

CO₂ laser deposition of diamond thin films on electronic materials

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Laser-induced pyrolysis has been utilized to create gas–surface chemical reactions necessary for diamond deposition on electronic materials. A 1200 W CO₂ gas laser has been used as an energy source for depositing diamond thin films from a gas mixture of CH₄ and H₂ in a chemical vapour deposition chamber. The substrate temperature was about 500 °C. The laser beam energy was largely absorbed by the gases that lead to their excitation and decomposition on contact with the nearby hot substrate. Raman spectroscopy and scanning electron microscope analysis revealed high quality, fine crystalline diamond structures.

1. Introduction

Diamond has many unique physical, mechanical and thermal properties (high hardness, highest thermal conductivity of any known material, excellent optical transparency from ultraviolet to infrared (u.v. to i.r.) range, chemical inertness, high stiffness, superior acoustical properties, very large band gap, and high elastic modulus) compared with other widely used semiconductors. Many of these properties such as thermal conductivity, optical transparency and breakdown field have already been effectively utilized to develop electrical and optical devices. However, the absence of an economical large-scale production of high quality films of diamond has limited its widespread application.

The applications of diamond thin films for the electronics industry are heat sinks for semiconducting devices, heat-dissipating printed circuit boards, temperature and radiation-resistant power semiconducting devices, transistors in motors and jet engines, and Schottky diodes. The most useful form of diamond for the electronics industry would be a film of single-crystal diamond on a non-diamond substrate. Since diamond is both a good thermal conductor and a good semiconductor, diamond microchips could be used successfully in high-speed devices.

Diamond thin films are created by a variety of chemical vapour deposition (CVD) procedures including plasma, microwave, hot filament, and ion beam from the vapour phase at low pressures and high temperatures [1]. The films generally possess characteristics close to that of natural diamond. Two major limitations of these processes include high substrate temperature and low deposition rate. Additionally, the lack of smooth surface, poor adhesion, and presence of graphite and hydrogen impurities in diamond films restrict these processes to be applied for many electronic components.

Laser-induced chemical reactions and physical processes are widely used to synthesize various thin films

of Si, W, Au, etc., on various substrates [2]. In laser-induced CVD (LCVD), the laser serves as an energy source for decomposing the gases and to raise the surface temperature of the substrate for deposition.

Lasers deposit thin films by pyrolysis and photolysis mechanisms of breaking the gaseous molecules. In laser pyrolysis used in this work (Fig. 1), the substrate is heated by a directed laser beam up to the desired temperature by controlling the power and irradiation time of the beam, while the chemical gases are decomposed by photothermal, and collisional excitation (with the hot surface) mechanisms. The laser-driven reactions are different from those initiated by other CVD sources for the same heat input because of the higher temperatures obtainable in the smaller reaction volume defined by the laser beam [2].

In this paper, we report a CO₂ laser CVD process for pyrolytic decomposition of hydrocarbon in the hydrogen environment to grow diamond. The significant features of this process are clean source of energy (no contamination of the diamond layer unlike hot filament method), low substrate temperature and high quality, fine crystalline diamond structures.

2. Experimental procedure

2.1. Laser

A CO₂ laser, operating in pulsed and continuous wave mode, was used in this work. The specifications of the laser system are given in Table I. A 127 mm focal length lens and an optical integrator were sometimes used to reduce the beam size.

2.2. Chemical vapour deposition chamber

The CVD chamber used in this work was made of stainless steel with ports for vacuum pumps, gas inlet and outlet, thermocouple connection, and the laser beam. A schematic diagram of the CVD chamber is shown in Fig. 2. The laser beam was external to the

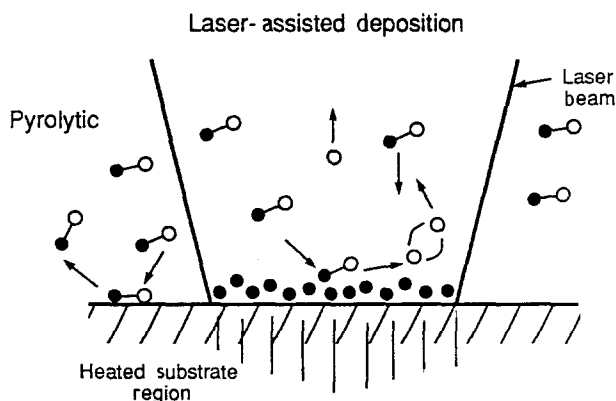


Figure 1 A schematic diagram showing the laser pyrolytic thermal decomposition of gaseous molecules at the substrate surface.

TABLE I Laser system

| | |
|-----------------------|---------------------------|
| Laser type | CO ₂ |
| Wavelength (nm) | 10 600 |
| Power (W) | 100–1200 |
| Pulse length | millisecond to continuous |
| Pulse repetition rate | continuous to 100 Hz |
| Beam size | 19 mm |
| Energy distribution | Gaussian |

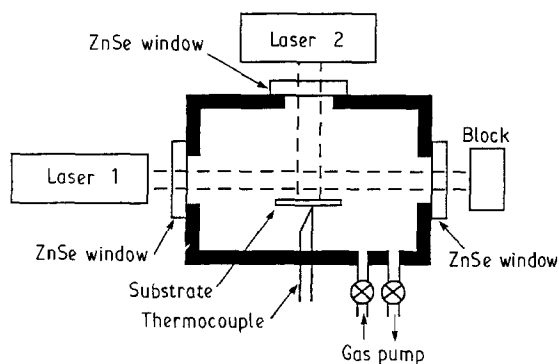


Figure 2 Experimental arrangement for laser CVD of diamond. Either normal beam (Laser 2) or parallel beam (Laser 1) was used.

chamber and was directed inside the chamber through a window. The window for the chamber was made of ZnSe. The laser beam was made either normal (laser 1) or parallel (laser 2) to the substrate surface. The gas was made to impinge at the substrate location where the laser beam was incident. A thermocouple was placed in contact with the substrate and the gas pressure was monitored by using a gauge. Provisions to control the gas flow were also made.

2.3. Substrates

The substrates studied were gallium arsenide (GaAs) and silicon (Si). GaAs had a thickness of 0.6 mm with an orientation of (100). GaAs was also doped with small amounts of silicon. Silicon with about the same thickness and (1 1 1) orientation was chosen because it has been proven by other CVD techniques that Si (1 1 1) is a suitable substrate for diamond deposition. The substrates were polished with 3–6 μm diamond powder and ultrasonically cleaned before laser deposition.

2.4. Processing

LCVD was performed by first evacuating the chamber to 1.3×10^{-4} Pa using mechanical and diffusion pumps and then passing a mixture of 2% CH₄ and 98% H₂ through the reaction area. The gas pressure and the flow rate were 1.3×10^4 Pa and 50 cc min^{-1} respectively. The laser beam was then incident either parallel or perpendicular to the surface of the substrate. In parallel radiation, the substrate surface was about 2 to 3 mm to the laser beam. The process parameters were varied as given below:

Laser power: 100 to 1200 W;

Beam size: 19 mm diameter unfocused beam, 6 mm square beam, 0.25 mm focused beam;

Beam mode: continuous wave and pulsed (1 to 100 Hz);

Deposition time: 15 min to 2 h.

2.5. Analysis

The deposited films were analysed by visual examination, scanning electron microscope, X-ray diffraction and Raman microprobe spectroscopy.

3. Results

Initially, the experiments were unsuccessful in depositing the diamond films. Several reasons account for the failure: specimen shattering, local heat concentration, improper control of gas flow, low laser power, breakage of window, short duration of test, low substrate temperature, high heating of the chamber, laser breakdown and so on. One of the major problems in using CO₂ laser is that the chamber becomes very hot in 30 min of deposition time. Since diamond nucleation requires longer than 30 min, the chamber was modified such that the tests could be run for 2 h or more. Experiments using focused beam and 6 mm square beam as well as pulsed beam did not yield any film. The parallel radiation method also did not generate any film.

The successful results were obtained by using an unfocused, continuous wave CO₂ laser beam with a power of 1200 W. Seeding of the substrate with diamond paste or powder for enhancing nucleation did not affect the results. The laser power was gradually increased from 0 to 1200 W in 1 h to prevent the shattering of substrate. The CH₄–H₂ gas mixture was flown at 50 cc min^{-1} for a pressure of 1.3×10^4 Pa. The deposition time was 2 h. The substrate temperature during the irradiation was 300 °C. There was no fracture of the substrate. Black deposits were observed in the zone heated by the laser beam.

Fig. 3 shows a scanning electron micrograph (SEM) of laser-deposited film on a silicon substrate that was not seeded with diamond powder. SEM shows the ball-like morphology of diamond. Fig. 4 is the corresponding Raman spectra showing a well-defined peak at 1332 cm^{-1} characteristic of diamond. Note that there are no other peaks seen in Raman spectra corresponding to diamond-like carbon or graphite indicating the purity of diamond film. Diamond film

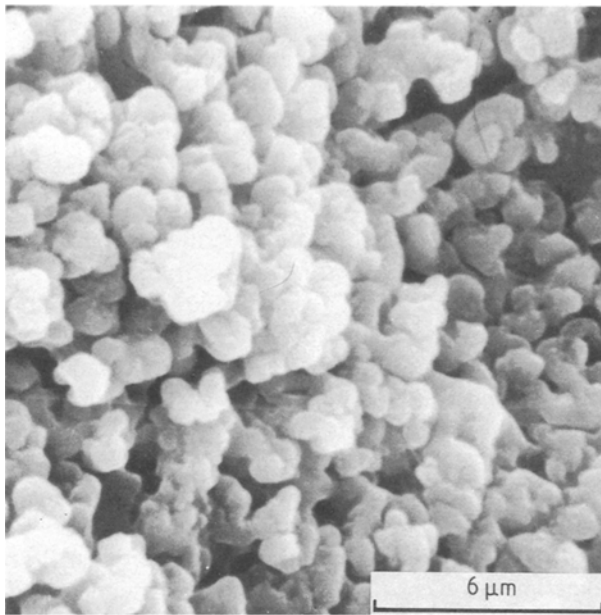


Figure 3 Scanning electron micrograph of laser-deposited film showing the ball-like morphology of diamond on silicon substrate.

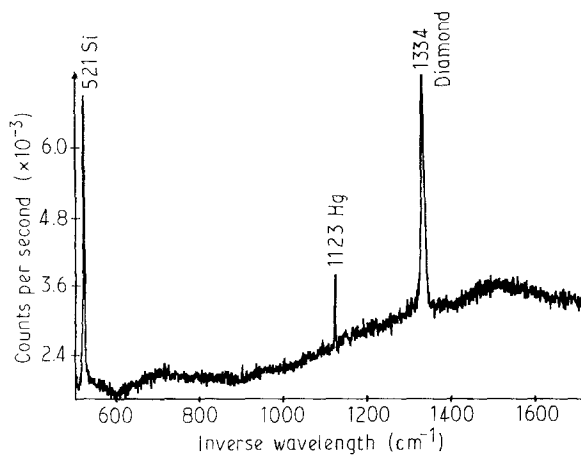


Figure 4 Raman spectrum of laser-deposited film shown in Fig. 3.

was also verified by X-ray diffraction pattern. The deposit surface coverage was 2 cm^2 while the deposition rate was about $2\text{--}3\ \mu\text{m h}^{-1}$. The experiment was repeated with a modification to confirm the reproducibility of diamond deposition. The modification was that the silicon substrate was seeded with diamond powder. SEM and Raman analysis confirmed the presence of fine crystals of diamond. Additionally, an increase in deposition was observed. When the same experiment was repeated for GaAs substrate, morphological features characteristic of diamond were observed and are shown in Fig. 5.

4. Discussion

It is clear from the experimental results that CO_2 laser is capable of growing diamond films on silicon and GaAs substrates from a gaseous mixture of CH_4 and H_2 . A literature review of laser-induced CVD for diamond deposition indicates that limited work has been carried out, all of which utilized an excimer laser and photolysis [3–5]. No work has been reported on

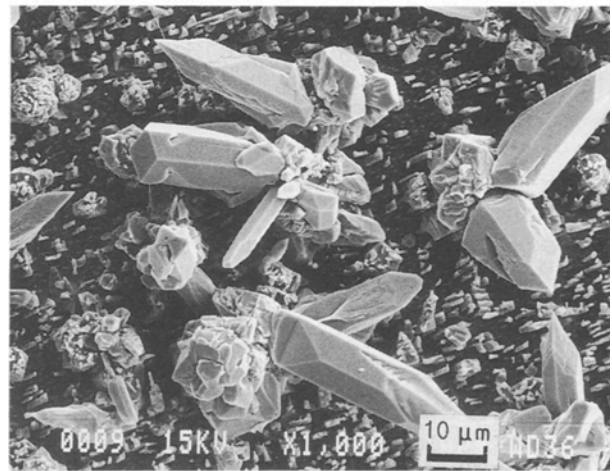
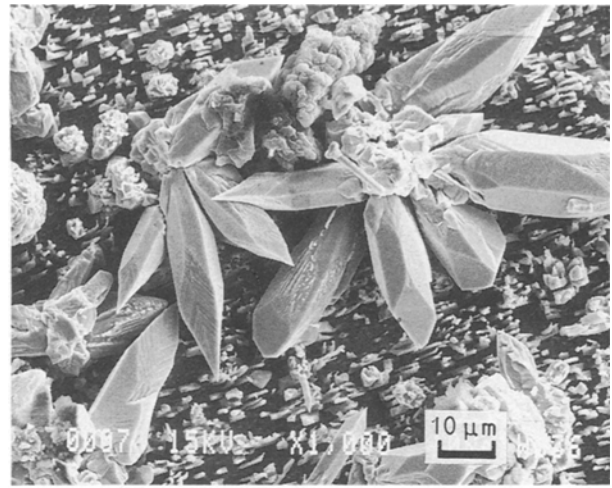


Figure 5 Scanning electron micrographs of laser-deposited diamond crystals on GaAs substrate.

the pyrolysis mode of depositing diamond although pyrolysis is, in general, more efficient than photolysis. Identification of diamond growth mechanism in CO_2 laser-induced CVD requires a knowledge of the laser pyrolytic processes. Photochemical reactions are ruled out with CO_2 lasers because the decomposition of CH_4 is possible only with photons whose wavelength is less than 160 nm [6].

In the pyrolysis (photothermal) process of diamond growth, the laser beam serves to heat the substrate surface and gaseous molecules leading to chemical reactions and physical processes required for deposition of films. The key issues in such reactions are energy transfer from photons into thermal and chemical and the kinetics and the dynamic processes involving energy acquisition, storage and decay. Laser light enhances chemical reactions either heterogeneously in adsorbate–adsorbent systems and at gas–solid interfaces or homogeneously within the surrounding media near solid surfaces. Homogeneous reactions occur near the substrate surface when the laser beam is parallel to the substrate surface. Reaction products are diffusion-driven towards the substrate surface giving rise to thin films. In our experiments with a parallel CO_2 laser beam to the substrate, no evidence of any film formation was observed which indicates any of the following possibilities: (1) decomposition of

CH₄-H₂ gases by the laser beam did not occur, (2) laser is able to decompose the gases but there is no activation of the substrate surface to allow diamond to nucleate.

Heterogeneously activated reactions take place when the laser beam is incident normal to the substrate surface. Reactions specifically occur at the gas-solid interface. Solid surfaces are potential sites for decomposing the gaseous molecules. Our experiments with normal incidence of CO₂ laser beam proved that diamond nucleation and growth require heterogeneously activated reactions. In heterogeneously activated laser CVD, the primary photon-stimulated surface interactions include the following.

4.1. Interaction of laser photons with gaseous species

In pyrolytic (photothermal) process, thermalization of the gaseous molecules by laser excitation is much faster than the decomposition reaction leading to a substantial temperature rise in the gaseous volume. The absorption spectra of H₂ and CH₄ gaseous molecules indicate that high temperatures may be reached in the gaseous volume because the frequency of CO₂ laser light matches strongly with the vibrational absorption of these molecules. Evidence in our experiments namely CO₂ laser heating of a silicon substrate with and without CH₄-H₂ gas mixture confirmed the absorption of laser energy by the gas. The temperature rise of the silicon substrate exceeded 1000 °C within few milliseconds of laser irradiation time if the gas mixture was absent. However, under the conditions of gas flow over the substrate, the temperature rise of the silicon substrate was only 500 °C even after the continuous radiation of CO₂ laser beam (1200 W power) for more than 1 h. Of course, the gas flow cooling of the substrate may also reduce the temperature of the substrate.

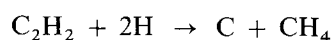
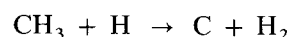
4.2. Photon interaction with the adsorbed species

Laser chemical processing is strongly influenced by the adsorption of reactants and reaction products which control the reaction rates, nucleation time, composition and morphology of films. Molecules on solid surfaces are adsorbed either physically or chemically. Decomposition of hydrogen occurs as a result of excitation (due to absorption of laser energy) and collision on the hot substrate and thereby leads to the formation of atoms and ions. Literature data indicates that hydrogen ions and atoms adsorb chemically on the silicon substrate if exposed [7]. The photons interact with the adsorbed species and cause densification of the hydrogen layer. Electronic and vibrational excitation of hydrogen gas molecules also increase the sticking coefficient. The adsorbed layer grows to form a continuous monolayer. The photon interaction with the adsorbed species may cause desorption, migration and change the nature of bonding or react with the solid surface causing deposition. CO₂ laser is capable of desorbing the gaseous

molecules by direct heating of the substrate, resonant excitation of an internal adsorbate vibration or resonant excitation of the external adsorbate-adsorbent vibration [8]. Thus a dynamic process involving adsorption and desorption occur.

4.3. Photon interaction and collisional excitation with the solid substrate

In semiconductors such as silicon, the excitation of the band gap by the laser cause an increase in chemical reaction rate. The excited CH₄ molecules collide with the hot substrate giving rise to a large number of decomposition products such as C₂H₂, C₂H, CH₃, C₂H₄ and CH₂ in the decreasing order as per the thermodynamic analysis of carbon-hydrogen binary system under the experimental conditions of 1.3 × 10⁴ Pa gas pressure and high temperatures. Both experimental work and simple thermodynamic calculations show that CH₃ and C₂H₂ are the species required for carbon deposition. Typical reactions are as follows:



The Gibbs energies of reactions shown above are nearly same for graphite and diamond, and hence it may be assumed that diamond and graphite deposit simultaneously. However, atomic hydrogen etches away the graphite by 20 to 50 times faster than diamond. In addition, laser photons may assist in etching the graphite through ablation. As a result high purity diamond films are generated through laser processing.

Lower growth rates as observed in this study for diamond are due to the lower laser powers used in this work. At low laser powers, the chemical reaction is governed by the kinetics rather than by mass transport [2]. Hence, nucleation and growth of carbon takes a long time.

5. Conclusions

A feasibility study utilizing CO₂ laser interactions with a 2% CH₄-98% H₂ gaseous mixture was conducted to deposit diamond thin films on electronic materials. A theory is also postulated to support the experimental observations. The principal conclusion is that superior quality, fine crystals of diamond can be grown on non-diamond substrates through CO₂ laser pyrolysis; the dimensions of the deposited zone and energy efficiency are, however, limited.

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