

# NANOSTRUCTURED DLC COATINGS FOR SELF-ASSEMBLY APPLICATIONS

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## Introduction

The singular characteristics of diamond-like carbon (DLC) thin films, concerning tribological and surfaces properties, are suitable for self-assembly applications. Usually, DLC thin films have been developed as protective coatings for sliding surfaces with relative motion. But, DLC coatings deposited on nanostructured surfaces also provide new potential for self-assembly applications. In particular, the addition of fluorine during the deposition of DLC deposited by pulsed DC plasma enhanced chemical vapor deposition (PECVD) has a significant effect on the surface energy and tribological characteristics, which accelerates the mechanisms involved in self-assembly processes. Among the multiple applications of DLC coatings we also found their biocompatibility and antithrombogenicity. Such properties make them candidates for a number of medical applications where wear-resistant coatings, such as prosthesis, or simply biocompatible parts are required.[1]

## Experimental

DLC thin films were deposited by means of pulsed-DC PECVD using CH<sub>4</sub> and CHF<sub>3</sub> (trifluoromethane) as carbon and fluorine precursors. This technology offers certain advantages over RF PECVD, because the deposition rate increases while DLC intrinsic stress reduces.[2] Also, in order to improve adhesion of DLC to the substrate, a layer structure composed by a thin layer of DLC and a gradient layer, combining CH<sub>4</sub> and CHF<sub>3</sub>, were deposited on the silicon surface before the deposition of a film of hydrogen-fluorinated amorphous carbon (a-C:H:F). The plasma reactor has a base pressure of 10<sup>-5</sup> Pa and the films were grown at 10 Pa in power regulation mode at 57 W, providing a negative peak voltage near to 1000 V and a power density of 1.3 W/cm<sup>2</sup> on the substrate. Pulse frequency and duty cycle were fixed to 100 kHz and 80%, respectively.[3]

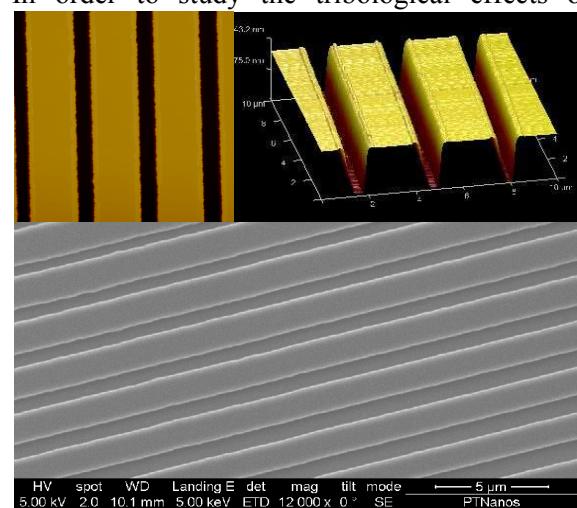
The surface characterization was carried out by microscopy observation, contact angle and tribology measurements. On the one hand, the exploration of the surface topography was performed by different optical and electronic

imaging techniques (interferometric and confocal microscopy, SEM, HR-SEM and AFM). On the other hand, contact angle was measured by a CAM 200 goniometer from KSV, and finally the friction measurements were performed using a CSM nanotribometer with a humidity controller. The applied load, 100 mN, was low enough to perform scans without damaging significantly the surface pattern.

## Results and Discussion

Low adherence, high stress and surface properties of DLC coatings can be modified with the incorporation of elements. Thus, the inclusion of Al, Fe, Ni, Nb or Ti metals reduces the surface free energy (SFE) of DLC, while W slightly increases it. In the case of no metals, the incorporation of O and N increases SFE, while Si and F reduce it. In the case of using compounds, the simultaneous addition of Si and O has more effect on the reduction of SFE than the incorporation of Si alone.[4] Among these elements, fluorine incorporation in DLC exhibits the highest water contact angles (more than 100°) and lowest surface energies (about 20 mJ/m<sup>2</sup>).[1]

In order to study the tribological effects of



**Figure 1.** SEM image of the lithographed silicon surface. AFM images of the lithographed silicon surface before the carbon deposition (left) and after (right).

fluorine, first, a surface patterning (Fig.1) was performed by laser lithography, and second, a relative flow of CHF<sub>3</sub> was set to 50, 75, 85 and

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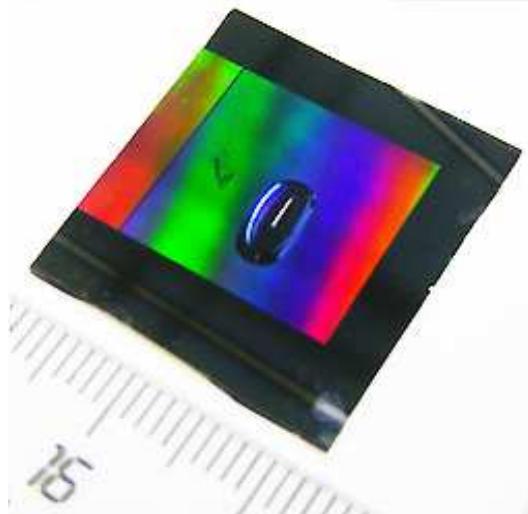
# Both authors have contributed equally in this work.

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90% versus the total gas flow ( $\text{CH}_4+\text{CHF}_3$ ) to produce a-C:H:F films on top of the patterned substrate. Large area patterns and direct writing on the substrate were performed with a mask-plotter DWL66 from Heidelberg Instruments. A lateral resolution as low as  $0.5\ \mu\text{m}$  could be achieved with a writing time shorter than in e-beam lithography. As an application of nanostructured DLC and fluorinated DLC coatings, we have focused on the self-assembly of submicron particles on coated surfaces. Then, by using wet technologies like Langmuir-Blodgett and spin-coater deposition, monodisperse and submicron silica particles were deposited on flat and on patterned surfaces.[5]

The lithographed and DLC coated substrates of silicon wafers were first laser lithographed and then coated by a DLC layer. An example of the structural and morphological characteristics of the explored samples is shown in Figure 1. Results show that DLC surface properties are dependent on the relative ratio between  $\text{CHF}_3$  and  $\text{CH}_4$  precursor gas concentration, resulting in high contact angles and low friction coefficients. DLC surface properties on lithographed surfaces such as hydrophobicity (Fig. 2) and wear show an anisotropic behavior related with the pattern geometry.

Another objective was to determine the ability of silica sub-micrometric particles to form



**Figure 2.** Image of the shape adopted by a water drop deposited on a patterned surface of a-C:H:F.

self-assembled arrays and to analyse the hypothetical benefits when DLC or fluorinated DLC were used. The formation of arrays and matrices of highly organized sub-micrometric colloidal particles (with a size in the range between  $10\ \text{nm}$  to  $1\ \mu\text{m}$ ) has attracted an extensive research interest due to their high versatility and their

consecutive potential applications. Wet fabrication of self-assembled monolayers (SAM), like spin-coating or Langmuir-Blodgett deposition, are ideal for producing high-quality macroscopic surface domains of monodispersed colloidal particles in a non-sequential process. These technologies suppose a clear advantage for large area applications in front of electron beam or ion beam lithography. But, our results show that the synthesis of colloids of high uniformity in size and shape (monodisperse) is a key factor to produce high quality arrangements by SAM. The consequences of a lack of uniformity or arrangement of particles affect directly the electrical, optical and magnetic properties of the resulting aggregates.[6] The attachment of silica particles will also depend on the roughness and the nanostructure of the surface.

## Conclusions

Applications of SAM on top of lithographed and fluorinated DLC films have been investigated. The results point to a significant effect of both patterning and a-C:H:F coating on the surface energy and tribological characteristics, which accelerates the mechanisms involved in self-assembly processes.

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