Growth of diamond-like carbon films using low energy ion beam sputter – bombardment deposition with Ar ions

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Abstract. An alternative to a widely used ion assisted deposition method has been developed where a single beam of low energy Ar ions is used to simultaneously sputter a graphite target and to bombard a growing film. By placing the substrate at low incident angles to the axis of the ion beam and therefore subjecting the growing film to the additional ion energy we aimed to promote the formation of \(sp^3\) bonding. \(sp^2\) rich amorphous carbon (a-C) and diamond-like carbon (DLC) films with significant fractions of \(sp^3\) bonding were formed by sputtering from a Kaufmann – type ion source. Experimental results revealed that when the substrate was placed at grazing angles to the incoming ions no DLC, but only polymeric a-C films were produced as a result of a secondary resputtering process. For DLC synthesis the optimal angles of the target and the substrate to the ion flux were found to be 30º and 0º respectively and the ion energies of 0.8 – 1.0 keV.

1. Introduction
Fabrication of DLC films commonly employs DC [1, 2] or RF [3] magnetron where films are produced by sputtering a solid graphite target by Ar plasma. Often ion beam sputtering is used to fabricate DLC where a directional beam of ions with the energy of several keVs is focused towards a graphite target creating a carbon flux; and frequently an additional beam is used to bombard the surface of a growing film that delivers extra energy to the densification process and thus promotes favourable morphological changes [4, 5]. A single, low energy nitrogen ion beam has been used by other workers [6, 7] to fabricate amorphous carbon nitride coatings by sputtering a solid carbon target and positioning a substrate parallel although some distance away from the central axis of the ion beam.

The objective of this investigation is to examine the suitability of a single ion beam deposition method for fabrication of DLC films, and to investigate whether positioning of a substrate at grazing angles to the ion beam results in beneficial structural changes in the synthesised films such as the increase of \(sp^3\) fraction.

2. Experimental methods
Films were deposited using CTP-700 high vacuum deposition system (Laserdyne Pty Ltd) fitted with a Kaufman–type ion source with a convex ion grids of 40 mm in diameter. Highly ordered pyrolytic graphite (HOPG) was used as the target material. A schematic of the film deposition is illustrated in figure 1.
Films samples were deposited onto Si <100> substrates under varying target-ion beam, $\alpha_t$ and substrate-ion beam, $\alpha_s$ incidence angles. The specific angles used were: $\alpha_t=15^\circ$, 30$^\circ$ and 45$^\circ$, and $\alpha_s=0^\circ$ (parallel to the ion beam flux), and 10$^\circ$. The working pressure of the system was approximately 4x10$^{-4}$ Torr. Ar of 99.999% purity was used as a sputter gas. The ion beam energy, $E_{Ar}$, was varied from 0.2 keV to 1.0 keV in 0.2 keV increments and beam current was 10 mA. Accelerator voltage was 190 V at 1.0 mA and the discharge was 60 V at 0.6 A. Film deposition time was 30±1 min.

A Kimmon 5161R–GS Raman spectroscope with He/Ca 325 nm laser was used to examine $sp^2$ and $sp^3$ bonding in fabricated films.

X-ray photoelectron spectroscopy (XPS), using a Kratos Ultra photoelectron spectroscopy with a monochromated Al $K_\alpha$ 1486.6 eV X-ray source, was used to obtain $C_{1s}$ spectra.

Scanning Electron Microscopy using AEI Quanta 200 electron microscope was employed to examine frontal and cross sectional surfaces of the films. All fabricated films were found to display smooth and flat surfaces that are featureless at 100 nm resolution and maximum films thickness was 1 $(\pm 0.02)$ µm for higher energy deposited films.

3. Results and Discussion

Atomic scale Monte Carlo (MC) simulation for Ar ions interacting with a HOPG target was performed using SRIM in order to optimize the sputtering geometry. The MC calculations were used to determine an optimal target sputtering angle(s) where the yield of ejected carbon ions per single Ar projectile ion is at maximum altogether with maximum energy for carbon ions. The appropriate target to the ion beam angle that also provides for increased ion beam flux was found to be approximately 30$^\circ$. However, at this $\alpha_t$ of 30$^\circ$ the average energy of produced carbon flux is less then 50 eV per single carbon ion. In order to form DLC a metastable increase in density is required that causes the local bonding to change to $sp^3$; in our experiments the use of an infringing ion beam was intended to accomplish this.

Figure 2 shows a deconvoluted UV Raman spectrum of a DLC film fabricated using 1.0 keV ions

![Figure 1](image1.png)  
**Figure 1.** Schematics of a single source ion beam sputter deposition with substrate grazing bombardment.

![Figure 2](image2.png)  
**Figure 2.** 325nm UV Raman spectra of a DLC film fabricated with $E_{Ar}=1.0$ keV, $\alpha_t=30^\circ$ and $\alpha_s=0^\circ$

![Figure 3](image3.png)  
**Figure 3.** The deconvolution of XPS $C_{1s}$ spectra of a DLC film fabricated with $E_{Ar}=1.0$ keV, $\alpha_t=30^\circ$ and $\alpha_s=0^\circ$
and sputtering angles set at $\alpha_{t}=30^\circ$ and $\alpha_{s}=0^\circ$. The spectrum in figure 2 was decomposed by fitting a Pearson VII (P VII) lineshape function to all constituent peaks [8]. The best fit was obtained when using the P VII width value $M$, of 5 for the $G$ peak and 3 for the $D$ and the $T$ peaks. The spectrum in figure 2 is clearly dominated by the $G$ peak ca. 1570 cm$^{-1}$ and corresponding to stretching vibrations of aromatic rings and olefinic chains. The $D$ peak is relatively small and found located at ca. 1390 cm$^{-1}$. The $T$ peak contributions are seen and the peak is positioned at ca. 1070 cm$^{-1}$. The relative intensity ratios for $I(D)/I(G)$ was 0.28 and $I(T)/I(G)$ was 0.15. Using the $I(T)/I(G)$ ratio and the $T$ peak position, cm$^{-1}$ it is easy to distinguish films with high $sp^{3}$ content. Using works of Ferrari and Robertson [9], an $I(T)/I(G)$ ratio below 0.2 indicates that the $sp^{3}$ content is likely to be below 30%, however an $sp^{3}$ content of about 50% corresponds to the $T$ band position at approximately 1070 cm$^{-1}$.

The $sp^{3}/sp^{2}$ ratio was obtained by decomposition of the XPS $C_{1s}$ core binding energy (BE) spectra onto two constituent functions corresponding to $sp^{2}$ and $sp^{3}$ carbon hybridized states. Figure 3 shows decomposition of $C_{1s}$ spectra for a DLC film fabricated when bombarded by 1.0 keV Ar ions and the target and the substrate angles of 30° and 0° (same DLC film as shown in UV Raman spectrum in figure 2). In addition to the two main $sp^{3}$ and $sp^{2}$ peaks $C$-$O$ and $C=O$ contamination peaks were fitted positioned at ca. 286.5 eV and ca. 288 eV [10, 11]. After subtracting the Shirley background, the $sp^{3}$ and $sp^{2}$ peaks we fitted with P VII function. The P VII value $M$, of 4 was used for carbon hybridised states and Gaussian lineshape was used for $C$-$O$ and $C=O$ peaks. The comparative BE spectral functions of graphite (100% $sp^{2}$) and natural diamond (100% $sp^{3}$) were used to calculate the $sp^{3}/sp^{2}$ ratio based on contributions from the respective area ratios of hybridised states [12, 13]. The $sp^{3}$ peak was found positioned at BE of 284.14 eV with FWHM$_{sp^{3}}$ of 1.15 eV and the $sp^{2}$ was at 284.9 eV with FWHM$_{sp^{2}}$ of 1.51 eV. The separation between the $sp^{2}$ and $sp^{3}$ constituents was 0.85 eV and it is in agreement within the separation range presented in recent publications [14, 15]. The $sp^{3}/sp^{2}$ ratio for the DLC films shown in figure 4 was 0.40±0.02. This result obtained using XPS measurements corresponds well with the approximate $sp^{3}$ value deduced from UV Raman measurements.

The $sp^{3}$ content (with an uncertainty of ±2 %) for all fabricated films is summarised in table 1.

| Ion energy, keV | Target and substrate to the ion beam axis sputtering angles, $\alpha_{t}:\alpha_{s}$ |
|----------------|-----------------------------------------------------------------------------------|
| 0.2            | ---                                                                                |
| 0.4            | --- $SiC$                                                                          |
| 0.6            | $\leq 7$ $SiC$                                                                    |
| 0.8            | 18 $SiC$                                                                           |
| 1.0            | $\leq 7$                                                                           |

All $sp^{3}$ values were derived from XPS $C_{1s}$ measurements. From table 1 it follows that at Ar ion beam energies below 0.6 keV it is not possible to fabricate DLC films but only $a$-$C$ and $SiC$ films. At the substrate grazing angle of 10° to the ion beam axis there were no DLC formed at any deposition energies independent of the angle of target sputtering. The inability to form DLC film is due to a secondary resputtering process. This resputtering is due to differentiation between sputtering energy for carbon and nucleation energies for $SiC$ and DLC; the energy of incident Ar ions is much higher than the threshold displacement energy of carbon atoms, while it is almost the same as or less than that of $SiC$ atoms [16].
4. Conclusion
DLC films can be synthesised on Si surface using a low energy ion beam sputter deposition, where a single ion beam is situated to sputter the carbon target at incident angles and the substrate is positioned parallel to the axis of the ion beam flux. In this arrangement the increase of incident ion energy promotes $sp^3$ bonding formation. However, positioning the substrate at grazing angles to the ion beam leads to a secondary resputtering process by the incoming ions and consequently no DLC films are formed.

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