

Diamond and diamond-like carbon in laser heated diamond anvil cell at 16.5 GPa and above 2000 K from pyrolytic graphite

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Diamond and diamond like carbon have been synthesized by direct conversion of pyrolytic carbon at pressure, 16.5 GPa and temperature, ~ 2000 K using a Laser Heated Diamond Anvil Cell (LHDAC) facility. The formation of diamond and diamond like carbon is confirmed by micro-Raman and scanning electron microscopy. The synthesised material has been found as opaque and colourless. The diamond crystals formed in this process are of micrometer size having regular facets. In this experiment, the diamond formation pressure is much lower than reported in shock pressure experiments.

Keywords: Pyrolytic graphite, Synthesis of diamond, Diamond anvil cell, Laser heating, Micro-Raman, Scanning electron image

1 Introduction

The synthesis of diamond and diamond-like carbon (DLC) materials is an area of intensive research¹⁻⁶. In addition to high pressure synthesis using catalytic solvents, the direct conversion of graphite to diamond has been reported and more recently, it has been suggested that the direct conversion of graphite to diamond can be accomplished by core-excitation using synchrotron X-rays⁷. The experimental conditions under which transparent diamonds were obtained from graphite have been explored in a multianvil apparatus³. Yusa *et al.*^{8,9}, have reported direct conversion of single crystal of graphite to hexagonal diamond (lonsdaleite). However, the *P-T* conditions under which different kinds of diamonds and diamond-like carbon formed in LHDAC are not well documented. Further, the formation of diamond or DLC depends heavily on quality of the starting material. Non-graphitizing amorphous carbon are normally difficult to transform into diamond¹⁰.

Yamada and Tanabe⁴ have found that the direct transition to diamond from pyrolytic graphite under shock pressure conditions occurs at 19.6 GPa. The study of formation of diamond like material is important because it has been seen that nano-crystalline diamonds obtained at high pressure-high temperatures has extreme hardness of ~120-145 GPa, matching with that of bulk diamond⁷. The DLC materials are hard, amorphous and contain a

significant fraction of sp³ bonded carbon atoms and have free energy minimum close to that of diamond. Static compression studies have concluded that they have density between diamond and graphite¹¹⁻¹⁵. In this paper, the synthesis of diamond from pyrolytic graphite under the action of high pressure and high temperature using LHDAC facility has been studied.

2 Experimental Details

The experiment was carried out by using LHDAC facility¹⁶. It consists of a Mao-Bell type diamond anvil cell (DAC) into which a CO₂ ($\lambda=10.6\mu\text{m}$) laser beam is focused to heat the sample. The DAC is mounted on a XYZ stage, in which motion along the X-Y directions (beam direction is Z) is brought about by two automated nanomovers. The DAC can be moved in steps as small as 10 nm with respect to the focused laser spot. By the controlled movement of the stage various regions of the sample are subjected to laser heating. Heating of the sample is observed by using a CCD based imaging system which offers a resolution of 640 * 480 dpi. Temperature and pressure are the two crucial parameters that are to be measured in a LHDAC facility. Temperature measurement is done by recording the black-body radiation spectrum of the hot, microscopic sample and utilizing Planck's law. Pressure is measured using the well-known ruby fluorescence method. The black body radiation of the sample and ruby fluorescence

spectra are recorded by feeding the signal through optical fiber into LN₂-cooled CCD based spectrometer^{16,17} (M/s Jobin-Yvon).

The temperature attainable in LHDAC setup is ~5000K. Since graphitization of diamond takes place at ~900K, sufficient thermal insulation has to be provided to the diamonds. Thus sample assembly is very crucial and has to be optimized for efficiently converting the incident IR beam into heat concentrated on the sample without much dissipation. After several attempts the sample assembly has been optimized as follows. Stainless steel gasket is preindented to a thickness of ~80 μm and a through hole of diameter ~150 μm is drilled in the centre. A small chip of pyrolytic graphite of ~100 μm is mounted on small pieces of ruby to insulate it from the diamond. Another ruby crystal, ~10-15 μm is placed in the sample chamber for pressure calibration. This hole is completely filled with liquid argon by a custom designed cryogenic argon loading facility¹⁸. Argon gas is preferred because it acts as good thermal insulator, IR window and also as pressure transmitting media. Figure 1a shows a typical sample assembly for laser heating inside the diamond anvil cell. Pyrolytic graphite is taken up to a pressure of 16.5 GPa by monitoring the ruby fluorescence peak. On this sample 10.6 μm CO₂ laser (120W) is focused for heating, the focal spot is ~30 μm . A persistent glow seen on the sample indicates that the coupling of the laser to the sample is very good. This efficient heating also validates the sample assembly procedure adopted. As the focal spot of the IR laser is small with respect to the sample size, radial temperature gradients are introduced. To reduce these temperature gradients, slow circular scan has been carried out employing the automated nanomover system¹⁹. While the sample was being laser heated, temperature measurement was carried out by spectro-radiometry and was found to be ~ 2000K. After ensuring that all the regions of the sample were brought in focus with the laser, the laser power is gradually turned off and pressure is released in steps to retrieve the sample for further studies. The laser heated sample contained in DAC is shown in Fig. 1(b).

3 Results and Discussion

On visual inspection of the retrieved sample using a 100X stereomicroscope, the laser heated sample showed little variation in its features. It showed signs of heating and some deformation of the initial

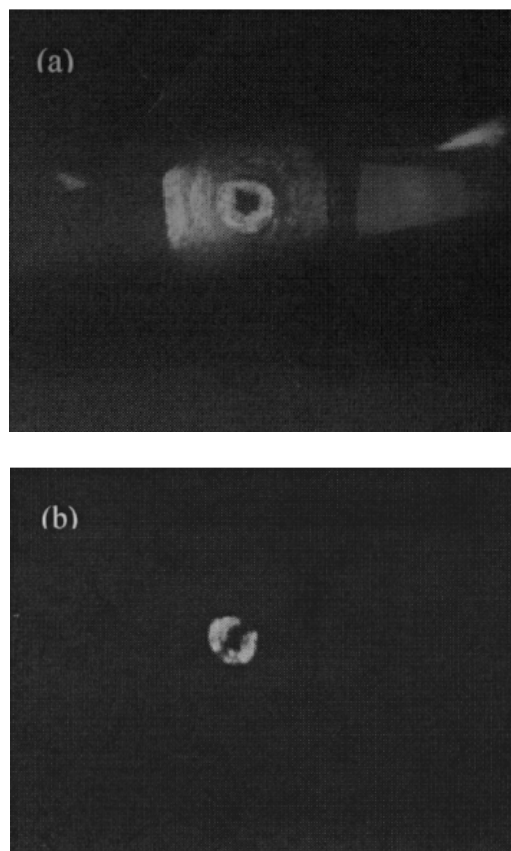


Fig. 1 — Sample contained inside the diamond anvil cell at 16.5 GPa, gasket through hole ~150 μm and sample ~80 μm : (a) before laser heating (b) after laser heating

morphology of the sample was observed. The morphology of the sample was having scars of laser heating. However, the material was completely opaque and colourless.

The carbon polymorphs can be unambiguously identified from their Raman spectra as its features of the Raman spectra depend on the ratios of sp^2 (graphite-like)/ sp^3 (diamond-like) bonds⁵. In order to investigate further micro-Raman was carried out by focusing the laser on various regions of the sample. On most of the regions of the sample double hump pattern was observed as shown in Fig. 2(a). This is well known feature of DLC, where the two peaks are named as G and D. The peak G is due to bond stretching of all pairs of sp^2 atoms and D is due to breathing mode of atoms in the rings. However, on some regions of the sample a Raman spectrum could be collected, clearly indicating sp^3 carbon bonding. The diamond Raman peak at 1331 cm^{-1} , was clearly riding on a typical DLC background as shown in Fig. 2(b).

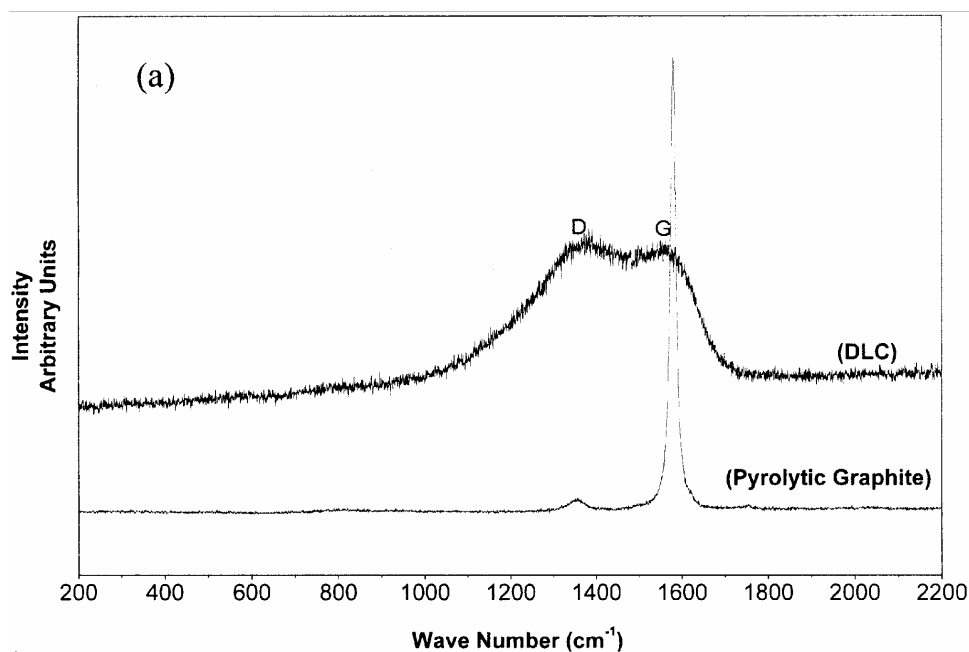


Fig. 2(a) — The micro-Raman spectra of laser heated sample having typical DLC characteristics

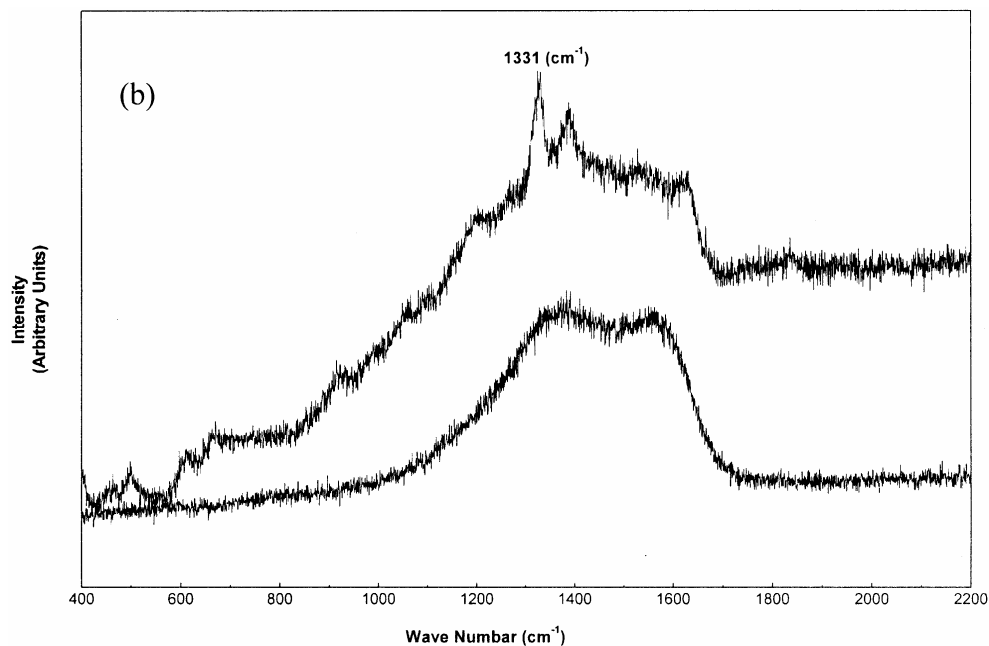


Fig. 2(b) — Micro-Raman spectra with diamond peak at 1331 cm^{-1} riding on DLC background

To see if the morphology of the sample is different in the regions where diamond like carbon is observed, the sample was coated with gold and observed under SEM. The scanning electron micrograph (Figs 3a and 3b) show the picture of the entire sample of dimension $\sim 70\text{--}80\text{ }\mu\text{m}$ across. The sample shows regions of layered structure at the edges, typical of

pyrolytic graphite. However, there are regions showing granular structure and small microcrystalline regions having regular facets. Figs 3c and 3d show the enlarged picture of such granules having very interesting shape and morphology. It can be seen that the granules are of $\sim 2\text{ }\mu\text{m}$ in size and have regular facets.

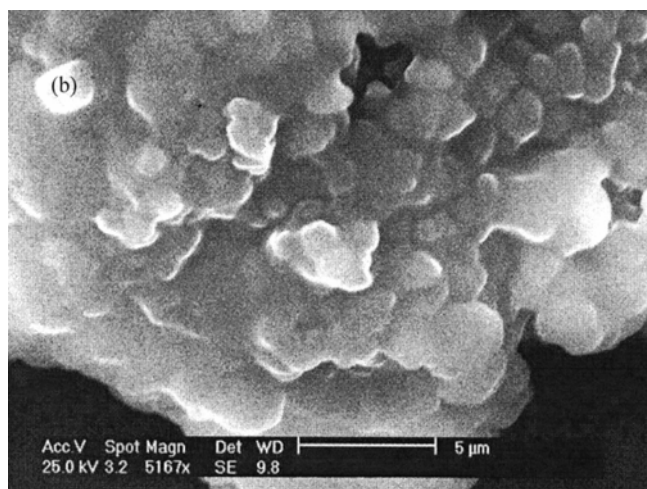
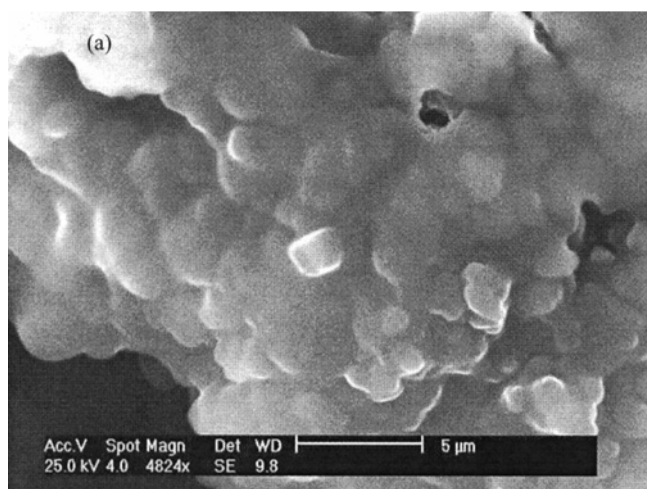


Fig. 3(a & b) — Low magnification SEM image of the laser heated sample

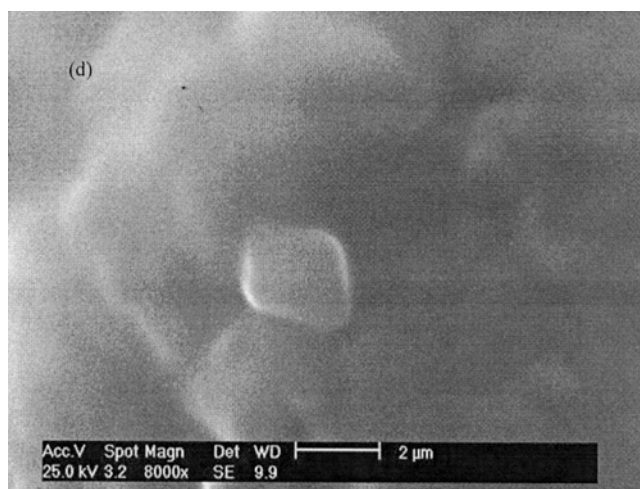
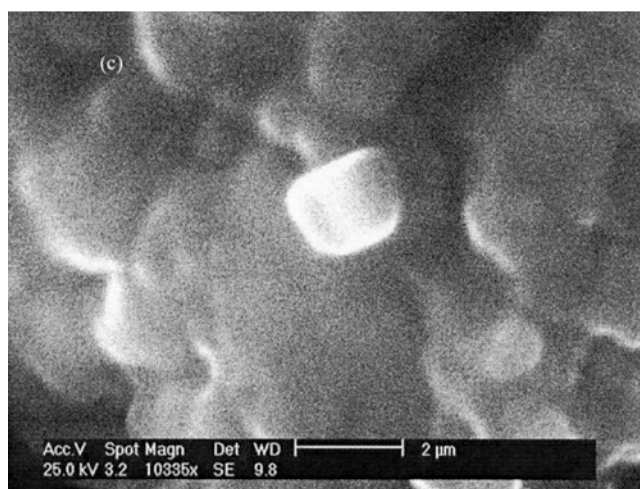


Fig. 3(c & d) — Magnified image of micrometer size granules of diamond showing square morphology

As compared to the shock induced experiment on direct conversion of pyrolytic graphite to diamond, the transition pressure observed in this static pressure experiment is much lower i.e., 16.5 GPa as against 19.6 GPa⁴. Further, in this static high pressure experiment the Raman signal from diamond is quite sharp and clear. Also, well faceted morphology of the diamond micro crystals have been observed. The shaded region shown in Fig. 4 indicates our experimental conditions. The location of the shaded region in the P - T diagram explains the non-observance of the transparent phase of the diamond.

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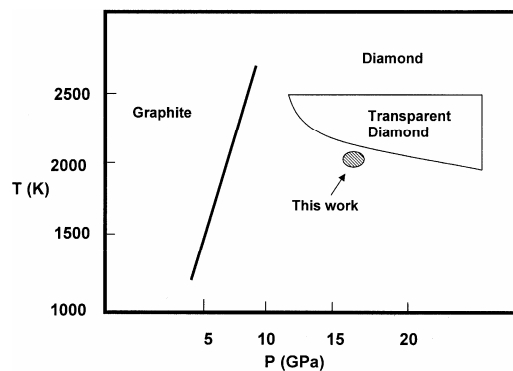


Fig. 4 — Schematic of synthesis conditions experimentally obtained (adapted from ref. 4)

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