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XPS and laser Raman analysis of hydrogenated amorphous carbon films

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Abstract

Hydrogenated amorphous carbon films were deposited in an RF parallel plate plasma reactor using various values of process pressure (10–50 mTorr) and DC self-bias (0–300 V). The films were then analysed by laser Raman spectroscopy (LRS) at 514.5 nm and X-ray photoelectron spectroscopy (XPS). Values for the ratio of sp^2:sp^3 bonded carbon in the various films were obtained by suitable fitting of the XPS carbon 1s energy peaks, using a three-curve fitting procedure, which recognises a portion of the peak attributable to CO surface bonding. The sp^3 content was found to depend upon the DC self bias (and hence the ion impact energy) during deposition, peaking at a value of 81% at approximately 150 V. The softer films grown at lower DC bias values still had an sp^3 content of approximately 70%. Microcombustion analysis showed that films deposited with low DC bias contained 7 at.% H compared to less than 2 at.% for films deposited at biases greater than 100 V. This high sp^3 content can be explained by H-termination of dangling bonds, suggesting that sp^3 content alone is not a reliable indication of film properties. Curve-fittings of LRS spectra of the films showed that the Breit–Wigner–Fano lineshape is inappropriate for use with hydrogen containing films. Fitting using a Gaussian profile gave precise values for the FWHM, intensity, and Stokes' shift of the G and D-peaks. A linear relationship between the intensity ratio of the D to G peaks and the width of the G peak was found for films deposited at high DC bias (with low H content), but not for films deposited at low DC bias. This is consistent with the increased H content of the films causing a change in the elastic constants and/or affecting the stress levels within the films.

Keywords: Diamond-like carbon; Laser Raman analysis; XPS; Film composition

1. Introduction

Diamond-like carbon (DLC) thin films are becoming increasingly important in many forms of industrial applications, including wear-resistant coatings for hard-disk drives and optical components, as well as in semiconductor devices [1–3]. However, the term DLC covers a range of materials with properties that can vary from those similar to graphite to those approaching those of natural diamond. Hydrogen-free DLC films (also known as amorphous carbon films, a-C [4], are believed to consist of a mainly graphitic sp^2 carbon matrix containing nm-sized clusters of sp^3 diamond-like carbon. Hydrogenated DLC films (also known as hydrogenated amorphous carbon films, a-C:H) add yet more degrees of complexity to the possible structure of the films [5]. One of the most crucial factors determining the film properties is the ratio of sp^2:sp^3 bonded carbon. In a-C films, laser Raman spectroscopy (LRS) can be used to determine this ratio [6], but in a-C:H films more sophisticated techniques such as electron energy loss spectroscopy (EELS) or X-ray photoelectron spectroscopy (XPS) often need to be used. In this paper we use XPS in conjunction with LRS to study the sp^2:sp^3 ratio in a-C:H films grown with a variety of ion impact energies and deposition conditions, and to gain an insight into the structure and bonding within these films.

2. Experimental

a-C:H films were deposited onto single crystal Si (100) substrates using a capacitively-coupled radio frequency (RF) parallel-plate plasma reactor. The process gas was methane (CH_4) at a flow rate of 30 sccm and a pressure ranging from 10–50 mTorr. RF power was used to strike a plasma and the ions were then accelerated onto the lower electrode by the DC self-bias. The substrate sat on the lower electrode, and the value of the DC bias in this system thus gives an approximate

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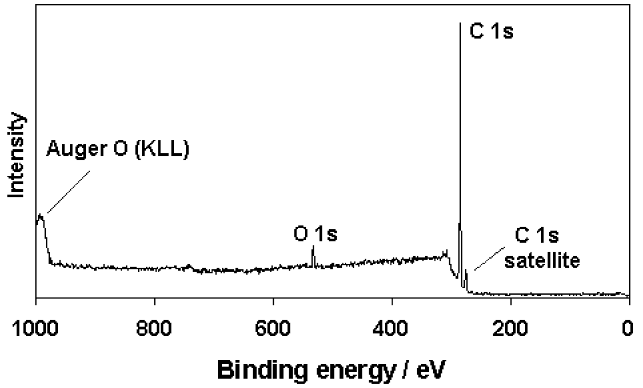

Fig. 1. An example of a wide XPS spectrum from an a-C:H film grown at 10 mTorr and with a DC bias of -100 V.

measure of the average impact energy of the carbon-containing ions upon the Si surface [7,8]. The a-C:H films were deposited for 30 min, yielding an approximate thickness of 0.5 μm, as measured by cross-sectional SEM. The films were smooth, and varied in hardness depending upon the DC bias used. Films deposited at DC bias values less than 100 V were soft and easily scratched, whereas those deposited at higher biases could not be scratched with tweezers.

XPS was performed using the Mg K-α-line, which analysed approximately the top 40 Å of the film. The spectra were dominated by the C 1s peak at approximately 285 eV (see Fig. 1). Calibration experiments using CVD diamond and graphite powder showed that the C 1s peak from diamond was located at 287 eV with a full-width half-maximum (FWHM) value of 1.1 eV, and that the C 1s peak from graphite was located at 284 eV (FWHM = 0.98 eV). The 3 eV separation between these two peaks is largely due to charging effects on the insulating diamond film, but is also partly due to the different chemical environment of the C 1s electron with respect to the hybridisation of the orbital. Also present was the O 1s peak at 531 eV, due to surface chemisorbed oxygen species. If it is assumed that all the oxygen atoms in these films are of the same hybridisation, then the difference in the energies of the O 1s peak in the diamond and graphite spectra should be equal to the shift of the diamond C 1s, due to charging effects. This difference was used to give an estimate of the offset due to charging, and was used to correct subsequent spectra. We note that this correction assumes that the surface charging is spatially homogeneous, which we believe is valid given the uniformity of the film deposition.

The lineshapes of the O 1s and C 1s peaks give information about the chemical bonding environment, and fitting these peaks to suitable functions allows this bonding information to be extracted. Previous workers [9] have fitted two Voigt curves, one corresponding to sp^2 hybridisation with a FWHM the same as that for graphite, and the other corresponding to sp^3 hybridisation with a FWHM the same as that measured for diamond. The ratio of Gaussian to Lorentzian functions comprising the Voigt profile should be the same as the ratio needed to get the best fit in the calibration spectra of diamond and graphite (after compensation for the charging effects). However, this method does not account for any C bonded to O (which might arise as a result of hydrocarbons, water, oxygen and other adsorbates picked up when the film was transported through air), and when applied to our spectra gave inconsistent values for the sp^2:sp^3 proportion. Merel et al. [10] attributed a peak at 285.6 eV which was 1.3 eV higher in energy than that of their sp^3 peak (E_{sp3}) to C bonded to O. We have therefore included this third curve to the fitting procedure, centred at an energy of ($E_{sp3}+1.3$) eV.

The curve fitting was done using XPSpeak 4.0 software, with Newton's iteration method and 300 iterations. The three-curve fitting procedure resulted in a much better fit to our data than the previous two-curve procedure. Fig. 2 shows an example of an XPS curve fitted using the (a) two-curve and (b) three-curve

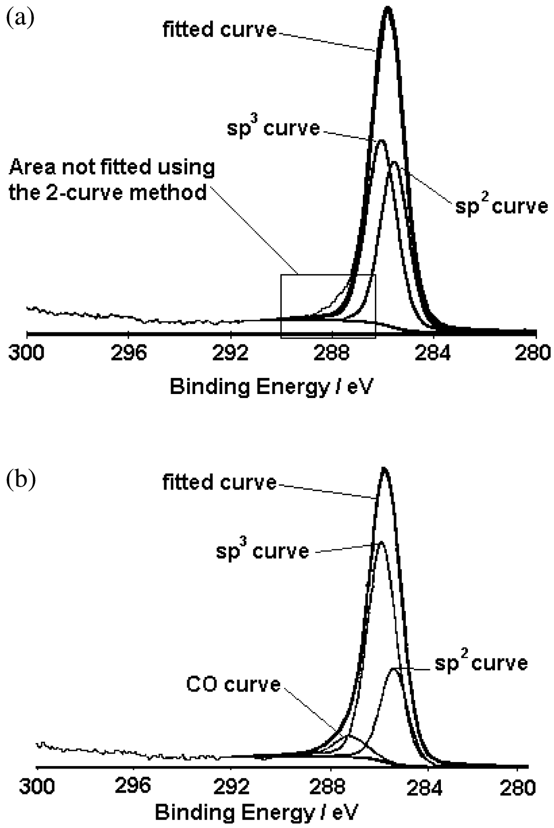

Fig. 2. Example of the fits of the C 1s peak from an XPS spectrum from Fig. 1, fitted using (a) the two-curve method and (b) the three-curve method.

methods. For our data, all curves were defined as 20% Lorentzian, 80% Gaussian (as used by Leung et al. [9]). The sp^3 peak was fitted allowing both the FWHM and the binding energy to vary, whilst the sp^2 peak had a variable FWHM but a position fixed at $(E_{sp3}-0.5)$ eV [9]. The C–O adsorbate peak was also fitted with a variable FWHM, but its energy was fixed at $(E_{sp3}+1.3)$ eV. It was found that the FWHM of both the sp^3 peak and the sp^2 peak tended to be wider than those from diamond and graphite. This has been attributed to environments within the DLC films with mixed sp^2 and sp^3 bonding. The FWHM of these peaks tended towards the values found by Leung et al., which were 1.4 eV for sp^3 carbon and 1.3 eV for sp^2 carbon. One feature of XPS analysis, which should be highlighted is that it is only the top few surface layers which are analysed. Therefore, any sp^2:sp^3 ratios calculated using XPS data will represent the surface values, and not necessarily those in the bulk. It is known that for ta-C films the surface layers are often slightly richer in sp^2 carbon than the bulk, and this may be true for a-C:H films also.

Microcombustion analysis was performed on three films grown with low, medium and high DC bias values to determine the H content of the film. For these experiments, the films were grown onto glass slides covered in Al foil. The Al foil was then dissolved in concentrated HCl (11.56 M) leaving inert DLC flakes floating on the surface. The mixture was filtered, washed with water and the flakes were left to dry overnight. Sufficient deposition runs were performed to obtain a few mg of solid DLC. Microcombustion then gave the ratio of C:H within the film to within 1%.

LRS was performed using a Renishaw 2000 spectrometer operating at a wavelength of 514.5 nm. The spectra were fitted using both Gaussian and Breit–Wigner–Fano (BWF) [11] lineshapes for both the G and D bands. The BWF lineshape is commonly used to provide an estimate of the sp^2:sp^3 ratio in hydrogen-free a-C films (from the asymmetry of the G peak in the absence of a D peak). Curve fitting with the BWF line shape has been used to measure this asymmetry, and to quantify it using a variable called the skewness factor, Q (where $1/Q \sim 0$ corresponds to a pure Lorentzian line shape). Gilkes et al. [12] have shown that films high in sp^3 content display much more symmetrical peaks, characterised by large (negative) values of Q. However, use of the BWF lineshape to fit G-peaks in LRS spectra of a-C:H films has yet to be reported.

3. Results and discussion

The percentage of sp^3 hybridised C in films grown at 10 mTorr as a function of deposition DC bias is shown in Fig. 3. The sp^3 content has a constant high value of approximately 70% for low biases, and then rises to a maximum at approximately 150–200 V, before rapidly decreasing at yet higher bias values. This can be explained, since at low DC bias values the ion impact energy is too small to disrupt the carbon network, and also too small to remove H from the film by sputtering. Thus, the films probably consist of a relatively soft hydrocarbon polymer. The surprisingly high sp^3 content could be explicable if many of the sp^3 carbon bonds are terminated by hydrogen atoms, rather than bonded to other C atoms. As the DC bias is increased, the ions now have sufficient energy to sputter H, and also to sub-plant. The C network close to the surface then rearranges itself to form C–C sp^3 bonds, producing a hard diamond-like film. At even higher ion impact energies, the C network is sufficiently damaged throughout the bulk that subsequent long-range reconstruction results in predominantly large graphitic sp^2 structures. These results are consistent with the findings of Fallon et al. [13] who found the highest sp^3 ratio in their hydrogen-free a-C films occurred at an ion impact energy of $\sim$100 eV. However, Fallon et al. found that the sp^3 content dropped sharply at ion impact energies of less than 100 eV. The results are also consistent with the models of Angus and Hayman [14] and Robertson [15], who showed that the kinetic energy of ions impacting the substrate at approximately 100 eV is dissipated into a very small near-surface volume, leading to preferential sp^3 structuring. Studies of a-C films grown by pulsed laser ablation of graphite also found that optimal conditions for growth of high quality DLC films with $>$90% sp^3-bonded C atoms involved impact energies $\sim$100 eV [16].

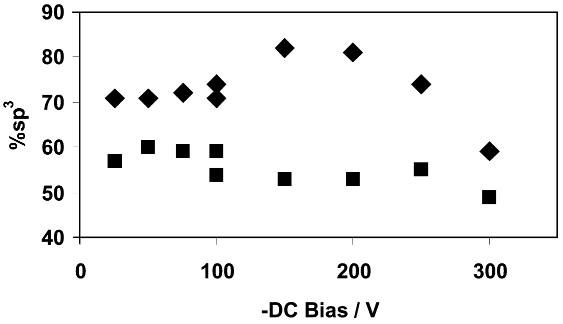

Fig. 3. The percentage of sp^3 hybridised C in films grown at 10 mTorr as a function of (negative) deposition DC bias as measured by XPS. The diamond-shaped markers show the values derived using the three-curve fitting method, and for comparison, the square-markers show the values obtained using the two-curve method of Leung et al. [9].

Microcombustion results provide extra evidence for this mechanism. Films deposited at a bias of −25 V contained considerably more H (7%) than those deposited at −150 V (3%) and −300 V (2%). This is consistent with the findings of Tamor et al. [17], who also found an increase in H content with decreasing DC bias in a-C:H films. Thus, for a-C:H films the conclusion

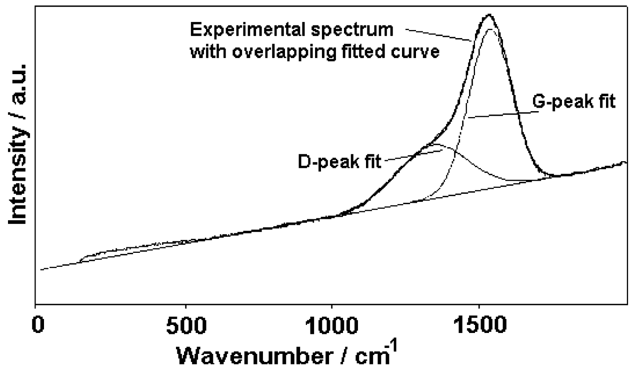

Fig. 4. A typical laser Raman spectrum (514.5 nm excitation) from an a-C:H film showing the prominent G peak (1580 cm^{-1}) and smaller shoulder (1350 cm^{-1}) due to the D band. The fitted curves are also shown.

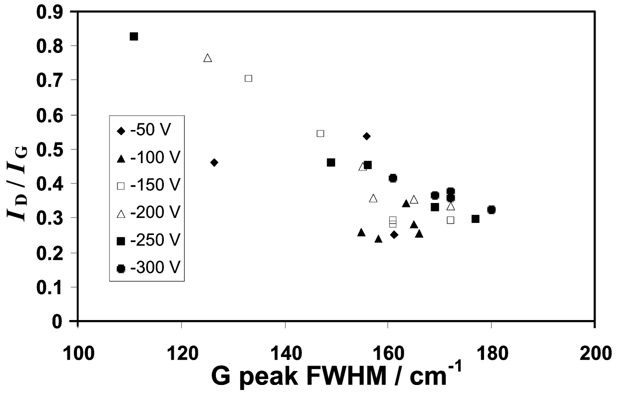

Fig. 5. The ratio of the intensities of the D peak, I_D, and G peak, I_G, plotted against the fitted G peak FWHM, for a number of different DC bias values. Different values for I_D/I_G and G peak FWHM were obtained for each DC bias value by changing the process pressure from 10–50 mTorr, which affected the ion impact energy and therefore the structure and composition of the films.

is that the sp^2:sp^3 C ratio alone is not a reliable estimate of the film structure or properties, since the sp^3 C could be bonded to either C or H.

Fig. 3 also shows a comparison of the sp^3 values that are obtained using the two-curve fitting method of Leung et al. [9]. By comparison with sp^3 values derived from the three-curve fitting method, these values are less precise, had greater day-to-day variability, and are not consistent with other experimental findings, such as the trends with hardness and H content. Also, the two-curve data cannot be rationalised using the theoretical models of film growth mentioned above. This suggests that the three-curve fitting method is a more precise way of obtaining sp^2:sp^3 ratios than previous methods.

A typical laser Raman spectrum from an a-C:H film is given in Fig. 4, showing the prominent G band (centred approximately 1580 cm^{-1}) and a smaller underlying D band shoulder (centred approximately 1350 cm^{-1}). The presence of the D peak in most of the spectra from these a-C:H films prohibited the use of a single BWF lineshape to quantify the sp^2:sp^3 ratio. However, some of the films that were grown at the lowest bias values gave spectra with only one G peak. These could be fitted to a BWF lineshape, but gave Q values of -1×10^{18}, so that $1/Q\sim0$. This suggests that the BWF fitting method is not appropriate for hydrogen containing a-C:H films due to their highly symmetrical G peak shape. A possible reason for this is that the presence of H within the films stabilises graphitic clusters by terminating dangling bonds on the aromatic rings.

Tamor et al. [17] state that for their spectra two Gaussians functions faithfully reproduced the peak structure, and therefore more elaborate line shapes were not needed. Following this procedure, the individual G and D peaks from our spectra were fitted with Gaussian line shapes to quantify their respective FWHM and peak heights. A plot of the ratio of the intensities of the D peak, I_D, and G peak, I_G, to the fitted G peak width is shown in Fig. 5, for a number of different DC bias values. Schwan et al. [18] have proposed that the G peak width is partially determined by the graphitic cluster size, and so a plot of I_D/I_G vs. G peak width should give a straight line. It can be seen in Fig. 5 that for films deposited at DC bias values greater than approximately -150 V, a linear relationship between G peak width and the I_D/I_G ratio is indeed observed. This suggests that at high ion impact energies the width of the G peak is strongly affected by the presence of aromatic clusters. However, for films deposited at DC bias values lower than -150 V, the data points are more clustered and show less of an obvious trend. This suggests that at these lower ion impact energies the graphitic clusters have much less influence upon the G peak width. One reason for this might be that the graphitic clusters now have H-terminated aromatic groups, rather than extended networks of graphene sheets. Another reason could be that the increased H content is affecting the elastic constants of the film and altering the stress levels. Schwan et al. also proposed that a-C:H films with G peak linewidths broader than 45 cm^{-1} have small aromatic clusters with size less than 10 Å. In our films, the very broad G peak width and I_D/I_G ratio of less than one, suggest that any aromatic clusters are less than 10 Å in size, and are thus probably composed of localised benzene-like or naphthalene-like structures.

4. Conclusions

We have shown that XPS and laser Raman spectroscopy can be used to derive structural information about the localised bonding with a-C:H films. The fact that films with apparently high sp^3 contents can have poor mechanical properties has been found to be due to the high H content of these films. This highlights the fact that sp^3 content alone is not a reliable measure of the properties of hydrogen containing DLC films. This might also hold true for DLC films containing other elements, such as those doped with N or P. We have also demonstrated use of the three-curve fitting method for XPS data gives precise values for sp^2:sp^3 ratios within the films, and gave values consistent with results from microcombustion and apparent hardness. Thus, we feel that compared to previous fitting methods, the three-curve method is a much more reliable and accurate method to reliably obtain such data from a-C:H films.

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