DIAMOND DEPOSITION FROM Ar-CO_2-CH_4 PLASMAS

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We have carried out the deposition of diamond from Ar-CO_2-CH_4 plasmas prepared using three types of discharges, dc plasma jet, microwave discharge and inductive rf discharge. The deposits from the microwave plasma only exhibited crystalline habit planes and were identified as diamond by XRD and Raman spectroscopy. In the microwave discharge, the dissociation of molecules would be suppressed and diamond deposition is possible.

INTRODUCTION

In usual, diamond is deposited from plasmas including hydrocarbons diluted with much amounts of hydrogen prepared using microwave discharge or dc plasma jet. The accepted interpretation of role of hydrogen is to make superequilibrium concentration of atomic hydrogen. Otherwise, carbon monooxide diluted with hydrogen was also used as carbon source to deposit diamond. Bachmann reported all the investigated gas compositions in a C-H-O triangular diagram and observed that the diamond yielding composition fell within a triangular region roughly centered on the H-CO line [1]. Otherwise, a mixture of CO and H_2 was observed as a product of the reaction between CH_4 and CO_2 in the microwave discharge [2]. This was a motivation for studying diamond growth using CH_4-CO_2 and C_2H_2-CO_2 gas mixtures in microwave plasmas by Balestrino et al.[3]. They observed a diamond deposition from the CH_4-CO_2 system in the microwave plasma. In this case, they also observed a sharp compositional threshold between the diamond-yielding range and the no-growth range. Optical emission spectra from CH_4-CO_2 plasmas which were similar to those from CH_4-H_2 plasma. On the other hand, Joeris et al. considered that most of the assumed roles of hydrogen in the diamond deposition would be possible with oxygen [4]. They also observed the diamond deposition from the Ar-CH_4-O_2 as well as Ar-CH_4-CO_2 microwave plasmas. We also deposited diamond from Ar-CO_2-CH_4-H_2 dc plasma jet and found the deposition of diamond from the plasma jet without hydrogen [5].

We have carried out the deposition of diamond from the Ar-CO_2-CH_4 plasmas prepared using three types of discharges, dc plasma jet (PJ), mirowave discharge (MW), and inductive rf discharge (RF), because plasma parameters are mutually considerably different among these discharges. In the present paper, the deposits obtained in the discharges are mutually compared with plasma conditions which were diagnosed using optical emission spectroscopy and electric double probe technique.

EXPERIMENTAL

The specimens used as substrates in diamond deposition were 15x10x1mm of molybdenum (purity, 99.9%) sheets which were polished, degreased and dried in vacuum. Purified argon, carbon dioxide and methane (purites, 99.9%) were used as plasma gases.

Three types of discharge apparatus were used for the diamond deposition.

dc plasma jet apparatus: The dc plasma torch was placed at the end of the steel reactor, with the metal sample placed on a water cooled copper holder. After the reactor had been evacuated below 10 Pa, argon was introduced through the plasma torch into the reactor, the pressure being maintained at 26 kPa. Carbon dioxide gas and methane gas were mixed in the desired ratio and introduced into the plasma jet just in front of the plasma torch in the reactor and the argon-carbon dioxide-methane plasma jets were generated. The gas composition was varied as Ar-CO_2(0.1-0.25 v/o)-CH_4(0.1-0.14 v/o). The total flow rate was kept at 720 $dm^3\ h^{-1}$. The dc power was 1.8 kW and the substrates were exposed to the plasma jet for a period of 2 h.

Microwave or rf discharge apparatus: The metal sample was placed on the fused silica holder and put in the fused silica discharge tube at a center of the cavity in the microwave discharge or of the inductive coil. After the discharge tube had been evacuated below 0.1 Pa, argon, carbon dioxide gas, and methane gas were mixed in the desired ratio and introduced into the discharge tube in the total flow rate of 1.2 $dm^3 h^{-1}$, the pressure being maintained at 2 kPa. The gas composition was varied as Ar-CO_2 (8.5-12.5 v/o) -CH_4(7.5-11.5 v/o). The microwave (2.45GHz) or rf (13.56) power was 200 W and the substrates were exposed to the plasmas for a period of 5 h.

During the discharge, the difference of the plasmas were diagnosed by means of electric double probe technique and optical emission spectroscopy. Surface temperatures of the substrates in the plasmas were measured using optical pyrometer. The deposits were characterized by means of SEM observation, X-ray diffraction and Raman spectroscopy.

RESULTS

Comparison of the deposits

dc plasma jet : A surface temperature of the substrate under impingement of the plasma jet was 1150 $\pm$ 20 K. Examples of characteristic results of the deposits from the dc plasma jet of Ar-CO_2(0.2 v/o)-CH_4(0.12v/o) are shown in Fig. 1-Fig. 3. The morphology of the deposits was identified by SEM observation and the micrographs are shown in Fig. 1. Amorphous deposits were identified and morphology did not changed with varying gas mixing ratio. X-ray diffraction patterns of the deposits are shown in Fig. 2. Weak diffraction line due to diamond (111) was observed from the plasma of CO_2/CH_4 =1.7. Raman spectrum of the deposit is shown in Fig. 3. Weak peak at about 1333 cm^{-1} due to diamond was observed with that at about 1340 cm^{-1} and 1600 cm^{-1} due to amorphous carbon.

Radiofrequency plasma : A surface temperature of the substrate in the plasmas was 1020 $\pm$20 K. Characteristic results of the deposits from the Ar-CO_2(11.5 v/o)-CH_4(8.5 v/o) are also shown in Fig. 1-Fig. 3. Sphere-like particles were only observed in the deposit as shown in Fig. 1. Diamond could not be identified in the X-ray diffraction pattern and in Raman spectra. The deposits were almost non-diamond materials as shown in Figs. 2 and 3.

Microwave plasma : A surface temperature of the substrate in the plasmas was 1150$\pm$ 20 K. Characrerristic results of the deposits from the Ar-CO_2(11.5 v/o)-CH_4(8.5 v/o) are also shown in Fig. 1-Fig. 3. The particles exhibiting cubo-octahedral habit planes was obtained as shown in Fig. 1. In the X-ray diffraction patterns, diffraction lines due to diamond were clearly observed as shown in Fig.2. The sharp peak due to diamond was identified in Raman spectrum as shown in Fig. 3.

As compared with the characteristic results of the deposits from the Ar-CO_2(11.5 v/o)-CH_4(8.5 v/o) (CO_2/CH_4=1.3) plasmas prepared using three types of plasmas, the diamond deposition was clearly observed in the deposit from microwave plasma. Therefore, a dependence of the deposit on the gas composition in the microwave plasma was investigated. Change of the SEM morphology with variation of gas composition is shown in Fig. 4 as an example. When the CO_2 concentration was lower than that in the case of Fig. 1, sphere-like particles were observed and a codeposition of amorphous carbon with diamond was suggested. In X-ray diffraction patterns as well as Raman spectra, peaks due to diamond decreased with decreasing CO_2 concentration. Otherwise, the deposit could not be observed in the deposition from the plasmas containing higher CO_2 concentration than 12.5 v/o (CO_2/CH_4=1.7).

Diagnostics of plasmas

Optical emission spectroscopy : Peak head intensities of identified species in the emission spectra from plasmas prepared three types of discharges at same concentration of carbon sources are given in Table 1. The intensities of CO as well as OH radicals in the spectra from the microwave plasma, in which the diamond formation was observed, were substantially stronger than those from other plasmas. Peak head intensities of identified species in the microwave plasma prepared varying gas composition is shown in Table 2. The peak head intensities of CO as well as OH radicals in the spectra would affect the deposits.

Electric Double probe technique : Electron energy, kTe, and ion density, n_i, of Ar plasmas prepared using three types of discharges estimated by electric double probe technique are given in Table 3. kTe in the microwave plasma was the highest values and that of rf plasma was slightly lower than that of microwave plasma. The value of kTe in the plasma jet was drastically lower than those in the other plasmas.

DISCUSSION

From the results obtained above, following phenomena were found in the diamond deposition from the Ar-CO_2-CH_4 plasmas prepared using three different types of discharges. (i) Microwave plasma was the most suitable to deposit diamond. (ii) Both electron energy and ion density were the highest in the microwave plasma. (iii) The diamond deposition took place in limited range of feed gas composition. (iv) The deposits corresponded with species observed in the plasmas.

Since microwave plasma and rf inductive plasma are cold plasmas, kTe as well as n_i are considerably higher than those in the plasma jet, which is pseude thermal plasma. Relative intensity of line due to the electron transition to metastable state of argon atom (4s $3p^0$, Em=11.6 eV) in emission spectra from the plasma jet was drastically stronger than those in the other plasmas and the dissociation and excitation of molecules were increased. On the other hand, the line intensity was very weaker than those in the other plasmas and the dissociation and excitation of molecules were suppressed. The density of the argon atoms at metastable state would determines the concetration of species in the plasmas. In the microwave plasma, small amounts of argon atoms at metastable state were contained and suitable amounts of intermediate products, especially CO and OH were contained.

In the diamond deposition from the Ar-CO_2-CH_4 microwave plasma, diamond deposition rate increased with increasing CO concentration and with decreasing C_2H_2

concentration in the plasma which were determined by quadrapole mass spectrometry [4]. The similar dependence of CO concentration, which was determined by optical emission spectroscopy, on the diamond deposition in the microwave plasma was observed in the present study.

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Table 1 Peak head intensities of identified species in three types of plasmas

Plasma	Rerative peak head intensity							
	Ar a)	CO b)	CH c)	OH d)	H e)	C2 f)	C g)	O h)
Plasma Jet	100	3	4	3	19	9	200	1
Microwave	3	14	2	13	3	3	-	-
RF	0.2	2	-	0.5	0.1	-	-	-

a) 4p-4s　b) B-A (0-0)　c) A-X (0-0)　d) A-X(0-0)

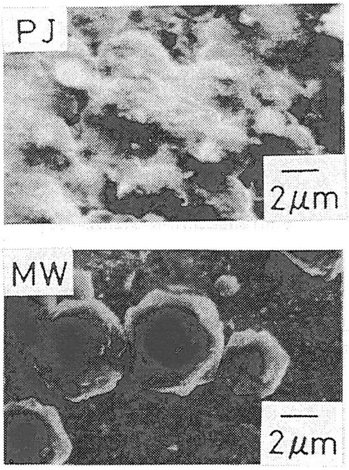
e) H β　f) A-X'(0-0)　g) 2p3s- $2p^2$　h) $2p^3 3p$-$2p^3 3s$

Table 2 Peak head intensities of identified speciesin the microwave plasma varying gas composition

CO2/CH4	Relative peak head intensity					
	Ar	CO	CH	OH	H	C2
0.7	3.0	6.3	2.2	3.5	3.3	6.8
1.0	3.4	10.5	2.2	8.2	3.4	3.4
1.3	3.4	13.6	1.7	13.0	3.4	2.8
1.7	3.5	15.0	0.9	32.1	4.1	0.7

Table 3 Electron energy (kTe) and ion density (ni) in the three types of plasmas

Plasma	kTe /eV	ni/10^{11} cm^{-3}
Plasma Jet	1.0	1.0
Microwave	13.0	9.8
RF	9.0	5.5



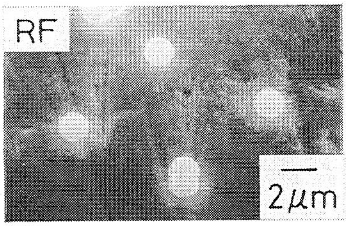


Fig. 1 Scanning electron micrograph of the deposits from Ar-CO2-CH4 plasmas prepared using three types of discharges.

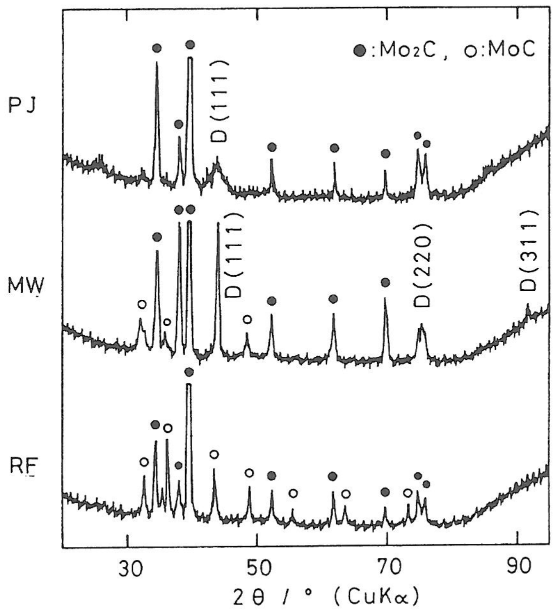


Fig. 2 X-ray diffraction patterns of the deposits from Ar-CO2-CH4 plasmas prepared using three types of discharges.

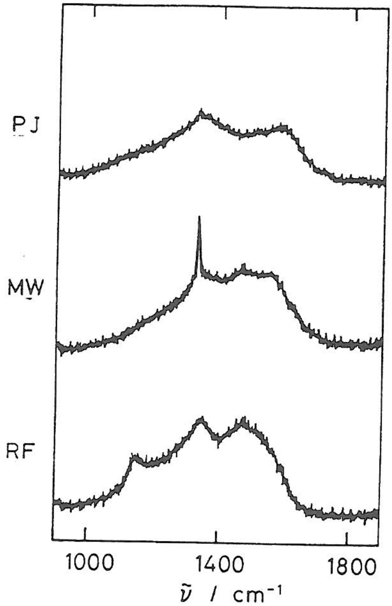


Fig. 3 Raman spectra of the deposits from Ar-CO_2-CH_4 plasmas prepared using three types of discharges.

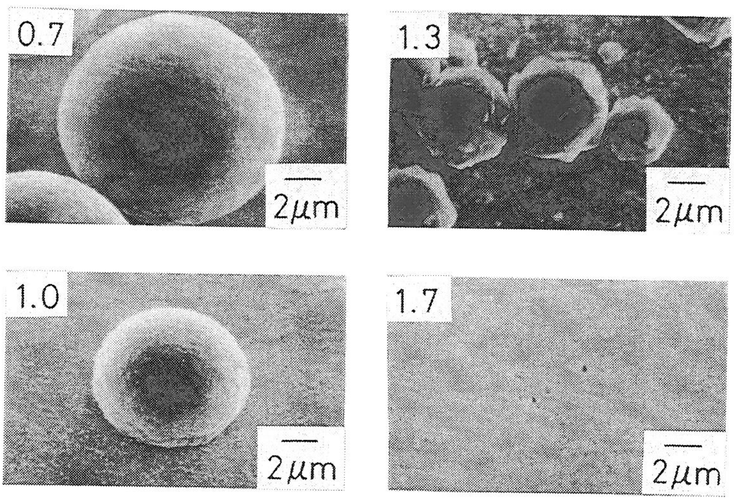


Fig. 4 Scanning electron micrograph of the deposits from Ar-CO_2-CH_4 microwave plasmas prepared varying gas composition of CO_2/CH_4=0.7-1.7.