

# DEPOSITION OF DIAMOND FROM CH<sub>4</sub>-H<sub>2</sub> PLASMA, (CH<sub>3</sub>)<sub>2</sub>CO-H<sub>2</sub> PLASMA, AND CO-H<sub>2</sub> PLASMA IN MICROWAVE DISCHARGE

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Using a microwave discharge, diamond was deposited on silicon wafers from (CH<sub>3</sub>)<sub>2</sub>CO(1 vol.%)–H<sub>2</sub> and CO(10 vol.%)–H<sub>2</sub> plasmas as well as CH<sub>4</sub>(1 vol.%)–H<sub>2</sub> plasma at a pressure of 1.3 kPa. The substrates were covered with carbonaceous films and particles having crystal habit planes were detected by SEM observation. Deposits were identified as diamond by the X-ray diffraction method as well as Raman spectroscopy. CH radicals were identified by emission spectroscopy, in all three types of plasmas. The existence of CH<sub>x</sub> (x=1–4) radicals in the plasmas was confirmed by mass spectroscopy. Moreover, H<sub>2</sub>O was also identified in both the (CH<sub>3</sub>)<sub>2</sub>CO–H<sub>2</sub> and CO–H<sub>2</sub> plasmas. From the correlation between the deposits and the species in the plasmas, it is believed that diamond is synthesized through the formation of CH<sub>x</sub> radicals in the plasma.

## 1. Introduction

Diamond thin films have been deposited from a methane–hydrogen mixture gas plasma prepared using microwave discharge<sup>1</sup>. In this procedure, methyl radicals prepared in the plasma would be precursors of diamond deposition<sup>2,3</sup>. In other research, diamond has been synthesized using a carbon monoxide and hydrogen mixture as plasma gas in a microwave discharge<sup>4</sup>. In this case, precursors other than methyl radicals were considered for the diamond deposition. Moreover, the deposition of diamond at higher rates has been achieved from acetone–hydrogen mixture gas by the thermal CVD method<sup>5</sup>.

Since hydrocarbons are formed from the mixture of carbon monoxide and hydrogen using a catalyst as well as in the microwave discharge<sup>6</sup>, diamond may be deposited from the mixture of carbon monoxide and hydrogen through hydrocarbons. We have studied the effect of the additive gases to methane in the deposition of diamond using microwave discharge and have found experimentally that diamond was synthesized through methyl radicals<sup>7</sup>, after which we have carried out the deposition of diamond from acetone–hydrogen

and carbon monoxide–hydrogen mixture gases.

In the present paper, we discuss the scheme of diamond deposition from methane–hydrogen, acetone–hydrogen, and carbon monoxide–hydrogen plasmas prepared using microwave discharge from the characterization of deposits together with the identification of species in the plasmas.

## 2. Experimental

The apparatus used in the deposition of diamond is the same as that reported previously<sup>7</sup>. Methane, carbon monoxide, and hydrogen were introduced into the quartz discharge tube from their respective cylinders through flow meters. Acetone was introduced using hydrogen as a carrier gas from liquid kept at a desired temperature. The mixing ratios of the gases were maintained as follows: CH<sub>4</sub>(1 vol.%)–H<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>CO(1 vol.%)–H<sub>2</sub>, and CO(10 vol.%)–H<sub>2</sub>. After the evacuation of the discharge tube below  $5 \times 10^{-2}$  Pa, the gas mixtures were introduced into the discharge tube at 20 sccm gas flow rate and the pressure in the discharge tube was maintained at 1.3 kPa. The microwave discharge was ignited and the discharge was carried out for 2 h under 200 W of power in every case.



characterization methods as approximately the same materials.

### Emission spectroscopy of plasmas

Emission spectra from the CH<sub>4</sub>-H<sub>2</sub> plasma, the (CH<sub>3</sub>)<sub>2</sub>CO-H<sub>2</sub> plasma as well as CO-H<sub>2</sub> plasma prepared using microwave discharge were obtained in the wavelength region between 600 and 200 nm. The observed electronic transitions in these three types of plasmas are summarized in Table 1. In the CH<sub>4</sub>-H<sub>2</sub> plasma, H atoms and CH and C<sub>2</sub> radicals were observed. In the (CH<sub>3</sub>)<sub>2</sub>CO-H<sub>2</sub> and CO-H<sub>2</sub> plasmas, CO and OH radicals were observed in addition to those observed in the CH<sub>4</sub>-H<sub>2</sub> plasma. The CO radicals would be the fragments of (CH<sub>3</sub>)<sub>2</sub>CO and excited species of CO molecules; the OH radicals would be the fragments of water molecules which were formed by the reaction between CO radicals and H<sub>2</sub> molecules or H atoms in the plasma. The relative intensities of the band heads of molecules and of the lines of the H atom in the emission spectra of the three types of plasmas are given in Table 2. The relative intensi-

Table 2. Relative intensities of band heads and line in the emission spectra from plasmas

	CH <sub>4</sub> -H <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO-H <sub>2</sub>	CO-H <sub>2</sub>
H: H $\beta$	100	100	100
CH: 4300 Å (0-0)	10	10	10
C <sub>2</sub> : Swan (0-0)	20	10	20
CO: 3rd. pos. (0-0)	N.D.*	5	10
OH: 3064 Å (0-0)	N.D.	1	20

N.D.\*: Could not be detected.

ties of H, CH, and C<sub>2</sub> are almost the same in all plasmas.

### Mass spectroscopy of plasmas

The mass spectra were taken for each plasma under 200 W of power input both with and without microwave discharge. The species in the discharge tube were introduced into the analyzing chamber which was kept at a pressure of an order of magnitude below 10<sup>-2</sup> Pa through an orifice 10–30  $\mu$ m in diameter. The mass spectra obtained in these three types of plasmas are shown in Fig. 3. In the spectra with discharge, H<sub>2</sub><sup>+</sup> and CH<sub>x</sub><sup>+</sup>

Table 1. Observed electronic transitions in plasmas by emission spectroscopy, from 600 to 200 nm

CH <sub>4</sub> (1 vol.%)–H <sub>2</sub> plasma		
H	Balmer series	H $\beta$ , H $\gamma$ , H $\delta$
CH	4300 Å system	A <sup>2</sup> $\Delta$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, Q heads)
C <sub>2</sub>	Swan system	A <sup>3</sup> $\Pi_g$ -X <sup>3</sup> $\Pi_u$ , $\Delta v=0$ (0-0, 1-1)
(CH <sub>3</sub> ) <sub>2</sub> CO(1 vol.%)–H <sub>2</sub> plasma		
H	Balmer series	H $\beta$ , H $\gamma$ , H $\delta$
CH	4300 Å system	A <sup>2</sup> $\Delta$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, Q heads)
	3900 Å system	B <sup>2</sup> $\Sigma^-$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, Q, R heads)
	3143 Å system	C <sup>2</sup> $\Sigma^+$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, 1-1, Q heads)
C <sub>2</sub>	Swan system	A <sup>3</sup> $\Pi_g$ -X <sup>3</sup> $\Pi_u$ , $\Delta v=0$ (0-0)
CO	E <sup>1</sup> $\Pi$ -A <sup>1</sup> $\Pi$ system	b <sup>3</sup> $\Sigma^-$ -a <sup>3</sup> $\Pi$ , $\Delta v=-2\sim 0$ (0-0, 0-1, 0-2)
		d <sup>3</sup> $\Delta$ -a <sup>3</sup> $\Pi$ , $\Delta v=1$ (1-0)
OH	3064 Å system	A <sup>2</sup> $\Sigma^+$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, 1-1)
CO(10 vol.%)–H <sub>2</sub> plasma		
H	Balmer series	H $\beta$ , H $\gamma$ , H $\delta$
CH	4300 Å system	A <sup>2</sup> $\Delta$ -X <sup>2</sup> $\Pi$ , $\Delta v=0$ (0-0, Q heads)
C <sub>2</sub>	Swan system	A <sup>3</sup> $\Pi_g$ -X <sup>3</sup> $\Pi_u$ , $\Delta v=0$ (0-0, 1-1)
CO	The Angstrom system	B <sup>1</sup> $\Sigma^-$ -A <sup>1</sup> $\Pi$ , $\Delta v=-3\sim 0$
	4th positive system	A <sup>1</sup> $\Pi$ -X <sup>3</sup> $\Sigma$ , $\Delta v=-11\sim -6$
	E <sup>1</sup> $\Pi$ -A <sup>1</sup> $\Pi$ system	b <sup>3</sup> $\Sigma^-$ -a <sup>3</sup> $\Pi$ , $\Delta v=-4\sim 0$
		d <sup>3</sup> $\Delta$ -a <sup>3</sup> $\Pi$ , $\Delta v=1$ (1-0)
OH	3064 Å system	A <sup>2</sup> $\Sigma^+$ -X <sup>2</sup> $\Pi$ , $\Delta v=0\sim +1$ (0-0, 1-1, 2-1)

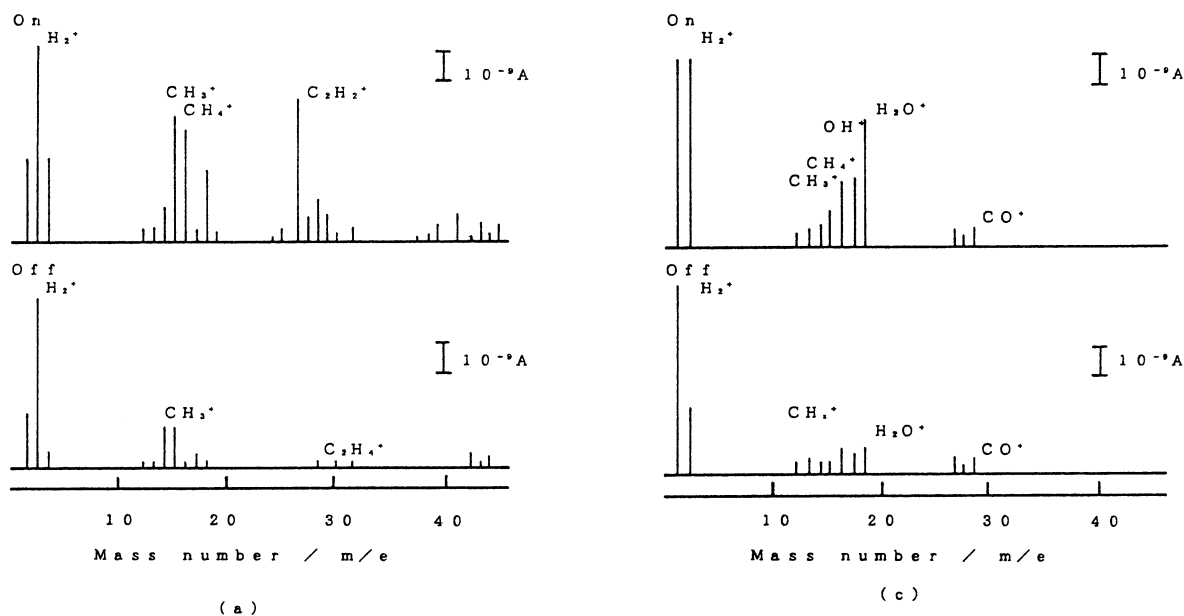


Fig. 3. (continued).

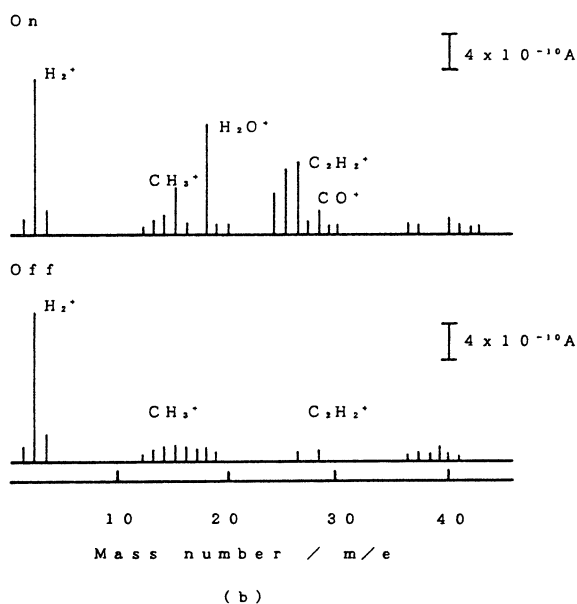


Fig. 3. Mass spectra of (a)  $\text{CH}_4(1 \text{ vol.}\%)\text{-H}_2$  plasma, (b)  $(\text{CH}_3)_2\text{CO}(1 \text{ vol.}\%)\text{-H}_2$  plasma, and (c)  $\text{CO}(1 \text{ vol.}\%)\text{-H}_2$  plasma. "On" and "off" mean during and before the microwave discharge.

( $x=1-4$ ) ions were identified in the  $\text{CH}_4\text{-H}_2$  plasma in addition to those from residual gases.  $\text{CO}^+$ ,  $\text{CH}^+$ , and  $\text{H}_2\text{O}^+$  ions were identified in the  $(\text{CH}_3)_2\text{CO-H}_2$  and  $\text{CO-H}_2$  plasmas in addition to those observed in the  $\text{CH}_4\text{-H}_2$  plasma. The increments of  $\text{CH}_x^+$ ,  $\text{OH}^+$ , and  $\text{H}_2\text{O}^+$  ions in the  $(\text{CH}_3)_2\text{CO-H}_2$  and  $\text{CO-H}_2$  plasmas suggest that these ions would be formed by the reaction between  $\text{CO}$  and  $\text{H}_2$  in the plasma and  $\text{CH}_x^+$  would be the precursor of the diamond deposition in all plasmas.

#### 4. Concluding remarks

In the methane-hydrogen, acetone-hydrogen, and carbon monoxide-hydrogen plasmas prepared using microwave discharge, diamond thin films were obtained. From identified species in the plasmas, it was suggested that diamond would be deposited from hydrocarbons, probably methyl radicals, created in the plasmas in all cases. The creation of the hydrocarbons in the carbon monoxide-hydrogen plasma is considered by the reaction between carbon monoxide and hydrogen,  $\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CH}_x$ , which is known as the Fischer-Tropsch reaction as reported previously<sup>6)</sup>.

*Acknowledgements.* The authors wish to thank Dr. M. Ohkubo of JASCO for performing the Raman spectroscopy of the deposits.

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