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Facile deposition of copper-doped diamond-like carbon nanocomposite films by a liquid-phase electrochemical route

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Copper-doped diamond-like carbon nanocomposite films have been facilely deposited by a liquid-phase electrochemical route from an acetonitrile solution of $[Cu(CH_3CN)_4]ClO_4$.

Diamond-like carbon (DLC) films are considered as promising materials with a wide variety of potential applications because of the similarity of their properties with those of diamond.[1,2] Doping the DLC films with metals (Me-DLC) could manipulate the electrical property of these films and create a two dimensional array of metal clusters within the carbon matrix. Such composite structures are of interest for use as nanoelectrodes in electrochemistry.[3,4] Additionally, many studies have shown that incorporating some metal elements into a carbon matrix could reduce intrinsic stress and improve adhesion of the DLC films,[4,5] thus increasing their use in industrial applications. Therefore, considerable efforts have been devoted to the deposition of Me–DLC films in recent years.[6–8] Co-sputtering and co-evaporation of metal whilst growing carbon films are the most popular methods to deposit these composite films. For example, Pt–DLC composite thin films were synthesized by a radio frequency (RF) sputtering deposition technique, and improved electrical conductivity and reduced film stress were obtained by the addition of platinum.[4] Copper/hydrogenated amorphous carbon (Cu/a-C:H) composite films have also been obtained by a hybrid deposition technique combining the plasma-enhanced chemical vapor deposition of carbon with the sputter-deposition of copper in argon–acetylene gas mixtures.[6] Although high quality and rapid growth rates have been achieved, many of these methods require complex experimental setups and high substrate temperatures.

A liquid-phase electrodepositing technique might be more attractive, due to such advantages as low deposition temperature, simplicity of experimental setup, and availability for coating on substrates with complex shapes. The possibility of deposition of DLC films by means of electrolysis of organic liquids such as acetonitrile,[9] dimethylsulfoxide[10] and lithium acetylide in dimethylsulfoxide[11] has been demonstrated recently. Apparently, metal is more easily deposited on the electrode surface under electrolysis conditions. So it is reasonable to achieve the co-deposition of metal and carbon although the deposition of Me–DLC films by an electrochemical route has not been reported up to now. To produce the expected properties, the primary task is to solve the distribution of metal clusters within the carbon film.

In this contribution, an electrochemical route to deposit copper doped diamond-like carbon (Cu–DLC) films from an acetonitrile solution of $[Cu(CH_3CN)_4]ClO_4$ at 1600 V and 60 °C has been reported. The choice of such copper dopant is based on the assumption that the interaction between the copper atom and acetonitrile molecules in $[Cu(CH_3CN)_4]ClO_4$ might be beneficial to the distribution of copper clusters within the carbon matrix. The reduced reaction of copper dopant will provide a beneficial micro-environment for the reaction of acetonitrile (especially those bonded to copper atoms), which will advance the growth of carbon species in the surroundings of the copper atoms and result in a good distribution.

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The dopant $[Cu(CH_3CN)_4]ClO_4$ was synthesized as previously reported,[12] and $[Cu(CH_3CN)_4]ClO_4/CH_3CN$ solution could be obtained by dissolving $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN. The experimental setup comprising an electrolytic cell system and deposition conditions are similar to those of depositing pure DLC films.[9] A cleaned Si substrate and a polished graphite plate were used as negative and positive electrodes, respectively. The distance between the two electrodes was set at 7 mm, and the films were deposited at 1600 V and 60 °C. A 30 mL volume of analytically pure acetonitrile was initially present in the reactor. Then, the copper salt solution was added dropwise to the reactor with stirring during the deposition. The content of copper in the film could be controlled simply by the drop rate and the concentration of the copper salt solution. Here, the concentration of the copper salt solution was 1.5 mM and the drop rate was controlled to keep current density in the range of 2.0–5.5 mA cm^{-2}, which was a little larger than that (1.0–3.5 mA cm^{-2}) when only the analytically pure acetonitrile was used as electrolyte. The electrochemical process was kept to 20 min, and a brown film could be observed even by the naked eye.

The chemical composition of the film was investigated by X-ray photoelectron spectroscopy (XPS), and the spectrum displays the characteristic peaks attributed to carbon and copper as well as to the contamination of oxygen. The C 1s peak showing a broad core line is at about 284.9 eV, which is in agreement with the known value of amorphous carbon (284.2–285.5 eV). The Cu 2p peaks at 933.5 eV ($2p_{3/2}$) and 952.9 eV ($2p_{1/2}$) show CuO character. This might be caused by oxidation of copper nanoparticles in the presence of atmospheric oxygen, which can be further confirmed by the presence of the O 1s peak at 530.3 eV. If estimated in terms of peak area and atomic sensitivity factors, the concentration of copper in the films expressed by the atomic number ratios, Cu/(Cu+C), is about 10.7 at%.

An Avatar-360 Fourier transform infrared (FTIR) spectrophotometer was used to probe the different C–H configurations. It can be concluded that hydrogen is contained in the film, and mainly bonds to sp^3-C according to the absorbance at 2854 cm^{-1} and 2925–2970 cm^{-1} in the range of 2800–3300 cm^{-1} characterizing the vibration of C–H bonds.

Since XPS probes few surface layers, the above XPS data cannot be regarded as strong evidence in favor of the formation of Cu–DLC films. More accurate information on the sample could be given by Raman spectroscopy which is probably the most ideal technique for analysis of carbon materials currently in use. Fig. 1 presents the Raman spectra of the sample. It can be seen that three peaks at 291, 341 and 627 cm^{-1} are related to CuO,[13] demonstrating the partial oxidation of Cu clusters in the presence of atmospheric oxygen, which is in agreement with the XPS results. A shoulder peak at 1360 cm^{-1} and a broad peak at 1550 cm^{-1}, identified with the so-called Raman D and G bands, respectively, should be attributed to amorphous carbon with diamond-like structure. Therefore this film is a typical Cu–DLC film. It is noted that the intensity ratio of the D to G bands (ID/IG) decreased remarkably, and the position of the G-band shifts to a smaller wavenumber in comparison with that of pure DLC films deposited under the same conditions (see inset of Fig. 1), which indicated that this film contained more sp^3 carbon atoms.[2,14] Additionally, a

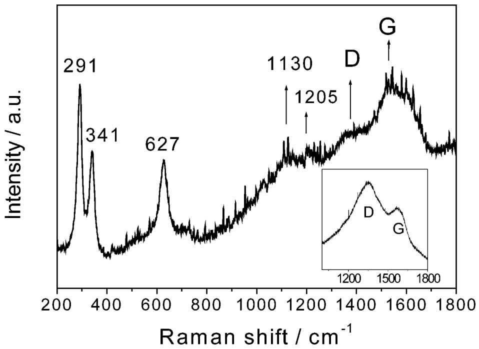

Fig. 1 Raman spectroscopy of the Cu–DLC film deposited at 1600 V and 60 °C. The inset is the Raman spectra of pure DLC film deposited under the same conditions.

broad peak at 1100–1140 cm^{-1} and a weak peak at about 1205 cm^{-1} could be discerned. The former is usually attributed to disordered sp^3 carbon phases and the latter peak was considered to be caused by amorphous diamond.[15–17] All of these results indicate that the addition of copper in the carbon films promoted the formation of sp^3 carbon atoms.

A JSM-5600LV type scanning electron microscope (SEM) was used to investigate the surface morphology of the deposited films, and the results showed that the film was composed of small grains about 100 nm in size. However, it is difficult to discriminate the copper nanoclusters from the carbon matrix. In order to investigate the distribution of copper clusters within the carbon matrix, the sample was deposited for 60 s on the copper mesh grid coated with a thin carbon film for transmission electron microscopy (TEM) observation. Fig. 2 shows the TEM images of the sample and the relevant electron diffraction (ED) pattern. It can be seen that the copper particles (small black dots about 5 nm in size) were well dispersed in the carbon matrix (Fig. 2a). A selected area electron diffraction (SAED) pattern (see inset of Fig. 2a) revealed by focusing an electron beam on the small black particles matches those of cubic metallic copper ((111), (220), (200)). However, the ED patterns from the carbon area that does not contain copper nanoparticles shows a diffuse halo, indicating the carbon species are amorphous materials. Fig. 2b is an image at low magnification, which shows the copper nanoparticles were dispersed homogeneously within the carbon network over a large area. Since the deposition process was only maintained for 60 s, the film did not cover the substrate completely. It was also noted that the copper nanoparticles and carbon species always appear together: they appeared in some areas and disappeared simultaneously in others, which indicated that the carbon species preferably grow on the surroundings of copper particles.

In summary, the first example of deposition of Cu–DLC nanocomposite films by a facile liquid-phase electrochemical route has been reported. The results of Raman spectroscopy showed that the addition of copper promoted the formation of sp^3 carbon atoms, and TEM images displayed copper nanoparticles as well dispersed within the amorphous carbon matrix in the nanocomposite films, which was considered to be related to the interaction between the copper atom and acetonitrile molecules in [Cu(CH$_3$CN)$_4$]ClO$_4$. This method provides a facile route to deposit Me–DLC films which potentially have applications in electrochemistry and tribology.

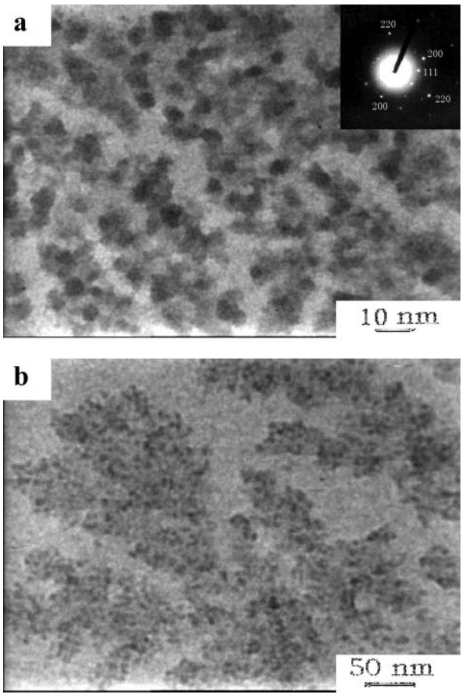

Fig. 2 TEM images of the sample deposited for 60 s on the copper mesh grid coated with thin carbon film; (a) is the magnified image of (b). The inset is a selected area electron diffraction pattern of copper nanoparticles.

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