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Production of nanocrystalline diamond by laser ablation at the solid/liquid interface

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Abstract

Diamond nanocrystals have been produced by the pulsed laser ablation of graphite at room temperature and pressure in two liquids (water and cyclohexane). This suggests that the mechanism for diamond formation maybe a result of the high-pressure, high-temperature conditions found within the cavitation bubbles in the ablation plume, rather than a chemical route such as etching of non-diamond species by OH.

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1. Introduction

Pulsed laser ablation (PLA) is a well-known method to produce thin films by ablating material from a solid target of known composition [1]. PLA usually occurs in vacuum, or sometimes in a background of inert gas such as Ar or more reactive gases such as ammonia or nitrogen. Recently a new variation of PLA has been reported whereby the target is immersed in a liquid medium, and the laser beam is focused through the liquid onto the target surface [2]. The interaction of the high-intensity laser pulse with the target surface produces an ablation plume of ejected material, in which the surface of the solid target and a small amount of the surrounding liquid are vaporised to form bubbles within the liquid. As more material is vaporised, the bubbles expand, until, at a certain critical combination of temperature and pressure, they collapse [3]. It is believed that when the bubbles collapse the species within are subjected to temperatures of thousands of Kelvin and pressures of several gigapascal, and that these extreme conditions are what allows novel materials to be created [3,4]. The conditions inside these bubbles are similar to cavitation bubbles generated by ultrasonic waves or by arc discharges under liquids. Ionisation and breakdown of components within the bubbles can occur, and the subsequent electron–ion recombination followed by radiative cascade can produce significant optical emission. The advantage of the laser-induced cavitation bubble method is that large amounts of a solid target can be vaporised and incorporated into the bubble as well as the liquid, allowing materials to be made that contain a mixture of atoms from the target and the liquid. Unlike the arc discharge method that requires the solid electrode material to be electrically conducting, the liquid-phase PLA (LP-PLA) method can utilise insulating target materials, allowing a much wider range of novel materials to be produced. The products are usually in the form of nanoparticles that remain suspended within the liquid medium, and can be isolated by filtration and evaporation of the liquid.

This novel LP-PLA technique has been used to produce a variety of materials, including diamond-like carbon films from liquid aromatic hydrocarbons [2], nanocrystals of carbon nitride by ablating graphite in ammonia solution [5] and nanometre-sized particles of Ti, Ag, Au, Si and TiC [6]. Recently, Wang et al. [7] converted hexagonal boron nitride crystals into cubic boron nitride crystals using this method. Nanocrystalline diamond has also been produced by LP-PLA using a graphite target along with water or acetone as the liquid medium [8–11]. The authors' main conclusions were that OH groups formed from the oxygen-containing liquids were etching non-diamond carbon species from the surface, thereby allowing diamond to form prefer-

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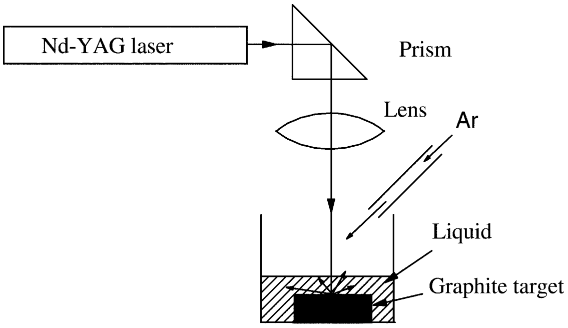

Fig. 1. Schematic diagram of the experimental setup used in this study.

entially. Thus, the OH was thought to be playing a role analogous to that of atomic hydrogen in conventional diamond CVD [12].

The aim of the present work is first to reproduce the findings of Ref. [11] to make diamond nanoparticles using water as the liquid medium, and then to explore the use of a non-aqueous, non-polar liquid medium. This tests the theory that OH species are necessary for diamond production in LP-PLA systems.

2. Experimental

Fig. 1 shows a schematic diagram of the apparatus. The laser light used was the first overtone from a Nd:YAG laser, at a wavelength of 532 nm. The maximum power was 130 mJ per pulse with a pulse duration of 10 ns at a repetition rate of 10 Hz. The beam was steered vertically downwards by a prism, and focused using a 25-cm-focal-length lens onto a solid target positioned in a glass reaction vessel. A long focal length lens was used to prevent liquid splashing onto the lens. The beam was focused down to a spot-size diameter of approximately 0.5 mm (giving a maximum fluence of 66 J cm^{-2}) by translating either the lens or the reaction vessel.

The target was a pure graphite disk of area 10 cm^2, with the top surface polished smooth. The target was placed in the bottom of the reaction vessel, and either deionised water or cyclohexane was poured into the vessel until it covered the target to a depth of ~1 cm. When using flammable liquids (such as cyclohexane), a continuous stream of Ar gas was flowed into the top of the reaction vessel to prevent possible combustion of the liquid.

Deposition usually lasted for 15 min, which corresponded to approximately 9000 laser shots. Some loss of liquid occurred during this time due to splashing and evaporation, and so the liquid level was periodically topped-up as necessary. Every laser pulse was accompanied by intense emission of visible light from the plume above the focal point. This light was captured via a telescope with a focal length of 20 cm (which was

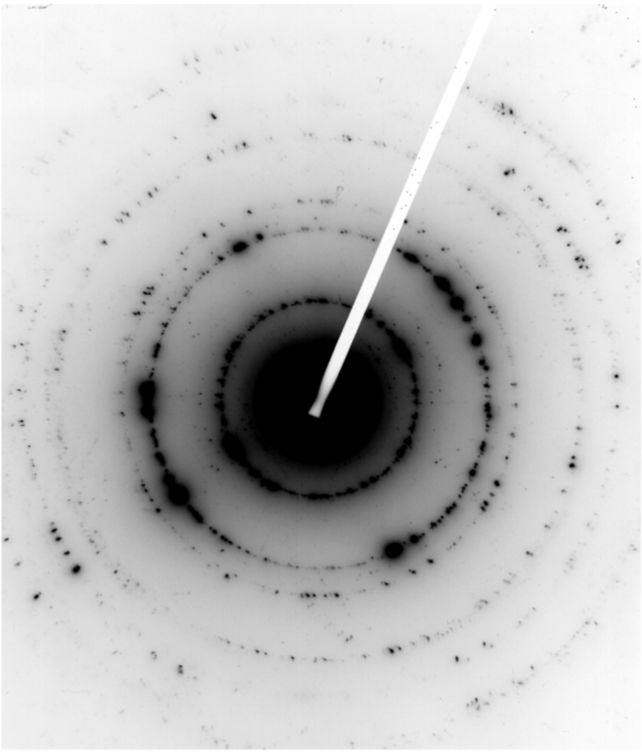

Fig. 2. A TEM ring pattern taken from a sample made from graphite ablated under water.

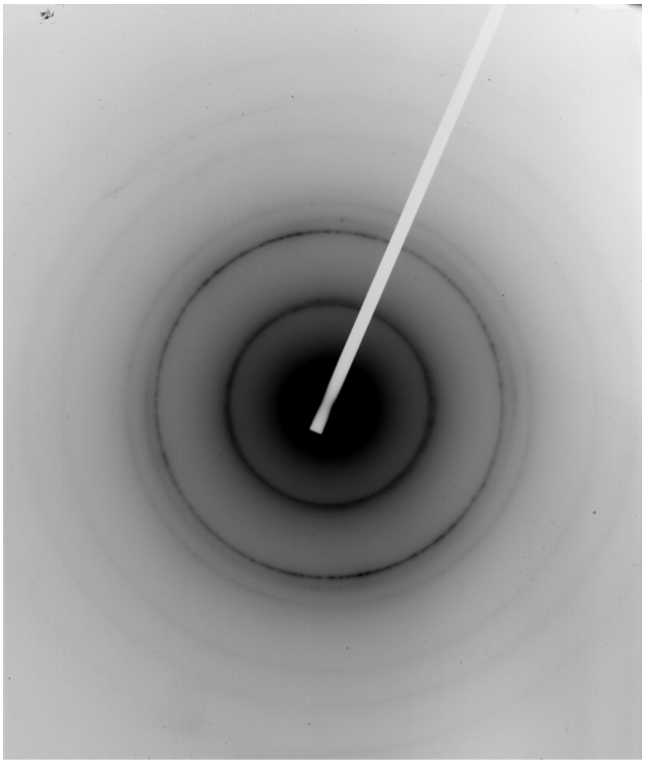

Fig. 3. A TEM ring pattern taken from a sample made from graphite ablated under cyclohexane.

Table 1
The plane spacings and lattice parameters calculated from the SAED data for sample A (deposited from graphite in water) and sample B (from graphite in cyclohexane), with those for diamond also given for comparison

Plane	Plane spacings (Å)			Lattice parameter (*a*, *b*, *c*) (Å)		
	Diamond	Sample A	Sample B	Diamond	Sample A	Sample B
1 1 1	2.059	2.156	2.082	3.60	3.734	3.606
2 2 0	1.261	1.250	1.225	3.60	3.536	3.465
3 1 1	1.075	1.074	1.048	3.60	3.562	3.476

focused onto the ablation plume). This was passed via a grating to a charge-coupled device detector via a quartz fibre optic bundle. The system used was an Oriel Instaspec IV, the monochromator had a 600 lines mm^{-1} ruled grating giving a resolution of 0.9 nm.

After deposition, the liquid often appeared slightly coloured (usually pale yellow) due to the suspension of nanoparticles. This liquid was pipetted off from the solid target and stored in air-tight vials prior to analysis. After deposition the graphite target surface had numerous pits caused by the ablation. These pits were approximately 0.5–1 mm wide and approximately 0.5 mm deep, and were randomly scattered over the surface in a radius of approximately 5 mm from the centre of the disk. This scatter was due to the laser beam being deflected as it passed through the moving gas–liquid ablation plume to strike different regions of the target.

Transmission electron microscope (TEM) analysis of the products was carried out by pipetting the liquid suspension onto a carbon-coated TEM grid, and allowing it to dry. For elemental analysis using energy dispersive X-ray (EDX) analysis, the products were dropped onto SiO_2-coated grids to ensure that the elemental fingerprint of the sample was from the sample and not from the TEM grid. Two TEM microscopes were used for the analysis, a JEOL 2010 and a Philips EM430, with electron source accelerating voltages of 200 and 250 kV, respectively. EDX spectra were taken on the JEOL 2010 with a windowless Oxford Instruments ISIS-310 EDX analyser utilising a Si detector.

Laser Raman spectra were taken using a Renishaw 2000 laser Raman Spectrometer at an excitation wavelength of 325 nm. Samples were prepared for Raman spectroscopy by putting several drops of the suspension on a glass slide and allowing the liquid to evaporate.

3. Results and discussion

In both the water and the cyclohexane experiments, the majority (≈95%) of the solid material found in the suspension was composed of the unchanged target material, namely, graphite. However, occasionally, nanocrys-

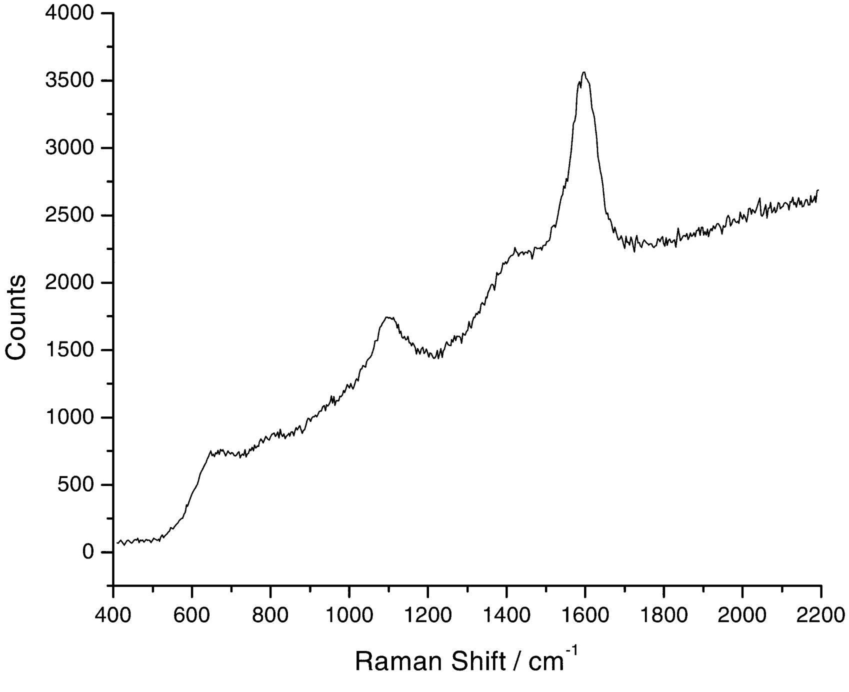

Fig. 4. A laser Raman spectrum taken from a sample made from graphite ablated under cyclohexane.

tals were found in small patches at the edge of larger pieces of graphite. Fig. 2 shows a selected area electron diffraction (SAED) ring pattern from nanocrystals following ablation of graphite under water (sample A). This ring pattern was analysed using a standard computer program [13], and the lattice plane spacings for the three inner rings were obtained. They corresponded well to the {1 1 1}, {2 2 0} and {3 1 1} planes of diamond, as can be seen in Table 1. From these plane spacings, the lattice parameter was determined. It was found to correspond to that of diamond [14]. EDX spectra indicated the presence of only C, Si and O in the area being studied (the Si and O are from the SiO_2 support grid). This result supports those of Yang et al. [8], and confirm that diamond may be produced by ablation of graphite under water.

Fig. 3 shows an SAED pattern from nanocrystals following ablation of graphite under cyclohexane (sample B). The plane spacings were measured as above, and again corresponded to those of diamond (Table 1). This result shows that it is not essential to have an oxygen-containing liquid to produce diamond by LP-PLA. This suggests that the mechanism for the production for diamond in LP-PLA systems proposed by Yang et al. [8], namely, the preferential etching of graphitic carbon by O and OH species, is not correct. These findings suggest that the mechanism is likely to be more physical in nature, such as that found in conventional high-temperature, high-pressure methods.

Laser Raman analysis of the material was difficult to perform as the minimum spot size of the laser Raman spectrometer was approximately 1 μm, and the crystal sizes were significantly smaller than this. A laser Raman spectrum is shown in Fig. 4. It shows a spectrum typical of disordered graphite, but at approximately 1150 cm^{-1} there is a broad peak that several authors have previously assigned to *trans*-polyacetylene [15,16]. However, this peak is also commonly seen in nanocrystalline diamond films grown by gas-phase CVD methods [16].

Fig. 5 shows optical emission spectra taken of the light-emitting region of the ablation plume. Unfortunately, most of the light emission was at the liquid/gas interface at the top of the reaction vessel. Peaks due to excited H, O and H_2O are visible when ablating under water in a background of air (Fig. 5b), but only from H when ablating under cyclohexane in a background of Ar (Fig. 5a). In both spectra the presence of the large peak from atomic H is interesting, since H is believed to be necessary for the growth of diamond in conventional gas-phase CVD methods. This suggests that atomic H maybe a common reagent necessary in both LP-PLA and CVD diamond growth, and that the growth mechanism may therefore be similar in both systems.

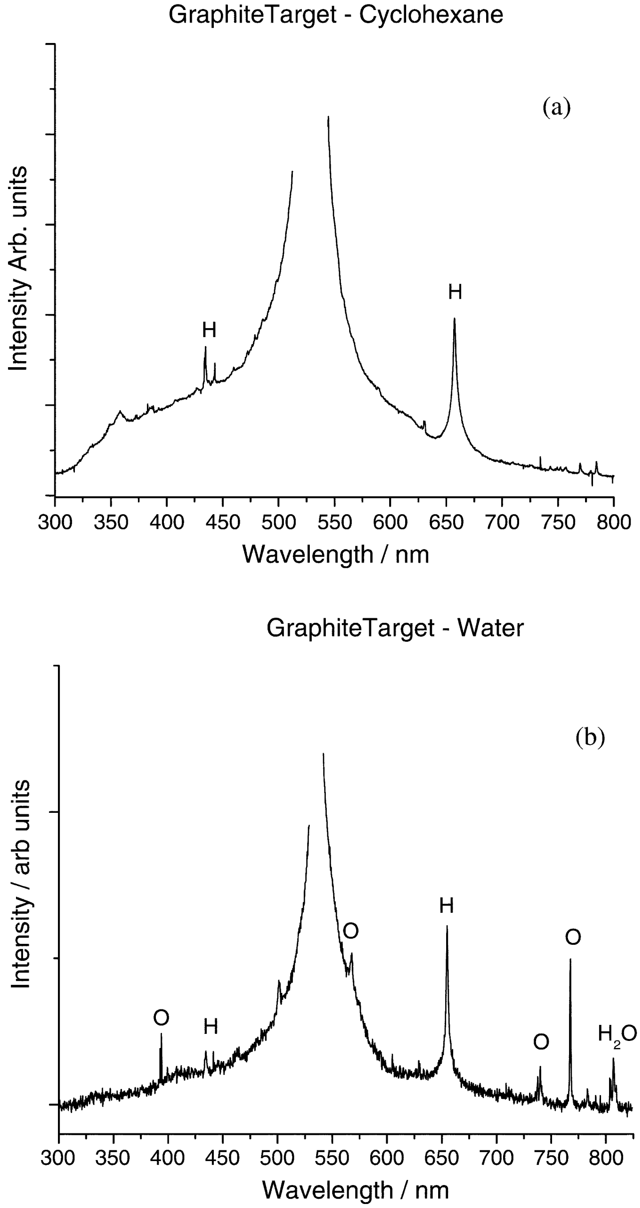

Fig. 5. Optical emission spectra of the light-emitting region of the ablation plume. Peaks were identified using standard reference data tables [17], and the NIST atomic spectra database [18]. Spectra are from ablation of graphite under (a) cyclohexane and (b) water. The large peak in the centre is from scattered light from the laser source at 532 nm.

4. Conclusions

The technique of LP-PLA shows great potential as a route to novel crystalline materials. We have demonstrated that diamond nanocrystals can be produced using both water and cyclohexane as the liquid media, although the yield is still very small. However, this technique is still in its infancy, with much of the parameter space yet to be investigated. Optimising the laser power, fluence, wavelength and focusing may improve yields substantially. Furthermore, by changing the composition of the target to include mixtures of other elements, such as P, B, Si, S, etc., as well as varying the composition of the liquid medium, this technique may allow nanocrystals of other potentially useful materials to be made, such as carbon nitride or carbon phosphide.

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