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X-ray reflectometry study of diamond-like carbon films prepared by plasma enhanced chemical vapor deposition in a low pressure inductively coupled plasma

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A B S T R A C T

In this work we probe the structural properties of amorphous hydrogenated carbon thin films prepared by plasma-enhanced chemical vapor deposition in a low pressure inductively coupled plasma using X-ray reflectometry in order to study the effect of varying the ion energy on the density of these films. The ion energy is varied by varying the RF power used to bias the substrate. It is shown that a very low ion energy is already sufficient to obtain a dense diamond-like carbon (DLC) film, in contrast with other deposition techniques where much higher ion energies are required to obtain a dense DLC film. The results of this study are corroborated by Raman spectroscopy and ellipsometry measurements. The X-ray reflectometry data analysis is detailed in order to highlight some methodological problems encountered during the data fitting which could lead to an incorrect interpretation of the measured curves.

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1. Introduction

Diamond-like carbon (DLC) films have been shown to be good candidates for various applications such as cutting tools, coatings of magnetic head and media of hard disk devices for their high hardness, high resistance to abrasion, low friction coefficient and high chemical inertness.

The properties of the deposited film are related to its density, sp^3 phase content, hydrogen content and internal layering in the film. Grazing angle X-ray reflectivity (XRR) is a nondestructive method, used widely for investigation of the structure of thin films and particularly the multi layered films [1]. This technique has been used in the past by various investigators to study hydrogen containing DLC films [2–7] determining thus the thickness and scattering length density. Libassi et al. [6] studied a variety of thin films of amorphous hydrogenated carbon and non-hydrogenated carbon in order to extract information on their densities, thicknesses and interfacial roughness. Kondrashov et al. [8] tried to combine ellipsometry and reflectometry to compare the structural properties of DLC films. Lemoine et al. [9] have combined several techniques with reflectometry to study in particular the thickness of thin carbon films. Junji et al. [10] have attempted to estimate the structure of DLC layers (thickness and density) deposited on silicon substrates by comparing several deposition techniques. Singh et al. [5] used XRR to investigate the effect of substrate bias on the formation of DLC films deposited by microwave electron cyclotron resonance. In this work we try to probe by X-ray reflectometry the structural properties of amorphous carbon thin films prepared by plasma enhanced chemical vapor deposition (PECVD) using an inductively coupled plasma (ICP) source operated in a methane plasma. In these plasmas CH_4 molecules are dissociated into CH_3 and H by electron impact. CH_3 can be further dissociated into CH_2 and H, CH_2 in CH and H and CH in C and H. Nevertheless, in low pressure plasmas, such as microwave electron cyclotron resonance (ECR) or ICP plasmas, it has been shown that CH_3 and CH_2 are the dominant neutral radicals, while CH_4^+ is the dominant positive ion. The film is expected to grow due to CH_x (mainly CH_3) adsorption on dangling bonds which are efficiently created by ion bombardment [11]. The structure and hardness of amorphous hydrogenated carbon films strongly depend on the energy of the ions impinging on the surface and values of 20 GPa (or even higher) are currently obtained for such hydrogenated amorphous carbon films. While DLC films deposited in rf capacitively coupled plasmas and microwave electron cyclotron resonance plasmas have been extensively studied, much less attention has been paid to carbon films deposited in ICP plasmas.

This study focuses on the structural changes within these films subject to the effect of varying rf power applied to the substrates and the corresponding DC self-bias voltage. The results are compared with those obtained by ellipsometry and Raman spectroscopy. Also some difficulties encountered when analyzing reflectivity curves for this kind of films are highlighted.

2. Materials and methods

2.1. Main characteristics of DLC films

DLC films are composed of sp2 hybridized (graphite type) and sp^3 (diamond-like) carbon atoms, with a significant fraction of sp^3 bonds;

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different types of DLCs can be distinguished: a-C, a-C:H, ta-C and ta-C: H. a-C, and a-C:H films contain a high proportion of sp^2 carbon, while tetrahedral amorphous carbon (ta-C: H or ta-C) has a majority of sp^3 bonds [12].

DLC films could present thus a wide diversity of chemical compositions giving them different properties approximating more or less those of diamond. The properties of carbon thin films depend on the relative proportions sp^2/sp^3 and the amount of hydrogen incorporated. The properties of diamond, graphite, C60 and different types of amorphous carbon are presented in Table 1.

2.2. Sample preparation

The most common methods for DLC film deposition are PECVD using methane based plasmas. Here, the carbon films were deposited in a low pressure (<1.33 Pa) radiofrequency (13.56 MHz) inductively coupled plasma. The PECVD reactor is described in detail in [13]. For the deposition of carbon films, methane is introduced at the top of the RF plasma source. The films are deposited on pieces of (100) silicon wafers located in the diffusion chamber on a substrate holder which can be biased by applying an RF power. The silicon samples were cleaned in an ultrasonic bath of acetone and rinsed in alcohol. Each deposit was preceded by a 10 minute plasma cleaning stage (pre-treatment) using an argon plasma at a pressure of 33 Pa, an rf power of 300 W and biasing the silicon substrate at −100 V. This pre-treatment allows to remove the native oxide SiO2 (3–4 nm thick) present on the substrate before the deposition phase and thus improves the adhesion of carbon film to the substrate, but it creates a very thin layer of amorphous Si. The DLC layer was then deposited under the following conditions: methane plasma at 8 Pa, 100 W applied to the helicon antenna and a variable RF power applied to the substrate, which should create the following stack: Si/amorphous Si/DLC layer. In the absence of the RF excitation, the substrate is at the floating potential (V_f) and the ion energy, equal to $e(V_p - V_f)$, where V_p stands for the plasma potential, was measured to be around 15 eV [14]. When an RF power was applied to the substrate, this latter was carried to a negative DC self-bias voltage, denoted V_b (in between −10 V and −200 V), which depends on the applied RF power. It allows to accelerate the positive ions impinging on the growing film to an energy equal to $e(V_p - V_b)$ while keeping a constant ion flux (fixed by the power coupled to the ICP plasma).

The aim of the study is to examine the effect of V_b on the density of these layers and to correlate this density with their structure. Each film is identified by the value of V_b: the film deposited at $V_b = -X$ V is hereafter denoted DLCX, while the film deposited at the floating potential is denoted DLC0.

The films were analyzed in situ by spectroscopic ellipsometry in the 1.5–5 eV range and ex situ by Raman spectroscopy and X-ray reflectometry. The spectroscopic ellipsometry measurements were performed in situ (under vacuum, after deposition) using a phase modulated UVISEL Jobin-Yvon Horiba ellipsometer operated in the 1.5–5 eV range. To analyze the ellipsometric data, the films were considered as one layer and were described using a model of Tauc–Lorentz [15,16] for biased films and a Cauchy model for the film deposited at the floating potential. Raman measurements were carried out on a Jobin–Yvon T64000 spectrometer using the 514.5 nm argon ion laser line.

The main deposition conditions of the studied samples and their thicknesses, estimated from spectroscopic ellipsometry measurements performed in situ, are compiled in Table 2.

Table 1
Comparison of amorphous carbon properties with those of reference materials, diamond, graphite, C60 and polyethylene according to Robertson [12].

	sp^3 (%)	H (%)	Density ($g.cm^{-3}$)	Gap (eV)	Hardness (GPa)
Diamond	100	0	3.515	5.5	100
Graphite	0	0	2.267	0	
C60	0	0		1.6	
Glassy carbon	0	0	1.3–1.55	0.01	3
Evaporated carbon	0	0	1.9	0.4–0.7	3
Carbon sprayed	5	0	2.2	0.5	
ta-C	80–88	0	3.1	2.5	80
a-C:H hard	40	30–40	1.6–2.2	1.1–1.7	20–10
a-C:H soft	60	40–50	1.2–1.6	1.7–4	<10
ta-C:H	70	30	2.4	2.0–2.5	50
Polyethylene	100	67	0.92	6	0.01

2.3. X-ray reflectometry

The reflectometry experiments were performed using a Bruker D5000 diffractometer with Cu-$K\alpha$ radiation. The time required to measure a reflectivity curve and determine the background noise was about 24 h. The reflectivity curves measured on these films have undergone the usual data reduction procedures [17]. Analysis of these curves was done using programs Motofit [18] and Parratt32 [19].

3. Results and discussion

3.1. Density profiles

In order to model the reflectivity data electron density models consisting of one, two and three layers were tested, since, in general, the structure of the DLCs cannot be described using a single layer density model. For sample DLC0, deposited at the floating potential, a model with two layers gives a satisfactory fit of the reflectivity curve, the introduction of a third layer leads to an equivalent profile. The two layers profile comprises a bulk layer, which represents about 98% of the total thickness of the film, and another layer in contact with the substrate that does not represent a layer of constant thickness but rather describes a density gradient at the interface substrate/layer mass.

For other samples, deposited with RF bias, it is necessary to use a density profile consisting of three layers to adequately describe the reflectivity curves for these samples. This profile includes a bulk layer, which represents between 90 and 96% of the total thickness of the film and two layers, one in contact with the substrate and the other to the sample surface, which represent no layers of constant thickness but which describe density gradients at the interface substrate/layer mass and layer mass/air. The description of the thin film in a three-layer model is similar to what was found by Singh et al. [5].

In Figs. 1 and 2 are presented two typical reflectivity curves measured on two samples that show models with two and three layers.

The reflectivity curve of sample DLC200, plotted in Fig. 3, does not show any Kiessig fringes, information on the thickness of the layer thus being lost. This is probably due to a thickness value exceeding the value which can be determined by the reflectometer. Indeed, the value of the thickness found by ellipsometry (348 nm) is at the upper detection limit of the experiment. The lower and upper limit of the thickness that can be determined by X-ray reflectivity is between 2 and 350 nm for Cu-Kα radiation and a standard laboratory

Table 2
The thicknesses (measured by ellipsometry) and the deposition conditions of the studied samples.

Reference sample	V_b (V)	Thickness (nm) Si (0.5 × 2 cm)	Deposition rate (nm/min)
DLC0	V_f	217	3.6
DLC10	−10	195	3.25
DLC20	−20	179	3.0
DLC50	−50	164	2.73
DLC80	−80	150	2.5
DLC120	−120	163	2.71
DLC200	−200	348	5.8

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