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Nanostructure and paramagnetic centres in diamond-like carbon: effect of Ar dilution in PECVD process

BJ Jones [1], S Wright [2], RC Barklie [2], J Tyas [3], J Franks [4], AJ Reynolds [1]*

1. Experimental Techniques Centre, Brunel University, Uxbridge, UB8 3PH, UK

2. School of Physics, Trinity College, Dublin 2, Ireland

3. Diameter Ltd, Brunel University, Uxbridge, UB8 3PH, UK

4. School of Engineering and Design, Brunel University, Uxbridge, UB8 3PH, UK

Abstract

Diamond-like carbon (DLC) films were deposited utilising plasma enhanced chemical vapour deposition (PECVD) with acetylene precursor, diluted with 0 – 45% argon. Electron paramagnetic resonance (EPR) measurements show the presence of one paramagnetic centre with no change in spin population over the range of film deposition conditions. However, the EPR linewidth decreases with increasing argon content of the precursor mix, suggesting an enhancement of motional narrowing due to an increase in electron delocalization, related to an increase in the sp^2 cluster size. Atomic force microscopy (AFM) measurements indicate the surface of the DLC is formed of nanoscale asperities of material. With radii of tens of nanometres for films deposited with zero argon, the size of the features increases with the argon dilution of the acetylene. Energy dispersive x-ray analysis and electrical measurements further elucidate the changes in film structure.

1. Introduction

Plasma enhanced chemical vapour deposition, PECVD, is one of the most highly used laboratory methods for production of diamond-like carbon, DLC, and other amorphous hydrogenated carbons, a-C:H. The process enables film deposition over a large area, combined with easily adjusted deposition parameters to facilitate production of films with tailored microstructure and properties [1].

The dilution of the PECVD precursor gases with argon [2, 3] is one of many parameters, which also include bias voltage, process temperatures and post-deposition annealing, that can be used to adjust the sp^2 / sp^3 ratio, hydrogen content, microstructure and properties of amorphous hydrogenated carbon films. Early work shows that clustering of the sp^2 regions, which may be in the form of olefinic chains or aromatic rings, is a crucial factor in determining the optical and physical properties of the amorphous carbon films [4, 5, 6].

Electron paramagnetic resonance (EPR) is a powerful tool to investigate the defects, such as dangling bonds, in carbon films, interfaces and substrates. The technique provides information on the spin-density, nature of defects and their interactions with the lattice [7], and can be related to the film microstructure and electron delocalization [8, 9]. A recent review [10] summarises previous work correlating the variation of paramagnetic spin density, linewidth and relaxation times, with a-C(:H) deposition conditions such as substrate temperature and bias voltage, as well as the relation to other properties including the optical band gap. EPR has also been utilised to show variation in electronic structure with the incorporation of additional elements, such as N, B, or W into amorphous carbons, either during deposition or through post-deposition ion implantation [9, 11, 12].

In addition to the electronic properties and chemical composition, the surface structure of DLC is important in a wide range of applications, for example in coating machine tools for use in dry, near-dry and oil-lubricated drilling [2, 13, 14]. In biomedical applications, the topography, composition and electrical properties are all of importance, in devices from sensors to hip joints, where DLC has been used as a diffusion barrier and to inhibit adhesion of bacteria such as *Staphylococcus epidermidis* [15].

In this article we investigate the variation of the argon content of the PECVD precursor gases and the effect on film micro- and nano-structure, surface and EPR signal, and relate this to the carbon bonding configuration and film properties.

2. Experimental

DLC films were deposited on high resitivity silicon by RF PECVD process in Diameter Ltd. The precursor gas was a mixture of acetylene, argon and tetramethylsilane (TMS). The ratio of argon to acetylene was adjusted by controlling flow rate of these gases individually. Substrates of (100)Si, measuring approximately 10mm × 5mm, were ultrasonically cleaned with acetone for 15 min and mounted on an electrode to which the negative bias voltage was applied. Prior to deposition, the chamber was evacuated to a background pressure below 8×10^{-5} torr. Substrates were sputter-cleaned for 15 minutes in an argon plasma with flow rate of 30 sccm, pressure of 8×10^{-2} torr and a bias voltage of 300 V. This reduces impurities on the substrates, through energetic argon ion bombardment. Subsequently, the bias voltage was adjusted to 450V and an interfacial layer was formed by adjusting argon flow rate to that used for the film deposition and introducing TMS with flow rate of 25 sccm. This layer enhances the adhesion of the film to the substrate. Once the interfacial layer was formed, the TMS gas flowing into the system was cut off, and acetylene gas at 60 sccm was introduced into the chamber. The argon flow rate and bias were maintained for film deposition.

The DLC films were deposited from argon diluted acetylene gas, the flow rate of argon was varied in different runs from 0 to 50 sccm with a constant rate of 60 sccm for acetylene. The deposition time was kept the same for all runs, to produce films approximately two micrometres in thickness; secondary ion mass spectrometry (SIMS) measurements and previous work on this system [2] show that the increase in argon concentration at this bias voltage may cause the film thickness to be decreased by up to 10% from the thickness deposited with zero argon dilution of the precursor.

EPR measurements were made at room temperature on a Bruker EMX machine, using 100kHz field modulation, a microwave frequency of approximately 9.9GHz (X-band) and a TM_{011} mode cavity. To avoid distorting the signal, measurements were conducted at a non-saturating power and the modulation field kept well below one third of the peak-to-peak linewidth of the narrowest feature in each spectrum [16].

Each g value was calculated by comparing the field position of the resonance with that of a resonance of known g value, in this case F^+ centres in MgO, with g=2.0023. The field range was calibrated with a proton NMR probe that also gave absolute field values. Spin populations were found by comparing the integrated area of the signal with that of a standard Varian sample of pitch in KCl; the absolute spin populations and average spin densities are estimated to be correct to within a factor of two, but their relative values are correct to within approximately 10%.

A Digital Instruments Dimension 3100 scanning probe microscope (SPM), operating in tapping mode with Veeco silicon probe and cantilever resonant at approximately 260kHz, was used to examine the surface topography of the DLC coating.

Simple resistance measurements were conducted using a Fluke 1520 mega-ohm meter; although this is a coarse evaluation method, with errors related to the probe contact and film thickness (reflected in the tabulated uncertainties), this is nevertheless a useful tool for initial appraisal.

Measurements of composition were conducted within a Zeiss Supra 35 VP field emission scanning electron microscope (FE-SEM) equipped with an Oxford Instruments Inca energy dispersive x-ray analyser (EDX). The SEM / EDX quantified elemental concentration values will depend on the calibration, which is complex for Ar; however, the relative values are correct to a greater level of certainty.

The electron accelerating voltage was decreased to bring the silicon EDX signal to zero to ensure that the penetration depth and depth of analysis were less than or equal to the film thickness. Thus the measurement of argon incorporation is only examining the film, not the substrate (which may well contain incorporated argon due to the cleaning process).

3. Results and Discussion

SEM EDX shows incorporation of Ar into the films varying from 0 to 0.44 at. %. The accelerating voltage and approximate density of the films show that the penetration

depth is approximately 1.5 to 2 microns, and as the Si signal has been reduced to zero by controlling the accelerating voltage, the analysis depth is entirely within the film thickness – this also demonstrates negligible deviation from nominal thickness. The levels of argon incorporated into the DLC films are detailed in table 1. This also shows the decrease in resistance of the films as argon dilution of precursor is increased.

Ar / sccm	ΔB_{p-p} / mT	Spin Population / 10^{16}	Surface roughness, R_a / nm	Peak density / μm^{-2}	Film resistance / MΩ	Ar content / at%
0	0.167	1.96	2.719	47.9	475±85	0
10	0.145	1.64	2.617	35.9	525±75	0.13
20	0.135	1.87	4.464	25.0	215±40	0.26
30	0.116	1.72	4.528	22.6	50±15	0.35
50	0.079	1.73	5.097	12.6	35±11	0.44

Table 1. Film structure, surface and properties as a function of argon content of precursor gas mix.

The electron paramagnetic resonance (EPR) spectra, as shown in figure 1, show a single Lorentzian line at g = 2.0026. This is characteristic of defects in carbon, and there is no contribution from the silicon substrate [8, 17, 18]. Earlier work has shown this line does not contain unresolved multiple elements [7, 19], and the g value and Lorentzian shape imply that the deposition process has not produced macroscopic graphitic regions; if randomly orientated graphite microcrystals had formed, the resonance line would be asymmetric and consist of a superposition of lines ranging in g value from 2.0026 to 2.0495 [20], very different from the single Lorentzian line observed.

This is in contrast to other ways of increasing the conductivity of DLC, for example with high doses of implanted ions [21, 22]. Assuming nominal thickness and uniform distribution of defects throughout the film [23] leads to a spin concentration of approximately $2x10^{20}$ cm^{-3} for all samples.

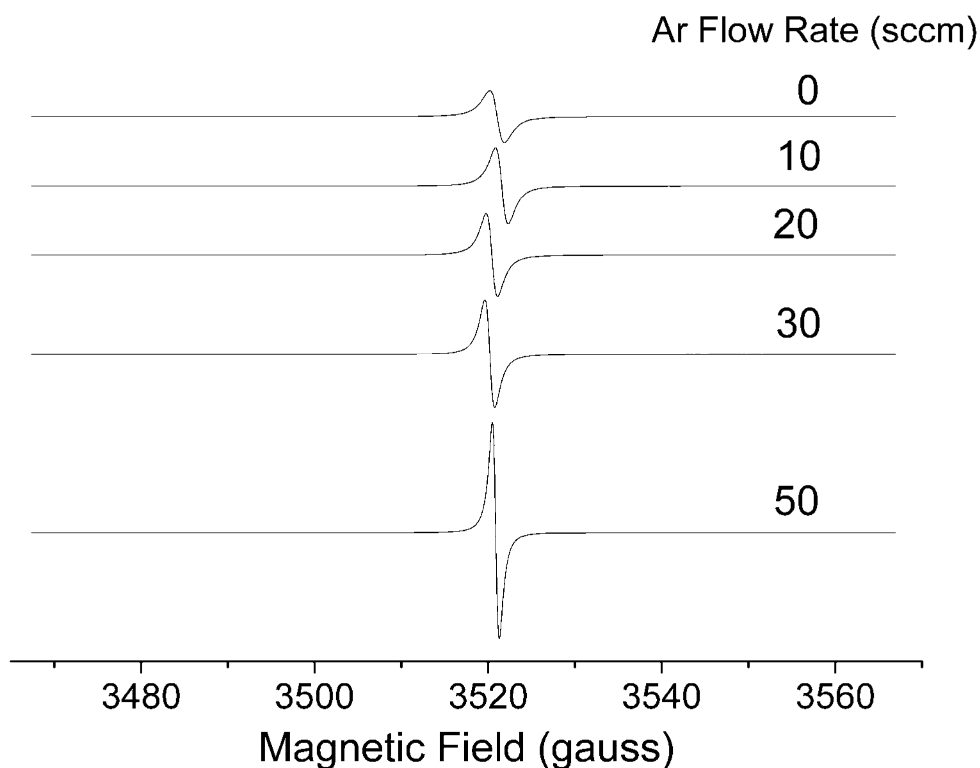

Figure 1. EPR signal variation with increased argon dilution of precursor.

The observed EPR linewidth of the film deposited with zero argon is considerably less than the linewidth of 1.6 mT that may be expected d ue to dipolar broadening from this spin density [16]; the linewidth further decreases with increased argon content of the precursor gas, as detailed in table 1, reaching 0.079 mT with 50 sccm of argon in the precursor gas mix. This reduction in linewidth may be attributed to motional or exchange narrowing, related to increased wavefunction overlap, due to increased size of sp^2 clusters. This is similar to the effect seen in DLC or polymer-like amorphous hydrogenated carbon, implanted with boron, nitrogen or carbon ions [8, 9].

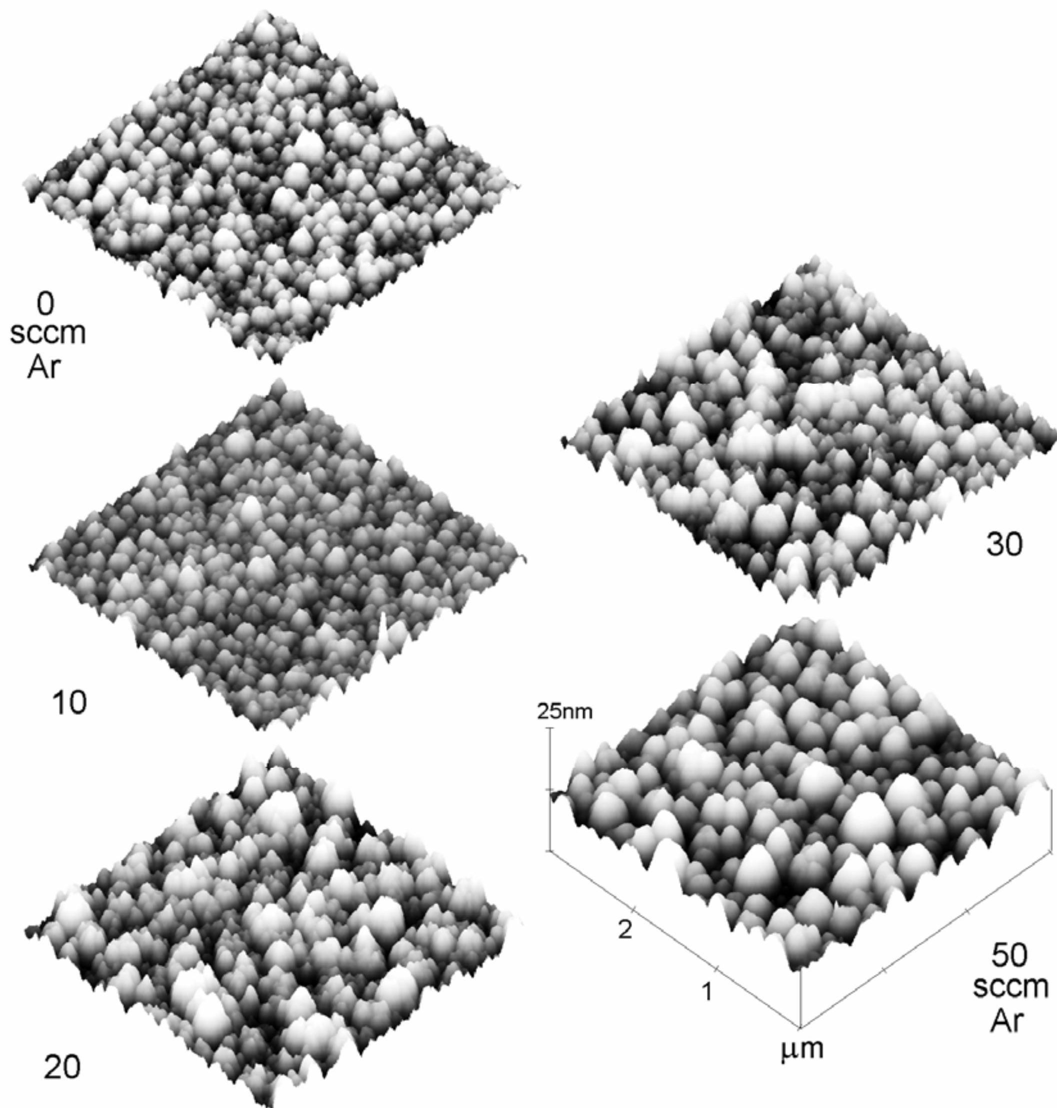

Figure 2. AFM images showing variation in surface topography with argon dilution of precursor.

This hypothesis is consistent with the decrease in film resistance, and with the analysis work of Valentini [3] who observed decreasing diamond-like properties in DLC films produced with increased argon dilution of methane precursor. The observed effects of varying argon content of precursor mix may be related to the process of incorporation of argon into the film, or to the variation in preferential deposition species as theorised by Riccardi [24] who showed preferential deposition of C_2 with increased Ar dilution of precursor gas, rather than hydrocarbons that are deposited when precursor mix has zero Ar content. Reduction in hydrogen content of

the deposited film would be consistent with an increase in sp^2 regions, as hydrogen acts to alleviate internal stresses inherent with sp^3 structure in a-C:H films.

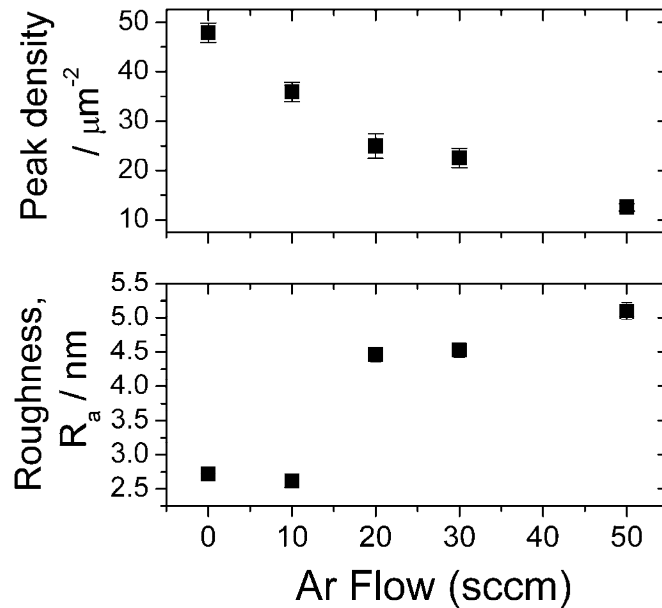

Figure 3. Variation in surface roughness and peak density with Ar dilution of precursor. The decrease in peak density indicates an increase in peak size.

The increase in argon concentration also results in changes to the physical structure of the film, as shown in the atomic force microscopy (AFM) images in figure 2. The film deposited with zero argon has a structure consisting of nanoscale asperities, with features of approximate size a few tens of nanometres. As the argon concentration of the precursor is increased, the average diameter of the features increases, indicated by an approximately linear decrease in the density of peaks per unit area, from ~50 to ~12 peaks per square micron. The surface roughness, measured as R_a, the mean z-direction deviation from the mean line, is also increased with increasing Ar; however, this appears as almost a step change at 20 sccm Ar, with R_a increasing from 2.6 nm for films deposited with zero and 10 sccm argon, to 4.5 – 5.0 nm for 20 – 50 sccm argon, as shown in figure 3. The minimal change in R_a seen above 20 sccm Ar, coupled with the continued decrease in peak density is consistent with the coalescence of peaks in this process regime. These issues may counter any decrease in friction

that might be expected from variation of sp^2 clustering of the films, this may explain the findings of Zolgharni [2] that there is a low optimum level of Ar in the PECVD precursor mix to produce films with decreased friction for drilling applications.

4. Conclusions

The electronic and surface structure of amorphous carbon films can be controlled by varying the argon content of the PECVD process precursor gas mix. DLC films produced with increasing argon dilution of the precursor mix lead to some incorporation of Ar into the DLC film, a narrowing of the EPR line, and an associated decrease in film resistance. This is consistent with motional narrowing of the EPR signal, resulting from increased wavefunction overlap, due to increased electron delocalization, in turn caused by increased clustering of the sp^2 structure. This is similar to that seen in observations of EPR linewidth in ion implanted a-C:H, [8, 9] but does not lead to the associated increase in defect concentration observed in these systems.

Simultaneously, the increased argon concentration in the precursor mix leads to an increase in roughness of the surface and increase in diameter of topographical features. This leads to a low optimum level of Ar in precursor mix for applications dependent on low friction surfaces, as observed by Zolgharni *et al.* [2] in dry drilling applications.

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