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## Formation of diamond-like carbon by fs laser irradiation of organic liquids

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### ABSTRACT

The high intensities generated in femtosecond (fs) laser interactions offers the possibility of novel formation routes for diamond and diamond-like carbon materials. Coulomb explosion, a common phenomenon in intensive fs irradiation, has recently been shown to lead to a direct graphite–diamond phase transition on the surface of graphite. In this paper we report the results of fs irradiation of a variety of liquid organic compounds at intensities in the Coulomb explosion regime. The products of laser-induced chemistry under these conditions have been studied using visual/surface enhanced Raman and transmission electron microscopy (TEM). Surface enhanced Raman spectra/TEM show that an intermediate diamond phase, trans-polyacetylene chains and amorphous carbon are present after fs irradiation of liquid alkanes. We also find that the diamond component can be enhanced by irradiation in the presence of certain transition metals; however the origin of this effect is still uncertain. Diamond films deposited in this way are found to exhibit a nano-assembled structure involving individual nanodiamonds extending over an area of about 1 cm<sup>2</sup>. This process represents a wet chemical method for room temperature formation of diamond-like carbon films

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### 1. Introduction

Three kinds of *s* and *p* orbital electron hybridizations allow carbon to form various allotropes, such as, carbyne, i.e. *sp*-bond linear carbon chains, *sp*<sup>2</sup>-bonded graphite/graphene, *sp*<sup>3</sup>-bonded diamond (cubic or hexagonal diamonds), fullerenes and carbon nanotubes with dominant *sp*<sup>2</sup>-bonds mixed with a small amount of *sp*<sup>3</sup> bonded material. The phase transition from graphite to diamond requires a high temperature and high pressure condition [1–3]. Commercial nanodiamonds synthesized through detonation possess a low *sp*<sup>3</sup> fraction and contain a large fraction of amorphous carbon so that purification has to be done in order to improve the concentration of *sp*<sup>3</sup>-bonded nanodiamonds [4,5]. Although there are some reports on the fabrication of nanodiamonds by laser irradiation of graphite [6], C<sub>60</sub> [7] and carbon nanotubes [8], problems remain concerning the high operating cost and low production rate using these methods. A simple, straightforward, nanodiamond synthesis procedure is still required.

Lonsdaleite is the *sp*<sup>3</sup>-bonded diamond phase of carbon with a hexagonal structure. It can be synthesized by static compression of crystalline graphite at ≈ 13 GPa and temperatures > 1000 °C [9]. Trace amounts of hexagonal diamond are extensively found in the crystalline boundary of chemical vapor deposited (CVD) diamond films, where it accommodates large anisotropic stresses [10]. Misra et al. successfully

deposited 88% hexagonal diamond films on strained gallium nitride-coated quartz substrates at 800 °C by hot filament CVD [11]. Another technique, involving the dissociation of methane molecules in water with nanosecond UV laser pulses (λ = 193 nm), only results in the formation of small amounts of diamond-like nanoparticles consisting of tetrahedral carbon with graphitic inclusions [12]. Recently, it has been found that a localized graphite–diamond phase transition can be induced by fs laser pulses due to the generation of high pressure and temperature in a laser-induced shock wave [2]. In this paper, we report a method for the fabrication of diamond-like carbon films in hydrocarbon solutions by irradiation with fs laser pulses.

### 2. Experimental

The output beam of a regenerative amplified Ti:sapphire laser operating at 800 nm, and producing 90 fs pulses at a frequency of 1 kHz was focused into a quartz cell containing 20 ml of organic hydrocarbon liquid by a 4 cm focal length lens. As the diameter of the focused beam was ≈ 10 μm, the resulting laser intensity was near 10<sup>15</sup> W/cm<sup>2</sup> at a pulse energy of 300 μJ. As shown in the inset in Fig. 1, a transition metal plate was immersed in the liquid and the laser was focused on its surface. The liquid was stirred during irradiation to ensure uniformity. The resulting diamond deposit was collected on the metal plate (unirradiated areas), a Si substrate or a transmission electron microscopy (TEM) Cu-grid coated with lacey films placed in the vicinity of the laser focus. This deposit took the form of a light grey film. The chemical composition and structure of deposited films were characterized using

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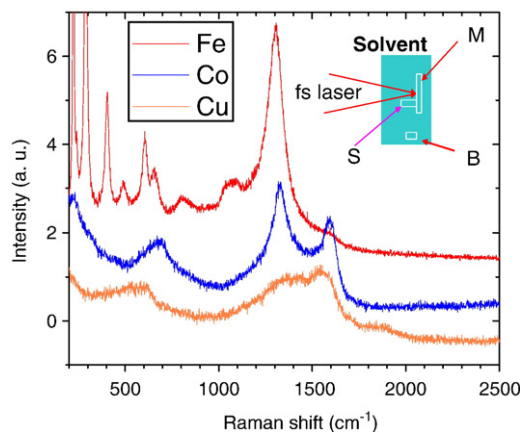


Fig. 1. Raman spectra of diamond films deposited in liquid hexane after fs laser irradiation of Cu, Co and Fe. Inset: deposition configuration.

visual Raman spectra with an excitation of 633 nm (He–Ne laser) and TEM. Molecular species in the obtained films were identified from surface enhanced Raman spectra (SERS) after in-situ deposition of 120 nm nano Ag films [13,14]. SERS spectra were recorded by focusing a 488 nm Ar ion laser beam into the resulting solution with a  $\times 50$  objective at an excitation power of 0.3 mW.

### 3. Results and discussion

Fig. 1 shows Raman spectra of carbon films deposited using different transition metal targets in HPLC (high-performance liquid chromatography) grade hexane. Carbon films deposited using Cu show spectra that are typical of tetrahedral amorphous carbon in which the G band (the stretching band of graphite) at  $1570\text{ cm}^{-1}$  overlaps with a D band (graphitic breathing mode) at  $1350\text{ cm}^{-1}$  [13]. A small bump near  $1900\text{ cm}^{-1}$  can be attributed to Raman scattering from carbynes accompanying Cu nanoparticles [13]. Carbon films deposited from Co show two modes near  $1320$  and  $1600\text{ cm}^{-1}$ , indicating the presence of a mixture of hexagonal diamond and microcrystalline graphite [13–18]. Carbon films deposited from Fe show a strong Raman feature at  $1308\text{ cm}^{-1}$  that can be attributed to hexagonal diamond [15–17]. However, the present Raman band displays a wider range of  $80\text{--}100\text{ cm}^{-1}$  than that of about  $20\text{ cm}^{-1}$  at FWHH (full-wide-at-half height) in the shock wave induced cubic-hexagonal structure phase diagram [16]. This probably indicates the presence of defect states and/or the mixture of other carbon compositions, such as, amorphous carbon. A weak band extending from  $1050$  to  $1140\text{ cm}^{-1}$  can be assigned to trans-polyacetylene chains [13,18]. The Raman peaks in the range of  $200\text{--}700\text{ cm}^{-1}$  can be attributed to  $\text{Fe}_2\text{O}_3$  with rhombohedral symmetry [19]. It is worth noting that pyrolytic amorphous carbon possesses two Raman modes centered at  $1355\text{ cm}^{-1}$  and  $1570\text{ cm}^{-1}$  [20]. In the present composition deposited with Fe the G band of graphitic phase degrades into a small kink at  $1570\text{ cm}^{-1}$ . It is thus evident that the presence of different metals can dramatically influence the final chemical binding states of carbon films. Fe is the proper choice for synthesizing diamond-like carbon in hexane.

Fig. 2 shows typical micrographs of hexagonal diamond films deposited in hexane after irradiation with a pulse energy of  $300\text{ }\mu\text{J}$  for 15 min. These films are assembled from individual nanoparticles with an average size of  $20\text{--}50\text{ nm}$ . Aggregated grains form larger structures with sizes up to several  $100\text{ nm}$ . These films cover a substrate area of  $\approx 1\text{ cm}^2$  and have a thickness of  $\approx 300\text{ nm}$ . Their thickness varies with distance and orientation relative to the focal point. Fig. 3 illustrates the high resolution transmission electron microscopy (HRTEM) imaging of a typical nanoparticle. The chemical composition analysis by X-ray energy dispersive spectrum evidences that the core of nanoparticle is

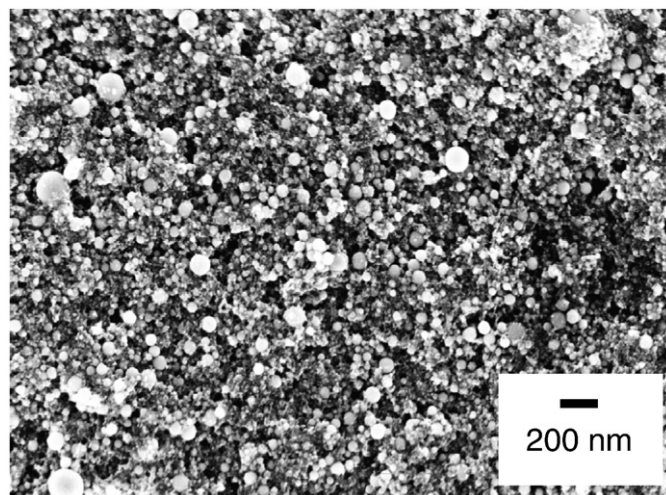


Fig. 2. Scanning electron microscopy (SEM) images for deposited nanodiamonds for Fe in hexane.

Fe with a low amount of oxygen, i.e., the partial oxidation of Fe, which corresponds to the Raman features of  $\text{Fe}_2\text{O}_3$ . A spherical carbon shell of  $5\text{--}10\text{ nm}$  in thickness is clearly observed. HRTEM imaging shows that the carbon shell is in a partial crystalline: the outer layer is amorphous carbon and the inter layer has an average fringe distance of  $0.257\text{ nm}$ . The fringe distance is remarkably smaller than  $0.345\text{ nm}$  of graphitic  $\{0002\}$  interplanar spacing while much larger than  $0.206\text{ nm}$  of diamond  $\{111\}$  lattice fringe spacing. This value is bigger than  $0.219\text{ nm}$  of  $\{002\}$  lattice fringe of lonsdaleite [21,22]. On the basis of Raman characterization, the present crystalline carbon phase could be an intermediate phase during the femtosecond laser-induced graphitic-diamond phase transition. Since its graphitic feature is suppressed (low G bands) the behaviors of this intermediate phase are more similar to a diamond phase. A further investigation with high resolution electron energy loss spectrum (EELS) is help to elucidate this issue. The related experiment is underway.

Additional experiments have shown that diamond films can also be synthesized in a variety of other hydrocarbon liquids, including acetone, methanol, and benzene when Fe is used as the substrate at

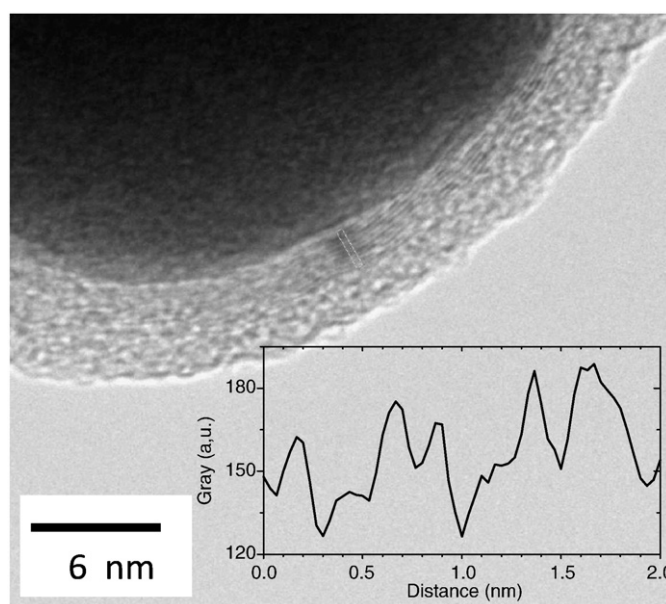
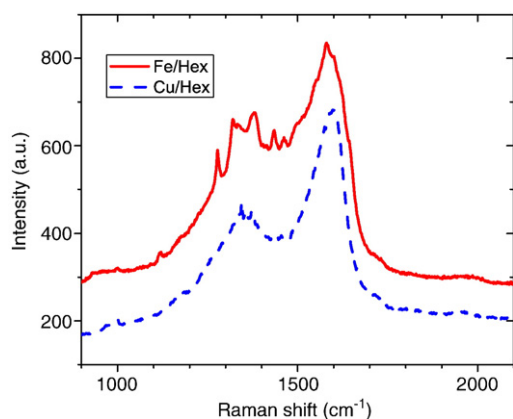


Fig. 3. High resolution TEM image of a Fe nanoparticle ablated in hexanes by femtosecond laser pulses. Inset: profile of lattice fringe of the carbon shell.



**Fig. 4.** Surface enhanced Raman scattering spectra for deposited films with the presence of Fe or Cu.

the laser focus. This suggests that the composition of the parent hydrocarbon is not critical in the formation of diamond-like carbon as the liquid only acts to provide as source of carbon. It is well known that pyrolytic carbon can be synthesized by heating hydrocarbons to 700–1200 °C [23] but pyrolysis is unlikely in our experiments because the interaction between fs pulses and molecules is a non-thermal process [2]. Some additional insight into the photolysis of liquid hydrocarbons by fs radiation can be obtained from SERS spectra. Fig. 4 shows SERS spectra of deposited films with the presence of Cu and Fe substrates. In both cases, amorphous carbon dominates as evident from the strong bands at 1370 and 1580  $\text{cm}^{-1}$ . The small bump at 1800–2200  $\text{cm}^{-1}$  show the characteristic Raman bands of carbynes [2,13]. This indicates that *sp*-bonded carbynes are one of the primary products of fs laser photolysis, independent of target composition. Fs irradiation of hexanes in the presence of Fe results in the formation of hexagonal diamond as evidenced by the Raman feature at 1315  $\text{cm}^{-1}$  together with trans-polyacetylene chains having Raman modes at 1120, 1180 and 1450  $\text{cm}^{-1}$ . It can be seen that irradiation in the presence of Cu only results in features attributable to trans-polyacetylene chains, without the characteristic spectral features of diamond. This suggests that Cu does not promote the formation of diamond-like carbon. It is important to point out that SERS Raman and conventional visual Raman (in Fig. 1) spectra yield different characteristic values of hexagonal diamond. This slight difference can be a result of different sensitivities of two measured methods. Besides, variable Raman features from 1306 to 1326  $\text{cm}^{-1}$  have been assigned to hexagonal diamond, possibly induced by defects and local stress [11, 15–17, 24].

The current experimental results suggest that the dominant mechanism in fs irradiation may be an ionization process initiated by Coulomb explosion which causes a step-wise dissociation of the precursor hydrocarbon molecules. This conclusion is supported by the direct observation of carbon species such as  $\text{C}^+$ ,  $\text{C}_2$  and  $\text{C}^{2+}$  by time of flight mass spectroscopy [25]. These species can act as fundamental building blocks in the growth of nanodiamond and carbynes [26,27]. In the dissociation process, chemical bonds will break in order of their binding energy. For example, the sequence of the primary dissociation

of acetone involves the sequential breaking of C–C, C–O and C–H bonds as the laser intensity is gradually increased [28]. To get elemental carbon and the  $\text{C}_2$  molecule, all hydrocarbon bonds must be dissociated. It has been previously found that a laser intensity of  $\approx 10^{15}$   $\text{W}/\text{cm}^2$  is required to dissociate C–H bonds [28] in simple hydrocarbons. This condition is approximately satisfied in the current experiments. As this laser intensity is close to the threshold for the Coulomb explosion of gas molecules, we attribute fs-induced dissociation in hydrocarbon solutions to this effect. It is still unclear how irradiation of Fe acts to enhance the formation of nanodiamond although it is well known that hexagonal diamonds are frequently present in iron meteorites [29]. The role of Fe as a catalyst of this process is worth further investigation.

#### 4. Conclusions

Nanostructured diamond-like films have been synthesized by fs laser dissociation of liquid hydrocarbons at room temperature. Microstructure and spectroscopic studies show that the crystalline diamond-like carbon is formed and coated on Fe nanoparticles. This new liquid-based synthetic route to diamond-like carbon films may open up novel applications for this material in a variety of fields. This work was supported by grants from the *Natural Science and Engineering Research Council of Canada* (NSERC).

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