

## The effect of ion energy on the deposition of amorphous carbon phosphide films

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### Abstract

A detailed study has been performed of diamond-like carbon films containing high concentrations of phosphorus deposited onto a variety of substrates. These ‘amorphous carbon phosphide’ films have been grown using RF plasma CVD at varying ion impact energies by changing the DC self bias on the powered electrode. X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS) have been used to determine changes in the chemical composition and chemical bonding structure of these films. UV/visible absorption spectroscopy employing the Tauc-plot method has determined the band gap change with varying ion energies. Results show the enhancement of C–P bonding ratios with deposition under high average ion energies, and also with the dramatic reduction in contaminant elements (O, H).

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### 1. Introduction

In the last 10 years the potential for materials similar to diamond-like carbon (DLC) has begun to be exploited. DLC is already used in several everyday applications, such as wear resistant coatings for razor blades and hard coatings for hard disk drives. There is now emerging interest in its application as an electronic material. However, in order to form useful semiconducting devices, the DLC films must be doped to control their conductivity. Doping with phosphorus to make n-type materials has been demonstrated in CVD diamond films [1], but, to date, there have been few studies on the effect of the addition of P to DLC films [2–7]. Most of the studies concerned have relatively low doping levels, of P, from ppm up to a few %, however, we recently reported [8] a CVD method that allowed carbon films to be deposited with P:C ratios up to 0.9. With such high P incorporation, it was no longer valid to call these CP<sub>x</sub> films ‘phosphorus doped DLC’; instead we described them as ‘amorphous carbon phosphide’. These films, however, were not crystalline, and still contained traces of O, as well as up to 10% H. Later work [9]

produced amorphous CP<sub>x</sub> films with P:C ratios up to 3:1, and with an optical band gap that was seen to decrease with increasing P content. However, the H content remained at approximately 10%, and careful handling of the samples was required to minimise their oxidation in air.

As well as having interesting electronic properties in their own right, the amorphous CP<sub>x</sub> films offer the possibility of achieving a crystalline version of carbon phosphide. Such a material may have properties similar to those of related phosphides and nitrides, such as GaP, GaN, BP, SiN, C<sub>3</sub>N<sub>4</sub>, etc., along with many potential applications in opto-electronics and hard coatings. The first step toward this goal is to optimise the CP<sub>x</sub> film deposition conditions in order to increase the number of C–P bonds within the structure. Theoretical studies [10,11] show that the crystalline carbon phosphide (of formula C<sub>3</sub>P<sub>4</sub>) would be likely to have a sp<sup>3</sup>-bonded structure. Thus, to make crystalline carbon phosphide, we require a dense network of C–P bonded material with high sp<sup>3</sup> content. However, this poses a problem, since Golzan et al. [5] showed that when DLC films were doped with small amounts of P, approximately 3%, the dopant destabilised the tetrahedral network in favour of an sp<sup>2</sup> bonded network. To counteract this ‘graphitisation effect’, it might be possible to optimise the ion

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impact energy during deposition to favour  $sp^3$  bonding. It is well known [12] that ions with impact energies of approximately 100 eV produce DLC films with the highest  $sp^3$  content. At these energies the ions can both sputter away H atoms efficiently, as well as subplant to cause  $sp^3$  bond formation in the uppermost layers. Below approximately 100 eV the ions do not have the sufficient energy to either sputter away H or to subplant, and the films that are deposited resemble long chain hydrocarbon polymers. At ion impact energies greater than 150–200 eV the ions can implant deeper into the film structure causing long range damage leading to graphitisation, and at even higher energies the majority of the film material may be lost through sputtering. This mechanism should also hold true for optimising the  $sp^3$  content of carbon phosphide films, but with the added complication of maintaining the correct C:P ratio. We therefore require incoming ions with sufficient kinetic energy to subplant, to form enough C–P bonds with high  $sp^3$  bonding character, and to sputter away H. As such, this paper reports the results of experiments which studied the effect of the variation of ion energies on the properties of the deposited  $CP_x$  film.

## 2. Experimental

Film deposition was carried out in a 13.56 MHz capacitively-coupled radio frequency (RF) parallel-plate plasma reactor, and a full description can be found in reference [8]. 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 30 sccm, the gas mixture was 25%  $PH_3$  and 75%  $CH_4$ , and the gas pressure was maintained at 20 mTorr. The RF power was 10–350 W, which was adjusted to maintain a constant (negative) DC self bias on the lower powered electrode (supporting the substrate) of between 25–350 V. The top-hat chamber design, with cathode/anode electrode area ratios of approximately 3:1, was such that under these reaction conditions the DC bias was a good measure of the average ion energy [13]. The duration of all deposition runs was 20 min, giving film thickness of approximately 200–600 nm (measured by an imaging focused ion beam). 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. Surface analysis of the films were 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.

X-ray photoelectron spectroscopy (XPS) was used to allow accurate quantification of the film composition and stoichiometry; the quantification of the instrument was checked in a previous study with Auger electron spectroscopy. XPS allows accurate quantification of all elements present with the exception of H. Elements detected were C, O and P. Signals from potential contaminants (such as N, Si, etc.) were not observed in any films used in this study.

Secondary ion mass spectrometry (SIMS) was used to identify the spatial uniformity of prepared films at the surface and in depth. As it is capable of detecting atomic and molecular ions, the relative level of the  $CP^-$  ion from different samples could be compared with the levels of other ions. It must be emphasised that SIMS is only semi-quantitative, and that the relative sensitivities of this method to various ions can vary by several orders of magnitude. SIMS depth profiles using  $Ga^+$  ion sputtering to etch through the film, allowed the variation of the elemental composition throughout the film, to be determined.

UV/visible absorption spectra was recorded over the range 200–600 nm on a Perkin–Elmer Lambda Bio 10 UV/VIS spectrometer, with a spectral resolution of 2 nm. The optical band gap was estimated by using the Tauc plot method [14].

## 3. Results and discussion

The films were examined using scanning electron microscopy (SEM) and by secondary electron emission from the SIMS and found to be smooth on a nm scale. Films that were left for a few hours in air tended to crack and delaminate, hence the requirement to keep them in a vacuum desiccator prior to analysis. This was especially true for films deposited at low DC bias (and hence lower average ion energy). The films were coloured in appearance; those deposited with DC biases, of up to  $\sim 250$  V, had a green/red appearance; whereas films deposited at higher bias values were either transparent or silver in colour. Imaging focused ion beam analysis was used to measure the film thickness. This showed that films deposited at bias values greater than 250 V were much thinner (typically 200–400 nm) than films grown at lower biases (typically  $> 500$  nm).

Fig. 1 shows a typical SIMS depth profile from a  $CP_x$  film. There is some oxygen present at the surface (we estimate the top few atom layers from the SIMS depth profile) due to oxidation of the film upon exposure to air. The presence of a signal from CP provides evidence for direct C–P bonding within the film. Apart from the surface oxidation effects, the CP counts increase going deeper into the film and then plateau, showing that below a depth of approximately 40 nm the film composition is uniform. The H content in the films grown at high bias values approaches the background

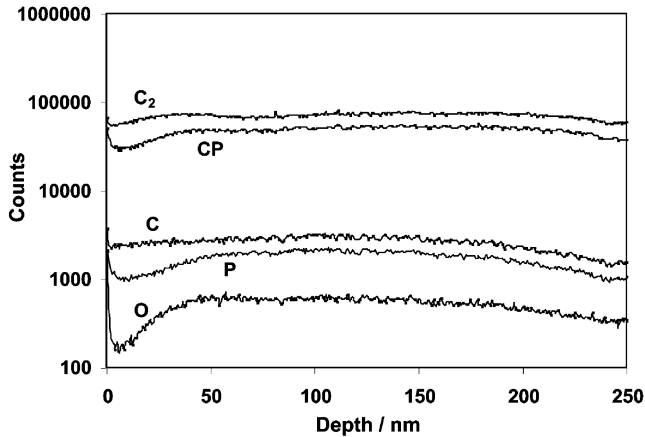


Fig. 1. A typical (negative ion mode) SIMS depth profile from a  $CP_x$  film grown at a DC self bias of  $-300$  V. Note that SIMS is at best semi-quantitative, since the absolute magnitudes of the signals cannot readily be calibrated. Thus, the heights of the signals cannot be compared relative to each other— just the variation in signal for each individual element with depth, shown as the percentage of the full-scale deflection of the channeltron for each ion. The surface has a different composition to the bulk due to oxidation/hydrolysis reactions with air. Below the surface the bulk has a fairly uniform composition with levels of H below the background detection limit.

level, showing that the films are virtually H-free. This is consistent with the DLC growth mechanism of Robertson et al. [12], where energetic incoming ions may sputter away hydrogen. Evidence for this is seen when the depth profiles are analysed. Since the composition of the bulk is relatively uniform below the point at

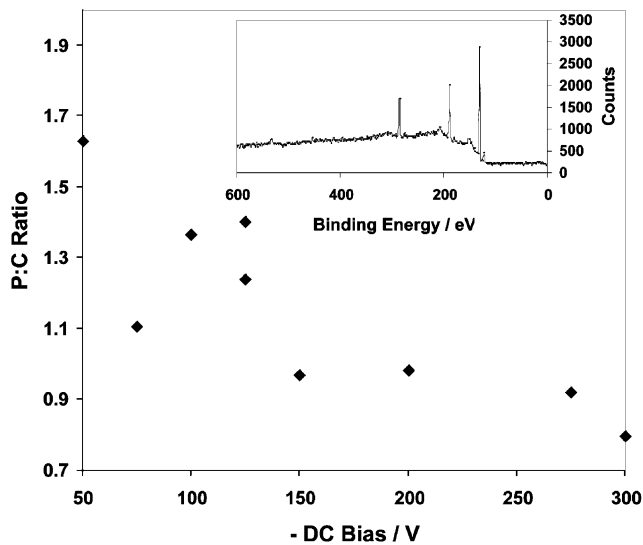


Fig. 2. P:C ratios measured by X-ray photoelectron spectroscopy (XPS) plotted against the (negative) DC bias voltage. Inset is a typical XPS spectrum, for a film grown at a DC self bias of  $-150$  V (corresponding to an average ion impact energy of approx  $150$  eV). The peaks present are:  $\sim 130$  eV P ( $2p_{3/2}$ ),  $\sim 192$  eV P ( $2s$ ),  $\sim 285$  eV C ( $1s$ ),  $\sim 530$  eV O ( $1s$ ).

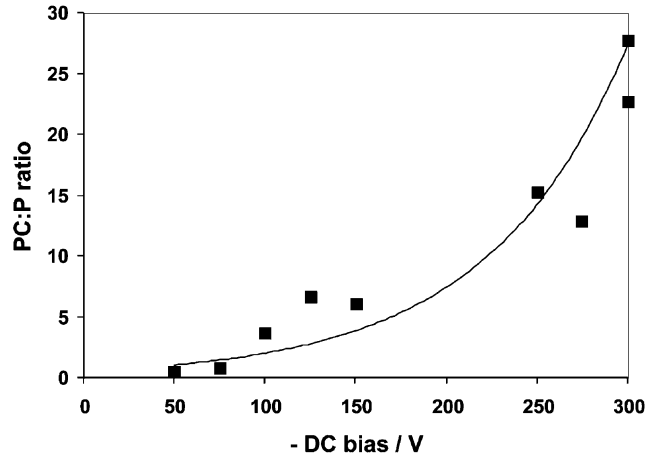


Fig. 3. CP:P ratios for films measured from SIMS depth profiles plotted against deposition DC bias.

which the CP signal plateaus, the ratio of P:C and PC:P counts (taken at or below this point) can give an indication of the type of bonding present in the films as a function of deposition conditions. Fig. 2 shows a plot of the P:C ratio measured by XPS of films grown at various bias voltages. The amount of P incorporated into the film decreased as the DC bias increased (became more negative). The reason for this is unclear, but it may be due to preferential sputtering of weakly bonded  $PH_x$  ( $x=0-3$ ) species from the surface compared to the more strongly bonded  $CH_x$  ( $x=0-3$ ) species. Fig. 3 shows that the PC:P ratio increases with increasing DC bias. The PC:P ratio is not a direct measure of absolute concentration, but rather a measure of relative counts, and gives an idea of the proportion of P that is directly bonded to C in the film, as opposed to phosphorus that is present as individual non-bonded P atoms or  $P_x$  clusters. Fig. 3 shows that at higher DC bias values, even though the absolute concentration of P is decreasing within the film, the P that remains is that which is bonded to C. Therefore, increasing the ion impact

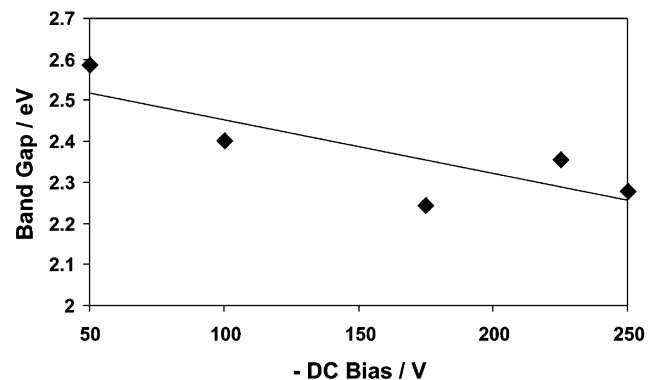


Fig. 4. The optical band gap of several films measured by the Tauc-plot method [14] as a function of deposition DC bias.

energies does, indeed, increase the C–P bonding within the film.

Fig. 4 shows the optical band gap of several films plotted against the DC bias. It is observed that the optical band gap decreases with increasing DC bias. This is consistent with the theoretical predictions [10,11] that fully  $sp^3$ -bonded crystalline carbon phosphide should have metallic character, (i.e. zero band gap), and suggests that increasing the ion impact energy leads to a higher degree of  $sp^3$  bonding in the films.

#### 4. Conclusions

$CP_x$  films have been grown that are virtually hydrogen free (below the ppm level detection limit of the SIMS), and virtually oxygen free. Increasing the DC bias, and hence the ion impact energy, during deposition has been shown both to increase the direct C–P bonding (by a mechanism involving preferential sputtering of non-bonded P species), and possibly to increase the degree of  $sp^3$  bonding within the film leading to a reduction in optical band gap. This holds out the promise that further optimisation of growth parameters may produce films with even higher degrees of  $sp^3$  C–P bonds, and maybe, eventually, the elusive crystalline carbon phosphide material itself. Other process parameters that have still to be investigated include the deposition temperature—since deposition onto a heated substrate may favour film crystallisation in situ—and post-deposition annealing in vacuum or inert atmospheres.

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