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Fabrication of Diamond Films by Microwave Plasma CVD at Low Hydrogen Concentration

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Diamond films are fabricated by a microwave plasma CVD method from gas mixture of low hydrogen concentration. Carbon mono-oxide and carbon di-oxide are fed as source gases with a small amount of hydrogen. When the hydrogen concentration ($H_2/(CO+CO_2+H_2)$) is higher than 10%, well faceted diamonds are observed on the whole at a Si(100) substrate($15\times15mm^2$). At the hydrogen concentration between 1.7% and 10%, diamonds are obtained only on the fringe area of the substrate, while sooty carbons deposit on the central area. At the hydrogen concentration less than 1.7% no diamonds can be fabricated. As the hydrogen concentration gets lower, the plasma ball becomes smaller and more greenish, i.e., in the optical spectra, the intensity of H and CH emission becomes lower and that of C and C_2 becomes higher.

Key words: diamond, microwave plasma CVD, hydrogen

1. INTRODUCTION

Diamond films have been fabricated by chemical vapor deposition (CVD) methods from gas phase [1-3]. Hot-filament CVD method and microwave plasma CVD are in common use with using hydrocarbon source gases diluted with hydrogen. A typical condition for diamond synthesis by the microwave plasma CVD method is as follows; methane(CH_4) source gas diluted with hydrogen(H_2) below 1%, a total gas pressure about 5kPa, a substrate temperature about 900℃ [4]. From the fact that diamond can be obtained from such the gas mixture, hydrogen is considered to play an important role during the growth of diamond. It has been considered carbons are given by decomposition of hydrocarbon gas and are deposited onto substrates with a large number of atomic hydrogens who will etch non-diamond phase. Then carbon atoms in diamond phase are left on the growing surface. For this reason, it requires a lot of hydrogens to fabricate diamond films of good quality [5-8]. Oxygen is also able to etch the carbon. It is reported that by adding oxygen(O_2) or carbon di-oxide(CO_2) to the reaction gas, or using carbon mono-oxide(CO) as a source gas, diamond films have been fabricated at low temperature and high speed.

In the reaction gas, however, it is necessary to contain a large amount of hydrogen atoms. Recently Yoshimoto et al. succeeded in fabrication of diamond in a hydrogen free condition by laser ablation of graphite target in oxygen ambience [9]. This success of the novel method for diamond growth indicates a possibility of different mechanism from the diamond growth in hydrogen.

In this work, to make it certain whether diamond can grow in a hydrogen free condition by a microwave plasma CVD, fabrication of diamond films at decreased hydrogen concentration is studied. Ramesham et al. reported that a diamond film of a poor quality was fabricated at a low hydrogen concentration of 6.54%[10].

2. EXPERIMENTAL

A Si(100) wafer cut in a square with sides of 15mm was used as a substrate. The substrate was cleaned with acetone and ethanol in an ultrasonic bath for 5 min in each, dipped in HF acid (5 vol%) to remove a surface oxide layer, agitated with diamond powder of 40 μm in size suspended in ethanol in the ultrasonic bath for 15min, and then cleaned with acetone and ethanol again. A schematic diagram of the microwave plasma CVD apparatus is shown in Fig.1. A reactor of a quartz

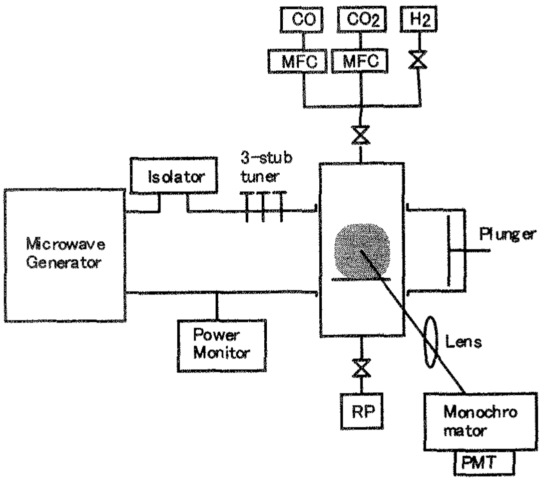


Fig. 1. Schematic of the experimental setup.

Table I Deposition parameters of diamond.

Sample	1	2	3	4	5
H_2 flow (sccm)	4.0	1.0~1.4	0.49	0.21	0.11
H_2 concentration (%)	25	7.7~10.4	3.9	1.7	0.91
Substrate temperature (℃)	960	1000	1000	1000	1050
Deposits and growth rate at center of substrate	Diamond 4 μ m/Hr	Diamond 6 μ m/Hr	Non Diamond	Sootlike	Sootlike
Deposits and growth rate at fringe of substrate	Diamond 1 μ m/Hr	Diamond 1.5 μ m/Hr	Diamond 3 μ m/Hr	Diamond 1 μ m/Hr	Nothing

tube of 36mm in diameter was set up and evacuated by a rotary pump to the base pressure of 8×10^{-1}Pa. The substrate was put on a sample stage of quartz supported in the reactor tube. A mixture of CO, CO_2, and H_2 gases was introduced to the reactor tube. The flow rates of CO and CO_2 fed through mass flow controllers were 12sccm and 0.02sccm, respectively. H_2 was controlled by a needle valve. The total pressure in the reactor tube was 5.33kPa. The substrate was located at 10mm below the center of a microwave resonator in which a microwave of 2.45GHz was introduced through a rectangular waveguide.

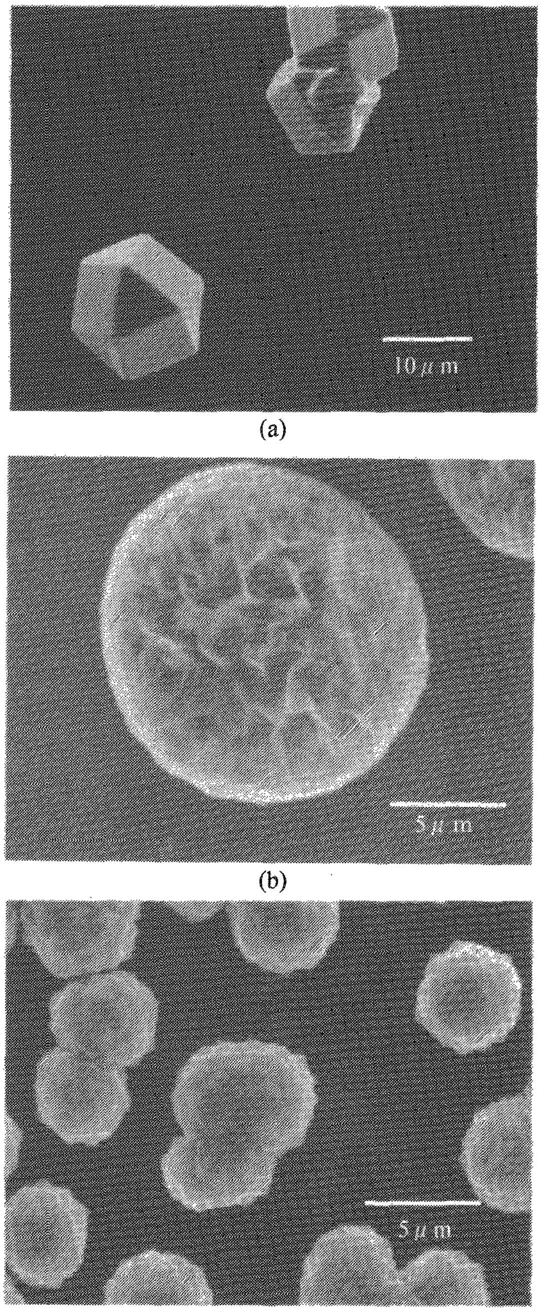
A plasma ball was maintained in the reactor tube by a microwave discharge. Microwave power was kept at about 500W in this work. The substrate was heated by the microwave plasma. The resulting temperature of the heated substrate was measured by an optical pyrometer through an observation window on the top of the reactor. The CVD process was carried out for 2 hours.

For characterization of the plasma, an optical emission spectroscopy (OES) measurement was carried out by a monochoromator(Shimazu SPG-100S). The optical emission from the center, or 10mm above the substrate, to a monochromator after being focused by a lens.

3. RESULTS AND DISCUSSION

Details on the deposition parameters are provided in Table I. The H_2 concentration is the ratio of H_2 flow rate to the total gas flow, i.e., $H_2/(CO+CO_2+H_2)$. The growth rate was estimated by measuring the diamond particle size on the scanning electron microscope(SEM) micrographs. The samples were investigated by micro-Raman scattering spectroscopy and identified as diamond by a sharp peak at 1332cm^{-1}.

Diamonds were deposited uniformly on the substrates of sample 1 and 2 as shown in Fig. 2(a). Figure 2(a) shows the SEM micrograph of the central part of sample 1. Sample 3 had black deposits in the central area of 8mm in diamiter. A SEM micrograph of the black deposits is shown in Fig. 2(b). Diamonds deposited on the fringe of the black deposits. A sooty black lump of 1mm height was deposited on the central area and a black thin film with diamond particles embedded was deposited on the fringe area of the black lump on sample 4. Figure 2(c) shows a SEM micrograph of the fringe area of sample 4. Sample 5 had the same sootlike deposit as sample 4, and nothing on



(a)

(b)

(c)

Fig. 2. SEM micrograph of deposits at
(a) center of sample 1 at H_2 concentration=25%
(b) center of sample 3 at H_2 concentration=3.9%
(c) fringe of sample 4 at H_2 concentration=1.7%

the fringe area.

At H_2 concentration more than 10%, diamonds were fabricated on whole the surface of the substrate. As H_2 concentration got lower, the deposits in the central area of the substrate became black. At H_2 concentration more than 1.7%, however, diamonds were still deposited in the fringe area of the black deposit in the central part. As the H_2 concentration was decreased below 1.7%, the black deposits became coarse and weak, or sooty deposits appeared.

Diamond growth rate increased and crystalinity deteriorated as H_2 concentration got lower due to insufficient etching of non-diamond phase during the growth. This result will support the growth mechanism of selective etching of non-diamond phase by atomic hydrogen.

During the deposition of sample 1 with 25% H_2, a white plasma ball spread to the reactor wall and covered whole surface of the substrate. With decreasing the concentration of H_2, plasma became greenish in color, smaller in size, and brighter due to increase in power density. The smaller plasma ball at lower H_2 concentration could not cover whole surface but only the center of the substrate.

Figure 3(a) and (b) show the optical emission spectra from the plasmas during the deposition of sample1 and 5, respectively. Both in the spectra, H α (Balmer line, 656.3nm), CH($A_2\Delta - X_2\Pi$, 431.4nm), OH($A^2\Sigma^+ - X^2\Pi$, 308.9nm), CO ($b\ {}^3\Sigma - a^3\Pi$, 3rd positive and 5B bands) , C(${}^1P^0 - {}^1S$, 247.9nm), C_2 ($A^3\Pi_g - X'^3\Pi_u$, swan bands) were observed. Emission peaks of H α and CH became lower and those of C and C_2 became higher, as the H_2 concentration got lower. The greenish plasma was due to the intense C_2 emission at lower H_2 concentration.

These results indicate the following. At lower H_2 concentration, C atoms could not be CH but C or C_2 in the plasma. Because of central part of the substrate was covered with the small plasma, in which had a large amount of C_2 and little atomic hydrogen were produced, the deposition of carbon was leading the selective etching of non-diamond phase. It has been expected that oxygen from decomposed CO would help the etching of non-diamond phase. In the result, however, it was insufficient for diamond growth in the small plasma at the lower H_2 concentration, and it resulted in sooty deposits. In the fringe area of the sooty deposits, apart from the plasma ball, the etching could match against the decreased flux of carbon due to the deposition of sooty carbon in the central area.

4. SAMMARY

Diamonds were fabricated by means of microwave plasma CVD from CO and CO_2 gas mixture with decreased amount of H_2. Diamond was fabricated on the whole substrate at H_2 concentration of more than 10%, while it was only in the fringe area of sooty deposits in the central part of the substrate at the lowest H_2 concentration of 1.7%.

With decreasing by H_2 concentration, plasma became greenish due to C_2 high emission intensity, and smaller in size resulting in localizing the deposition.

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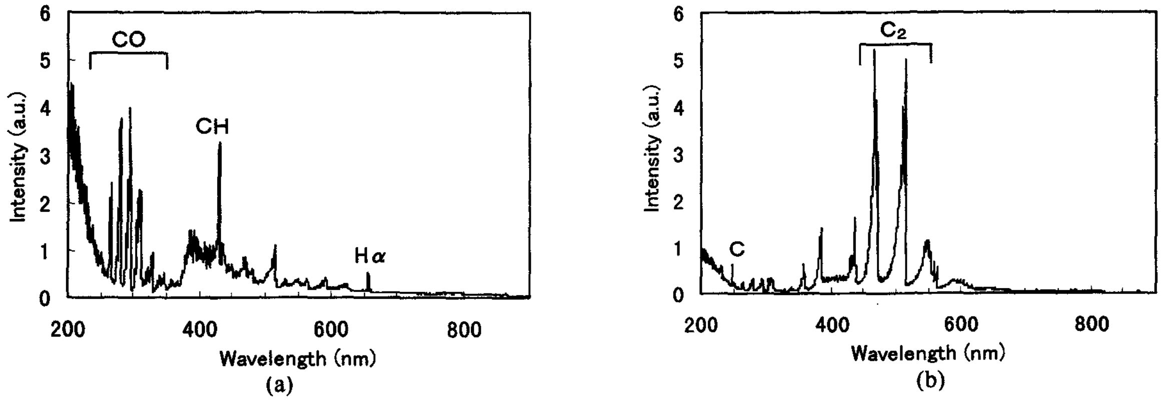

Fig. 3. Emission spectra of plasma during deposition of (a) sample 1 and (b) sample 5.

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