

## DIAMOND SYNTHESIS BY LASERS: RECENT PROGRESS

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Recebido em 6/7/11; aceito em 10/2/12; publicado na web em 15/6/12

This paper provides an up-to-date critical review of methods for diamond synthesis by lasers. A provisional classification of synthesizing methods is carried out, in order to present a varied and heterogeneous experimental work that is as clear as possible. Laser diamond CVD methods involve chemical processes in a carbon-containing system induced by specific absorption of laser radiation, while diamond PVD methods involve physical processes induced by an intense, highly-directed laser beam. Different methods involving coupled, simultaneous action of lasers and classic CVD agents are suggested and discussed as prospective approaches for diamond synthesis.

Keywords: diamond synthesis; CVD; lasers.

### INTRODUCTION

Many advantageous properties of diamond – maximal or minimal in comparison with properties of other materials – make this a strategic material important for science and technology, yet whose mainly use was hitherto as a jewel. Mechanical and thermal properties of diamond have long been exploited, while the development of technology had not yet enabled other applications, such as optical and electronic, with a goal to attain use of the most delicate – biocompatible properties. Obtaining such a valuable material has attracted great scientific interest and led to many studies, involving extensive skills and efforts. Diamond can be synthesized by many methods in the region of its thermodynamic stability (high pressure, high temperature, HPHT) as well as in the region of its thermodynamic metastability (low pressure, low temperature). HPHT methods yield bulk material (grit), whereas low pressure and low temperature methods (Chemical Vapour Deposition, CVD) produce thin coatings and powders. HPHT methods are centered on the idea of reproducing terrestrial genesis of diamond. Dynamic compression of non-diamond carbon requires pressures up to 150 GPa and temperatures higher than 3000 °C, static compression requires pressures up to 20 GPa and temperatures up to 3000 °C, while the use of catalysts – solvents for carbon, reduces pressure and temperature values to around 5 GPa and 1300 °C. At low pressure and low temperature diamond can be synthesized from the gaseous phase, starting with reactants at a high chemical potential. Atomic hydrogen which possesses an extremely high chemical potential, has a very important role in the growth chemistry of metastable diamond: it takes part in activation of carbon species – diamond precursors, etches non-diamond carbon and stabilizes a growing surface of diamond. A particular set of varied and inventive methods for diamond synthesis, which predominantly apply in the region of its thermodynamic metastability, are methods that use lasers. As a laser is a specific source of electromagnetic radiation, it is used to promote a reaction in the system containing carbon in any aggregation form. Properties of laser radiation important in diamond synthesis are: high intensity, high directionality (i.e. low beam divergence) and monochromaticity (important for gaseous spectroactive precursors).

This paper outlines a provisional classification of the published

work on diamond synthesis by laser – based on laser radiation characteristics – by way of review. This provides some background and clarifies the varied and heterogeneous experimental work. Laser CVD methods, with an emphasis on spectroactivity of gaseous constituents of a working mixture for diamond synthesis, are described first. Heterogeneous nucleation of diamond, either by pyrolysis or photolysis, takes place on a selected substrate, while homogeneous nucleation – without the substrate – occurs in the gaseous diamond precursor which strongly absorbs the applied radiation. The creation of conditions for diamond synthesis in plasma by lasers is presented separately. All these methods may be considered successful in that they showed a proper Raman spectrum and SEM evidence of diamond. However, some of these methods suffer from an inability to grow continuous films over larger areas, while others produce diamond powder in a bulk of non-diamond carbon. Subsequently, laser PVD methods for diamond synthesis which involve physical processes induced by an intense, highly directed laser beam are described. Ablation in a vacuum or inert gas produces diamond-like films, while ablation in rarefied (diluted) reactive gas allows the obtention of diamond films. Ablation of a solid target immersed in a liquid medium enables synthesis of nanocrystals of thermodynamic metastable phases, due to special conditions that occur in plasma on the solid/liquid interface, namely high pressure, high temperature, high density and high cooling velocity of plasma. A final section presents possible solutions for diamond synthesis by laser in their joint, simultaneous action with classic CVD methods, that may allow the technique to be applied more generally.

### LASER CVD METHODS

Chemical Vapour Deposition (CVD) is a technique for growing solid films on a substrate by gas-phase and surface reactions. Chemically reactive species in CVD are produced by introducing energy into the system, for example, by heating (e.g. hot filament), by electrons (e.g. glow discharge) or by photons (e.g. laser). Laser CVD methods for diamond synthesis can be performed in a gas which does not absorb the laser radiation and thus a substrate is required (photothermal process), and/or can be carried out in gas which absorbs the laser radiation specifically with and without the substrate (photolytic, i.e. photochemical process).

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### Heterogeneous nucleation (pyrolysis, photolysis)

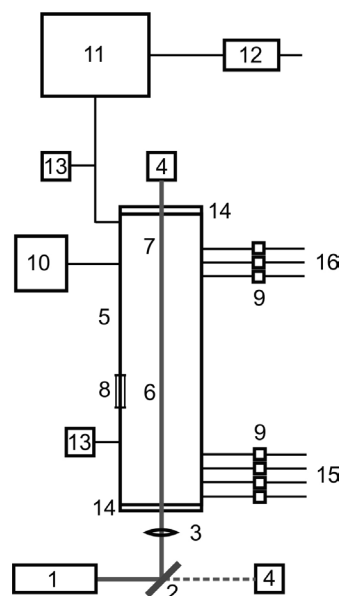
In the photothermic/pyrolytic laser deposition of diamond by use of an unfocussed, continuous wave (cw) CO<sub>2</sub> laser beam with a power of 1200 W, the Si and/or GaAs substrate is heated to the desired temperature by controlling the laser power and irradiation time.<sup>1</sup> The process gases CH<sub>4</sub> (2%) in H<sub>2</sub>, which do not absorb the laser radiation, decompose by collisions with the hot surface. Heterogeneous nucleation of diamond occurs by reactions of dissociated species which are adsorbed, desorbed, diffused and deposited. SEM analysis and Raman spectrum evidenced deposited diamond films.

In a case where a gaseous diamond precursor does not absorb the laser radiation, deposition (by photolytic mechanism) is nevertheless possible, by use of a sensitizer – a gas-mediator which absorbs the laser radiation and then transfers the absorbed energy to the gaseous diamond precursor. Diamond deposition on monocrystalline Si (100) from a mixture of CO (95%) and CH<sub>4</sub> (5%) is done<sup>2</sup> by use of the CO laser operating on its lower vibrational transition ( $\lambda \approx 5 \mu\text{m}$ ). The mechanism responsible for diamond deposition is the resonant single photon absorption of CO, followed by V-V redistribution of the absorbed energy by collisions. The CO laser power is deliberately restricted by an intracavity Q switch, in order to confine energy dissipation through CO dissociation (which were evident by Swan band-emission of C<sub>2</sub> clusters formed in the gas phase), and to enhance energy transfer onto CH<sub>4</sub>. Hyperdilution with H<sub>2</sub> is not necessary in this case. Diamond stems from the excited CH<sub>4</sub>, or from reactive fragments C<sub>x</sub>H<sub>y</sub>. SEM images disclosed faceted diamond particles, and Raman spectrum showed the characteristic diamond peak.

In a case where the gaseous precursor absorbs the laser radiation, diamond synthesis proceeds by multiphoton dissociation and subsequent reactions of fragments with gaseous medium. Diamond deposition on monocrystalline Si (111), from the mixture of CO (1%) and H<sub>2</sub> (99%) is achieved<sup>3</sup> using an ArF laser ( $\lambda = 193 \text{ nm}$ ). Carbon monoxide is decomposed by a multiphoton process of the relatively long-lived (4.4–9.5 ms) a<sup>3</sup>Π state (which is not significantly populated), i.e. via transition a<sup>3</sup>Π←X<sup>1</sup>Σ<sup>+</sup> (Cameron bands), providing fragments necessary for diamond deposition. Substrate heating is not necessary as the deposit is situated “downstream” of the laser irradiated region. Raman microprobe and SEM analysis proved the deposited particles (sizes in the order of 5–10 μm) were diamond.

### Homogeneous nucleation (photolysis)

Diamond synthesis in the gaseous phase directly, without the substrate, is also possible. Molecules of the gaseous precursor absorb the laser radiation resonantly and, if the laser radiation intensity is sufficiently high, are subjected to multiphoton dissociation. Secondary reactions in the gas phase produce diamond. Homogeneous synthesis of diamond is carried out<sup>4–7</sup> from ethylene, by a selected line (10.532 μm = 10P14) of the cw CO<sub>2</sub> laser radiation at a power of 42 W. The beam was focussed by a ZnSe lens, giving a beam diameter of 0.86 mm in the focal plane and intensities in the range 6000–8000 W cm<sup>-2</sup>. A scheme of an experimental set-up is given in Figure 1. Upon absorption of 17 photons per C<sub>2</sub>H<sub>4</sub> molecule, hydrogen elimination and acetylene formation result. The reaction mechanism for homogeneous nucleation of diamond is proposed in five steps, via 1,3-butadiene to cis-octaline and/or cis-hexaline, which is the postulated reaction nucleus of diamond lattice (neglecting a double bond). Diamond powders with grain size up to 18 μm (depending on working conditions – total pressure, gas composition, gas flow rates) were obtained in large amounts of non-diamond carbon. Diamond characterization was done by TEM analysis and electron diffraction (because of low yields).



**Figure 1.** Schematic diagram of a flow reactor for homogeneous diamond synthesis by CO<sub>2</sub> laser: 1- CO<sub>2</sub> laser, 2- partially transmitting mirror, 3- ZnSe lens, 4- power meter, 5- flow tube made of stainless steel, 6- reaction zone, 7- reduction zone, 8- window, 9- mass flow controllers, 10- external heating device, 11- separation of solid and gaseous products, 12- rotary vacuum pump, 13- manometer, 14- NaCl window, 15- reactant and inert gas lines, 16- gas lines for reducing agents. Adapted from refs. 4-7

### Plasmatrons

Lasers can be used for creating and sustaining plasma at atmospheric pressure, without need for a special reaction chamber, vacuum, hydrogen, substrate pretreatment, etc. Plasma created by lasers contains various chemical reactive species and very hot electrons, which all form a unique environment for diamond growth. High grow rates are accomplished, up to 1 μms<sup>-1</sup>. Two procedures are described in the literature. In the QQC process,<sup>8</sup> (3 or) 4 pulse lasers work in the open air, at laboratory P-T conditions. Two ultraviolet (excimer) and two infrared (Nd:YAG and pulsed CO<sub>2</sub>) lasers are directed through an opening of a ring-shaped nozzle supplied with CO<sub>2</sub> (precursor) and N<sub>2</sub> (shielding) gases, situated at a set distance from the substrate holder. Triggering lasers generate the instantaneous plasma around the workpiece to be coated. The Raman spectrum taken on a cutting tool coating certified the presence of diamond and SEM photos showed the characteristic diamond morphology.

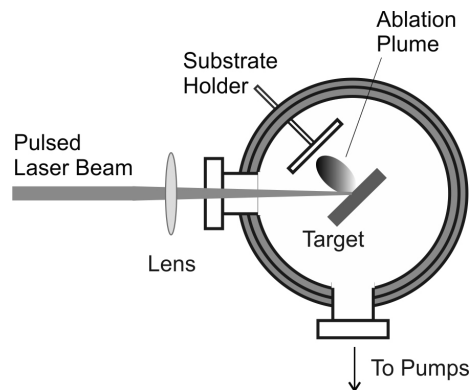
Another procedure, so-called photon-plasmatron,<sup>9</sup> makes use of the 2.5 kW cw CO<sub>2</sub> laser to sustain stationary optical discharge in a gas stream, exhausting over a substrate into air. Nano- and polycrystalline diamond films were deposited on tungsten substrates from an atmospheric-pressure gas mixture Xe(Ar):H<sub>2</sub>:CH<sub>4</sub>. Raman and SEM evidence verified good quality faceted diamond crystallites produced under optimum conditions.

### LASER PDV METHODS

Treatment of a solid target by an energy flux in a vacuum – sputtering, evaporation, ablation/erosion – and subsequent condensation of a vaporized form of the material onto the target produces coatings by the Physical Vapour Deposition (PVD) technique. PVD methods yield generally diamond-like phases and are usually coupled with other methods – the synergy is accomplished – with the aim of obtaining diamond.

### Ablation in vacuum and rarefied gases

Ablation is instantaneous vaporization of the thin layer of material from the target surface by intensive, pulsed laser radiation. Excimer lasers working on different wavelengths in the UV region (308 nm, XeCl; 248 nm, KrF; 193 nm, ArF) are typically used, but lasers working in other regions can also be used such as: in VIS (532 nm, frequency-doubled Nd:YAG), near IR (1064 nm, fundamental Nd:YAG), mid IR (10.6  $\mu\text{m}$ , CO<sub>2</sub> laser) regions. Ablation is carried out in a vacuum ( $\approx 10^{-6}$  mbar) or at low pressure in an inert gas. The graphite target is mounted near (and parallel to) the substrate. The laser beam focused on the target produces a plasma cloud-plume (containing the ablated material), which spreads symmetrically around a perpendicular axis to the target surface, and then settles, i.e. precipitates at the substrate surface. A schematic of a typical apparatus can be seen in Figure 2. Deposited films have different content of sp<sup>3</sup> hybridized carbon, and depending on working conditions possess a certain crystalline range or nano-smooth character.<sup>10,11</sup> If ablation is performed in a reactive gas having etching ability for sp<sup>2</sup> hybridized carbon – hydrogen or oxygen – the resulting deposit is diamond.<sup>12-15</sup>



**Figure 2.** Schematic diagram of an apparatus for pulsed laser ablation in vacuum. Adapted from ref. 11

### Ablation in liquids – plasma quenching

Ablation of a solid target immersed in liquid enables synthesis of nanocrystals of thermodynamic metastable phases, due to special conditions that occur in plasma at the solid/liquid interface,<sup>16</sup> namely high pressure, high temperature, high density and high cooling velocity of plasma. In the course of the process, the focused laser beam interacts with the target surface and the layer of the surrounding liquid. The plasma plume created by target ablation in liquid consists of microbubbles of the liquid filled with particles of the target material (e.g. atomic clusters sp<sup>2</sup> and their ions). Microbubbles grow, expand with material supply up to a certain critical value, and then collapse. Species inside collapsing microbubbles are subjected to temperatures of thousands of Kelvin and pressures of several GPa, which allow synthesis of phases stable under such extreme conditions (sp<sup>3</sup>). By condensation of plasma which cools in the surrounding liquid, nanoscale crystals are formed, because the growth time (i.e. time of plasma quenching/microbubbles collapsing) is so short. Exactly in this short period of time, the thermodynamically favourable and kinetically accessible reaction occurs, which leaves the “frozen” nanoresult. The described mechanism of reactive plasma quenching for diamond synthesis<sup>16-18</sup> may be complemented by the presence of atomic H/atomic O – active promoters from the classic CVD methods – which are detected by the OES technique in the light emitting region of the plasma plume.<sup>19</sup> The yield of nanodiamond particles in

the ablation product was estimated at about 5%, with the remainder being graphitic particles ejected from the target.<sup>19</sup>

Early investigations of diamond synthesis by CO<sub>2</sub>-laser heating of the hydrocarbon drops/carbon black particles falling through the focal point, followed by drastic cooling are presented in an extensive monograph.<sup>20</sup> Ibidem, synthesis of diamond (without laser) in the high-temperature Ar-flow containing the gaseous carbon precursor (C<sub>2</sub>H<sub>2</sub>), subjected to abrupt cooling (by expanding through a Laval nozzle) is also disclosed. Although not intending to constitute a detailed review of the work on diamond synthesis by reactive quenching, we will still mention another example of diamond coating growth by fast quenching associated with pulsed laser annealing.<sup>21</sup> Firstly, the pretreatment of a Cu substrate is performed by implantation with high-energy C<sup>+</sup> ions to a high dose at room temperature, and subsequently the Cu substrate is irradiated by a pulsed XeCl laser to melt and rapidly solidify – laser anneal – the implanted regions. The authors stressed that optimum quenching rates were not achieved using cw-lasers. Defect-free, single crystal diamond films obtained over areas up to several squared micrometers were characterized by electron diffraction, SEM, Rutherford backscattering/ion channeling, as well as Auger and Raman spectroscopies.

### HYBRID METHODS – SYNERGY OF LASERS AND CLASSIC METHODS

The joint, simultaneous action – or synergy – of different lasers with various CVD and PVD methods is achieved with the aim of synthesis and deposition of diamond coatings. The laser synergy partner, due to its specific characteristics, can participate in the synthesis in several ways, i.e. in the photothermic/pyrolytic way and in the photolytic way. The classic method – conceptionally and experimentally simpler – is usually chosen as another synergy partner. The hot filament CVD method, coupled with lasers or working independently (i.e. unassisted) is the most often used approach because of its versatility, scalability, low cost and ease of performance.<sup>22</sup>

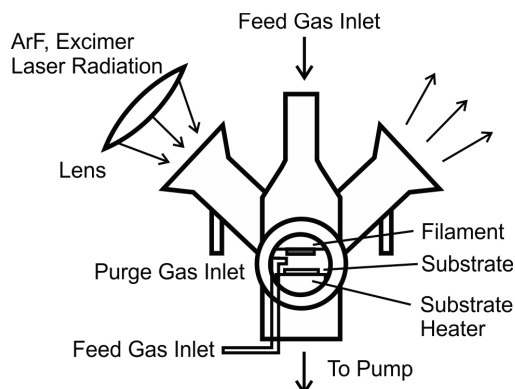
#### Synergy with hot filament CVD method

In a spectroinactive atmosphere, several different lasers coupled with the hfCVD method have been used. The focused laser beam of an Ar-ion laser (514.5 nm) was used for selective heating of a Si substrate during the hot filament deposition, and obtaining spots of high-quality diamond (or/and high-quality graphite).<sup>23</sup> A pulse, frequency-doubled Nd:YAG laser (532 nm) coupled with the hot filament method, enhanced<sup>24</sup> and enabled rapid nucleation of diamond on a Si substrate.<sup>25</sup> Focused radiation of a cw Nd:YAG laser (1064 nm) produced localized heating of a W substrate and deposition of a diamond (or graphitic) disc<sup>26</sup> by the hot filament CVD method onto the selected location. By joint action of an infrared pulse/cw CO<sub>2</sub> laser (10.6  $\mu\text{m}$ ) and the hot filament method diamond particles were synthesized onto a Si substrate.<sup>27</sup> Ablating the graphite target in pure hydrogen at an optimum pressure of 27 mbar, an XeCl laser (308 nm) coupled with the hot filament, deposited a high-quality diamond coating onto the Si substrate.<sup>28</sup>

In a spectroactive precursor atmosphere, a thorough and detailed study of the joint, simultaneous action of a UV pulse laser and hot filament CVD has been performed.<sup>29</sup> Many samples (24) were processed and many experimental conditions were varied: two wavelengths (308 nm, XeCl and 193 nm, ArF) at a range of intensities (20-200 mJ cm<sup>-2</sup>), three carbon sources [(CH<sub>3</sub>)<sub>2</sub>CO, CCl<sub>4</sub>, CH<sub>4</sub>] with different absorption strength and maxima, variety of gas flow rates (150-670 cm<sup>3</sup> min<sup>-1</sup>) and gas introduction geometries. A scheme of a reactor which enables sample irradiation at a 45° angle is shown



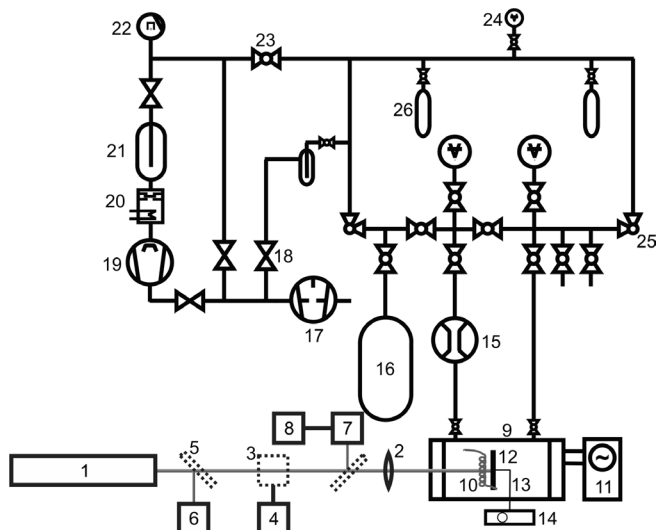
in Figure 3. The deposited materials were analyzed using optical microscopy, SEM, scanning Auger microprobe and microRaman scattering. Diamond films with regions of suppressed growth at the irradiated locations were obtained. The use of pulsed UV irradiation during filament-assisted diamond CVD has proven effective in suppressing nucleation and subsequent diamond growth. The mechanism of diamond suppression was thought to be via removal of nucleation sites, either by ablation or site blockage.



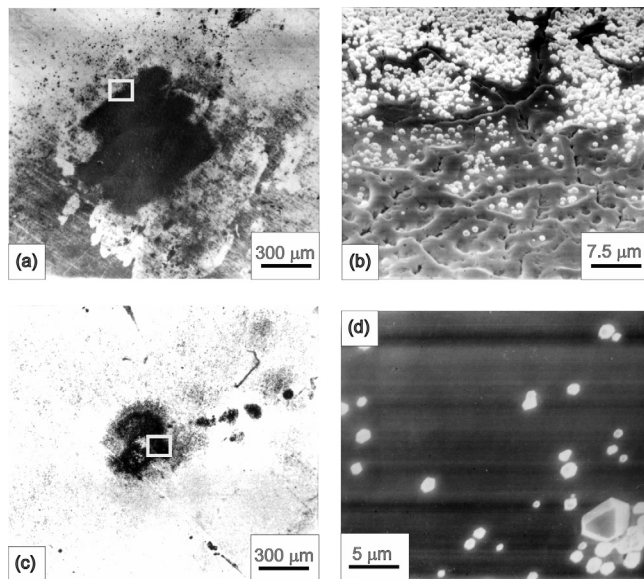
**Figure 3.** Scheme of a reactor which enables irradiation of a substrate/target at a 45° angle, used in hot filament - ArF laser synergy. Adapted from ref. 29

In the appropriate spectroactive precursor atmosphere, an IR pulsed laser and a hot filament CVD method acted jointly (in the synergy).<sup>30</sup> The experimental set-up, shown in Figure 4, consisted of a reaction cell with a hot filament and the pulse CO<sub>2</sub> laser, set opposite each other at the same optical axis. The reaction cell with the hot filament was coupled to a glass vacuum apparatus equipped with pumps, pressure gauges and a gas flowmeter. Gaseous mixture of C<sub>2</sub>H<sub>4</sub> (0.5%) in H<sub>2</sub>, contained in a gas cylinder, was introduced into the system during the experiment. The filament formed as a coil was supplied with electrical current from the a.c. mains through variable transformers. Before deposition, the filament was carburized in order to reduce its evaporation and to fix its distance from the substrate. The substrate was mounted at a distance from the filament of about 5 mm. Substrate temperature during the experiment was measured by a thermocouple at the rear of the substrate. The radiation of the pulse TEA CO<sub>2</sub> laser was focused by a ZnSe lens onto the target-substrate mounted in the reaction cell at a distance from the filament of around 1-2 mm. Laser operating characteristics were as follows: pulse power (at a spike) = 0.5 MW, pulse duration (FWHM) = 120 ns (initial spike), ≈2 μs (pulse "tail"), repetition rate ≈3 Hz, spectral output wavelength = 10.6 μm, multimode working regime, spot size at a focus = 1-2 mm<sup>2</sup>, beam incidence angle at surface = 90°. Characterization of the resulting diamond coatings carried out by SEM is shown in Figure 5a-d. Diamond coatings obtained from the spectroactive precursor atmosphere (0.5 % C<sub>2</sub>H<sub>4</sub> in H<sub>2</sub>) were rarefied in the proximity of the laser spot, while the latter was completely "cleaned" of diamond by the action of the focused laser radiation (Figure 5a,b). Deposition impoverishment was also found in the reflection spot created simultaneously<sup>31</sup> (Figure 5c,d). It was suggested that deposition impoverishment in the irradiated regions (in contrast to the unirradiated regions) was due to the laser absorption in ethene, which drew out the diamond precursor from the hfCVD process in another reaction channel.<sup>30,31</sup>

Impoverishment/suppression effects in diamond deposition were observed in the synergy experiments of hot filament CVD with pulsed lasers. Generally, an excitation level of the spectroabsorbing diamond precursor depends on laser power, i.e. on the rate of energy (photons) supply. The pulsed lasers used in the laser-hot filament



**Figure 4.** Experimental set-up used in a synergy hot filament-CO<sub>2</sub> laser comprises following elements: 1- CO<sub>2</sub> laser, 2- ZnSe lens, 3- power meter, 4- digital electronic module, 5- plane mirror, 6- spectrum analyser, 7- photon drag detector, 8- digital oscilloscope, 9- reaction cell made of stainless steel, 10- Ta filament, 11- power supply, 12- substrate, 13- thermocouple, 14- multi-meter, 15- flowmeter, 16- gas cylinder containing working mixture, 17- rotary pump, 18- metal valve, 19- diffusion pump, 20- vapour oil baffle, 21- trap cooled with liquid N<sub>2</sub>, 22- Penning gauge, 23- stopcock (glass or PTFE), 24- pressure gauge, 25- right angle stopcock, 26- glass tube. Components depicted with dashed lines are used in separate experiments for determination of laser working parameters



**Figure 5.** Diamond coating of synergy obtained from C<sub>2</sub>H<sub>4</sub> (0.5%) in H<sub>2</sub>: (a) whole laser spot produced by a direct beam; (b) enlarged detail indicated in (a); (c) whole laser spot produced by the reflected beam; (d) enlarged detail indicated in (c). Adapted from ref. 30,31

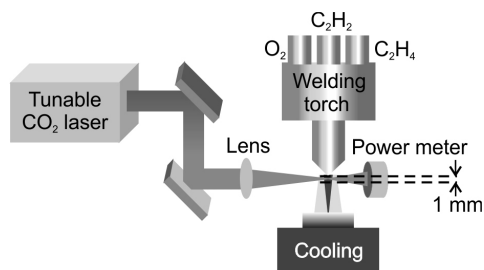
CVD synergy possess high power concentrated in a laser pulse and therefore break chemical bonds very effectively, but the overall amount of the energy delivered in a given period of time is not high. The pulsed TEA CO<sub>2</sub> laser delivered a total energy of 4 kJ for the 2.5 h duration of the synergy experiment,<sup>30</sup> while the ArF laser working simultaneously with the hot filament furnished the system with 27 kJ for 2.5 h.<sup>29</sup> However, elevating the laser power in the synergy laser-hot filament (regardless of quantity and rate of energy delivery)

can affect only the spectroabsorbing diamond precursor. The latter then suffers a photolytic change, i.e. it is directed to the photolytical reaction channel. Pyrolysis (photolysis) of ethene by the radiation of the CO<sub>2</sub> laser yields acetylene, which can give different final products, such as diamond nanopowder,<sup>4-7</sup> or carbon nanopowder,<sup>32</sup> depending on experimental conditions (pressure, gas flow regime, laser power density). Thus, the constituent of the gaseous mixture of the synergy experiment which does not absorb the applied radiation (hydrogen – diatomic, homonuclear molecule<sup>33</sup>) does not suffer any influence of the laser. At the same time, processes induced by the hot filament (pyrolysis of all gaseous species on the filament) deposited diamond in the filament activity region. This means that the diamond coating which grows at locations of common and simultaneous action of the CO<sub>2</sub> laser and the hot filament will contain discontinuities and rarefied regions. Therefore, laser-hot filament synergy can serve as a method for producing diamond coating with a specific pattern – locations free of diamond deposits and locations with diamond deposits.

### Synergy with combustion flame CVD method

Another classic method for diamond synthesis – combustion flame CVD – was investigated in the synergy with a cw CO<sub>2</sub> laser. A commercial welding torch working with a spectroinactive flame mixture C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub>, coupled with a cw CO<sub>2</sub> laser, deposited polycrystalline graphite structures.<sup>34</sup> Different key parameters of the synergy process were varied and explored: laser power (300–800 W), beam incidence angle, arrangement of the torch and the laser, gas flow ratio, gas flow rate, etc. FE-SEM, XRD, and TEM techniques were used to characterize the results obtained.

A modified, spectroactive composition of the standard combustion flame mixture allowed the obtention of high-quality diamond coatings.<sup>35-39</sup> The welding torch was used to generate a C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> combustion flame with gas flow ratio of C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> = 1:1:2. A focused beam from the powerful (800 W), tunable cw CO<sub>2</sub> laser was passing through the flame, in parallel with the substrate around 1 mm from the nozzle tip. A scheme of the experimental set-up is depicted in Figure 6. The deposition or irradiation time was 15 min. The strong resonant vibrational excitation (on a laser line 10.532 μm = 10P14) of C<sub>2</sub>H<sub>4</sub> was achieved, and the laser energy was coupled directly into the flame (followed by measurements), that was manifested as conspicuous enhancement of the deposited diamond coating in comparison with the coating deposited without the laser action. Optical images of the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flames irradiated with the selected laser lines, SEM images and corresponding Raman spectra of the resulting diamond coatings were shown in order to corroborate diamond deposition enhancement by the synergy of CO<sub>2</sub> laser-combustion flame CVD.



**Figure 6.** Experimental set-up of a synergy combustion flame CVD–CO<sub>2</sub> laser. Adapted from ref. 36

The choice of ethene as a partial substitute for acetylene in the combustion flame mixture was of multiple value. As a well-known, very strong absorber of CO<sub>2</sub> laser radiation,<sup>40,41</sup> C<sub>2</sub>H<sub>4</sub> enabled drawing

of the laser energy into the flame. For 15 min irradiation time, the CO<sub>2</sub> laser working at a power of 800 W delivered 720 kJ to the flame. This is many times greater than the energy delivered by the pulse lasers for a 10-fold longer working period (15 min: 150 min).<sup>29,30</sup> The most important fact is that ethene was photolysed to acetylene<sup>4-7,32,42</sup> by absorbing the CO<sub>2</sub> laser radiation. Hence, consuming ethene through photolytical decomposition during laser-combustion flame synergy allowed supplying the combustion flame with a fuel. Moreover, the initial composition of the combustion flame mixture C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> = 1:1:2 may be modified to a slightly acetylene-rich flame, which is favourable for diamond deposition.<sup>43</sup> In such a way, the laser pyrolysis of ethene was converted spontaneously to the diamond-forming combustion flame, i.e. the process of an “incomplete combustion” was completed to the true, full combustion. The latter ensured continuous production of an indispensable etchant of non-diamond carbon. The irradiation of the combustion flame CVD by the CO<sub>2</sub> laser beam afforded an essential energy coupling, i.e. coupling of the laser photon energy and flame chemical energy, which resulted in intensifying chemical processes, consequently producing diamond coatings of high quality at a considerably higher deposition rate.

A recapitulation of all experimental parameters which are considered in diamond synthesis by lasers is given in Table 1.

**Table 1.** Experimental/working conditions considered in diamond synthesis by lasers

Laser: wavelength, λ [nm]; working regime pulse/cw; beam energy [J]; focused/unfocused beam; beam incidence angle on a substrate/target (45°, 90°, 180°)

– Laser CVD methods:

Laser (characteristics indicated above);  
Diamond precursor spectroactive/spectroinactive in H<sub>2</sub>;  
Substrate/without a substrate;  
Reaction cell/open atmosphere.

– Laser PVD methods:

Laser (characteristics indicated above);  
Target;  
Diluted gas/liquid;  
Substrate/without a substrate;  
Reaction cell (confined reaction volume).

– Synergy of laser-classic CVD methods:

Laser (characteristics indicated above);  
Typical working conditions of the classic CVD method (diamond precursor in H<sub>2</sub>, activating agent, total pressure, gas flow rate, substrate).

## CONCLUSIONS

Diamond is a technologically important material due to its valuable properties, applicable to many different fields of science and industry. A number of methods for diamond synthesis has been developed, both in a region of its thermodynamic stability as well as in the region of its thermodynamic metastability. A use of lasers for diamond synthesis in the region of high pressures and high temperatures settles on its use as an intense heating source. In the region of low pressures and low temperatures, lasers can involve (through their characteristic of monochromaticity) chemical reactions, with purpose of diamond synthesis. By a proper choice of the spectroactive diamond precursor, classic methods of the chemical vapour deposition, well-established in diamond synthesis, can receive the laser energy and transfer it to chemical processes of diamond synthesis. Recent research work of a synergy seems to meet an essential for synthesis of diamond in its metastability region: presence of reactive species at a high chemical potential (an etchant of non-diamond carbon, carbon containing species) as well as a way to accept and exploit additional

energy supply from a laser. Hopefully future studies will show this approach to be a feasible.

## ACKNOWLEDGMENTS

This work has been financially supported by the Ministry of Science and Technological Development of the Republic of Serbia, under projects 172019 and 45014.

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