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Optical emission spectroscopy as a process-monitoring tool in plasma enhanced chemical vapor deposition of amorphous carbon coatings - multivariate statistical modelling

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ABSTRACT

Production of Diamond-Like Carbon (DLC) nanocoatings using plasma enhanced chemical vapor deposition is studied by Optical Emission Spectroscopy (OES) as a plasma diagnostic technique. The objective of the current research is to establish a predictive model of DLC properties using a multivariate analysis method. This model is based on OES data instead of process parameters, which are reactor dependent and accordingly, their effect on the plasma deposition process may vary from one reactor to another. The predictive potential of OES is evaluated using partial least square regression (PLSR) analysis. The results show that OES derived data are capable of replacing some process parameters to predict the DLC properties. The perspective of PLSR modelling and OES application for the development and monitoring of a structurally graded DLC coating is also discussed.

1. Introduction

Diamond Like Carbon (DLC) is a general term that covers a wide range of amorphous carbon materials including amorphous carbon (a-C, a mix of sp^2 and sp^3 hybridized carbon), tetrahedral amorphous carbon (ta-C) with up to 90% of carbon in sp^3 hybridization (diamond-like structure) and their hydrogenated variants (a-C:H and ta-C:H) [1–3]. Therefore, the sp^3/sp^2 ratio and H-content determine the final DLC structure and properties. However, a high sp^3 content of a DLC coating provokes a high internal compressive stress within the coating, which restricts film thickness and its application in harsh conditions. Annealing [4,5], doping with different types of metallic elements [6–8] and multi-layer or structurally graded DLC [9–11] have been proposed to attenuate the internal stress and to improve the coating's mechanical behavior. The latter has the benefit of tailoring the properties of the coating according to the desired application.

Designing a graded coating requires to know the correlation between the structure of nanocoating and the plasma process parameters. Several researchers have studied the effects of process parameters such as plasma power, pressure, etc. on the properties of DLC coatings [12,13]. However, the relationship between such parameters and plasma characteristics, which directly affect a coating's structure, differs from one reactor to another depending on each reactor's configuration. Consequently, reproducing identical coatings in different plasma setups involves a tedious trial and error procedure. One avenue to overcome this problem consists in correlating some of the plasma characteristics in terms of plasma specie densities and energies, as measured through plasma diagnostic tools, with the DLC coating properties.

Several plasma diagnostic methods have been used to study carbon containing plasmas; such as electrostatic probes [14–16], optical emission spectroscopy (OES), optical absorption spectroscopy [17–20], and mass spectroscopy [21–23]. Each of these plasma characterization methods has pros and cons. For instance, the Langmuir probe is a common method for evaluating electron energy distribution inside the plasma. However, it is an intrusive characterization method, which means that it somewhat perturbs the plasma environment. On the other hand, OES extrinsically probes the plasma and provides information about temperatures (electronic, vibrational, and/or rotational) and densities of excited species. Although being advantageous at first sight,

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this technique requires to make some hypotheses related to the energy distribution of the plasma species as well as the mechanisms of excitation [24,25].

In this context, this article aims to compare both the deposition process parameters and OES data as predictive tools to monitor DLC structure and its mechanical properties. However, since the plasma parameters, optical spectroscopy results, and coating properties are highly correlated, the common regression methods cannot demonstrate the effects of each independent parameter on the resulting dependent variables. Therefore, a partial least square (PLS) regression modelling, which is consistent with effects causing changes in the investigated system [26], is employed to find the correlation between either the plasma process parameters or OES data with some of the DLC structural and mechanical properties.

1.1. Statistical analysis – PLSR

Projection to Latent Structure/Partial Least Square Regression (PLSR) is a practical mathematical tool to study a data space when numerous, correlated, noisy and sometimes missing data are available. It extracts the latent structure of independent (X) and dependent (Y) data set by finding new coordinate system for X and Y based on orthogonal vectors (called Principal Components (PC) or Latent Variables) along which there is minimum variance between the projected observations. The PCs are the best descriptors of each data space (X or Y). This new coordinate system is calculated in such a way that it assures the highest possible covariance between X and Y spaces. Therefore, a PLSR model describes at the same time the data structure at predictive (X) and predicted (Y) matrices as well as the correlation between these two [26].

A PLS model begins by following decompositions of X and Y matrices [26] (when there are N observations with K variables in X and M responses in Y):

$$X_{NxK} = T_{NxK} + P^{T}_{AxK} + E_{NxK} \quad (1)$$

$$Y_{NxM} = U_{NxA} C^{T}_{AxM} + F_{NxM} \quad (2)$$

$$T_{NxA} = X_{NxK} W^{*}_{KxA} \quad (3)$$

T and U are called score matrices for X and Y, respectively, and bear the A principal components of the X and Y matrices in their columns. P and C are called loading matrices. E and F are the residuals of the model for X and Y, respectively. W* is called the weight matrix of PLSR and contains those combinations of X variables that are the most predictive of Y.

In PLSR, the T and U matrices are calculated in such a way that a high level of correlation between them is assured. Therefore, T is also a good predictor of Y:

$$Y_{NxM} = T_{NxA} C^{T}_{AxM} + G_{NxM} \quad (4)$$

A combination of Eqs. (3)–(5) will be used for the purpose of process prediction:

$$Y_{NxM} = X_{NxK} W^{*}_{KxA} C^{T}_{AxM} + G_{NxM} = X_{NxK} B_{KxM} + G_{NxM} \quad (5)$$

This latter equation allows determining the B matrix that contains the regression coefficients. More details on PLSR is provided by Wold [26].

2. Materials and methods

Amorphous carbon films were deposited using an inductively coupled radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) reactor (FLR1200, Plasmionique Inc., Varennes, QC, Canada) over silicon wafers. Fig. 1 depicts a schematic setup of the plasma reactor. Methane (CH_4) was used as the source of carbon and hydrogen. A separate low frequency power supply was employed to induce ion acceleration toward substrates by applying a self-rectified negative bias voltage to the sample holder (as a cathode) with respect to the chamber wall (as the Anode). A UV–Vis spectrometer equipped with a 300 lines per mm grating (HR4000CG-UV-NIR, Ocean Optics Inc. Dunedin, FL, USA) was used to record the UV–Visible spectra between 200 and 1100 nm with a spectral resolution of ~0.5 nm.

2.1. Pre-deposition process

Silicon substrates were wiped with acetone and then fixed over the substrate holder in such a way to ensure proper electrical conductivity between the substrate holder disk and samples during the deposition process. Argon etching (at 100 W, 20 sccm, 6.7 Pa, and a bias voltage of −100 V for 15 min) for contamination removal and hydrogen etching (at 100 W, 10 sccm, 6.7 Pa, and a bias voltage of −150 V for 15 min) for surface activation were carried out prior to deposition.

2.2. DLC deposition

A constant flow of 7 sccm of CH_4 provided the required carbon source to build-up the diamond-like coating during 30 min of deposition. Four experimental parameters were studied in this research; plasma RF power (P), plasma power mode (M) (either continuous or pulse mode at 100 Hz and duty cycle of 50%), pressure (p), and applied bias voltage (V_b).

2.2.1. Determination of deposition parameters

The four experimental parameters mentioned above were employed at two different levels (high/low), as described in Table 1. This range of values allowed the deposition of DLC coatings with a variety of structural and mechanical properties.

2.2.2. Design of Experiments

A fractional factorial design method was employed to determine the combination of experimental parameters for each deposition condition and to reduce the number of experiments [27]. Therefore, 8 observations (Table 2) with 3 replicates were performed. This allowed to build-up the training set of experiments that will be used to develop the statistical model.

The range of values has been determined based on literature [27], technical limitations, and a series of preliminary tests. For example, at a bias voltage of < 50 V, the incident carbon species do not carry enough energy to form a dense sp^3 structure over the substrate. Therefore, the resulting coating would not be stable. However, when they got accelerated at very high bias voltage (over 200 V), they induce intolerable internal stresses to the coating that make it delaminated.

The lower value for the pressure and plasma power are the minimum values which are capable of igniting and keeping a steady state plasma medium, according to our experimental setup. Their high values are determined based on our experimental setup limitations.

Supplementary sets of coatings were also deposited for evaluation of the model prediction power (prediction set). As may be seen in Table 2, the combinations of experimental parameters for the prediction set were different from those of the training set.

2.3. DLC characterization methods

2.3.1. Profilometry

The thickness of coatings was measured using a stylus profilometer (DektakXT, Bruker, USA) with a force of 3 mg applied to a 12.5 μm Rc stylus via a step-height technique. The internal compressive stress was calculated by measuring the surface curvature before and after deposition using the same surface profilometer and the Stoney's method [28].