

Synthesis of carbon films with diamond-like structure by electrochemical oxidation of lithium acetylide

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Electrochemical oxidation of lithium acetylide in aprotic media affords carbon films containing a high fraction of sp³-type C bonds; the growth conditions and the photoelectrochemical behaviour of these films were investigated.

Much recent attention has been focused on the diamond-like carbon (DLC) films which are considered as promising materials for electronic, optical, and wear protection applications^{1–3} because of similarities of their properties to those of diamond. These similarities, which are caused fundamentally by the fact that a greater part of DLC consists of a local sp³ bonding configuration, ensure superior features such as chemical inertness, hardness, low friction and high thermal conductivity. The use of conductive DLC films as electrodes has also been of great interest due to very low capacitive background currents and a wide potential window in aqueous solutions⁴ – these open up fresh opportunities for various electroanalytical applications.⁵

DLC films can be deposited using various chemical and physical vapour deposition techniques such as filament-assisted chemical vapour deposition,⁶ filtered cathodic vacuum arc,⁷ microwave plasma-assisted deposition,⁸ mass-selected ion beam deposition⁹ and pulse laser deposition.¹⁰ On the other hand, there are few known reports describing attempts at utilising electrolysis of organic liquids for DLC film deposition despite the fact that the liquid deposition techniques, from the viewpoint of practical use, have many advantages such as an availability for large area deposition and a low deposition temperature. Recently, the possibility of deposition of DLC films by means of electrolysis of methanol has been demonstrated;¹¹ this deposition process, which occurs at high voltages (2–3 kV) and at high current densities (15 A cm⁻²), is to be considered rather as an electrochemical plasma-assisted anodic carbonization of organics. It has also been reported that the anodic oxidation of acetylene in liquid ammonia yields transparent fragile carbon films exhibiting an electron diffraction pattern similar to that of diamond; however, the deposition rate showed by this process does not exceed 2 × 10⁻³ μm h⁻¹.¹²

In this work we demonstrate the possibility of utilizing anodic oxidation of lithium acetylide in dimethyl sulfoxide for electrochemical growing of carbon films containing a high fraction of sp³ hybridized sites.

To prepare the C₂HLi/DMSO solution, acetylene was passed through lithiated DMSO obtained by dissolving lithium hydride in DMSO at 70 °C. The electrochemical deposition of carbon films has been carried out from a 0.1 M C₂HLi + 0.01 M Bu₄NClO₄/DMSO electrolyte under potentiostatic or galvanostatic conditions. As the electrodes, cathode-sputtered 100 nm platinum films at <111> silicon single-crystal wafers were used. The potentials were measured against an aqueous Ag/AgCl, Cl⁻(sat.) reference electrode connected to the electrolysis cell through a salt bridge.

It is seen from Fig. 1 that an effective oxidation of lithium acetylide occurs at potentials more positive than about -0.5 V. The prolonged electrolysis of C₂HLi/DMSO solution is accompanied with the formation of the hard transparent film. As evidenced by Auger electron spectroscopy (AES) the film consists entirely of carbon (carbon content ca. 96%). The discharge of lithium acetylide at the carbon-modified surface occurs at higher overvoltages than at the bare platinum and the completion of carbon monolayer formation manifests itself as a pronounced anodic peak on the potentiodynamic polarization curve (Fig. 1). According to the AES depth profiling measurements, the electrolysis of C₂HLi/DMSO solution for 30 min under galvanostatic conditions at *i* = 400 μA cm⁻² leads to the formation of a ca. 50 nm thick carbon film, only a mere increase in the film thickness being observed during the further anodization. During the course of electrolysis, the electrode potential exhibits a gradual shift in the anodic direction (Fig. 1) that can be attributed to the increase of overvoltage for C₂HLi

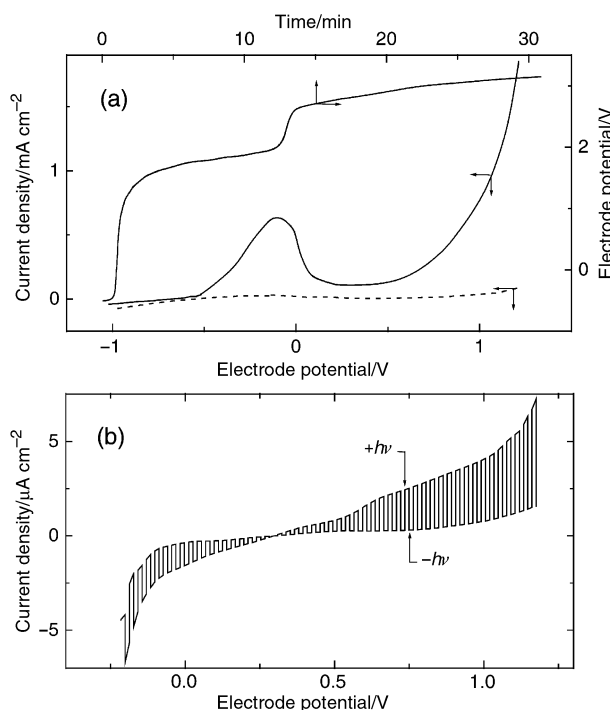


Fig. 1 (a) Current vs. time (galvanostatic conditions, *i* = 400 μA cm⁻²) and current vs. potential (potentiostatic conditions, scan rate *dE/dt* = 2 mV s⁻¹) dependencies for anodic oxidation of lithium acetylide (0.1 M) in Bu₄NClO₄/DMSO at Pt electrode. Dashed curve corresponds to the sweep in a supporting electrolyte. (b) Potential dependence of photocurrent in aqueous buffered (pH 4.4) solution for carbon film grown under galvanostatic conditions. Full spectrum of 120 W medium-pressure Hg lamp; chopped illumination; *dE/dt* = 5 mV s⁻¹.

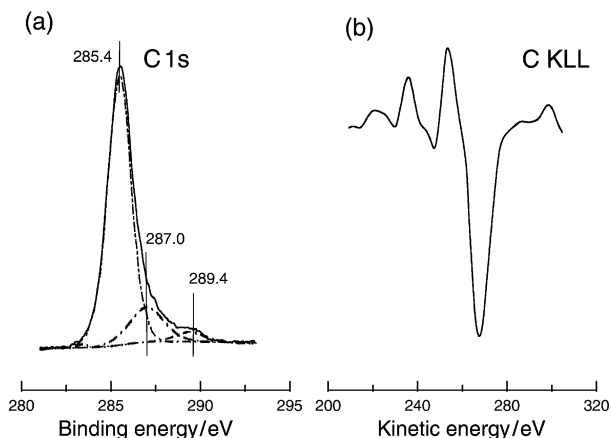


Fig. 2 (a) Spectrum of C 1s photoelectrons and (b) the first-derivative spectrum of X-ray excited C KLL Auger electrons for a carbon film grown under galvanostatic conditions. The Au 4f line of freshly evaporated gold was used as reference.

oxidation, while a step at the chronoamperometric curve corresponds to the moment when the anodic decomposition of DMSO becomes dominant and the film growth terminates. The transparent carbon films similar to those obtained at platinum were also successfully grown on F-doped SnO₂ and nickel electrodes.

The photoelectrochemical experiments (potentiostatic conditions, potential given vs. Ag/AgCl) carried out in aqueous solution (acetate buffer, pH 4.6, 20 °C) have shown that under illumination with the whole spectrum of a 120 W medium-pressure mercury lamp the electrochemically-grown carbon film generates an anodic current of approximately 20 μA cm⁻² at a potential of 1.2 V (Fig. 1). The anodic photocurrent was about two times larger in the acetate-containing solution (0.1 M CH₃CO₂H + 0.1 M CH₃CO₂Na + 0.25 M Na₂SO₄) as compared with the solution containing only Na₂SO₄. This fact can be explained by the effective acceptance of photogenerated holes by the acetate, a well known hole scavenger. This process significantly facilitates the transport of the photogenerated carriers through the carbon–solution interface. At a potential of ca. 0.3 V, an anodic photocurrent changes its direction and a cathodic photocurrent is evident under cathodic bias (Fig. 1). Photocurrent magnitude was not found to exhibit a pronounced influence on film thickness.

It seen from Fig. 2(a) that the C 1s photoelectron spectrum of electrochemically-deposited carbon film exhibits a main peak at 285.4 eV, *i.e.* at higher binding energies than those typical of amorphous carbon and hydrogenated carbon containing a high concentration of sp² sites.¹³ A narrow C 1s peak (FWHM = 1.6 eV) points to the presence of a single C–C bonding phase, while a shoulder to the higher-binding-energy side of the C 1s spectrum can be assigned to carbon atoms bonded to oxygen. On the other hand, a large O 1s photoelectron peak composed of double signals with maxima at 532.9 and 534.2 eV indicates the presence of the other oxygen species (*e.g.* adsorbed DMSO). The AES and X-ray photoelectron measurements show very little evidence for the presence of sulfur (*ca.* 3 at.%) and nitrogen (<1 at.%) at the surface of the carbon film grown under galvanostatic conditions. The S 2p photoelectron spectrum is composed of at least two signals peaking at 164 and 168.9 eV. This points to the fact that the observed contamina-

tion of the carbon surface is due to the adsorption not only of the electrolyte components but also of some other sulfur-containing species produced during electrolysis.

Further information on the carbon state in the electrochemically-grown carbon film was obtained from the X-ray excited Auger electron spectra (XAES). The XAES measurements, which are known to be much less destructive as compared to the conventional AES experiments,¹⁴ have shown their suitability for the elucidation the form of carbon at a surface.¹³ The main energy feature of the XAES spectrum is a peak at 262 eV, which coincides very closely with the energy of the major transition in the XAES spectrum of DLC.¹³ Fig. 2(b) shows C KLL, the first-derivative Auger spectrum obtained from the XPS line. The maximum in the derivative spectrum is located at *ca.* 253 eV which is typical of amorphous carbon and hydrogenated carbon films.^{13,15} A secondary feature at *ca.* 241 eV, which is generally identified as an energy loss peak,¹⁵ is also observed in the spectrum, while the high-energy shoulder at *ca.* 247 eV is attributable to the contamination of the carbon surface by oxygen.

A narrow C KLL line at *ca.* 265 eV, possessing no secondary features on the high-energy side, implies complete absence of KVV transitions involving π electrons which are typical of sp² coordination. As a result, the energy distance between the maximum of the positive-going excursion and the excursion and the minimum of the negative-going excursion, which was unambiguously indicated as a fingerprint of the different arrangement of carbon atoms,^{13,14} does not exceed 14 eV. This value is very close to the peak-to-peak width of the main transition of diamond (13 eV),¹⁴ whereas the graphite spectrum is characterized by a far larger width (*ca.* 23 eV) between the negative and the positive maximum peak. The observed peculiarities of the X-ray excited Auger electron spectrum point to the fact that the electrolysis of lithium acetylide solution leads to the formation of the diamond-like carbon films almost free from sp²-bonded carbon.

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