

Review Report

GR/M12339/01:

Fundamental Studies of Laser Ablation as a Route to Hard Carbon Films

1. Background/context

Interest in, and use of, pulsed laser ablation (PLA) as a route to depositing thin films (of, e.g., metals, carbon, oxides and other ceramics, ferroelectrics and high- T_c superconductors) on a wide variety of substrate materials at room temperature, continues to grow rapidly.¹ Film formation by pulsed laser deposition (PLD) was actually first reported as long ago as 1965, but many details of the chemical physics involved in the deposition process are still far from completely understood. The process is often envisaged as a sequence of steps, initiated by the laser radiation interacting with the solid target, absorption of energy and localised heating of the surface, and subsequent material evaporation. The properties and composition of the resulting ablation plume may evolve, both as a result of collisions between particles in the plume and through plume-laser radiation interactions. Finally the plume impinges on the substrate where incident material may be accommodated, rebound back into the gas phase, or induce surface modification (via sputtering, compaction, sub-implantation, *etc.*). Such a separation has conceptual appeal, but is necessarily over-simplistic. Furthermore, the laser-target interactions will be sensitively dependent both on the nature and condition of the target material, and on the laser pulse parameters (wavelength, intensity, fluence, pulse duration, *etc.*). Subsequent laser-plume interactions will also be dependent on the properties of the laser radiation, while the evolution and propagation of the plume will also be sensitive to collisions, and thus, to the quality of the vacuum under which the ablation is conducted and/or the presence of any background gas. Obviously, the ultimate composition and velocity distribution (or distributions, in the case of a multi-component ablation plume) of the ejected material is likely to be reflected in the detailed characteristics of any deposited film.

The present program of work was targeted at studies of pulsed laser ablation of graphite at 193 nm, and the subsequent deposition of diamond like carbon (DLC) films – with and without added dopant species like B, N or S. Graphite was identified as an attractive target material for fundamental studies of PLA, both because of its intrinsic elemental simplicity and because of the wide potential applicability of hard hydrogen-free DLC films. It has been the subject of several previous investigations; indeed, graphite was one of the first target materials to be ablated when the pulsed ruby laser first became available. Studies of the PLA of graphite at long excitation wavelengths (e.g. 1064 nm) have shown the ablation plume to contain a high proportion of small carbon cluster species (ions and neutrals);²⁻⁴ DLC films so formed have been reported as containing up to ~70% sp^3 (tetrahedrally) co-ordinated C atoms, but only at laser intensities approaching $10^{10} \text{ W cm}^{-2}$.⁵ In contrast, the plume resulting from PLA induced using short wavelength UV laser radiation (e.g. at 193 nm) is dominated by atomic species (C neutrals and ions),⁶⁻⁸ and high quality DLC films containing >90% sp^3 bonded C atoms have been reported using much lower intensities ($\sim 5 \times 10^8 \text{ W cm}^{-2}$).^{5,9-12} Such observations accord with the view that high (~100 eV) impact energies encourage formation of dense sp^3 (rather than graphitic) networks in the deposited film,^{5,13-18} and that high ejection velocities are a feature of electronic (*i.e.* UV) rather than thermally driven material ablation. Nonetheless, it was clear to us that many details of the ablation process, including, for example, factors which affect the plume composition and properties, and how these in turn influence the resulting film characteristics, demanded further study. To this end, we proposed a program of work employing a quadrupole mass spectrometer (QMS) with ion energy analysis, capable of analysing the identity and kinetic energy of neutral species, and positive and negative ions within ablation plumes focusing, initially, on graphite ablation, then progressing to investigations of PLD of doped hard carbon films. In the event, the energy analysis capabilities of the QMS system proved disappointing, to say the least, and it was necessary to implement a variety of alternative, and additional, diagnostics in order to progress these issues (and provide a sufficient body of data for the graduate students). These are described in parts 2 and 3 below.

2. Key advances and supporting methodology

3. Project plan review

These two aspects of the program are inextricably linked and it has thus proved convenient to roll them together. This Section thus contains a description of the QMS system, its limitations with regard to kinetic energy (KE) analysis, and steps taken to try and alleviate them. We then describe the range of additional strategies implemented in order to address the fundamental objectives of the original application, and results obtained thus far from studies of PLA and PLD of graphite, both in vacuum and in the presence of added nitrogen and sulfur and, most recently, from the PLA and PLD of ZnO.

The quadrupole mass spectrometer, a HAS-5PL-4353 system from Hiden Analytical, was selected on the basis of its advertised capability for energy analysing ions or neutrals of any user selected mass. Figure 1(a) shows a schematic of the ablation apparatus, and Fig. 1(b) shows a more detailed view of the QMS design, which consists of extraction, source and electrostatic analysis regions, a quadrupole mass filter, and a detection region incorporating a secondary electron multiplier. The QMS apparatus was developed specifically for plasma diagnostic applications, and designed to function in two modes; as a residual gas analyser (RGA, whereby neutral species are ionised by electron impact in the source region) and as a secondary ion mass spectrometer (SIMS). We have used the QMS quite extensively as a simple mass spectrometer both for ions and neutrals in the ablation plume, in time-gated mode (synchronised with the firing of the ablation laser). In SIMS mode, for example, we were able to show that the ionic component within the plume resulting from 193 nm ablation of graphite in vacuum is dominated by $^{12}\text{C}^+$ and $^{13}\text{C}^+$ ions (in natural isotopic abundance), supplemented by a small peak at $m/z = 6$ (attributable to $^{12}\text{C}^{2+}$ ions). This finding was crucial to our investigations of the validity of the kinetic energy distributions returned by the QMS (see below). The option of applying a (user selectable) positive potential to the extractor region has proved to be a useful and workable route to recording mass spectra of neutrals, in RGA mode,

even when the plume contains a significant ionic fraction (with the same m/z as the neutral of interest). Thus we were able to identify neutral gas phase CS_2 ($m/z=76$) species when ablating graphite/sulfur samples – which provided important clues regarding the mechanism of S incorporation in DLC films formed by laser ablation methods (see below).

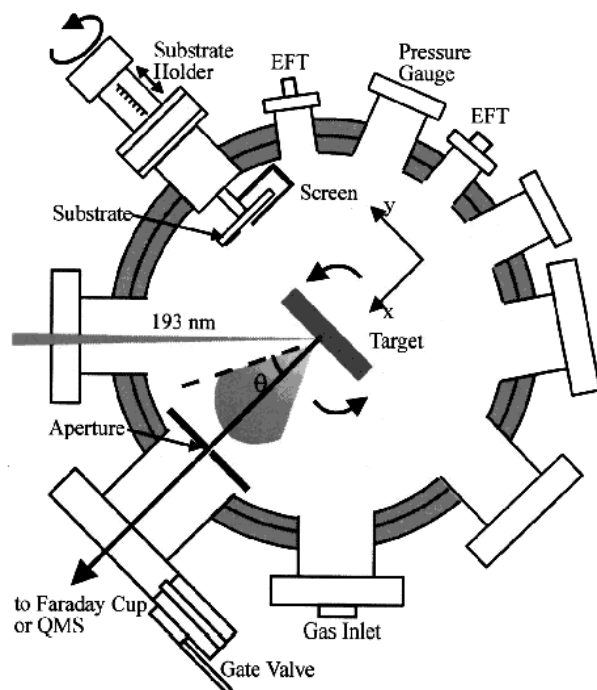


Figure 1(a). A schematic diagram of the ablation apparatus.

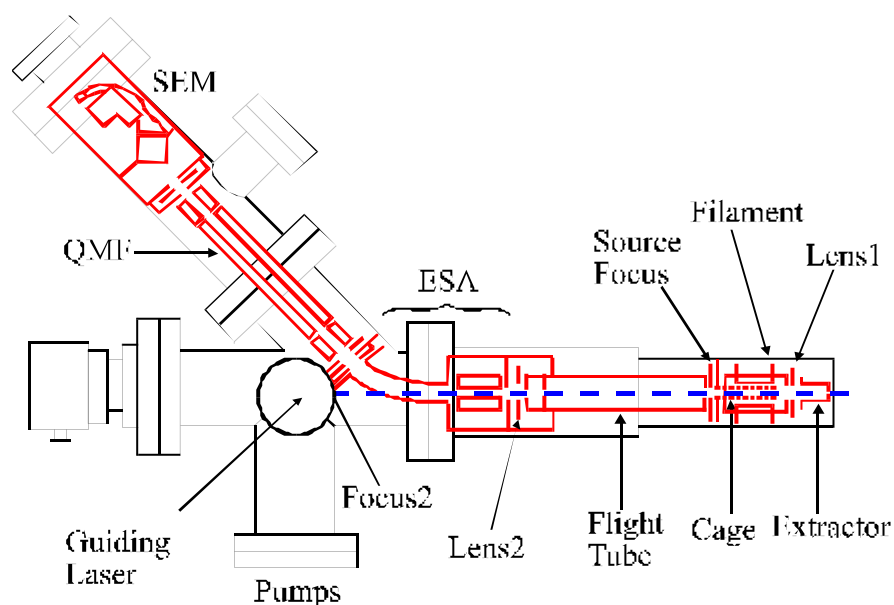


Figure 1(b). Detailed view of the QMS design.

However, much of the novelty of the proposed program required that we were able to determine the KE distribution of mass-selected components within the plume, and this has proved much more challenging than the manufacturers, or their sales literature, would lead one to expect. Optical emission measurements by ourselves, and others, have shown that ions in ablation plumes can have very broad KE distributions, spanning the range 0–200 eV or more.^{5,19} Working with a Cs ion source, provided by Hiden, we were able to confirm the energy calibration of the spectrometer, but the KE distribution of the Cs^+ ions from this source is not known. Our initial observations, both with the Cs^+ ion source and with ions formed by PLA, were that the form of the measured ion KE distributions was critically dependent upon the voltage settings applied to the various elements in the extraction and source regions. Lacking a well characterised ion source, we had no way of determining which (if any) was the true KE distribution. We tackled this problem in two ways.

On the experimental front, we designed and built a Faraday cup detector, coupled it to the ablation chamber in place of the QMS, and measured high resolution (4 ns bin widths) time-of-arrival (TOA) spectra of ions formed in the 193 nm PLA of graphite in vacuum. Knowing, from the mass spectroscopic measurements, that almost all of these ions had $m/z=12$, it was a trivial exercise to convert the measured TOA spectrum into a KE distribution. This was then compared with the ‘equivalent’ KE spectrum derived using the QMS. Obtaining the latter was a fairly painstaking process, involving the recording of overlapping 20 eV sections of the

full KE spectrum, with the various applied voltages re-optimised to ensure maximum transmission in each case, which were subsequently spliced together. Figure 2(a) displays a C^+ ion KE distribution from 193 nm PLA of graphite in vacuum obtained in this way and, for comparison, Fig.2(b) shows the ion KE distribution obtained with the Faraday cup detector. Ratioing the two results could, in principle, provide one measure of the KE dependence of the mass spectrometer transmission.

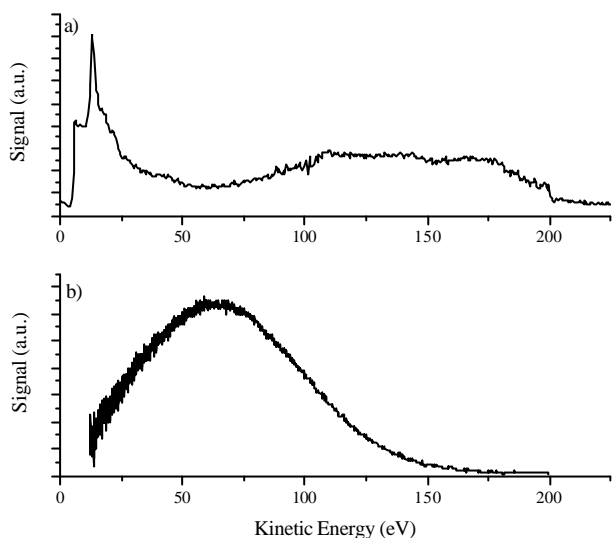


Figure 2. (a) A C^+ ion KE distribution from 193 nm PLA of graphite in vacuum obtained by splicing together overlapping 20 eV sections each recorded with optimised applied voltages throughout the QMS system, and, (b) for comparison, the ion KE distribution obtained with the Faraday cup detector.

To understand the problem better, we also modelled the energy-dependent transmission function using the SIMION code. Hiden provided a potential array file describing the front end of the mass spectrometer, and student Frederik Claeysens (FC) wrote a Monte Carlo add-in program that allows calculation of trajectories for individual ions, with any user-selected initial KE, as a function of initial position (within the 2mm-diameter entrance orifice) and angle (up to 4° off the centre axis of the spectrometer). These trajectory calculations, which are still approximate, in as much that they only treat individual ions and thus include no allowance for space charge effects, showed the electric field gradients in the region between lens 1 and the source region to have a huge, KE dependent, effect on the subsequent trajectory of any ions with non-zero off-axis velocity. In theory, the solution to this problem is to limit the detected ions to that small sub-set that propagate along the centre axis of the spectrometer. Such a modification was attempted, with help from Hiden, by introducing a small diode laser, the output beam from which defines the centre axis of the spectrometer and facilitates alignment of this axis with the irradiated spot on the target, and by incorporating a series of small apertures that define accurately the centre axis of the flight tube. Inevitably, however, there is a trade-off between aperture size and transmitted signal strength, so the problem of the KE dependent transmission can only be reduced, not solved. Indeed, after these modifications, it was found necessary to increase the filament lengths in the ioniser region to ensure sufficient sensitivity in RGA mode. For these reasons, progress towards determining mass selected ion and neutral KE distributions with this mass spectrometer, and the way these distributions vary with process conditions, has been much less successful than hoped. Given the lack of ion sources with well characterised broad KE distributions, it remains an open question whether any such KE distribution has been (or can be) definitively characterised in this way.

The above saga spanned the best part of 2 years, during which time it became imperative that the project student acquire data complementary to that targeted in the original proposal. To this end we carried out extensive studies of the plume accompanying PLA of graphite at 193 nm in vacuum, using a combination of wavelength, temporally and spatially resolved optical emission spectroscopy (OES), together with Faraday cup and Langmuir probe measurements of charged particle production, as a function of process conditions (*e.g.* laser fluence, angle of incidence, detailed target composition, *etc.*)¹⁹ The optical emissions are seen to extend much further (in both space and time) than can be reconciled with any model that assumes that the emitting states are populated solely during the laser ablation pulse. Various explanations were considered, and the observation rationalised by assuming that the emitting species arise via electron-ion recombination processes, stabilised by a third body in the early stages of plume expansion, and subsequent radiative cascade from the high Rydberg states that result from such associations. Emission from neutral C atoms was observed to be distributed symmetrically about the surface normal, whereas the C^+ emission – evident only at the higher incident fluences – was found to be localised in the solid angle between the propagation axis of the ablating laser pulse and the surface normal. Time-of-flight (TOF) and time gated imaging studies of the optical emission (see Fig.3, for example) provided measures of the expansion characteristics of emitting neutrals and ions within the plume. Electrostatic probe measurements enabled determination of the ion (and electron) yields and velocity distributions, as a function of scattering angle, and the dependence of these measurables on the incident pulse energy. These results, in turn, served as input for a simple two dimensional (2-D) model which provides a rationale for the observed anisotropy of the C^+ emission in terms of preferential multiphoton excitation (and ionisation) of C atoms in the leading part of the expanding plasma ball that are exposed to the greatest incident 193 nm photon flux.

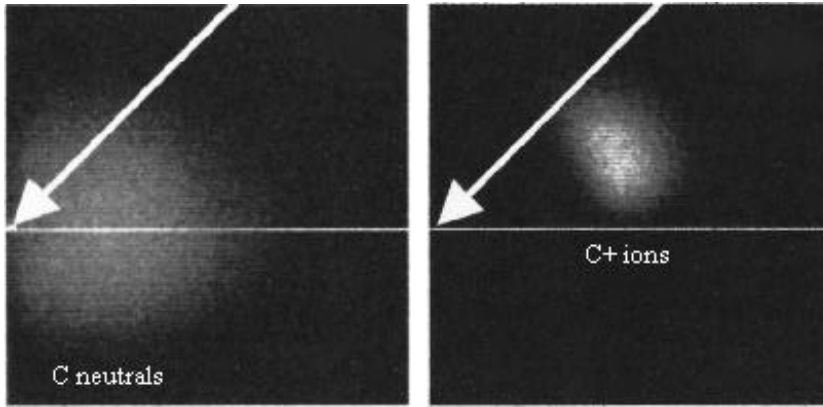


Fig.3. Time-gated images ($\Delta t = 100$ ns centred at $t = 630$ ns after the laser is incident on the target) of the optical emission from (left) slow moving C neutrals ($\lambda > 780$ nm) and (right) fast moving C⁺ ions (426 nm) following PLA. The laser (indicated by the arrow) is incident at 45° to the surface normal (indicated by the horizontal white line, with the surface of the graphite target being the left hand vertical edge of the picture).

In May 2001 the opportunity arose for FC to make a one month visit to work with Prof Demetrios Anglos at the Institute for Electronic Structure and Laser at FORTH, Heraklion, and to carry out complementary studies of graphite ablation, in vacuum, at 248 nm, using ns, ps and fs laser pulse durations, again using wavelength and time resolved OES to investigate emitting components within the ablation plume, and the way they varied with incident laser intensity. Nanosecond pulsed ablation was found to give a distinctively different optical emission spectrum from that observed with the two shorter pulse durations. Emissions attributable to electronically excited C*, Cⁿ⁺* and C₂* fragments were identified in the former (as in the 193 nm ns laser studies in Bristol), while the spectra obtained when using the shorter duration, higher intensity pulses contain an additional line attributable to C²⁺* species but none of the C* emission lines. Again, we deduce that each atomic emission is a step in the radiative cascade that follows when an electron recombines with a Cⁿ⁺ species (where n is one charge state higher than that of the observed emitter) formed in the original ablation process. Broad-band visible radiation attributable to black-body emission from larger particulates, was also observed following ablation with all three laser pulse durations. Time-gated imaging studies allowed estimation of the velocity distributions of each of the emitting species within the plume, and their variation with incident laser fluence and/or intensity. The deduced multi-component structure of the plume emission following excitation with short duration laser pulses was rationalised in terms of contributions from both non-thermal and thermal mechanisms for material ejection from the target. Use of longer duration (nanosecond) laser pulses offers the opportunity for additional laser-plume interactions, which we believe are responsible for much of the emission seen in the ns PLA of graphite.

Particulates tend to be endemic in the PLA of graphite and most other target materials, and are generally incorporated in the deposited film – to the detriment of most film properties. For this reason, there continues to be much interest both in their origins, and in strategies by which they can be minimised.²⁰ As part of our Bristol-based work we specifically compared and contrasted DLC film growth by 193 nm PLA of both graphite and CVD diamond targets, in vacuum. The latter were grown in-house, in a DC arc jet reactor in a project supported by EPSRC (GR/L63341) and De Beers Industrial Diamond Ltd.²¹ The resulting films, and the post-ablated targets, were analysed by laser Raman spectroscopy (LRS) and scanning electron microscopy (SEM), and their field emission properties investigated via I - V curves measured in a home-built test station. In all regards, similarities outweighed differences. LRS confirmed that PLA induced graphitisation of the diamond surface. Films grown from both targets showed similar (~ 30 V μm^{-1}) emission threshold voltages. Once above threshold, however, films deposited from CVD diamond showed the steeper slope (dI/dV). This finding correlates with the (somewhat unexpected) observation that films deposited using the CVD diamond target actually contain the higher density of macroparticles. This, we suspect, was a function of the specific polycrystalline CVD diamond films used, which were deposited at high (> 100 $\mu\text{m hr}^{-1}$) growth rates, and thus include many more small voids than material grown at more traditional (~ 1 $\mu\text{m hr}^{-1}$) rates. Rapid heating of process gas trapped in such voids leading to localised material explosion is generally recognised as one of the most likely causes of particulate ejection during PLA.

Notwithstanding the shortcomings of the QMS, we have actually made substantial progress towards many of the aims summarised in the original proposal. In the case of pulsed UV laser ablation of graphite, we have found alternative strategies by which to determine much about the KE and angular distributions of emitting ions and neutrals, the ways these vary with incident fluence and intensity, and the various mechanisms that contribute to material ejection from the target and electronic excitation of the plume. A key issue still to be answered is the contribution that ‘dark’ ground state material, arising as a result of thermally driven ablation, makes to the plume, and the characteristics of any resulting film. We have attempted to investigate the expansion characteristics of these particles using the QMS. The KE distribution of neutral particles with $m/z = 12$, detected in RGA mode with +20 V on the extractor (which should repel all nascent C⁺ ions in the plume with KE < 20 eV) is found to peak at ~ 3 eV. If correct, such a result would necessitate some considerable revision of the present consensus view as to what constitutes the optimal plume content for deposition of DLC films with high sp^3 content – a view that is based very much on OES measurements of emitting C⁺ ions.^{5,13-18} We argue that these are actually signatures of nascent C²⁺ ions, which are subjected to considerable acceleration in the early stages of plume expansion and reach terminal velocities much greater than those of thermally ejected particles which are neutral throughout their existence as gas phase species. Of course, we also confirm the presence of high KE ionic material both by OES and the electrostatic probe measurements, but suspect that this represents only a small fraction of the material that contributes to the eventual film.

Our application also proposed investigation of doping the hard carbon films *in situ* with, for example, N, S or B atoms. Thus far we have investigated the first two of these possibilities. N doping is being investigated by ablating graphite in a low background pressure of N₂, both with and without additional activation with a DC plasma discharge. OES reveals intense CN(B[?] X) emission

when the background N_2 is activated by the discharge (Fig.4), indicating substantial gas phase chemistry and the desired C-N bond formation *en route* to the substrate. Inevitably, the material deposition rate falls with increasing background pressure and the resulting films are softer (the particles impact with less KE); we are still juggling the process conditions (pressure, discharge conditions, target-substrate distance, substrate temperature, *etc*) to try and optimise the deposition rate whilst still retaining significant N incorporation – as revealed via IR absorption analyses of films deposited on KBr substrates^{22,23}. Systematic conductivity and field emission testing of these N doped DLC films will follow.

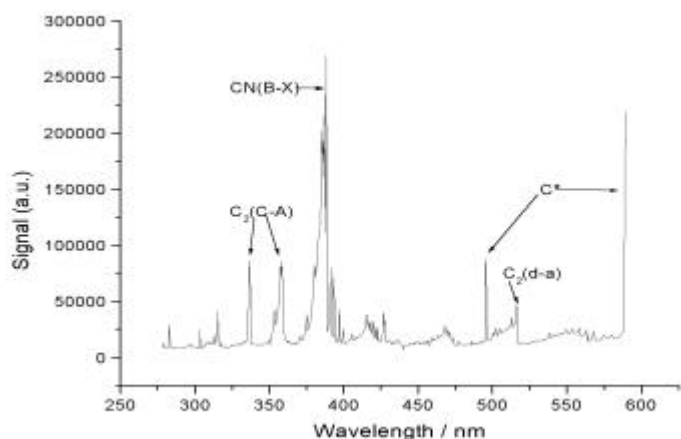


Fig.4. CN(B? X) emission spectrum observed during PLA of graphite in the presence of an N_2 discharge.

Various strategies have been investigated for incorporating S atoms in the DLC films corporation. Mixtures of finely divided sulfur and graphite failed to solidify into a pellet when cold pressed, even at loads $> 10 \text{ ton/cm}^2$. Inclusion of a small amount of adamantane ($C_{10}H_{16}$) aided compaction, but the resulting pellet tended to shatter when placed under vacuum. The most reliable and controllable procedure identified to date, involves preparation of a thin sulfur strip (by cold pressing, or by melting powdered sulfur), that is then mounted radially onto an existing graphite target on a stage rotating at 1 rpm. Similar strategies have been used for metal doping DLC films;²⁴ in both cases the dopant concentration can be varied simply by changing the strip width and thus the relative exposure times of the two components. Obviously, calibration experiments have had to be performed to establish their relative ablation rates – not surprisingly, given their very different boiling points, we find that sulfur ablates more efficiently than graphite when irradiated at 193 nm. A number of additional subtleties have been identified, however, which we are currently investigating further. Post-ablation EDAX analysis shows no significant re-deposition of sulfur onto the graphite part of the target surface, or vice versa. However, mass spectrometric analysis of the low ($\sim 10^{-4}$ Torr) background pressure that builds up during ablation of a rotating C:S target reveals formation of neutral CS_2 ($m/z = 76$) molecules, most obviously at the start of a graphite ablation phase. These gas phase species are assumed to arise from preferential sputtering of previously deposited sulfur (both on the substrate and, inevitably, the walls of the ablation chamber). Such an expectation accords with the results of preliminary TRIM calculations, and are an inevitable reflection of the lower surface displacement energy of atomic sulfur (2.88 eV/atom, *cf.* 7.8 eV/atom for carbon atoms in a graphite lattice²⁵). XPS and Auger spectroscopy have both been used to analyse the composition of S-doped DLC films grown at room temperature. At low fluences (5 J cm^{-2}), the S:C ratios in the films are some 2.5 \times the S:C aspect ratio on the rotating target. This ‘excess’ falls as the incident fluence is increased, however. This is understandable, given the very different melting temperatures of the two materials (386 K for sulfur, *cf.* $\sim 4300 \text{ K}$ for carbon). SEM analysis (Fig.5) reveals the deposited films to be smooth, save for occasional needle- or tube-like macroparticles, which EDAX mapping show to be sulfur rich. Similar filamentary structures have also been observed in films grown from microwave activated CS_2/H_2 and $CH_4/H_2S/H_2$ mixtures in our laboratory and are very much an area of current research in our group.

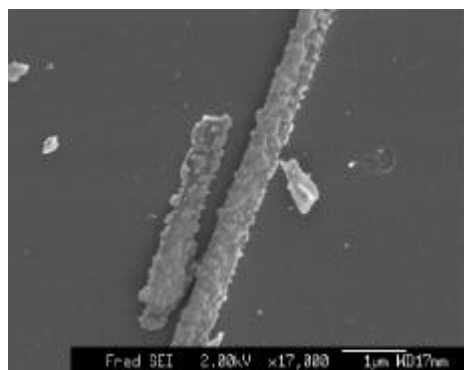


Figure 5. SEM picture of needle-like particles found on the surface of S-doped DLC films after PLD from C:S targets.

The original project abstract indicated that the programme would be extended to studies of polymer ablation at its later stages but, given the difficulties of obtaining quantitative information from the QMS, our recent efforts have been focused on 193 nm ablation of a somewhat simpler, two component, system, ZnO – both in vacuum and in low background pressures of both O_2 and N_2 . Again, the ablation plume has been analysed by wavelength and temporally resolved OES, by electrostatic probe measurements and, as best as possible, using the QMS. XRD shows that the resulting films are largely amorphous if deposited at room temperature, but to be *c*-axis aligned if deposited in a low background pressure (10 mTorr) of O_2 and at elevated ($> 400^\circ\text{C}$) substrate temperatures –

even on substrates like Si and quartz where the growth is not epitaxial. Investigations of the 193 nm PLA of (and PLD from) pure ZnO targets, and commercial ZnO targets containing 2% Al₂O₃ and Ga₂O₃ are ongoing as part of GR/R40333/01, which started in 4/01.

4. Research Impact and Benefits to Society

The proposed research identified two principal objectives: to provide a better understanding of important mechanisms involved in pulsed laser ablation and subsequent film deposition, and to optimise film properties, especially with regard to electron emission. Progress with regard to the former aspect has been very pleasing, notwithstanding the limitations of the QMS. By working through a progressively more complex series of target materials (graphite, CVD diamond, Al and Cu (not discussed here), graphite + sulfur, graphite in background N₂ and, most recently, ZnO, with and without background pressures of O₂, we have succeeded in identifying recognisable signatures of laser-target and laser-plume interactions, explored the roles of thermal and electronic contributions to the ablation process and the way these vary with both laser and target parameters, developed protocols for unravelling sub-structure within the ablation plume, characterising velocity and KE distributions, and provided explanations for the extent and duration of the electronic emissions that accompany almost all PLA processes. Progress towards optimisation of film properties, especially with regard to electron emission, is reflected by the recent invitation to form part of a successful DTI/LINK bid (AEROFED) in which Smiths Industries Aerospace, Brimar Ltd, ourselves and Bath University have joined forces in an 'evaluating a research opportunity to realise a low voltage, field emission display for use as a multi-functional avionic flat panel'. Our role is to focus particular attention upon films of N-doped DLC, boron nitride and semiconducting ZnO doped with Al or Ga.

5. Explanation of Expenditure

The sub-division of expenditures turned out very much as expected at the outset. The modest overspend is mainly attributable to the welcome, but unbudgeted, significant increase in the approved annual stipend for project students during the period of the grant. Informal conversations with EPSRC staff lead us to understand that this will be treated as a legitimate overspend by the grant-holder and will be reimbursed accordingly.

6. Further Research and Dissemination Activities

Aspects of this work have been presented at the following meetings:

- ?? American Vacuum Society ICMCTF'99, San Diego, CA, U.S.A., April 1999,
- ?? COLA'99 – 5th International Conference on Laser Ablation, Göttingen, Germany, July 1999,
- ?? Gordon Conference on Laser Ablation, New Hampshire, U.S.A., July, 2000,

at invited seminars at University of Surrey (2/2000), Manchester Metropolitan University (5/2000) and Cambridge University (May 2000), and at less formal presentations at Smiths Industries Aerospace (12/2000), FORTH, Crete (5/2001), University of Birmingham (8/2001).

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