss of lighter components, such as H, leaving a film composed solely of C and P. Such a film might then only need to be recrystallised by, say, a high temperature sintering process, to form crystalline carbon phosphide — a material which has yet to be synthesised by normal chemical routes, but as shown by Fig. 1, is predicted to have extraordinary hardness and useful optoelectronic properties [17].

Acknowledgments

References

[1] J. Robertson, C.A. Davis, Diamond Relat. Mater. 4 (1995) 441.

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

[3] M.Y. Chen, P.T. Murray, J. Vac. Sci. Technol. A 16 (1998) 2093.

[4] S. Koizumi, M. Kamo, Y. Sato, et al., Diamond Relat. Mater. 7 (1998) 540.

[5] D.I. Jones, A.D. Stewart, Phil. Mag. B 46 (1982) 423.

[6] V.S. Veerasamy, G.A.J. Amaratunga, C.A. Davis, A.E. Timbs, W.I. Milne, D.R. McKenzie, J. Phys.: Condens. Matter 5 (1993) L169.

[7] A. Helmbold, P. Hammer, J.U. Thiele, K. Rohwer, D. Meissner, Philos. Mag. B72 (1995) 335.

[8] M.M. Golzan, D.R. McKenzie, D.J. Miller, S.J. Collocott, G.A.J. Amaratunga, Diamond Relat. Mater. 4 (1995) 912.

[9] C.A. Davis, Y. Yin, D.R. McKenzie, et al., J. Cryst. Solids 170 (1994) 46.

[10] T.Y. Leung, W.F. Man, P.K. Lim, W.C. Chan, F. Gaspari, S. Zukotynski, J. Non-Cryst Solids 254 (1999) 156.

[11] M-T. Kuo, P.W. May, A. Gunn, M.N.R. Ashfold, R.K. Wild, Diamond Relat. Mater. 9 (2000) 1222.

[12] J. Tauc, in: F. Abeles (Ed.), Optical Properties of Solids, 1972, p. 270.

[13] J. Chastain (Ed.), Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp, 1992.

[14] P.W. May, D. Field, D.F. Klemperer, J. Phys. D: Appl. Phys. 26 (1993) 598.

[15] D. Field, D.F. Klemperer, P.W. May, Y.P. Song, J. Appl. Phys. 70 (1991) 82.

[16] P.W. May, D. Field, D.F. Klemperer, J. Appl. Phys. 71 (1992) 3721.

[17] D.C.W. Shapton, BSc Thesis, School of Chemistry, University of Bristol, Bristol, UK, 2000.