Controlled Nucleation & Growth of Semiconductor Diamond

UHV surface analytical measurements of film growth have been coupled with novel precursor chemistry to study the effect of precursor chemical structure on the efficiency of diamond film nucleation and growth. The goal is to optimize source gases and substrate surface preparation methods for both doped and undoped diamond film nucleation and growth, enabling the use of diamond in field emission, semiconductor, and optoelectronic applications. "Surface perfection" of the diamond substrate was found to be a crucial factor in CVD of sp2-free diamond deposition. Exposure of a diamond (100) surface to CO at high temperature (900°C) resulted in propagation of the diamond surface and extreme smoothing as monitored by RHEED. Growth was apparently linked to an inadvertent impurity, iron, which may have catalyzed the decomposition of CO. Improved nucleation and growth rates from non-hydrogen-containing carbon sources may be achievable with catalysis by transition metals. We intend to use this discovery in Phase II to develop diamond emitters for flat panel displays, UHV analytical instruments, and microwave vacuum electronics.
FINAL REPORT

Controlled Nucleation and Growth of Semiconducting Diamond

Contract N00014-90-C-0139

Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, CT 06810

C. P. Beetz, Jr.
Principal Investigator

Bo-Yang Lin
Research Scientist

Research Sponsored By

The Strategic Defense Initiative/Innovative Science and Technology

Managed By

Office of Naval Research

Advanced Technology Materials, Inc.
7 Commerce Drive
Danbury, Connecticut 06810
203-794-1100; FAX 203-792-8040
# TABLE OF CONTENTS

Controlled Nucleation and Growth of Semiconducting Diamond

### INTRODUCTION

<table>
<thead>
<tr>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
</tr>
</tbody>
</table>

### EXPERIMENTAL

<table>
<thead>
<tr>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

### RESULTS

<table>
<thead>
<tr>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
</tr>
</tbody>
</table>

- CH₄ Pyrolysis on Diamond (100) and Polycrystalline Diamond Films 7
- Ketene (CH₂CO) Pyrolysis on Diamond (100) 12
- CO and CO₂ Pyrolysis on Diamond (100) 12
- Exposure of the Diamond Surface to O₂ 19

### CONCLUSIONS AND FEASIBILITY ASSESSMENT

<table>
<thead>
<tr>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
</tr>
</tbody>
</table>

---

Figure 1. The morphology (a) and Raman spectrum (b) of the polycrystalline diamond film. Raman feature at ~ 520 cm⁻¹ is due to the Si substrate. 6

Figure 2. RHEED pattern for the virgin single crystal diamond surface before any CH₄ exposure. 7

Figure 3. Auger spectra of (a) diamond (sp³) and (b) graphite (sp²) surfaces. 8

Figure 4. Auger spectra of (a) smooth diamond and (b) cratered surfaces after exposure to CH₄ at 900°C. 9

Figure 5. SEM of the single crystal diamond surface after CH₄ exposure. The dark regions are where SIMS craters were sputtered into the surface. The difference between the flat and cratered region is reflected in the different contrast in the SEM. Diamond regions are much brighter than the graphite ones. 10

Figure 6. RHEED pattern produced upon exposure of diamond (100) surface to CO. 13

Figure 7. RHEED pattern produced upon exposure of diamond (100) surface to CO at 900°C. Weaker lines may be due to BCC iron. 14

Figure 8. EDS of film produced upon exposure of diamond (100) to CO. 15

Figure 9. X-ray diffraction pattern of film produced upon exposure of diamond (100) to CO. 15

Figure 10. IR spectrum of film produced upon exposure of diamond (100) to CO. 16

Figure 11. UV/VIS spectrum of film produced upon exposure of diamond (100) to CO. 16

Figure 12. IR and UV/VIS spectra of film produced upon exposure of diamond (100) to CO after H₂SO₄ etching. 18
INTRODUCTION

The effect of precursor chemical structure on the efficiency of diamond film nucleation and growth is largely unknown. Our approach to the problem couples UHV surface analytical measurements of film growth with novel precursor chemistry. Long term, we hope to be able to optimize source gases and substrate surface preparation methods for both doped and undoped diamond film nucleation and growth. Understanding these important issues will lead to the use of diamond in field emission, semiconductor, and optoelectronic applications.

Diamond has been deposited on a wide variety of substrates using various chemical vapor deposition (CVD) techniques, such as hot filament assisted CVD,\(^1\) DC,\(^2\) RF,\(^3\) and microwave assisted CVD,\(^4\) oxyacetylene torch,\(^5\) thermal plasmas and direct pyrolysis.\(^6\) The growth morphologies, in relationship to carbon concentration, growth temperature and substrate material using different methods are very similar, indicating a common nucleation and growth mechanism. Although various factors have been identified for the growth of \(\text{sp}^2\) free diamond, the importance of surface defects has so far escaped attention.

We have carried out a series of pyrolysis experiments under UHV conditions on diamond surfaces having varying degrees of perfection. In these experiments, we have explored several different chemical precursors whose decomposition chemistries are very different, methane, carbon monoxide and carbon dioxide. These experiments are analogous to the atmospheric pressure carbon monoxide and methane pyrolysis experiments on diamond powders.\(^7\)\(^,\(^8\)

According to the C-H-O phase diagram which defines the regions of diamond film growth, we would not expect to observe diamond growth upon pyrolysis of pure methane.\(^9\) However, since \(\text{CH}_4\) is the most commonly used gas for the growth of diamond, we performed the methane pyrolysis experiments as a reference for

---

comparison with similar experiments using compounds whose decomposition lead to species having very different reactivities.\textsuperscript{10,11}

We unexpectedly found that "surface perfection" of the diamond substrate appeared to be a crucial factor in CVD of sp\textsuperscript{2}-free diamond deposition. We recognize that the term "surface perfection" is ambiguous; we will define it to mean the overall crystallographic perfection of the lattice, including possibly the effects of surface roughness.

Exposure of a diamond (100) surface to CO at high temperature resulted in extreme smoothing as monitored by RHEED. The diamond surface was propagated under conditions of exposure to CO at T~ 900°C. Growth was apparently linked to an inadvertent impurity, iron, which may have catalyzed the decomposition of CO.

\begin{thebibliography}{11}
\end{thebibliography}
The experiments were carried out in a UHV system with a base pressure of $3 \times 10^{-10}$ torr. The system consisted of growth and analysis chambers, separated by a gate valve, which allowed in-situ Auger analysis of the grown surfaces without exposing them to air. The growth chamber was equipped with a RHEED apparatus, a quadrupole mass spectrometer, and a gas inlet and dosing system. Gas flow was controlled via a leak valve. The local gas pressure at the surface during dosing was estimated from the gas flow rate and the system geometry. The background pressure during dosing was approximately $3 \times 10^{-4}$ torr.

A polished (100) oriented 4 x 8 x 0.25 mm natural type IIa single crystal diamond plate was obtained from Dubbeldee Harris Diamond Corp. of New Jersey. The original diamond was too insulating to carry out Auger measurements. A very thin layer of very lightly boron doped diamond was homoepitaxially deposited on the surface using hot filament assisted low pressure CVD (0.5% CH$_4$ in H$_2$) to create a slightly conducting surface. The thickness of the boron doped layer was about 200Å. The doped film was featureless when viewed in the SEM at 30Kx magnification.

Previous UHV experiments had been carried out on the diamond which did not produce any observable changes on the diamond surface. Prior to the CH$_4$ pyrolysis experiments, SIMS measurements were carried out on the diamond creating three 1x1mm craters approximately 2000Å deep. The crater surfaces were featureless under 30Kx magnification in the SEM.

Before carrying out the pyrolysis experiments, the natural type IIa single crystal diamond was cleaned using the following series of chemical treatments: (1) chromic acid at 180°C; (2) H$_2$O$_2$ and NH$_3$OH 1:1 solution; (3) nitric:HF:acetic (1:1:1) acid; (4) D. I. water and acetone rinses followed with drying in filtered argon. This cleaning procedure removed any non-sp$^3$ carbon from the surface accompanied by only minor etching of the diamond.

We also conducted CH$_4$ pyrolysis experiments using as a substrate a polycrystalline CVD diamond film approximately 10μ thick, grown on a silicon substrate. The diamond film was grown by hot filament assisted CVD under the following conditions:

- Pressure: 14 Torr
- CH$_4$ : H$_2$: 0.5 : 99.5
- T$_{substrate}$: ~800°C
- T$_{filament}$: 2100°C
At the end of the CVD growth run, the gas was replaced by pure H\textsubscript{2} for 10 minutes before turning off the hot filament to ensure the removal of any sp\textsuperscript{2} carbon on the surface. The film morphology is shown in Figure 1a, and the Raman spectrum of the film is shown in Figure 1b. The absence of any feature at around 1550 cm\textsuperscript{-1} in the Raman spectrum indicates that there is very little sp\textsuperscript{2} carbon in the film.

During the pyrolysis experiments, the single crystal diamond and the polycrystalline film were heated by a tantalum filament resistor placed directly under the samples. The substrate temperatures were measured by placing a thermocouple directly on top of the diamond surface. The temperature of the single crystal diamond was also measured using a pyrometer focused on the unpolished edge of the diamond plate. The temperatures measured by the thermocouple and the pyrometer agreed within 30°C.
Figure 1. The morphology (a) and Raman spectrum (b) of the polycrystalline diamond film. The Raman feature at ~520 cm\(^{-1}\) is due to the Si substrate.
RESULTS

CH₄ Pyrolysis on Diamond (100) and Polycrystalline Diamond Films

Throughout the pyrolysis experiment with the type IIa diamond substrate, the structure of the single crystal surface was monitored by RHEED. Before CH₄ exposure the RHEED pattern consisted of Kikuchi lines as well as a faint 1x1 pattern (Figure 2). RHEED patterns close to the crater region were not much different. However, this did not necessarily indicate that the crater surfaces were of the same quality as the flat regions because the electron beam on the sample was much longer than the crater dimension, which was a result of the low angle of incident of the electron beam. We believe that the crater surfaces have a nanoscale roughness as the result of sputtering.¹²,¹³

Figure 2. RHEED pattern for the virgin single crystal diamond surface before any CH₄ exposure.

Auger electron spectroscopy was used to identify the chemical nature, i.e., sp³ or sp² carbon, of the different surfaces. The Auger fine structure of the C KLL peak

---

has been shown to be sensitive to the various allotropes of carbon.\textsuperscript{14} Auger spectra of diamond (sp\textsuperscript{3}) and graphite (sp\textsuperscript{2}) surfaces measured in our system, using the C KLL line, are shown in Figure 3. It is known that for sp\textsuperscript{2} carbon, the peak (peak 1) closer to the main KLL dip is much smaller than the peak at lower energy (peak 2). Peak 1 appears only as a shoulder on the sp\textsuperscript{2} spectrum, whereas the opposite is true for a sp\textsuperscript{3} carbon surface. A change in the relative intensity of peaks 1 and 2 indicates the growth of a sp\textsuperscript{2} carbon on the diamond surface or a conversion of the diamond surface carbon structure. The inset in Figure 3 shows the C KLL spectra for natural diamond, graphite and amorphous carbon from reference 14.

![Figure 3. Auger spectra of (a) diamond (sp\textsuperscript{3}) and (b) graphite (sp\textsuperscript{2}) surfaces. Inset is high resolution spectra taken from reference 13.](image)

In our experiments, pure methane was exposed at background pressures of up to \(-3\times10^{-4}\) torr onto the single crystal diamond (100) surface at 900°C. Little change in the Auger spectrum was found on the flat portions of the (100) surface with 3\times10^{10} L of exposure, whereas in the sputter crater region only sp\textsuperscript{2} carbon species were observed in the Auger spectrum (Figure 4). The RHEED pattern from the

flat region still showed the same pattern with a slight increase in the background intensity, whereas the pattern in the crater region was hardly observable.

![Auger spectra of (a) smooth diamond and (b) cratered surfaces after exposure to CH$_4$ at 900°C.](image)

**Figure 4.** Auger spectra of (a) smooth diamond and (b) cratered surfaces after exposure to CH$_4$ at 900°C.

SEM also showed the difference between the flat and the crater surface regions. Since the secondary electron yield of diamond is greater than that of graphite, diamond normally appears much brighter in the SEM. As shown in the SEM image in Figure 5, the flat regions were considerably brighter than the sputter craters. Before the CH$_4$ exposure, no differences were seen in the SEM images between the two regions. These SEM results were also consistent with the formation of sp$^2$ carbon in the cratered regions.
These results indicated that surface perfection played a crucial role in the formation of sp² carbon upon pyrolysis of CH₄. The regions outside the sputter craters were atomically flat or at least consisted of large atomically flat areas. The crater surfaces were atomically rough as a result of ion bombardment during the SIMS analysis. It is also conceivable that the rough crater surface had non-sp² structural defects contributing to the formation of sp² carbon. Any sp² surface carbon should have been etched away during the extensive ex-situ surface cleaning. (Recall that AES measurements after the cleaning showed only sp³ carbon.)

To test the hypothesis that surface roughness contributed to sp² carbon formation, pyrolysis of CH₄ was carried out on the polycrystalline CVD grown diamond film. We expected that the polycrystalline diamond films would have numerous structural defects, especially at the grain boundaries. As a result of these defects, sp² carbon should form on the polycrystalline diamond film upon CH₄ exposure.

No ex-situ cleaning treatment was carried out on the film before loading it into the UHV chamber. The surface should have been free of any sp² carbon, a result of the hydrogen etch at the end of the film growth run. The Auger spectrum of the surface of the CVD film was identical to that of ex-situ cleaned single crystal
diamond. After exposure to $4 \times 10^9$ L of CH$_4$ at 900°C (a factor of 10 less than in the single crystal experiment), the surface was completely covered with sp$^2$ carbon as indicated by the Auger line shape. Since the surface was initially free from sp$^2$ carbon species, the difference in the nucleation and formation of sp$^2$ carbon between the flat portion of the single crystal and the polycrystalline film was most likely a result of the differences in surface perfection. Although the polycrystalline surface consisted of both (100) and non-(100) grains, we do not believe that crystallographic orientation played an important role in the nucleation of the sp$^2$ carbon species in our experiments. This result provides an additional support to our speculation that there is a strong correlation between surface perfection and the formation of sp$^2$ carbon.

Diamond growth was not observed on the single crystal diamond after $3 \times 10^{10}$ L of CH$_4$ exposure at 900°C. In these experiments, a 3x3mm (100) diamond was mechanically clamped onto the larger diamond plate. It was reasonable to expect that if growth occurred, a step would have been created between the covered and exposed portion of the larger plate. After the 24 hour exposure experiment, a surface profilometer was used to identify any possible growth step between the region masked by the smaller diamond plate and the exposed region. The profilometer had a 50Å resolution and no growth was found at the limit of the resolution of the instrument. However this finding does not rule out the possibility of growth by direct pyrolysis since the growth rates reported by Eversole$^{15}$ and Angus et al.$^{16}$ by direct pyrolysis of methane, methane/hydrogen mixtures were on the order of 100-200Å/hr at pressures ~100 times larger than those used in our experiments, so our expected growth rates would be on the order of 2Å/hr. Thus the expected film growth is at or below the limit of our ability to detect.

CH$_4$ exposures were repeatedly carried out at temperatures below 900°C, neither graphite nor growth was found on the flat diamond surfaces. We do not know if sp$^2$ carbon would form at temperatures below 900°C on defective surfaces.

At low to moderate pressures, sp$^2$ carbon is the more stable carbon phase. It may also be kinetically more favorable for sp$^2$ carbon to form. In the regions having enhanced surface imperfection, such as the sputter craters, decomposition of the CH$_4$ occurs and sp$^2$ carbon is deposited. In the atomically flat areas, the deposition rate of sp$^3$ carbon is very small, so that measurable film thicknesses were not attainable over the course of the experiment. This observation may also

---

help to explain the preference of sp$^2$ carbon to form at the grain boundary regions in CVD diamond films.$^{17}$

Although we do not know the exact nature of the defects that are responsible for nucleating sp$^2$ carbon growth, i.e. dislocations, stacking faults, or high densities of ledges due to macroscopic roughness, our results can be understood in quite general terms. Under the pyrolysis conditions, the residence time of the impinging species is very small on smooth surfaces. Surface imperfections may increase residence times; the probability of multiple collisions on the surface may be increased or the critical cluster size may be reduced. Either may lead to stable nuclei.$^{18}$

Finally, our experiments were inconclusive in providing direct evidence for the growth of sp$^3$ carbon on diamond (100) by direct pyrolysis of methane.

**Ketene (CH$_2$CO) Pyrolysis on Diamond (100)**

It was our intention to use ketene as a source of methylene in order to study the interaction of the methylene radicals with the diamond surface. We attempted to prepare ketene by gas phase pyrolysis of acetone and to trap the ketene in a trap maintained at 77K. In our hands, the ketene, if it had been produced, polymerized. The approach was abandoned until Phase II.

**CO and CO$_2$ Pyrolysis on Diamond(100)**

We proceeded to take a look at the effects of CO and CO$_2$ exposure. Curiously, the initial experiments in which $10^4$L of CO was exposed to the diamond surface at nominally 700°C produced the best RHEED pattern ever observed in our laboratory (Figure 6). Streaks were clearly visible in the RHEED pattern. The pattern gradually faded away with time and further annealing and exposure to CO up to 900°C did not improve the pattern.

Streaking in the RHEED pattern indicated that the atomically flat areas of the surface were relatively large. Diamond surfaces are usually covered with hydrogen that produces 2x1 and 1x2 pattern. Since RHEED of diamond surfaces normally does not show streaking, it is possible that the 2x1 and 1x2 domains are

---

19 Later experiments call the absolute value of the temperature measurement into question.
relatively small. If the observed streaking upon exposure to CO were a result of desorption of surface hydrogen and the elimination of small domains, exposing the streaking surface to hydrogen should eliminate the streaks. However, the streaks remained visible even after $10^4$ L of hydrogen exposure at 900°C.

![RHEED pattern](image)

Figure 6. RHEED pattern produced upon exposure of diamond (100) surface to CO.

We attempted to reproduce the initial result without success. That the streaking pattern did not appear with further CO exposure may have been a result of changed surface conditions with respect to the original diamond, which was only treated with standard ex-situ cleaning procedures. To explore this possibility, another ex-situ cleaning was carried out. However, exposing the new surface to CO under nominally the same conditions did not produce the streaking pattern. We repeated the experiment; this time when we took the sample to ~900°C, the streaking of the RHEED pattern occurred again. The different outcome of the earlier experiments at was attributed to a low substrate temperature. The observation of the changes in the RHEED pattern immediately raised the question of whether the extreme smoothing of the diamond surface was due to addition or removal of carbon.

A high dosage CO experiment was carried out; the total exposure time was 8 hours and the base pressure was maintained at $1.5 \times 10^{-4}$ torr. Two pieces of diamond (100), one 3x3mm and the other 4x8mm in size, were held together by a stainless steel clip. The smaller diamond was clamped over part of the surface of the larger diamond plate. This was done to mask an area on the large diamond surface so that a profilometer scan could be performed after the exposure.
experiment to determine whether or not the diamond surface grew as a result of the exposure. The heating was carried out by a Ta strip heater directly beneath the larger diamond.

After 4 hours, a beautiful RHEED pattern with clear streakings was found. The pattern showed a second weaker feature with an in-plane lattice constant approximately 17% smaller than diamond (Figure 7). This feature was tentatively identified as BCC Fe which has a lattice constant 19.6% smaller than diamond. The observed larger in-plane lattice constant for BCC Fe may have been due to the influence of the underlying diamond which has a much larger lattice constant. The presence of Fe was either due to redeposition of Fe from Fe(CO)₅ produced by reaction of CO and the hot steel clip or due to diffusion.

![Figure 7. RHEED pattern produced upon exposure of diamond (100) surface to CO at 900°C. The weaker lines may be due to BCC iron.](image)

Auger spectra taken in-situ immediately after the exposure showed both the carbon and iron signals. This result indicated that either the Fe layer was very thin (one monolayer or so) or that it formed isolated islands. EDS (Figure 8) showed only traces of Fe. X-ray diffraction result (Figure 9), which shows a total absence of any other peaks besides those of diamond. The intensity resolution in X-ray is 1 in 3000 with respect to diamond signals. Clearly, the amount of Fe was minimal.
Surface profilometer measurements indicated that a ~ 500Å layer was grown on the diamond surface. EDS and X-ray diffraction data indicated that this 500Å layer is entirely carbon, most likely diamond. No extraneous peaks were seen in the IR, (Figure 10) and UV/visible (Figure 11) reflection and transmission spectra. The transmission through the diamond appeared somewhat attenuated possibly due to the presence of iron on the surface. The attenuation is not surprising since the appearance of the diamond is transparent with a slight gray tint coloration.
Figure 10. IR spectrum of film produced upon exposure of diamond (100) to CO.

Figure 11. UV/VIS spectrum of film produced upon exposure of diamond (100) to CO.
Since Auger, EDS and X-ray results indicated that the diamond was on the surface, we attempted to etch away any surface Fe with $\text{H}_2\text{SO}_4$. After etching, the sample looked transparent with only a slight tint. A faint footprint of the smaller diamond could be seen on the larger diamond. Surface profilometer measurements now showed that the film was approximately 300Å thick, not 500Å. The difference may have been due to measurement discrepancies due to surface roughness (100Å) or to thinning of the layer as a result of etching. IR and UV/VIS spectra showed less attenuation (Figure 12) after the etch. SIMS analysis showed the presence of iron.\textsuperscript{20}

Similar observations have been made in which methane was thermally decomposed on diamond powders precoated with a thin layer of Fe, Ni, Co, Mn, or FeNi alloy.\textsuperscript{21} The growth rates reported using methane were $\sim10x$ larger than those we report for Fe mediated growth from CO. In the previous work employing methane, the Fe was reported to act as a mobile transfer medium which aided in decomposition of the methane and facilitated the transition from carbon in the vapor phase to a precursor and subsequent transition to carbon in the solid metastable diamond phase.\textsuperscript{21}

\textsuperscript{20} Dr. Charles Magie at Charles Evans East.
Figure 12. IR (upper) and UV/VIS (lower) spectra of film produced upon exposure of diamond (100) to CO after H$_2$SO$_4$ etching.
Exposure of the Diamond Surface to O₂

In all low pressure CVD growth of diamond, both sp³ and sp² carbons are created on the growth surface and the non-sp³ carbon is etched away. In these hydrogen based growth systems, the etching of the non-diamond carbon is carried out by hydrogen atoms whose creation requires a great deal of energy such as the presence of a plasma or the use of a hot filament. A large energy consumption is needed in diamond growth to produce the atomic hydrogen which is the predominant factor in the cost of diamond growth. A process in which the non-diamond component can be etched preferentially with less energy is, therefore, very much needed. From this respect, O₂, which etches both diamond and graphite, may be a viable alternative, since it is known that the etching rate of graphite by O₂ is higher than diamond.

However, if O₂ creates an sp² carbon on the growing surface the deposition cannot be of pure diamond.

To study what happens in the O₂ diamond system, the diamond (100) surface was exposed to 10⁴ L of oxygen at temperatures between 30°C and 900°C. No conversion of sp³ carbon to sp² was found by Auger. The only change was the addition of a small amount (approximately 2% of a monolayer) of oxygen on the surface at temperatures above 200°C. No significant changes in the RHEED pattern were seen. This experiment indicated a) that oxygen does not convert diamond into graphite; or b) that the formation of graphite on the surface is rapidly etched away. The finding is encouraging, since it indicates that in the presence of oxygen, sp³ surface exists which can be nucleation sites for further diamond growth. Experiments using dilute CH₄ in H₂ with the assistance of O₂ will be carried out to explore the possibility in diamond growth using this combination.
CONCLUSIONS AND FEASIBILITY ASSESSMENT

We unexpectedly found that "surface perfection" of the diamond substrate appeared to be a crucial factor in CVD of sp$^2$-free diamond deposition. We recognize that the term "surface perfection" is ambiguous; we will define it to mean the overall crystallographic perfection of the lattice, including possibly the effects of surface roughness. The quality of semiconductor homoepitaxial layers was strongly influenced by surface preparation.

Exposure of a diamond (100) surface to CO at high temperature resulted in extreme smoothing as monitored by RHEED. The diamond surface was propagated under conditions of exposure to CO at T~ 900°C. Growth was apparently linked to an inadvertent impurity, iron, which may have catalyzed the decomposition of CO. Improved nucleation and growth rates from non-hydrogen-containing carbon sources may be achievable with catalysis by transition metals. We intend to use this discovery in Phase II to develop diamond emitters for flat panel displays, UHV analytical instruments, and microwave vacuum electronics.