DIAMOND SYNTHESIS IN A MW PLASMA JET

Yoshitaka MITSUDA and Toyonobu YOSHIDA

Department of Metallurgy and Materials Science, Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Using a MW plasma jet, diamond was successfully synthesized from an Ar–H₂–CH₄ system at a higher rate (30 μm/h) on a larger area (25×25 mm²). The growth rate was in proportion to the substrate temperature and/or CH₄/H₂ volume ratio up to 1200°C and/or 10 vol% respectively. Moreover, we have employed in-situ mass spectroscopy of the chemical species on the substrate surface during deposition. A large amount of 15 and 16 m/e was found on the substrate surface during deposition, which was mainly due to CH₄. A small amount of CₓHₓ was also detected in addition to CH₄ as a species including carbon atoms. In comparing the mass spectra before discharge, CₓHₓ was considered to be generated in plasma. The intensity of CH₄ on the substrate surface, however, was higher than that of CₓHₓ. At this stage, however, the correspondence was not clear between the mass spectra of any species and the deposition rate of diamond in regard to the CH₄/H₂ ratio.

1. Introduction

In the early 1960’s, diamond was successfully grown on seed diamond in a thermodynamically hindered region using the chemical vapor deposition method (CVD)¹,². To date, diamond has been grown on various kinds of substrates in a pressure range of a few kPa, by filament CVD³, by plasma CVD using microwaves (MW)⁴,⁵ or radio-frequency (rf)⁶ devices. Recently, it has also been deposited at atmospheric pressure using inductively coupled rf plasma, and its growth rate reached about 1 μm/min, which was 60 times higher than any other previous method⁷.

However, there is very little information from in-situ species measurements taken at the growth interface. Several investigators have tried to diagnose chemical species during diamond growth using emission spectroscopy⁵,⁸ or absorption spectroscopy⁹, although they could not conclude what is the key species for diamond formation. In order to investigate the chemical mechanism of diamond growth, we need to get more information on the gas phases during diamond growth.

In this paper, therefore, we have investigated diamond synthesis at atmospheric pressure from an Ar–H₂–CH₄ system using a MW plasma jet, which was so large that we could easily use a complex instrument for in-situ measurement. So we have employed mass spectroscopy of chemical species on the substrate surface for analysis of the diamond growth environment.

2. Experimental

Figure 1 shows the experimental apparatus with the quadrupole mass spectroscopy system (QMS). The MW plasma jet torch, which has been described previously¹⁰,¹¹, was connected to an airtight chamber with a water-cooled substrate holder. The plasma jet was generated at atmospheric pressure and blown into the chamber. Table 1 shows the experimental conditions investigated here. CH₄ was added to the plasma as a reactant, and a (100) Si wafer (25×25 mm²) was set on the holder as the substrate.

The Si substrate was pre-treated by the mechanical blasting method¹² using #100 SiC powder, because substrate pretreatment made the number density of nucleation sites much higher. The substrate was set on the holder about 60 mm from the torch nozzle and was heated by the plasma jet directly. The substrate temperature was measured by a radiation pyrometer (λ=0.9 μm) through a
pyrex window, though it was not calibrated with regard to the substrate emissivity.

In-situ mass spectroscopy was employed to diagnose the surface chemical species during diamond deposition. The QMS system connected with the nozzle of a tandem differential pumping system, which served as a substrate holder at the same time, as shown also in Fig. 1. The diameters of the orifice and the skimmer in the nozzle were 50 μm and 100 μm, respectively, and the gap between the orifice and skimmer was about 1 cm. The pressure inside the nozzle and the mass analyzer was approximately maintained at 2×10⁻¹ Pa and 1×10⁻⁴ Pa, respectively. The species were ionized in the ionizing chamber and were analyzed from 1 to 150 m/e. The mass spectra were measured before and during the discharge.

### 3. Results and discussion

#### 3.1 Diamond depositions

Diamond particles or films were successfully synthesized on Si substrate. According to Auger electron spectroscopy (AES), these deposits consisted of only carbon, and there was no contamination from the electrode materials. The AES spectrum of carbon was in good agreement with that of natural diamond. Moreover, the structure of this deposit was identified by X-ray diffraction (XRD) and Raman scattering spectroscopy. The d spacings calculated from the results of XRD coincided with the values reported for natural cubic diamond\(^{12}\). No other peaks except for diamond and Si substrate were detected from any samples. The Raman spectra had a sharp peak of about 1333 cm\(^{-1}\), which agreed with the value of 1332.5 cm\(^{-1}\) reported for diamond\(^{13}\). A small broad peak centered at around 1550 cm\(^{-1}\) was also observed due to the presence of amorphous carbon. It seemed that the obtained samples consisted of many diamond particles and a little amorphous carbon.

Figure 2 shows the dependence of the film deposition rate on the CH\(_4\)/H\(_2\) volume ratio. The deposition rate was almost in proportion to the CH\(_4\) concentration. However, under conditions of a CH\(_4\) concentration above 5 vol%, amorphous carbon was also deposited in addition to diamond. Because the morphology of deposits was not drastically changed, almost all of the deposit seemed to be diamond in the case of a high CH\(_4\)/H\(_2\) ratio.

![Deposition Rate vs. CH\(_4\)/H\(_2\) Ratio](image)

**Fig. 2.** The dependence of deposition rate of diamond film on CH\(_4\)/H\(_2\) ratio. (Pressure 0.1 MPa, Ar 10 SLM, H\(_2\) 20 SLM, MW power 5.0 kW).
Figure 3 shows the dependence of the linear growth rate of the average particle diameter on the substrate temperature. It was found that the growth rate increased according to the substrate temperature up to the melting point of the substrate material. The substrate temperature was able to be controlled properly by regulating the MW input power or the substrate position. The circle symbols in Fig. 3 show the case of the substrate temperature varied by the adjustment of the MW input power, while the square symbols show the case by the substrate position. In either case, the growth rate was governed only by the substrate temperature.

3.2 QMS spectra

Mass spectroscopy was carried out on the Ar–H₂–CH₄ gas mixture before and during deposition. All spectra were normalized by Ar partial pressure, that is, the intensity of each chemical species was divided by the intensity of 40 m/e for every mass spectra. Figure 4 shows the typical normalized QMS spectra of chemical species on the substrate surface; (a) before and (b) during discharge. Ionic species could not be detected in this case. Mass numbers of 16–18, 28, 32 and so on were also detected in the background spectra of QMS, so these species were due to the presence of H₂O, N₂ or CO, and O₂. The mass spectra observed for the Ar–H₂–CH₄ gas flow showed the presence of H₂ (m/e=2), CH₃ (n=0–4, m/e=12–16) and Ar (m/e=20, 40). On the other hand, the mass spectra observed for plasma showed the presence of C₂Hₙ (n=0–8, m/e=24–30) added to the case of the gas flow. From comparison of the two spectra, C₂H₂ was considered to be generated in plasma. The intensity of CH₃ on the substrate surface, however, was higher than that of C₂H₂.

Figure 5 shows the dependences of normalized mass spectra of several species on the CH₄/H₂ ratio; (a) before and (b) during discharge. In Fig. 5(a), the intensities of 15 and 16 m/e were in proportion to the CH₄/H₂ ratio, and their gradient was about equal to a unit. So 15 and 16 m/e were parent and fragment peaks of CH₄, respectively. On the other hand, in Fig. 5(b), these intensities were not in proportion to the ratio and, moreover, the intensity of 15 m/e was higher than 16 m/e, compared with Fig. 5(a). This fact means that 15 m/e was detected due to the presence of CH₃ as well as the fragment peak of CH₂. However, we cannot at this stage conclude that diamond is formed by CH₃, because there is a possibility that

![Fig. 3. The dependence of deposition rate of diamond film on substrate temperature. (Pressure 0.1 MPa, Ar 10 SLM, H₂ 20 SLM, CH₄ 0.6 SLM).](image-url)
CH₃ was formed in the nozzle of the QMS, due to the rather high pressure in the nozzle.

4. Discussion

Now we can know the amount of chemical species on the substrate surface during deposition. Since diamond was formed at atmospheric pressure, some investigators had emphasized that the key species of diamond was the carbon atomic radical. However, even if thermal plasma was used for the formation of diamond, large amounts of CH₄ were detected on the substrate surface and it seems that CH₄ reached the substrate surface through plasma without decomposition or with partial decomposition up to CH₃. But it was not clear whether the CH₄ on the substrate surface was detected without decomposition through plasma or the CH₄ was generated in the plasma by some recombination mechanisms.

The mass spectra in Fig. 5 were measured under the same experimental conditions as those in Fig. 2, which shows the dependence of the deposition rate on CH₄/H₂. However, the dependence of the mass spectra of any species on the CH₄/H₂ ratio in Fig. 5 did not correspond to the deposition rate curve in Fig. 2. So, at this stage, we cannot determine which species is the key species for diamond. By increasing the vacuum level in the QMS nozzle, more exact amounts of chemical species will be known during diamond deposition, which means the possibility of determining the key species for diamond formation.

5. Conclusions

The conclusions of this paper were as follows:

1. Using a MW plasma jet, diamond particles and films were deposited at higher rates (10 μm/h) on larger areas (25×25 mm²).

2. Using the MW plasma jet, diamond could be grown in proportion to the substrate temperature and/or the CH₄/H₂ volume ratio up to 1200°C and/or 10 vol%, respectively.

3. The QMS spectra of the chemical species on the substrate surface could be detected during diamond deposition.

4. Mainly CH₄ was detected on the substrate surface during deposition. A small amount of C₂H₂ was also detected in addition to CH₄ as species which include carbon atoms.

REFERENCES

12) ASTM X-ray powder diffraction data file, 6-675.