Deposition of Nanostructured Diamond-like Carbon Films on Al Substrate by Facile Electrochemical Route

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Diamond-like carbon (DLC) films were deposited on Al substrate by electrolysis of dimethylsulfoxide (DMSO) at relatively low voltage (150 V). The morphology of the sample was investigated by SEM, indicating that the film was composed of compact grains about 100 nm. The analysis of the films by XPS, FTIR, and Raman spectroscopy revealed that the deposits are typical hydrogenated DLC films.

Numerous research efforts have been made on the diamond-like carbon (DLC) films during the past two decades because they have potential applications on the protective optical or tribological coatings owing to their excellent mechanical and tribological properties. Various physical and chemical deposition techniques such as pulse laser deposition,[1] microwave plasma-assisted deposition,[2] filament-assisted chemical vapor deposition,[3] mass-selected ion beam deposition,[4] have been widely used to grow these films. Although high quality and rapid growth rate have been achieved, applications of these gas-phase deposition are limited to some extent because of the complexity of experimental setup and the high substrate temperature.

Recently, particular attention[5–8] has been focused on liquid-phase synthesis of DLC films by an electrochemical method on account of its merits of simplicity of the experimental setup and availability for coating on substrates with complex shapes. Several kinds of solvents such as methanol,[5] acetonitrile,[9] and *N,N*-dimethylformamide (DMF)[10] have been used to deposite carbon films, demonstratting that liquid-phase deposition is indeed a feasible method in synthesis of DLC films. However, the carbon sources are very limited and a high applied voltage (1–3 kV) is necessary in these processes. It has also been reported that DLC films could be deposited by anodic oxidation of acetylene in liquid ammonia[6] or lithium acetylide in dimethylsulfoxide[8] at low voltage. However, these methods involve the use of acetylene or liquid ammonia, which makes it difficult to operate. Moreover, the deposition rate is so low that the process has to continue several hours. So it is very necessary to search a facile method to deposit DLC films from the viewpoints of industrial applications and scientific studies.

In this contribution, DMSO was selected as the electrolyte for the first time to deposit DLC films on Al substrate. The choice of such organic solvent is based on the fact that DMSO with two equivalent methyl groups bonding directly to the strong polar group has larger dipole moment and dielectric constant in comparison with the carbon sources used before. DMSO is so easily polarized, becomes $(CH_3^{\delta+})_2—SO_2^{\delta-}$. The C–S bonds in these polarized molecules could break even at relatively low voltage, and produce methyl cation (CH_3^+) that could react on some active sites of the negative electrode surface and at last would lead to the formation of DLC films according to previous studies.[11,12]

The experimental setup comprised an electrolytic cell system, which is similar to that reported by Wang et al.[5] A cleaned Al substrate and a polished graphite plate were used as the negative and positive electrodes, respectively. The distance between two electrodes was set to 7 mm. Before deposition the substrate was treated in NaOH (0.05 M) for 5 min and then cleaned by ultrasonic treatment in deionized water and acetone, sequentially. Contrary to previous work, analytically pure dimethylsulfoxide (99.5%) was used as the electrolyte and the voltage applied to the two electrodes was only 150 V in this work. The deposition was performed at 75 °C for 100 min. After deposition the sample was cleaned in acetone.

A JSM-5600LV type scanning electron microscopy (SEM) was used to investigate the surface morphology of the deposited films. The composition of the sample was characterized by an Axis Ultra X-ray photoelectron spectrometer (XPS), an Avatar-360 Fourier transform infrared (FTIR) spectrophotometer and a T-6400 type Raman spectrometer with an argon ion laser (514.5 nm).

In the course of experiment, it was noted that the current density varied in the range of 1.0 to 8.5 mA·cm^{-2} and pale gray films could be observed on both sides of Al substrate even by naked eyes when the deposition time is about 30 min. In order to get thick film, the deposition progress was kept for 100 min. Figure 1 presents the SEM micrograph of the sample. It can be seen that the film is continuous and composed of compact grains with an average size of 100 nm.

XPS survey spectrum of a typical sample is shown in Figure 2. It has a striking C 1s peak and O 1s peak. The peak of O 1s might mainly result from the contamination of the sam-

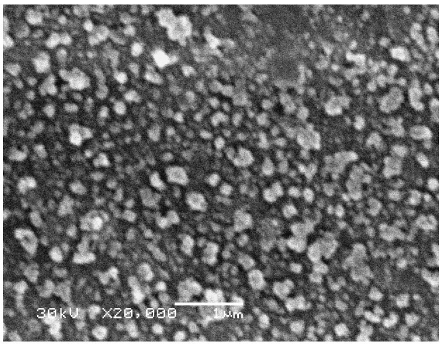

Figure 1. SEM image of the deposited film. Scale bar: 1 µm.

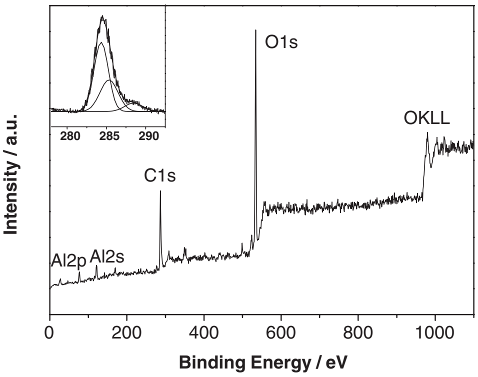

Figure 2. XPS survey spectrum of the sample. The inset is the C 1s XPS spectrum of the sample.

ple in the open air and/or the oxidized surface of the substrate, which is common for the spectrum of such films.[8,13] The peaks of Al 2p and Al 2s are very weak and should be caused by the substrate. It is noted that within the detective sensitivity of XPS, no obvious signal from S atom could be detected although it is directly bonded to C atom in the precursor electrolyte, and this indicates that the C–S bonds in DMSO molecules must break during the deposition, which is in accordance with our assumptions.

The inset of Figure 2 shows the C 1s XPS spectrum of the deposited film, which was deconvoluted into three lines peaks. The peaks at 284.3 and 285.3 eV correspond to sp^2 and sp^3 carbon atoms, respectively. According to the corresponding peak area, it can be inferred that the ratio of sp^2 to sp^3 is about 1.5:1. A third peak of much smaller intensity at 288.4 eV has also been noted and should be related to chemical bonds with surface oxygen.

As XPS is insensitive to hydrogen, FTIR measurement was carried out on the sample to probe the different C–H configuration. It can be concluded from the inset of Figure 3 that hydrogen is contained in the film and mainly bonds to sp^3 carbon atoms according to the absorbance in the region of 2800–3000 cm^{-1} assigned to the vibration of C–H bond.

Conclusive evidence for the identification of the sample as DLC film was provided by the Raman spectroscopy that has an ability to distinguish between different forms of carbon. The Raman spectroscopy of an electrodeposited film on Al is shown in Figure 3. A shoulder peak at 1355 cm^{-1} and a broad peak at 1560–1600 cm^{-1}, identified with the so-called Raman D and G bands, respectively, indicate that the films are typical DLC films. Generally, the broad peak at 1560–1600 cm^{-1} is attributed to sp^2-C, and the peak at 1355 cm^{-1} is designated to disordered carbon, i.e., the bond-angle disorder in the sp^2 graphite-like microdomains induced by linking with sp^3-C atoms as well as the finite crystalline sizes of sp^2 microdomains.[14] Therefore the deposits is a typical hydrogenated DLC film with mixted structure containing sp^2 and sp^3.

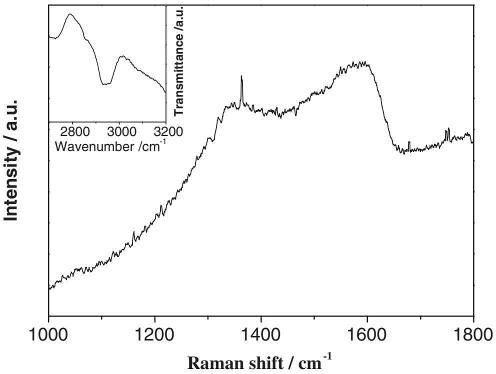

Figure 3. Raman spectrum of the film deposited on Al. The inset is the FTIR spectrum of the sample.

In the course of experiment, it was also found when the DMSO electrolyzed in above process reassumed as the electrolyte, it only needs about 5 min to get an entire layer of film that could be observed even by naked eyes. The details of such phenomenon are not clear. We suppose that it may be related to the structure change of the electrolyte during the deposition. Apparently, a higher deposition rate was achieved and the carbon source could be reused in this method, which would be very significant from the viewpoint of practical use.

In conclusion, a facile method has been reported to deposited hydrogenated diamond-like carbon films on Al substrate from DMSO, which not only avoided the use of gas but also decreased the required applied voltage remarkably. It seemed that DMSO is superior to the carbon sources used so far.

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