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Towards new binary compounds: Synthesis of amorphous phosphorus carbide by pulsed laser deposition

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ABSTRACT

We have recently undertaken comprehensive computational studies predicting possible crystal structures of the as yet unknown phosphorus carbide as a function of composition. In this work, we report the synthesis of amorphous phosphorus–carbon films by pulsed laser deposition. The local bonding environments of carbon and phosphorus in the synthesised materials have been analysed by x-ray photoelectron spectroscopy; we have found strong evidence for the formation of direct P–C bonding and hence phosphorus carbide. There is a good agreement between the bonding environments found in this phosphorus carbide material and those predicted in the computational work. In particular, the local bonding environments are consistent with those found in the β-InS-like structures that we predict to be low in energy for phosphorus:carbon ratios between 0.25 and 1.

1. Introduction

There has been much interest in carbon nitride since the prediction that β-C_3N_4 should have a hardness equal to or greater than diamond [1]. However, synthesis of this material has proven to be difficult and success to date has been limited to mixtures of the α- and β-C_3N_4 phases in the form of nanoparticles and nanocrystals embedded in an amorphous network [2–4]. For this reason, in recent work we have used computational approaches to study related materials, including carbon nitrides with a lower nitrogen:carbon ratio [5]. We have also undertaken a detailed computational study of possible crystalline forms of phosphorus carbide [6–9]. By studying structures for a range of compositions, we have been able to predict the preferred local bonding environments of carbon and phosphorus as a function of composition [6]. When the phosphorus content is low, the preferred type of structure is phosphorus-doped graphite (Fig. 1a), in which the carbon is sp^2 hybridised, the phosphorus is two-coordinated and, formally, there are delocalised electrons. However, when the phosphorus content is $\gtrsim 20$ at%, the preferred structures contain sp^2 hybridised carbon and four-coordinated, formally hypervalent phosphorus (Fig. 1b and c). We call structures with these local bonding environments β-InS-like, regardless of stoichiometry, because for the 1:1 stoichiometry the structure with these local bonding environments has the same space group and atoms at the same special positions as the β-InS structure. These structures can also be considered as phosphorus-substituted graphite with P–P bonds between the phosphorus atoms in adjacent layers. In these "pillared" or β-InS-like structures, it is also possible for phosphorus to occupy the three-coordinate sites and carbon the four-coordinate sites, but this is higher in energy than the reverse. Another type of structure considered in the computational studies is pseudocubic-like, in which the carbon is sp^3 hybridised and the phosphorus is three-coordinated (Fig. 1d). Structures of this type generally have a relatively high energy of formation from the pure elements, although they may be the preferred type of structure when the phosphorus content is high (>50 at%) [6]. We are now interested in testing these theoretical predictions of preferred local bonding environments by synthesising phosphorus carbide materials.

Phosphorus-doped carbon and phosphorus carbide films have been previously produced by ion implantation of trimethylphosphine into polyethylene [10], RF plasma CVD [11–13], cathode arc deposition [14], pulsed laser deposition [8] and magnetron sputtering [15]. However, the formation of crystalline phosphorus carbide has not been observed. These experimental reports suggest that the incorporation of small quantities of phosphorus into carbon favours sp^2 hybridised carbon over sp^3 [16,17], consistent with our predictions. Combined experimental and computational studies of fullerene-like phosphorus carbide have

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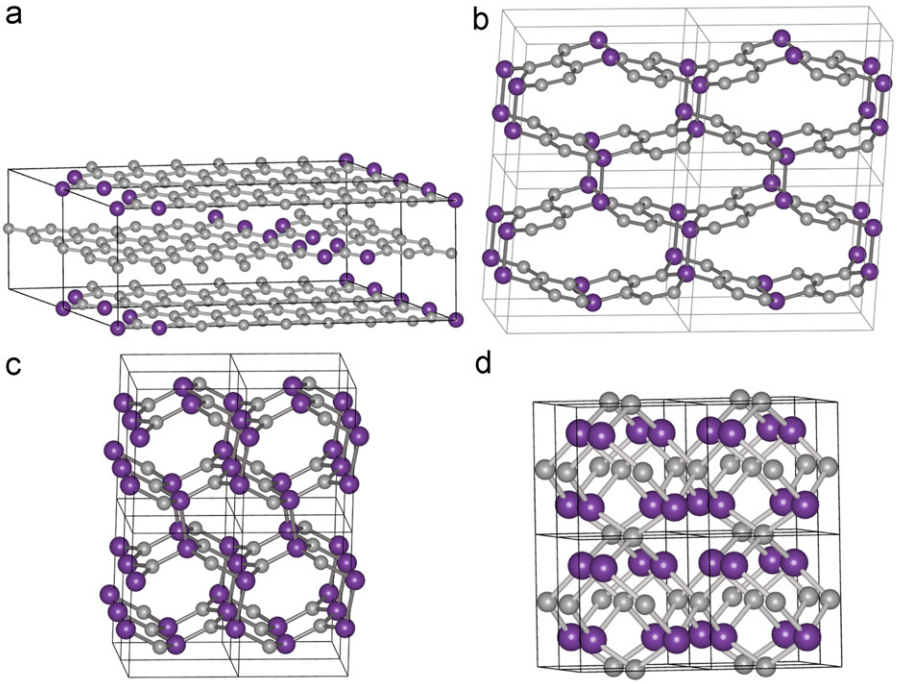

Fig. 1. Preferred structures for different P_xC_y compositions: (a) phosphorus-doped graphite for P_4C_{27}; (b) β-InS-like structure for PC_3; (c) β-InS-like structure for PC; (d) pseudocubic-like structure for P_4C_3. The light grey and the darker purple atoms are carbon and phosphorus, respectively, and the black lines show the unit-cell boundaries. Images of structures were produced with VESTA [21]. (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

also been reported previously [15,18–20]; the results indicate that the preferred structures when the phosphorus content is low include highly curved graphene sheets. This is consistent with our prediction that graphite-like structures are usually distorted and buckled, with the phosphorus adopting a pyramidal geometry [6].

These previous experimental reports suggest that phosphorus carbide materials have applications as semiconductors, electrochemical electrodes, electron field emitters and tribological coating materials [13,15–17,20]. It has been found that incorporation of phosphorus in amorphous carbon films significantly increases conductivity, resulting in materials that are promising as electrode materials for electroanalysis [14]. Also, phosphorus carbide thin films have been studied as biocompatible coatings. For example, Kwok et al. [22–24] reported an improved haemocompatiblity of phosphorus-doped diamond-like carbon (DLC) films compared to undoped DLC films. Additionally, the studies of Kelly et al. [25] and Regan et al. [26] indicate that phosphorus-doped DLC thin films exhibit good neurocompatibility and enhanced neuronal adhesion compared to undoped DLC.

2. Experimental methods

Phosphorus–carbon films were deposited on n-type single crystal (100) silicon ($\sim 1\ \mathrm{cm}^2$) substrates by pulsed laser deposition. Targets for ablation were produced by pressing a mixture of red phosphorus and graphite powder under a 10 t load to form a disc with a diameter of 16 mm. Targets were made with a phosphorus content up to 37 at%. The target was mounted on a rotating stage in a stainless steel chamber evacuated to $\sim 10^{-6}$ torr. The output of an ArF excimer laser (Lambda-Physik, Compex 201, 193 nm wavelength, 10 Hz repetition rate, ~25 ns pulse length) was focused onto the target; the focal spot size on the target was $\sim 1\ \mathrm{mm}^2$, giving an incident energy fluence of $\sim 8\ \mathrm{J\,cm}^{-2}$ ($\sim 3 \times 10^8\ \mathrm{W\,cm}^{-2}$). The deposition time was 20 min. The silicon substrate was mounted perpendicular to the target surface normal at a distance of ~9 cm from the target. Substrates were heated both during and after film deposition (while still under vacuum in the deposition chamber) by placing a 250 W incandescent light bulb behind the substrate; a thermocouple was attached to the substrate to allow the temperature to be monitored. The films were analysed by scanning electron microscopy (JEOL JSM 5600LV), which showed that they were dense with a smooth, featureless surface. The film thickness was measured by atomic force microscope (Bruker Multimode) imaging over a step in the film created by masking part of the substrate during deposition. The thickness increased as the phosphorus content increased, due to the higher ablation rate of phosphorus compared with carbon [8], and was typically ~30−100 nm.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition of the outer few nanometres of the deposited films. Areas of $\sim 4\ \mathrm{mm} \times 3\ \mathrm{mm}$ on each sample were analysed with a Thermo Fisher Scientific Escascope spectrometer, with an Al$K\alpha$ (1486.6 eV) X-ray source operated at 280 W (14 kV, 20 mA). The analyser had a pass energy of 30 eV; the use of a relatively high pass energy was necessary for an adequate count rate. Wide-scan survey spectra were obtained between binding energies of 1000 eV and 0 eV with a step size of 1.0 eV. Subsequent higher energy resolution scans over variable binding energy ranges with 0.1 eV steps were recorded for specific elements of interest (C 1*s*, O 1*s* and P 2*p*). The operating vacuum during analysis was $\sim 5 \times 10^{-9}$ mbar.

Fityk version 0.8.6 software was used for peak fitting and quantitative analysis [27]. The relative quantities of carbon, phosphorus and oxygen in the samples were determined from the peak areas, which were weighted by atomic sensitivity factors of 1.00, 2.85 and 1.25 for carbon, oxygen and phosphorus, respectively. All spectra were corrected for charging effects with respect to the carbon 1*s* peak for sp^2 carbon at 284.6 eV [28–30]. To quantify the different bonding environments, the carbon 1*s* and phosphorus 2*p* peaks were fitted with a linear background and a series of pseudo-Voigt functions. A Shirley background was