Liquid-phase Electrodeposition of Diamond-like Carbon Films on Conducting Glass Substrates Using a Low Deposition Voltage at Room Temperature

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By using formamide as the carbon source, an attempt was made to electrodeposit diamond-like carbon (DLC) films on indium tin oxide (ITO)-coated glass plate substrates at a low constant voltage and room temperature. The structures and morphologies of the films were analyzed by Raman spectroscopy and field-emission scanning electron microscopy.

Diamond-like carbon (DLC) has unique chemical, optical, mechanical, tribological, and electrical properties, and thus DLC films have offered tremendous opportunities in many technical applications, such as bioelectronic, biomedical, and molecular-scale tribology and as a self-alignment layer for liquid crystal displays (LCDs).[1–5] The usual synthesis methods of DLC films include chemical vapor deposition (CVD) and physical vapor deposition (PVD), such as photoinduced chemical vapor deposition,[6] vacuum arc deposition,[7] radio-frequency magnetron sputtering,[8] plasma-enhanced deposition,[9] pulsed laser deposition (PLD),[10] and so forth. Although high quality and rapid growth rate have been achieved, the application of the gas-phase synthesis is limited by the complexity of the experimental setup and usually the high substrate temperature required.

In the field of DLC technology, the electrodeposition of DLC films in liquid phase has the potential for great scientific and technological usefulness. This is due to that the liquid deposition technique, from the viewpoint of practical use, has many advantages such as low deposition temperature, less consumption of energy, the possibility to deposit coatings of large area on intricate surface using rather simple technical devices, and the possibility to control the reaction rate by adjusting the deposition parameters. These reasons gave an impetus to a number of investigations, which have demonstrated the possibility of DLC films formation by electrolysis of organic solvents (alcohols, dimethylformamide (DMF), and acetonitrile) or their mixture with water under a high deposition voltage (2–3 kV).[11–17] Meanwhile, Novikov and Dymont[18] and Shevchenko et al.[19] have reported that the DLC films can be fabricated by electrolysis of acetylene in liquid ammonia and anodic oxidation of lithium acetylide in dimethyl sulfoxide (DMSO) at a very low voltage (<5 V), respectively. Although the electrolysis voltage is low, the use of liquid ammonia or acetylene gas and the low deposition rate restrict the further application of these techniques. Thus, the development of an alternative route to prepare DLC films under mild condition is highly desired.

In this letter, by using formamide (FA) as the carbon source, an attempt was made to direct electrodeposit DLC films on conductive glass substrates in FA using a low deposition potential at room temperature.

The apparatus used in the experiments was a traditional electrolytic cell system with two electrodes. An indium tin oxide (ITO)-coated glass plate (resistance $\leq 20\,\Omega\,\mathrm{cm}^{-2}$) with a flat ($Ra = 0.2$ nm) surface and an area of $2.0\,\mathrm{cm}^2$, which was previously cleaned by sonication in acetone, ethanol, and ultrapure water, was used as the negative electrode. The counter electrode was a platinum plate with an area of $6\,\mathrm{cm}^2$. Analytical pure (99.5%) FA was used as the electrolyte. The electrodes were placed parallel with a distance of 10 mm into the FA solvent, and a constant potential of 5 V was applied at room temperature by an Arbin MSTA4+ multichannel galvanostat/potentiostat. The as-deposited films were dried under ambient conditions.

Figure 1 shows the time dependence of the current density in FA at a constant deposition voltage of 5 V and room temperature. During the deposition process, the current density decreased remarkably from 4.25 to $2.75\,\mathrm{mA\,cm}^{-2}$ in about 5 min, and thereafter it had almost no change. When the deposition process was stopped after 30 min, the resistivity of the deposited film was in the $10^6\,\Omega\,\mathrm{cm}$ range. Therefore, the insulating film deposited on the conductive glass seems to have led to the remarkable decrease of current density within 5 min. The color of the film changed from brown to grey as the deposition time increases. Finally, a grey film with a high sticking force was obtained on the ITO-coated glass substrate in FA.

Laser Raman spectroscopy is usually applied to characterize diamond, graphite, and other materials related to carbon.[20] Raman measurements were made by a Reinshaw RM2000 type microscopic confocal Raman spectrometer in which a 632.8 nm radiation of a He-Ne laser was focused on a spot of 5 µm in diameter. The typical spectrum of the films deposited from FA is identical (as shown in Figure 2). After curve fitting, it is found that there exist two broad peaks near 1580 and $1370\,\mathrm{cm}^{-1}$ as seen in Figure 2, which can be assigned to G (graphite) and D (disorder) modes, respectively, which indicate that the films

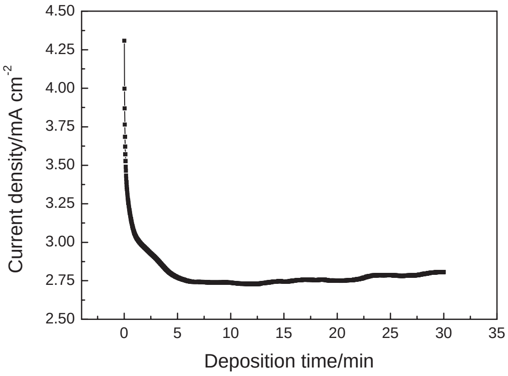

Figure 1. Time dependence of the current density during the electrodeposition process in FA.

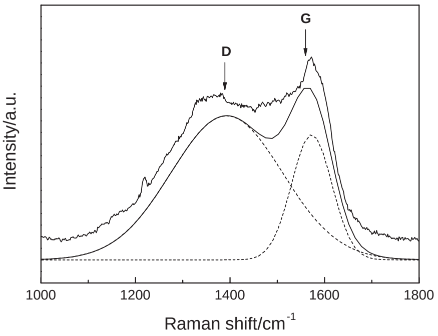

Figure 2. Typical deconvoluted Raman spectrum of the DLC film electrodeposited on the ITO substrate using a Gaussian line shape.

are typical DLC films. The G peak is attributed to the stretching vibration mode of any pair of sp^2 sites, whether in sp^2 chains or in aromatic rings. The D peak is attributed to the breathing mode of those sp^2 sites only in sp^2 rings. Thus, the Raman parameters, such as I_D/I_G and G band position (ω_0), are critical data used to characterize the different amorphous carbon structures. From the Gaussian curve fitting procedure, the I_D/I_G intensity ratio of the as-deposited DLC films can be calculated to be 3.173, higher than that of DLC films deposited from other organic solvent, such as acetonitrile (2.208), DMF (2.195), and methanol (1.726) under high deposition voltage (>2 kV),[16] indicating that the high amount of sp^3 C atomic sites in the as-deposited DLC films.

The surface morphology of the deposits was tested by a Hitachi S-4700 field emission scanning electron microscope (FE-SEM). The surface morphologies of the films deposited from FA at different deposition time are shown in Figure 3. From Figures 3a and 3b it can be seen that the film deposited at 10 s is composed of small and compact balls with an average size of approximately 20 nm and that the surface is even and smooth. As the deposition time increases, the surface of the film becomes rougher and the average size of the surface carbon balls grows to ca. 200 nm (Figures 3c and 3d). Thus, the surface roughness of the film can be easily controlled by adjusting the deposition parameters.

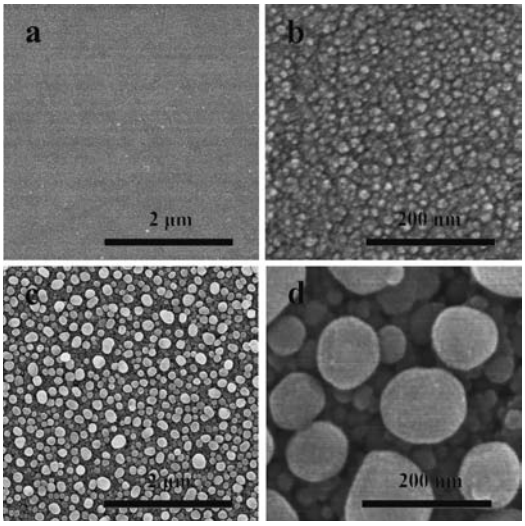

Figure 3. FE-SEM images of DLC films electrodeposited on the ITO substrates with the deposition time of (a, b) 10 s and (c, d) 30 min.

Diamond-like carbon films have been successfully deposited on ITO-coated glass substrates in FA by electrodeposition at a low constant voltage and room temperature. Raman spectrum indicates that the film contains more sp^3 C and is more diamond-like. The surface morphology and roughness of the as-deposited film can be easily tailored by adjusting the deposition parameters. The results may indicate a general method for the selection of the organic solvent in order to prepare high quality DLC films by electrodeposition at a low voltage and near room temperature.

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