A New Thin Film Deposition Process by Cathodic Plasma Electrolysis

Thierry Paulmier[a], Emad Kiriakos[a], John Bell[a], Peter Fredericks[b]

[a] *Built Environment and Engineering Research Centre, School of Mechanical, Manufacturing and Medical Engineering, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia*
[b] *Science Research Centre, School of Physical and Chemical Science, Queensland University of Technology, GPO Box 2434, Brisbane, QLD 4001, Australia*

A new plasma deposition process, called Atmospheric Pressure Plasma Deposition (APPD), has been developed for the deposition of diamond-like carbon, titanium and silicon films. This paper describes the process and presents the structural properties of diamond-like carbon produced by this technique.

1 Introduction

A new deposition method, Atmospheric Pressure Plasma Deposition (APPD), has been developed, which combines galvanic processes and plasma-chemical phenomena. Unlike other plasma deposition techniques, the process occurs in liquid precursors and the plasma is thus confined to the cathode in a superheated vapour sheath surrounded by the liquid phase. This method, previously used in anodic configuration for the deposition of oxide films [1-2], allows (in cathodic configuration) the production of a wide range of films, such as carbon, titanium and silicon films.

2 Experimental set-up

The basic process of APPD is the electrolysis of a solvent at high voltage. In our test facility, we use a direct current power supply (Bertran 105-02R) with a maximum voltage of 2000 V and a maximum electric power equal to 1kW. The electrodes can be cylindrical or flat. For the deposition of diamond-like carbon films (DLC), the electrolytic solution is composed of ethanol (50-90 % in volume), water, potassium chloride and phosphate buffer. The anode area is significantly larger than the cathode area (12 times) in order to concentrate the current density and create both the vapour sheath and the glow discharge around the cathode. A sampling system has been installed on the facility to collect liquid during the process. The liquid is then analysed by Gas Chromatography – Mass Spectrometry (GC-MS). The precipitate formed during the process is separated from the solution and then analysed by infrared and Raman spectroscopy. The films have been analysed by Scanning Electron Microscopy (SEM) and Raman spectroscopy.

3 Results and discussion

3.1 The phenomenology

The current-voltage characteristics of the APPD allow the different physico-chemical mechanisms occurring during the process to be distinguished (Fig. 1). The first stage is characterized by a steep increase of the current with the increasing voltage. This stage corresponds to the Joule heating of the solution. During this stage, the electrochemical reactions induce the production of oxide precipitates and a large number of small bubbles on the cathode. When the temperature reaches the temperature of vaporization of the solvent, the cathode is blanketed by bubbles which form a vapour sheath (stage 2). The conductivity of this overheated sheath is much lower than the liquid conductivity, so the voltage drop mainly occurs in the gas phase causing a strong decrease of the electric current.

The electric field is very high (from 50 to 1000 kV/m), which induces the breakdown of the gas (stage 3). The cathode emits a large number of electrons which ionize the gas. When the voltage is sufficiently high, the number of produced electrons compensates the electrons lost by collisions, the glow discharge is initiated and a plasma gas is formed. If the voltage is higher, the glow discharge is converted to a powerful arc discharge, which destroys the film.

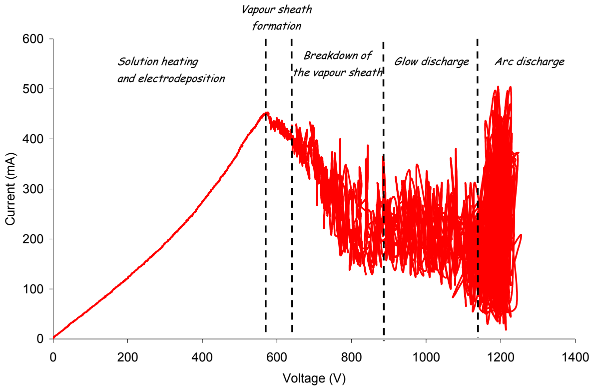
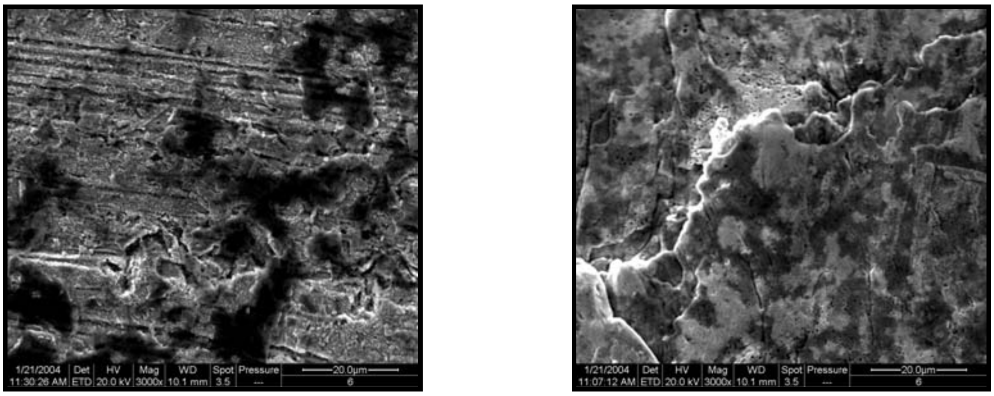


Figure 1: Current-Voltage characteristics of the APPD process.

3.2 The film properties

The atmospheric pressure plasma deposition allows the rapid deposition of dense hydrogenated carbon films. Fig. 2 shows the evolution of the morphology of the produced films on the substrate. Fig. 3 shows the Raman spectrum obtained on the edge. The structure of the film changes drastically as a function of its distance from the edge. In the vicinity of the edge, we observe the presence of DLC precursors (peaks at 1360 and 1470 cm^{-1}) [3]. The middle of the substrate is mainly composed of nanocrystalline graphite. The glow discharge is located at the edge of the substrate and is thus an important factor for the formation of DLC films.



(a) *(b)*

Figure 2: SEM pictures of DLC films. (a) 5 mm from edge, (b) 1 mm from edge. Solution: ethanol (90 vol. %) + water (10 vol. %), Voltage: 1700 V, Treatment time: 3600 s.

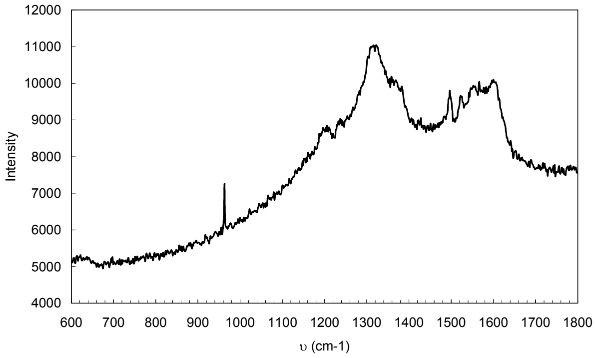


Figure 3: Raman spectrum of the carbon film at 1mm from the edge.

3.3 The physico-chemical processes

The analysis by GC-MS of the solution, sampled during the process, shows that the glow discharge is responsible for complex chemical processes. The plasma-liquid interaction induces the formation of heavy organic compounds (Table 1), resulting in dissociation, ionisation, fragmentation and polymerisation processes. The precipitates formed during the process have been analysed by Raman spectroscopy revealing the presence of nanocrystalline graphite and oxide compounds (between 400 and 800 cm^{-1}) produced by electrochemical reactions. In the gas phase, the plasma is responsible of the formation of ionised species which are implanted in the substrate. The high temperature of the plasma induces melting and phase changes in the pre-deposited oxide film.

Table 1: Organic compounds produced by the plasma-liquid interaction (GC-MS analysis)

Acetaldehyde, Formaldehyde, Methanol, 1,3-Butadiene, 2-Propanol, 1-Propanol, Ethyl acetate, 2-Butanol, Butadienylacetylene, Acetic acid hydroxy-ethyl ester, 1,1-Diethoxy-Ethane, Ethylene glycol, 1,2-Propandiol, 2,3-Butandiol, 1,3-Butandiol, Phenylethyne, 1,3-Propandiol, Methylphenylacetylene

4 Conclusion

The atmospheric pressure plasma deposition has been developed for the rapid production of carbon and titanium films. The glow discharge is responsible for several complex chemical reactions and thermal effects on the substrate which are essential for the deposition of the films. This process combines electrolytic and plasma chemistry to produce, at relatively low cost, interesting films for a large range of applications (wear resistant coating, electronics, biomedical, renewable energies).

References

[1] A. L. Yerokhin, X. Nie, A. Leyland, A. Matthews and S. J. Dowey, Plasma electrolysis for surface engineering, Surface and Coatings Technology, **122**, 73 (1999)

[2] X. Nie, A. Leyland, H. W. Song, A. L. Yerokhin, S. J. Dowey and A. Matthews, Thickness effects on the mechanical properties of micro-arc discharge oxide coatings on aluminium alloys, Surface and Coatings Technology, **116-119,** 1055 (1999)

[3] A. Zaitsev, Optical Properties, Handbook of Industrial Diamonds and Diamond Films, Chapter 7, edited by Mark A. Prelas (Marcel Dekker Inc., New York), 227 (1998)