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Diamond synthesis from methane–hydrogen–water mixed gas using a microwave plasma

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Fine particles of diamond or diamond-like carbon were synthesized from methane–hydrogen–water mixed gas using a microwave plasma. The growth rate was several times as fast as that of methane–hydrogen mixed gas, which is the conventional method to prepare diamond from the gas phase. Promotion of the methane decomposition reaction and the removal reaction of byproduct graphite by OH radicals produced in the plasma were credited with enhancing the rate.

1. Introduction

Diamond is a desirable material because of its high hardness, thermal conductivity, electrical resistance and optical transparency. Considerable attempts have been made to synthesize it from the gas phase using various techniques, such as chemical vapour deposition (CVD) [1], plasma-induced vapour deposition (PCVD) [2] and ion-beam methods [3]. A mixed gas composed of methane and hydrogen has been used as feed gas in the conventional gas-phase decomposition method. On the other hand, Hirose and Terasawa [4] have used an acetone and hydrogen mixed gas to synthesize fine particles or film-like diamonds, at a high growth rate of 1 to $10\,\mu\mathrm{m\,h^{-1}}$, using a hot-filament CVD method. Some proposals were made as to the cause of the enhanced rate. These included easier decomposition of acetone as compared to methane, the effect of oxygen, etc., but no firm conclusion was drawn.

In the present investigation, diamond synthesis from a mixed gas composed of methane, hydrogen and water has been carried out. The effect of water addition to the mixed gas on diamond growth is reported for various conditions.

2. Experimental details

A schematic illustration of the experimental apparatus is shown in Fig. 1. A single-crystal silicon wafer (5 mm × 5 mm) was used as a substrate. The substrate was washed with hydrogen fluoride solution and placed on a porous silica glass plate in a silica tube (inner diameter: 18 mm; length: 300 mm). After evacuation to 10^{-1} Pa, a gas mixture composed of methane, hydrogen and water was introduced into the tube. Water content in the gas was varied by changing the temperature of the bubbling bottle. Methane–hydrogen mixed gas was also used as a feed gas to clarify the effect of water addition. Microwaves (2.45 GHz) were supplied through a resonator to generate a plasma in the tube. The reaction temperature was controlled to a predetermined value by adjusting the voltage supplied to a heater. The effects of microwave energy on the thermocouple were proved to be small by pyrometer measurements.

The pressure of the reaction tube was measured with a Pirani gauge. After the reaction, observation of the products on the silicon substrate was made using a scanning electron microscope (SEM) and the identification of the deposits was made by X-ray diffraction analysis and Raman spectroscopy.

Raman spectra were measured using the 488 nm line of an argon ion laser for excitation. Experimental conditions are summarized in Table I.

3. Results and discussion

3.1. Effect of water addition

Typical SEM pictures of the reaction products obtained from CH_4–H_2 and CH_4–H_2–H_2O systems under the same conditions are shown in Fig. 2. Small ball-like and larger cube-like particles are seen for the CH_4–H_2 and CH_4–H_2–H_2O systems, respectively. The sizes of the latter particles are three or four times those of the former. Few X-ray diffraction peaks are observed for deposits from the CH_4–H_2 system, besides those due to the silicon substrate. Raman spectra of these deposits show a broad peak at $1550\,\mathrm{cm^{-1}}$ which is very similar to the reported value for diamond-like carbon or i-carbon [5]. On the other hand, in the water-containing mixture prominent X-ray diffraction peaks are observed at interlayer spacings (*d* values) of 0.208, 0.127 and 0.108 nm which correspond to (1 1 1), (2 2 0)

TABLE I Experimental conditions

Substrate temperature (° C)	450 to 900
Pressure (Pa)	13 to 530
Feed gas (vol %)	
CH_4	1 to 10
H_2O	0 to 6.8
H_2	99 to 83.2

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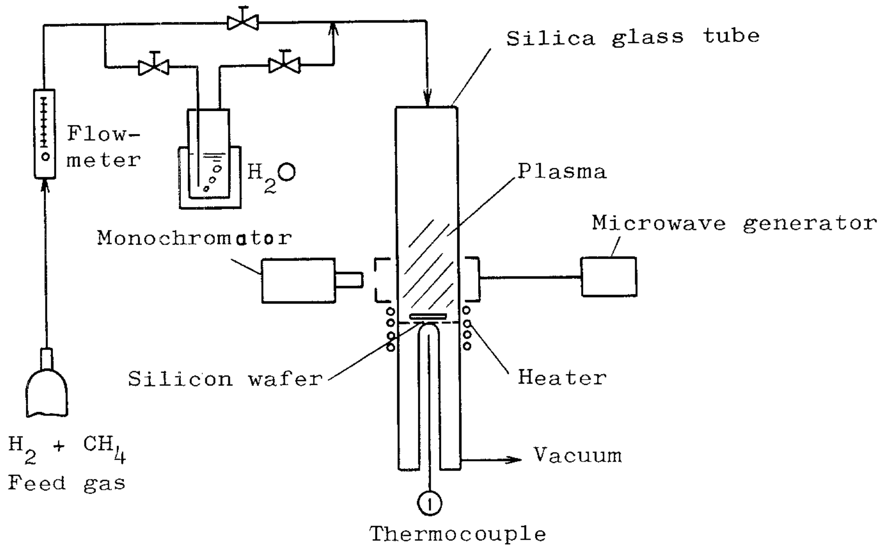

Figure 1 Experimental apparatus.

and (3 1 1) planes of diamond. The peaks at *d* values of 0.312 and 0.163 nm are due to the silicon substrate. The X-ray diffraction intensity ratios of 100 : 27 : 16 are also in good agreement with those for diamond reported elsewhere [6]. Raman spectra of the deposit from the CH_4–H_2–H_2O system shows a sharp peak very close to the value of 1332.5 cm^{-1} reported for natural diamond [7]. The broad peak is due to diamond-like carbon. These results indicate that the deposits from the CH_4–H_2–H_2O system are composed of diamond and diamond-like carbon. Although it seems that the amount of diamond-like carbon is larger than that of diamond based on the Raman spectra, this is not so, because the exciting argon laser ray cannot penetrate the deposits beyond several tens of nanometres due to the strong absorption by diamond-like carbon. Only surface-layer information is obtained from the Raman spectra for samples containing amorphous carbon such as diamond-like carbon.

In order to examine the effect of water addition on diamond growth, the emission of plasma from CH_4–H_2 and CH_4–H_2–H_2O systems was measured. The results are shown in Fig. 3. Excited hydrogen molecules, hydrogen atoms of the Balmer series (Hβ, Hr) [8], CH_2 and CH radicals are found in the spectra of the CH_4–H_2 mixed gas. In the case of CH_4–H_2–H_2O mixed gas, excited carbon monoxide molecules and OH radicals are found in addition to those in the CH_4–H_2 plasma. CH_3 radicals are not detected in these spectra. The intensities of the CH to Hβ radicals increase conspicuously with water addition to the CH_4–H_2 mixed gas. The results indicate that the decomposition of methane is promoted by water addition.

A possible mechanism of diamond formation from CH_4–H_2–H_2O mixed gas, based on plasma spectroscopy, is shown in Fig. 4. Hydrogen and water in the feed gas are dissociated into H and OH radicals by excited electrons in the plasma. Methane is dehydrogenated to CH_3, CH_2 and CH radicals by H and OH radicals or excited electrons produced in the plasma. These hydrocarbon radicals are adsorbed on the silicon substrate and thermally decomposed to diamond, diamond-like carbon (i-carbon) and graphite. The rate of graphite formation may be much larger than that of diamond or diamond-like carbon on account of the stable phase of graphite. However, graphite is selectively removed from the surface because it is much

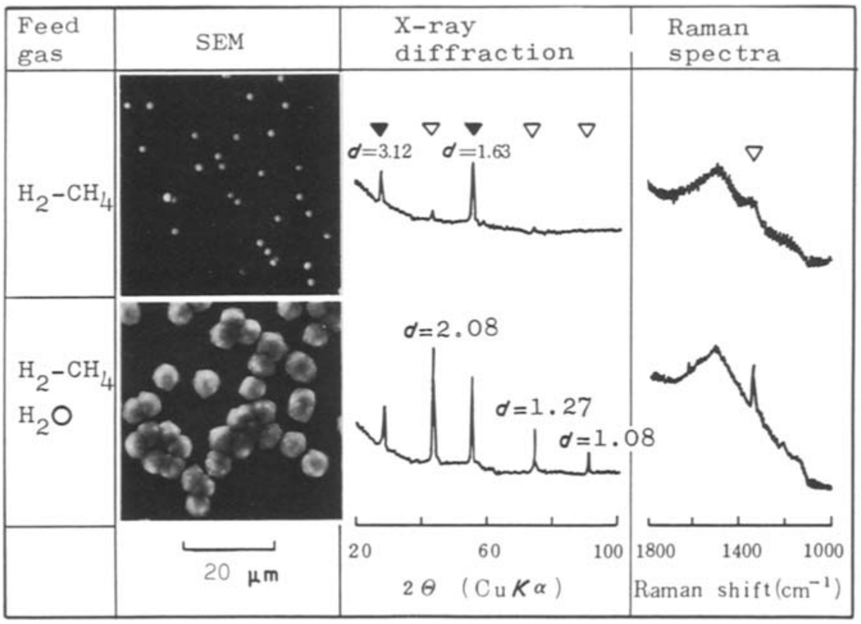

Figure 2 Deposits from CH_4–H_2 and CH_4–H_2–H_2O systems. (▼) Silicon, (▽) diamond.

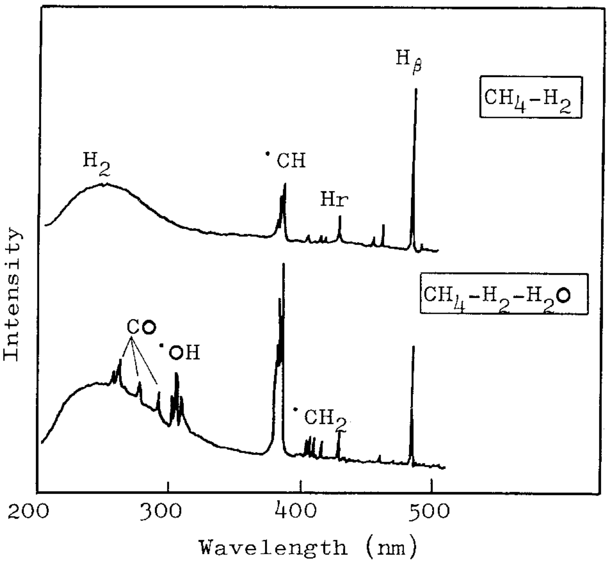

Figure 3 Plasma emission spectra of CH_4–H_2 and CH_4–H_2–H_2O mixed gases.

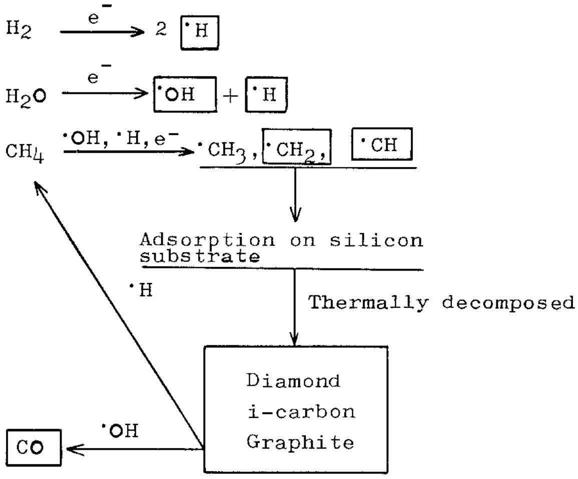

Figure 4 A possible mechanism of diamond formation from CH_4–H_2–H_2O mixed gas. Excited species detected in the plasma emission are enclosed by boxes.

more reactive towards H and OH radicals than diamond or diamond-like carbon, which leaves the latter two species behind. When H and OH radicals are present in relatively larger amounts, diamond-like carbon is also removed and only diamond remains. The effect of water addition can be considered as promotion of the methane decomposition and graphite removal reactions.

3.2. Effect of water vapour concentration

The concentration of water vapour was changed from 0 to 6.8 vol % under otherwise constant experimental conditions (10 vol % methane; 750° C substrate temperature; 265 Pa pressure). The growth rate of particles increases rapidly on addition of 1.3 vol % of water, but no increase in the growth rate of particles is observed for larger additions as shown in Fig. 5. X-ray diffraction studies of particles produced for water contents from 1.3 to 6.8 vol % show similar patterns. It is not clear at the present time why changing the water concentration from 1.6 to 6.8 vol % has no effect on diamond growth.

3.3. Effect of methane concentration

Experiments were carried out by changing the concentration of methane from 1 to 10 vol % under constan pressure, substrate temperature and water content The results are summarized in Fig. 6. No deposits are obtained for 1 vol % CH_4, which is the usual concentration of methane used to prepare diamond by PCVD with CH_4–H_2 mixed gas [2]. Deposited carbon including diamond must be removed by reaction with H and OH radicals in the plasma. This fact suggests that OH radicals have a greater reactivity towards deposited

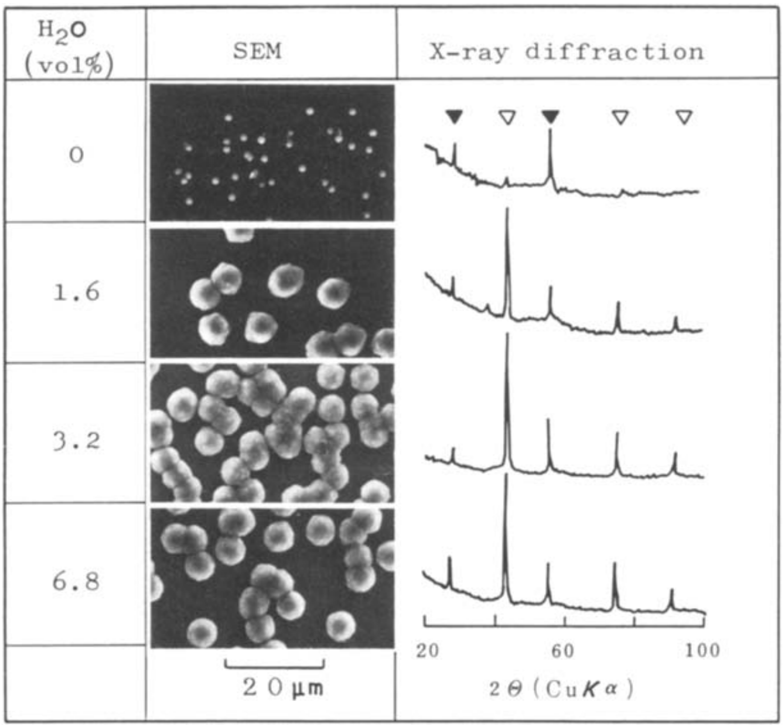

Figure 5 Effect of water concentration on diamond formation. (▼) Silicon, (▽) diamond.

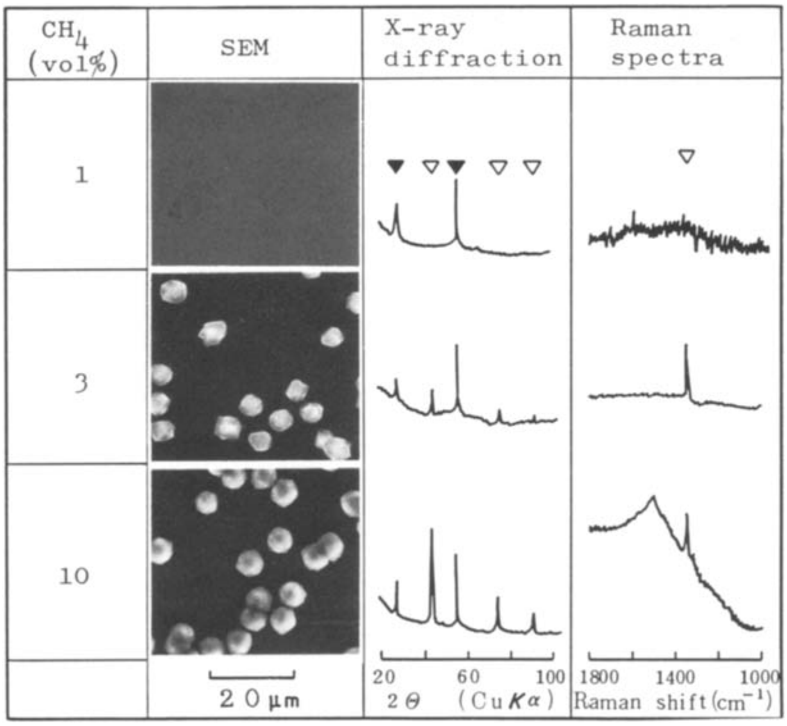

Figure 6 Effect of methane concentration on diamond formation. (▼) Silicon, (▽) diamond.

carbon than H radicals. As the concentration of methane is increased to 3 vol %, well-defined particles are formed. The deposits are identified as a clear diamond, judging from X-ray diffraction and Raman spectra analyses. As the methane concentration is increased even more, the growth rate of the particles increases but the morphologies of the particles changes from well-defined to cube-like. The particles prepared from 10 vol % CH_4 show the coexistence of diamond and diamond-like carbon.

In order to prepare pure diamond, it appears that the methane concentration is an important factor.

3.4. Effect of substrate temperature

The effect of substrate temperature on diamond formation is shown in Fig. 7. On increasing the substrate temperature, the number and size of deposits have a tendency to increase. On the other hand, the morphologies of deposits change from well-defined to cube-like or ball-like. The fact that the diamond formation rate increases with increasing temperature supports our way of thinking, that hydrocarbon radicals adsorbed on the silicon substrate surface are decomposed thermally to carbon as shown in Fig. 6. In the experiments, diamond is formed at as low a

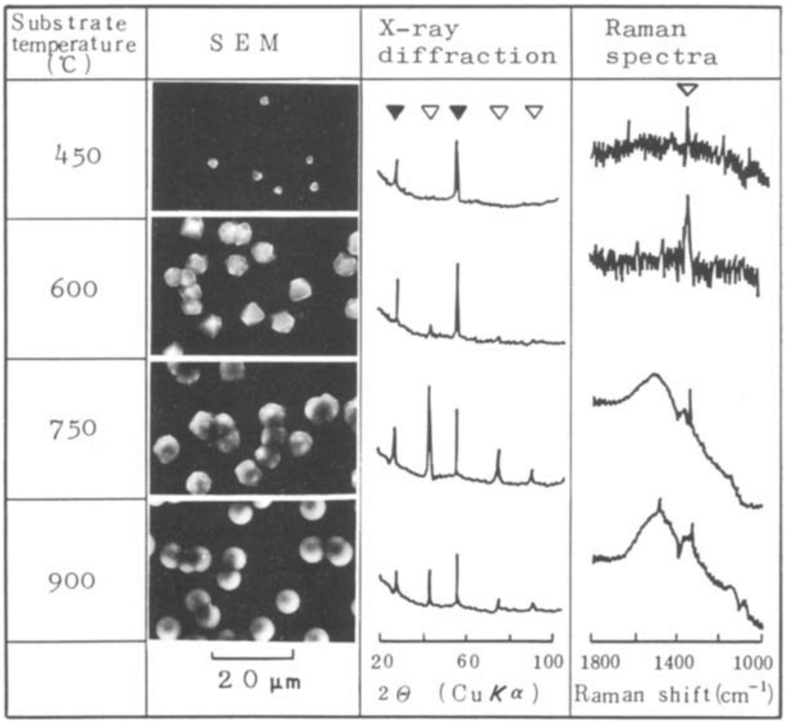

Figure 7 Effect of substrate temperature on diamond formation. (▼) Silicon, (▽) diamond.

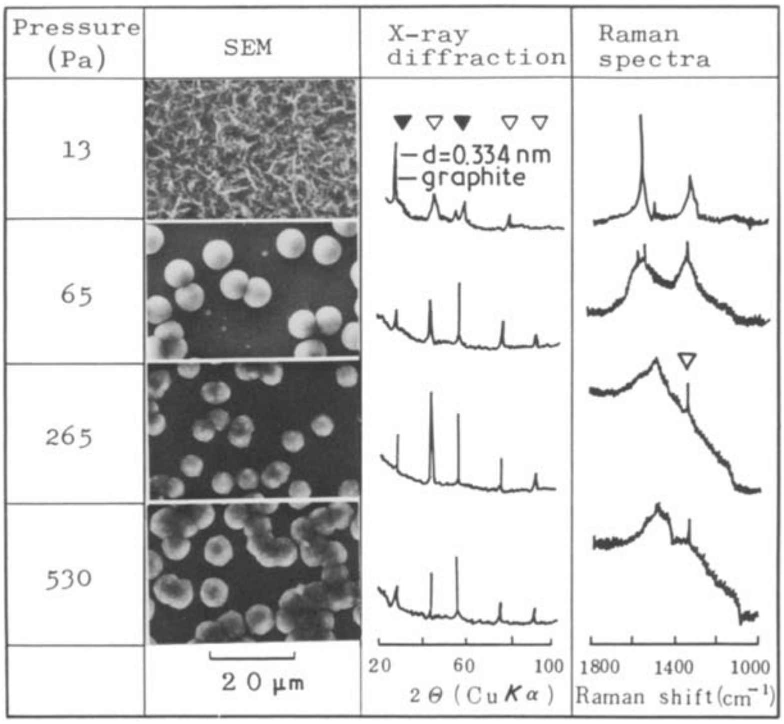

Figure 8 Effect of pressure or gas flow rate on diamond formation. (▼) Silicon, (▽) diamond.

substrate temperature as 450° C. No diamond formation has been reported at a substrate temperature below 600° C for the PCVD method using CH_4–H_2 gas.

It appears that water addition reduces the substrate temperature necessary for diamond formation.

3.5. Effect of pressure and flow rate

In the apparatus, the reaction pressure was changed by controlling the flow rate under a constant evacuation speed. Therefore, lower pressure means a lower flow rate. Pressures of 13 and 530 Pa correspond to $10\,cm^3\,min^{-1}$ and $300\,cm^3\,min^{-1}$ at STP, respectively. Soot-like deposits are seen on the substrate at 13 Pa pressure as shown in Fig. 8. X-ray diffraction of the deposits at a d value of 0.334 nm can be ascribed to graphite. Raman spectra of the deposits show two peaks at 1360 and $1580\,cm^{-1}$ which are similar to the reported values for disordered pyrolytic carbon from hydrocarbon [9], except for differences in their intensity and width. Although disordered pyrolytic carbon has nearly equal intensity for the two peaks, and their peaks are broad, in the present case the peak intensity is much stronger at $1580\,cm^{-1}$ than at $1360\,cm^{-1}$, and the peak at $1580\,cm^{-1}$ is sharp. It can be attributed to the co-existence of graphite, which also has a rather sharp Raman peak at $1580\,cm^{-1}$ [9]. Under a low gas pressure and flow rate, the rate of graphite or disordered carbon formation is higher than that of removal and consequently graphite and disordered carbon remain. It seems that a high plasma density under a low gas pressure promotes the decomposition of methane. It is important in preparing diamond that the feeding rate of hydrocarbon radicals to the substrate is made slower than the removal reaction rate of byproduct graphite.

At higher pressures than 13 Pa, diamond and diamond-like carbon are formed instead of graphite or soot-like carbon. The growth rate of the particles increases slightly with increasing pressure.

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