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Argon and hydrogen plasma influence on the protective properties of diamond-like carbon films as barrier coating

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ABSTRACT

Diamond like carbon (DLC) films are becoming materials of choice for mechanical and corrosion protection barrier films due to their excellent properties of low-friction and chemical inertness. As DLC functional properties are strictly dependent on process parameters, different DLC coatings have been deposited onto silicon substrates by Plasma Enhanced Chemical Vapour Deposition (PECVD) evaluating the effect of the variation of argon and hydrogen gas flows on the coating resistance properties. It has been observed that the hydrogen variation is the main factor affecting the DLC films resistance in aggressive environments, while DLC samples deposited by varying Ar showed significant delamination phenomena. These differences have been related to the morphological and microstructural characteristics of DLC films taking into account for the specific role of both Ar and H_2 in the mechanism of DLC formation. In particular, it has been observed that the resistance against corrosive environment for DLC coatings may be related to the compressive residual stress values in conjunction with surface and structural properties of the film. This can be considered an understanding at the atomic scale providing the key for the optimization of the protective coating performance.

1. Introduction

In the last decades, the requirement to use effective protective coatings for nanoscale practises has driven modern research to design more durable ultra-thin anticorrosion and protective films with specific functional surface, such as water wetting, self-cleaning and antibacterial properties [1–3].

To date, the most common approaches to prepare coatings with functional surface properties are: chemical and electrochemical methods [4–7], lithography [8], CVD [9,10] or PVD technologies [11,12], and surface plasma modification [13,14]. The last one is particularly enticing as it enables to achieve a desired surface functionality while retaining the mechanical properties of the bulk [15–17]. Further added-value is also given by the fact that plasma is a “dry” technology, intrinsically ecological, and environmentally friendly, and the physico-chemical modification of the surface can be carried out also at low temperatures, allowing treatments for thermo-sensible materials, such as plastics, polymers and organic substrates [18].

Among the protective coatings that can be prepared by plasma modification, diamond-like carbon (DLC) is of particular interest: it is constituted by amorphous carbon containing hydrogen and carbon bonded in mixed sp^2 and sp^3 electronic configurations [19]. Furthermore, DLC-based materials have attracted much attention for their unique properties such as relatively high hardness, low friction coefficient, high thermal stability, optical transparency, excellent abrasion resistance, wide band gap, high resistivity, high dielectric strength, good thermal conductivity and good bio-compatibility [20,21]. Moreover, at room temperature, DLC films show low water permeability, are chemically inert to any solvent and present good resistance against acids (even strong acid mixtures), alkalis or organic mixtures [22]. This renders DLC films ideal choices as thin protective coatings even in extreme environmental conditions also for nanoscale-based applications [23,24]. Recently, Faraldi et al. [25,26] have employed nano-structured DLC films prepared by Plasma Enhanced Chemical Vapour Deposition (PECVD) for metallic artefacts protection against atmospheric corrosion and have preliminarily shown that, by adopting certain deposition procedures, it is possible to produce high-quality DLC coatings for the long-term preservation of metallic artefacts even under uncontrolled environmental conditions [25,26].

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DLC thin films, on the other hand, find application also in silicon-based nanotechnologies, as for example, protective materials for Silicon-based Micro- or Nano-electromechanical technologies (MEMS/NEMS) [27]. MEMS devices are used in different technological areas, like biomedical, environmental, transportation, manufacturing, robotics, space sciences, computing systems etc. However, silicon suffers some drawbacks: very large friction coefficient, high surface energy, high wear rate and narrow band gap energy, which cannot fulfill all of the material properties of MEMS. Under some extreme conditions, such as high temperature or aggressive environment, silicon hence may fail. For these reasons, silicon should be coated by a suitable protective coating, such as DLC, having a good adhesion to substrate and good resistance to delamination in aggressive conditions.

In this context, it must be pointed out that protective behaviour strictly depends on mechanical and microstructural properties of the material. The presence of flaws or pores in the film can lead to a worsening of interface adhesion, delamination and spalling of coatings, and the subsequent exposure of the substrates to the environment [28–31]. As a consequence, the presence of structural defects may act as a pathway for aggressive (external) agents to penetrate through the barrier coating and start a localized aggression of the substrate. It is mandatory, therefore, to assure the optimal deposition parameters in barrier coating preparation to avoid the formation of defective film that can then delaminate or not have a good adherence.

It is well known that DLC properties are strongly affected by the relative population of sp^2 and sp^3 hybridizations of the carbon atoms involved. Since the carbon sp^2/sp^3 ratio can be varied by tuning some experimental parameters, it is possible to impart to the DLC layer the required properties just changing opportunely the deposition parameters [32]. In this contest, we focused our attention on the effects of Ar and H_2 partial pressures on DLC barrier resistance when exposed to different environmental aggressive conditions. We carried out PECVD depositions of DLC films on silicon substrates by varying the Ar and H_2 flows, while keeping constant all the other experimental conditions, i.e. CH_4 flow, plasma power, deposition temperature and film thickness. Then, DLC films were exposed to several aqueous environments at different temperatures and for different exposure times and the resulted film adhesion and resistance to delamination have been evaluated.

Results indicate that differences in gas flow reactive plasma deeply affect film barrier properties. Consequently, a full investigation of film microstructure has been carried out to relate the DLC performances as protective coatings to the structural properties. The knowledge of correlations between protective behaviour and structural properties could be determinant for improving DLC resistance by simply optimizing the parameters deposition. These findings are expected to be a useful guide in designing and optimizing corrosion resistant coatings.

2. Material and methods

2.1. Diamond-like carbon deposition

The home-made PECVD system, used for the film deposition, consists of a capacitively coupled asymmetric plasma reactor, driven by a 13.56 MHz RF power generator connected to the upper electrode and controlled by an integrated impedance matching network. Further details on the RF plasma system can be found elsewhere [33,34].

DLC films were deposited at room temperature onto 1.5 × 1.5 cm (100) Si substrates, placed on the upper RF electrode.

The silicon substrates were previously cleaned in an ultrasonic bath with isopropyl alcohol for 10 min and, before deposition, have been additionally etched “in situ” by a 10 sccm hydrogen plasma at a pressure of 10^{-2} mbar and an RF power of 50 W for at least 600 s, in order to remove residual contaminants from the substrate surface and to optimise deposition conditions of the DLC.

Films have been deposited at 50 W RF power, using a fixed CH_4 flow of 40 sccm and by varying alternatively (i) the Ar gas flow rate in the range 0–100 sccm (DLC-Ar serie, H_2 flow rate constant and equal to 20 sccm) and (ii) the H_2 flow rate in the range 0–20 sccm (DLC–H_2 serie, Ar flow rate constant and equal to 50 sccm). Time deposition has been slightly varied in order to obtain DLC films of 500 nm in thickness, accordingly to the film growth rate. The substrate has been kept at room temperature (300 K) and controlled by a thermocouple. The working pressure, dependent on the gas flow, has been varied in the range of $2–5 \times 10^{-1}$ mbar with a consequently Bias Voltage variation in the range 200–240 V. All the gases used in the plasma cleaning and deposition processes are of 5.0 purity.

2.2. Growth rate

The film growth rate evaluation was carried out on 30 min of deposition time; the corresponding thickness, that turned out to be in 500–700 nm range, depending on the different deposition parameters, was evaluated by a KLA Tencor profilometer.

According to the growth rate values, the corresponding deposition time has been chosen in order to obtain DLC films of about 500 nm in thickness. Moreover, the analysis of variation of growth rate has been used to correlate the growth mechanism to the surface properties of DLC barrier coatings

2.3. Accelerated adhesion tests

Resistance-to-delamination of the coatings has been determined by accelerated tests carried out by expositing the DLC films to different water solutions. First of all, DLC-Ar and DLC-H_2 sets underwent a humidity test at 50 °C for 24 h using a home-made static humidity chamber. Then, the best sample of each set has been immersed in (a) a saline water solution (NaCl 0.9%) at 25 °C and at 50 °C over different time (2 h, 12 h, 24 h), and (b) in acid (HCl pH = 1.0) and basic (NH_4OH pH = 14.0) solutions at room temperature for 24 h.

After the immersion tests, film adhesion has been assessed by observing the number and extension of failures, such as blistering and delamination, through a Leica MZ FLIII optical microscope, equipped with a Leica DFC 320 digital camera. Images were digitally analysed using ImageJ in order to quantify the amount (area %) of sample which did not experience blistering/delamination/degradation during the test.

2.4. AFM

Morphological characterization of DLC films has been carried out by Atomic Force Microscopy (AFM) through a Dimension 3100 atomic force microscope equipped with a Nano Scope IIIa, controller (Veeco, Santa Barbara, CA) operating in tapping mode. Silicon nitride (TESP) probes with a resonant frequency of around 300 kHz and a nominal spring constant of 20/80 N m were employed (Veeco, Santa Barbara, CA). A scan rate of 0.3−1 Hz at a resolution of 512 pixels/line was employed. Background interpolation and surface roughness parameter calculation was performed with Gwyddion 2.40 (http://gwyddion.net/).

Reported root mean squared area roughness (S_q) values are the average of at least three different regions, with the standard deviation of these measures as the uncertainty.