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DC-Plasma-assisted Synthesis of Diamond and Alumina Using Liquid

Takeyuki Suzuki,* Toshihiko Ishihara, Tomonori Shimosato, Tsutomu Yamazaki and Satoshi Wada

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

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Abstract

A new approach was proposed for the DC-plasma-assisted ceramic synthesis using liquid as starting materials. The method consists of generating a plasma between the substrate (electrode) and the liquid phase. Plasma-assisted deposition above the liquid surface of a water–ethylene glycol solution yielded diamond on anode substrate under a constant applied voltage. The morphology and quality of diamond changed from mirror-ball particle with disordered graphite to high-quality film with prolonged deposition. Heating a cathode wire by discharge in an aqueous solution of aluminum nitrate produced α-alumina coatings without post-annealing under atmospheric pressure. Deposition stopped automatically when the whole wire in the solution was covered with alumina. The growth rate of the alumina coatings ranged 1–10 μm min^{-1}. © 1997 Elsevier Science Limited.

1 Introduction

In a low-pressure diamond synthesis by chemical vapor deposition (CVD),[1] carbon-containing species are fed into the reaction chamber and substrates are heated assisted by hot-filament or plasma. Thus, raw materials are limited to molecules with high vapor pressures, typically gases. Therefore, a variety of liquids are left unused in the conventional CVD. If a plasma can be generated close to the liquid surface, liquids with relatively high vapor pressures can also be served as starting materials and this will give us a wide selection of raw materials. One such way is to heat a cathode in an electrolyte solution under atmospheric pressure. The method is known as contact glow-discharge electrolysis[2] or electrolytic heating[3] where the cathode is surrounded by a thin vapor sheath in the solution and heated by discharge through the sheath [Fig. 1(a)]. However, deposition by electrolytic heating of tungsten wires in ethanol solutions produced glassy or disordered graphitic carbon and no diamond was observed.[3] Taking account of the facts that diamond growth is enhanced by electrically biasing the substrate holder positively with respect to the filament in hot-filament method[4] and that substrate placed on the anode yielded diamond in DC plasma CVD,[5] a method was undertaken to apply a high DC voltage between the anode substrate in the gas phase and the liquid surface under reduced pressure [Fig. 1(b)]. This yielded diamond using a water–ethylene glycol solution, however, the chemical reaction in the solution resulted in the change of the deposition parameters.[6] The present paper deals with a search for an electrolyte solution and diamond synthesis under a constant applied voltage. Further, to see whether or not the electrolytic heating can be applicable to other ceramic synthesis, alumina deposition was carried out.

2 Experimental

2.1 Diamond

DC plasma CVD above the liquid surface was carried out under reduced pressure. The glass reaction chamber was evacuated using an aspirator and a vacuum controller. Hydrogen was introduced at a rate of 100 SCCM to prevent the risk of explosion. The solution was cooled and circulated. The surface level of the solution in the reaction chamber was kept constant with the aid of a reservoir which was set in the circulation circuit. Cathode was a graphite block and anode was a copper rod. The distance between the substrate and the

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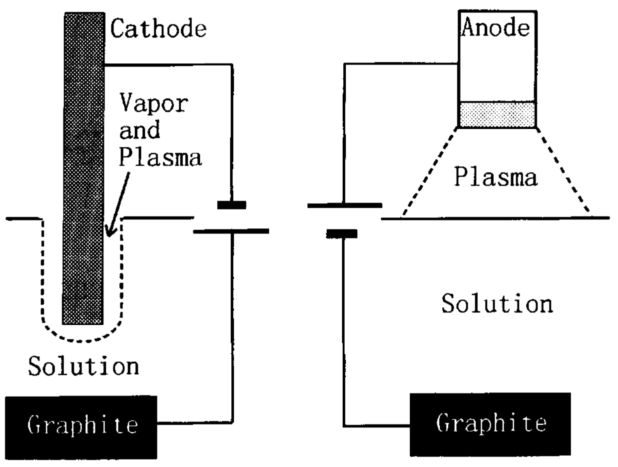
*To whom correspondence should be addressed.



(a) (b)

Fig. 1. Schematic illustration of the DC-plasma-assisted CVD using liquid. (a) Electrolytic heating in the liquid and (b) CVD above the liquid surface.

solution was 8 mm. Molybdenum disk and tungsten carbide disk containing 12% cobalt were used as substrates whose dimensions were 4 mm in diameter and 1 mm in thickness. Prior to deposition no pretreatment was conducted on the substrate. The amount of evaporation loss was measured from the reduction of the solution in the reservoir. The temperature of the liquid was measured by a thermometer inserted in the reservoir. A preliminary examination was carried out for a solution suitable as an electrolyte under a constant applied voltage using molybdenum substrates. Solutions tested were aqueous solutions of methanol, ethanol, n-propyl alcohol, n-butyl alcohol, glycerol, dimethyl sulfoxide (DMSO), sucrose and ethylene glycol; these were mixed with 0·1 mol% potassium acetate. The deposits were examined by optical microscopy, scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and Raman spectroscopy. The 514·5 nm line of argon–ion laser was used to induce the Raman spectrum.

2.2 Alumina

Deposition by electrolytic heating was carried out in air under atmospheric pressure. The reaction vessel was a beaker whose wall was cooled with ice-water. Anode was a graphite block and cathode was a tungsten wire of 0·5 mm in diameter. The wire was dipped gradually into the solution down to 5 mm by a linear head under a constant applied voltage. The electrolyte was a mixture of deionized water and aluminum nitrate. The surface level of the solution was kept constant by adding the solution to compensate for the evaporation loss. The deposits were examined by optical microscopy, scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD).

3 Results and Discussion

3.1 Diamond

Table 1 shows the concentration, applied voltage and observation for each of the solutions. Solutions of methanol, ethanol and n-propyl alcohol showed a vaporization too intensive to continue the deposition, phase separation in the n-butyl alcohol solution was not desirable for the stable discharge, highly viscous 60 mol% glycerol solution yielded few diamond particles under 1400 V in 30 min, DMSO solution gave out an offensive odor and sucrose solution showed no evidence of diamond formation. Thus, a water–ethylene glycol solution was chosen; it was a mixture of 19·9 mol% deionized water and 80 mol% ethylene glycol containing 0·1 mol% potassium acetate. Influence of the deposition time under a constant applied voltage was then examined using a tungsten carbide substrate containing 12% cobalt. Deposition was carried out under 1350 and 1450 V for 30, 60 and 120 min. Figure 2 shows the SEM images of deposits as functions of deposition time and applied voltage. Raman spectra from corresponding deposits are shown in Fig. 3. A sharp diamond peak was observed at 1335 cm^{-1} (c, d, f) or at 1333 cm^{-1} (a) together with the broad peaks of disordered graphite bands[7] centered around at 1350 cm^{-1} and 1600 cm^{-1}. It was observed that longer deposition have changed the diamond from the agglomeration of mirror-ball like particles with disordered graphite to high quality films. Similar mirror-ball morphology was also observed

Table 1. Deposition on molybdenum substrate under a constant applied voltage using aqueous solutions mixed with 0·1 mol% potassium acetate. Deposition was carried out up to 60 min as long as the stable discharge continued

Material	*Concentration (mol%)*	*Voltage (V)*	*Observation*
Methanol	40, 60	900–1000	Vaporization
Ethanol	10–99·9	1000–1700	Vaporization, graphite, carbon particle
N-propyl alcohol	5–40	900–1500	Vaporization, graphite, whisker
N-butyl alcohol	25	1200	Phase separation
Glycerol	20–60	750–1400	Viscous, diamond (60 mol%, 1400 V)
DMSO	20, 80	900, 1500	Sulfide deposition
Sucrose	Saturation	800	Substrate etching
Ethylene glycol	20–80	600–1500	Diamond (80 mol%, 1300–1500 V)

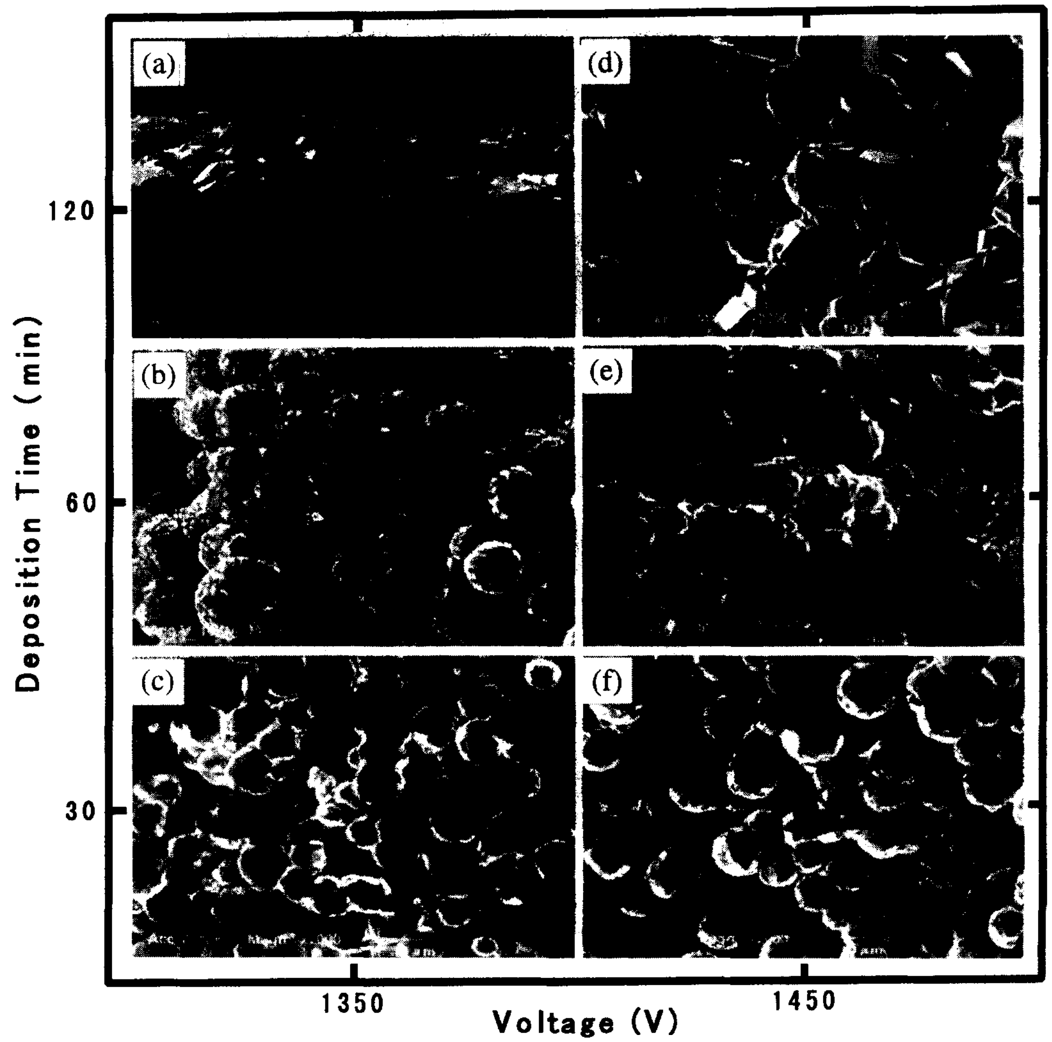


Fig. 2. SEM images of deposits as functions of applied voltage and deposition time. Deposition was carried out under a constant applied voltage on the tungsten carbide substrate containing 12% cobalt.

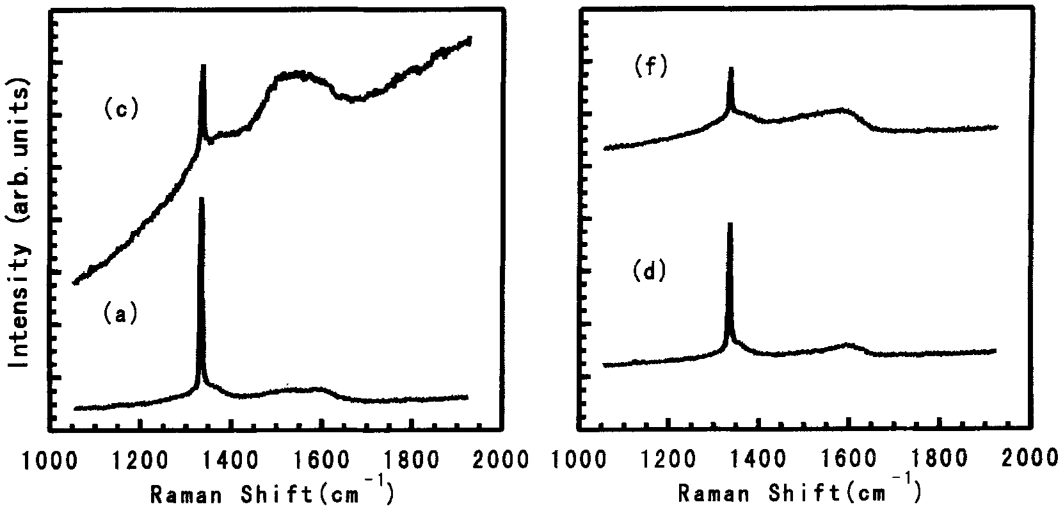


Fig. 3. Raman spectra from deposits shown in Fig. 2.

in diamond deposited on molybdenum substrate for 30 and 60 min. Although diamond was thus deposited, it was distributed locally at the periphery of the substrate. Reliable temperature could not be measured by optical pyrometer. During the deposition under a constant applied voltage, both the current and the pressure have increased as a result of the chemical reaction in the solution. For example, during the deposited for 2 h under 1450 V, the (current, pressure) changed from

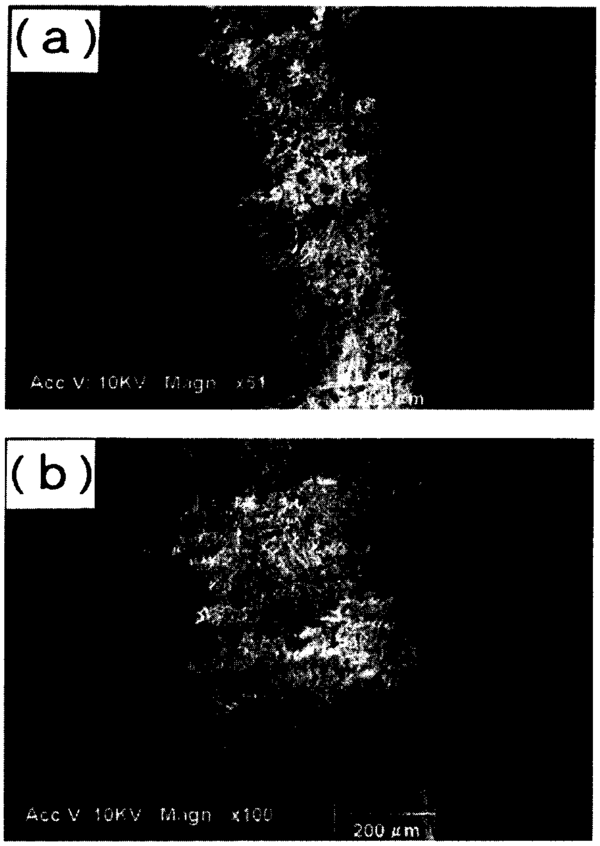


Fig. 4. SEM images of alumina coatings on the tungsten wire dipped 5 mm in the aqueous solution of 1 mol% aluminum nitrate under 150 V. Deposition stopped automatically in 5 min. (a) Surface morphology and (b) cross-sectional picture with higher magnification.

(210 mA, 33 kPa) to (300 mA, 51 kPa). The liquid temperature did not exceed 40°C and the amount of the liquid loss was 220 ml. These changes induced the apparent substrate temperature. Thus, deposition under a constant substrate temperature, or more practically, deposition under a constant current is preferable and this is under way. What is striking is the high carbon concentration of 20 at% in the solution. In the typical CVD using the H_2–CH_4 system, the carbon concentration is generally less than 1 at%. Although the probable preferential sputter-evaporation of water may reduce the carbon concentration in the gas phase, diamond formation in the present method is rather similar to that of the combustion flame method,[8] where 30 at% carbon is fed with the comparable amount of oxygen. For detailed discussion, we need the knowledge of the time-varying chemical species in the gas and liquid phases.

3.2 Alumina

At the moment the wire tip touched the solution the discharge heating started. XRD analysis showed that electrolytic heating produced α-alumina without post-annealing. When the alumina covered the whole surface of the wire in the solution, the discharge stopped automatically. The deposition time up to the auto-stop was 5 min in 1 mol% aluminum nitrate solution under 150 V, 15 min in 0·5% solution under 150 V and 25 min in 1% solution under 100 V. Figure 4 shows the SEM images of the 5 min auto-stop sample. Deposited alumina exhibited rugged surfaces. The growth rate of coatings ranged 1–10 μm min^{-1}. The current behavior was almost the same for these samples. For the 25 min sample, the initial current of 700 mA soon decreased to a constant value of 250 mA. The evaporation loss of the solution was 20 ml. The liquid temperature increased to 65°C in 25 min. It is to be noted that deposition by electrolytic heating using magnesium nitrate solution produced magnesia coatings on tungsten wire in like manner.

4 Concluding Remarks

DC-plasma-assisted CVD using aqueous solutions was demonstrated above and in the solution for the synthesis of diamond and alumina.

4.1 Diamond

Plasma was generated above the liquid surface under a constant applied voltage. Aqueous solutions of glycerol and ethylene glycol produced diamond on molybdenum substrate. Influence of the deposition time on the morphology and quality of diamond on tungsten carbide substrate was studied under 1350 and 1450 V using the solution of 80 mol% ethylene glycol. The diamond changed from mirror-ball like particles with disordered graphite in 30 min to better quality films in 120 min. They were deposited locally on the periphery of the substrate. The current and the vapor pressure increased during the deposition under a constant applied voltage.

4.2 Alumina

Deposition by electrolytic heating was carried out using a tungsten cathode wire of 0·5 mm in diameter, which was dipped 5 mm in an aqueous solution of aluminum nitrate. Plasma was generated by discharge through the thin vapor sheath between the cathode and the liquid phase. It yielded α-alumina coatings without post-annealing. When the whole surface of the wire in the solution was covered with alumina, the deposition stopped automatically. Deposited alumina exhibited rugged surfaces; the growth rate of alumina coatings ranged 1–10 $\mu m\,min^{-1}$.

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