JOURNAL OF MATERIALS SCIENCE 25 (1990) 1246–1250

Diamond synthesis from CO–H_2 mixed gas plasma

YUKIO SAITO, KOUJI SATO, KENICHI GOMI, HIROSHI MIYADERA
Hitachi Research Laboratory, Hitachi Ltd, Hitachi-shi, Ibaraki, Japan 319-12

Particulate or film-like diamond was prepared on silicon substrates from CO–H_2 mixed gas using a microwave plasma technique. The growth rate of diamond without graphite and amorphous carbon, as measured by Raman spectroscopy, was $9\,\mu m\,h^{-1}$ for particles and $4\,\mu m\,h^{-1}$ for flims. These values were larger than those in other source gas systems, such as CH_4–H_2, CH_4–H_2–H_2O and CH_3OH–H_2. The good formation rate and high quality of diamond in the CO–H_2 system was attributed to acceleration of methyl radical formation by the reaction of excited CO and H_2 molecules and removal of by-product graphite by OH radicals in the plasma.

1. Introduction

Several methods to prepare diamond from the gas phase have been developed. They include chemical vapour deposition (CVD) [1], thermo-filament CVD [2], plasma CVD [3], electron-assisted plasma CVD [4], and laser-induced CVD [5]. In all of these, CH_4 or a CH_4–H_2 mixture has been used as a source gas. A study on the source gas system has been made by Hirose and Terasawa [6] using a thermo-filament CVD method. They reported that organic compounds such as CH_3OH, CH_3COCH_3 and CH_3CHO are good source gases for the promotion of diamond growth rate and purification. We have also been studying source gas systems, and have reported that the CH_4–H_2–H_2O system is good for diamond synthesis with a high formation rate and purity [7]. The above-mentioned source gases all include the methyl group.

On the other hand, we have found that diamond can be made at a rather high deposition rate using a microwave plasma method from a CO–H_2 mixture, which does not include methyl groups [8]. A similar result has also been reported by Ito *et al.* [9], but details of the source gas system were not examined.

In the present study, diamond particles or films were synthesized on silicon substrates from CO–H_2 plasma under various experimental conditions and the diamond growth rate compared with the results obtained from other source gas systems such as CH_4–H_2, CH_4–H_2–H_2O and CH_3OH. The diamond formation mechanism from the CO–H_2 system was also investigated.

2. Experimental procedure

The microwave plasma CVD apparatus used in the present experiments is shown in Fig. 1. A silica glass tube (i.d. 40 mm; length 1000 mm) was used as a reactor. A single-crystal silicon wafer (20 mm diameter), with a mirror finish, was used as the substrate on which the diamond particles were deposited. To obtain film-like diamond, the substrate was polished with diamond paste (particle size 1 μm). These substrates were held at about the centre of the reaction tube by a columnar substrate holder. After evacuation of the tube by a rotary pump, CO and H_2 were supplied to the tube through the mass flow meter. In separate experiments, CH_4–H_2, CH_4–H_2–H_2O and CH_3OH–H_2 mixed gases were also fed to the tube to clarify the behaviour of the CO–H_2 system regarding the diamond growth rate. H_2O and CH_3OH were vaporized into the feed gas by a bubbling method and the concentration was varied by changing the bubbling bottle temperature.

Microwaves (2.45 GHz) were introduced into the tube and a plasma of the mixed gas was generated. The substrate was heated to several hundred degrees centigrade by microwave power and the temperature was controlled at a predetermined value by a gas cooler when necessary. The temperature was measured using a pyrometer. After reaction, products on the silicon substrate were observed by scanning electron microscopy (SEM) and identified by low-angle X-ray diffractometry and Raman spectroscopy.

The experimental conditions are summarized in Table I.

TABLE I Experimental conditions

Feedstock gas	CO (2.5 – 100%) + H_2 CH_4 (0.5 – 3%) + H_2 CH_4 (1 – 10%) + H_2 + H_2O CH_3OH (1 – 10%) + H_2
Total gas flow rate	50 – 100 $cm^3\,min^{-1}$
Microwave power	0.3–0.7 kW (2.45 GHz)
Pressure	1.3–6.7 kPa
Substrate temperature	700–900° C
Substrate	Si (100), 20 mm diameter

3. Results and discussion

3.1. Synthesis conditions

Diamond synthesis conditions from CO–H_2 plasma were first investigated. Fig. 2 shows SEM photographs of deposits on the silicon substrate polished

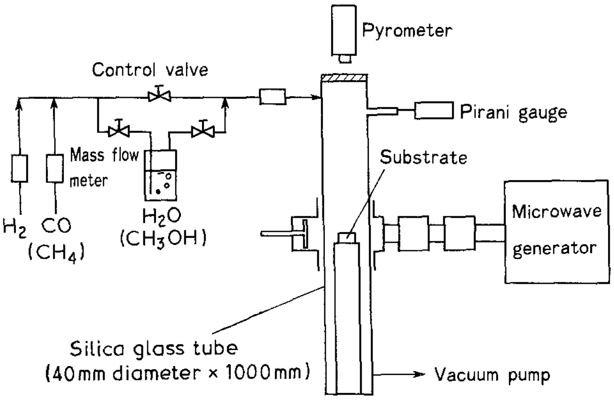

Figure 1 Experimental apparatus.

with diamond paste. These products are obtained by changing the CO concentration from 5% to 100% under constant temperature (800° C), pressure (5.3 kPa) and reaction time (1 h). Polycrystal-like deposits can be seen clearly for CO = 5%. Crystal grains of the deposits become obscure as the CO concentration increases, and the products at CO = 100% show fine flower-like shapes. Low-angle X-ray diffraction patterns and Raman spectra corresponding to these deposits are shown in Fig. 3. Up to CO concentrations of 50%, the 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) and (3 1 1) planes of diamond [10]. But the width of the diffraction peaks increases with CO concentration. This result means that the crystallinity of the deposited diamond become less as the CO concentration increases. The Raman spectra also show this trend clearly. Only one sharp Raman peak corresponding to diamond is observed at 1332 cm^{-1} in the films prepared at CO concentrations of 5 and 10%. This peak and another broad one at around 1530 cm^{-1}, derived from amorphous carbon (or i-carbon) [11] are observed in the films obtained at CO concentrations of 30 and 50%. Deposits at CO = 100% shown only the X-ray diffraction and Raman spectra due to graphite. The desirable CO concentrations to prepare pure diamond are considered to be 5 to 10% based on the above results.

Desirable temperatures and reaction pressures were also investigated. Suitable temperatures and pressures for diamond preparation from the $CO-H_2$ system are 750 to 850° C and 4 to 6 kPa which are much the same as those of the CH_4-H_2, $CH_4-H_2-H_2O$ and CH_3OH-H_2 systems.

3.2. Comparison of source gas systems

Fig. 4 shows SEM photographs of deposits on mirror finished silicon substrate from CH_4-H_2, $CH_4-H_2-H_2O$, CH_3OH-H_2, and $CO-H_2$ systems under the same conditions of temperature (800° C), pressure (5.3 kPa), and reaction time (1 h). The concentrations of carbon source gas shown in the figure are different for each system. The carbon concentrations chosen are those suitable to prepare pure diamond with a high growth rate in each of the systems. Particles deposited from each system have well-defined characteristics. Low-angle X-ray diffraction and Raman spectroscopy of the deposits reveal that the deposits are diamond and exclude amorphous carbon and graphite. The predominant crystal faces appearing are (1 1 1) and (1 0 0) faces of diamond. Cubo-octahedral and twinned crystals are observed. On the other hand, the particle size is conspicuously different in each system. Particles made from $CH_4-H_2-H_2O$, CH_3OH-H_2 and $CO-H_2$ systems are several times larger than those made from the CH_4-H_2 system. The largest particles are those made from the $CO-H_2$ system and their growth rate is about 9 $\mu m\,h^{-1}$.

Fig. 5 shows the relationship between the diamond growth rate and carbon concentration in each system.

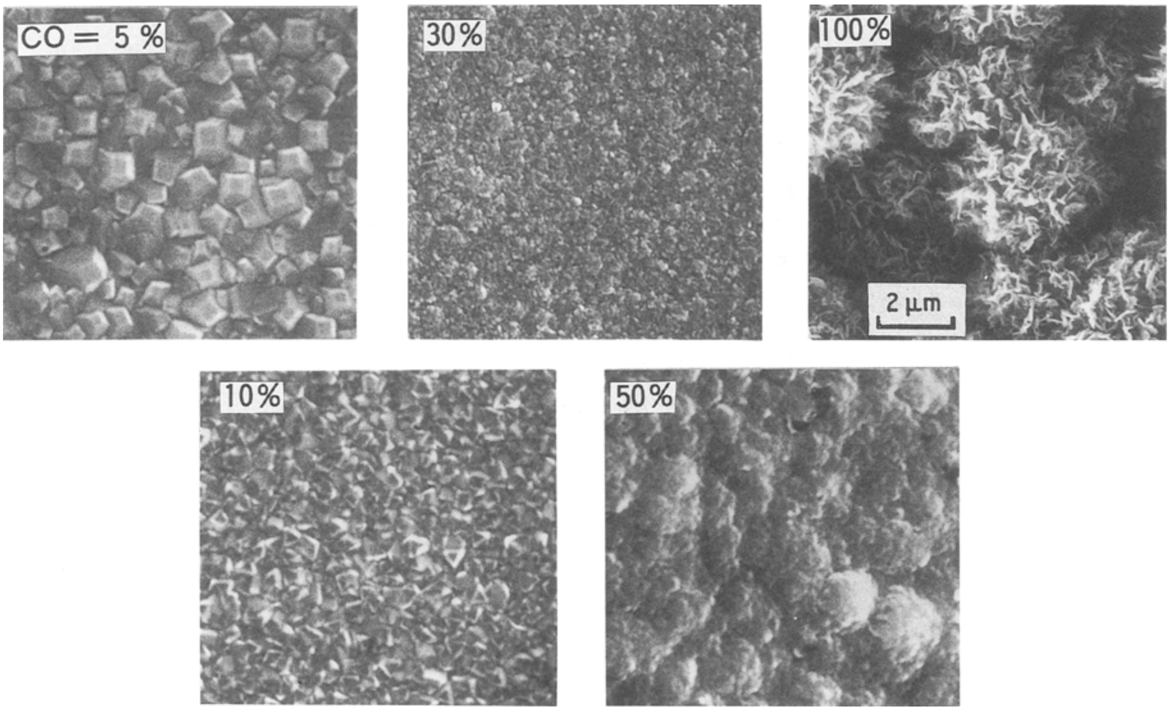

Figure 2 Scanning electron micrographs of deposits on the silicon substrate formed under various CO concentrations at 800° C, 5.3 kPa, 1 h.

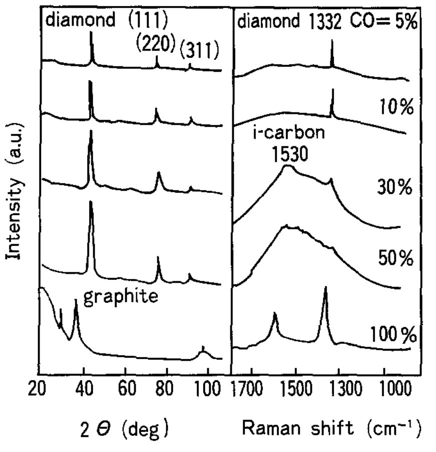

Figure 3 X-ray diffraction patterns and Raman spectra of the deposits shown in Fig. 2.

in the CH_4–H_2 system, amorphous carbon-free diamond films are formed for under 1% carbon concentration, but the films obtained at 3% carbon concentration contain amorphous carbon, based on the Raman spectroscopy data of these films. The diamond film growth rate is about $0.5\,\mu m\,h^{-1}$. In the CH_4–H_2–H_2O and CH_3OH–H_2 systems, diamond films are obtained at the higher carbon concentration of 3%. The diamond formation rate is about $2\,\mu m\,h^{-1}$ which is about four times as fast as that in the CH_4–H_2 system. However, the films obtained at a carbon concentration of 10% include amorphous carbon. In the present CO–H_2 system, no deposits are observed at CO = 1%. At CO = 3%, slight deposits are seen. Diamond films free from amorphous and graphite carbon are obtained at up to 10% CO concentration. The growth rate at CO = 10% is about $4\,\mu m\,h^{-1}$ which is the fastest among the inspected systems. Diamond-like films composed of diamond and amorphous carbon are formed at higher CO concentrations of 50%. The CO–H_2 mixed gas is a good system to prepare pure diamond at a high growth rate using the microwave plasma technique.

3.3. Formation mechanism

A diamond formation mechanism from the CH_4–H_2 system has been presented by Tsuda *et al.* [12]. They described the methyl radical or cation methyl radical as the key species for diamond crystal growth from the gas phase. This is reasonable, considering the system's thermo-dynamics. In this study, diamond formation was proposed via methyl radicals in the CO–H_2 system which has no methyl group in the molecules. In this section, diamond formation from CO is considered. Fig. 6 shows plasma emission spectra of CH_4(1%)–H_2, CH_4(3%)–H_2–H_2O(1.6%), CH_3OH(3%)–H_2, and CO(10%)–H_2 systems. Excited hydrogen molecules, hydrogen atoms of the Balmer series ($H\beta$, $H\gamma$), and CH and CH_2 radicals are found in the plasma. On the other hand, excited carbon monoxide molecules and OH radicals are found in the CH_4–H_2–H_2O, CH_3OH–H_2 and CO–H_2 systems in addition to those species in the CH_4–H_2 system. The relative intensity of the excited carbon monoxide molecules and OH radicals to $H\beta$ are different. The relative intensities in the CO–H_2 system are two or three times larger than those of the CH_4–H_2–H_2O and CH_3OH–H_2 systems.

A possible mechanism for diamond formation from CO–H_2 plasma is shown in Fig. 7. Hydrogen and carbon monoxide molecules are excited by accelerated electrons produced in the plasma and part of the excited species is dissociated into H, C and O radicals. Methyl radicals can be formed through two routes. One is the source of the direct reaction between C and

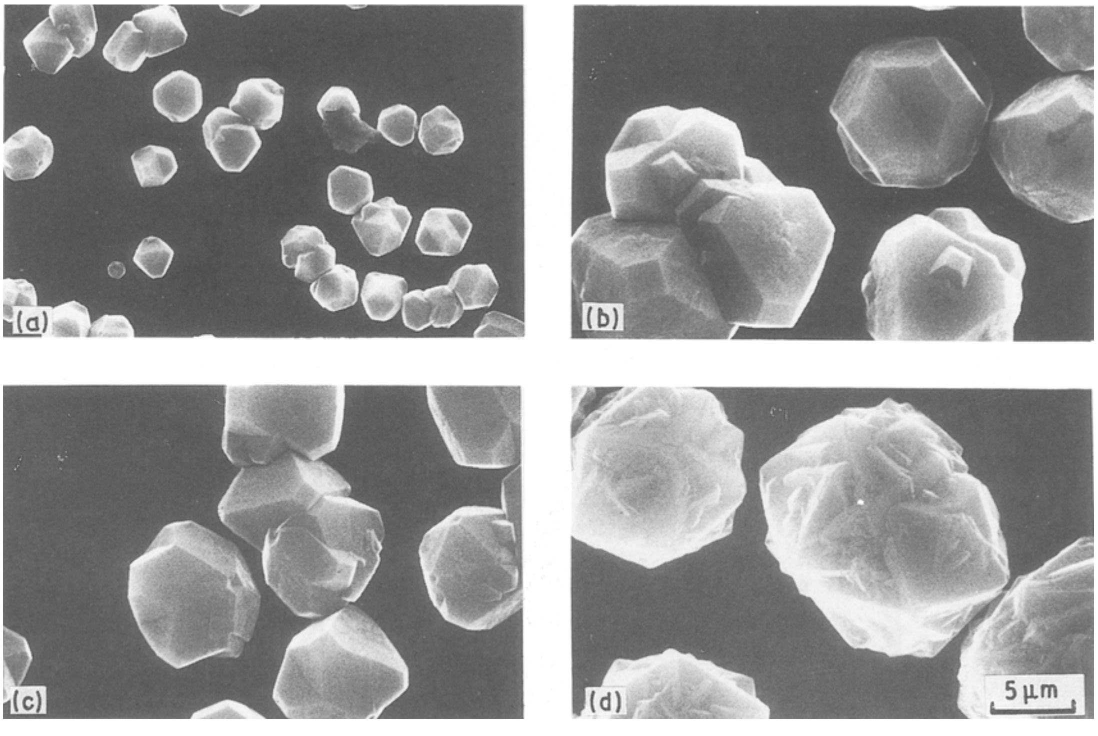

Figure 4 Scanning electron micrographs of deposits prepared under the same conditions (800° C, 5.3 kPa, 1 h) for each system: (a) CH_4 (1%) + H_2; (b) CH_4 (3%) + H_2 + H_2O; (c) CH_3OH (3%) + H_2; (d) CO (10%) + H_2.

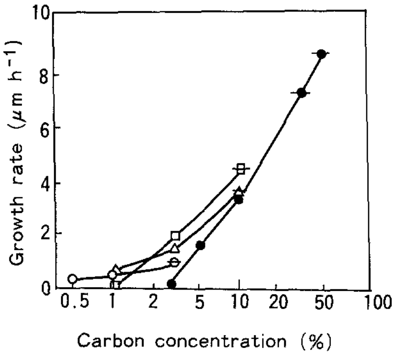

Figure 5 Comparison of diamond film growth rates: (○) CH_4–H_2; (△) CH_3OH–H_2; (□) CH_4–H_2–H_2O; (●) CO–H_2; (——) contained i-carbon.

H radicals. But the reaction cannot explain the high diamond formation rate in the CO–H_2 system compared to the CH_4–H_2 system, because a high methyl radical formation rate is not expected on account of the much larger bond energy of C = O (975 kJ mol^{-1}) compared to that of CH_3–H (435 kJ mol^{-1}). Another possible source is the reaction between excited carbon monoxide and hydrogen molecules. Carbon monoxide reacts with excited hydrogen molecules or radicals to form atomic carbon and water. The atomic carbon reacts with hydrogen molecules or radicals to form methyl radicals and other radicals such as methylene and methyne. These radicals are adsorbed on the substrate surface and thermally decomposed to diamond, amorphous carbon and graphite. Diamond can be formed from methyl radicals which have a tetrahedron structure like diamond. Amorphous carbon and graphite are more reactive towards H and OH radicals than diamond [13], so these carbons are removed selectively and diamond remains.

The next two experiments support the proposed diamond formation via methyl radicals in the CO–H_2 system. Methane is detected in the exhausted gas from the plasma reactor by gas chromatograph analysis. Methane formation is attributed to the reaction of the methyl radical and hydrogen or hydrogen atoms. Diamond is not formed from CO–O_2 mixed gas plasma under various CO concentrations. Only graphite is found by low-angle X-ray diffraction. This result indicates that diamond cannot be formed from carbon atoms. The higher rate and purer diamond formation in the CO–H_2 system compared to CH_4–H_2, CH_4–H_2–H_2O and CH_3OH–H_2 systems is ascribed to the following two reasons. (1) The methyl radical formation rate is hastened by the reaction of excited carbon monoxide and hydrogen molecules which does not take place in the CH_4–H_2 system. Concentrations of excited carbon monoxide and hydrogen molecules in the CO–H_2 plasma are higher than in the CH_4–H_2–H_2O and CH_3OH–H_2 systems shown in Fig. 6. (2) The removal reaction of the by-products of amorphous and graphite carbon is also hastened by OH radicals. The OH radicals are more reactive towards the carbon by-products than by H radicals [13] and their concentration is higher than in the CH_4–H_2–H_2O and CH_3OH–H_2 systems shown in Fig. 6.

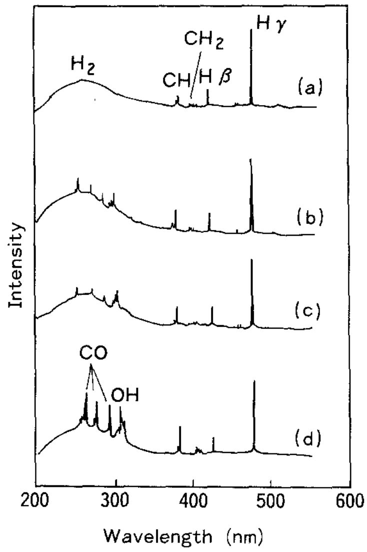

Figure 6 Plasma emission spectra of each system under microwave power of 0.7 kW and pressure of 1.3 kPa. (a) CH_4 (1%) + H_2, (b) CH_4 (3%) + H_2 + H_2O, (c) CH_3OH (3%) + H_2, (d) CO (10%) + H_2.

The higher diamond formation rate in the CH_4–H_2–H_2O and CH_3OH–H_2 systems compared to the CH_4–H_2 system may also be ascribed to the formation of excited carbon monoxide and hydrogen molecules.

4. Conclusion

The CO–H_2 feed gas system was investigated and compared with other systems of CH_4–H_2, CH_4–H_2–H_2O and CH_3OH–H_2 as source gases for diamond formation rate and purity; the CO–H_2 system was best. Diamond growth rates of 9 μm h^{-1} for particles and 4 μm h^{-1} for films were obtained. The high formation rate and quality of the diamond obtained in the CO–H_2 system must be due to the acceleration of the methyl radical formation rate by the reaction of excited CO and H_2 molecules and the removal reaction of by-product carbon by OH radicals produced in the plasma.

Acknowledgement

The authors thank Dr Kenichi Souma, Hitachi Research Laboratory, Hitachi Ltd, for assistance with the plasma emission spectra measurements.

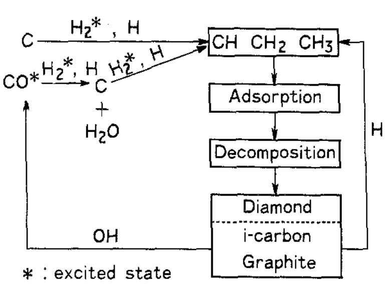

Figure 7 A possible mechanism of diamond formation from CO–H_2 plasma.

References

1. B. V. DERYAGUIN, D. V. FEDOSEEV, V. M. LYKUANOVICH, B. V. SPITSYN, V. A. RYANOV and A. V. LAVRENTYEV, *J. Cryst. Growth* **2** (1968) 380.
2. S. MATSUMOTO, Y. SATO, M. TSUTSUMI and N. SETAKA, *J. Mater. Sci.* **17** (1982) 3106.
3. M. KAMO, Y. SATO, S. MATSUMOTO and M. SETAKA, *J. Crysal Growth* **62** (1983) 642.
4. A. SAWABE and T. INUZUKA, *Appl. Phys. Lett.* **46** (1985) 146.
5. K. KITAHAMA, K. HIRATA, H. NAKAMATSU, S. KAWAI, N. FUJIMORI, T. IMAI, H. YOSHINO and A. DOI, *ibid.* **49** (1986} 634.
6. Y. HIROSE and Y. TERASAWA, *Jpn J. Appl. Phys.* **25** (1986) 519.
7. Y. SAITO, K. SATO, H. TANAKA and K. FUJITA, *J. Mater. Sci.* **23** (1988) 842.
8. Y. SAITO, K. SATO, H. TANAKA and K. FUJITA, Kokai Tokkyo Koho (Japanese Patent), 62-265197 (1987).
9. K. ITO, T. ITO and I. HOSOYA, *Chem. Lett.* **4** (1988) 589.
10. ASTM X-ray powder data file 6-675 (American Society for Testing and Materials, Philadelphia, Pennsylvania, 1956).
11. G. GAUTHERIN and C. WEISSMANTEL, *Thin Solid Films* **50** (1978) 1642.
12. M. TSUDA, M. NAKAJIMA and S. OIKAWA, *Jpn J. Appl. Phys.* **26** (1987) 527.
13. H. TANAKA, Y. SATO, Y. SAITO and H. MIYADERA, International Symposium on Plasma Chemistry, Tokyo, August 1987, edited by K. Akashi and A. Kinbara (Ionic Ltd, Tokyo, 1987) p. 2463.

Received 4 October 1988
and accepted 28 February 1989