Diamond growth from a CO/CH₄ mixture by laser excitation of CO: Laser excited chemical vapor deposition

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We report for the first time, diamond growth from a mixture of 95% CO and 5% CH₄ without gas phase hyperdilution of H₂. Such a mixture has not been previously reported to yield diamond by any of the existing methods (hot-filament chemical vapor deposition, plasma assisted chemical vapor deposition, or flame synthesis). In this paper we describe our observations of diamond growth at low pressures from vibrational excitation of CO in a CO/CH₄ mixture by irradiation from a CO laser operating on its shorter wavelengths. We refer to this technique as laser excited chemical vapor deposition.

I. INTRODUCTION

Diamond has been synthesized by a variety of techniques at low pressures. However, most of these processes involve deposition of trace amounts of carbon containing species in large amounts of hydrogen (typically less than 5% of the hydrocarbon in more than 95% of hydrogen). An exception is deposition from CO/H₂ mixtures where the CO partial concentration can be as high as 30%. Recently, there have been two reports of methods that do not require this hyperdilution in hydrogen. The first method involves the use of halocarbons, in which the halogens presumably play the same role as hydrogen. The second technique reportedly involves the saturation of carbon atoms in the surface layers of an immiscible substrate such as copper, followed by pulsed laser irradiation. The rapid annealing of the substrate surface apparently results in carbon atom desorption, and subsequent crystalline agglomeration at the surface. Although both of these techniques await reproduction by other groups, they do represent a line of thinking away from the mainstream.

Mixtures of alcohol and acetone, and alcohol and water have also been used to deposit diamond. However, in these latter systems, significant amounts of H atoms, or OH radicals are formed and present. This is undesirable since such species can be readily accommodated into the diamond film, thereby affecting its properties.

In this paper, we report on a novel technique for the synthesis of diamond from the gas phase. It involves excitation of the vibrational modes of CO (X' ¹Σ⁺ ground electronic state) using a CO laser operating on its lower, if not lowest, vibrational transitions. This technique has been pioneered over the past several years by Rich and co-workers, Brechignac & Martin, and Urban and co-workers for studying various nonequilibrium molecular energy transfer processes with applications to discharges, flames, and supersonic expansions.

We wish to point out at the outset that the process described herein is not a multiphoton dissociation process, but rather a resonance single-photon absorption phenomenon followed by redistribution of the absorbed laser energy by anharmonic vibration-to-vibration (VV) collisions. This redistribution of the input laser energy among the vibrational modes can result in highly vibrationally excited CO (up to energies on the order of 9 or 10 eV). In the most highly VV-pumped cases, dissociation of the CO molecules is limited due to rapid vibration-to-electronic (VE) transfer from the X' ¹Σ⁺ manifold to the ¹Π manifold. Furthermore under such highly VV pumped conditions, the vibrationally excited CO reacts to form C and CO₂ in the gas phase. Subsequent recombination to form C₂ is visibly evident from the C₂ Swan band emission. In the present experiments however, the VV pumping of the CO is purposely restricted so as to limit the production of carbon clusters (such as C₂) in the gas phase. Thus, in the experiments discussed here, there is no visible emission from the gases or other objects in the growth chamber. We report here on the successful deposition of diamond from such optically pumped CO/CH₄ mixtures without the need for gas phase hyperdilution with hydrogen or some other halogen. In order to distinguish the method presented herein from other existing processes that may or may not utilize lasers, we refer to the technique as laser-excited chemical vapor deposition (LECVD).

This article is organized as follows: The experimental apparatus is discussed next, followed by the experimental results, and a discussion of the implications of our findings.

II. EXPERIMENTAL APPARATUS

The CO laser utilized in these experiments consists of a LN₂ cooled discharge tube that was designed and built at The Ohio State University. The laser gas mixture consisting primarily of He with trace amounts of N₂, air, and CO, is precooled prior to injection into a nominal 10 kV, 23 mA dc discharge. cw operation can be achieved with lasing on the v=2→v=1 and other higher transitions. Lasing on the v=1→v=0 transition can be triggered by an intracav-
FIG. 1. Shown here is a typical spectrum of the CO laser used in the experiments reported here. The line designations have been given following the notation that $P_{r}(m)$ denotes a lasing branch transition from level $(v=n+1, J=m-1)$ to level $(v=n, J=m)$, where $v$ and $J$ are the vibrational and rotational quantum numbers respectively.

A schematic of the experimental setup is shown in Fig. 2(a), and a schematic of the substrate holder and heater assembly is shown in Fig. 2(b). The CO (99% pure CP grade from Linde Specialty Gases) is passed through a molecular sieve type 5A (Zeolite from Union Carbide) and mixed with CH$_4$ (99.99% UHP grade from AGA). This mixture is then introduced inside the six arm cross parallel to the laser beam. The molecular sieve serves to remove Fe(CO)$_3$ and Ni(CO)$_4$ which are common contaminants arising from the gas cylinders in which CO is usually stored. A substrate is suspended above the focused laser beam, and the heating is accomplished radiatively from a tungsten filament which is hidden from view by the substrate. The tungsten filament does not contact the substrate. The inverted geometry is used because the translational temperature in the focal volume can range anywhere from 300 to 800 K, and given the slow gas flow rates in the six arm cross, natural or free convection is at least as important as forced convection.

In the experiments reported here, single crystal Si(100) wafers approximately 2 cm$^2$ in size were used as substrates. As pretreatment, these were physically abraded with 4–8 μm sized diamond particles suspended in glycerol, rinsed in deionized water, acetone, cleaned in a methanol bath in an ultrasound cleaner for 4 min, characterized, and then placed in the cell. This method of substrate preparation has been found to be effective in dislodging most, if not all, of the abrasive particles. The abrasion pretreatment was used principally to reduce nucleation time and avoid long run durations. Such pretreatment has been shown in the past to enhance nucleation of diamond, likely through the presence of residual seed crystals.

Therefore, the abraded substrates were characterized thoroughly before growth using scanning electron microscope (SEM) imaging, survey Raman spectroscopy, as well as Raman spectroscopy using a microprobe. In the few very rare cases where a diamond particle could be detected by SEM imaging (see Fig. 3 before growth), no Raman peak near 1332 cm$^{-1}$ could be detected even with the microprobe beam focused on the particle. This is because the residual particle was on the order of 4–8 μm or smaller in size. Since the size of the focused Ar$^+$ beam is no smaller than about 10–20 μm, the scattered signal from small isolated particles could not be picked up by our instrument.
FIG. 3. SEM micrographs of the substrate surface before and after growth in a 95% CO/5% CH₄ mixture with laser excitation.

Following this thorough surface characterization before growth, the sample was then placed on the substrate holder inside the six arm cross.

III. EXPERIMENTAL RESULTS

We report here in detail on the case consisting of CO with trace amounts of CH₄ flowing in the growth chamber (six arm cross). The specific run conditions were total P=50 Torr, CO volume flow rate of 95 sccm, CH₄ volume flow rate of 5 sccm, and an indicated thermocouple temperature of 440 °C. This indicated thermocouple temperature was measured using a chromel-alumel thermocouple in an inconel sheath, placed approximately 2 mm from the substrate front surface. The thermocouple reading was calibrated separately using an Omega thermal lacquer. Thus, the estimated substrate temperatures were between 600 and 700 °C. Once the CO and CH₄ flows were established via mass flow controllers (Edwards High Vacuum Model 825), the laser beam was directed into the cell and focused approximately 1 cm below the substrate surface. Power measurements before and after the cell indicated that about 1 W of the incident 2.3 W was absorbed by the CO. It is important to note that not all of the 1 W is absorbed in the focal region. This is because the CO upstream of the focal region does absorb some of the incident radiation, so that the absorbed laser energy at the focal region will be less than 1 W. The Si substrate was then resistively heated from the back by a 12 mil tungsten wire. After run durations of about 4 h, the samples were removed and analyzed using SEM imaging and Raman spectroscopy (microprobe analysis). The SEM images before and after growth by LECVD are shown in Fig. 3. The images reveal the presence of additional particles after the LECVD run, which appear to be faceted. In fact, such facets are sometimes seen in diamond crystals grown using hot-filament chemical vapor deposition (HFCVD). However, conclusive evidence is provided by Raman microprobe data shown in Fig. 4. As can be seen from Fig. 4, a sharp well defined line at 1336 cm⁻¹ characteristic of diamond is evident. Also visible in Fig. 4 is the silicon peak at 524 cm⁻¹. It is important to emphasize that such a diamond line was obtained using the Raman microprobe from all of the crystallites after growth. The scattered signal from the deposited particles was detected primarily because they were clustered together in groups covering a region whose size was on the order of 50–60 μm. EDS (energy dispersive x-ray spectroscopic) analysis was also employed to deter-

FIG. 4. Typical Raman microprobe spectrum of deposited particles.
mine the elemental composition and revealed the presence only of silicon and carbon.

As a control and further verification that the CO laser and not the heating is the responsible agent in LECVD, a sample pretreated in precisely the same manner as described in Sec. II was placed in the chamber and exposed to the same flowing gas mixture (95 sccm of CO and 5 sccm of CH4) at 50 Torr. The substrate was heated as before, to an indicated temperature of 440 °C for 4 h but with no laser excitation of the CO. The SEM images from this control sample before and after growth, as well as the Raman microprobe spectra show no growth at all. Two other controls were substrates having undergone the same pretreatment and heated to the same substrate temperature, but subjected to an optically pumped 95% CO/5% H2 gas mixture and 100% pure CO, respectively. These two latter runs also did not reveal growth of diamond.

IV. DISCUSSION
A novel technique, LECVD of diamond which utilizes the selective excitation of the vibrational modes of the CO molecule in a CO/CH4 mixture has been presented. The technique presented here does not require the usual gas phase hyperdilution with hydrogen or a halogen, that is employed by other existing deposition methods. Although our present results were obtained with large amounts of CO relative to the CH4, the CO does not appear to be incorporated into the deposited diamond (confirmed by EDS elemental analysis). This is in stark contrast to existing systems that employ large amounts of hydrogen, oxygen, or other halogens for diamond synthesis.

The present results indicate several important findings:
(1) Hyperdilution of the gas phase with hydrogen is not strictly necessary for diamond growth.
(2) The CO laser excitation of the CO molecule is necessary for diamond growth in the present experiment. This does not, however, necessarily mean that the deposited carbon originated from the CO. Based on our preliminary studies, the deposited diamond originated from the trace amounts of CH4 in the gas mixture.
(3) We believe at this time that the laser energy absorbed by the CO was transferred to the CH4 with subsequent deposition of diamond either from excited methane or from a subsequent dissociated or reacted fragment (C2H2). We base this on the fact that diamond could not be grown from a similar CO/H2 mixture.
(4) No evidence was found for codeposition of diamond with other forms of carbon.

This work underscores the importance of understanding detailed state-resolved (i.e., as function of vibrational or rotational quantum number) kinetics. Additional spectroscopic and detailed kinetics investigations into the responsible mechanisms for diamond synthesis by LECVD are presently underway.

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