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CVD Diamond Grown by Microwave Plasmas in Mixtures of Acetone/Oxygen and Acetone/Carbon Dioxide

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Diamond has been deposited on silicon and molybdenum substrates by microwave plasma enhanced chemical vapor deposition technique in acetone/oxygen and acetone/carbon dioxide mixtures. A narrow C/O ratio around 1:1 was found necessary for diamond to be deposited under our deposition conditions. Diamond of good quality was deposited at rates exceeding 25 $\mu\text{m/hr}$. By the use of high-power-density microwave plasmas, diamond deposition using these two mixtures has been achieved at substrate temperatures up to around 1300°C. A comparison between the diamond deposition process using these two mixtures without additional hydrogen gas and the traditional diamond deposition process using the mixture of methane and hydrogen will be discussed.

KEYWORDS: Acetone, oxygen, carbon dioxide, diamond deposition

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INTRODUCTION

The most popularly used gas mixtures for the chemical vapor deposition (CVD) of diamond are hydrocarbons diluted in hydrogen. In most cases, hydrogen is of a very high percentage in the gas mixture and the diluted hydrocarbon gas is the source of carbon. In this study, diamond deposition using binary gas mixtures of acetone/oxygen and acetone/carbon dioxide without hydrogen dilution is investigated.

The region for diamond growth is indicated in the C-H-O diagram presented by Bachmann et al. [1] between two lines. The first line connects the H corner with the point with $C/O=1.33$ (or $C/(C+O) \approx 0.57$) on the C-O sideline. The second line connects the H corner with the point with $C/O=0.82$ (or $C/(C+O) \approx 0.45$) on the C-O sideline. For gas mixtures with $C/O > 1.33$, non-diamond carbon (amorphous carbon, graphite, etc.) tends to grow. The "no growth" region has $C/O < 0.82$. Pure carbon monoxide, CO, is at the location with $C/O = 1$, which is the midpoint of the C-O sideline. Carbon dioxide, CO₂, is located at the point with $C/O=0.5$.

The location for acetone is determined by the intersection of two lines: the line connecting the O corner with C₂H₄, and the line connecting the C corner with the point with $O/(O+H)=1/7$, as shown in Figure 1. In using acetone and oxygen, the data points for the gas mixtures are located between the O corner and the data point corresponding to acetone on the line connecting the O corner with C₂H₄ as shown in Figure 2. Both the acetone/oxygen and the acetone/carbon dioxide lines pass through the diamond growth region in the acetone-rich part. The appropriate fractions of C, H, and O in a gas mixture is useful for selecting the least expensive, nonpoisonous, and nonpolluting gases for diamond deposition. Understanding the influence of the deposition conditions such as the deposition temperature, the power density of plasma, the concentrations of active gas feeds and the carrying gas, and the total gas pressure on the shape and location of the diamond growth zone is therefore desirable.

Acetone/oxygen and acetone/carbon dioxide are chosen as the source gas mixtures for diamond deposition because the cost for a high flow rate of hydrogen can be avoided. Unlike using dangerous gases such as carbon monoxide, there is less concern in poisonous or polluting issues when oxygen, carbon dioxide, and acetone are used.

EXPERIMENTAL SETUP AND PROCEDURE

Diamond films were deposited by microwave plasma enhanced chemical vapor deposition (MPECVD). The schematic diagram of the microwave plasma CVD system used for this study is shown in Figure 3. An industrial 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 in. thick was used to separate the reactor from the waveguide. Ports on the reactor were used for gas inlets, the exhaust port, and viewing windows. Reactant gases used in this study were acetone, oxygen, and carbon dioxide. Electronic mass flow controllers were used to control the gas flow rates. A mechanical pump was used to pump down the reactor before any gas was fed into the chamber and to maintain the total pressure at a desired value. The deposition temperature was monitored by aiming an optical pyrometer at the surface of the substrate through one of the viewing windows.

Molybdenum (9mm in diameter, 2 mm thick) and silicon (7 x 7 mm, cut from 3" diameter silicon wafer) were used as substrates without diamond seeding. The substrate holder was water-cooled and heated by the microwave plasma alone during the process. By varying the microwave power, the temperature of the substrate was controllable between 600 and 1400°C.

When acetone and oxygen were used, acetone was the carbon source. The C/O ratio studied was in the range of 0.89-1.5. The flow rate for oxygen was between 4 sccm and 7 sccm. For acetone, flow rates from 4 sccm up to 8.4 sccm were studied. Microwave

power in the range of 300 to 1300W was used. The total gas pressure in the reactor was in the range of 30 ~ 120 Torr.

In the case of acetone and carbon dioxide mixtures, the ratio of C/O ratio studied was in the range of 0.93~1.64. The flow rate for acetone was between 3 sccm and 12 sccm. For carbon dioxide, the flow rate was between 3.7 sccm and 15.3 sccm.

DIAMOND FILMS GROWN FROM ACETONE/OXYGEN PLASMAS

For C/O ratios in the range of 0.89-1.28, the ratio of C/O=1.03 leads to a broader parameter space for diamond growth. At gas pressures around 35 Torr, the quality of the deposit depends significantly on the substrate temperature. At C/O=1.03, and gas pressure less than 40 Torr, diamond was obtained at temperatures up to 1200°C, but not at 1350°C. Diamond films of better quality were obtained at higher total gas pressures and higher plasma power densities. Figure 4 shows the SEM photographs of deposits at 1050 °C, 1235°C, and 1350°C substrate temperatures for a total gas pressure in the range from 80 Torr to 120 Torr. Continuous diamond films can be deposited within 20 minutes at a rate of greater than 24 $\mu\text{m/h}$.

For a higher ratio of C/O=1.11 (acetone: 8.4sccm, oxygen:7sccm) and a gas pressure of 90 Torr, cauliflower-like deposit was obtained at 1100°C. For substrate temperatures higher than 1200°C, only graphite was obtained.

Inside the reactor, the size of the plasma ball changes with the microwave power and the gas pressure. At the same microwave power input, higher pressures would reduce the size of the plasma ball and thus increase the power density. Figure 5 shows the growth rate versus deposition temperature at two different gas pressures for the C/O ratio of 1.03. The figure shows that the rate of change of growth rate versus substrate temperature is higher at a higher pressure. Figure 6 shows the relationship between the growth rate and the microwave power. As indicated by the curve, higher microwave power leads to higher growth rates.

Figure 7 shows the Raman spectra of carbon films deposited from acetone/oxygen plasmas at 970°C substrate temperature in C/O ratio of 1.03, 1.08, and 1.11. The gas pressures were between 30 and 55 Torr. The surface morphologies of these deposits were shown in Figure 8. As both figures show, at this deposition temperature, diamond films were obtained when C/O=1.03 and C/O=1.08.

Figure 9 and 10 show the deposits obtained from a fixed C/O ratio of 1.03 under a low power density condition at different substrate temperatures ranging from 1000 to 1350°C. With a low power density, diamond grows at temperatures up to 1200°C. When higher pressures were used, the size of the plasma ball decreased. The result was the increase in power density of the plasma. Diamond films deposited from high power density at C/O=1.03 were shown in Figure 11 and Figure 12. Compared to what is deposited at a low power-density, diamond grows better at high substrate temperatures when a higher power-density plasma is applied.

DIAMOND FILMS GROWN IN ACETONE/CARBON DIOXIDE PLASMAS

It was found that the parameter range for diamond deposition from acetone/carbon dioxide was narrower than that for acetone/oxygen. From the C-H-O diagram, CO₂ is located at C/O=0.5 on the C-O sideline and acetone is inside the C-H-O triangle. The line connecting acetone and CO₂ crosses the diamond domain with the ratio of acetone/CO₂ in the range of 0.21~1.146. However, it is found that a molar ratio of acetone/CO₂=0.5~0.93 is needed for diamond growth. In terms of the ratio of C/O, the range is from 1 to 1.4. When the C/O ratio is below 1, no growth was obtained. Soot and fiber-like deposit were formed for C/O greater than 1.4. At the ratio of C/O=1.4, substrate temperature of 1030-1130°C, and pressure at 46 Torr, graphitic fibers longer than 10µm were found on the deposit. Although a gas mixture with a C/O ratio in the range of 1~1.295 may have diamond growth on the substrate, the growth conditions are very restrictive. At the ratio

of $C/O=1$, the process parameter range for diamond growth is the broadest. Figure 13 shows SEM photographs for films deposited with $C/O=1$ at 720°C, 42 Torr, and 1200°C, 57 Torr.

Raman spectra of diamond films deposited from acetone/carbon dioxide plasma at $C/O=1$ at a low power density, and substrate temperature of 720, 880, 980, and 1080°C were shown in Figure 14. The temperature range for diamond growth is from 720°C up to around 1100°C. When gas mixtures of the same C/O ratio of unity were used in a high power-density environment, the diamond growth region ranged from 840°C to 1200°C, as shown in Figure 15 and 16. Figure 17 shows the pressure and substrate temperature range in which diamond has been deposited using acetone and carbon dioxide as the feed gas with $C/O=1$. Under similar conditions (substrate temperature and pressure), but with a different ratio of $C/O=1.2$, no diamond was deposited.

SUMMARY AND CONCLUSION

High quality diamond grows more easily from acetone/oxygen than from acetone/carbon dioxide. The gas mixtures comprising of acetone and oxygen have a broader process parameter range for CVD diamond than that provided by acetone and carbon dioxide. The growth rates from acetone/oxygen or acetone/carbon dioxide do not show much difference and can be 25 $\mu\text{m/h}$ or higher. While using acetone/oxygen for diamond deposition, we have found that the diamond growth domain is quite broad. However, when gas mixtures consisting of carbon dioxide were used, tighter control over the ratio of acetone to carbon dioxide is necessary. If the C/O ratio in acetone/carbon dioxide is not well controlled, soot and graphitic fibers can form on the substrate at a rate greater than 25 $\mu\text{m/h}$. Good quality diamond growth has been observed for atomic ratio of $C/O < 1.1$. Beyond the atomic ratio of $C/O > 1.2$, diamond deposition is still possible but the growth conditions are quite restrictive.

Diamond deposition using acetone/oxygen or acetone/carbon dioxide differs from that using hydrogen/hydrocarbon mixtures primarily in the roles played by atomic hydrogen. In acetone/oxygen and acetone/carbon dioxide plasmas, the source of atomic hydrogen is from the dissociation of acetone alone. Without atomic hydrogen dissociated from molecular hydrogen and the smaller amount of atomic hydrogen from acetone, other radicals may share the roles of atomic hydrogen. Oxygen in the plasma may lead to the formation of OH radical as well as atomic oxygen. The existence of atomic oxygen and OH radical are important in growing diamond films from both the acetone/oxygen and acetone/carbon dioxide plasmas. From the results of Raman spectra and SEM photographs of the diamond films obtained in this study, it is likely that atomic oxygen preferentially etch non-diamond carbon components effectively. The growth rate of diamond from acetone/oxygen plasma is slightly higher than that from acetone/carbon dioxide plasma. This may be attributed to more atomic oxygen in the acetone/oxygen plasma than that in the acetone/carbon dioxide plasma. In high power density plasma, a growth rate of more than 10 $\mu\text{m/h}$ was achieved at temperatures higher than 1300⁰C by using acetone/oxygen. This was not obtained from the acetone/carbon dioxide plasma. The best C/O ratio for diamond deposition is close to unity. Although acetone-carbon dioxide line crosses over the "diamond growth" region wider than acetone-oxygen line does, it appears that a tighter control is needed when acetone/carbon dioxide is used. Generally speaking, the boundaries for diamond domain change from one deposition condition to another. The acetone/oxygen and acetone/carbon dioxide have been proven as effective gas mixtures for CVD of diamond. Without the need of a high flow rate of hydrogen, the cost for diamond production may be reduced without much sacrifice of the quality of the diamond film and the deposition rate.

REFERENCE

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

FIGURE CAPTIONS

Figure 1. C-H-O phase diagram and location of acetone.

Figure 2. Lines of acetone/oxygen and acetone/carbon dioxide in the C-H-O diagram.

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

Figure 4. SEM photographs for diamond films deposited from acetone/oxygen at C/O=1.03 under (a) 1050°C, 100 Torr, (b) 1235°C, 120 Torr, and (c) 1345°C, 80 Torr.

Figure 5. Growth rate of diamond films versus deposition temperature at two gas pressures: 63 Torr and 82 Torr.

Figure 6. Growth rate of diamond films versus net microwave power from acetone/oxygen plasma at C/O=1.03.

Figure 7. Raman spectra of diamond films deposited from acetone/oxygen plasmas at 970°C substrate temperature in C/O ratio of (a) 1.03, (b) 1.08, and (c) 1.11.

Figure 8. Surface morphology of carbon films deposited from acetone/oxygen plasma at 970°C substrate temperature in C/O ratio of (a) 1.03, (b) 1.08, and (c) 1.11.

Figure 9. Raman spectra of diamond films deposited from acetone/oxygen plasma at C/O=1.03 and substrate temperature of (a) 1000°C, (b) 1200°C, and (c) 1350°C.

Figure 10. Surface morphology of diamond films deposited from acetone/oxygen plasma at C/O=1.03 and substrate temperature of (a) 1000°C, (b) 1200°C, and (c) 1350°C.

Figure 11. Raman spectra of diamond films deposited from acetone/oxygen plasma at C/O=1.03 and substrate temperature of (a) 1050°C, (b) 1250°C, and (c) 1350°C.

Figure 12. Surface morphology of diamond films deposited from acetone/oxygen plasma at C/O=1.03 and substrate temperature of (a) 1050°C, (b) 1250°C, and (c) 1350°C.

Figure 13. SEM photographs for diamond films deposited from acetone/carbon dioxide at C/O=1.0 and (a) 720°C, 42 Torr, and (b) 1200°C, 57 Torr.

Figure 14. Raman spectra of diamond films deposited from acetone/carbon dioxide plasma at C/O=1 and substrate temperature of (a) 720°C, (b) 880°C, (c) 980°C, and (d) 1080°C.

Figure 15. Raman spectra of diamond films deposited from acetone/carbon dioxide plasma at C/O=1 and substrate temperature of (a) 840°C, (b) 930°C, (c) 1100°C, and (d) 1200°C.

Figure 16. Surface morphology of diamond films deposited from acetone/carbon dioxide plasma at C/O=1 and substrate temperature of (a) 840°C, (b) 930°C, (c) 1100°C, and (d) 1200°C.

Figure 17. Diamond domain in P-T space for deposition in acetone/carbon dioxide plasma at C/O=1.0.

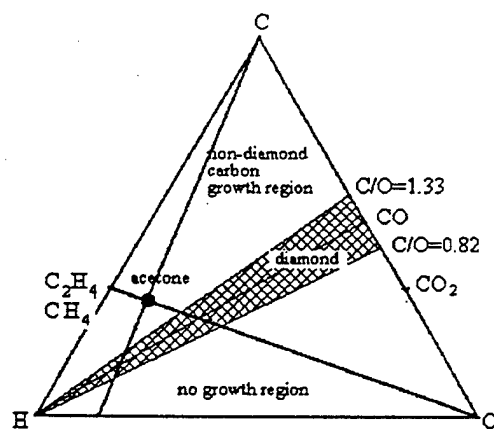


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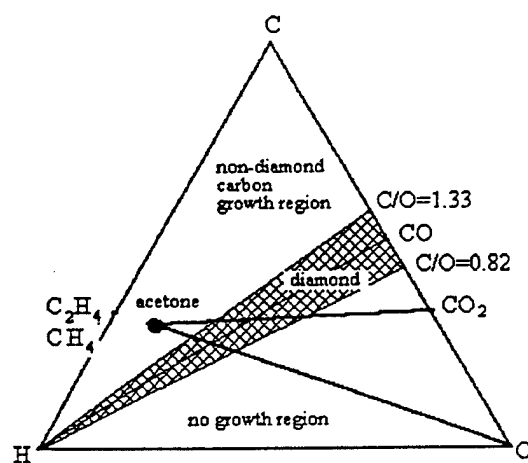


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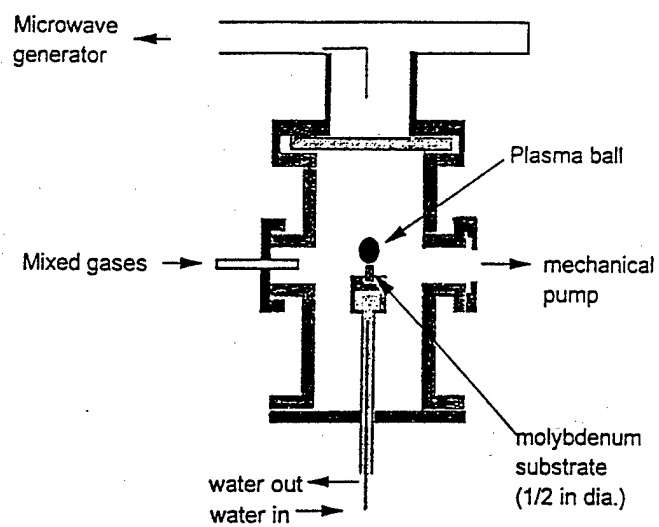


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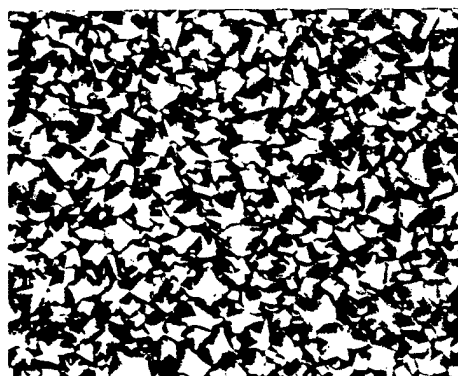
(a)

10 μm



(b)

10 μm



(c)

Fig. 4

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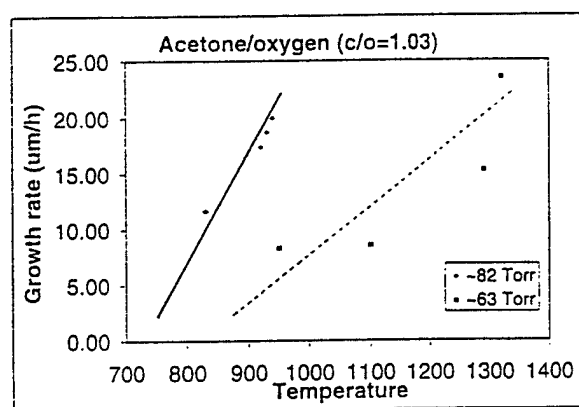


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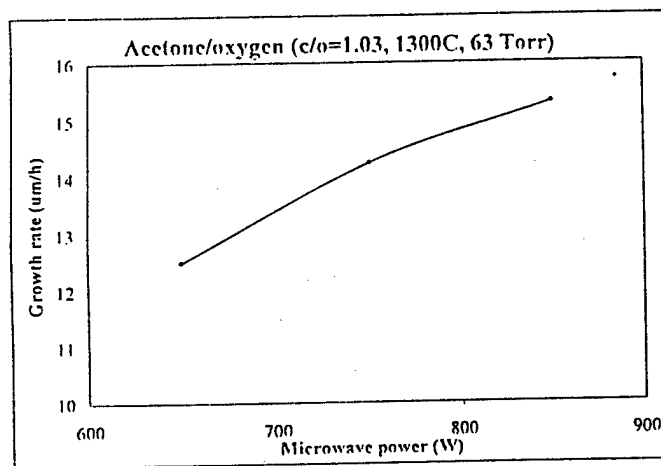


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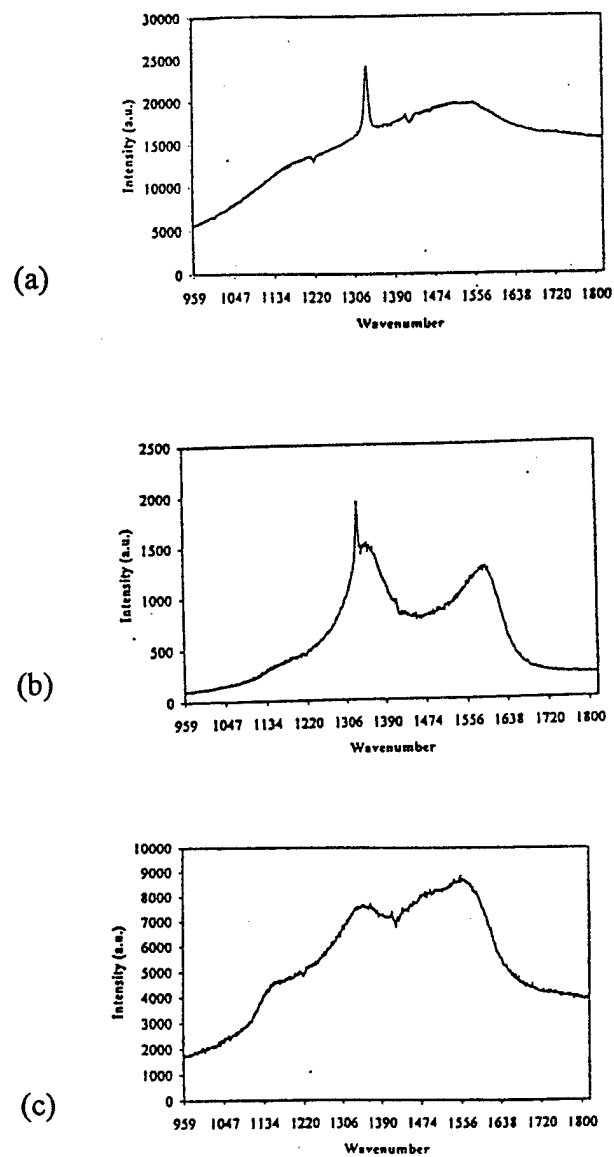


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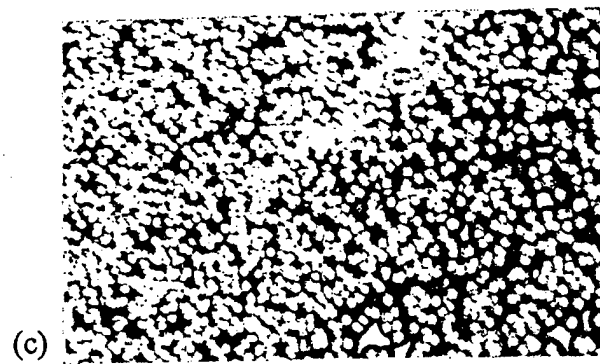
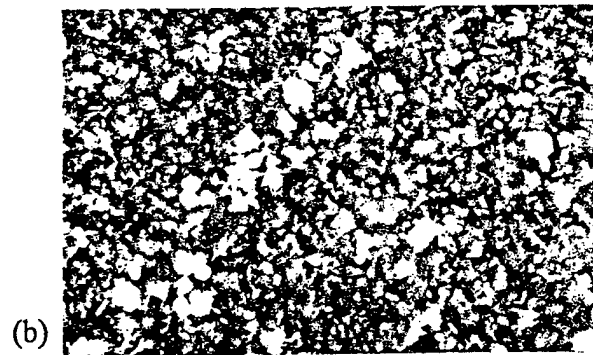
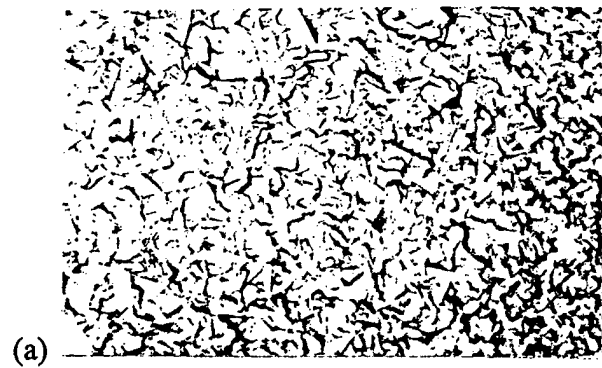
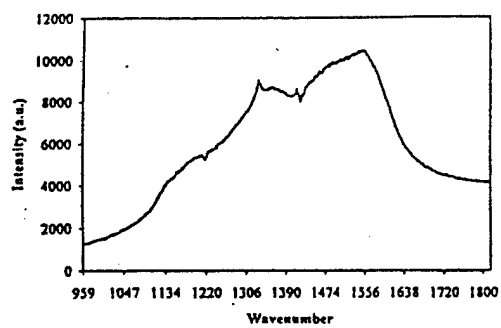
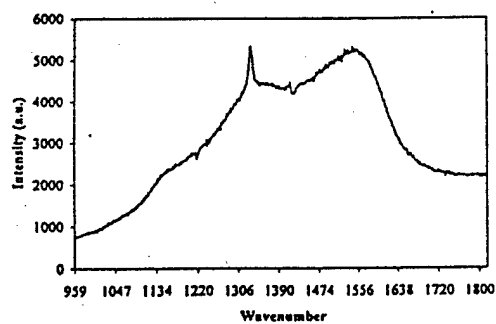


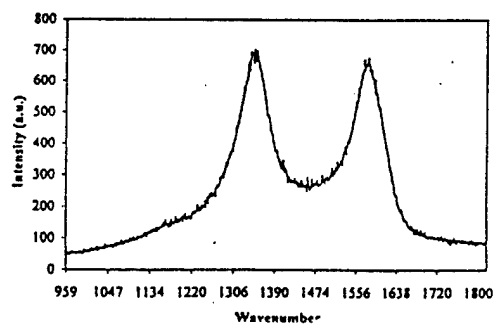
Fig. 8. Tsan-Heui Chein and Yonhua Tzeng,



(a)



(b)



(c)

Fig. 9. Tsan-Heui Chein and Yonhua Tzeng,

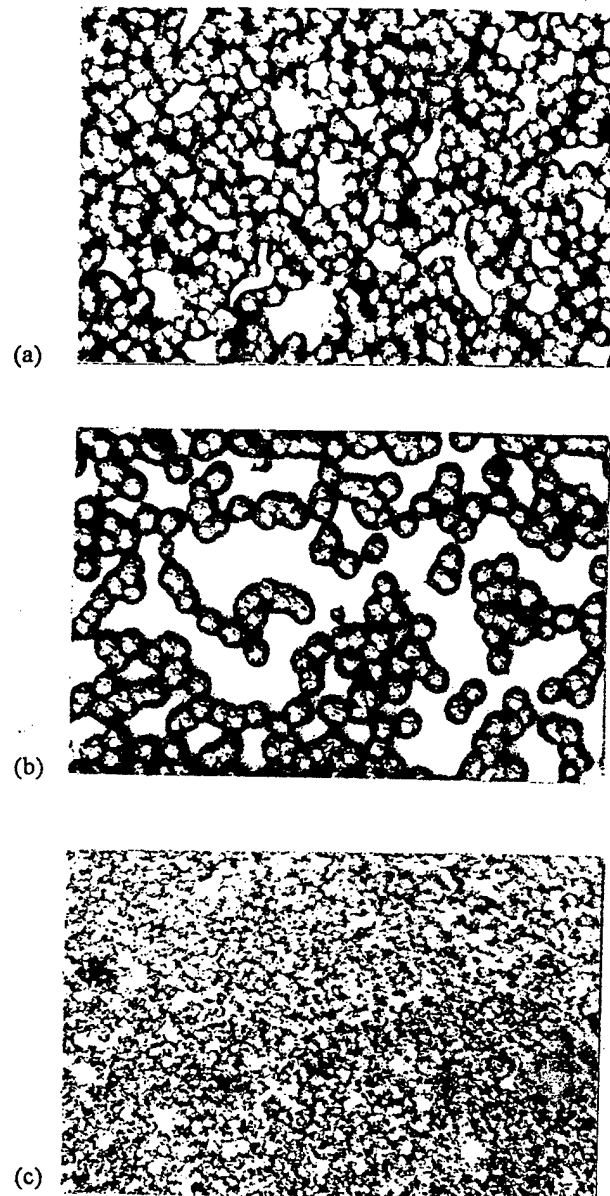


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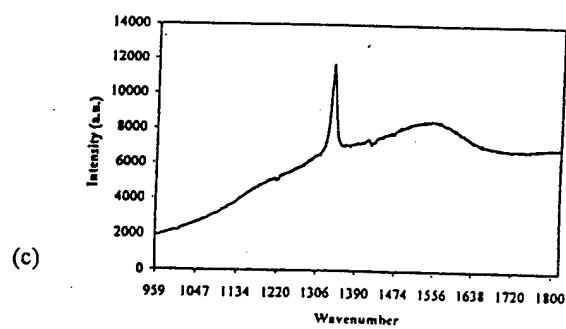
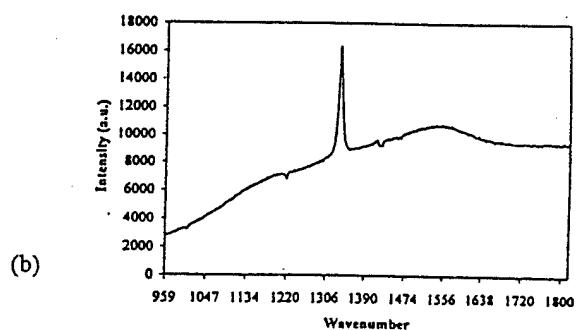
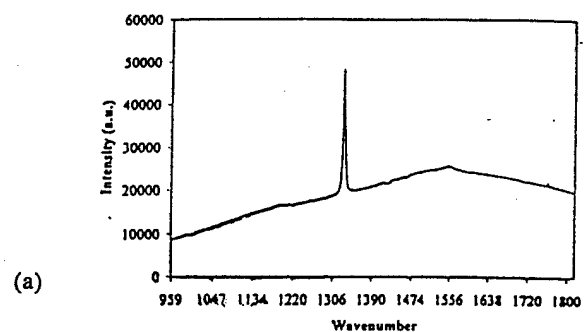


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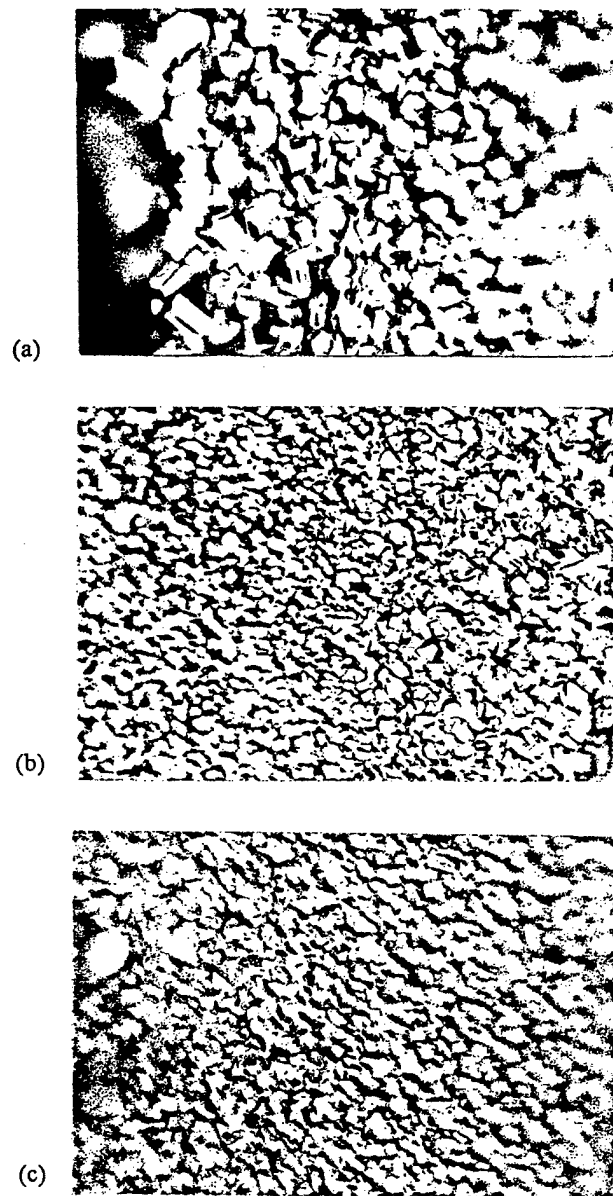


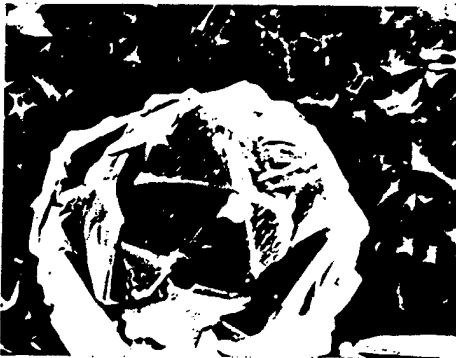
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(a)

10 μm



(b)

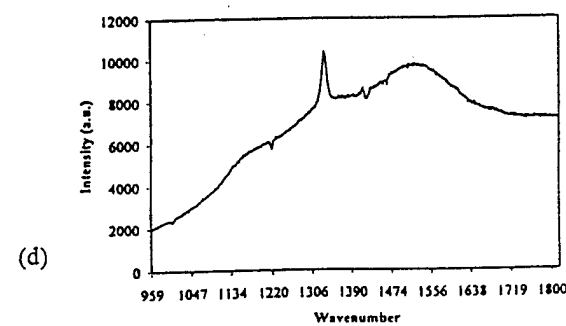
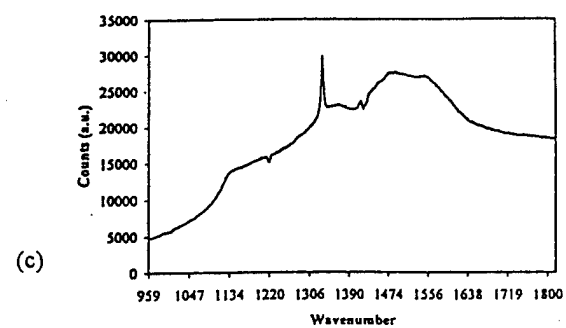
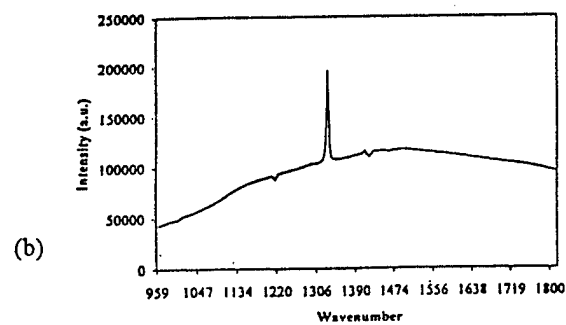
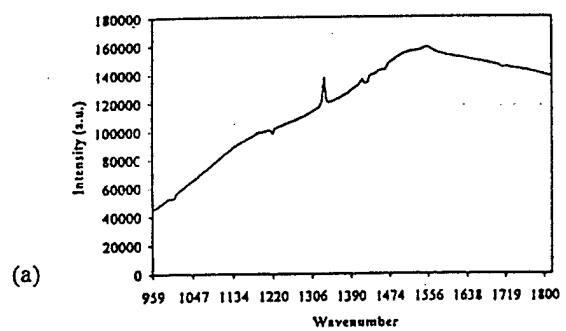


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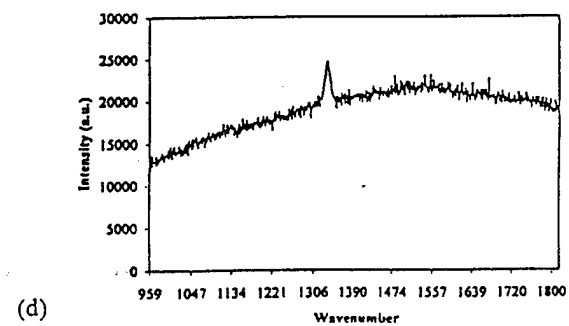
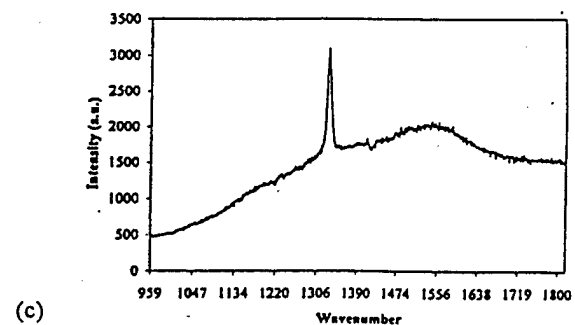
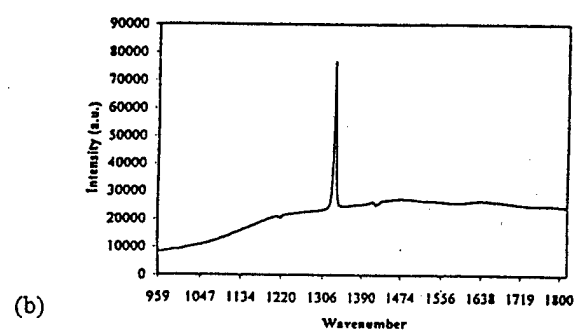
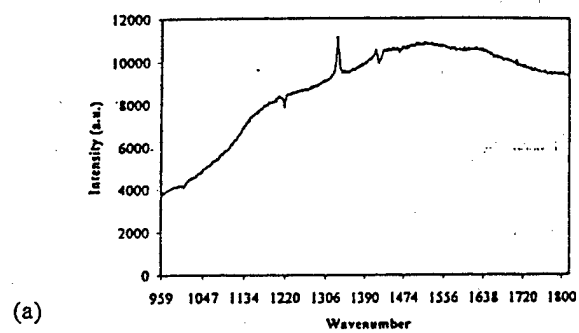
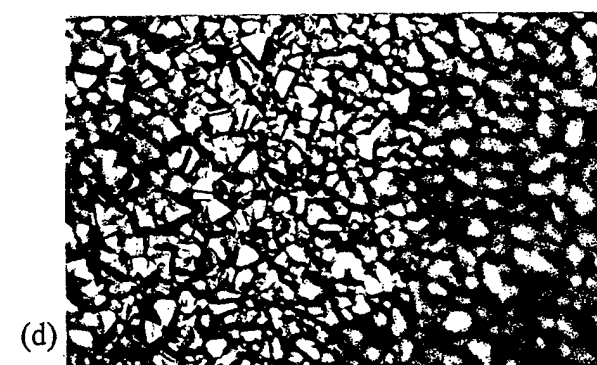
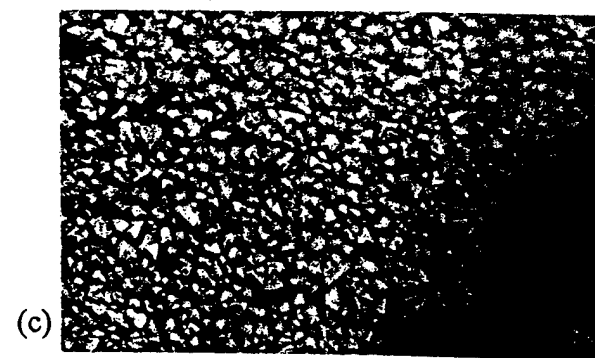
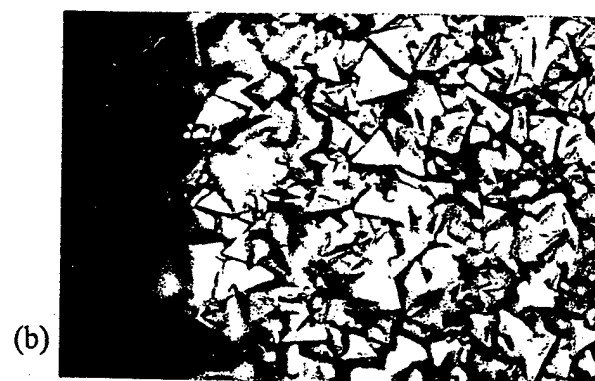
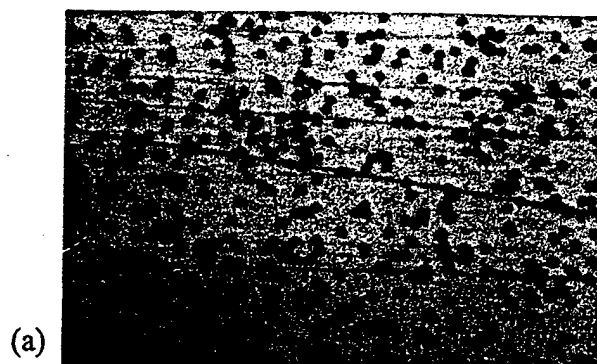


Fig. 15 Tsan-Heui Chein and Yonhua Tzeng,



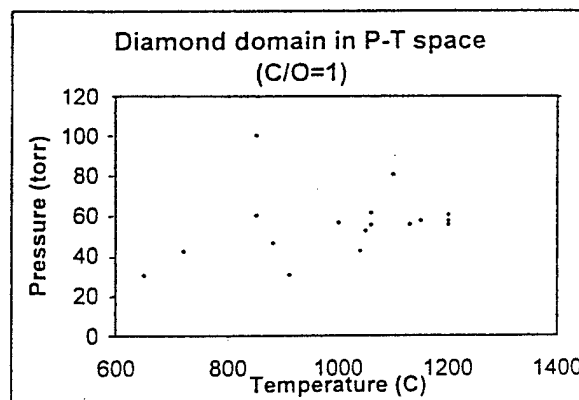


Fig. 17

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