

Time Evolution in Radiation Intensities of C₂ and H Spectra in Ar/CH₄/H₂ Pulse Modulated Induction Thermal Plasmas for Diamond Film Deposition

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Abstract. The present paper describes the first trial application of an Ar/CH₄/H₂ pulse modulated induction thermal plasma (PMITP) to polycrystalline diamond film deposition on a silicon substrate. The PMITP system has been originally developed by our group to control the heat flux and densities of chemical species in thermal plasma treatment. Polycrystalline diamond film was successfully deposited on a 25×25 mm² Si(100) substrate using the PMITP. Spectroscopic observation was carried out to measure the time evolution in the spectral intensity from the PMITP irradiated to the Si substrate. We found that the C₂ molecular spectra have strong intensities at 4–7 ms after rise-up of the coil current, while the H spectral line has much high intensity at 6–12 ms in a 15 ms modulation cycle. This implies that the PMITP produces repetitive irradiation from different chemical fields in one modulation cycle, which may effectively provide diamond film deposition.

1. Introduction

The inductively coupled thermal plasmas (ICTPs) have been widely adopted as effective heat and chemical species sources for various materials processings such as syntheses of diamond films [1], thermal barrier coatings [2], fullerene synthesis [3], and surface modifications, etc. The ICTP has some advantages like their high enthalpy and high radical density without any contamination.

To obtain a further effective radical source, we have previously developed a series of modulated induction thermal plasma system including a pulse-modulated induction thermal plasma (PMITP) system and an arbitrary-waveform-modulated induction thermal plasma (AMITP) system [4, 5]. The PMITP and AMITP are established by the coil current amplitude of the order of several hundreds amperes modulated almost into a rectangular or other waveforms. Such a millisecond modulation can perturb the thermal plasma markedly, and then it can change the temperature and radical densities as well as the gas flow field in the thermal plasma in time domain [4]. It also produces chemically non-equilibrium effects even in high-temperature and high-pressure plasmas [4, 6]. We found actually that the Ar-N₂ PMITP provides simultaneous control of the increased nitrogen radical flux and the decreased enthalpy flow by chemically non-equilibrium effects in application to surface modification [6]. Such a modulated induction thermal plasma has further possible other applications to be effectively adopted.



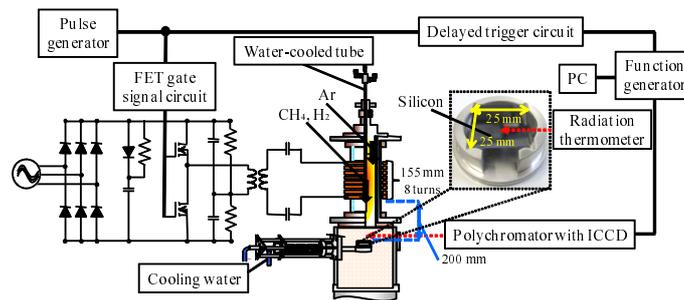


Figure 1. Schematic diagram of experimental system.

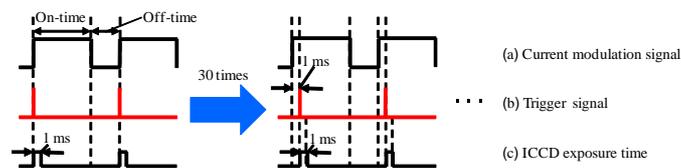


Figure 2. Timing chart in spectroscopic observation.

This paper describes the first results on application of the PMITP to polycrystalline diamond film deposition. A several kW-class Ar-CH₄-H₂ PMITP was adopted to fabricate polycrystalline diamond film on a Si (100) substrate. A polycrystalline diamond film was successfully deposited almost uniformly on a 25×25 mm² Si(100) substrate using the PMITP, whereas it could not be deposited using a non-modulated plasma with the same heat flux. Spectroscopic observation was carried out to measure the time evolution in the spectral intensity from the PMITP irradiated to the Si substrate. Strong C₂ molecular spectra were found during the first stage in the on-time and then strong H atomic line was observed during the successive stage in the on-time of the PMITP. This implies that a carbon film is deposited at the first stage, and then a deposited graphite film is chemically etched by hydrogen atom to leave a diamond film in one modulation cycle.

2. Experimental

2.1. Experimental arrangements

Figure 1 shows the PMITP system and also the spectroscopy observation system used in the present work. The rf power source for PMITP is operated with metal-oxide semiconductor field emission transistors (MOSFET). The rated power of the source and the fundamental rf frequency are 30 kW and 450 kHz, respectively. This power source can modulate the output electric current amplitude of several hundreds of amperes into a rectangular waveform. The rise time of the current amplitude modulation is 80 μs with a delay time less than 1 μs. The modulated coil current has four modulation control parameters: the quantity ‘On-time’ which is the time duration with higher current level (HCL), and ‘Off-time’, the time duration with lower current level (LCL) as indicated in [7]. We also defined the shimmer current level ‘SCL’, as a ratio of LCL/HCL. The 100%SCL condition corresponds to non-modulation condition. In addition, the duty factor (DF) is set to a ratio of the on-time to one modulation cycle: DF= ‘on-time’ / (‘on-time’ + ‘off-time’).

The configuration of the plasma torch is the same to our previous work [7]. It has two coaxial quartz tubes. The inner diameter of the interior quartz tube is 70 mm; its length is 330 mm. Argon gas was supplied as a sheath gas along the inside quartz tube. Into the plasma torch, a water-cooled tube was inserted from the plasma torch head along the center axis. Through this tube, CH₄/H₂ gas mixture was injected to the plasma. The tip position of this water-cooled tube was set between 5-th and 6-th turns of the coil. This means that CH₄/H₂ gas mixture was directly injected into high-temperature region

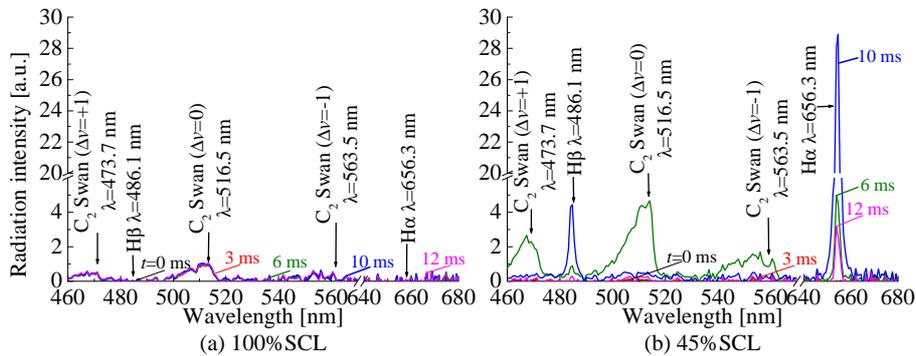


Figure 3. Radiation intensity observed at 5 mm above Si substrate.

in the thermal plasma. The direct injection of CH_4/H_2 gas mixture to the high temperature region can cause its complete decomposition. Downstream of the plasma torch, a Si (100) substrate with a size of $25 \times 25 \text{ mm}^2$ was located. The distance between the substrate surface and the coil end was 200 mm. This substrate surface is directly irradiated by an Ar/ CH_4/H_2 PMITP. The irradiation of the PMITP also increases the surface temperature. This surface temperature of the Si substrate was measured with a radiation thermometer. As pretreatment processes of the Si substrate surface, it was scratched with diamond powder of $5.6 \mu\text{m}$ in ethanol using an ultrasonic cleaning device.

Spectroscopic observation was carried out to measure the emission spectra from the PMITP. The observation position was 195 mm below the coil end, which corresponds to 5 mm above the substrate surface. The observation size was $2.5 \text{ mm}\phi$. To measure emission spectra at different timings against the coil current modulation, we used a delayed trigger circuit and a polychromator with an ICCD (HAMAMATSU: PMA-20). Figure 2 schematically illustrates the timing chart of (a) the pulse generator signal for the coil current modulation, (b) the delayed trigger signal for the ICCD, and (c) the ICCD exposure signal. First, the ICCD was operated at 0 ms just after transition from LCL to HCL. The exposure time of the ICCD was set 1.0 ms. At the same timing against the modulation signal, the same measurement was done 30 times to obtain the averaged value of the radiation intensity of spectra. After this measurement, the timing of the ICCD exposure was shifted by 1 ms using the delayed trigger circuit for the next timing measurement. Similarly, the timing of the ICCD exposure was shifted by every 1 ms in the modulation cycle to obtain time evolution in the averaged radiation intensities of emission spectra from the PMITP.

2.2. Experimental conditions

In the present work, the modulation cycle was fixed at 15 ms. The DF of the modulated coil current was set at 67%. Only the SCL was changed at six values from 45% to 100%. One purpose of the present work is to find the modulation effect on the diamond deposition. The surface temperature of Si substrate was thus controlled to be fixed to be $1,000(\pm 20)^\circ\text{C}$ for any modulation conditions. The fixed surface temperature was realized by carefully regulating a base input power, i.e. the time-averaged input power, for any modulation conditions. For example, the 100% SCL condition required 9.3 kW for input power to obtain the surface temperature of 1000°C , while 14 kW in time-averaged power was needed for the 45% SCL condition. Irradiation time of Ar- CH_4 - H_2 PMITP was set to six hours.

The flow rate of Ar sheath gas was fixed at 65 L min^{-1} (liters per minute). The center gas flow rate of CH_4 and H_2 gas mixture through the water-cooled tube was set at 0.03 L min^{-1} , and 3 L min^{-1} , respectively. The pressure inside the chamber was controlled at 180 Torr with an automatic feedback control.

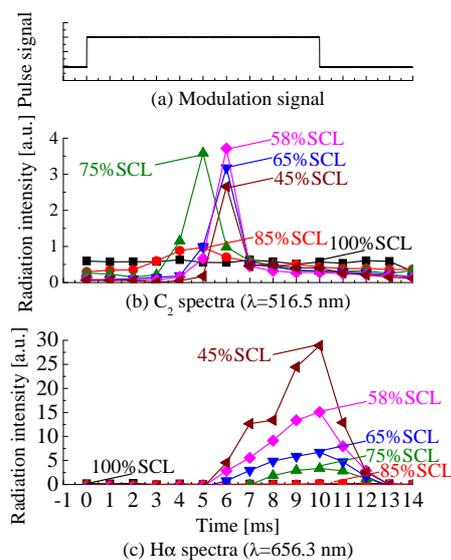


Figure 4. Time evolution in (a) modulation signal, radiation intensity of (b) C₂($\Delta\nu = 0$) ($\lambda=516.5$ nm), (c) H α ($\lambda=656.3$ nm) in different coil current modulation.

3. Results and discussion

3.1. Ar-CH₄-H₂ PMITP spectroscopic observation at 5 mm above Si substrate

Figure 3 shows the emission spectra observed at 5 mm above the Si substrate at timings of $t=0, 3, 6, 10$ and 12 ms, for (a) 100%SCL (non-modulation condition), and (b) 45%SCL (modulation condition). The timing $t=0$ ms against the modulation signal corresponds to the timing just after transition from LCL to HCL. For 100%SCL, C₂ Swan system around wavelengths of 473.7 nm and 516.5 nm can be seen. However, those intensities are relatively low and they are almost unchanged with time because of non-modulation condition. On the other hand, for 45%SCL, i.e. a large modulation condition, C₂ Swan system around 473.7 nm and 516.6 nm has higher intensities especially at $t=6$ ms. In addition, H atomic lines at 486.1 nm and 656.3 nm have higher intensities at $t=10$ ms.

Figure 4 shows time evolution in (a) modulation signal, (b) the radiation intensity of C₂($\Delta\nu = 0$) ($\lambda=516.5$ nm), and (c) the radiation intensity of H α ($\lambda=656.3$ nm) in different modulation conditions, i.e. in different SCLs. As seen, the non-modulated plasma with 100%SCL provides a certain constant intensity from C₂ molecular spectra, and a low intensity of H atomic line. On the other hand, for PMITP, reducing SCL produces changing intensities of the C₂ spectra and also the H atomic line. The radiation intensity of the C₂ molecular spectra increases with time from $t=4$ ms to $t=7$ ms, and it has a peak around $t=5-6$ ms almost irrespective of SCL condition. Concerning the H atomic line, it has a higher intensity from $t=6$ ms to $t=12$ ms for different SCLs. One interesting point is that it has a peak at $t=10$ ms almost independently of modulation conditions. The above measurement results implies that the PMITP irradiates a particle flux including C₂ around $t=4-7$ ms, and then H flux to the substrate around $t=6-12$ ms to the substrate. The irradiation of this alternative kinds of chemical species fluxes with C₂ molecules and H atom in one modulation cycle is one feature of the present method using the PMITP. Furthermore, this irradiation repeatedly occurs by modulation cycle.

According to the equilibrium composition calculation of C-H system, molecules C₂ is produced around 5000–6000 K, while H atom is done around 6000–8000 K by thermal dissociation. Thus, C₂ is produced at the boundary between the high-temperature plasma and the cold gas, whilst H is created at high-temperature region. On the other hand, the PMITP provides a modulated gas flow. Thus, this gas flow created by the PMITP transfers C₂ around the edge of the plasma to the substrate first. After that, H atoms in the high temperature region of the PMITP is transported to the substrate. The roles of C₂ flux and then H flux in one modulation cycle will be discussed later.

Next is the SCL dependence on these radiation intensities. Reducing SCL from 100% to 58% increases the radiation intensity of C₂ spectra. However, a further reduction in SCL to 45% decreases that

intensity. This is because 45%SCL condition has a higher instantaneous input power to the PMITP during the on-time, which may lead to higher dissociation degree of C_2 molecules. This 45%SCL condition contrarily produces more H atoms by higher thermal dissociation of CH_4 and H_2 .

3.2. SEM images and Raman spectroscopy

Figure 5 presents the SEM images of the Si substrate surface after Ar- CH_4 - H_2 PMITP irradiation in different shimmer current levels SCLs: (a) 100%SCL (non-modulated plasma), and (b) 45%SCL (modulated plasma). These SEM images were taken at the center of each substrate. In the SEM image for 100%SCL, several particles of around 3 micron in size were sparsely deposited on the Si substrate. On the other hand, for 45%SCL condition, a film with polycrystalline diamond structure was deposited and grown on the Si substrate. From other experiments on 1 hour irradiation of Ar- CH_4 - H_2 PMITP, we found that reducing SCL from 100% to 45% decreased the diamond particle size formed, and in addition that the particles were rather densely deposited on the substrate. The thickness of the deposited diamond film in Fig. 5(b) was estimated to be $5.6 \mu m$ for 45%SCL.

The deposited particles or film were analyzed using Raman spectroscopy. The upper panel in Fig. 6 shows the Raman shift spectra of the Si substrate surface after Ar- CH_4 - H_2 PMITP irradiation for two conditions: (a) 100%SCL (non-modulation), and (b) 45%SCL. These were measured at the center of each substrate. It can be seen that 100%SCL condition obtains not only Raman peak of disordered or diamond ($k=1334 \text{ cm}^{-1}$) but also strong peaks from the Si ($k=520 \text{ cm}^{-1}$) and strong G band ($k=1590 \text{ cm}^{-1}$, graphite). A slight shift of diamond Raman peak ($k=1332 \text{ cm}^{-1}$) may be due to the internal stress of diamond [9]. On the other hand, an important point that we emphasize in this paper is that the deposited film under 45%SCL condition has only diamond Raman peak ($k=1328 \text{ cm}^{-1}$), and there is no peaks from Si and graphite. This result indicates that use of PMITP can fabricate a pure polycrystalline diamond film on the Si substrate. Another interesting point is the uniformity of the deposited film. The lower panel in Fig. 6 depicts the Raman shift spectra measured at the edge of the Si substrate irradiated by PMITP (a) with 100%SCL (non-modulation), and (b) with 45%SCL. For 100%SCL, only Raman shift peak from Si were found. On the other hand, the 45%SCL condition offers only Raman shift peak from diamond, and it is almost the same to that measured at the center of the substrate. This means that almost uniform film was obtained by using the PMITP. From the spectral measurement and deposited film analysis, we infer the following phenomena: The PMITP supplies a higher density flux including C_2 etc to be irradiated to the substrate at timing $t=4-7 \text{ ms}$ in the modulation cycle. This flux fabricates a carbon film consisting of sp^2 hybridized carbons (e.g. graphite, graphene, fullerene etc.), and also sp^3 hybridized carbons (e.g. diamond) and more carbon-based particles. After that, at timing of $t=6-12 \text{ ms}$, the PMITP transports a high density hydrogen radicals to the substrate. The high density hydrogen flux effectively chemically-etches carbons with weaker bonds, for example, through sp^2 hybrid orbitals from the substrate. Whereas, only sp^3 hybridized carbon film is left on the substrate to create a polycrystalline

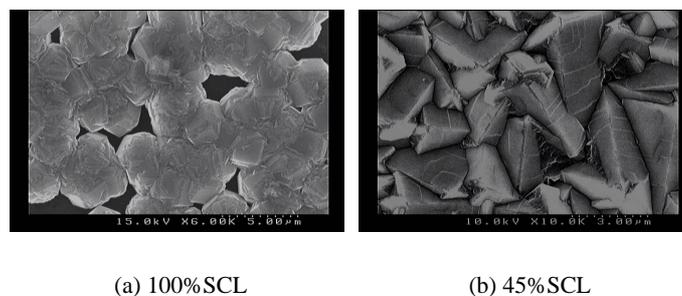


Figure 5. SEM images of the Si substrate surface at the center after Ar- CH_4 - H_2 PMITP irradiation (a) 100%SCL (non-modulated plasma), (b) 45%SCL.

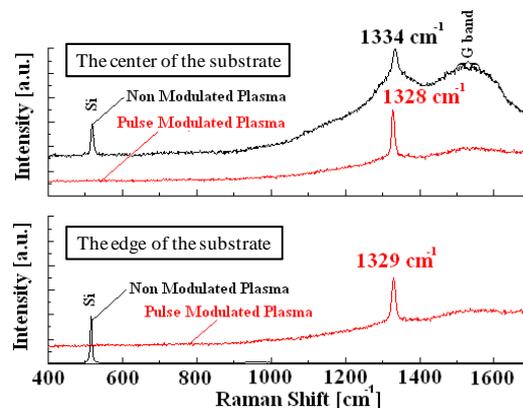


Figure 6. Raman shift measured at the center and edge of the Si substrate irradiated by non-modulated plasma or PMITP with Ar-CH₄-H₂ gas mixture.

diamond film.

4. Conclusions

This paper describes the application of the Ar-CH₄-H₂ pulse modulated induction thermal plasma (PMITP) to polycrystalline diamond film deposition on a Si substrate. The polycrystalline diamond film was successfully deposited on the Si substrate using the PMITP, while the non-modulated plasma could not deposit it under the same heat flux condition to the substrate. Spectroscopic observation was conducted at 5 mm above the Si substrate to measure time evolutions in the radiation intensities of both C₂ and H spectra. The results indicated that in one modulation cycle with the on-time/off-time of 10/5 ms, the intensity of C₂ has a peak at 4–7 ms after the rise-up of the coil current, and H atomic line has an intensity peak around 10 ms. This result implies that the PMITP provides a particle flux dominated by carbon-related chemical species and a flux dominated by H radicals, which are irradiated to the substrate, separately.

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