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Characterization of Diamond-like Carbon Films on Si-Wafer Deposited by DC Plasma CVD.

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Abstract — Diamond-like carbon(DLC) thin films were prepared by DC plasma chemical vapor deposition of methane and hydrogen gas mixtures on Si(111) wafer with changing discharge current, reaction pressure, methane content and substrate temperature. Thus deposition conditions to obtain good-quality DLC films were determined as follows; 480 mA, 32 Torr, 1.0 vol %, and 850℃ by using scanning electron microscope and laser Raman spectrophotometer. The DLC films are composed of ball-like grains consisted of most sp^3 carbon bonds and have a refractive index 2.2 nearly equal to that of the natural diamond. It was also found that the hydrogen coverage is vital for the growth of DLC films.

요 약 — 메탄과 수소 혼합가스로 직류 플라즈마 화학 증착법(DCPECVD)을 이용하여 방전전류, 반응압력, 메탄농도 및 피착체의 온도를 변화시키면서 다이아몬드 유사탄소박막(DLCF)을 Si(111)-웨이퍼 위에 합성하였다. 주사전자 현미경(SEM)과 레이저 Raman 스펙트로포토메터로 확인된 양질의 DLCF를 얻는 조건은 방전전류, 반응압력, 메탄농도, 그리고 피착체의 온도가 각각 480 mA, 32 Torr, 1.0 vol % 및 850℃ 였다. 이 DLCF는 대부분 sp^3 탄소 결합으로 된 구형의 알갱이들로 구성되어 있고, 그 굴절률은 2.2로 천연 다이아몬드와 비슷한 값을 가지고 있다. 또한 DLCF 성장에서 수소피복이 매우 중요한 것으로 밝혀졌다.

1. Introduction

A large number of experimental methods for diamond-like carbon(DLC) film synthesis [1-4] in the low pressure condition have been developed because simple bulk diamond [5, 6] synthesized under high pressure is not enough because of its diffcult processing of the parts in a complete unit in its industrial applications.

Diamond is easily converted into graphite and graphitic carbon by heating under atmospheric and reduced pressure. Several researchers have shown that this degradation from diamond into graphite is depressed by hydrogen [7]. Therefore, the DLC films can be obtained by the chemical vapor deposition(CVD) method [8, 9] using methane or other hydrocarbon with hydrogen gas mixtures, the excess component of which should be hydrogen gas. Among hot filament thermal CVD [8, 10], RF plasma CVD [9], microwave plasma CVD [4], electron-assisted CVD [11] and DC plasma CVD [12], DC plasma enhanced chemical vapor deposition(PECVD) is most promising because of the rapid growth rate of the DLC films [13].

Mania *et al.*[14] proposed that the methyl radical having an sp^3 hybrid orbital was favourable for the synthesis of diamond like films and the presence of radicals with a sp^2 bond favoured graphite structure. Tachibana *et al.*[15] showed that the main species in the plasma of CH_4-H_2 gas mixtures were CH_3 and H radicals.

Although the DLC films have been synthesized by the various deposition techniques mentioned above, very little is known for the growth process of the DLC films, and as a result process optimization has not been achieved [16, 17].

Accordingly, the purpose of the present work is to obtain an optimum growth conditions for high quality DLC films on Si-wafer with CH_4/H_2 plasma using DC PECVD. At the same time, we controlled deposition conditions such as discharging current, total pressure, methane concentration and substrate temperature to get high quality DLC films. Surface morphology and bond character of the DLC films synthesized with the deposition conditions were investigated by means of scanning electron microscope(SEM), Raman spectrosphotometer and XRD.

2. Experimental

2.1. Materials:

(111)-oriented oxygen-doped P-Si wafers cut into 10×10×0.5 mm were used as substrates. The Si-wafers were scratched for 10 minutes with diamond paste containing diamond particles 8 μm in diameter. The Si-wafers were chemically washed with acetone in an ultrasonic vessel and rinsed with HF solution (HF : H_2O = 1 : 9) several times to remove impurities, then thoroughly washed with distilled water. Mixed source gases used in this experiment were CH_4(99.99%) and H_2(99.999%).

2.2. Apparatus and experimental procedures

The CVD apparatus for the preparation of the DLC films on the Si-wafers were composed of a cylindrical vacuum chamber 50 cm in both diameter and length, gas feeding parts with mass flow controllers, and evacuating components. The vacuum chamber made of stainless steel was evacuated with an oil diffusion pump coupled with a rotary pump. An oil filtering component was set up between the chamber and the diffusion pump to keep away oil vapor from it and a trap was located between the diffusion pump and rotary pump to capture unreacted chemical species.

A DC diode composed of two parallel plate electrodes was set up in the chamber to produce plasma from the CH_4 and H_2 gas mixture and prepare diamond like carbon films on the substrate. The cathode and anode of the diode were made of copper and stainless steel respectively. The distance from the cathode to the anode was controlled to 1 cm to maximize efficiency of deposition. The substrate was located on the anode with circulating water cooling components to keep its temperature constant because it was heated to 950℃ due to temperature of plasma.

Before deposition, the chamber was evacuated to 2×10^{-7} Torr, then H_2 gas was fed for sputter cleaning of the substrate for 30 minutes at 35 Torr. The source gas, methane and hydrogen were introduced to prepare the DLC films. Typical experimental conditions of the DLC film preparation were total pressure; 23~32 Torr, DC discharge current; 200~480 mA, flow rate of H_2; 100~400 sccm, flow rate of CH_4; 2~20 sccm, methane concentration; 0.2~5 vol %, substrate temperature 730℃ ~900℃ and reaction time; 10 hours.

2.3. Chatacterization of DLC films

The refractive index of the DLC films deposited on the Si-wafer was measured by ellipsometry (Gaertner L116A). The surface morphology of the deposited DLC films was observed by the scanning electron microscope (SEM, Akasi DS-130S). The bonding nature of the DLC films was characterized by using micro Raman spectrophotometer (A Spectra Physics model 165) which was composed of argon ion laser, Raman U-1000 double monocromator, Hamamatsu R943-02 photomultiplier tube and Hamamatsu C1230 photon counter, discriminator, and XRD (Philips model X-pert).

3. Results and Discussion

The effects of synthesis parameters such as discharge current(Id), total pressure in the reaction chamber, methane content of CH_4-H_2 mixture, substrate temperature and reaction time were controlled to produce high quality DLC films. Fig. 1 shows SEM images of DLC films deposited on Si(111) wafers under the four discharge currents 200 mA(a), 300 mA(b), 400 mA(c), and 480 mA(d), which were fixed with changing discharge voltage from 360 V to 400 V respectively at keeping other synthesis conditions constant, such as 1 vol % CH_4, 850℃, 32 Torr, and 10 hours. The colour of the plasma of the CH_4-H_2 mixture was gradually changed into

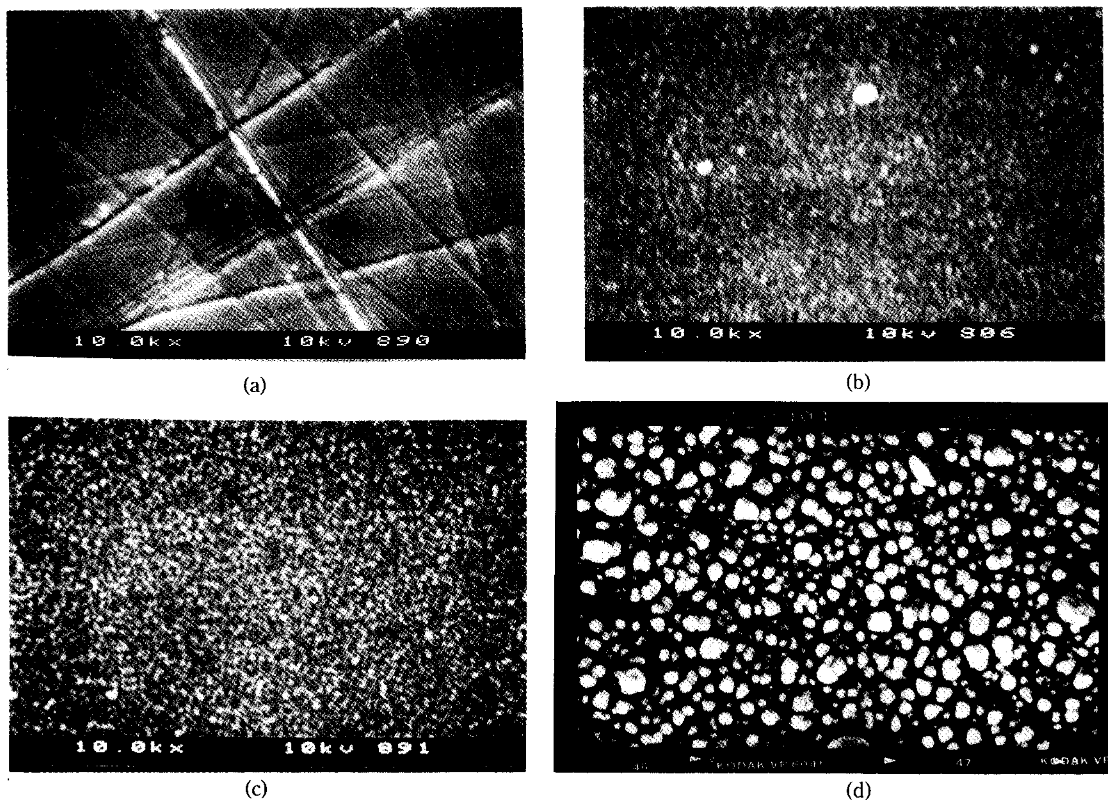

Fig. 1. The SEM photographs of DLC films at various discharge currents; (a) 200 mA, (b) 300 mA, (c) 400 mA, (d) 480 mA at CH_4 content, 1.0 vol %; substrate temperature, 850℃; reaction pressure, 32 Torr, and reaction time, 10 hours.

bright-blue with increasing discharge current. The DLC films were not synthesized on the Si-wafer when the discharge current was increased up to 200 mA. But small grains were observed on the Si-wafer when Id was 300 mA and their average diameter was increased from ca. 0.17 μm to ca. 0.33 μm as shown in Fig. 1 and 2 when Id was increased from 300 mA to 480 mA. The DLC films have a grain-like structure and their sizes increase with increasing discharge current. These phenomena suggest that the elevation in Id results in an increase of the reactive chemical species dissociated by the colliding electrons and hydrogen radicals required for the preparation of the diamond [18].

A typical cross-sectional view of the DLC films indicates that the film is rather uniform in thickness; ca. 0.33 μm as shown in the bright region of the upper part of Fig. 3. A growth rate of the

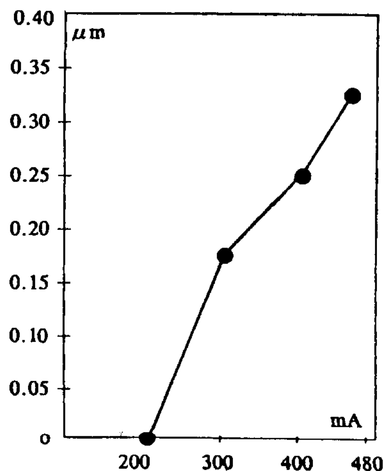

Fig. 2. The grain size of DLC films as a function of discharge currents at CH_4 content, 1.0 vol %; substrate temperature, 850℃; reaction pressure, 32 Torr, and reaction time, 10 hours.

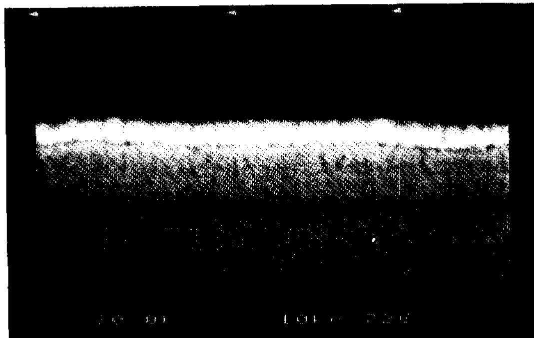

Fig. 3. A typical cross-sectional view of DLC films prepared at discharge current, 480 mA; CH_4 content, 1.0 vol %; substrate temperature, 850℃ ; reaction pressure, 32 Torr, and reaction time 10 hours.

DLC film was calculated to be ca. 33 nm/h from the average value of their thickness observed in repetitive experiments. The growth rate of DLC films in this work is about 5 times faster than that of diamond films deposited on Al substrate at Id= 300 mA [18].

There are some peak assignments of the Raman spectra of the DLC films deposited at different discharge currents in Fig. 4, where a broad line A at 1334 cm^{-1} arises from sp^3 C bonds of the DLC film and a narrow peak B occurring in the 1610 cm^{-1} does from sp^2 C bonds of a graphite and other structures of carbon which had intervened as impurity in the preparation of the DLC films.

The peak at 1334 cm^{-1} is attributed to the single triply degenerate zero center optical phonon(F_{1g} symmetry) associated with fourfold coordinated sp^3 bonded carbon atoms [19], which corresponds to the metastable phase of crystalline carbon, i.e., diamond which has only a sharp single Raman peak at 1332 cm^{-1}. However, the width of this Raman peak is broader compared to natural diamond. Such a broadening may be explained as being due to reduction in the phonon lifetime owing to an increase in the density of defects in the diamond phase [20]. The Raman peak at 1610 cm^{-1} can be assigned to the sp^2 bonded carbon atom to indicate the presence of some amount of graphitic carbon because of the small amount of blue shift of the peak position from 1575 cm^{-1} which is the characteristic peak position

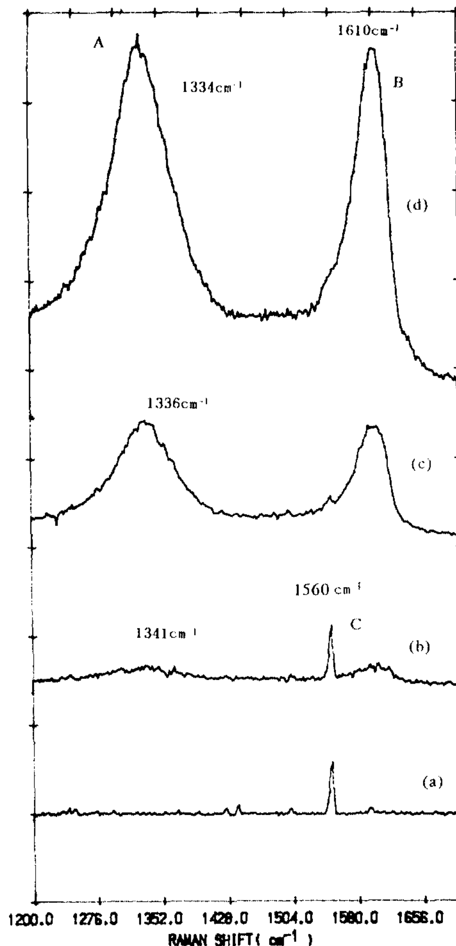

Fig. 4. The Raman spectra of DLC films at various discharge currents; (a) 200 mA, (b) 300 mA, (c) 400 mA, (d) 480 mA at CH_4 content, 1.0 vol %; substrate temperature, 850℃ ; reaction pressure, 32 Torr, and reaction time, 10 hours.

[21] of single crystals of graphite to 1610 cm^{-1}. This fact may be interpreted as being caused by disorder-induced changes in the phonon density of states in carbon film [21]. It may be mentioned that Raman spectra have particular sensitivity to the sp^2 bonding component because the Raman cross section of graphite is about 50 times [22] that of a diamond which has only sp^3 bonding structure. From these facts, we can propose an empirical equation from which we can define DLC film.

$$R(sp^3)=\frac{I(sp^3)}{I(sp^3)+0.02\ I(sp^2)}\times 100\% \quad (1)$$

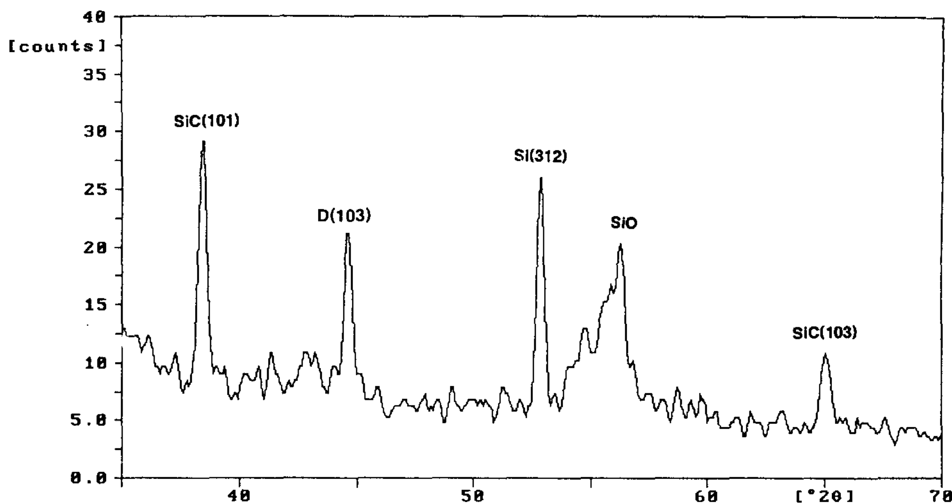

Fig. 5. X-ray diffraction pattern of DLC film; at 850℃ discharge current, 450 mA; reaction pressure, 32 Torr; CH_4 content, 1.0 vol %, and reaction time 10 hours.

where $R(sp^3)$ denotes a relative Raman peak ratio of sp^3 bonded carbons of amorphous carbon(a-C) film, and $I(sp^3)$ and $I(sp^2)$ are intensities of Raman peaks for the sp^3 bonded carbons and sp^2 bonded carbons in the a-C films respectively. If the $R(sp^3)$ value of a-C film is more than 90% it can be said that the film is DLC film. All $R(sp^3)$ values of Fig. 4 (d), Fig. 6(c), Fig. 7(d) and Fig. 8(c) Raman spectra are more than 90%, therefore all films in this study are DLC films.

Even in the microcrystalline and amorphous states, DLC films retain some of the unique physical and chemical properties of single crystal diamond like high transparency in the visible range, hardness, high thermal conductivity and chemical inertness. The a-C films deposited on Si-wafer in this experiment have high transparency and refractive index 2.2 which is nearly equal to 2.4 of the natural type IIA diamond [23] and so these films have been considered to be DLC films.

An x-ray diffraction pattern of the a-C film is shown in Fig. 5. The a-C film grown on si(111)-wafer has a D(103) orientation which are assignable to diamond structured carbon and a number of other peaks such as SiC(101) and SiC(103) etc., This fact is another evidence, that the film is DLC film.

The sharp line C at 1560 cm^{-1} corresponds to the third-order line of a silicon substrate.

The intensities of peaks, A and B were gradually enhanced and the peak C disappeared with increasing discharge current. Since the Raman scattering efficiency of sp^2 C bond is about 50 times greater than that of sp^3 C bond, we can conclude that the DLC films are mainly composed of sp^3 C bonds which are characteristic structure of the diamond [24].

Some SEM photographs and Raman spectra of the DLC films were represented in Fig. 6 and 7 respectively at various total reaction pressures such as 23, 29, and 32 Torr. The colour of plasma became gradually bright-blue with increasing reaction pressure and changing the discharge current. The grain size of diamond-like carbon having ball-like struture is increased from ca. 0.33 to 1 μm and the nucleation density is enhanced as shown in Fig. 5. These facts can be proved by the increase of Raman peak intensity of DLC films represented in Fig. 6 because the reactive chemical species such as energized electrons and hydrogen radicals in the plasma are increased with elevating reaction pressure. When the total reaction pressure is over 32 Torr, the plasma itself was not generated in our experimental condition.

The Raman spectra of DLC films are shown in

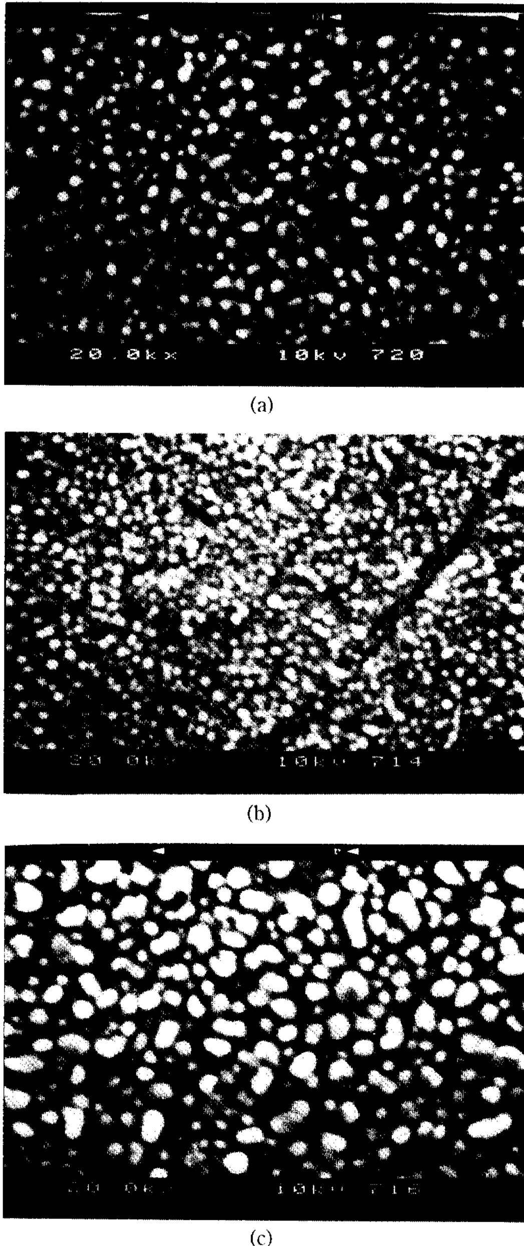

Fig. 6. The SEM photographs of DLC films at various reaction pressures; (a) 23 Torr, (b) 29 Torr, (3) 32 Torr at discharge current, 480 mA; CH_4 content, 1.0 vol %; substrate temperature, 850 ℃, and reaction time 10 hours.

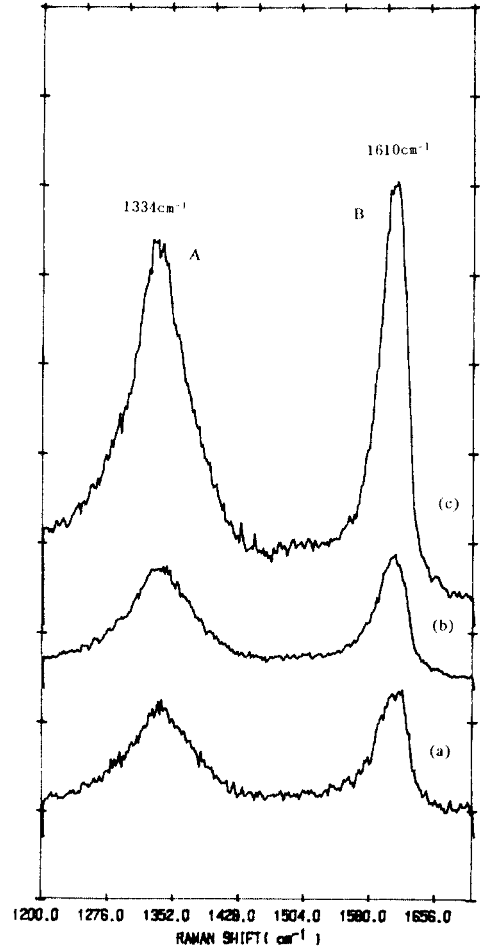

Fig. 7. The Raman spectra of DLC films at various reaction pressures; (a) 23 Torr, (b) 29 Torr, (c) 32 Torr at discharge current, 480 mA; CH_4 content, 1.0 vol %; substrate temperature, 850 ℃, and reaction time, 10 hours.

Fig. 8 at various CH_4 contents under discharge current; 480 mA, pressure, 32 Torr and substrate temperature, 850℃. The CH_4 contents of CH_4-H_2 mixture to generate plasma were 0.2, 0.5, 0.7, 1.0 and 5.0 vol %. The colour of plasma changed from thin-blue into deep-blue with increasing CH_4 content. The growth rate of the DLC films is directly proportional to methane concentration in the range of 0.2~1.0 vol % since the chemical species such as CH, CH_2 and CH_3 etc. to take part in the reaction of DLC preparation increase with increasing CH_4 content. But the peaks A and B of Raman spectra of DLC films were relatively decreased and broadened, and the sharp C peak mentioned above appeared at 1560 cm^{-1} when CH_4 content was over 5.0

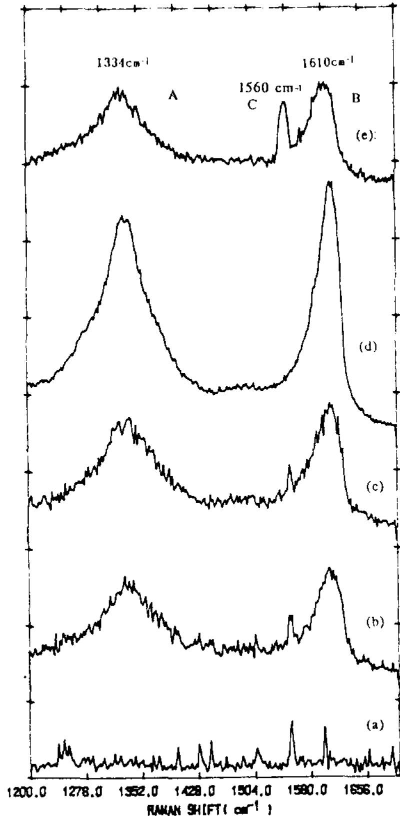

Fig. 8. The Raman spectra of DLC films at various CH_4 contents; (a) 0.2 vol %, (b) 0.5 vol %, (c) 0.7 vol %, (d) 1.0 vol %, (e) 5.0 vol % at discharge current, 480 mA; reaction pressure, 32 Torr; reaction temperature, 850℃ and reation time 10 hours.

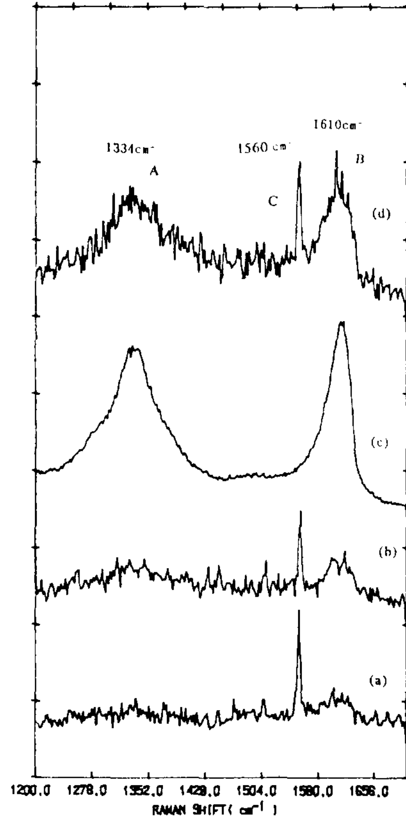

Fig. 9. The Raman spectra of DLC films at various reaction temperatures; (a) 730℃, (b) 800℃, (c) 850℃, (d) 900℃ at discharge current, 450 mA; reaction pressure, 32 Torr; CH_4 content, 1.0 vol %, and reaction time 10 hours.

vol %. These facts support that an active hydrogen radical of CH_4/H_2 plasma remove formation of graphitic carbon to help DLC synthesis [25, 26]. It is 1.0 vol % that the optimum CH_4 content of CH_4/H_2 plasma is in need of the good-quality DLC film preparation in this work.

The effect of substrate temperature on DLC film deposited on Si-wafer was shown in Fig. 9 under discharge current, 480 mA; pressure, 32 Torr, and CH_4 content, 1.0 vol %. The growth rate of DLC films enhances gradually with increasing temperature in the range of 730℃ ~850℃. In this temperature range, it is distinct from decrease of the height of the peak (c) compared with the height of the peak (d) in Fig. 8 that the substrate is more and more covered with DLC film. In general, DLC film is deposited on substrate when the reaction species colliding with the substrate are thermally excited to high energy levels to get over activation energy barrier [22]. Consequently, the increase in the growth rate of DLC film can be caused by the thermal excitation of the reactive species and formation of active sites on the surface of the substrate. From the intensity and width of the two characteristic peaks at 1334 cm^{-1} (peak A) and 1610 cm^{-1} (peak B) of the DLC films shown in Fig. 9, we can easily find that the growth rate and crystallinity of the films are very sensitive to reaction temperature. With increase in reaction temperature up to 850℃, the growth rate and crystallinity of the films increa-

ses and seems gradually better respectively. On the other hand, with further increase in reaction temperature, the growth rate and crystallinity begin to decrease and degrade. These phenomena can be explained as that the carbon solubility on the surface of the substate in the high temperature region decreases, while the carbon concentration in the gas phase is nearly constant. In addition, these facts support the amount of CH bonding on diamond surfaces increased with the temperature of treatment below 900℃ but the amount of the CH bonding decreased above 900℃ because the hydrogen coverage vital step in the growth process of DLC films decreased above 900℃ [28, 29].

Under the present experimental conditions, the good-quality DLC films are obtained with deposition conditions of discharge current, 480 mA; reaction pressure, 32 Torr; methane content, 1.0 vol %, and substrate temperature, 850℃. DLC films deposited on Si-wafer in the optimum conditions consist of ball-like grains and have a refractive index 2.2 which is nearly equal to 2.4 of the natural type IIA diamond.

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