REPORT DOCUMENTATION PAGE	Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
18-05-2012	Final Report	1-Nov-2010 - 31-Oct-2011

4. TITLE AND SUBTITLE
Final Technical Report for Proposal Number 59187MSDRP: Experimental Study of Diamond Nucleation by Plasmon Assisted Chemical Vapor Deposition

5a. CONTRACT NUMBER
W911NF-11-1-0003

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
0620BJ

6. AUTHORS
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5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
California Institute of Technology
Sponsored Research MC 201-15
California Institute of Technology
Pasadena, CA 91125 -

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
59187-MS-DRP.1

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT
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15. SUBJECT TERMS
CVD, plasmon, diamond

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Boyd
UU	UU	UU	UU		19b. TELEPHONE NUMBER 626-395-4123

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

Report Title

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Final Technical Report for Proposal Number 59187MSDRP, *Experimental Study of Diamond Nucleation by Plasmon Assisted Chemical Vapor Deposition*

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Caltech

May 18, 2012

Abstract

The efforts over the performance period focused on the nucleation of diamond by plasmon assisted chemical vapor deposition, characterization of diamond nanoparticles, and direct conversion of the polymer poly(hydridocarbyne) to diamond. We adapted the hot-filament CVD methods used in conventional CVD diamond to our plasmon assisted CVD (PACVD) setup and explored the growth of diamond using in situ Raman spectroscopy. With the addition of the filament, we were able to observe carbon deposition and etching of amorphous carbon. We were able to form diamond-like carbon. For comparison, we examined commercially available diamond nanoparticles of varying percent sp^3 bonding with visible and UV Raman spectroscopy. As an alternative route to diamond nucleation, we synthesized poly(hydridocarbyne) (PHC), and used it as a carbon source for PACVD. In situ Raman spectroscopy taken during plasmon heating pyrolysis of PHC in open air indicated transformation of the polymer from amorphous carbon to what we believe is hexagonal diamond.

Statement of the Problem

Diamond had remarkable properties. However, formation of diamond films can currently only take place at high temperatures. This precludes a wide range of materials from being coated with diamond. The goal of this project was to explore a low temperature means of nucleating diamond using plasmon assisted chemical vapor deposition (PACVD). If successful, this could allow the formation of diamond on temperature sensitive materials.

Summary of Important Results

PACVD of Diamond

Our first approach was to combine conventional diamond CVD techniques with plasmon assisted CVD (PACVD). Traditional methods for diamond incorporate flows of methane and hy-

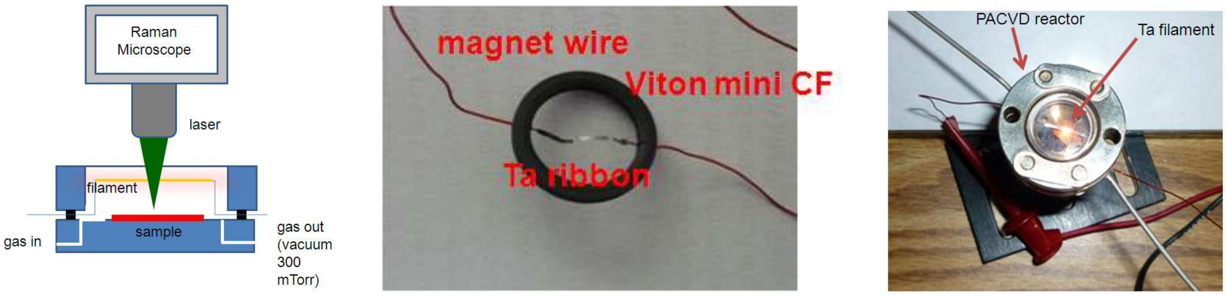


Figure 1: a) Schematic of the modified PACVD reactor b) A Viton gasket modified to hold the hot-wire filament in the PACVD reactor c) Working filament in the reactor cell.

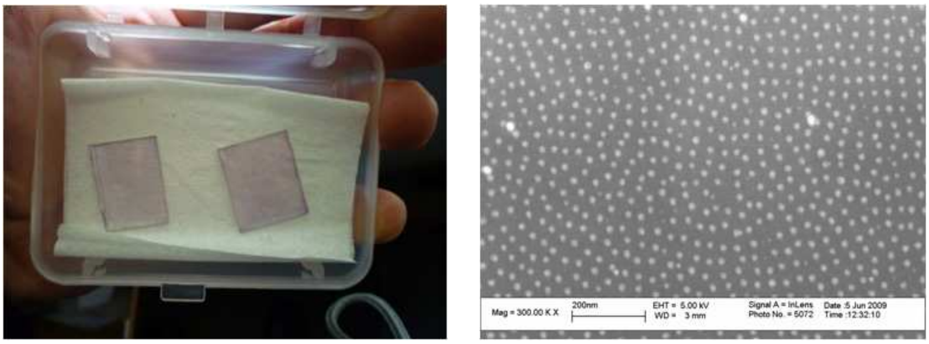


Figure 2: a) Glass coated with gold nanoparticles via BCPL b) Representative SEM image of gold nanoparticles produced by BCPL.

drogen over a heated substrate; a hot filament is incorporated into the process to produce atomic hydrogen. Atomic hydrogen is used to etch away amorphous carbon and facilitate carbon sp^3 bond formation. Heating the substrate is also necessary and can be provided by conventional means e.g. a furnace. In our approach, the heating would be supplied by the plasmon heating of gold nanoparticles.

We modified our existing PACVD flow reactor for diamond growth. A schematic of the reactor is shown in Figure 1-a. The reactor is based on mini two Conflat flanges with the top one being viewport and the bottom one incorporating small stainless steel tubing. The setup setup allows for flows of methane and atomic hydrogen over the sample, while heating is driven by laser induced plasmon heating through the viewport. The system vacuum pressure and gas flows were under computer control. In addition, the same excitation laser for plasmon heating was also used to measure the Raman spectra during deposition. A filament was added to the system. The filament was constructed from magnet wires that were run through a Viton gasket and were spot-welded to the filament, Figure 1-b. This allowed for a vacuum to be maintained, which is necessary to operate the filament for extended periods. Figure 1-c shows the working filament in the reactor.

The substrates used in these studies were glass microscope slides coated with gold nanoparticles. The particles were produced in our lab block copolymer lithography (BCPL). BCPL is a self assembly technique that allows for large-area, low-cost, uniform coatings of nanostructures. Shown in Figure 2-a are images of glass coated with gold nanoparticles via BCPL and Figure2-b representative SEM image of gold nanoparticles produced by BCPL.

We examined the effects of the hot-filament on PACVD deposited carbon. We had previously demonstrated that it was possible to deposit amorphous carbon by PACVD with methane as a carbon source while monitoring the deposition with *in situ* Raman spectroscopy. With the addition of the filament to the system, we observed etching of amorphous carbon. Shown in Figure 3 are in situ Raman spectra demonstrating this. The initial spectrum (green) was taken with with flowing hydrogen only, and the second spectrum (red) is the difference spectrum, taken 200 s later under the same flow and with the hot-filament. The red peak is referenced to the initial carbon peak, and the negative peak indicates etching of the amorphous carbon by atomic hydrogen.

We compared the performance of different filament materials. It is well known in the diamond literature that different filament materials can effect the production rate of atomic hydrogen. Shown in Figure 4 are in situ measurements taken during carbon deposition with a tantalum filament. The filament is tantalum and the temperature is estimated to be 700 °C. The gas flows are H_2 25 sccm; CH_4 1 sccm. The system pressure is 300 mTorr. The laser is 532 nm focused to about 10 micrometers. The spectral features are: 1332 cm^{-1} (diamond) and 1551 cm^{-1} (G band- amorphous carbon). The amorphous carbon feature dominates the spectrum.

We tested the performance of a tungsten filament. Shown in Figure 5 is an in situ measurement taken during carbon deposition with a tungsten filament. The filament temperature is estimated to be 700 °C. The system pressure is 300 mTorr. The laser is 532 nm and is focused to about 10 micrometers. The spectral features are: 1332 cm^{-1} (diamond) and 1551 cm^{-1} (G band- amorphous carbon). These spectral features are more pronounced than with the Ta filament. The absence of a singular peak at 1332 cm^{-1} and relative heights of the D and G peaks indicate that deposition is most likely diamond-like carbon. A time series analysis of the Raman peaks of this growth is shown in Figure 6. These results show the the diamond peak did sharpen and increase in area relative to the D and G peaks.

These results are encouraging. Growth of diamond-like carbon is possible via hot filament PACVD. Additional experiments could be conducted over longer growth times. This would require improvements in the hot-wire arrangement (or other source of atomic hydrogen) so that it could run for extended periods i.e. hours rather than tens of minutes

Characterization of Diamond Nanoparticles

In an effort to determine the detection limits of in situ Raman spectroscopy, we made ex situ Raman measurements of diamond nanoparticles. We examined the Raman spectra of commercially available nanodiamond (Dynalene Inc). Two grades of powders were examined with 50 % and 98 % sp^3 bonding. The size of the particles was approximately 5 nm. The particles were examined with 244 and 532 nm excitation. We do currently do not have 244 nm capabilities on our current system, and The UV Raman measurements were made with a Raman system outside of our laboratory. Shown in Figure 7 are Raman spectra of the particles. The particles with varying bond content exhibited distinct spectral responses. The 98% sp^3 particles show a sharp resonance at 1332 cm^{-1} with 244 nm excitation. This sharp resonance is not seen with 532 nm excitation. However, there is a small diamond peak in this spectra that can be useful for indicating the presence of diamond. The 50% sp^3 particles show spectra similar to that of amorphous or diamond like carbon due to a resonance of the sp^2 bonds with visible excitation.

These measurements show that UV Raman excitation could be useful for monitoring the early stage of diamond nucleation down to at least 5 nm. They also show that visible Raman excitation will at least detect the presence of diamond nucleation as long as there is small

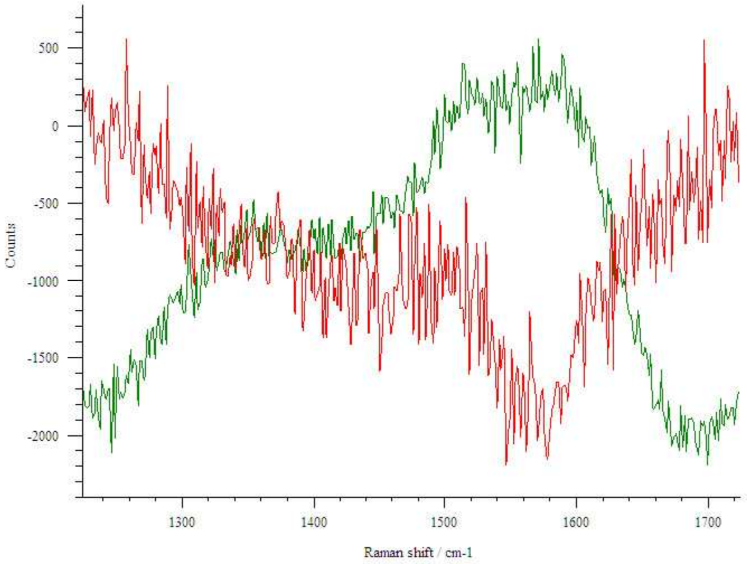


Figure 3: In situ Raman spectra demonstrating etching of amorphous carbon via hot filament. The green spectrum is taken prior to turning on the filament. The red spectrum is the difference between the initial and final spectrum. The negative peaks indicate removal of amorphous carbon by the atomic hydrogen produced by the hot filament.

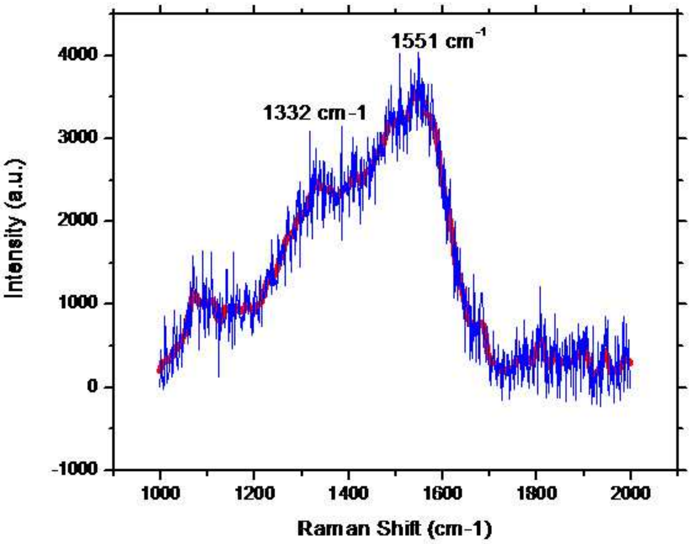


Figure 4: In situ Raman measurements during PACVD deposition with a tantalum filament. The small diamond peak is formed suggesting some fraction of diamond-like carbon.

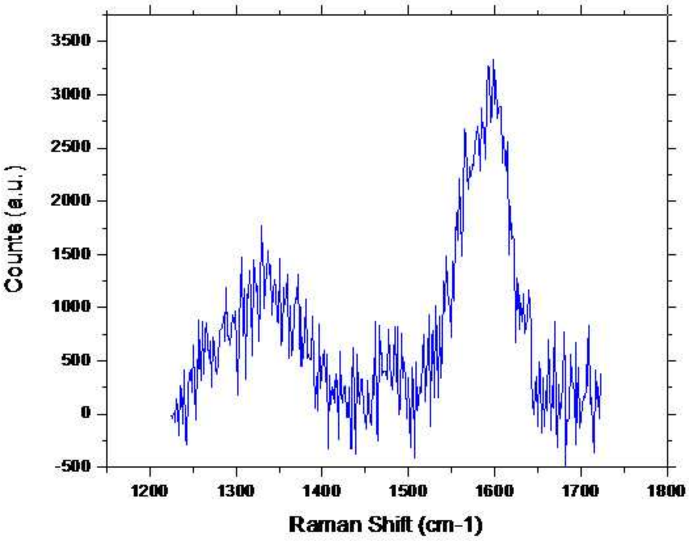
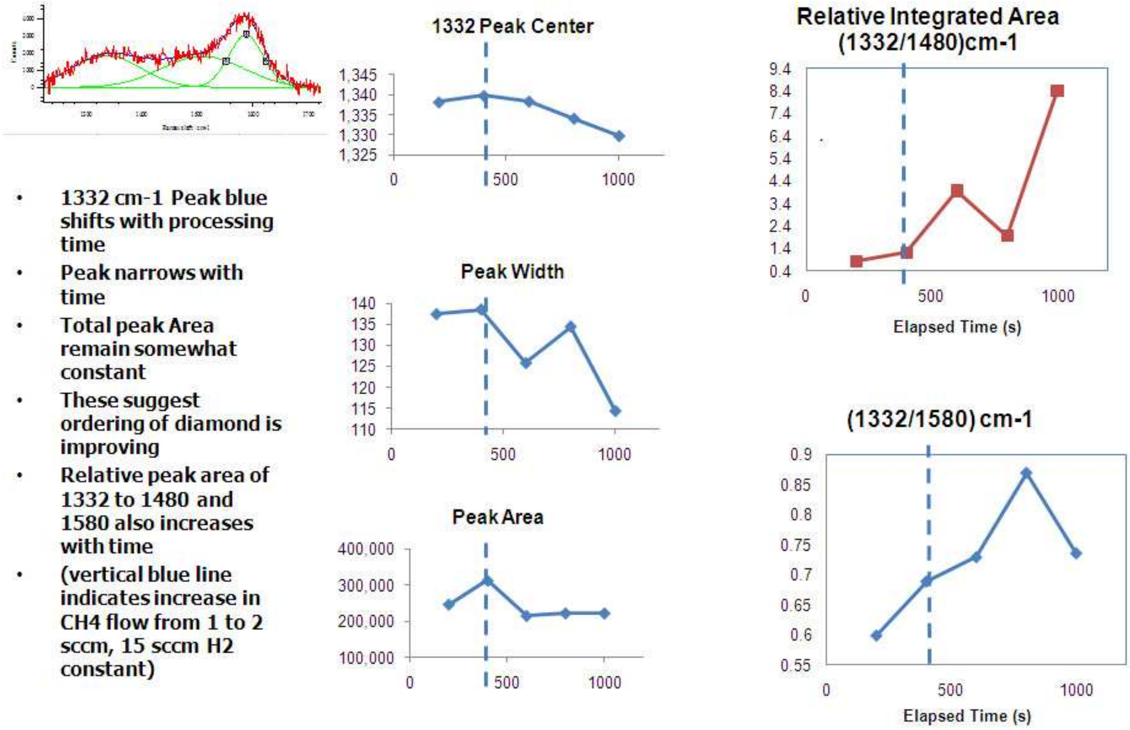


Figure 5: In situ Raman measurements during PACVD deposition with a tungsten filament. The spectrum indicates the formation of diamond-like carbon.



- 1332 cm-1 Peak blue shifts with processing time
- Peak narrows with time
- Total peak Area remain somewhat constant
- These suggest ordering of diamond is improving
- Relative peak area of 1332 to 1480 and 1580 also increases with time
- (vertical blue line indicates increase in CH4 flow from 1 to 2 sccm, 15 sccm H2 constant)

Figure 6: Time series analysis of the Raman spectra during growth with a tungsten filament.

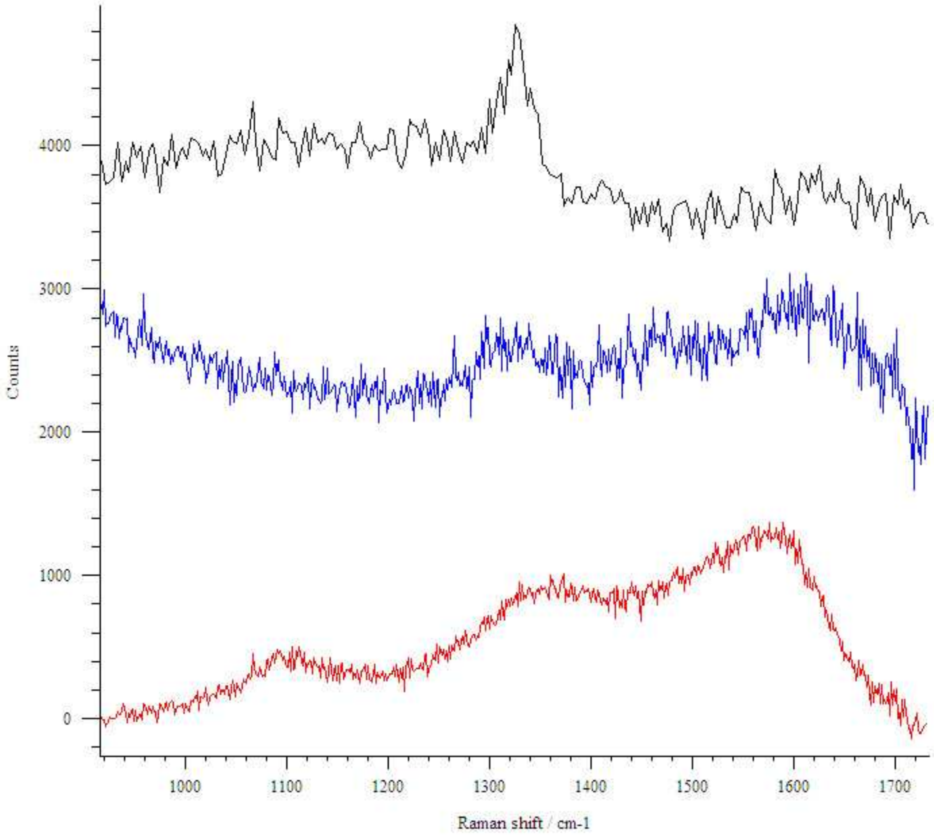


Figure 7: Raman spectra of commercial diamond nanoparticles. 98% sp^3 with 244 nm excitation (black, top), 98% sp^3 content taken with 532 nm excitation (blue, middle), and 50% sp^3 taken with 532 nm excitation (red).

amount of amorphous carbon present. These measurements allowed us to compared the 532 nm Raman spectra of the diamond NP with the in situ measurements that we made.

We explored etching of the diamond nanoparticles by atomic hydrogen. Shown in Figure 9 are a series of Raman spectra of the diamond nanoparticle with 98 % sp^3 bonding taken while the filament is on. Figure 9 shows that both the carbon and diamond peaks diminish with time. This indicates that the NDs are being etched by atomic hydrogen. The etching also indicates that the rate of atomic hydrogen will need to be managed during growth.

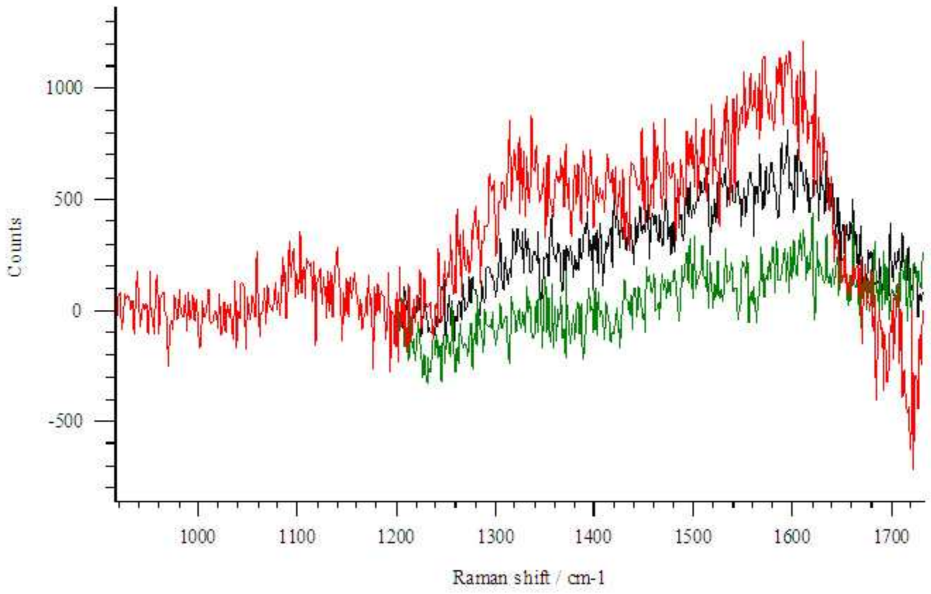


Figure 8: Raman spectra of commercial diamond nanoparticles while exposed to the hot filament.

Plasmon Heating of Graphite Powder

We explored plasmon heating of crystalline graphite power. The graphite G band is known to be temperature sensitive. We observed a downshift in the peak energy with increasing laser power, Figure 9. The maximum laser power that we could apply before the graphite exhibited a D (disorder) band was 0.76 A. We used published data to relate these downshifts to the increase in temperature. Everall et al. (Carbon, 29, 2, 1991, p 133) obtained the temperature dependence of the G frequency of graphite using a microscope heating stage. Using these results we were able to calibrate changes in the G band with laser power. The maximum temperature before the onset of disorder was 661 °C. This temperature was achieved with approximately half the available laser power on our system. This suggests that higher temperatures are possible with our PACVD existing system.

Growth of Diamond from PHC

An alternative to vapor phase formation of diamond is direct conversion of a polymer. Poly(hydridocarbyne) (PHC) is an sp^3 bonded polymer. It was first developed by Visscher et al.(Science, 260,1993, p1496). An avantage of the polymer conversion approach is that the polymer coated, dipped, spun, or sprayed onto the part to be coasted. The polymer can be converted to diamond by pyrolysis. However, the conversion temperatures are comparable to growth temperatures of CVD diamond ~1000 °C. The first publication of PHC only produced diamond like carbon.

A challenge with PHC is its synthesis, which is very involved, especially for non-chemists. However, a new, simple synthesis route has recently been developed by Nur et al (J Mater Sci (2009) 44:2774-2779).) The authors of this work claimed that PHC synthesized by their method can produce diamond upon pyrolysis at 1000 °C. With help from a Caltech chemist, we were able to follow their procedure and produce PHC in our lab.

We applied plasmon heating to PHC and measured the response in real time with Raman

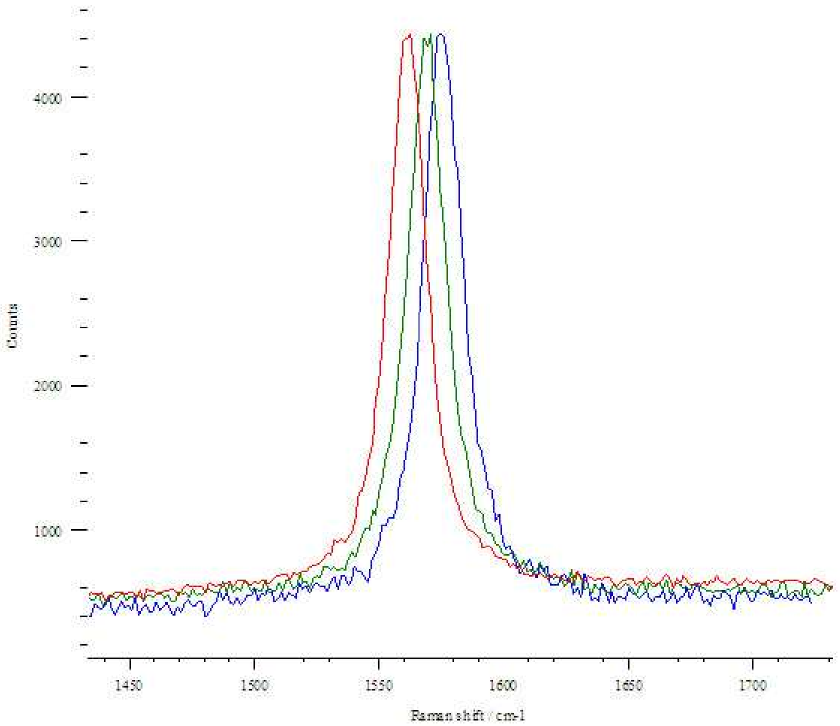


Figure 9: Down-shift of the G band of crystalline graphite powder with laser power. The peak position of the G band is, 1576 cm^{-1} (blue) 0.5 Amp, 1569 cm^{-1} (green) 0.7 Amp and 1560 cm^{-1} (red) 0.76 Amp. Beyond 0.76 Amp, disorder of the particles was observed. The graphite particles were on glass substrates with 30 nm gold nanoparticles.

spectroscopy. We were able to observe dramatic changes in the PHC with plasmon heating. Figure 10 (left) shows the time evolution (bottom to top) of Raman spectra during synthesis. Bottom spectrum (red) is typical of amorphous carbon with the G peak 1600 cm^{-1} larger than D peak at 1340 cm^{-1}. With time, the two become equal, and eventually the G peak disappears and the D sharpens and shifts. Figure 10 (right) shows sharp peak at 1310 cm^{-1} that results. This single peak indicates the polymer was transformed from an amorphous to a crystalline state. At this point it is not clear whether the deposits are primarily hexagonal diamond or cubic diamond. The width of this peak, which is much wider than that of natural diamond, suggests that the deposit is not single crystal, i.e. poly crystalline and or contains defects.

Using higher laser processing powers, we observed that the peak could be shifted up to high wavenumbers, e.g. 1318 cm^{-1}. We also noticed that in the outer wings of the beam, where the laser intensity is less, the polymer did not fully convert, and it was only at the center of the beam where polymer was fully converted. Direct pyrolysis of PHC at 1000 °C in an open air furnace did not produce diamond.

A visible change in the PHC could also be seen. Upon transformation by plasmon heating to a crystalline state, as observed by Raman spectroscopy, the polymer would change from from a dull brown paste to what appeared to be small crystallite. Shown in Figure 11 is an optical image a crystallite taken with a 100 X objective. Further examinations of the deposits will be needed to fully characterize the microstructure.

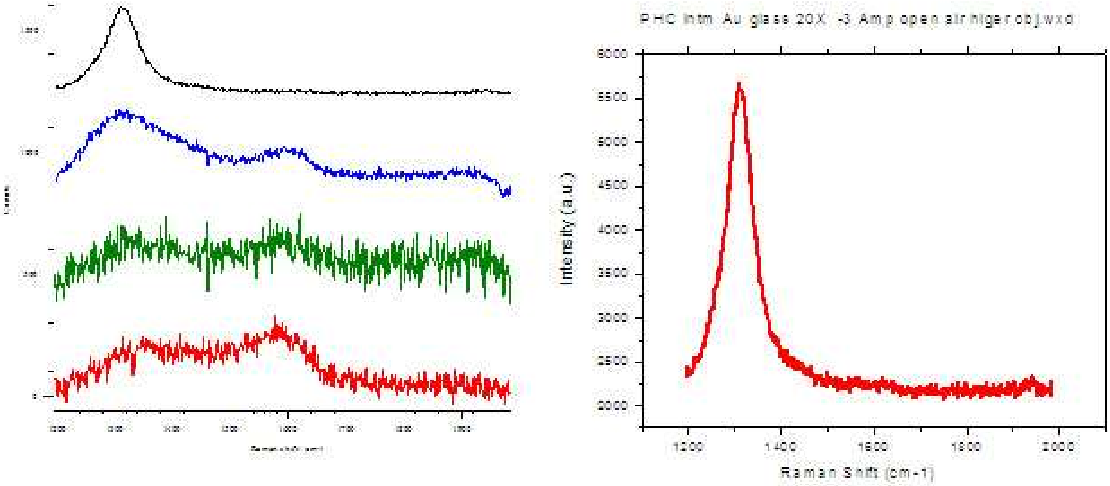


Figure 10: Raman spectra of taken during plasmon heating of PHC. Time evolution (bottom to top) of Raman spectra during synthesis. (left) Bottom spectrum (red) is typical amorphous carbon with G peak 1600 cm^{-1} larger than D peak at 1340 cm^{-1}. With time, the two become equal, and eventually the G peak disappears and the D sharpens and shifts. Expanded view final spectrum showing sharp peak at 1310 cm^{-1} (right).

Figure 11: An optical image of a crystallite formed from plasmon heating of PHC. This image was taken with a 100 X microscope objective.

Summary

We explored plasmon heating as method to nucleate diamond via vapor phase. We established that carbon can be deposited by PACVD from from a gaseous carbon source. We observed that the hot filament allowed amorphous carbon to be etched. We also observe that plasmon heating can provide substantial heating of graphite. PACVD combined with traditional hot-wire diamond CVD was able to produce diamond-like carbon. However, the experiments were limited by the stability of the home-made filament, which in turn, constrained the duration of the growth time to tens of minutes. Improvement in the hot-wire filament or replacing with the filament with plasma source set-up would allow more precise control of the process and a longer duration of the project.

We explored the detection of limits Raman spectroscopy for diamond nucleation. Commercial diamond nanoparticles of varying sp^3 content were examined with visible and deep UV Raman. UV Raman was able to see a sharp resonance in particles as small as 5 nm. Visible Raman was mostly sensitive to amorphous carbon peaks. However, a small diamond feature was discernable when there was very high sp^3 bond content. We observed that the diamond NPs were etched by the filament. From the deposition and studies of diamond NPs, we can conclude that the incorporation of deep UV Raman would be valuable in the study of diamond nucleation and growth process. While visible Raman would be in detection of the growth of high quality diamond only.

With regards to the vapor phase nucleation of diamond, we believe that the each of necessary components for creating and detecting diamond nucleation are possible with PACVD. Further work will be necessary to bring these elements together to produce high quality diamond.

Direct conversion of PHC to diamond provides an interesting alternative to vapor phase deposition. We demonstrated that it is possible using plasmon heating to convert PHC from an amorphous carbon to what we believe is a crystalline state. However, further characterization of the deposits will be required to establish the exact nature of the deposits. Our ability to further characterize the PHC deposition is currently limited. Larger sample area, which would allow x-ray diffration or EELS, and or deep UV Raman would be valuable characterization tools.