22P062-P

Irradiation of $Ar/CH_4/H_2$ Pulse Modulated Induction Thermal Plasmas to Si Substrate

変調制御した高熱流$Ar/CH_4/H_2$誘導熱プラズマのSi基板照射実験

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The silicon substrate was irradiated by $Ar/CH_4/H_2$ Pulse Modulated Induction Thermal Plasma (PMITP) at 15 kW. The irradiated surface of the substrate was analyzed by a scanning electron microscope (SEM) and Raman spectroscopy. Results showed that the substrate irradiated by the PMITP had a sharp peak at 1328 cm^{-1} which indicates diamond of Raman shift, while the substrate by the non modulated thermal plasmas has a large G-band. The SEM results showed that polycrystalline diamond films were grown almost uniformly in 25x25 mm^2 in case of PMITP.

1. Introduction

The inductively coupled thermal plasma (ICTP) is widely used for many material processings [1,2] because of its high enthalpy and high reaction activity. To obtain a further effective radical source with high controllability of the gas temperature, we have developed a pulse-modulated induction thermal plasma (PMITP) system [3]. This PMITP system can modulate the coil current amplitude of the order of several hundreds amperes. On the other hand, much attention has been paid to carbon materials including graphene, carbon nanotube, fullerene, DLC and diamond. The diamond is a promising material, for example, for surface coating with high hardness. This report describes results on a trial irradiation test of a high pressure high-power $Ar/CH_4/H_2$ PMITP to the Si substrate. It was found that use of the PMITP provided the uniform polycrystalline diamond films deposited on the Si substrates, although the non-modulated thermal plasma does non-uniform one.

2. Experimental setup and conditions

Fig. 1 illustrates a configuration of the plasma torch for PMITP. The plasma torch is composed of two coaxial quartz tubes with a 330 mm length. Argon gas was supplied as a sheath gas along the inside quartz tube. Experimental conditions are summarized in Table 1. Methane and hydrogen gas mixture was supplied through a water-cooled stainless steel tube inserted from the top of the plasma torch. Total gas flow rate including CH_4/H_2 mixture was fixed at 70 slpm. Methane gas flow rate and hydrogen gas flow rate was fixed at 30 sccm and 3 slpm, respectively. Pressure in the chamber was fixed at 180 torr. The quantity 'On-time', which is the time duration with higher current level (HCL), was set to 10 ms, and 'Off-time', the time duration with lower current level (LCL), was set to 5 ms for PMITP. We also defined 'SCL', shimmer current level as a ratio of LCL/HCL [3]. The SCL was set to 100% and 40%. The condition 100%SCL is equivalent to non-modulated condition. A water-cooled specimen holder was installed downstream of the chamber, where a silicon substrate was put. The silicon substrate has a size of approximately 25×25 mm^2. Input power to the non-modulated plasma and the PMITP was adjusted to make the substrate temperature 980 ^oC in each. Thus, the input power was 9.3 kW for the non-modulated plasma, whilst it was 14.5 kW for the PMITP. The substrate temperature was measured by a radiation thermometer from the observation window. The irradiated surface of the substrate was analyzed by Raman spectroscopy and the scanning electron microscope (SEM). To study the gas composition around the substrate, a quadrupole mass spectrometer (QMS) was used to detect gases around the substrate surface from $Ar/CH_4/H_2$ PMITP. Irradiation time was six hours.

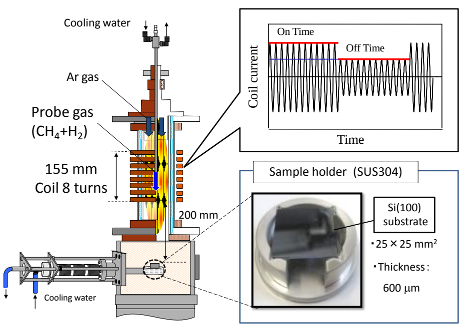


Fig.1. Schematic diagram of plasma torch and chamber.

Table 1. Growth conditions

Gas flow rate Ar/ H_2/ CH_4	67/3/0.03 slpm
Substrate	Si (100)
Substrate temperature	980°C
Total gas pressure	180 torr
Input power	
Non Modulation(100%SCL)	9.3 kW
Pulse Modulation(40%SCL)	14.5 kW

3. Results and discussions

3.1 The *surface of substrates irradiated by PMITP*

Fig.2. (a) and (b) shows photos of the Si substrate surface irradiated by the induction thermal plasma. In case of non-modulated plasma irradiaiton, carbon films were non-uniformly deposited on the substrate surface. On the other hand, the PMITP offers almost uniform carbon films grown in region 25 x 25 mm^2. Fig.3 shows a SEM image of the surface irradiated by the PMITP, which indicates polycrystalline film there.

3.2 *Raman spectra*

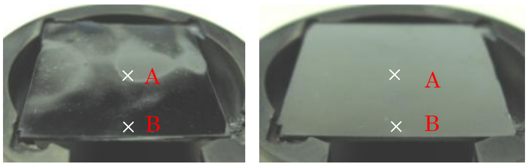
Fig. 4 shows the Raman spectra of the carbon films irradiated by the non-modulated plasma and the PMITP. This figure includes Raman shift results for two positions on Si substrate designated by A(center) and B(edge) in Fig.2. For the non-modulated plasma, the peak at 520 cm^{-1} was found on both position A and B. This peak comes from the silicon of the substrate. The band at 1580 cm^{-1} is attributed to the graphite which has been assigned to the predicted E_{2g} C-C stretching mode. The Raman line at 1334 cm^{-1} is the characteristic signature of the diamond structure [4]. These peaks cannot be found in position B. On the other hand, only the sharp Raman spectra peak around 1328 cm^{-1} could be measured for the substrate irradiated by the PMITP. This peak can be clearly seen for two positions A and B. The peak at 520 cm^{-1} disappeared, which indicates that the components of the graphite (shown at 1550 cm^{-1}) decreased by using PMITP.

3.3 *Mass spectra*

Fig.5 shows the mass spectra measured around the substrate using a QMS to study gas composition irradiated. This figure implies that use of the $Ar/CH_4/H_2$ PMITP decreased the CH_4, CH_3, CH_2 and CH density as compared to the non-modulated thermal plasmas. We expect from this figure that the dissociation of CH_4 was promoted by the PMITP.

4. Conclusion

Polycrystalline diamond was deposited on Si(100) substrate using $Ar/CH_4/H_2$ PMITP. The substrate by the PMITP shows a sharper peak of diamond at 1328 cm^{-1} in Raman spectra as compared to non-modulated thermal plasmas. The PMITP provided more uniform polycrystalline diamond films grown in 25 x 25 mm^2.



(a)Non modulation (b)Pulse Modulation

Fig.2. The surface of Si substrates irradiated by induction thermal plasma.

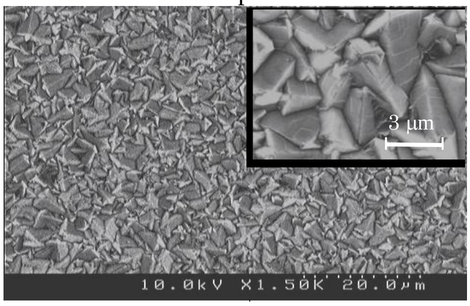


Fig.3. SEM images of the surface polycrystalline diamond films deposited on Si(100) by PMITP.

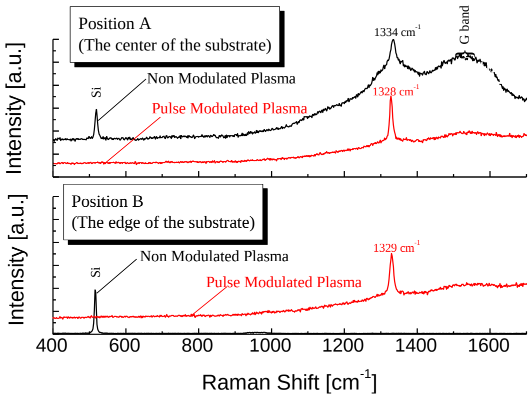


Fig.4. Raman spectra of carbon films on silicon substrates.

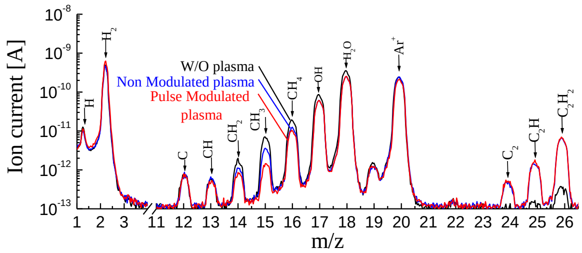


Fig.5. Mass spectrum of $Ar/CH_4/H_2$.

Acknowledgments

The authors are grateful to Dr. Haruyuki Yasui for performing Raman spectroscopic analysis.

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