REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE April 30, 1999	3. REPORT TYPE AND DATES COVERED May 1, 1998 – April 30, 1999

4. TITLE AND SUBTITLE

Synthesis of Diamond in High Power-Density Microwave Methane/Hydrogen/Oxygen Plasmas at Elevated Substrate Temperatures

5. FUNDING NUMBERS

Grant N00014-98-1-0571

6. AUTHOR(S)

7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES)

Auburn University
Department of Electrical Engineering
200 Broun Hall
Auburn, AL 36849

8. PERFORMING ORGANIZATION REPORT NUMBER

2

9. SPONSORING / MONITORING AGENCY NAMES(S) AND ADDRESS(ES)

Colin E. Wood
ONR 312, Office of Naval Research
Ballston Center Tower One
800 North Quincy St., Arlington, VA 22217-5660

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release

12. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Effects of elevated substrate temperatures and oxygen additive on the chemical vapor deposition of diamond are presented. High power-density microwave plasmas in a high concentration of methane diluted by hydrogen led to high diamond growth rates at elevated substrate temperatures up to around 1450C. With the addition of a small amount of oxygen (less than 2%), diamond films deposited at substrate temperatures higher than 1450C at 30 um/hr were achieved. At substrate temperatures higher than 1600C, diamond nucleation density is low. However, diamond grows well and forms high quality diamond crystallites.

14. SUBJECT TERMS

Diamond, microwave plasma, high temperature

15. NUMBER OF PAGES
32

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT unlimited

Synthesis of Diamond in High Power-Density Microwave Methane/Hydrogen/Oxygen Plasmas at Elevated Substrate Temperatures

Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng
Department of Electrical Engineering
Auburn University, Auburn, Alabama 36849 USA

Effects of elevated substrate temperatures and oxygen additive on the chemical vapor deposition of diamond are presented. High power-density microwave plasmas in a high concentration of methane diluted by hydrogen led to high diamond growth rates at elevated substrate temperatures up to around 1450^0C. When methane and hydrogen were the only reactant gases and the substrate temperature was higher than 1450^0C, graphitic deposits started to show up. With the addition of a small amount of oxygen (less than 2%), diamond films deposited at substrate temperatures higher than 1450^0C at 30 um/hr were achieved. Diamond deposited at substrate temperatures exceeding 1600^0C was achieved on molybdenum substrates. At such high temperatures, diamond grows well but nucleation density was low. Raman spectra and surface morphologies of diamond films are correlated with the growth conditions.

INTRODUCTION

Diamond has many unique properties that makes it an ideal material for a broad range of applications. In some applications, thick and inexpensive diamond is needed. Therefore, a high-rate diamond deposition process is desirable. Although some techniques, such as dc arc jets and combustion flames, have been proven to be able to deposit diamond films at high rates, the deposition cost is high and good uniformity on a large area is still difficult to achieve. Microwave plasma enhanced chemical vapor deposition technique (MPECVD) has advantages over others because the process is relatively stable and reproducible results can easily be obtained. It is, therefore, important that we study high growth rate diamond deposition by the MPECVD method.

The substrate temperature is a very important parameter in the diamond CVD process. There has been a suggestion for the growth of diamond at temperatures up to about 1400^0C [1]. However, most CVD diamond processes have been carried out at substrate temperatures in the range of 500-1000^{0}C [2,3]. The power density of the plasma is another key parameter for MPECVD. The power density is dependent on the applied microwave power, the total gas pressure, and the volume of the plasma. Table I shows the typical deposition conditions for traditional low power-density MPECVD and for high power-density MPECVD. For traditional low power-density MPECVD, diamond growth rate increases with substrate temperature when the substrate is about1000^{0}C or lower. Many researchers have reported that at substrate temperatures above 1200^{0}C, graphite instead of diamond was deposited. This is true because most of those MPECVD diamond processes use low power-density plasmas. The conditions used for a typical low power-density MPECVD of diamond restrict the achievable diamond growth rates, the temperature range in which diamond grows, and the quality of the diamond films. By using a high power-density plasma, we were able to extend the diamond growth domain to a higher substrate temperatures and allow the application of higher methane concentrations.

2

One of the important parameters in chemical vapor deposition of diamond is the concentration of hydrocarbon gas in the gas mixtures. Among various hydrocarbon gases that have been used for diamond deposition, methane is the most popular carbon source. The concentration of methane in the gas mixture influences the growth rate, the surface morphology, and the quality of a diamond film as well. The diamond growth rate is directly related to the concentration of methane within a limited range. A higher concentration of methane in the gas mixture may increase the deposition rate as well as the graphitic components in the deposit. It has been reported that 6% methane concentration in hydrogen led to good crystallinity and surface morphology for a diamond homoepitaxial process [4] while the typical concentrations of methane in the gas mixtures for diamond deposition are less than 5%. The diamond growth rates obtained under low concentrations of hydrocarbon gas and low power-density of microwave plasmas are few micrometers per hour at most.

Bachmann *et al.* [5] summarized diamond CVD results from a number of authors. The data included the use of gas mixtures that led to successful diamond deposition and those failed to produce any diamond. The data was plotted in the form of the overall concentrations of carbon, hydrogen, and oxygen in a triangular diagram. The phase diagram shown in Figure 1, to be called the C-H-O diagram in the following discussion, is an equilateral triangle with each side representing the atom fractions of the gas phase composition of the C-H, H-O, and O-C binary systems. The diagram is divided into three regions: "non-diamond growth" region, "diamond growth" region, and the "no growth" region. Only graphite and/or amorphous carbon are deposited in the "non-diamond growth" region. The "diamond growth" region is bounded by two lines: (1) the first line connects point H and the point with $C/(C+O) \approx 0.57$ on the C-O sideline, and (2) the second line connects point H and the point with $C/(C+O) \approx 0.45$ on the C-O sideline. The locations for the end points of these two lines on the C-O sideline, when expressed in terms of C/O ratio, are 1.33 and 0.82, respectively. For gas mixtures with $C/O > 1.33$,

non-diamond carbon (amorphous carbon, graphite, etc) tends to grow. The "no growth" region has C/O < 0.82. Carbon monoxide, CO, is located at C/O = 1, which is at the midpoint of the C-O sideline. Most hydrogen-rich mixtures are located at coordinates very close to the H corner. Gas mixtures with less than 5% methane diluted in hydrogen are located on the C-H sideline with H/(H+C) > 0.977 or C/H < 0.024. The C-H-O diagram is a summary of experimental results available at the time of publication. Carbon monoxide, CO, is located within the diamond domain. However, although many attempts to depositing diamond from pure CO have been made, no diamond growth has been reported [6,7].

Typical concentrations of methane or other hydrocarbon gases used for plasma enhanced CVD of diamond without oxygen additive are less than 5%. The locations for the data points representing those gas mixtures in the C-H-O phase diagram are on the C-H sideline. Methane is located on the C-H line at H/(H+C) equal to 0.8. The presence of hydrogen in the gas mixtures tends to move the location of the data points toward the H endpoint (H/(H+C)=1). In other words, the locations for hydrogen diluted methane containing gas mixtures are between H/(H+C)=0.8 and 1 on the C-H side line. Fig. 2 shows the enlarged hydrogen-rich corner of the C-H-O diagram [5]. The location for a 5% concentration of methane in hydrogen is at H/(H+C)=0.977. For gas mixtures containing 3% or less of methane in hydrogen, their H/(H+C) values are larger than 0.985, which is very close to the end point of the upper border of diamond growth region. According to Figure 2, the diamond domain on the C-H line is limited to a short section near the H-corner. If oxygen is added to the gas mixture, all data points will move away from the C-H sideline into the C-H-O diagram. This study employed high density microwave plasmas in a high concentration of methane diluted by hydrogen. The H/(H+C) values for 16%, 50%, and 80% methane diluted by hydrogen are 0.935, 0.86 and 0.818, respectively, as shown in Fig. 2. These points are located on the C-H sideline but are outside of the "diamond growth" region. Although these data points can be moved from the C-H sideline into the

"diamond growth" region inside the C-H-O diagram by adding some oxygen, oxygen additive was found to be not necessary for diamond deposition within an appropriate range of experimental conditions. Results from this work suggest that "diamond growth" zone in the C-H-O diagram expands when the power density of the microwave plasma is high.

EXPERIMENTAL SETUP

Diamond films were deposited by microwave plasma enhanced chemical vapor deposition (MPECVD). The schematic diagram of the microwave plasma CVD system used in this study is shown in Fig. 3. A microwave magnetron with output power up to 6kW was used to deliver microwave power through a rectangular waveguide and an antenna to the reactor. A quartz window of ¼ inch thick was used to separate the low pressure side of the reactor from the waveguide. Ports on the reactor were used as gas inlets, the exhaust port, and viewing windows. Reactant gases used in this study were methane and hydrogen with optional addition of a small amount of oxygen. Electronic mass flow controllers were used to control the gas flow rates. A mechanical pump was used to pump down the reactor before gases ware fed into the chamber. The deposition temperature was monitored by aiming an dual color optical pyrometer at the surface of the substrate through one of the viewing windows.

Water cooled molybdenum (Mo) rods of 1/2 inch in diameter were used in this experiment as the substrates. Because the high melting point of molybdenum, it is a convenient substrate material for studying high temperature diamond deposition. Before a Mo rod was mounted in a water-cooled substrate holder, one end of the rod was polished to a mirror finish and used for diamond growth. For comparison, some substrates used in this experiment were seeded with diamond while others were not. Diamond seeding was done by rubbing the polished Mo surface with diamond paste (1 μm) followed by ultrasonic cleaning. The total gas flow rate was 500 sccm and the reactor pressure was

kept at around 130 Torr. In contrast to the typical methane of less than 5% diluted in hydrogen, 16% methane diluted by hydrogen was used as the gas mixture for deposition. Microwave power between 1400 and 1750 W was applied. The deposition temperature was controlled by adjusting the output power of the microwave generator and was measured by an optical pyrometer. The readings of the optical pyrometer were later calibrated with the readings from a thermocouple inserted into a molybdenum substrate which was heated up by a resistive heater. Deposition periods ranged from 45 minutes to 26 hours. The deposited diamond films were characterized by means of a scanning electron microscope (SEM). Raman spectra for diamond films were used to examine the crystalline quality of the deposits. The growth rates were determined via optical microscopy.

RESULTS AND DISCUSSION

The dependence of diamond growth rate in high power-density microwave plasmas at 500°C and 900°C substrate temperatures on the concentration of methane is shown in Fig. 4. At these substrate temperatures, diamond growth rates increase with the concentration of methane. The higher substrate temperature results in a higher growth rate. Graphite instead of diamond was usually deposited at substrate temperatures above 1200°C by a low power-density microwave plasma. By using a high power-density microwave plasma, diamond can grow at the substrate temperature of 1500°C with 1% methane diluted in hydrogen. As shown by curve (a) in Fig. 5, the growth rate increases with the substrate temperature up to 1200°C and starts to decrease when the substrate temperature exceeds 1200°C. One of the differences between a low power-density microwave plasma and a high power-density plasma is that a higher concentration of methane can be used for high power-density MPECVD of diamond. Also shown in Fig. 5 is the growth rate for 16% methane in hydrogen. The growth rate of diamond increased

monotonically with increasing substrate temperature up to around 1500°C in a high concentration methane/hydrogen, high power-density microwave plasma.

The surface morphology of diamond films deposited at 150 Torr and 900°C with different concentrations of methane are shown in Fig. 6. Fig. 7 shows the corresponding Raman shifts. Clear crystal facets are shown even with 50% methane diluted in hydrogen. At 80% concentration of methane in hydrogen, (Fig. 6(e)), crystal facets are not so clear but the Raman shift (Fig. 7(e)) identifies the existence of diamond. With 100% methane, ball-like deposits are formed (Fig. 6(f)) and a tiny diamond feature is found in the Raman spectrum (Fig. 7(f)). At a 16% concentration of methane diluted by hydrogen and 100 to 150 Torr gas pressures, surface morphology and Raman spectra of deposits at different substrate temperatures are shown in Fig. 8 and Fig. 9, respectively. Diamond films grown at high rates have been obtained in 16% methane/hydrogen plasma. The sharp peak of the diamond feature appears in Fig. 9 (a)-(c). The diamond feature is still distinguishable for deposits made at 1450°C, but not for deposits made above 1500°C. Only non-diamond features are observed when substrate temperatures are greater than 1500°C. The growth rates are as high as 50 μm/h (Fig. 5(b)) at a substrate temperature of 1500°C.

The challenge in the use of a high concentration of methane in the gas mixture for achieving high diamond growth rate is how to maintain the quality of the diamond. A combination of high concentration of methane and high power-density plasma with small oxygen additive may provide a solution for achieving this goal.

It has been reported that the addition of oxygen to a methane/hydrogen plasma [8,9,10] can affect the diamond growth by (1) enhancing the growth rate of diamond films, (2) improving the quality of diamond films, and (3) expanding the parameter space allowed for diamond deposition. Some of the reported growth rates are in the order of tens of μm per hour. Under similar conditions, by adding oxygen to the gas mixtures, the pressure and temperature regions suitable for diamond formation have been extended [11]. Results contrary to previously mentioned ones have also been reported, such as: no

observation in the enhancement of growth rate of diamond or a prolonged deposition time in the presence of oxygen.

In this study, CVD diamond deposited in the presence of oxygen in the reactant gases was obtained at temperatures as high as 1620°C. The deposition rate was examined as a function of substrate temperature between 900°C and 1600°C. Fig. 5(c) shows the growth rate versus substrate temperature. For comparison, the results from 1% and 16% methane/hydrogen plasma without the addition of oxygen to the gas mixture are also shown in Fig. 5(a) and (b), respectively. The growth rates obtained with oxygen additive are lower than those without the addition of oxygen.

We also investigated the dependence of the diamond growth rate on the concentration of oxygen additive and the deposition temperature. Oxygen of 1.6%, 2.4%, and 3.2%, respectively, was added to the methane and hydrogen mixture in this study. With a 1.6% O_2 additive, good quality diamond films were deposited at a rate up to 30 μm/h at 1420°C. The growth rate for 3.2% oxygen additive was about 50% lower than that for 1.6% oxygen additive. The diamond growth rate on a newly polished, unseeded Mo surface with methane not being fed into the reactor until the substrate had been heated by the oxygen/hydrogen plsama to the desired deposition temperature was close to 30 μm/h at deposition temperatures ranging from 1300°C to 1550°C.

When the deposition started with all reactant gases (methane, oxygen, and hydrogen) fed simultaneously into the chamber at the beginning of the process at a substrate temperature exceeding 1530°C, no clear crystal facets could be found on the deposit no matter the substrate was seeded with diamond or not. The resulting deposits were black in color, soft, and could easily be wiped away using a sandpaper. Clear (100) and (111) crystal facets on diamond deposition at temperatures exceeding 1530°C were found only when the reactant gases were not fed into the reactor simultaneously. This was done by either adding oxygen and methane to the hydrogen plasma or adding methane to the oxygen/hydrogen plasma after the plasma had been started for about 10 minutes and

the desired deposition temperature had been reached. The gas feed sequence has apparently affected the initial nucleation phase which subsequently led to different carbon deposition.

At substrate temperatures exceeding 1600°C, only individual diamond particles or island-like noncontinuous films formed on Mo substrates. Diamond crystals could be deposited at substrate temperatures as high as 1620°C when the Mo substrate was exposed to an oxygen/hydrogen plasma for more than 10-25 minutes followed by the addition of methane to the plasma. Fig. 10 shows some diamond crystals grown at such conditions. The growth rate was as high as 50 μm/h according to the grain size. Fig. 11 shows diamond films deposited at 1550°C at pressures around 130 Torr with methane added to the oxygen/hydrogen plasma after the substrate has been heated to the deposition temperature.

An intense first order Raman peak for diamond at 1332 cm^{-1} was observed on the growth side of the films while two broad bands centered at around 1350 and 1580 cm^{-1} in Raman shifts were observed on most of the substrate side of the deposited films and in some grain boundaries. Fig. 12 shows the Raman shifts of samples deposited through three different gas feed processes. The deposition temperature was around 1550°C. Curve (a) in Fig. 12 is for the film deposited when all the reactant gases were fed into the reactor at the same time at the beginning. Curve (b) is for the film deposited when O_2 was added later to the CH_4/H_2 plasma and curve (c) is for the film deposited when CH_4 was added later to the O_2/H_2 plasma. Curves (b) and (c) show the characteristics of diamond while curve (a) does not show such a feature. The Raman shifts for the substrate side of deposits are shown in Fig. 13. When methane was added in a later stage to the oxygen/hydrogen plasma, the substrate side had a better quality of deposition than that corresponding to the other two gas feed sequences.

Microwave power density is the one of the most important process parameters for the high growth-rate diamond deposition. The percentage of the dissociated hydrogen

increases with the microwave power density of the plasma. It is believed that with atomic hydrogen sufficiently supplied in a high power-density plasma, the effects of atomic hydrogen on promoting diamond growth are greatly enhanced and, therefore, high growth-rate diamond deposition becomes possible. High microwave power density generates much more atomic hydrogen than what would exist in a typical low power-density MPECVD process making it possible for diamond deposition at high substrate temperatures and with high methane concentrations.

When mapping the data points for gas mixtures with the concentrations of 16%, 50%, and 80% methane diluted in hydrogen (H/(H+C) =0.935, 0.86 and 0.818) respectively, they are located on the C-H side of the C-H-O diagram as shown in Fig. 2. Fig. 2 is the enlarged section of the H corner. As pointed out by Bachmann et al., the "diamond growth" region is not a true triangle. The short sideline covers most of the region with less than 5% methane in hydrogen commonly used in low power-density PECVD. Apparently, points for 16%, 50%, and 80% methane in hydrogen are located in the "non-diamond growth" region." However, as stated before, diamond films were successfully deposited by using more than 16% methane in hydrogen. The apparent value of H/(H+C) or C/H ratio calculated from the gas feed is not the accurate determining factor. It is the actual ratio of atomic hydrogen to (H+C) that determines the deposition process. The influence by the addition of oxygen, the substrate temperature, the power density of the plasma, and the total gas flow rate on diamond deposition has been discussed. Results from this study show that: (1) diamond can grow in the "non-diamond growth" region" in the original C-H-O diagram shown in Fig. 1; and (2) diamond grows at temperatures above 1300°C. The "diamond growth" region shown in Fig, 1, should have its upper border pushed upwards into the "non-diamond growth" region when a high microwave power density is applied. The observed upper limit in the substrate temperatures for diamond growth appears to be the consequene of poor diamond

nucleation on foreign substrates at high temperatures. Homoepitaxial growth of diamond may allow even higher substrate temperatures than what is reported in this work.

SUMMARY

The high growth rate of diamond deposition is mainly due to the high power density used for deposition. A high concentration of atomic hydrogen plays important roles in the nucleation and growth of diamond.

When methane and hydrogen are the only reactant gases and the substrate temperature is higher than 1450°C, graphitic deposits are obtained. With the addition of a small amount of oxygen, diamond films deposited at temperatures higher than 1450°C at high rates (30μm/h) were obtained. Diamond grows well at temperatures exceeding 1600°C, forming smooth (100) surfaces. Obviously, the existence of oxygen in the gas mixture makes high temperature diamond deposition more favorable. The deposition characteristics at substrate temperatures above 1600°C depend on the sequence in which the reactant gases are introduced. By feeding gases in a proper sequence, well faceted diamond was deposited on Mo at substrate temperatures as high as 1620°C. However, at substrate temperatures exceeding 1600°C, individual diamond particles or island-structured noncontinuous films rather than continuous films tend to be formed on Mo substrates, due to a low nucleation density on Mo substrates. To obtain continuous diamond film on foreign substrates at temperatures exceeding 1600°C, we may use a two-step process. In the first step, high nucleation density at a low or medium substrate temperature is achieved. The second step is to grow diamond at a high growth rate using a high substrate temperature. A small amount of oxygen also assists in growing high quality CVD diamonds in a methane/hydrogen plasma. Diamond growth rate decreases if more than 2% of oxygen additive is included in the feed gases under our experimental conditions.

REFERENCES

[1] J.J. Lander and J. Morrison, Surf. Sci. 4, 241 (1966).

[2] J.C. Angus, in Proc. of 1st International Sym. on Diamond and Diamond-like Films, Edit. by J.P. Dismukes, et al. P. 1 (1989).

[3] N. Fujimori and A. Hara, in Proc. of 1st International Sym. on Diamond and Diamond- like Films, Edit. by J.P. Dismukes, et al. P. 1 (1989).

[4] H.Shiomi, Y.Nishibayashi, H.Nakahata, T.Imai and N. Fujimori, Proc. of 36th Meeting of Sco. of Jpn. Appl. Phys., 458 (1989).

[5] P.K. Bachmann, D. Leers, and H. Lydtin, Diamond and Related Materials, Vol. 1, pp. 1 (1991).

[6] H.J.Hibshman, U.S. Patent 3371996 (1968), filed 1964.

[7] Y. Saito, K. Sato, K. Gomi, and H. Miyadera, J. Mater. Sci. Vol. 25, pp. 1246 (1990).

[8] Y. Saito, K. Sato, H. Tanaka, K. Fujita, and S. Matuda, J. Mater. Sci., 23, 842 (1988).

[9] Y. Hirose and Y. Terasawa, Jpn. J. Appl. Phys., 25, L519 (1986).

[10] Y. Liou, A.Inspektor, R.Weimer, D. Knight, and R.Messier, J. Mater. Res., 5, 2305 (1990).

[11] T. Kawato and Ken-ichi Kondo Jpn. J. Appl. Phys., Vol. 26, pp. 1429 (1987).

TABLE I. Parameters used in typical MPECVD and this study

	Typical	This study
Pressure	few Torrs to tens of Torr	up to 150 Torr
CH_4 (vol. %)	< 6%	1-100%
Temperature	<1000^{0}C	up to 1620^{0}C
Microwave power density	low	high
Growth rate	few μm/h	tens of μm/h

FIGURE CAPTIONS

Figure 1. C-H-O diamond deposition phase diagram.

Figure 2. Locations for hydrocarbons near the enlarged hydrogen-rich corner in C-H-O diagram.

Figure 3. Schematic diagram of MPECVD system used in this study.

Figure 4. Growth rate versus CH_4 concentration at temperatures of (a) 500^0C and (b) 900^0C.

Figure 5. Growth rate versus substrate temperature in (a) 1% and (b) 16% CH_4 in H_2, and (c) 16% CH_4 + 1.6% O_2 in H_2.

Figure 6. SEM photographs of diamond films grown from different concentrations of methane at 900^0C and 150 Torr.

Figure 7. Raman spectra of diamond films grown from different concentrations of methane at 900^0C and 150 Torr.

Figure 8. SEM photographs of diamond films grown at different temperatures in 16% methane/hydrogen plasmas at pressures between 100 and 150 Torr.

Figure 9. Raman spectra of diamond films grown at different temperatures in 16% methane/hydrogen plasmas at pressures between 100 and 150 Torr.

Figure 10. Diamond grown at substrate temperatures of 1600^0C and higher: (a) CH_4 was added to O_2/H_2 plasma after substrate had been heated to 1600^0C for 5 minutes, and (b) CH_4 was added to O_2/H_2 plasma after the substrate had been heated to 1600^0C for 20 minutes.

Figure 11. Diamond films deposited at 1550^0C at around 130 Torr. 16% CH_4 was added to the oxygen/hydrogen plasma after the substrate had been heated to the deposition

14

temperature.

Figure 12. Raman spectra for diamond films (growth side) deposited using different gas feed processes: (a) All gases were fed into the reactor simultaneously, (b) O_2 was later added to the CH_4/H_2 plasma, and (c) CH_4 was later added to the O_2/H_2 plasma. The substrate temperature was 1550^0 C and the pressure was around 130 Torr.

Figure 13. Raman spectra for diamond films (substrate side) deposited using different gas feed processes: (a) All gases were fed into the reactor simultaneously, (b) O_2 was later added to the CH_4/H_2 plasma, and (c) CH_4 was later added to the O_2/H_2 plasma. The substrate temperature was 1550^0C and the pressure was around 130 Torr.

Fig. 1.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

100% CH₄ 0.8
80% CH₄

Non-diamond carbon
growth region

50% CH₄

0.9

Diamond growth region

16% CH₄

No growth region

H
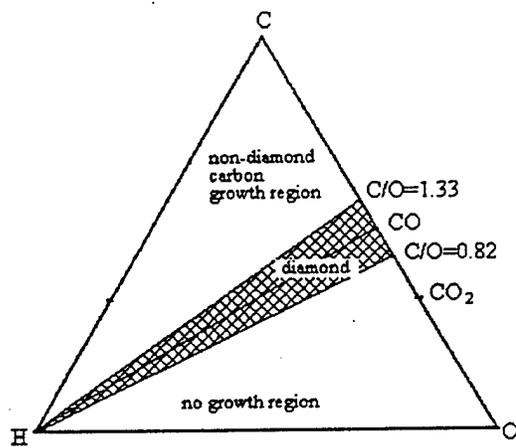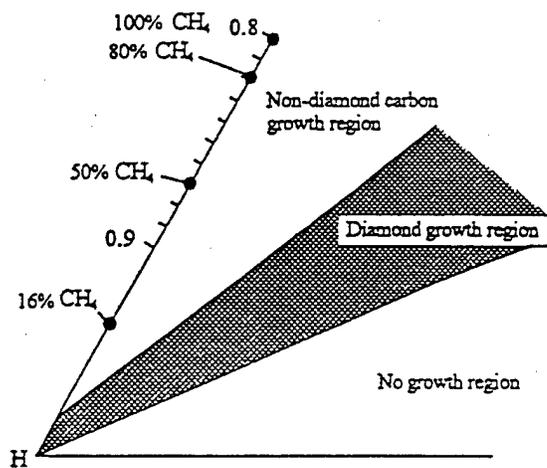
Fig. 2.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

Fig. 3.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(a) 500 °C — Growth rate (μm/h) vs CH₄ concentration (%)

(b) 900 °C — Growth rate (μm/h) vs CH₄ concentration (%)
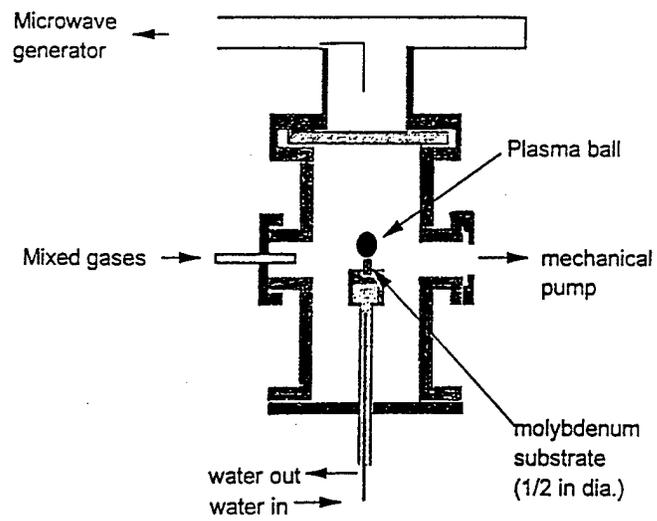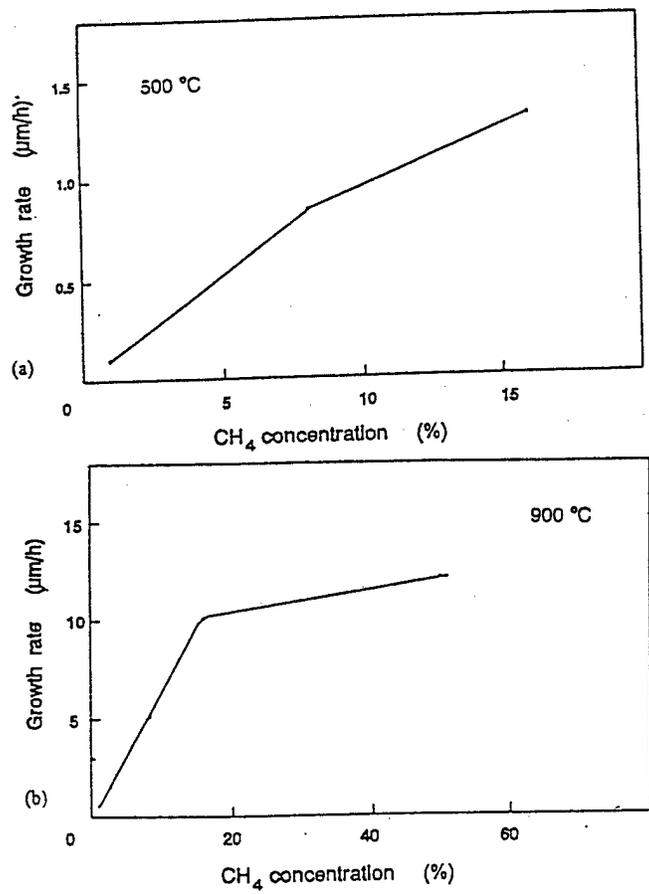
Fig. 4.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,
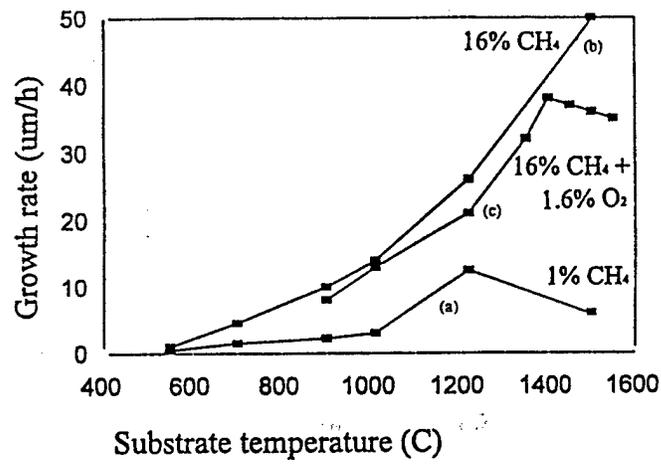
Fig. 5.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,
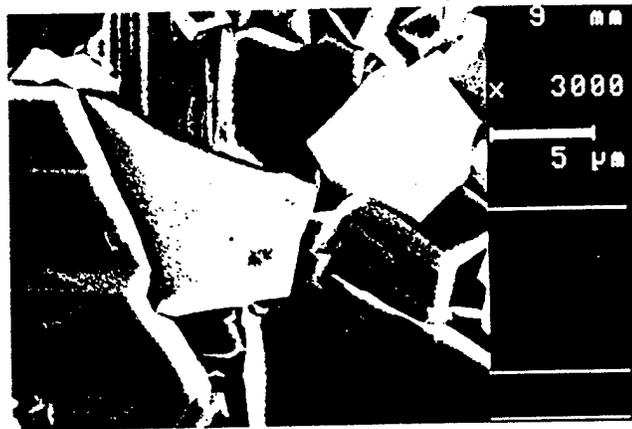
(a)   1% CH₄
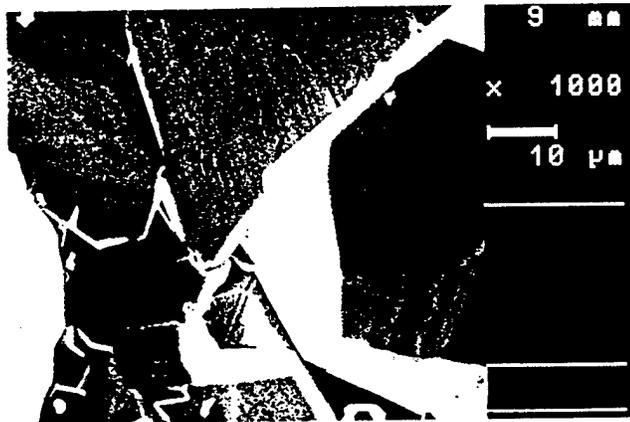
(b)   3% CH₄

(c)   16% CH₄

Fig. 6(a),(b),(c) Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,
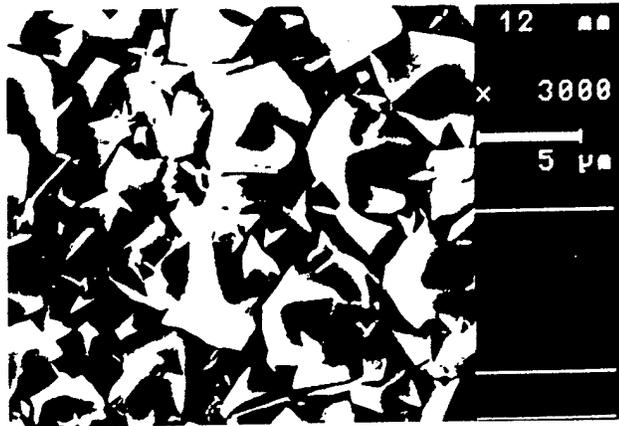
(d)　　50% CH$_4$

(e)　　80% CH$_4$

(f)　　100% CH$_4$

Fig. 6(d),(e),(f) Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(a)

(b)

(c)

Fig. 7 (a),(b),(c).   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(d)

50% CH₄ — Intensity (Counts) vs Raman Shift (cm⁻¹)

(e)

80% CH₄ — Intensity (Counts) vs Raman Shift (cm⁻¹)

(f)

100% CH₄ — Intensity (Counts) vs Raman Shift (cm⁻¹)
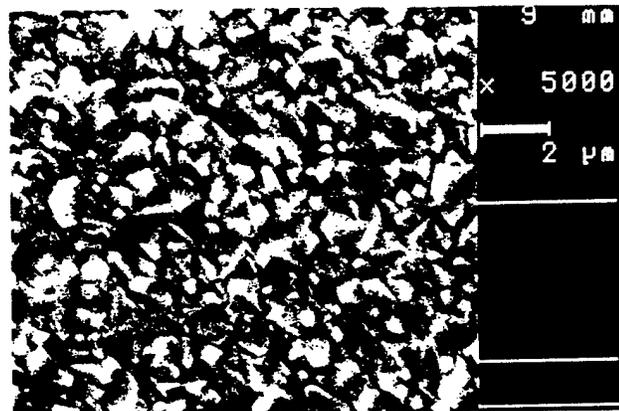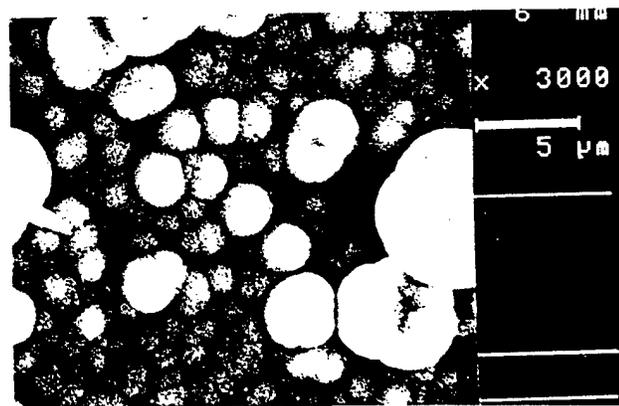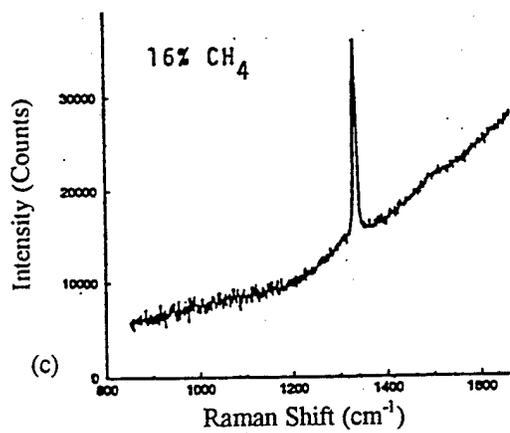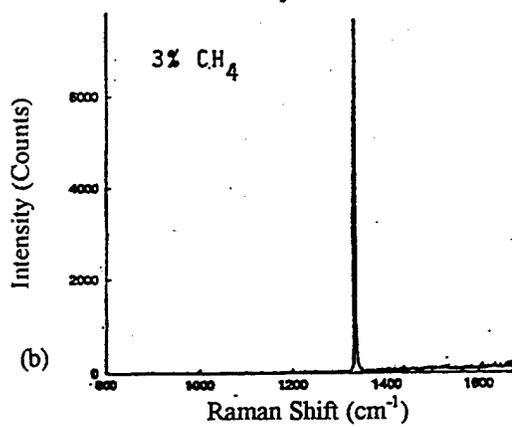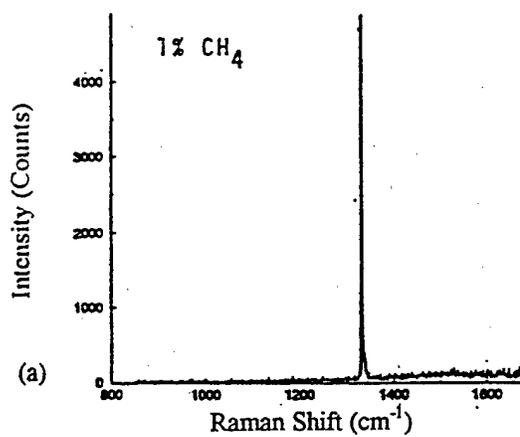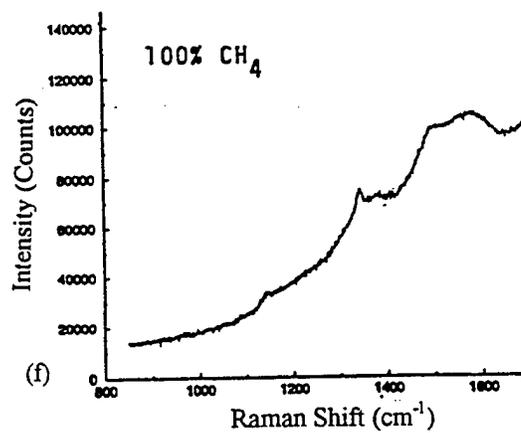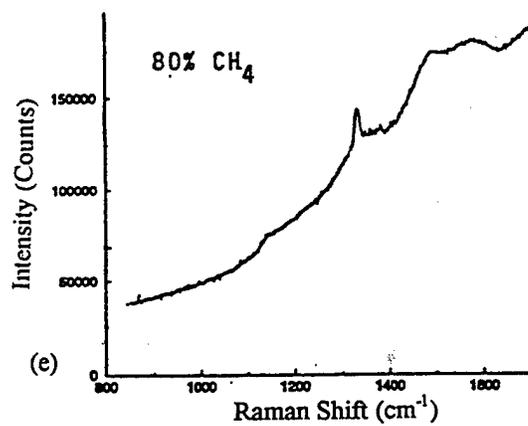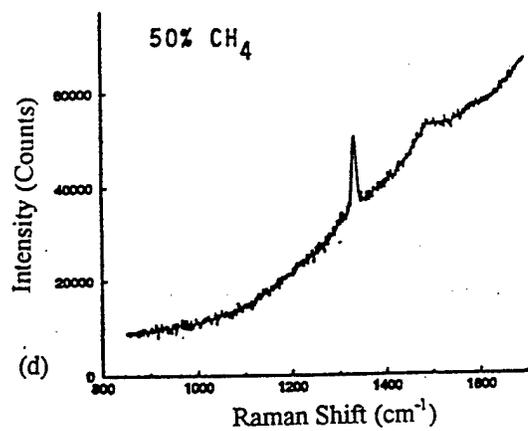
Fig. 7 (d),(e),(f).   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(a)   550⁰C

(b)   700⁰C
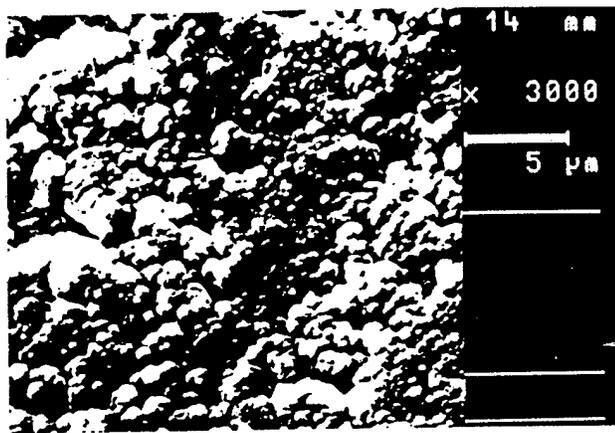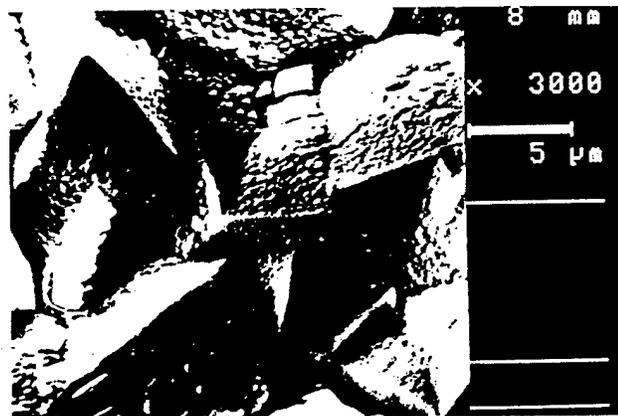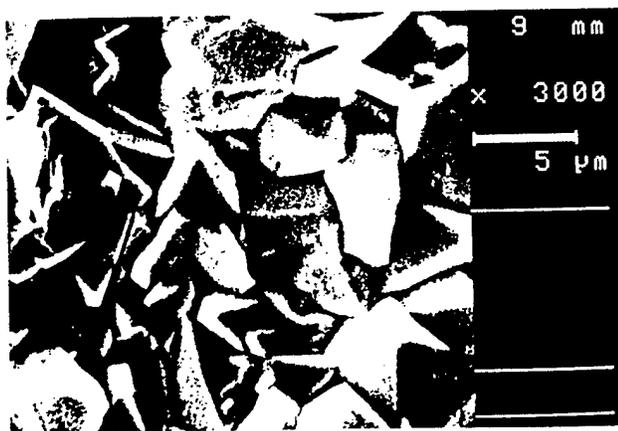
(c)   900⁰C

Fig. 8(a),(b),(c) Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(d)   1200⁰C

(e)   1450⁰C

(f)   1600⁰C

Fig. 8(d),(e),(f) Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,
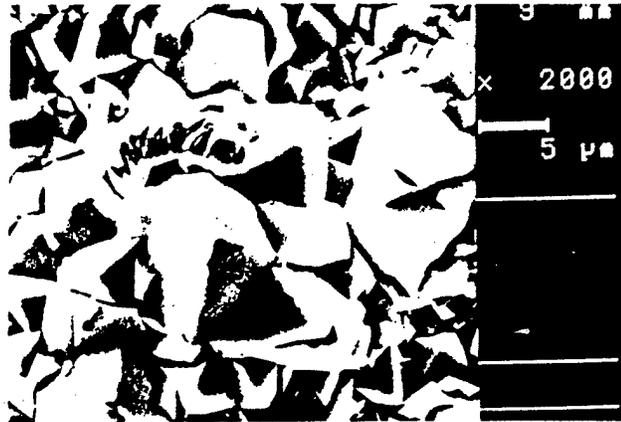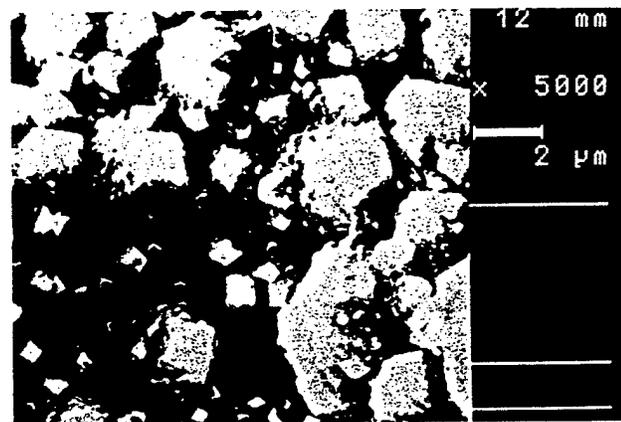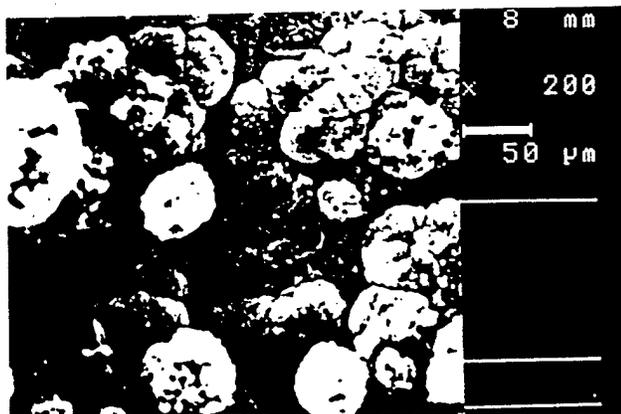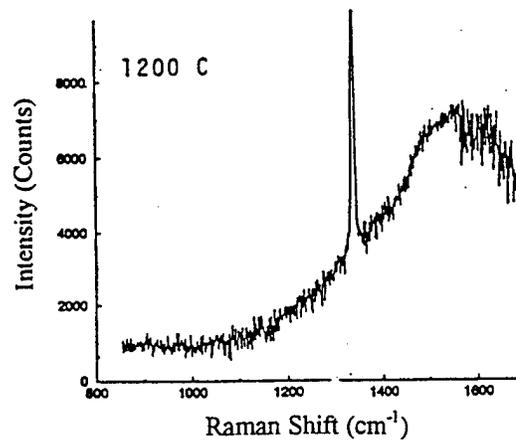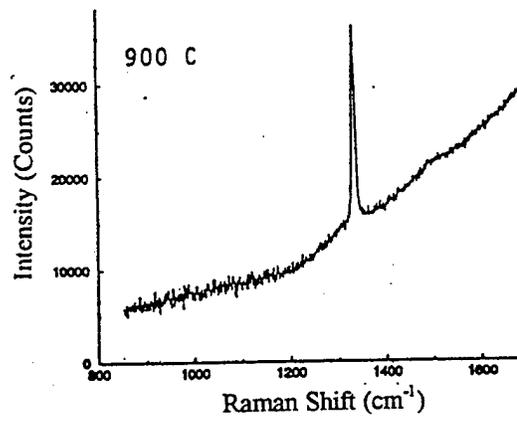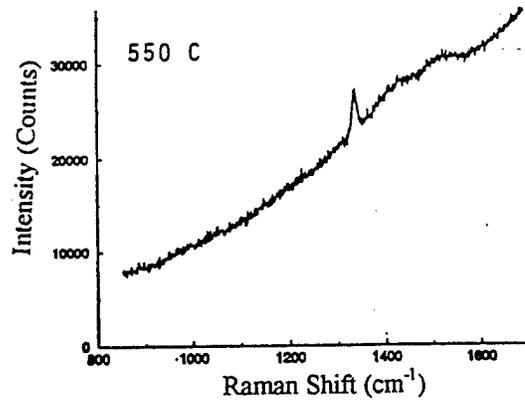
Fig. 9 (a),(b),(c).   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,
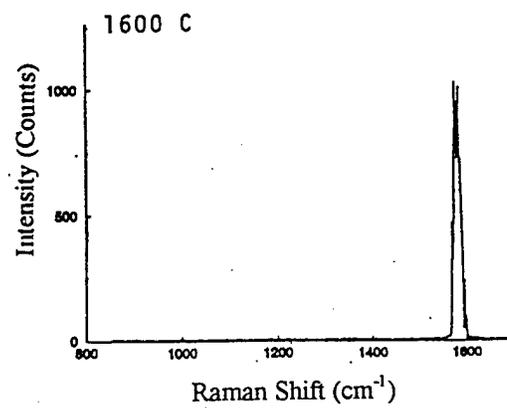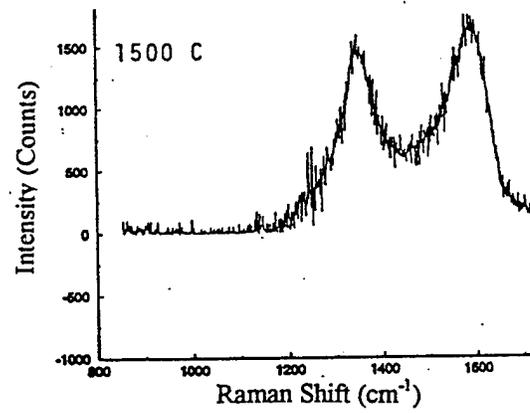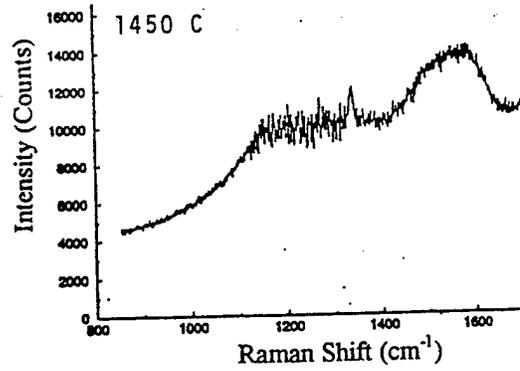
Fig. 9 (d),(e),(f).   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

(a)

20 µm
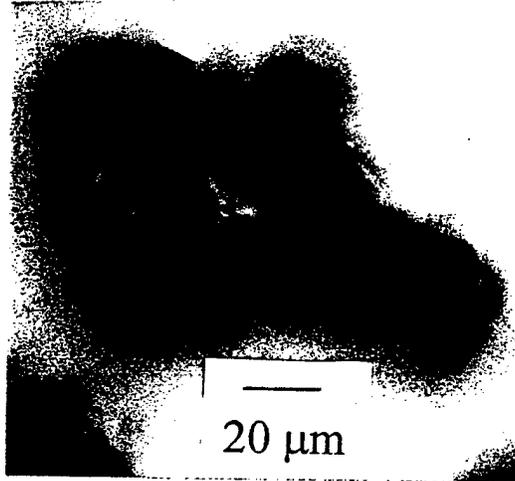
(b)

Fig. 10.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

Fig. 11.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

Intensity (A.U.)

(a)

(b)

(c)

800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800

Raman Shift (cm^{-1})

Fig. 12.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,

Intensity (A.U.)

(a)

(b)

(c)

300 900 1000 1100 1200 1300 1400 1500 1600 1700 1800

Raman Shift (cm^{-1})

Fig. 13.   Tsan-Heui Chein, Jin Wei, and Yonhua Tzeng,