



UNIVERSITAT DE BARCELONA



DEPARTAMENT DE FÍSICA APLICADA I ÒPTICA

c/ Martí i Franquès, 1, 08028 Barcelona

**THIN FILM STRUCTURES OF DIAMOND-LIKE CARBON
PREPARED BY PULSED PLASMA TECHNIQUES**

Carles Corbella Roca

Memòria presentada per optar al grau de Doctor

Barcelona, novembre de 2005



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Programa de doctorat: Tècniques Instrumentals de la Física i la Ciència de Materials

Bienni: 2001-2003

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Als meus pares i al Jordi

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Outline of this thesis

The study of synthesis of diamond-like carbon (DLC) thin films and their subsequent characterisation are the goals of this thesis. Hard, low-friction and wear-resistant DLC films, either in the form of amorphous carbon (a-C) or amorphous hydrogenated carbon (a-C:H), have been used as protective coatings and solid lubricants in a great variety of applications. Plasma-enhanced chemical vapour deposition (PECVD), cathodic arc and sputtering physical vapour deposition (PVD) are the most employed deposition techniques of this material.

An important disadvantage shown by DLC films is their high compressive stress, which limits their adherence to substrate if their thickness approaches 1 μm . Among the proposed solutions are the deposition of a metallic buffer layer, the preparation of composition-graded films and multilayer structures. This work deals with the strategy of incorporating metal atoms in the carbon network via reactive sputtering physical vapour deposition (PVD). This leads to metal containing DLC (Me-DLC) films with a more relaxed structure. On the other hand, the use of pulsed high-power suppliers has also been considered. The main advantages of this technology are to reduce intrinsic stress, increase deposition rate and make production more cost effective. This thesis reports the preparation of DLC-based films by means of these two plasma techniques, as well as data concerning chemical, structural, morphological, optical and mechanical properties. The contents of each chapter are summarized below.

Chapter 1 – Introduction

DLC shows mechanical properties similar to diamond. Thus, a general introduction to protective and hard coatings is given in this chapter. A brief history of hard coatings is reviewed, followed by examples in industry and hardening mechanisms of thin films. The second section deals with the role of plasma technology for material treatment and deposition.

Chapter 2 – Diamond-like carbon

This chapter presents the topic material. After an atomic description, the main carbon structures (diamond, nanotubes, etc) are listed, emphasizing amorphous carbon and its properties. The main thin film growth models of DLC are discussed in the second part. Finally, the chapter gives an overview of the applications of this material.

Chapter 3 – Experimental set for deposition

In this chapter, the deposition systems have been presented. First, the reactor used to grow DLC by pulsed-DC PECVD is described. The second section deals with the chamber for the preparation of Me-DLC, and its alternative setup to deposit multilayers. This chapter finishes with the description of the used substrates and of the Langmuir probe employed to measure the plasma parameters.

Chapter 4 – Thin film characterisation techniques

The aim of this chapter is to present the methods which provided the experimental results analysed in this thesis. The characterisation of the deposited films involves structural, optical and mechanical properties of DLC, which have been related to technological parameters of deposition stage.

Chapter 5 – Plasma characterisation with a fast Langmuir probe

This is the first chapter of experimental results. The methane glow discharge responsible of PECVD DLC films is analysed through an electrostatic probe. Plasma parameters have been obtained from the analysis of I(V) scans concerning RF and pulsed-DC glow discharges. Tracking of parameters in the latter case required the construction of a time-delay circuit.

Chapter 6 – Characterisation of pulsed-DC DLC films

This chapter discusses the growth and properties of DLC films prepared by pulsed-DC PECVD method. The analysed properties are microstructure (Raman, XRR), hydrogen content (FTIR, EA), surface (AFM, contact angle) and mechanical properties (stress, nanoindentation, micro-scratch, wear, LFM).

Chapter 7 – DLC structures from RF magnetron sputtering

In this chapter, the preparation and characterisation of multilayer structures grown by sputtering are reported. Microstructure (Raman, TEM, XRR), crystallinity (XRD), and mechanical properties (stress, hardness, micro-scratch) are the studied properties.

Chapter 8 – Metal containing DLC films prepared by pulsed-DC reactive magnetron sputtering

The last chapter analyses several aspects of Me-DLC films. Special emphasis has been made in nanostructure of growth patterns (TEM) and crystallinity (HRTEM, XRD). Other studied properties are composition (XPS, SIMS, EPMA), optical behaviour (spectroscopic ellipsometry and transmittance), electric conductivity (four-point probe method), and surface and mechanical properties (AFM, contact angle, stress, micro-scratch, nanoindentation).

