are specially homonuclear diatomic molecules whose absorption frequencies do not lie in the easily accesible spectral region. In Figure 4, the simulated CARS spectra of N_2 at two different rotational temperatures are presented. The spectra show distinct shapes for different rotational temperatures from which the rotational population distributions can be deduced. As shown in the figure, the CARS technique can serve as a sensitive measure of the rovibrational distribution of the molecules of interest in the ground electronic states. In addition to the precise energy distribution of the products, the initial states of the reactants should be specified to study chemical dynamics in detail. The stimulated Raman scattering can pump the molecules in the desired rovibrational states by tuning the Stokes frequency. Thus the initial states of the reactants can be prepared as well as identified in this process. In our laboratory, various chemical and photochemical reaction dynamics have been studied by this technique.

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Synthesis of Diamond-Like Carbon Films on a TiO_2 Substrate by DC-Discharge Plasma Enhanced Chemical Vapor Deposition

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A diamond-like carbon (DLC) film was produced on a TiO_2 substrate using a plasma enhance chemical vapor deposition (PECVD) method. The CH_4-H_2 plasma was produced by applying 400 V DC. The DLC film with the best crystalline structure was obtained when the concentration of CH_4 in H_2 was 0.75 percent by volume and total pressure was 40 torr. The presence of the diamond structure was confirmed by Raman spectroscopy, X-ray diffraction, and scanning electron microscopy methods. It was found that the diluting gas H_2 played an important role in producing a DLC film using a PECVD method.

Introduction

The hard or diamond-like carbon films have attracted a rapidly growing interest in the past few years because of their unique properties. Their characteristic properties are[1~3] high electrical resistivity of the order of 10^3-10^{12} Ωcm, extreme hardness, high optical transparency over a wide spectral range, especially in IR region, chemical inertness to both acids and alkalies, and a high refractive index.

Diamond-like carbon (DLC) films are metastable amorphous materials. They can be synthesised by various methods such as ion beam deposition (IBD),[4] sputtering,[5] chemical vapor deposition (CVD),[6] and *rf*- or *dc*-plasma CVD methods.[7] These methods employ a variety of carbon bearing solid or gaseous source materials.[8] The gas-phase synthesis of diamond has clear advantages over the high-pressure and high-temperature method. It is possible to grow the film on large area substrates and highly pure diamond-like carbon can be obtained. DLC films contain sp^3-, sp^2- and even sp^1 coordinated carbon atoms and sometimes have medium range order. Depending on the precursor materials, many of these films contain a significant amount of hydrogen from

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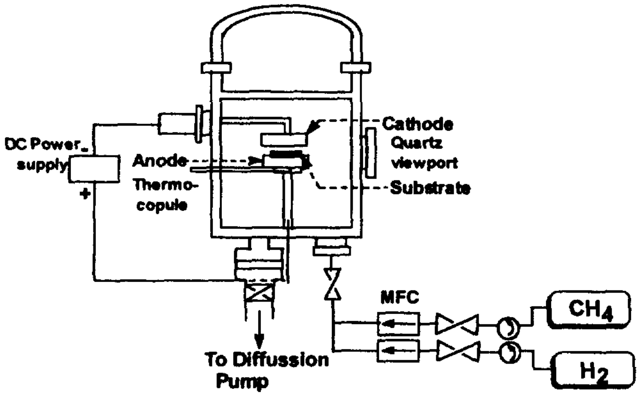

Figure 1. Schematic diagram of a DC-discharge PECVD system.

less than 10% to 60%.[9,10]

Diamond-like carbon films have been deposited on various substrates such as Si, Mo, W, Ni, α-Al_2O_3, stainless steel and NaCl single crystal. The growth of DLC films is greatly affected by the chemical and physical properties of substrates. We tried to deposit DLC films on a TiO_2 substrate. Titanium oxide is widely used for catalysts, electronic devices, sensors and wear-resistance materials. The deposition of DLC films on ceramic materials is gaining more interest. The DLC film can modify the electronic and optical properties of ceramics. In addition to that, the DLC/TiO_2 system can be used as a model system to study adhesive forces between the DLC coating and the substrate. We deposited DLC films a TiO_2 using CH_4-H_2 plasma produced by DC-discharge.

The DC-discharge Plasma Enhanced Chemical Vapor Deposition (PECVD) process is an effective method for producing high-density electrons to excite the active species on substrates. It is possible to produce diamond at relatively low T_s (Substrate Temperature).[11] The potential advantages of PECVD are (1) lower deposition Temperature, (2) less sensitivity to deposition temperature, (3) the capablilty of introducing high concentrations of dopant species without affecting the deposition rate, and (4) high rates for film deposition.[12]

Properties of the DLC films range from graphitic to diamond-like depending on the experimental condition. The aim of the present investigation is to determine the optimum experimental conditions to make good quality diamond-like carbon on a TiO_2 ceramic substrate.

Experiment

The experimental set-up of the PECVD equipment used in this study is shown schematically in Figure 1. The vacuum chamber was made of stainless steel and was pumped with an oil diffusion pump. The CVD apparatus was equipped with mass flow controllers and a DC power supply. A DC diode consisting of two parallel circular plates was set up in the chamber to produce plasma. The cathode and the anode of the diode were made of stainless steel and copper, respectively. The plasma was produced by applying 400 V between the cathode and anode.

A TiO_2 pellet was used as a substrate. The thickness of the pellet was 1 mm and the diameter was 10 mm. The TiO_2 substrate was cleaned with acetone in an ultrasonic vessel and rinsed with a HF solution (HF : H_2O=1 : 10) several times to remove surface impurities, and then washed thoroughly with distilled water. The TiO_2 substrate was mounted on the anode. The anode was cooled down by operating circulating water cooling system when the plasma was on. The substrate temperature (T_s) was measured using a thermocouple mounted just below the substrate holder (anode). The observed temperature was somewhat lower than the substrate temperature because of low thermal conductivity of the ceramic substrate.

Table 1. Typical experimental conditions for a growth of DLC films

Variation	Typical condition
Substrate	TiO_2 (rutile)
Reaction gas	CH_4-H_2 mixture
CH_4 (in H_2) (vol%)	0.25-5
Total pressure (torr)	10-40
Substrate temperature (℃)	1050-1200
Reaction time (hr)	4-20
Discharge current (mA)	450-480
Electrode distance (cm)	1

The TiO_2 substrate was sputter-cleaned for 30 minutes using H_2 plasma before the DLC film deposition. The mixture of CH_4 and H_2 gas was introduced into the reaction chamber as a source gas to prepare the DLC films on the TiO_2 pellet. The pressure and composition of reaction gas mixtures was controlled using mass flow controllers and the pressure was monitored by a digital manometer. A typical deposition conditions are listed in Table 1.

The physical and chemical properties of DLC films such as crystallinity, bond nature, and surface morphology have been investigated using X-ray diffraction (XRD ; model X-pert), Raman Spectroscopy, and Scanning Electron Microscopy (SEM ; Akasi DS-130S). Raman Spectra were measured with a Spex 4103 spectrometer using the 514 nm line of an argon ion laser for excitation.

Results and Discussion

Effect of methane concentration. It was generally observed that the methane concentration in hydrogen strongly affected the film quality. We investigated the effect of gas composition on the DLC film growth. Figure 2 shows the change of Raman spectra of DLC films deposited on TiO_2 substrates as a function of the methane concentration. The concentration of methane was determined as the flow rate of methane divided by the total flow rate of hydrogen and methane mixture. The total pressure was 37 torr and deposition was continued for 20 hours. In Figure 2, the 1334 cm^{-1} feature can be readily assigned as the first-order Raman mode of sp^3-type C-C streching. The features at 1402 cm^{-1} and 1606 cm^{-1} correspond to sp^3-type amorphous carbon and sp^2-type amorphous carbon respectively.

Raman spectroscopy is most widely used to characterize diamond and carbon films.[13~14] Raman analysis has become

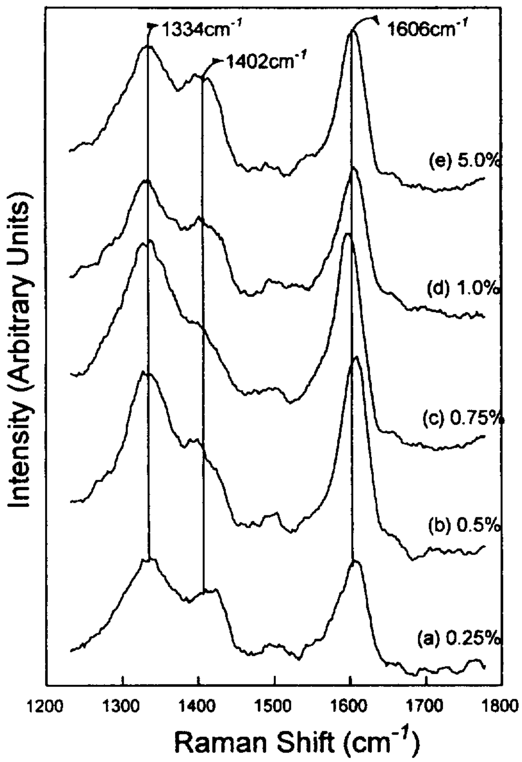

Figure 2. The Raman spectra of DLC films. The concentration is the volume percent of CH_4 in H_2. Total pressure was 37 torr and the flow rate was 400 sccm. The film was deposited for 7 hours.

accepted by the CVD diamond community as the benchmark analytical method for determining the presence of diamond and other forms of carbon. It is non-destructive, fast, needs little or no sample preparation, and affords positive identification of all carbon structures. The spectra obtained from CVD carbon films have generally focused on the appearance of the first-order Raman mode of diamond (sp^3-type bonding) at 1334 cm^{-1}. Other features of carbon, diamond-like carbon, and the diamond film appear in the Raman spectra in the spectral range from 1350 to 1600 cm^{-1}. They are associated with carbon structures such as graphite[15] (sp^2-type bonding) and amorphous carbon. The presence of a 1334 cm^{-1} feature in the Raman spectrum generally allows one to identify the diamond structure.

Based on Raman analysis, we can determine that the carbon layer deposited on TiO_2 is composed of both sp^3-type carbons and other carbonaceous species. However, one difficulty may arise in the interpretation of the relative scattering intensities of Raman features observed in the spectra of DLC films. The intrinsic Raman intensity of the sp^2 type carbon relative to the diamond is quite different. The Raman scattering efficiency of crystalline diamond[16] is $(4.9\text{-}6.0)\times 10^{-7}$ cm^{-1} and that of crystalline graphite[17] is $(3.0\text{-}4.3)\times 10^{-9}$ cm^{-1}. The Raman scattering efficiency for the sp^2-bonded carbon is expected to be more than 50 times greater than that for the sp^3-bonded diamond. This results in an enhanced sensitivity of disordered sp^2 carbon over sp^3 diamond. Based on relative intensities of sp^3 and sp^2-type carbon feature, we can conclude that the DLC film deposited on TiO_2 is mostly composed of sp^3 carbon bonds which are frameworks of diamond.

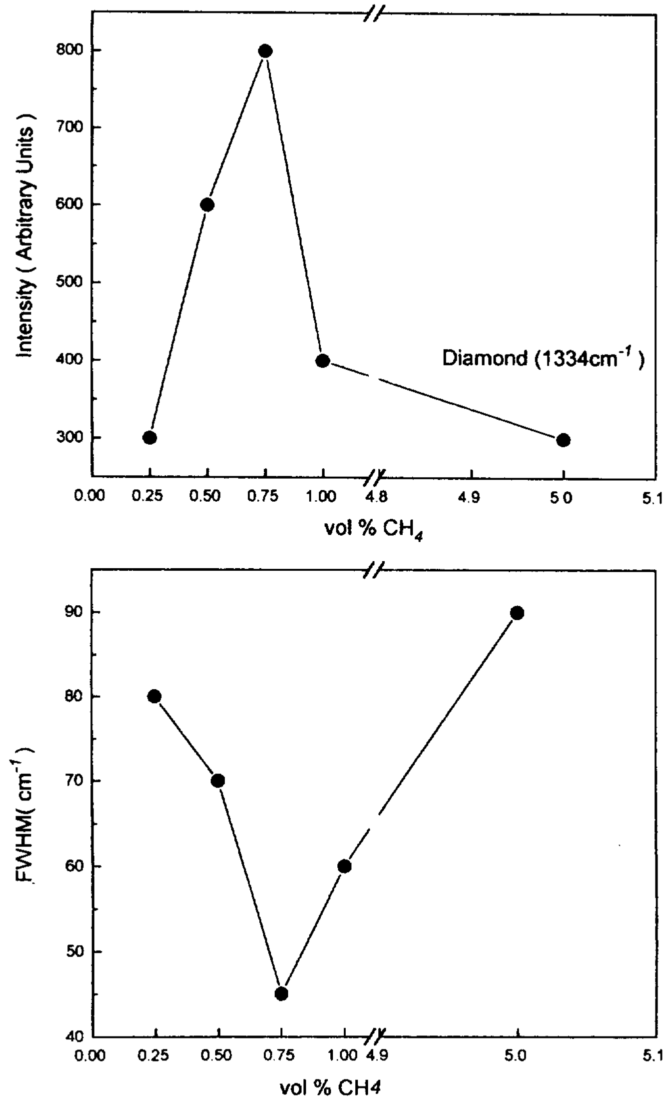

Figure 3. Change of the diamond Raman feature at 1334 cm^{-1} as a function of CH_4 concentration in H_2; (a) peak intensity, (b) full width at half maximum.

The concentration of methane in hydrogen affected the chemical property and the growth rate of DLC films on TiO_2. The crystalline DLC film was produced when the methane concentration was 0.75% by volume in hydrogen. It was determined by inspecting Raman spectra of DLC films. Figure 3 shows the peak intensity and the peak width at half maximum (FWHM) of the diamond reflection with respect to the CH_4 concentration. The full width at half maximum (FWHM) of the peak is very sensitive to the crystal stucture. The peak would be broadened by structural distortion such as defects. The 1334 cm^{-1} feature gives the smallest value when the CH_4 concentration is 0.75 vol%. This suggests that the crystalline quality of the diamond particles is optimum when the CH_4 concentration is 0.75 vol%. The growth rate of the DLC film is also the highest when the CH_4 concentration is 0.75 vol%. Increase of the CH_4 concentration may increase the active carbon species in plasma to produce the carbon

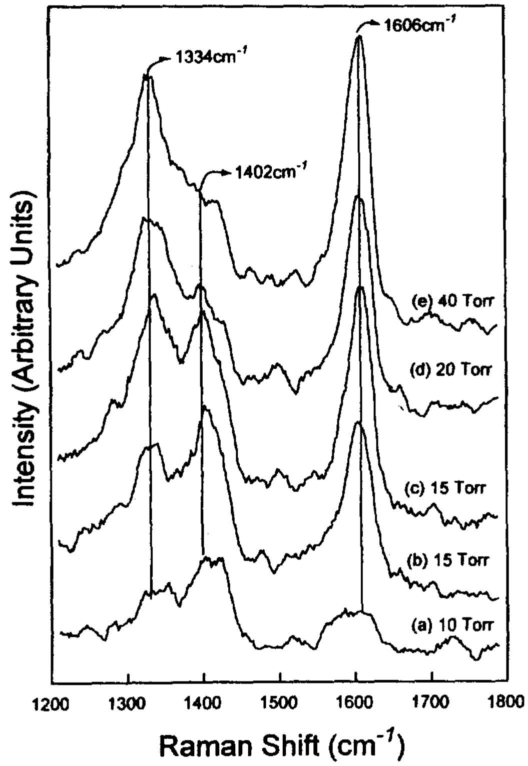

Figure 4. Change of Raman spectra of DLC films as a function of total gas pressure. The CH_4 concentration was 1 percent in H_2. The film was deposited for 10 hours.

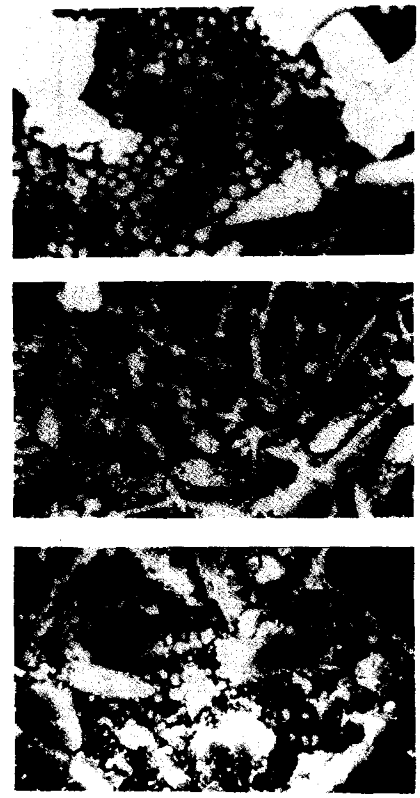

Figure 5. SEM photographs of DLC films. The concentration of CH_4 was 1 vol% in H_2 and total pressure was (a) 10 torr, (b) 20 torr, and (c) 40 torr.

film on the substrate. However, the optimum condition to produce the chemical species for the diamond-like carbon film is very sensitive to CH_4/H_2 ratio as described in detail later. In our experimental condition, the optimum concentration of CH_4 in H_2 was 0.75% by volume.

Effect of Pressure. We investigated the effect of the total gas pressure on the growth of the DLC film on TiO_2. We changed the total pressure from 10 to 40 torr with the same methane concentration. The reaction pressure was changed by controlling evacuation speed and the concentration of methane was 1 vol%. When total reaction pressure was increased the relative intensity of diamond Raman feature at 1334 cm^{-1} to sp^2 carbon phase at 1606 cm^{-1} increase as shown in Figure 4. The Raman feature around 1400 cm^{-1} is related to the amorphous carbon structure. It clearly indicates that the crystallinity of the diamond particles was enhanced with increasing total reaction pressure in the pressure range used. The intensity ratio of the diamond feature (1334 cm^{-1}) to the sp^2 carbon feature (1606 cm^{-1}) was the highest when the total pressure was 40 torr. The morphology of deposits was investigated using SEM. As Figure 5 shows, the surface of the carbon deposit is mainly composed of amorphous phase when the total pressure was 10 torr. As the total pressure was increased, ball-like DLC particles showed up. When the pressure was 40 torr, the morphology of the surface became well-defined ball-like particles. The grain size of the particle was about 1 μm when the pressure was 40 torr. We have not investigated at pressures higher than 40 torr because of the difficulty to generate plasma.

It was generally observed that the quality and the growth rate of the DLC film is greatly affected by the total pressure. When the pressure is high, the mean free path of the particles in the plasma becomes short. The temperature of heavy species such as radicals, molecules, atoms and ions increases up to the temperature level of electrons due to frequent collisions. High pressure is advantageous to create a plasma with abundant active species because of the equilibra between electrons and heavy particles. However, diffusion toward the surface requires time and some of the active species vanish because of recombination. It may cause an increased number of recombinations and prevented many active particles from arriving at the surface. The optimum pressure for diamond-like carbon deposition is related to the balance between generation and recombination of these active species.

Effect of Deposition Time. We investigated the change of DLC film morphology at extended plasma exposure. Figure 6 shows the X-ray diffraction profiles of DLC films made by exposing to CH_4-H_2 plasma for 4, 10 and 20 hours. The concentration of CH_4 was 0.75 vol% by volume in H_2 and the total pressure was 40 torr. As deposition time increased, new X-ray diffraction peaks showed up in addition to peaks of the TiO_2 substrate. The most obvious change is the increase of the intensity of the peak at $2\theta=44^0$. This peak corresponds to the diffraction of the diamond (111) plane. The presence of the diamond (111) peak in XRD paterns clearly shows that the DLC film is mainly composed of sp^3 carbon frameworks. This agrees very well with interpretation of Raman spectra we made.

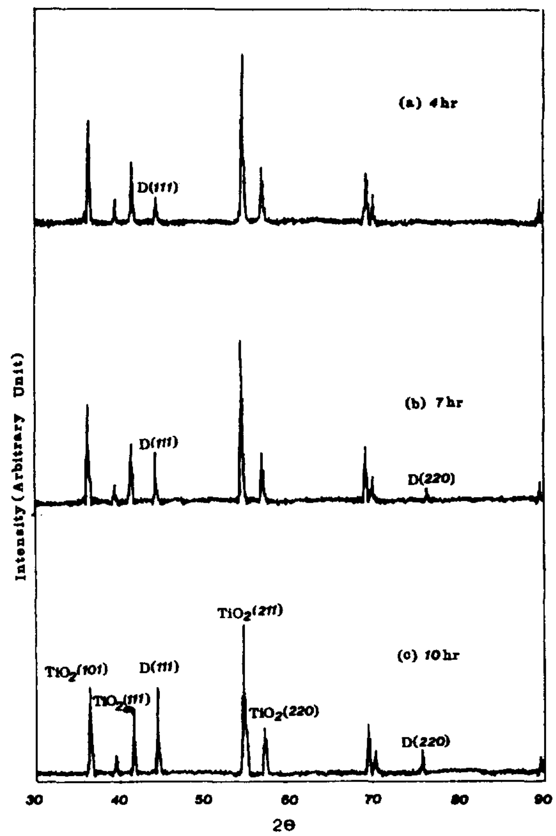

Figure 6. XRD patterns of DLC films after deposition for (a) 4 hours, (b) 7 hours, (c) 10 hours. The concentration of CH_4 was 0.75 vol% in H_2 and total pressure was 40 torr.

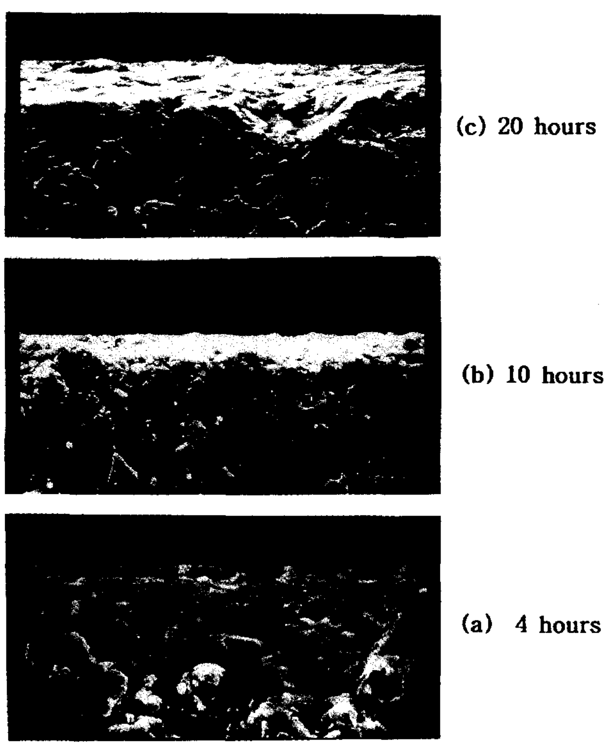

Figure 7. Cross-sectional SEM photographs of DLC films after deposition for (a) 4 hours, (b) 7 hours, (c) 10 hours. The concentration of CH_4 was 0.75 vol% in H_2 and total pressure was 40 torr.

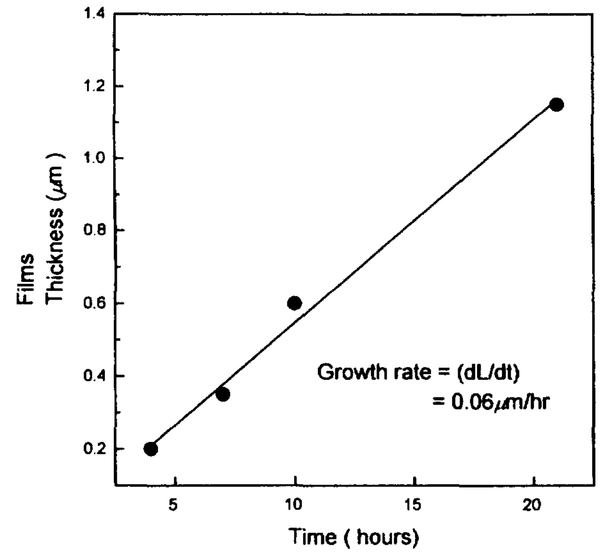

Figure 8. DLC film thickness against deposition time. The concentration of CH_4 was 0.75 vol% in H_2 and total pressure was 40 torr.

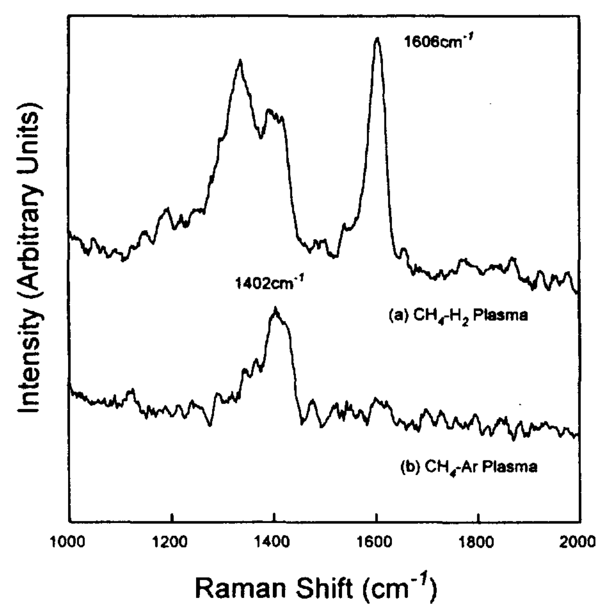

Figure 9. Raman spectra of DLC films showing the effect of diluting gases on the quality of DLC films. (a) 0.5 percent of CH_4 in H_2. (b) 0.5 percent of CH_4 in argon. Total pressure was 37 torr.

Figure 7 shows the fractured cross section of DLC films. Continuous films are obtained after a duration of 20 hours. Figure 8 shows the thickness of diamond-like films against deposition time. The thickness of diamond-like films is directly proportional to the deposition time. This indicates that diamond films are deposited in the steady state under the experimental condition. In this work, the growth rate is about 0.06 μm/h. This is consistent with the X-ray diffraction profiles obtained at different deposition time as indicated in Figure 6.

Effect of Hydrogen. It was generally found that H_2

played an important roll when the CH_4 plasma was used to produce diamond films. Hydrogen not only helps produce plasma effectively but affects directly the structural and chemical property of the diamond film. We tried to investigate the roll of hydrogen by changing the diluting gas from hydrogen to Ar.

Experiments were carried out by using argon instead of hydrogen under otherwise identical experimental conditions (0.5 vol% methane ; 37 torr pressure ; flow rate 400 sccm). Raman spectra of CH_4-H_2 and CH_4-Ar systems are shown (a) and (b) in Figure 9 respectively. No diamond peaks at 1334 cm^{-1} were obtained for CH_4-Ar system.

In order to investigate the role of H_2 gas, attention was paid to the emission of hydrogen atomic radical. Excited hydrogen molecules, hydrogen atoms of the Balmer series (H_β, H_γ) CH_2 and CH radicals are adsorbed on the substrate and thermally decomposed to form diamond, diamond-like carbon and graphite.[18] The rate of graphite formation may be much grater than that of diamond or diamond-like carbon because of the stable phase of graphite. However, graphite is selectively removed from the surface[19] because it is much more reactive towards H radicals than diamond or diamond-like carbon which leaves the latter behind. Unfortunately, however, the mechanism of diamond growth is not clear at this stage. The role of H_2 gas can be considered as promoter of the methane decomposition and graphite removal reactions.

Conclusion

Based on the results and discussion given above, the follwing conclusion can be made:

(1) A DLC film was successfully produced on the TiO_2 substrates using PECVD method. The source material was the mixture of CH_4 and H_2 and the plasma was produced by applying 400 V DC.

(2) The diamond struture was identified by several analytical methods ; 1334 cm^{-1} feature in Raman spectra, diamond (111) peak in XRD, and the ball-like structure in SEM.

(3) The diluting gas H_2 was found to play an important role in producing DLC films.

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