Diamond synthesis by plasma jet above a liquid surface

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Abstract

A new approach was proposed for the low-pressure diamond synthesis on high-resistant substrates using liquids as starting materials for carbon sources. The principle is to generate a DC plasma between the copper nozzle and the negatively-biased liquid surface under reduced pressure. The discharge continued with an applied voltage between 1.5 and 2 kV and at pressures between 30 and 50 kPa using a mixture of water– ethylene glycol solution. Plasma thus generated was led onto the silicon substrate placed horizontally and 1 mm over the nozzle top. The deposits distributed almost concentrically centered at the point directly above the nozzle axis. After deposition for 1 h, well-faceted diamond was formed in a limited region. The growth rate of the diamond film was 10 μm/h. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Since the development of low-pressure diamond synthesis, a variety of deposition methods are proposed.[1] In the chemical vapor deposition (CVD), diamond is generally formed by exposing the heated substrates to decomposed chemical species from the mixture, for example, of CH_4 and H_2 assisted by hot-filament or plasma.[2,3] Sometimes, carbon sources such as CH_3OH, C_2H_5OH, CH_3COCH_3 and $C_2H_5OC_2H_5$ are fed into the reaction chamber as gases by evaporating the corresponding liquids outside the reaction chamber.[4] Recently, a new method was proposed in which liquid is directly introduced in the chamber to produce the vapour by sputtering the liquid with charged species, i.e. by inducing a DC discharge between the metal substrate and the liquid surface under reduced pressure.[5] This method allows us to use a variety of liquid state organic compounds with relatively low vapour pressures as starting materials. The significance of introducing the oxygen- and nitrogen-containing organic compounds is clearly demonstrated by Hirose and Terasawa,[4] where diamond films with good crystalinity and high quality were obtained at growth rates of 8–10 μm/h which is 10 or several tens times faster than the thermal CVD method using oxygen-free feed gases. Our previous study has demonstrated that diamond could be prepared on metal substrates using a water–ethylene glycol solution.[6,7] However, in this method, the metal substrate worked also as positive electrode and thus the highly-resistant materials could not serve as substrates. Even with the semiconductor substrate of silicon, the trial failed. The silicon melted partially as soon as the discharge started. This was due to the positive temperature dependence of the conductivity in the semiconductor. The current path concentrated to the highest temperature zone, thus leading to its fusion by the Joule effect. Because the diamond deposition on insulators and semiconductors has a practical importance, a new approach is proposed in which the role of the substrate and the electrode is separated. The present report describes a plasma jet generation above the liquid surface and its application to diamond synthesis on silicon substrate.

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2. Experimental

Deposition was carried out using an apparatus similar to that reported elsewhere,[5–7] except the reaction chamber. The glass chamber was modified to generate the plasma jet as shown schematically in Fig. 1. The chamber was divided in two by a partition of water-cooled copper plate. The lower-room was for the plasma generation and the upper for the deposition. A copper nozzle was set at the center of the partition. The lower surface of the copper partition was covered with a thin mica plate to prevent the extra discharge from occurring. The distance between the nozzle and the solution was 8 mm. Prior to ignition, the upper-room was evacuated with an aspirator and hydrogen gas was introduced in the lower-room at a flow rate of 100 SCCM. The solution was biased negatively from the DC power source via graphite block immersed in the solution and the nozzle was grounded via partition. By applying a high DC voltage, plasma was generated. The sputter-evaporation of the solution increased the pressure in the lower-room and the plasma was expelled into the upper-room through the nozzle. The upper-room pressure was monitored by a vacuum gauge. Thus the plasma jet was generated and carried onto the 0.4 mm thick silicon substrate placed horizontally and 1 mm over the nozzle top. The substrate was cut from the n-type (100) wafer with a resistivity of 3~4 Ω cm. The substrate was cooled in contact with a copper block. The copper block was cooled with a running water. The substrate temperature was measured by a thermocouple attached at the back surface of the substrate center. The compositional selec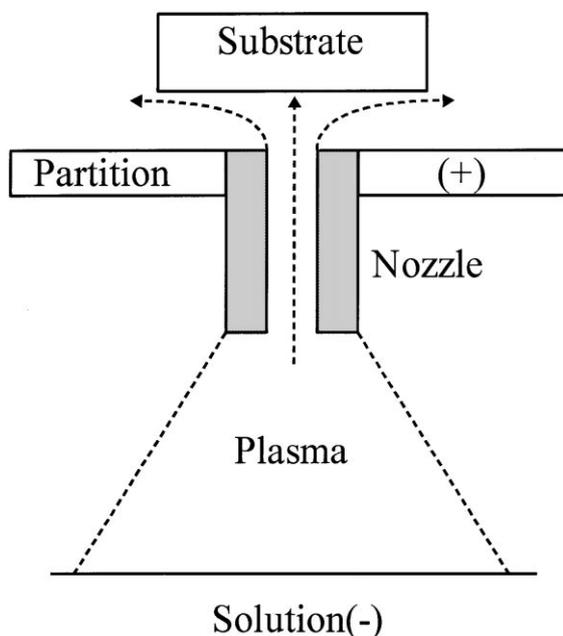tion of the solution for depositing diamond was based on our previous work.[7] A water–ethylene glycol solution was chosen as an electrolyte; it was a mixture of deionized water and 70 mol% ethylene glycol (purity: 99.5%) containing 0.1 mol% potassium acetate (purity: 97%). The solution was circulated and cooled. The surface level of the solution was kept constant with the aid of a reservoir. The deposits were examined by optical microscopy, scanning electron microscopy (SEM) and Raman spectroscopy. The 514.5 nm line of argon-ion laser was used to induce the Raman spectrum.

3. Results and discussion

Several tests with various nozzle dimensions showed that a copper pipe of 2 mm inner diameter, 4 mm outer diameter and 4 mm long could produce a plasma longer than for 1 h. Thus this dimension was mostly employed throughout the experiment. Table 1 shows the typical process factors for diamond formation under a constant applied voltage of 1550 V. Because similar results were obtained under different voltages between 1.5 and 2 kV, deposit analysis of a typical example was described. During the deposition, a pale blue jet was observed to blow up from the nozzle and the jet made the substrate red-hot. The small red spot fluctuated as the plasma fluctuated. This made the temperature measurement difficult. So the measured temperatures, 680~730°C, were regarded as the averaged values that the moving hot-spot has established on the substrate. Instantaneous temperature of the hot-spot may be very high, however there was no indication of substrate melting. On the substrate, the deposits distributed almost concentrically centered at the point directly above the nozzle axis; this defined the deposition radius R. Fig. 2 shows the SEM image of deposits distribution where seven spots (A–H) are indicated and Raman spectra from the corresponding spots are given in Fig. 3. No deposit was observed within the area of $R < 0.5$ mm (A). Well-faceted deposits were observed only at the narrow region of the periphery of $R \approx 0.5$ mm (C, D). A sharp Raman peak at 1333 cm^{-1} confirmed the formation of diamond. Outside the diamond region, 0.5 mm $< R < 2.5$ mm, disordered graphite developed (F–H). They showed a broad Raman peak centered at 1350 cm^{-1} and another broad peak centered

Fig. 1. Schematic illustration of the DC plasma jet CVD using liquid. The reaction chamber is divided in two by a partition.

Table 1
Typical process factors for diamond synthesis. Deposition was carried out using 70 mol % ethylene glycol solution

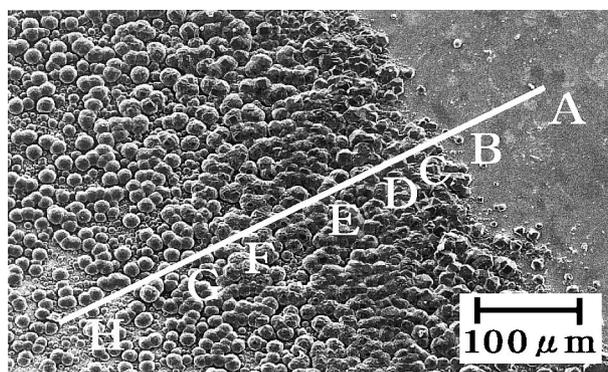| Substrate	Silicon wafer
Deposition time (h)	1
Applied voltage (V)	1550
Current (mA)	390–410
Upper-room pressure (kPa)	35–45
Liquid loss (g)	215
Conductivity of solution (S/m)	0.02 → 0.05

Fig. 2. SEM micrograph of deposits distribution. Upper right is near the jet center and no deposit is observed Raman analysis was carried out along the line from A to H.
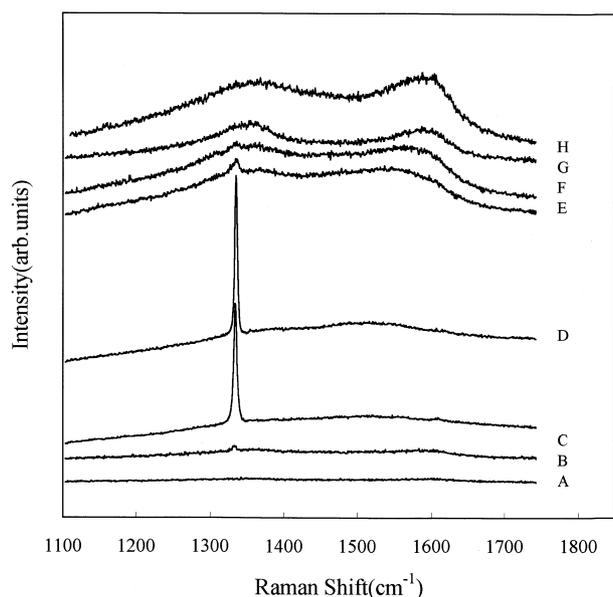

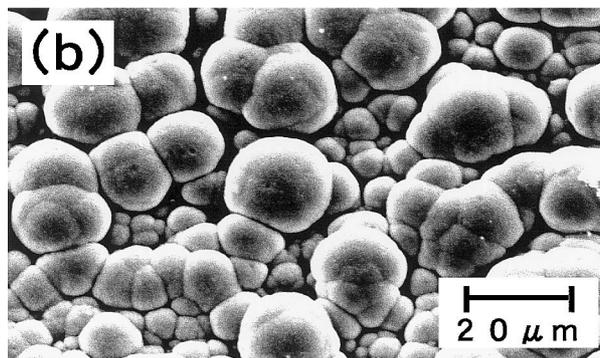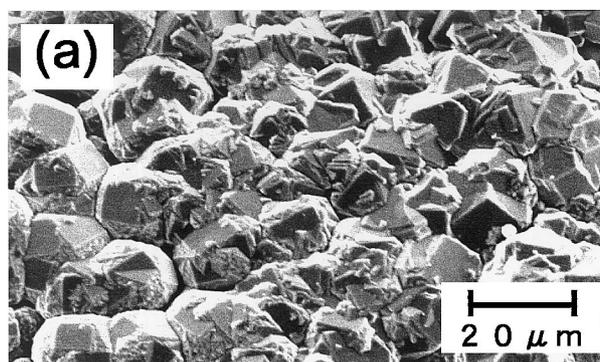Fig. 3. Raman spectra from deposits corresponding to the seven spots in Fig. 2.

Fig. 4. SEM micrographs of typical morphology: (a) well-faceted diamond near D in Fig. 2; (b) rounded surface of disordered graphite near G in Figs. 2 and 3.

around 1600 cm^{-1}.[8] Typical morphology of faceted diamond and rounded disordered graphite is given in Fig. 4. The Raman spectrum of disordered graphite (G in Fig. 3) is very similar to diamond-like carbon (DLC) except the larger half-width of the peak of the present deposits.[9] A cross-sectional view of the SEM showed that the growth rate of the diamond and disordered graphite films was almost identical; it was 10 μm/h or somewhat higher. The deposits distribution reflects the distribution of temperature and chemical species in the jet. It is generally reported that diamond growth occurs at substrate temperatures between 500 and 1200°C in the hydrocarbon–hydrogen system; growth at above 1200°C and below 500°C leads to graphite and DLC, respectively.[10] Supposing the similar tendency in our water–ethylene glycol system because diamond is produced at temperatures lower than 1100°C,[7] it may be

that the abundant hydrogen atoms and oxygen atoms (or oxygen molecules) in the jet core have entirely etched the graphitic deposits at the central region ($R <$ 0.5 mm). Diamond formation in a very limited region indicates the occurrence of a steep temperature gradient on the substrate rather than a sharp compositional change in the jet. The disordered graphite outside the diamond region may be the result of low substrate temperatures. Production of more stable plasma jet will enable the accurate temperature measurement and this is underway. The liquid temperature did not exceed 50°C after deposition for 1 h. The conductivity of the solution before and after deposition is given in the table. Initial conductivity of 0.02 S/m increased to 0.05 S/m after the discharge for 1 h. Hickling[11] has shown that the compositional change of the solution is the result of the positive ions entering the solution with energy as high as 100 eV. The same ion bombardment also induces the sputtering of the solution and produces a variety of chemical species in the gas phase. Although the liquid composition satisfies the diamond forming atomic ratio of C/(C + O) = 0.45 in the C–H–O phase diagram,[12] neither the compositional relationship between the solution and the gas nor the spectroscopic analysis of the gaseous species are examined yet. Regardless of this complexity involved, it is interesting to estimate the jet speed V in a very simplified model. Assuming that the plasma behaves as an ideal gas having pressure P and

temperature T in the plasma region in Fig. 1 and that the generated gases consist of their original molecules, i.e. $xC_2H_6O_2 - (1-x)H_2O$, the amount of the solution evaporated is

$$\frac{M \times 10^3}{62x + 18(1-x)} \text{ (mol)}$$

where M (kg) is the liquid loss in 1 h and 62 and 18 are the molecular weights of ethylene glycol and water, respectively. This corresponds to the gas volume of

$$\frac{186MT}{(x + 0.41)P} \text{ (m}^3\text{)}$$

The volume is equal to the total jet volume passing the nozzle for 1 h. Therefore,

$$V = \frac{0.066MT}{(x + 0.41)PD^2}$$

where D is the nozzle diameter.

For the present 70 mol% ethylene glycol system, putting $x = 0.7$, $M = 0.215$ Kg, $T = 1473$ K, $P = 4 \times 10^4$ Pa and $D = 2 \times 10^{-3}$ m, it yields $V = 120$ m/s. Although the calculation neglects the further decomposition of water and ethylene glycol and the pressure difference between the upper- and lower-room, it indicates a very high jet velocity. In fact, the silicon substrate had to be fixed firmly for not to be blown away by the jet impact. A set-up which can diminish the distribution of temperature and chemical species in the jet will help deposit diamond on a larger scale.

4. Concluding remarks

DC plasma jet was generated under reduced pressure by applying a high voltage between the copper nozzle of 2 mm inner diameter and the liquid surface of water–ethylene glycol mixture. The silicon substrate was placed horizontally and 1 mm over the nozzle. The deposits distributed almost concentrically centered from the point directly over the nozzle axis. This defined the deposition radius R. Deposition for 1 h at an applied voltage of 1550 V showed no deposit in the central region, $R < 0.5$ mm. Well-faceted diamond was formed at the periphery of $R \approx 0.5$ mm. Outside the diamond region, 0.5 mm $< R < 2.5$ mm, disordered graphite deposited. The jet speed was roughly estimated to be 120 m/s.

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