Characterisation of Diamond-Like Carbon (DLC) laser targets by Raman spectroscopy

D.Haddock¹, T Parker¹, C Spindloe¹ & M Tolley¹

¹Science and Technology Facilities Council, Rutherford Appleton Laboratory, Harwell Oxford, Chilton, Oxon, OX11 0QX, UK

E-mail: david.haddock@stfc.ac.uk

Abstract The search for target materials suitable for High Power Laser Experiments at ultra-low thicknesses (below ten nanometres) is ongoing. Diamond-Like Carbon is investigated as an answer for a low-Z material that can survive target chamber pump-down and laser pre-pulse. DLC was produced using Plasma-Enhanced Chemical Vapour Deposition, using with varying gas flow mixtures of argon and methane. The methane plasma deposits amorphous carbon onto the substrate and the argon plasma re-sputters the weakly bonded carbon leaving a high proportion of diamond-like bonding. Bonding natures were probed using Raman spectroscopy; analysis of the resulting spectrum showed that flow rates of 40sccm/60sccm methane to argon produced DLC films with a diamond-like (sp³) content of ~20%. Increasing the methane gas flow decreased this value to less than 5%. DLC foils were processed into laser targets by method of float off; using a sodium chloride release layer and lowering into water, this was then lifted onto an array of apertures allowing for laser irradiation of the material with no backing. DLC with 20% sp³ content showed superior yield when compared to other materials such as metals and some plastics of the same thickness, with ~70% of the target positions surviving the float off procedure at <10nm. As a result of this work DLC targets have been available for a number of experiments at the Central Laser Facility.

1. Introduction

Target Fabrication at the Central Laser Facility supplies solid targets to experiments at the Gemini and Vulcan Petawatt laser systems at Rutherford Appleton Laboratories. There has been a significant increase in demand for ultra-thin <10nm low Z foils for experiments in ion acceleration with potential future applications in medicine, fusion science and astronomy simulations.[1] As a response to this demand Target Fabrication gained the capability to produce Diamond-Like Carbon by Plasma Enhanced Chemical Vapour Deposition (PECVD).

Diamond-Like Carbon is an amorphous carbon film with a significant fraction of sp³ bonding. sp³ bonding is the covalent bonding exclusively found in diamond. “sp” notation donates a hybridisation of the s and p atomic orbitals with sp being a single electron from the s orbital and three from the p. sp² bonding is two electrons in the p orbital and is found in graphite, leaving a free electron between sp² bonded layers. These two bonding types present in DLC are probed by Raman spectroscopy.

Sub 10nm foils inherently suffer from considerable yield issues when suspended across a window in the production phase, once put inside the chamber they are subject to pressure from the pump-down cycle of the target chamber and the presence of a laser pre-pulse. Diamond-Like Carbon is an ideal
choice to address yield issues as it possesses the material properties of diamond but in the form of a thin film coating. [2]

DLC is produced by PECVD and the bonding nature of the resulting thin films is probed by Raman Spectroscopy. In this discussion the relationship between coating parameters and resulting bond nature is linked to the suitability for laser targets.

2. Production of Diamond-Like Carbon by Plasma Enhanced Chemical Vapour Deposition

The coating plant used was a modified RIE80 Etch system. It is fitted with a RF 600W at 13.56MHz power supply. Gas flow rate is controlled via an automatic pressure control valve at the rear of the chamber and mass flow controllers constrain the incoming gas which is introduced for the top chamber by a shower head configuration. Plasma is created by discharge between two electrodes.

For deposition of DLC; firstly the substrates are cleaned by an Oxygen plasma clean (300mbar 150W) in the PECVD plant. Next, by method of thermal evaporation, sodium chloride is coated onto the substrate. Sodium chloride acts as a release layer for the resultant DLC film. When lowered into water the NaCl dissolves and the DLC sits on the surface tension of the water, this can then be lifted onto a target array which has multiple individual target positions.

The coated substrate is placed inside the PECVD chamber for DLC coating. The plasma in process is a gas mixture of methane and argon. The methane plasma deposits amorphous carbon with some inclusion of bonded hydrogen onto the substrate, the Argon plasma re-sputters weakly bonded sp² carbon atoms and leaves a higher proportion of sp³ content.

A typical coating uses a gas flow rate into the chamber of 40sccm methane and 60sccm argon, with a constant chamber pressure of 300mbar at 300W power and a process time of 300s. This produces a DLC coating less than 10nm thick.

<10nm DLC using these process parameters produces a film that is robust enough to survive open areas of 500um diameter allowing for use in laser experiments, yield across an array of 500um holes is typically 60-80% at this thickness. This is superior to any other material processed in this manner. Trailing metals such as aluminium and copper at this thickness is futile and no successful float offs are achieved. The float off method has been successful in producing foils with flatness across a 500um hole with surface deviations of only a few microns, this is achieved by using a small raised area surrounding the hole, during drying; tensile stress pulls the foil flat over the open aperture.

Figure 1 Modified RIE80 etch system for DLC coating. Touch screen console can be seen on the left and gas feed line can be seen on the wall at the rear. The target chamber is the black cylinder in the centre and measures 30cm diameter.

Figure 2 Ternary phase diagram of amorphous carbons. The three corners correspond to diamond, graphite and hydrocarbons respectively. Ta-C:H or tetra-hedral amorphous carbon is an alternative name for DLC. [3]
An alternative technique to manual float off is being developed by Christopher Spindloe at the Central Laser Facility and it is expected that this will eventually replace the manual method. This uses a substrate of silicon on which the target material is deposited, this is then etched from the rear through the silicon to leave the target foil with no backing. This has been successful with Atomic Layer Deposition deposited materials at thicknesses of ~5nm with material such as tantalum Nitride. The drawback to the method is this does not produce the flatness across the target achievable with the float off procedure; this is often a critical tolerance for laser experiments.

3. **Characterisation of DLC by Raman Spectroscopy**

Raman spectroscopy was used to characterise the bonding nature of the foils produced by PECVD. This technique allows the ratio of diamond-like ($sp^3$) to amorphous bonding ($sp^2$) to be estimated. Raman spectroscopy utilises the Raman shift to probe vibrational modes in a sample; the phonon vibrations are unique to the bonding present. A Raman shift is an inelastic scattering of light with vibrational modes in which the laser light is shifted (Raman shifted) to a slightly different wavelength. The background reflected light is eliminated using gratings and the Raman shift is plotted against relative intensity to give a spectrum. In visible Raman spectroscopy of diamond-like carbon the $sp^3$ bonding prominence cannot be probed directly as $sp^2$ sites are strongly resonant and therefore dominate the spectrum. However it has been shown that the relative intensities of the so called D and G peaks is indicative of $sp^3$ content [4].

Using a Renishaw 514nm excitation source at a power of 0.01mW the spectrum was fitted to Gaussian approximations in Origin pro 8, with which the intensities of the spectrum peaks could be compared. There are two prominent peaks one at around 1355cm$^{-1}$ the so called D peak, which is due to the breathing of graphitic-like rings, this only occurs where the graphite rings have room to stretch, and so does not occur in continuous sheets of graphitic rings. The other prominent peak is the G peak which is around 1516cm$^{-1}$, this does not require the presence of 6-fold graphite rings and so occurs at all $sp^2$ sites. Broadly speaking I(D) (integrated intensity) increases with increasing disorder moving from graphitic dominate carbon to nano-crystalline graphite and amorphous carbon. I(G) tends to keep relatively consistent intensity but undergoes a two stage process with its relative wavenumber position. The peak position moves to lower wavenumbers with increasing bond disorder but moves higher again when creation of $sp^3$ chains occurs. Using these two indicators $sp^3$ to $sp^2$ ratio can be reliably inferred.[3]
Figure 3 Typical Raman spectrum taken from the produced DLC. The smaller peak on the left around 900 cm\(^{-1}\) is the secondary Silicon peak and is present due to the silicon substrate on which the film was coated. The D Peak is around 1355 cm\(^{-1}\) and the G peak is around 1516 cm\(^{-1}\). I(D)/I(G) and the position of the G peak are the most informative factors in analysing the relative \(sp^3/sp^2\) ratio.

Figure 4 The three-stage model of the variation of the Raman G position and the D-to-G intensity ratio, with increasing disorder. The dotted left-pointing arrows in (b) mark the non-uniqueness region in the ordering trajectory. (c) Shows the data for as-deposited amorphous carbon collated from literature: Tamor & Vassel (1994) and Ferrari and Robertson (2000) plotted against \(sp^3\) ratio as measured by NMR, EELS [4]
Using the data from Robertson and Ferrari 2004 in figure 4(c) a comparative analysis can be made with the DLC coatings produced by PECVD. The coating parameter of interest was the ratio of the inlet flow gases: methane and argon.

**Figure 5** Diamond-Like Carbon produced with differing Methane/Argon flow rates, plotted against the relative intensities of the D and G peaks in the resulting Raman spectrum. The error in the D/G intensity ratio is high due to the error in the fitting of Gaussian peaks to the spectrum data.

**Figure 6** Diamond-like carbon produced with differing Methane/Argon flow rates, plotted against the position of the Gaussian fitted G peak in the resulting Raman spectrum.

Figures 5 and 6 confirm that decreasing the flow mixture ratio of methane to argon has a measurable effect on the resulting Raman spectrum especially for G peak position but the trend is unclear for D/G peak intensity potentially due to the errors in Gaussian fitting undertaken. Comparing the data to that shown in figure 4(c) it can be seen that the relative intensity ratio of the D and G peaks corresponds to a coating in the region of 40-60% \( sp^3 \) content. From the G peak a decrease in G peak position corresponds to an increase from 40-60% \( sp^3 \) content. This confirms predictions of a higher argon inclusion in the plasma process re-sputtering the weakly bonded \( sp^2 \) carbon and only partially ablating the \( sp^3 \) bonded carbon. [5]

The suitability for laser targets was tested by mounting foils over multiple 25 position target arrays. During the “float off” mounting procedure; it could be seen how many target positions remained
complete and unbroken. It was seen that DLC coatings with a higher inferred $sp^3$ ratio had better yield than those of lower $sp^3$ ratio at ultra-thin thicknesses (~3-30nm). However, at higher thicknesses (100nm and above) the DLC coatings with high $sp^3$ ratio showed cracking under internal stress and had considerable yield issues. Between 30nm and 100nm no significant difference was observed in target yield. These results are purely observational over number of repeats and need to be quantified by means of strength/pressure testing.

**Conclusion and future work**

Diamond-Like Carbon has been successfully fabricated as a laser target for use at the Central Laser Facility and fielded on a number of experiments on the Gemini high repetition rate laser system. DLC was created by Plasma Enhanced Chemical Vapour Deposition using varying methane and argon gas flows into the process chamber. Post characterisation of the bonding present in DLC foils was carried out by Raman Spectroscopy. The analysis showed that by increasing the Argon ratio in process increased the resultant $sp^3$: diamond-like bonding present. By comparing bonding nature to observed survivability across a target array it was seen that the higher $sp^3$ bonding present produced a foil that showed better yield than that of a lower $sp^3$ content.

Future work aims at investigating methane in the plasma process at the 10-30% range, initial trials have seen very low coating rates at lower methane inclusion but a new power supply is being trialed.

**References**

[1] Kiefer D, Yeung M, Delzanis T and Foster P S. Relativistic electron mirrors from nanoscale foils for coherent frequency upshift to the extreme ultraviolet 2013 *Nat. Coms.* 4 1763

[2] Liu Y, Erdemir A and Meletis E I. A study of the wear mechanism of diamond-like carbon films *Surface & Coatings Technology* 82 48-56

[3] Ferrari A C and Robertson J. 2004 Raman spectroscopy of amorphous, nanostructured, diamond–like carbon, and nanodiamond *Phil. Trans. R. Soc. Lond.* 362 1824

[4] Ferrari A C and Robertson J 1999 Interpretation of Raman spectra of disordered and amorphous carbon *American Phys. Soc.* 61 96-106

[5] Filik J, May P W, Pearce S R J, Wild R K and Hallam K R. 2003 XPS and laser Raman analysis of hydrogenated amorphous carbon films *Diamond and Related Materials* 12 974-978