CONCLUSIONS

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1) A pulsed-DC methane glow discharge has been studied by Langmuir probe measurements in time-resolved mode. The coupling of a time-delay circuit facilitated an accurate monitoring of plasma parameters within a pulse of 100 kHz frequency and a positive pulse time of 2 μs.

2) The higher energies and stronger ionisation rates achieved by pulsed-DC methane discharges lead to an enhancement in the values of plasma parameters as compared with those of RF methane discharges. An initially single electron population splits in the negative-going part of the pulse, where the hot group achieves 10 eV. The ion and electron densities have the same order of magnitude ($2\text{-}4\cdot10^{10}$ cm^{-3}) and their maxima do not match within the pulse, although they appear with a constant delay.

3) Well-adhered, low-stressed 1-μm-thick a-C:H films with diamond-like properties (DLC) were deposited at room temperature by PECVD at growth rates up to 60 nm/min in pulsed-DC methane discharges at 10 Pa and operated at pulse frequencies between 100 and 200 kHz. Another variable was the amplitude of peak voltage, which ranged from -400 to -1400 V.

4) XRR arises as an exhaustive structural characterisation technique for DLC films. The data concerning mass density points to the growth of more compact films as the ion bombardment energy increases. Morphological and tribological characterization on surface by AFM also highlights the tuning effect of the high energy plasma on roughness and nanofriction coefficient of DLC.

5) The diamond-like character of the a-C:H films has been manifested by both Raman and FTIR spectroscopies. Moreover, the high hardness (24 GPa), low compressive stress (1-1.5 GPa), low friction coefficient (~ 0.05), high critical load (> 20 N) and low wear rate (~ $5\cdot10^{-16}$ $m^3m^{-1}N^{-1}$) achieved by these DLC films constitute mechanical properties adequate for their performance as protective coatings.

6) The pulsed-DC technique with asymmetric bipolar waveform is an advanced technology for the PECVD of DLC films, and provides an alternative to conventional RF-PECVD. The dependence of film properties on pulse parameters permits the optimization of the DLC characteristics with a view to specific mechanical applications.

7) Multilayer W/a-C coatings with regular bilayer structure have been prepared at room temperature by sequential RF magnetron sputtering using graphite and W targets, in either continuous wave or square-wave modulated mode. The sequential orientation of the sample-holder through a stepper motor, which is communicated to a PC interface, permitted the deposition of stacks of up to 30 bilayers with period below 5 nm.

8) TEM and XRR analyses accounted for the formation of multilayered structures with sharp interfaces and a well-defined period. The first technique is time-consuming due to the procedure of sample preparation for cross-section views, while the second one also reveals the regular modulation of alternating phases and provides the multilayer period from diffractogram analysis.

9) The characterisation of W/a-C structures indicates the following improvements in the mechanical properties with respect to a-C single layers: lowering of the compressive stress, better adherence to the substrate, and increase in hardness and elastic modulus. These results open the possibility of using the W/a-C structures as protective coatings. The multilayer films studied may also find applications in soft X-ray reflecting systems.

10) Films of metal containing DLC (Me-DLC) have been produced by reactive magnetron sputtering using pulsed-DC power from different metal targets (Mo, Nb, Ti, W) and RF bias using different gas mixtures of methane and argon. The properties of the films have been changed from metallic behaviour to a DLC one by varying the methane flow rate from 0 to 25%. The Me-DLC films are generally uniform in composition.

11) The structure of Me-DLC films changes with metal and its content, as verified by TEM analysis. W- and Nb-DLC show typically a columnar growth, Ti-DLC is spontaneously structured in multilayers and Mo-DLC has a granular pattern. Cross-section HRTEM

images reveal that Me-DLC structures are nanocomposite-like, consisting on a distribution of nanocrystallites embedded in an amorphous matrix.

12) SAED and XRD scans account for the formation of metal carbide (MoC, NbC, TiC, WC_{1-x}) nanocrystallites in the Me-DLC samples. Their density and size (up to 6 nm) show a decrease when carbon is abundant, owing to a progressive predomination of amorphous DLC in C-rich samples. From the analysis of UV-visible and IR spectroscopic ellipsometry, it can be seen that the optical properties of the films are switched in a wide range from a metallic behaviour to a DLC one. The activation energy of DC electric conductivity constitutes another parameter for the metallic character.

13) For each metal forming a Me-DLC structure, RMS surface roughness is of the order of the nanocrystal size and reaches a maximum at intermediate compositions. The maximum of contact angle is around 80º and decreases smoothly at higher metal contents. SECPM images reveal a non-homogeneous metal distribution on the surface, variable with composition.

14) The adhesion of Me-DLC to the substrate has been improved due to a reduction in compressive stress (< 0.1 GPa for W-DLC). Friction coefficient (< 0.03) is lower than the corresponding to PECVD DLC, and critical load overcomes 20 N. Hardness is comprised between 8 and 22 GPa, which is lower than the value of DLC (24 GPa). In conclusion, Me-DLC films are suitable for hard coating applications requiring low stress, low roughness, moderate hydrophobicity and low friction coefficient. Their tuneable electric properties can also make them attractive for electric devices applications (antifuses).