

# Electrodeposition of DLC films on carbon steel from acetic acid solutions

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In this paper the electrodeposition of DLC films on carbon steel from aqueous acetic acid solutions and their structural and mechanical characterization are reported. The process is performed at room temperature at relatively low cell voltages (from  $-8$  to  $-20$  V) with entirely environmentally friendly chemicals. Qualitative and quantitative evaluation of C hybridisation type have been performed by Raman spectroscopy. Microhardness and adhesion of the supported electrodeposited films have been measured by micro-indentation and scratch-testing. Notably, ductile failure was found to correspond to a wide range of film growth conditions. The corrosion resistance of DLC-coated steel has been assessed by electrochemical impedance spectrometry in a neutral chloride solution. Optimal electrodeposition conditions were identified for the formation of high-quality DLC films *ca.* 270 nm thick with a high content of diamond-coordinated carbon and an ideal combination of hardness and adhesion; films formed under these conditions also confer some degree of corrosion protection to the steel substrate.

**Keywords:** DLC, Electrodeposition, Acetic acid, Raman, Scratch-testing

## Introduction

Applying a hard coating to a surface can improve the resistance to wear and environmental degradation for mechanical and tribological applications. In recent years, diamond-like carbon (DLC) films have attracted interest in the mechanical engineering community because of their unique properties and characteristics such as high hardness, high thermal conductivity, high chemical inertness and high corrosion resistance. The deposition of DLC films has been accomplished by a large number of different methods among which the more extensively documented are: chemical vapour deposition (CVD), physical vapour deposition (PVD) and ion-beam laser processing techniques.<sup>1–10</sup> However, these techniques have disadvantages such as requirement of high voltage, high vacuum and therefore high cost. Thus, an alternative simple, scalable and low-cost method for the deposition of DLC films would be very important. Electrodeposition offers us a novel route of synthesis for DLC films; in 1992, for the first time Namba<sup>11</sup> used electrochemical methods to deposit DLC films on silicon substrates. In his study, DLC films have been deposited on silicon substrates from ethanol

solutions at temperatures from room to 70°C, by ramping the potential from 0 to  $-1.2$  kV and obtaining current densities growing from 0 to 5 mA cm<sup>-2</sup>. After this seminal work, the electrolytic method has been successfully employed to deposit DLC films from different organic solvents such as: methanol, ethanol, acetone and DMF.<sup>11–13</sup> Notwithstanding the advantages of the electrochemical approach with respect to the competing physical methods, in these researches, DLC coatings have been deposited at low temperature, but with a high potential difference between the anode and cathode which greatly increases the difficulty of controlling the growth process.

More recently, A.K. Pal *et al.*<sup>4,15</sup> proposed a simple electrodeposition technique using formic acid, acetic acid (CH<sub>3</sub>COOH) and deionised water as the electrolyte; electrolysis was carried out with voltage in the range 2.5–30 V, corresponding to current densities between 10<sup>-3</sup> and 10<sup>-5</sup> A cm<sup>-2</sup>. By this method, diamond phase and amorphous carbon films were both formed, as revealed by Raman spectroscopy. This approach, employing both low potential and low temperature, allows a notable simplification of the setup and process control.

As far as the structure of DLC films is concerned, they have been reported to be generally amorphous and homogeneous, but some micro or nano-crystalline inclusions of all carbon forms are typically found in the amorphous matrix. During film deposition, the carbon atoms can combine at the surface to form all possible combinations of sp<sup>1</sup>, sp<sup>2</sup>, and sp<sup>3</sup> bonds, the trigonal (sp<sup>2</sup>) or tetrahedral (sp<sup>3</sup>) configurations

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