

Process parameters for diamond synthesis assisted by DC plasma using a water-ethylene glycol solution

T. SUZUKI, M. TSUKADA, T. YAMAZAKI, S. WADA, T. NOMA

Department of Applied Chemistry, Faculty of Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan

E-mail: takeyuki@cc.tuat.ac.jp

Influence of the liquid composition, concentration of the potassium acetate, substrate-liquid distance and liquid layer thickness on the diamond formation were surveyed under a constant current for deposition during 1 h. Optimum deposition conditions were found to be 0.1 mol % potassium acetate, 8 mm substrate-liquid distance and 10–20 mm liquid layer thickness. Diamond forming liquid composition was then examined under a constant substrate temperature. It ranged from 60 to 99.9 mol % ethylene glycol; end compositions showed a poor yield. A constant substrate temperature was maintained under a constant current for temperatures lower than 900 °C. However, an important current reduction was required during the deposition to keep the substrate temperature higher than 1000 °C. © 1999 Kluwer Academic Publishers

1. Introduction

In a low-pressure diamond synthesis, the source materials are fed into a reaction chamber as gaseous species. Thus carbon-containing starting materials have been limited to gases or liquids with high vapor-pressures [1]. In order to have a wide selection of liquids including those with low vapor pressures, new methods by electrolysis [2] and electrolytic heating [3] have been carried out. However, they failed to yield diamond. Another method consists of generating DC plasma between the anode substrate and the liquid surface under reduced pressure. In this method, the liquid is sputter-evaporated by an intense bombardment from the high energy positive ions in the plasma. Gaseous species thus generated work as source materials and chemical vapor deposition (CVD) takes place on the substrate. The new DC plasma CVD above the surface of a water-ethylene glycol solution yielded diamond [4]. Then, the effect of the deposition time on the morphology and quality was investigated and, further, a preliminary examination was carried out for a solution suitable as an electrolyte under a constant applied voltage [5]. However, the process parameters are still ambiguous. For example, the substrate temperature and the pressure have changed with deposition time under a constant applied voltage due to the chemical reaction in the solution. Leaving aside the chemical reaction in the solution, we must clarify the other process parameters in order to determine the best design for the apparatus and find out how it works. Thus the present paper describes the dependence of the diamond formation on the liquid composition and the electrode position using a water-ethylene glycol solution.

2. Experimental

Fig. 1 shows the schematic illustration of the apparatus. The reaction chamber was made of a glass cylinder of 5 cm in diameter and 15 cm in length both ends of which were covered by rubber stoppers. The chamber was evacuated by an aspirator through a cold trap and a vacuum regulator. The pressure was measured by a vacuum gauge. The solution was cooled and circulated at a rate of 150–180 ml/min. A reservoir was set in the circulation circuit to compensate for the evaporation loss of the solution. The gas phase of the reaction chamber and that of the reservoir was connected by a bypass to prevent the falling liquid from flowing backward; it served to keep the flat surface of the solution. The anode was a copper pipe of 4 mm in outer diameter; it was cooled with running water of a constant flow rate. The substrate was attached to the bottom of the anode pipe by suction with another aspirator through the inner hole of the pipe. The substrate was a tungsten disc of 4 mm in diameter and mostly 1 mm in thickness; 5 mm long pillar was employed only for the temperature measurement. No pretreatment was conducted on the substrate prior to deposition. Hydrogen was introduced around the substrate at a rate of 100 sccm. The cathode was a graphite disc of 4 cm in diameter. By momentarily touching the liquid surface to the substrate, discharge started and the solution was sputter-evaporated and served as feed gas. At the same time, hydrogen was generated from the graphite cathode by electrolysis. The amount of evaporation loss of the solution was measured from the reduction of the solution in the reservoir. The liquid temperature was measured by a thermometer inserted in the reservoir.

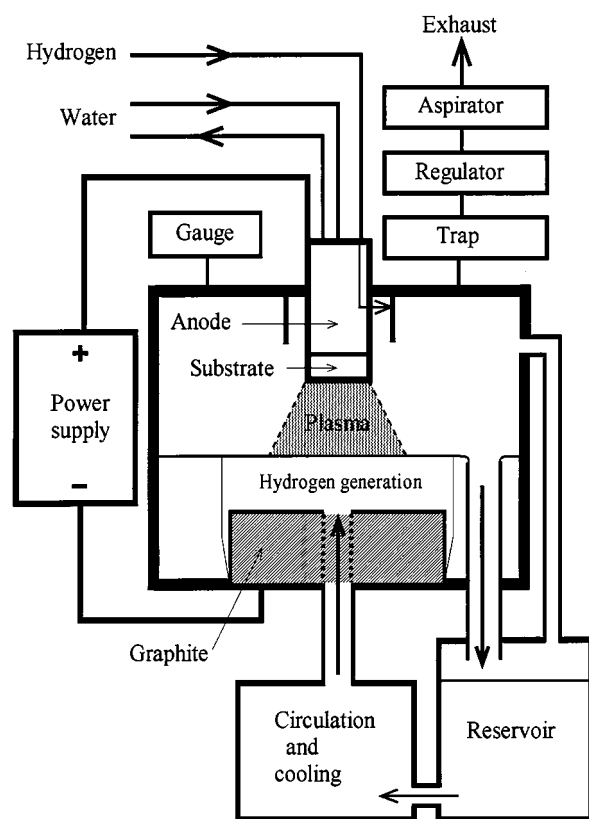
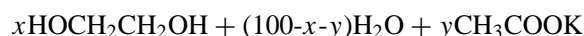


Figure 1 Schematic illustration of the experimental arrangement.

The solution was a mixture of ethylene glycol (purity: 99.5%), deionized water and potassium acetate (purity: 97%). The composition is given in mol % as follows.



Deposition was carried out first under a constant current for 1 h as long as the stable discharge continued, because of its ease of the manipulation, then under a constant substrate temperature using an optical pyrometer. The deposits were examined by optical microscopy, scanning electron microscopy (SEM) and Raman spectroscopy. The 514.5 nm line of an Arion laser was used to induce the Raman spectrum.

3. Results and discussion

The discussion follows neglects the hydrogen bubbles in the solution. The rate of hydrogen generation by electrolysis was calculated, supposing Faraday's law holds, to be at most 4 sccm under the present experiment. This rate is negligibly small compared with the 100 sccm of the inlet hydrogen. Only a small portion of the substrate surface being covered with diamond in most samples, the effective substrate area was regarded to be unchanged throughout the deposition.

3.1. Conductivity of the solution

Because the ethylene glycol contained 0.5% impure chemical species, an examination was carried out first to know whether it is possible to change the conductivity of the solution appreciably by adding a small amount of the potassium acetate. Fig. 2 shows the conductivity

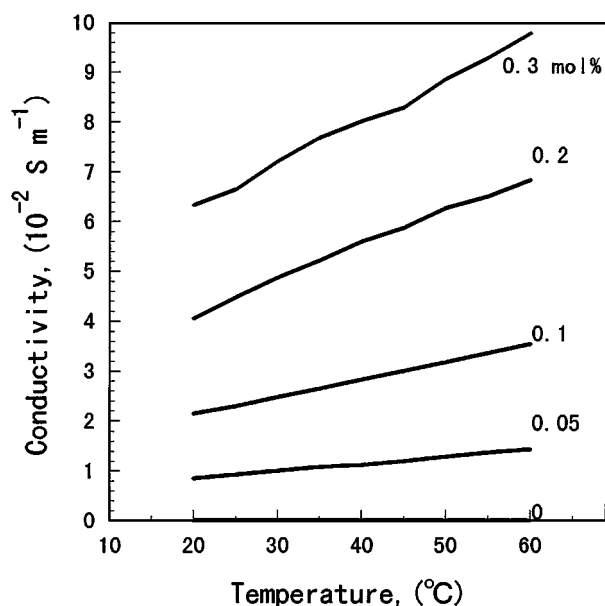


Figure 2 Influence of the potassium acetate concentration on the conductivity of 70 mol % ethylene glycol.

of 70 mol % ethylene glycol solutions. The conductivity ranged on the order of 10^{-2} S m^{-1} in solutions with 0.05–0.3 mol % potassium acetate. Solutions with no potassium acetate exhibited a very poor conductivity of less than $6 \times 10^{-5} \text{ S m}^{-1}$. It was clearly observed that even the addition of as small as 0.05 mol % potassium acetate was effective to increase the conductivity. Higher ethylene glycol concentration reduced the conductivity; the conductivity decreased to about a half in solutions containing no water. On the other hand, deposition increased the conductivity. For example, the conductivity of the 70 mol % ethylene glycol with 0.1 mol % potassium acetate increased twice after deposition for 1 h under 260 mA. Generally, 1 h deposition of solutions containing 0.1 mol % potassium acetate increased the conductivity 2–3 times. After the series of the present experiments, it became clear that the initial conductivity of about $2 \times 10^{-2} \text{ S m}^{-1}$ was desirable for a stable discharge during 1 h under a pressure range of 30–60 kPa. Solutions with higher or lower conductivity showed an increased discharge instability.

3.2. Deposition under a constant current

3.2.1. Standard deposition

As a standard reference, the deposition was carried out under a fixed electrode position using solutions containing 0.1 mol % potassium acetate. The substrate-liquid distance (the distance between the substrate and the liquid surface) was set to 8 mm and the liquid layer thickness (the distance between the liquid surface and the graphite cathode) was 20 mm. Fig. 3 shows the diamond forming current region. The temperature and the evaporation loss of the solution were less than 40°C and 100–200 ml, respectively in 1 h at the highest current region. The evaporation loss increased with increasing current and ethylene glycol concentration. This induced an increased vapor pressure and led to a discharge instability. Most SEM images and Raman spectra of diamond were similar to those given elsewhere [5]. The diamond region gave the widest current span at 70 mol %

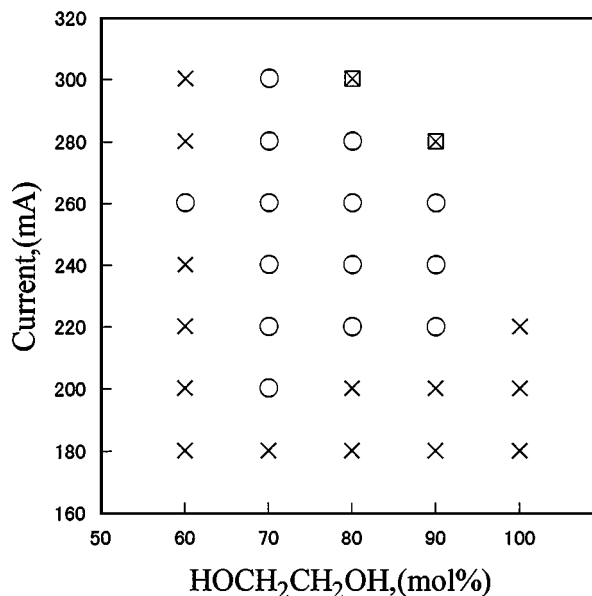


Figure 3 Diamond forming region in the system water-ethylene glycol mixed with 0.1 mol % potassium acetate under a constant current: (○) diamond in 1 h deposition; (×) no diamond in 1 h deposition; (⊗) no diamond, discharge stopped in less than 1 h.

and the region reduced with higher ethylene glycol concentration. Deposition with current lower than the diamond region generally produced graphite whiskers. Contrary to the wide diamond region of 70 mol %, the 60 mol % solution scarcely yielded diamond. This sharp contrast may be interpreted as follows. Although the gas phase chemical species are not equal to the liquid composition, supposing that the atomic fraction of carbon and oxygen is similar in both phases, the rule proposed by Bachmann *et al.* [6] holds true in our results. The rule predicts that the diamond domain exists at the higher C/(C + O) atomic fraction than 0.40–0.45. In our initial solution, the atomic fraction is 0.43 and 0.45 for 60 and 70 mol % ethylene glycol, respectively. Thus the atomic fraction of 60–70 mol % solution falls on the boundary, however, the 60 mol % solution is more distant from the diamond domain. As for the substrate temperature, see Section 3.3. Further discussion will be done with the experimental knowledge of chemical species in the gas phase.

3.2.2. Concentration of the potassium acetate

Because the diamond forming region was found to be the widest in the composition of 70% ethylene glycol, deposition was carried out using this composition with 0.05–0.3 mol % potassium acetate at each 0.05% step. The substrate-liquid distance and the liquid layer thickness were fixed to 8 and 20 mm, respectively. Potassium acetate concentration strongly influenced the diamond formation. Diamond region was the widest at 0.1 mol % (Fig. 3), the current range of 220–260 mA yielded diamond at 0.15 mol %. However, other potassium concentration rarely produced diamond. The lowest concentration of 0.05 mol % gave diamond only at 280 mA. For concentration higher than 0.2 mol %, the discharge instability increased greatly and except for

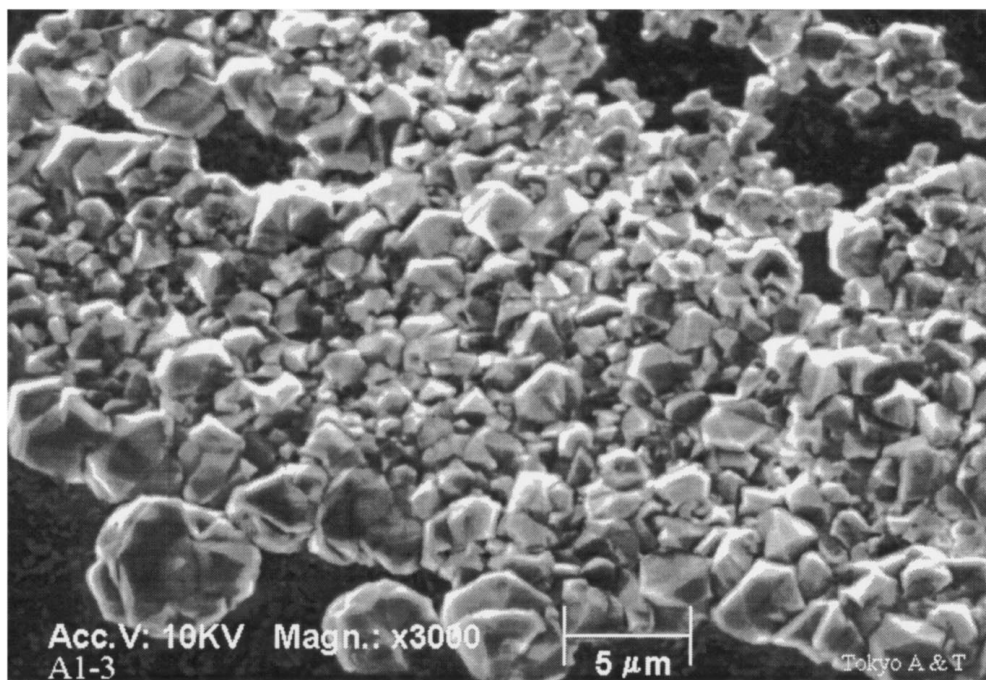
the (300 mA, 0.3 mol %) sample, which was prepared by an intermittent discharge for 30 min, no diamond was observed. Although most Raman spectra were similar to those given elsewhere [5], diamond in the (300 mA, 0.3 mol %) sample exhibited a peculiar Raman spectrum as shown in Fig. 4. The sharp peak at 1336 cm⁻¹ and a broad peak around at 1600 cm⁻¹ clearly indicate that diamond was formed with disordered graphite [7], however, coexisting peaks at 1419 cm⁻¹ and at 1752 cm⁻¹ are identified neither as disordered graphite nor as non-diamond carbon [8]. It is to be noted that J. Stiegler *et al.* [9], using microwave plasma assisted CVD with CH₄/CO₂ mixtures, have also reported a similar but broader unidentified peak at approximately 1420 cm⁻¹ at the lowest substrate temperature of 300 °C where the diamond peak has just vanished.

3.2.3. Substrate-liquid distance

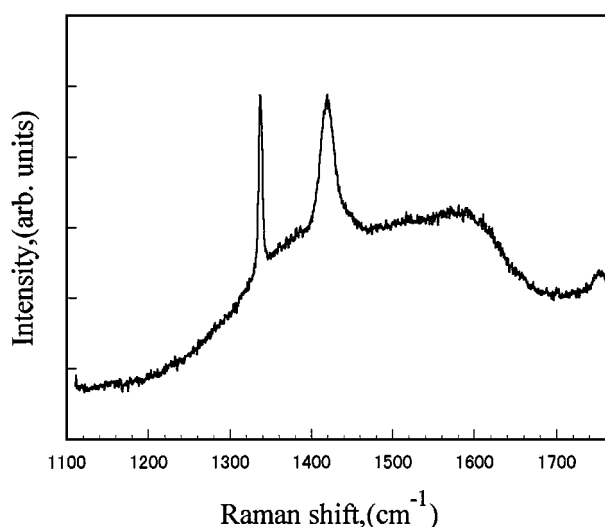
Deposition was carried out with the liquid layer thickness of 20 mm using the 70 mol % ethylene glycol with 0.1% potassium acetate under the varying substrate-liquid distance. Fig. 5 shows the diamond formation region. With 1 mm distance, the discharge changed to a high current mode with a low total resistance (applied voltage divided by deposition current) of less than 3 kΩ. The discharge was stable even under the atmospheric pressure. Thick deposits was identified as disordered graphite [7] by Raman spectroscopy. With other distances, glow discharge induced the best results at 8 mm; diamond yield was limited to high current region at 4 mm and discharge instability occurred at 12 mm with a high total resistance of 7–8 kΩ.

3.2.4. Liquid layer thickness

The aim of this work was to know the minimum liquid layer thickness to carry out the deposition. Deposition was carried out using a solution containing 0.1 mol % potassium acetate with a constant substrate-liquid distance of 8 mm. Diamond forming region was compared under the varying liquid layer thickness of 5, 10 and 20 mm. With the 5 mm layer thickness, the ignition became difficult and plasma stopped in a few minutes as a result of the discharge instability. Diamond region at the 10 mm layer thickness was somewhat narrower but similar to that of 20 mm layer thickness (Fig. 3); the 60 mol % ethylene glycol solution yielded no diamond. Better discharge stability at 10–20 mm layer thickness than that at 5 mm may be attributed to the liquid layer resistance. The initial liquid resistance of 5 and 10–20 mm thickness was calculated to be 110 and 220–440 Ω at 25 °C, respectively from the conductivity data in Fig. 2. The liquid resistance of 110 Ω is probably too small. It will be worthwhile to put a buffer resistance of 200–300 Ω in series to stabilize the discharge. Contrary to our expectation that the total resistance will increase with the liquid layer thickness under a given current, no definite relation was observed between the two factors. Experimentally, the total resistance lay between 5–7 kΩ. The value is far greater than the liquid resistance. Thus, a small change in the plasma state was supposed to have hindered the influence of the liquid resistance. In fact, the plasma state changed in a subtle



(a)



(b)

Figure 4 SEM image and Raman spectrum of a sample prepared with intermittent discharge for 30 min under 300 mA using 70 mol % ethylene glycol with 0.3 mol % potassium acetate.

way not only by the substrate setting but also by the distance adjustment.

3.3. Deposition under a constant substrate temperature

So far, the substrate temperature was neglected and, instead, the current was used as a measure for the diamond forming parameter. The following temperatures should be regarded as mere estimates, because the optical pyrometer was always adjusted to the value of the tungsten emissivity and no correction was made on the graphite deposition. Deposition was carried out under the substrate-liquid distance of 8 mm and the liquid layer thickness of 20 mm; the solution contained always 0.1 mol % potassium acetate. Fig. 6 shows the change of the current with time to maintain the constant substrate temperatures of 900–1100 °C in 70 mol % ethylene gly-

col solutions. The first 10 min was the transition period necessary to stabilize the temperature. It was observed that to keep the substrate temperature at 900 °C, it was enough to maintain the current at 240 mA. However, to keep the substrate temperatures higher than 1000 °C, an important current reduction was required. This is the reflection of the chemical reaction in the solution which was induced by the intense positive-ion bombardment at the liquid surface. Diamond forming region is given in Fig. 7 as functions of liquid composition and temperature. It corresponds to Fig. 3. Comparison of these figures predicts that diamond can be yielded at temperatures lower than 850 °C. Diamond was scarcely observed in the end compositions of 60 and 99.9 mol % ethylene glycol. The best diamond coverage of about 30% was found in the temperature range from 950 to 1050 °C at 90 mol %. Further study is underway for a search of a solution suitable as an electrolyte.

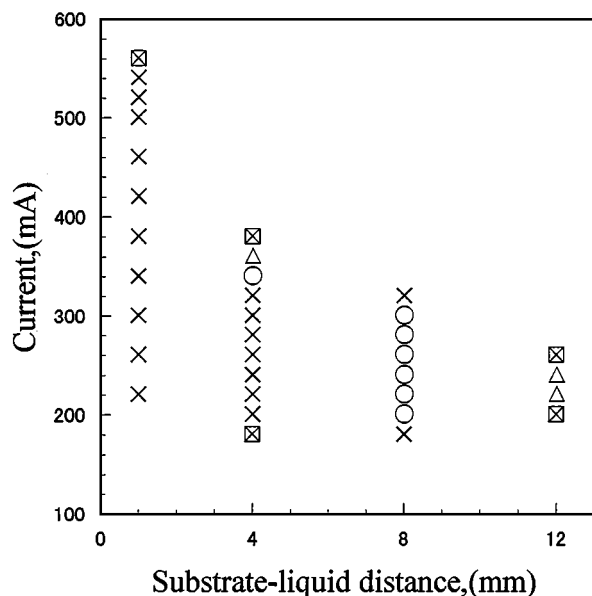


Figure 5 Influence of substrate-liquid distance: (O) diamond in 1 h deposition; (Δ) diamond, discharge stopped in less than 1 h; (\times) no diamond in 1 h deposition; (\otimes) no diamond, discharge stopped in less than 1 h.

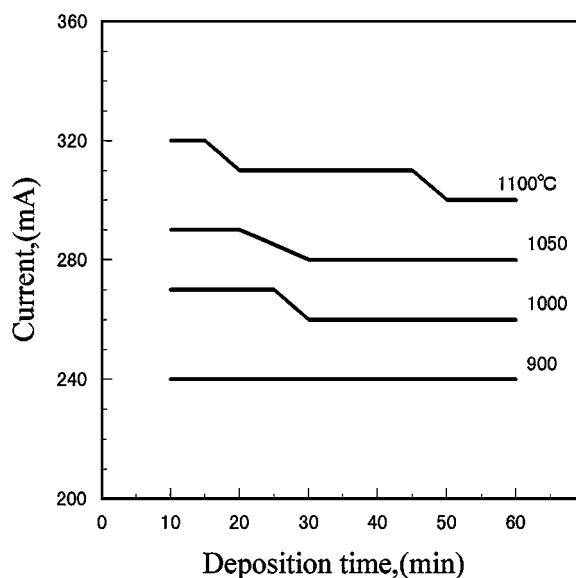


Figure 6 Change of current during deposition under a constant substrate temperature.

4. Conclusions

Optimum process parameters were investigated for diamond synthesis assisted by DC plasma using a water-ethylene solution. Deposition was carried out for 1 h under a pressure of 30–60 kPa. The results were as follows.

1. Potassium acetate concentration of 0.1 mol%, giving the initial liquid conductivity of about $2 \times 10^{-2} \text{ Sm}^{-1}$, was desirable for a stable discharge.

2. Substrate-liquid distance of 8 mm showed the best glow discharge. Shorter distance of 1 mm changed the discharge to a high current mode and no glow discharge was observed. Longer distance of 12 mm induced a plasma instability.

3. Liquid layer thickness of 10–20 mm generated a stable plasma. Thinner or thicker thickness induced a discharge instability.

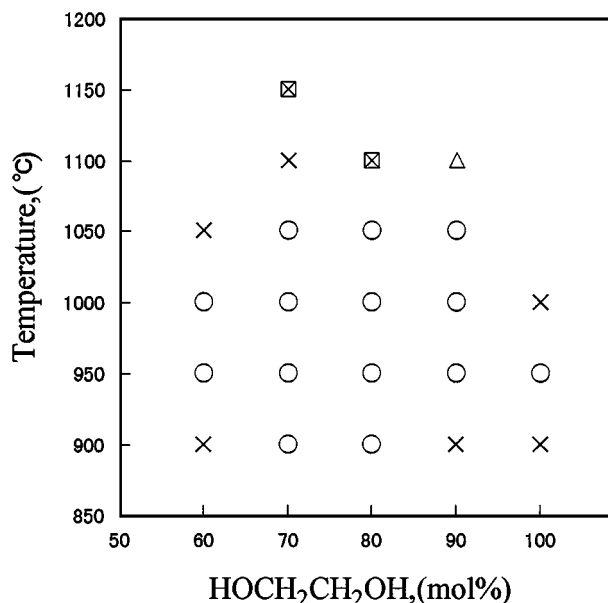


Figure 7 Diamond forming region in the system water-ethylene glycol mixed with 0.1 mol% potassium acetate under a constant substrate temperature: (O) diamond in 1 h deposition; (Δ) diamond, discharge stopped in less than 1 h; (\times) no diamond in 1 h deposition; (\otimes) no diamond, discharge stopped in less than 1 h.

4. Diamond forming composition ranged from 60 to 99.9 mol% ethylene glycol; end compositions showed a poor yield. The best yield of about 30% coverage was observed at 90 mol% between 950 and 1050 °C.

5. A constant substrate temperature was maintained under a constant current for temperatures lower than 900 °C. However, an important current reduction was required during the deposition to keep the substrate temperature higher than 1000 °C.

Acknowledgement

This study was partly supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan (No. 07555680).

References

1. T. D. MOUSTAKAS, in "Synthetic Diamond," edited by K. L. Speae and J. P. Dismukes (John Wiley & Sons., New York, 1993) p. 145.
2. T. SUZUKI, Y. MANITA, T. YAMAZAKI, S. WADA and T. NOMA, *J. Mater. Sci.* **30** (1995) 2067.
3. T. SUZUKI, T. NOMA, S. WADA, T. YAMAZAKI, Y. MANITA and T. YANAI, *ibid.* **31** (1996) 3743.
4. T. SUZUKI, T. ISHIHARA, T. YAMAZAKI and S. WADA, *Jpn. J. Appl. Phys.* **36** (1997) L504.
5. T. SUZUKI, T. ISHIHARA, T. SHIMOSATO, T. YAMAZAKI and S. WADA, *J. Eur. Ceram. Soc.* **18** (1998) 141.
6. P. K. BACHMANN, D. LEERS and H. LYDTIN, *Diamond and Related Materials* **1** (1991) 1.
7. F. TUINSTRAN and J. K. KOENIG, *J. Chem. Phys.* **53** (1970) 1126.
8. M. RAMSTEINER and J. WAGNER, *Appl. Phys. Lett.* **51** (1987) 1355.
9. J. STIEGLER, T. LANG, M. NYGAED-FERGUSON, Y. VON KAENEL and E. BLANK, *Diamond and Related Materials* **5** (1996) 226.

Received 19 June
and accepted 23 December 1998