CHEMISTRY LETTERS, pp. 589-592, 1988.

Diamond Synthesis by the Microwave Plasma CVD Method Using a Mixture of Carbon Monoxide and Hydrogen Gas (I)

Kazuomi ITO, Toshimichi ITO, and Ikuo HOSOYA

Department of Planning and Development, Idemitsu Petrochemical Co., Ltd.

The authors have succeeded in diamond synthesis by a microwave plasma chemical vapor deposition (plasma CVD) method using a mixture of CO and H_2 gas, which had been thought to be difficult to achieve. The growth rate when using CO as the feedstock gas is about several times faster than that when using CH_4.

Diamonds are synthesized conventionally by the vapor phase method, by various kinds of plasma, using hydrocarbon-hydrogen mixed gas,[1] hydrocarbon-hydrogen mixed gas to which H_2O,[2] O_2,[3] or CO[4] was added, a mixture of oxygen-containing organic compounds such as alcohols or acetones and hydrogen, or a mixture of

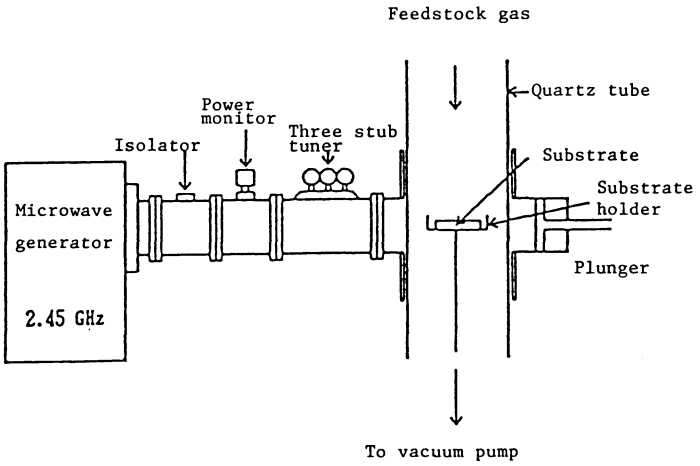

Fig. 1. Schematic diagram of plasma CVD apparatus.

Table 1. Experimental conditions

Microwave frequency	2.45 GHz
Microwave power	300 to 500 W
Feedstock gas	CO + H_2
CO/(CO + H_2)	5 to 100 vol%
Total flow rate	100 SCCM
Gas pressure	5.3 kPa
Substrate temp	900 °C
Substrate	Si (100)

nitrogen-containing organic compounds such as amines and hydorgen gas.[5] It is presumed that these reactions proceed via methyl radicals.[6,7]

The authors attempted diamond synthesis using, as the feedstock gas, CO gas which is generally thought to be difficult to use for diamond synthesis, and were successful. It is assumed from these findings that this reaction may proceed by a mechanism not explained by the conventional methyl radical theory alone.

Figure 1 shows a sketch of the diamond synthesis apparatus by the microwave plasma CVD method. The apparatus is almost similar to that developed by Kamo et al. in the National Institute for Research in Inorganic Materials.[1]

Table 1 shows the conditions of diamond synthesis. Microwave power was controlled to maintain the temperature of the substrate at 900 °C. The surface of the silicon used as the substrate was scratched with diamond power. The reaction product deposited on the silicon substrate was observed mainly by scanning electronic microscopy (SEM) and its structure was evaluated by Raman spectroscopy and X-ray diffractiometry.

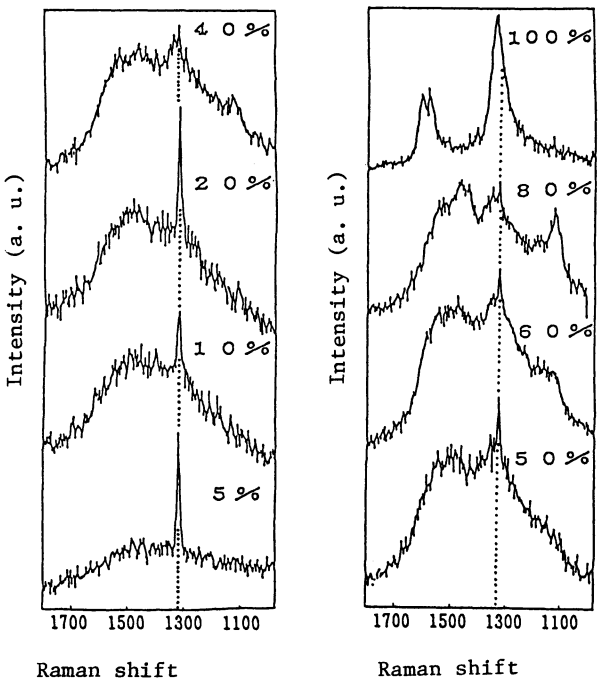

Fig. 2. Raman spectra of deposited films with various CO concentrations.

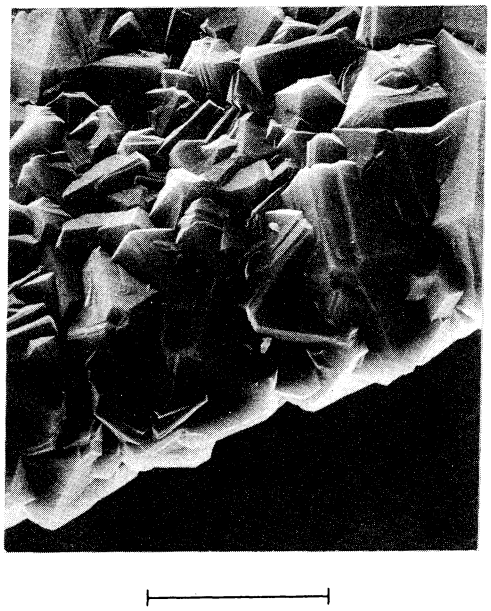

Fig. 3. A SEM image of a diamond thin film obtained at a CO concentration of 20 vol%.

Figure 2 shows the CO-concentration dependence of the Raman spectra of the thin films deposited from the CO-hydrogen mixed system using the microwave plasma CVD method on the silicon substrate. Only a sharp Raman peak was observed at 1332 cm^{-1} from the film obtained at a CO concentration of 5 vol%. The peak for diamond is observed at 1332 cm^{-1} up to a CO concentration of 80 vol%, while a wide range spectra at around 1550 cm^{-1} derived from noncrystalline carbon (i-carbon) appeared at a CO concentration up from 10 vol%. It is concluded that pure diamond was synthesized at a CO concentration of 5 vol% and diamonds could be synthesized up to a CO concentration of 80 vol%.

The peak for diamond is generally observable up to a CH_4 concentration of about 1 vol% in a CH_4-hydrogen mixed system, while diamond was deposited up to high CO concentrations in a CO-hydrogen mixed system.

Figure 3 shows the SEM image of diamond thin film synthesized at a CO concentration of 20 vol%. A thin film with euhedral crystals is observed. The growth rate was estimated at 1.6 μm/h from the SEM image. The growth rate when using CO was about several times faster than that when using CH_4.

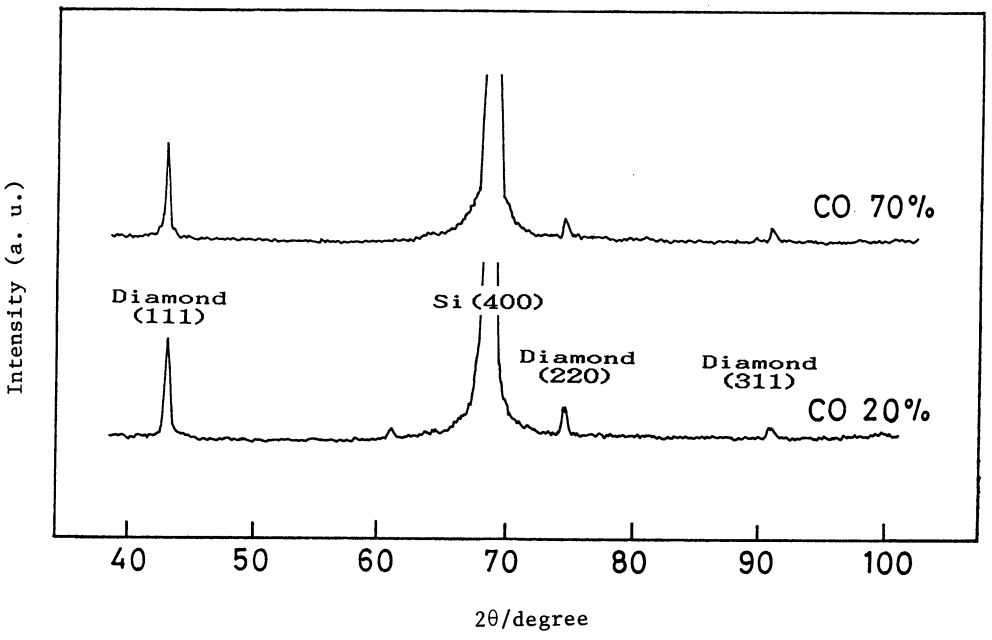

Fig. 4. X-Ray diffraction patterns of thin films obtained at a CO concentration of 20 vol% and 70 vol%.

Figure 4 shows the X-ray diffraction patterns of the thin films obtained at a CO concentration of 20 vol% and 70 vol%. These diffraction patterns are in good agreement with the reported values of natural diamond. In neither of them was a peak corresponding to graphite observed.

From the above findings, there is no doubt that diamonds can be synthesized from CO. However, it is unlikely that methyl radicals could be formed in the gas system of CO and H_2 mixtures under those experimental conditions. It is necessary to explain this diamond synthesis by a reaction mechanism other than the conventional one. The reaction mechanism will be reported separately.

References

1) M. Kamo, Y. Sato, S. Matsumoto, and N. Setaka, J. Cryst. Growth, 62, 642 (1983).
2) Y. Saito, K. Sato, H. Tanaka, and K. Fujita, Proceedings of 1st Diamond Symposium, 1987, 67.
3) T. Kawato and K. Kondo, Jpn. J. Appl. Phys., 26, 1429 (1987).
4) Y. Hirose, Y. Terasawa, K. Takahashi, I. Matsushima, and K. Arai, Proceedings of the 47th Autumn Meeting, Jpn. J. Appl. Phys., 1986, 287.
5) Y. Hirose and Y. Terasawa, Jpn. J. Appl. Phys., 25, L519 (1986).
6) R. Mania, L. Stobierski, and R. Pampuch, Cryst. Res. Technol., 16, 785 (1981).
7) M. Tsuda, M. Nakajima, and S. Oikawa, J. Am. Chem. Soc., 108, 5780 (1986).

(Received December 11, 1987)