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Deposition of diamond-like carbon films by electrolysis of methanol solution

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By electrolysis of the methanol solution, an attempt was made to deposit diamondlike carbon (DLC) films on silicon substrate at temperature of less than 60 °C. Substrates were negatively biased with a dc potential of 0 to −3000 V. IR spectra showed that the O–H, C–H, and C–O vibration bands of electrolyte decreased remarkably after electrolysis and a new peak characterized as the C=C bond appeared. The deposited films were characterized as DLC films by Raman spectroscopy. © *1996 American Institute of Physics.* [S0003-6951(96)00534-7]

Thin films of diamondlike carbon (DLC) have recently attracted much interest for their potential use as hard, wear-resistant films, and optical coatings. The methods known for depositing DLC films, such as chemical vapor deposition,[1] pulsed-laser deposition,[2] and ion-beam sputtering,[3] are all vapor deposition techniques. Using these techniques, high quality films and rapid growth rate have been achieved. However, deposition of DLC films in the liquid phase is seldom reported.

There is experimental evidence that most materials which can be deposited from the vapor phase can also be deposited in liquid phase using electroplating techniques and vice versa.[4] Enlightened by this conclusion, Namba[5] first attempted to grow diamond phase carbon films in the ethanol solution at a temperature less than 70 °C. In his article, however, only x-ray photoelectron spectroscopy results had been shown to indicate that there was carbon phase in the films, no obvious evidence could be seen to confirm that diamond or DLC films had been obtained. Suzuki *et al.*[6] recently made an attempt to deposit carbon films by electrolysis of a water-ethylene glycol solution. Graphitic carbon had been obtained according to their Raman spectra. Nevertheless, ethylene glycol is a viscous solution, which will cause some difficulty in cleaning substrates after deposition. Since DLC films synthesized in the liquid phase has significant scientific and technological implications, it is worth pursuing research with other electrolytes.

In this letter, a film deposition is attempted in methanol solution by the techniques of electrolysis. Methanol is selected because its polarizability and conductivity are stronger than those of ethanol, and the structure of methanol is even closer to that of diamond. Fourier transform infrared (FTIR) spectroscopy was used to compare the original methanol solution and the electrolyzed solution. The deposited films were examined by scanning electron microscopy (SEM) and Raman spectroscopy.

A schematic diagram of the system is shown in Fig. 1. Analytically pure methanol (99.5%) was used as electrolyte. A silicon (100) substrate with a size of $15\times20\times0.3$ mm^3 was mounted on the negative electrode. Before deposition the substrates were dipped in the mixture of dilute HNO_3–HF solution for a few minutes and then cleaned by ultrasonic treatment. The distance between the substrate and positive electrode was set to 10 mm. The potential applied to the substrate could be changed from 0 to −3000 V under a constant temperature.

In Fig. 2 the current density is plotted as a function of applied potential at a temperature of 60 and 50 °C. It increases linearly with the applied potential, however, at the potential above 2400 V, the heating effect of current increases remarkably, which will cause some difficulty in controlling the solution temperature. Namba[5] thought that the substrate current played an important role in film formation from an organic solution. The conductivity of electrolyte is indeed an important factor during electrolysis, which is the reason methanol is selected as an electrolyte in our experiment. Namba used ethanol as electrolyte, and the maximum current density was only 5 mA/cm^2, whereas in our experiment, the current density exceeded 20 mA/cm^2.

The FTIR spectrum of the electrolyte solution electrolyzed for 60 h is obviously different from that of the original methanol solution. The comparison is shown in Fig. 3. From the figure it can be seen that the O–H, C–H, and C–O vibration bands decrease remarkably after electrolysis. By comparison with the O–H stretch band of the original metha-

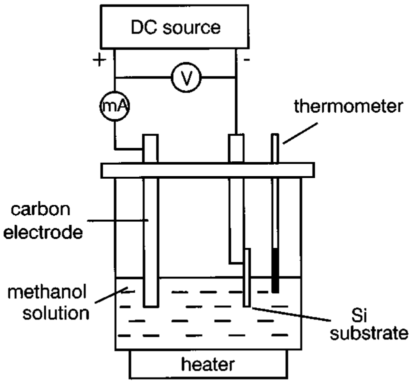

FIG. 1. Schematic diagram of the deposition system.

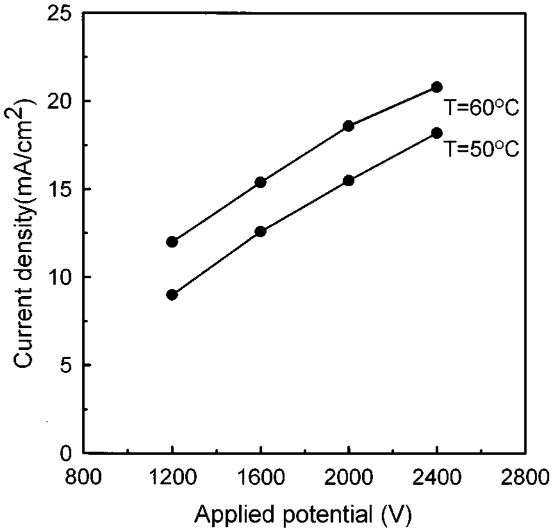

FIG. 2. Current density of the substrate versus applied potential. T: temperature of the solution.

nol solution (~3350 cm^{-1}), the O–H stretch band of the electrolyzed solution (~3450 cm^{-1}) shifts to high wave number direction by ~100 cm^{-1}, which indicates a transformation trend from the associated O–H bond to nonassociated O–H bond.[7] The most interesting phenomenon is that a new band appears at about 1625 cm^{-1}, which is a characteristic stretch band of the C=C bond.[7] We speculate that it may be the transition state of C–C bond from perfect to breakage. From Fig. 3, we can conclude that most of the carbon related bonds may have been broken after electrolysis for 60 h. Some of the broken carbon composition was deposited on the Si substrate. The rest remained in the solution in the form of C=C bond. Further research is being carried out to analyze the chemistry of electrolyte solution after deposition.

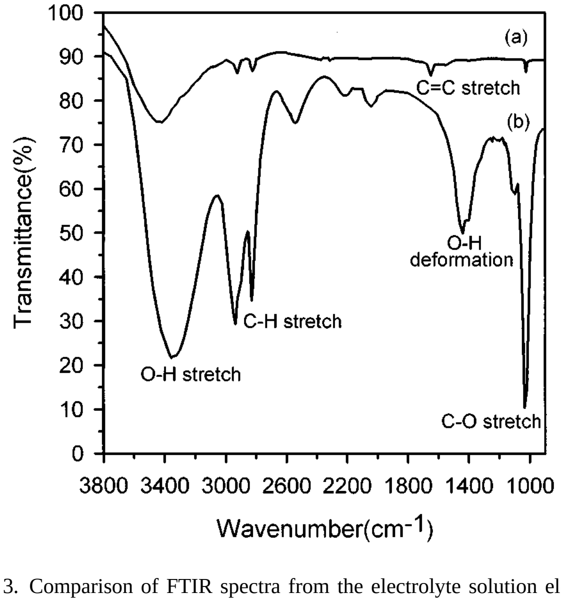

FIG. 3. Comparison of FTIR spectra from the electrolyte solution electrolyzed for 60 h and the original methanol solution, (a) electrolyzed solution, (b) original methanol solution.

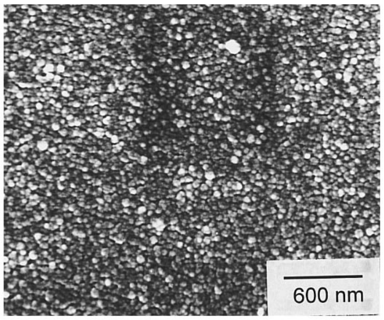

FIG. 4. SEM micrograph of the film deposited for 10 h at 1600 V at 60 °C.

The average thickness of the films increased almost linearly with the substrate current density or applied potential, and was also effected by the temperature. The thickness of the film deposited at 1600 V at 60 °C for 10 h was 0.8 μm.

Figure 4 shows SEM micrograph of the deposited film. In this case, the film was deposited for 10 h at 60 °C with an applied potential of 1600 V. From the figure it can be seen that film is composed of small, compact grains. The average grain size is about 60 nm.

Raman spectroscopy is the most important tools for characterizing diamond and DLC material. Raman spectra of the deposited films, obtained using the 514.5 nm line of Ar$^+$ laser, are shown in Fig. 5. Figures 5(a) and 5(b) are for films deposited for 10 h at 1600 V at a temperature of 50 and 60 °C, respectively. Similar spectra have been shown previously to the DLC films prepared by pulsed laser deposition.[2] The film shown in Fig. 5(a), shows two bands at about 1350 and 1580 cm^{-1}, identified with the disordered graphite band (called the *D* line) and the single-crystal graphite band (called the *G* line), respectively.[8,9] The width of the *D* line combined with its intensity relative to the *G* line changes with the disorder.[8–10] Based on this approach, a wide band in the *D* frequency region in Fig. 5(b) reflects a large disorder of a band angle[8] and a difference of their average from 120° in the sp^2 rings of graphite.[9] An increase in the intensity of the *D* line arises from a breakdown of the wave-vector selection rule in microcrystalline graphite.[10] Thus, the films deposited at 60 °C are more diamondlike than those deposited at 50 °C. The effect of temperature on the quality of the films is being investigated. A weak band at about 1610

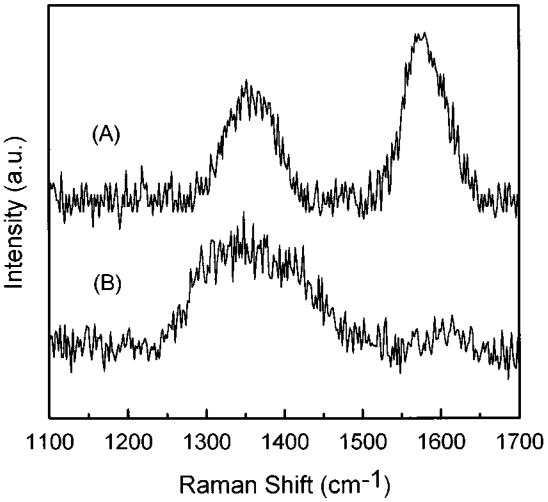

FIG. 5. Raman spectra of films deposited for 10 h at 1600 V at the solution temperature: (a) 50 °C and (b) 60 °C, respectively.

cm^{-1} is also shown in Fig. 5(b). This band may be due to the G line that moves slightly upwards in frequency.[11]

In summary, we have shown that the DLC films can be deposited in methanol solution by the electrolysis technique. We believe that diamond films may be obtained in the liquid phase by improving technology in the near future.

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