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PARTICLE -GROWTH IN HYDROGEN-METHANE PLASMAS

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Abstract

Particle growth and the behavior of particle clouds in hydrogen-methane capacitively-coupled rf plasmas are investigated. At room temperature most for different wall temperatures and gas compositions of these particles are due to flakes of layers delaminated from the electrode surfaces. Heating of the electrodes up to 800 K and dilution by hydrogen (up to H_2:CH_4 = 20:1) suppresses the production of the particles from the electrode surfaces. The electron temperature in the particle levitation region is controlled by introducing an additional electrode made from a grid (= gridded electrode) in between the levitation electrode and the driven electrode. If we introduce diamond seed particles (~2.8 μm in diameter) into the plasma with the gridded electrode in place, we observe nucleation of new grains (~100 nm) on the surfaces of the diamond particles. On the other hand, without the gridded electrode we don't observe nucleation but growth of amorphous carbon films on them.

Keywords: diamond growth; complex plasma; plasma CVD

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1. Introduction

Fine particles in plasmas have attracted strong interest because they form complex (dusty) plasmas which are a multicomponent system consisting of charged and neutral components. In complex plasmas we find many differences from usual particle-free plasmas, for example Coulomb crystals of fine particles [1,2], wave propagation [3] in Coulomb crystals and so on, because the fine particles have rather small charge to mass ratios. The presence of heavy charged particles leads to the appearance of additional spatial and time scales compared with usual plasmas.

Nucleation and growth of diamond films have attracted great interest because diamond has many unique properties, such as large thermal conductivity, chemical inertness, high electrical resistivity and so on [4]. Several methods have been reported for the production of diamonds by using plasma chemical vapor deposition (PCVD) techniques. It is commonly accepted that methyl radicals are an important precursor and atomic hydrogen plays a very important role for the deposition of diamond films. However, in conventional plasmas the reactive gas is highly dissociated providing many different kinds of radical species because the electron temperature is relatively high. If the electron temperature is controlled, a suitable condition can be chosen for the chemical reactions. In weakly ionized plasmas, it is difficult to change the electron temperature if the geometry, gas species and working pressure are fixed. For controlling the electron temperature, K. Kato et al. developed a grid method [5]. Furthermore, it has been found that the electron temperature plays an important role for diamond deposition [6] and a-Si:H process [7].

In this paper we discuss two points. The first is the behavior of levitated particles spalled from the electrodes. The second is treatment of levitated diamond particles in hydrogen-methane plasma.

2. Experimental

The experimental setup is shown in Fig. 1. The experiments are carried out in parallel-plate capacitively-coupled radio frequency (rf) discharge plasmas. We use a three electrode assembly with the electrodes, 10 cm in diameter, being oriented horizontally. This assembly is installed in a chamber about 80 cm in diameter. The upper electrode is the driven electrode where an rf power of up to 170 W at a frequency of 13.56 MHz is supplied through impedance matching circuits. The lower electrode, which is electrically floating, is for particle levitation. On the lower electrode we put an additional plate electrode (5 mm in thickness) with a hole 2 cm in diameter in order to confine the particles electrically. An additional electrode made from a grid (=gridded electrode (15 lines/inch)) is placed in between the levitation electrode and the driven electrode. All electrodes are made of stainless steel. The distance between the electrodes is 5 cm each. The plasma is ignited between the upper electrode and the gridded electrode, which divides the plasma volume in two regions, plasma-production region and particle-levitation region. In the case without the gridded electrode, the main counter electrode is the wall electrode (coaxial heater). The high energy electrons produced in the plasma-production region can penetrate through the gridded electrode only if they can overcome the ion sheath in front of it. In the particle-levitation region they lose their kinetic energy through ionizations and collisions with molecules. In the particle-levitation region there is no rf electric field to accelerate electrons, therefore, we have a low electron-temperature plasma in this region [5,6]. This procedure to control the electron temperature was investigated in detail by Shimizu and coworkers [5,6]. According to these references, we assume that the electron temperature with and without the gridded electrode is ~3 eV and ~0.5 eV, respectively. The electron density is estimated to ~10^9 cm^{-3}.

Particles are introduced into the levitation region by a particle dispenser. After introducing the particles, the dispenser is retracted from the plasma region. The particles

used in this study are diamond particles with a mean diameter of 2.8 micron, which have different shapes with distinct edges and facets. Typically, particles are levitated from 5 mm to 20 mm above the levitation electrode. The particle charge is estimated to be ~10^3 from the electron density, the electron temperature, and the particle size [2]. To collect levitated particles from the plasma volume, we use a NFP (negatively charged fine particle) collector [8], because it is difficult to distinguish levitated seed particles from delaminated particles if they are collected from the lower electrode surface. In order to measure the levitated particle number we use an Ar^+ laser (wavelength 514.5 nm, output power 100 mW) and a photodiode. The particle cloud is illuminated by the laser and the scattered light is detected with the photodiode through an optical filter under an angle of 90 degree. The particle number is proportional to the intensity of the scattered light. The linear proportionality of intensity and particle number was checked experimentally.

The chamber is evacuated to 2×10^{-4} Pa. Before the growth experiments, a pure hydrogen plasma is ignited at 100 Pa for 1 hour to clean the particle surface. In this study, we use hydrogen and methane for the growth experiments. For the cleaning of the electrodes, oxygen is used. During the growth experiments the upper electrode and lower electrode are heated to 810 K and 800 K, respectively. This slight temperature difference is selected to compensate the convection force on the particles, which is directed upwards, by thermophoretic force. We assume that the levitated particles have a temperature similar to that of the surrounding wall.

3. Experimental results and discussions

At first, we discuss particles, which are generated in the plasma and at the electrode surfaces. In hydrogen-methane (95 %/5 %) plasmas with the electrodes at room temperature, we observed the formation of a particle cloud a few 10 minutes after igniting the plasma. Before this experiment, the surface of the electrodes is cleaned by

an oxygen plasma for 4 hours. After cleaning, we confirm that for 1 hour in a pure hydrogen plasma there is no particle cloud. Then the hydrogen plasma is switched off and the chamber is evacuated. In the following, we introduce the mixture gas and ignite the plasma. For these kinds of experiments, most of the particles levitated are amorphous carbon flakes, delaminated from the surface of the upper two electrodes. An example of such particles is shown in Fig. 2. The thickness is around 100 nm.

Figure 3 shows the evolution of the particle number without seed particles. In this experiments we use two sets of the gas composition; i) methane only and ii) hydrogen and methane with a mixing ratio of 95/5 (up triangles in Fig. 3) both at a pressure of 100 Pa. The latter condition is the same as that for the diamond-particle-growth experiments described later. The absorbed rf power is 100 W. The evolution of particle number strongly depends on the temperature of the surrounding electrodes. At high electrode temperature, the deposition rate of amorphous carbon is low [9]. Therefore, the number of particles delaminated from the electrode surface decreases if the temperature of the electrodes increases. Above 800 K the number of particles is less than one fifth of that at room temperature. If during the diamond particle growth experiments the number of the particles which originate from the surface of the electrode would be large, they could continuously displace the initial diamond particles. In Fig. 3 a horizontal line at 690 a.u. in vertical axis shows the intensity of a typical diamond-particle cloud at 800 K. After about 8 hours of plasma operation, the number of delaminated particles is less than one third of that of the diamond particles. If we use the H_2/CH_4 gas mixture as mentioned above, the density is even lower. This means that the delaminated particles don't significantly disturb the diamond-particle clouds during plasma treatment.

In the following, we describe the plasma treatment of diamond seed particles. Figure 4 shows scanning microscope images of the diamond particles after 8 hours plasma treatment with the hydrogen-methane (95 %/5 %) gas mixture. The absorbed rf

power is 170 W and the electrodes are heated to 810 and 800 K as described in Sect. 2. Before using the mixture of hydrogen and methane, we produce a pure hydrogen plasma at the same pressure in order to clean the surface of the diamond particles. Figure 4a is for the case of the plasma without the gridded electrode and b with the gridded electrode. In Fig. 4a we see that no nucleation occurs on the surface of the diamond particle. However, on the top surface of the particle we can see a thin film which peels off the surface. Moreover the color of the treated particles changes from white to light brown. This film is most probably amorphous carbon which is similar to the particles from the electrode surfaces. The brownish color is typical of amorphous, hydrogenated carbon films. On the other hand, we observe nucleation of new particles in Fig. 4b. The size of the new particles is up to 100 nm. Since the shape of the new particles is three-dimensional with distinct edges, the material of the new particles could be diamond, but this has not yet been confirmed. Inserting the gridded electrode changes the plasma parameters, especially it decreases the electron temperature. If the electron temperature decreases, two effects can be expected. One is the reduction of the dissociation of methane. In the low-electron-temperature plasma, the reaction, $CH_4 \rightarrow CH_3 + H$, is dominant and the production of CH_2 is limited. Therefore, the dominant hydrocarbon radical at the surface is the CH_3 radical. The other effect is the decrease of the ion-bombardment energy. The electron temperature determines the sheath potential in front of the material which is electrically floating. The sheath potential decreases with decreasing electron temperature. Therefore the ion energy decreases. Both effects are beneficial for nucleation of new diamond particles on the surface of the seed particles.

A difference of the growth is observed for levitated particles and particles placed on the lower electrode. Figure 5 shows particles exposed at the lower electrode for the same condition as for Fig. 4b. On the surface of the particles a thin film is grown similar to the film in Fig. 4a. The color of the particles treated on the lower electrode is

light brown similar to the particle color in Fig. 4a. We assume that the flux of neutral reactive species towards the lower electrode is identical to that towards the levitated species. In fact, the levitation region is only a few mm in front of the lower electrode. But in front of the lower electrode we have a higher sheath potential. The sheath potential in front of the lower electrode is ~20 V higher than that around the particles. This was determined by measuring the floating by measuring the floating potential of the lower electrode and the floating potential of a Langmuir probe installed in the particle-levitation region. We suppose that the observed difference between Fig. 4b and Fig. 5 is due to the difference in ion bombardment. The ion bombardment may differ in flux as well as energy. According to the measurements of the floating potential, the energy of ions impinging on the levitated particles is about 20 eV lower, but the flux could also be lower than that of the electrode. Kozuma et al. [10] have shown that ion bombardment at higher ion energy can prevent diamond nucleation. Although their results can not be directly applied to our situation, this is a possible explanation of the observed differences.

4. Conclusions

Particle growth and the behavior of the particle clouds in hydrogen-methane capacitively-coupled rf plasmas were investigated. We determined the evolution of particle number for several surface temperatures and gas compositions. We found that heating of the electrodes and dilution with hydrogen can suppress the production of particles from the electrode surfaces. The deposition rate of amorphous carbon on the electrodes decreases if the electrodes are heated. If we introduce diamond particles in the particle-levitation region with the gridded electrode in place, we observe nucleation of small new particles on the surface of the diamond particles. On the other hand, we don’t observe nucleation of new grains, but film growth on them in the experiments without the gridded electrode. This is attributed to the difference of the plasma

parameters in the levitation region by installing the gridded electrode which causes a change of the sheath potential around the levitated particles. We also find that no nucleation occurs on particles put on the lower electrode. This result supports that the nucleation depends on the sheath potential.

Acknowledgments

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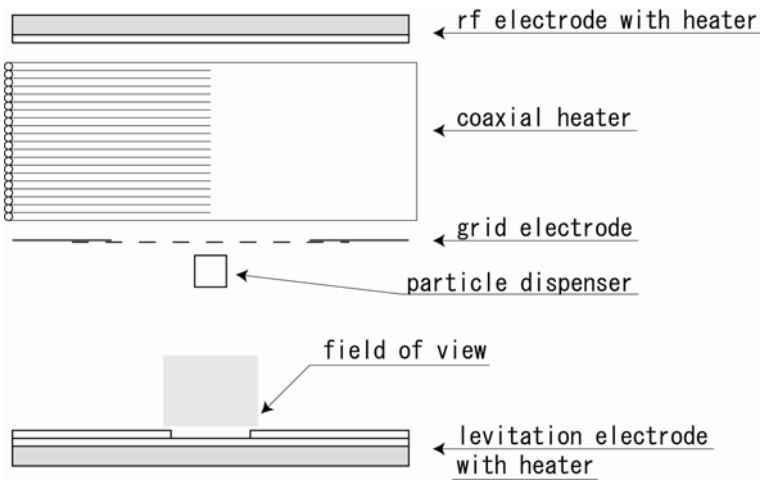

Figure 1. Experimental apparatus. The electrode diameter is 10 cm, the electrode distance is 5 cm each. The particle dispenser is normally retracted from the plasma. It is only inserted in the plasma during the introduction of species.

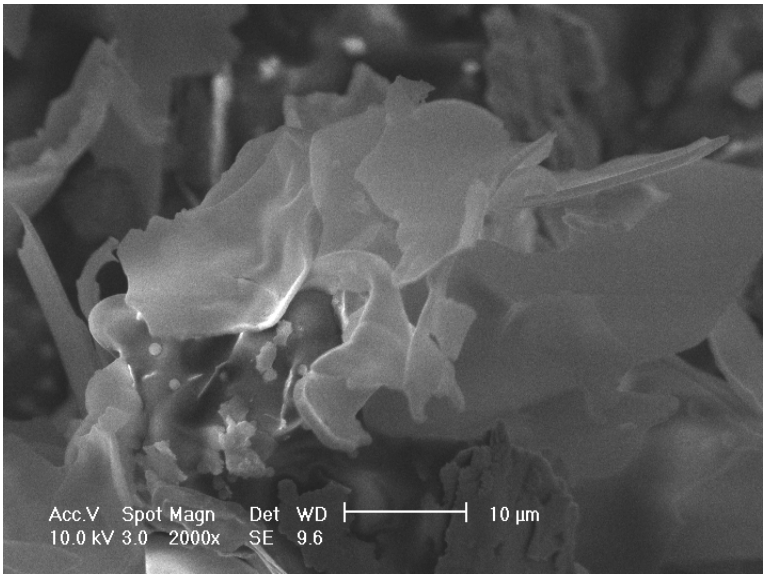

Figure 2. Scanning electron microscope image of delaminated particles.

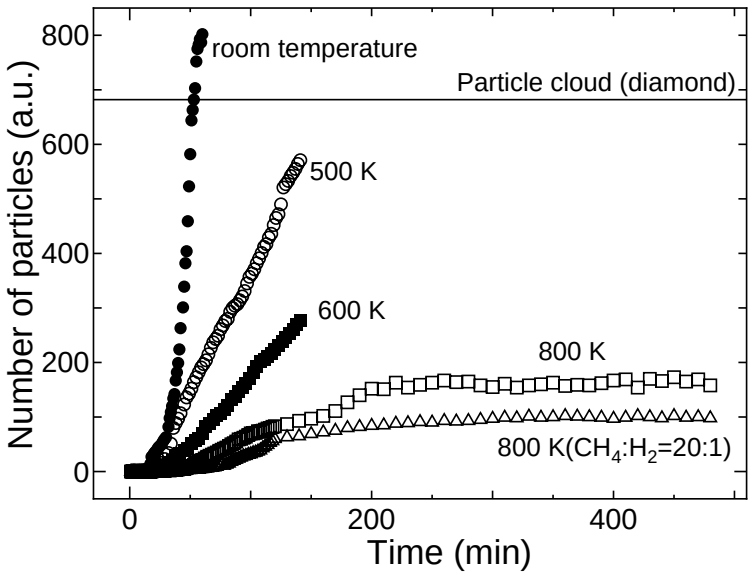

Figure 3. Evolution of particle number for different temperatures of the electrodes and gas compositions. The up triangles are for a H_2/CH_4 mixture (95/5). All other data are for pure methane.

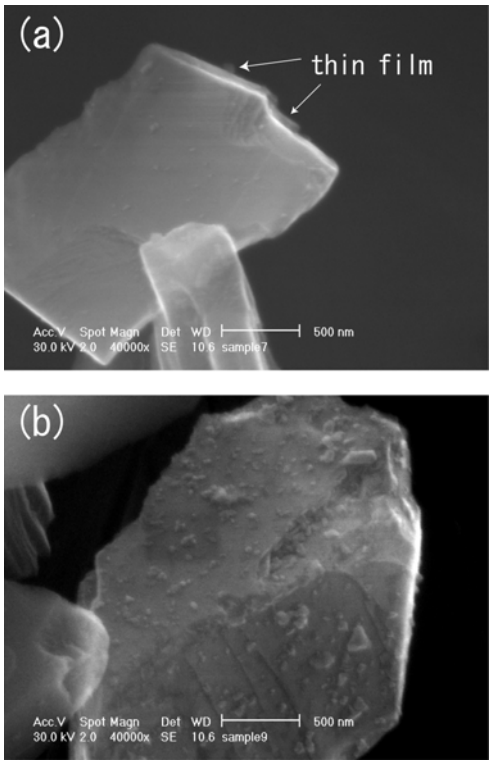

Figure 4.

Scanning electron microscope images of diamond particles after plasma treatment without gridded electrode (a), with gridded electrode (b). In (a) a thin film is observed on the upper side of the particle. New nucleation of small grains is observed on the surface of the particle in (b). The size of the grains is up to 100 nm.

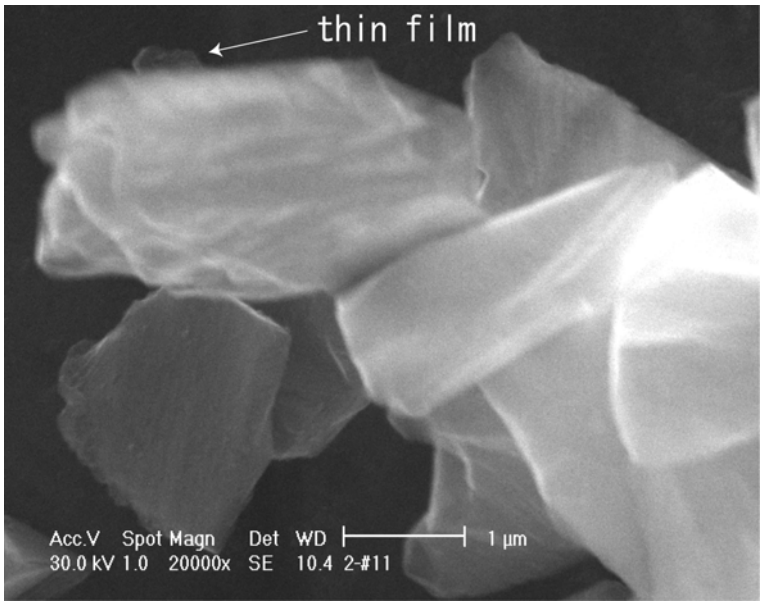

Figure 5. Scanning electron microscope image of diamond particles exposed on the lower electrode.