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Experimental confirmation of charged carbon clusters in the hot filament diamond reactor

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Abstract

The hypothetical nanometer sized charged diamond clusters, which were predicted in the charged cluster model [Journal of Crystal Growth 62 (1996) 55], were experimentally confirmed in the hot filament diamond chemical vapor deposition (CVD) process by the combination of a Wien filter and an ion mobility analyzer. Under typical processing conditions for CVD diamond, negatively charged clusters composed of hundreds of atoms were measured. The mass distribution showed a peak at $\sim$3000 atomic mass unit with a gas mixture of 1.5% CH_4–99% H_2. The number density of the negatively charged clusters was estimated to be $\sim 10^6\,mm^{-3}$.

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Since diamonds can be synthesized relatively easily with a high growth rate using gas activation methods such as the hot filament [1,2] and plasma [3,4] processes, intensive studies have been conducted in this area. Atomic hydrogen was suggested to play a critical role in the low-pressure synthesis of diamond [2,5,6]. The atomic hydrogen hypothesis states that atomic hydrogen etches graphite much faster than diamond, which results in the dominant formation of diamond. However, Hwang et al. [7] reported that the atomic hydrogen hypothesis contradicts thermodynamic concepts and suggested that the dominant nucleation of diamond should be approached by the capillary effect in the nucleation stage. This thermodynamic contradiction was pointed out as a thermodynamic paradox by Yarbrough [8]. Hwang and Yoon [9] also suggested that the experimental observation of diamond deposition with simultaneous graphite etching contradicts the second law of thermodynamics if the deposition unit is atomic carbon. They suggested that this paradox could be avoided by assuming that diamond clusters nucleate in the gas phase

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where they subsequently become the growth unit of diamond films.

Based on these analyses and other experimental evidence, Hwang et al. [10,11] suggested the charged cluster model as the growth mechanism for the low-pressure synthesis of diamonds. In the model, charged diamond clusters composed of hundreds to thousands of atoms are suspended like colloidal particles in the gas phase during the diamond chemical vapor deposition (CVD) process and these clusters are the growth unit of a diamond crystal. The model was successfully extended to the silicon CVD process [12,13] and recently charged silicon clusters were experimentally confirmed [14]. Although the charged cluster model can explain many unusual phenomena taking place in the diamond CVD process, the existence of these hypothetical clusters has not yet been confirmed during the diamond CVD process. Experimental confirmation would be critical to the validity of the charged cluster model. In this letter, we report experimental confirmation of these hypothetical charged clusters containing a few hundred carbon atoms under typical processing conditions for diamond in the hot filament reactor.

In order to confirm the presence of charged clusters, a molecular beam sampling technique [15] was used, where the gas in the filament reactor was extracted through an orifice (1.2 mm in diameter) into the second chamber followed by a skimmer (2.0 mm in diameter) into a third chamber. By two-stage differential pumping, the reactor pressure was kept at 800 Pa and the pressure in the third chamber was < 0.0013 Pa. This three-chamber system is shown schematically in Fig. 1. A gas mixture of 1.5% CH_4–98.5% H_2 was supplied to the reactor at a rate of 20 sccm (standard cubic centimeter per minute) with a filament temperature of 2373 K. The distance between the orifice and the filament was 5 mm. The orifice was made of aluminum, which was connected to a water-cooled brass plate. Because of the high thermal conductivity of aluminum, the temperature of the orifice could be kept below 623 K even when the orifice was only 5 mm away from the hot filament. However, when a 1 mm thick molybdenum plate was placed over the orifice, the temperature increased to 1023 K and there well-crystalline diamonds were deposited.

The extracted gas or clusters have supersonic velocities. If these species are charged, they will be

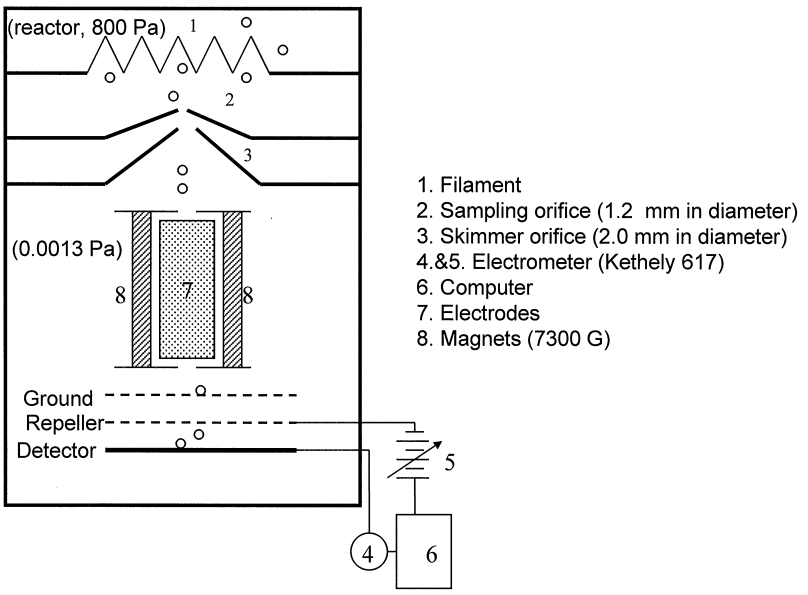

Fig. 1. Hot filament CVD system with a Wien filter and an ion mobility analyzer.

repelled by the application of like bias. Large and small charged clusters have, respectively, high and low kinetic energies. Charged species, which have a higher kinetic energy than the applied voltage, will impact on the detector where their flux can be measured as an electric current. Therefore, the measured current decreases with increasing repelling voltage. The energy distribution of the charged clusters is obtained by differentiating the measured current variation with respect to the repelling voltage. In order to derive the mass distribution from the energy distribution, the velocity of the clusters needs to be known. For this purpose, a Wien filter, which is a velocity selector, was used. Therefore, if the energy distribution is measured after the Wien filter, a mass distribution can be obtained.

Appreciable current was measured in the velocity range of 500–1000 ms^{-1}. Mass distributions for various selected velocities were measured. Four of them are shown in Fig. 2(a). The total charged cluster mass distribution is the sum of the data for all selected velocities, which is shown in Fig. 2(b). Since the lower filtering limit of our Wien filter is $\sim$2000 amu, data below this value are not shown.

Nearly all the clusters were negatively charged and the number of positively charged clusters was negligible in the hot filament diamond CVD reactor used in this study. This fact indicates that the source of charge must be electrons emitted from the hot filament. The distribution peak in Fig. 2(b) is $\sim$3000 atomic mass units (amu). This mass would correspond to $\sim$250 carbon atoms if the clusters consist solely of carbon.

The total current of the charged clusters on the detector was $\sim$200 nA. If it is assumed that the ejection velocity is 1000 ms^{-1}, the number density of the negatively charged clusters in the reactor was $\sim 10^{6}\,mm^{-3}$ at a filament temperature of 2373 K and a pressure of 800 Pa. However, considering the space charge effect [15] between the orifice and the detector, the number density of charged clusters in the reactor is expected to be larger than this estimation.

In conclusion, the hypothetical charged clusters, whose existence in the diamond CVD reactor was suggested by the charged cluster model, were experimentally confirmed. The presence of these clusters avoids the thermodynamic paradox of diamond deposition and simultaneous graphite etching, as these clusters are the growth unit of a diamond film. The charged cluster model may also apply to other crystal or thin-film systems. It appears from this and other studies [13,14,16] that crystal growth by charged clusters is a general mechanism in many thin-film processes and in some cases of solution growth.

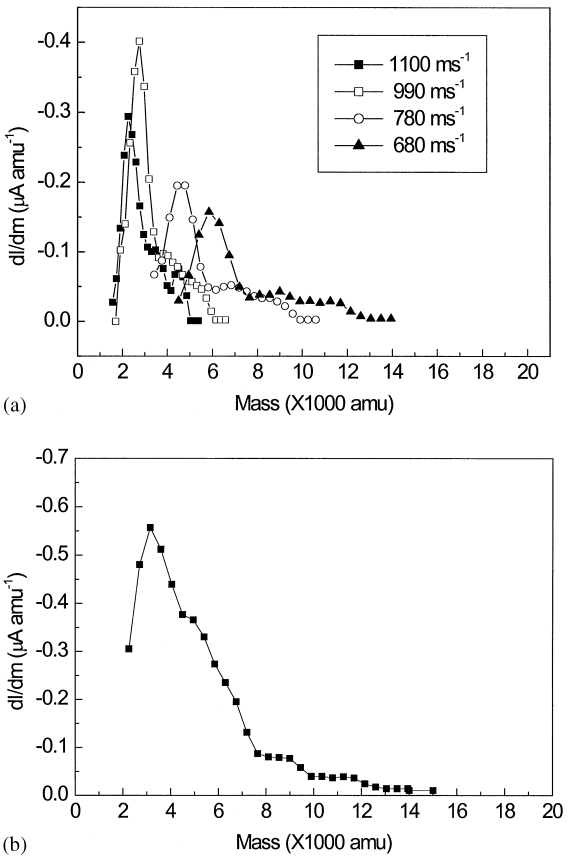

Fig. 2. Mass distribution of negatively charged carbon clusters extracted from the hot filament reactor (a) for four selected velocities by a Wien filter and (b) for the sum of the mass distributions for all measured velocities.

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