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Deposition of carbon films by electrolysis of a water–ethylene glycol solution

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An attempt was made to deposit carbon films by electrolysis of a water–ethylene glycol solution. Carbon plate and an *n*-type silicon substrate were dipped in the solution and a high d.c. potential was negatively applied on the silicon substrate. Some deposits were observed in the region between the boiling point curve and the line approximately 50 °C below and parallel to the boiling point, when electrolysis was carried out at 1 kV for 6 h. For higher potentials of 1.4–2.0 kV and longer electrolysis of 12 h, some samples showed a broad X-ray diffraction peak and Raman peaks, corresponding to graphitic carbon.

1. Introduction

Diamond and diamond-like carbon films are generally prepared from the gas phase in a variety of methods, such as ionized deposition [1], chemical vapour deposition [2, 3] and oxyacetylene combustion [4], and have been reviewed in [5]. Although high quality and rapid growth rates are achieved, gas phase synthesis requires the substrate temperature to be at least several hundred degrees centigrade. Reduction of the temperature will prevent damage of the substrates, and will also allow the use of low melting substrates, such as plastics. The possible use of low melting substrates will significantly enlarge the application field of diamond or diamond-like carbon films.

The pioneering work of Namba [6] showed that films were successfully deposited from liquid ethanol at a temperature as low as 50 °C. However, the choice of a suitable liquid was limited. Among the electrolytes of trichloroethylene, ethanol, acetone and benzene, only ethanol gave an interesting result. Since liquid phase synthesis has significant implications for the science and technology of carbon films, it is worth pursuing research with other electrolytes. This led to the electrolysis of the binary system H_2O–$HOCH_2CH_2OH$ (ethylene glycol) reported here.

2. Experimental procedure

The experimental arrangement for preparing films is shown schematically in Fig. 1. The positive electrode was a carbon plate. The negative electrode was an *n*-type ⟨1 0 0⟩ silicon substrate, with a resistivity of $3 \sim 4\,\Omega$cm and a size of $5 \times 30 \times 0.4$ mm^3. The substrate was cleaned in deionized water and then in an HNO_3–HF solution by ultrasonic treatment. The back of the silicon was covered with an insulating adhesive tape. Both electrodes were mounted to the copper plates with the aid of polytetrafluoroethene (PTFE) sealing tape. The distance between the electrodes were set to 4 mm using a PTFE spacer. The boiling point of the system H_2O–$HOCH_2CH_2OH$ was increased smoothly from 100 °C of water to 198 °C of ethylene glycol. The silicon substrate was immersed 5 or 10 mm into the solution in a 300 ml beaker. The constant potential applied to the substrate was 0.4–2.0 kV, under a constant temperature of 0–150 °C. The deposits were examined by optical microscopy, X-ray diffraction (XRD), using CuK$_\alpha$ radiation, scanning electron microscopy (SEM) and Raman spectroscopy.

3. Results and discussion

3.1. Survey at 1.0 kV

The first step was to find the deposition region. Deposition was judged as the point at which more than several per cent of the silicon surface was covered with deposits, including apparent organics, under the optical microscopy. Fig. 2 shows the formation region of deposits when electrolysis was carried out at 1.0 kV for 6 h. Occurrence of deposition was observed in the limited region between the boiling point curve and the line approximately 50 °C below and parallel to the boiling point. The colour of the deposits varied with composition and temperature; e.g. black with 6.5 mol % ethylene glycol at 100 °C, to pale yellowish of pure ethylene glycol at 140 °C. Fig. 3 gives the current density under 1.0 kV at 80 °C for 6 h. The current depended strongly on the concentration in the water-rich side. When the ethylene glycol was less than 40 mol %, the current density was 10–30 mA cm^{-2}, whereas for higher concentrations than 50 mol %, it remained within 2–6 mA cm^{-2}. The current fluctuation with time was mainly attributed to deposition and also to change of the liquid

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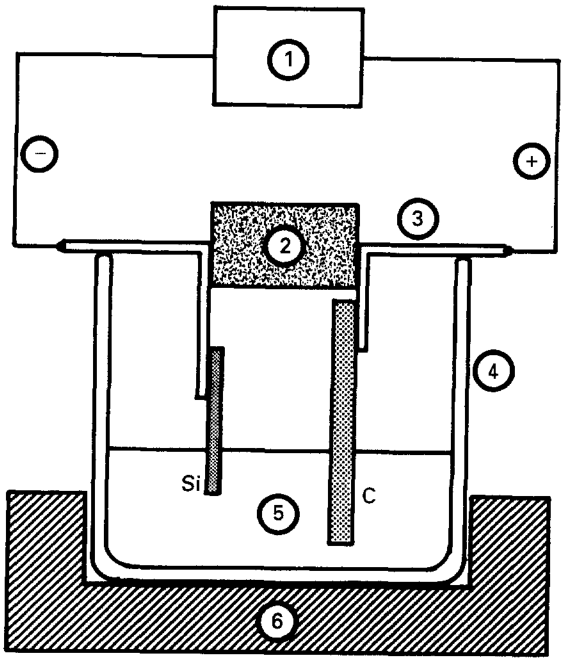

Figure 1 Schematic illustration of the experimental arrangement: (1) d.c. source, (2) spacer, (3) copper plate, (4) beaker, (5) solution, and (6) heat bath.

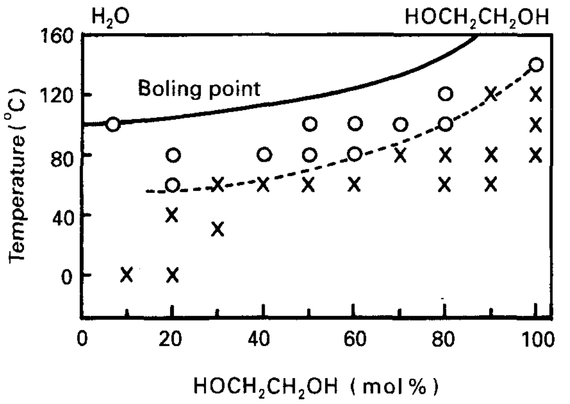

Figure 2 Formation region of deposit treated for 6 h under 1.0 kV as roughly judged from optical microscopy: (O) some deposits; (×) no deposits.

composition during electrolysis. In this 1 kV series, vaporization of the solution was compensated with that of the same composition. Electrolysis produced gases on both electrodes. Although, the role of atomic hydrogen has been extensively studied in gas phase synthesis [7], this is not discussed in the present study.

3.2. Pure ethylene glycol

Thus far, the deposition region was surveyed at 1.0 kV. The influence of higher potential, or temperature, for pure ethylene glycol was then examined. It was found that a black film was deposited even under 0.4 kV at 150 °C or under 2.0 kV at 130 °C in 3 h. Deposition was very sensitive to the liquid temperature.

3.3. 70 mol % ethylene glycol

After several trials with 40–90 mol % ethylene glycol under varying conditions, a 70 mol % ethylene glycol

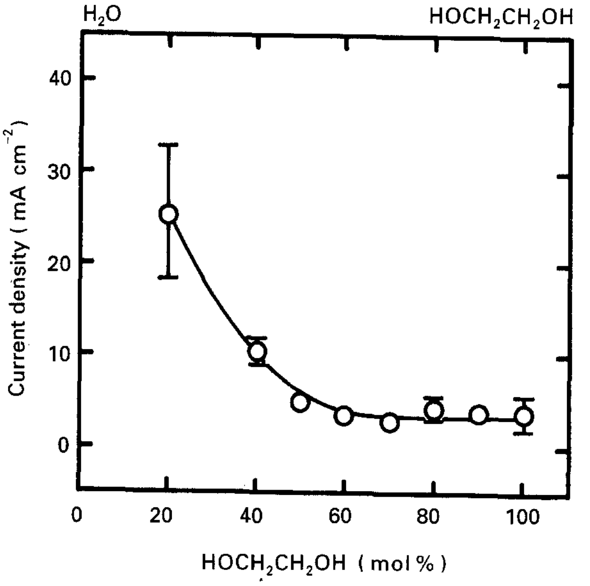

Figure 3 Current density at 80 °C when electrolysis was carried out at 1.0 kV for 6 h.

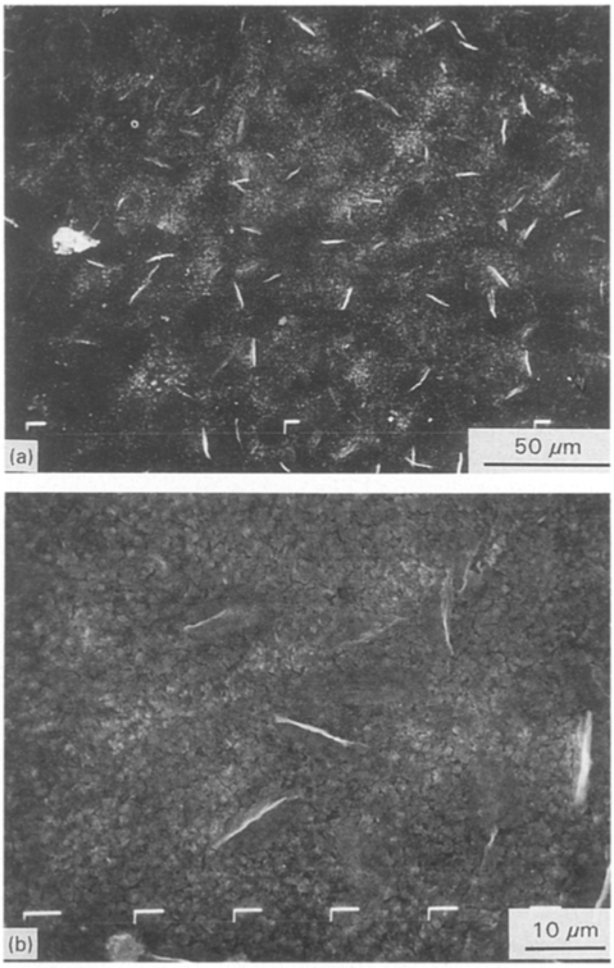

Figure 4 SEM for the 70 mol % ethylene glycol deposit treated for 12 h under 1.6 kV at 120 °C, showing bright particles dispersed in a black matrix: (a) bright line corresponds to bright particle under optical microscopy, (b) matrix consists of 1 μm size particles.

solution was chosen to characterize the deposited films. Electrolysis was carried out at 120 °C for 12 h under varying potentials of 1.4–2.0 kV. The current density was 10–30 and 15–50 mA cm^{-2} at 1.4 and

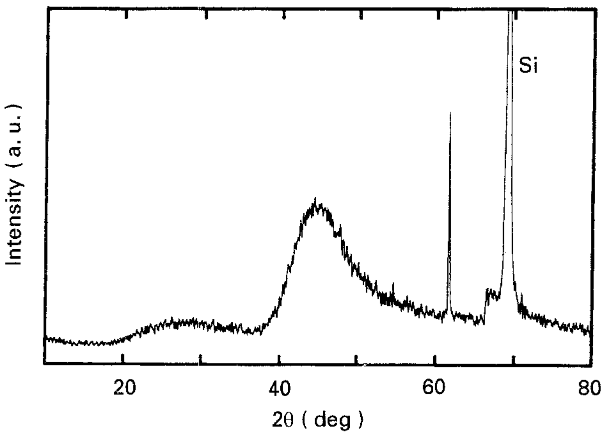

Figure 5 XRD pattern for the 70 mol % ethylene glycol deposit treated for 12 h under 2.0 kV at 120 °C.

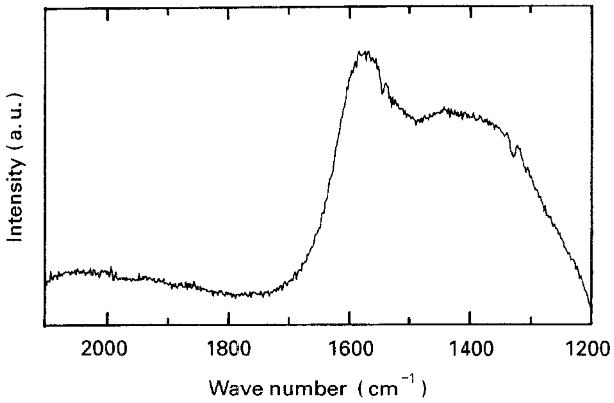

Figure 6 Raman spectrum for the 70 mol % ethylene glycol deposit treated for 12 h under 1.6 kV at 120 °C.

2.0 kV, respectively. The general trend showed an increase of current density with time. In this series, vaporization of the solution was compensated for by the addition of pure water. The thickness of the films was less than 1 μm. To the eye, the deposit's appearance was that of a multicoloured interference pattern of light; with higher potential, the deposit had a blackish appearance. In these films, bright particles were dispersed in a black matrix under the optical microscopy. SEM micrographs (Fig. 4) showed bright lines instead of bright particles (Fig. 4a); and, for 1.6 kV sample, the black matrix consisted of an agglomeration of ~ 1 μm size particles (Fig. 4b). These films showed a similar XRD pattern and that of 2.0 kV is shown in Fig. 5. The sharp peaks at $2\theta \sim 62$ and 69° are from the Si reflections due to the K_β and K_α radiation, respectively. The broad peak at $2\theta \sim 44°$ can be attributed to disordered graphitic carbon. The Raman spectrum of the 1.6 kV sample is shown in Fig. 6. It gives further information about the structure of the deposit. The broad peak centred around 1574 cm^{-1} is commonly attributed to the presence of graphitic or sp^2 hybridized carbon [7]. Interpretation of the broad shoulder centred at 1400 cm^{-1} needs further evaluation.

4. Conclusions

Carbon films were deposited on silicon by electrolysis of the binary system water–ethylene glycol. The deposition region was surveyed and the deposits were characterized by optical microscopy, SEM, XRD and Raman spectroscopy. The results were as follows.

1. Some deposits were observed between the boiling point curve and the line approximately 50 °C below and parallel to the boiling point when electrolysis was carried out at 1.0 kV for 6 h.
2. Deposition was very sensitive to the liquid temperature.
3. Films of graphitic carbon were deposited from the 70 mol % ethylene glycol solution at 120 °C when electrolysis was carried out at 1.4–2.0 kV for 12 h.

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References

1. T. MORI and Y. NAMBA, *J. Vac. Sci. Technol.* **A1** (1983) 23.
2. M. KAMO, Y. SATO, S. MATSUMOTO and N. SETAKA, *J. Cryst. Growth* **62** (1983) 642.
3. J. C. ANGUS and C. C. HAYMAN, *Science* **241** (1988) 913.
4. Y. MATSUI, A. YUUKI, M. SAHARA and Y. HIROSE, *Jpn. J. Appl. Phys.* **28** (1989) 1718.
5. W. A. YARBROUGH, *J. Amer. Ceram. Soc.* **75** (1992) 3179.
6. Y. NAMBA, *J. Vac. Sci. Technol.* **A10** (1992) 3368.
7. W. R. L. LANBRECHT, C. H. LEE, B. SEGALL, J. C. ANGUS, Z. LI and M. SUNKARA, *Nature* **364** (1993) 607.

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