Low friction a-SiC coatings deposited by microwave PACVD: from plasma characterization to materials and mechanicals properties

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Plasma CVD is commonly used for the growth of thin films as it offers the possibility to grow materials at medium temperature. However, the knowledge of the basic processes involved in the process is rather limited, particularly when a complex precursor, such as Tetramethylsilane (TMS), is used. Our studies are thus focused on the establishment of correlations between the process parameters and film microstructure and properties. In this paper, hard amorphous hydrogenated SiC materials are deposited as thin films for tribological applications in a microwave plasma-activated CVD reactor (microwave-PACVD). The initial gas-mixture is composed of Argon/TMS (TMS = Si(CH3). Using a two-levels factorial Design Of Experiment (DOE), three main process parameters were found to be determining at the process control. They strongly influence both the film composition and mechanical properties (hardness, elastic modulus, friction coefficient versus steel). These parameters are : i) the distance (d') between the precursor injection and the substrate surface, this parameter is of major importance as it controls the residence time in the plasma flow hence the nature of the chemical species that impinge on the growing surface; ii) the substrate temperature and iii) the TMS percentage in the argon / TMS mixture. Large variations of the film properties and composition are observed according to these parameters: $0.45 < Si/C < 1$; $18 < H$ %at. < 30 ; $8 <$ Hardness (H) < 23 (GPa) ; $60 <$ elastic modulus (E) < 185 (GPa) ; $0.08 <$ friction coefficient (μ) < 0.4.

In order to improve our insight into the deposition mechanism of the film, optical emission spectroscopy (OES) was carried out to identify the nature of the gaseous species produced in the reactive plasma. The changes versus (d') of the relative amounts of emitting species such as H, Si+, H2, CH, C2, SiH and SiC2 highlight competitions in the plasma flow between decomposition of the precursor and recombination of the produced species. The increase of the emitting intensities of Si+, H and CH species as a function of (d') up to 40-50 mm, is explained by the dissociation of the input precursor along the plasma through direct collisions with electrons. As the maximum intensity of the C2 species is observed at a higher (d') value than that of CH species, it may be concluded that TMS dissociation produces CHx radicals that combine to form C2Hy species. For increasing residence times, the increase of the emitting intensity of SiC2 (Si-C-C) species and the correlative decrease of the intensity of CH, SiH, Si+, C2 species reveal the presence of complex products (SiC2Hy) formed by recombination of simpler ones (CHx, SiHx and C2Hy). The comparison between the emission of SiH and CH similar bands shows that hydrogen is mainly carried to the growing surface by (CHx) species rather than silicon species ([SiHy] << [CHx]). Finally, H2 is partly formed from H atoms recombination in the plasma flow.

These in-situ measurements are not sufficient to establish a sequential mechanism due to the complexity of the Argon/TMS plasma, but some obvious relationships between the C, Si and H bearing molecules can be observed and correlated with the main features of the growing film :

- the presence in the gas phase of species including C-C and Si-C bonds (CxHy and SiC2Hy) is in agreement with the C-C and Si-C bonds detected in the films from XPS C1s peak analysis (variable rates of C-Csp2, C-Csp3 (CHn) and C-Si (ordered and disordered) are distinguished), and FTIR analysis (Si-CHn and CHn groups are pointed out)
- the incorporation of Si-Si or Si-H bonds into the film is low due to limited amounts of Si+ and SiH species in the plasma (probably low [Si2Hy])
- hydrogen amount in the film decreases as (d') increases due to H recombination into H2 in the plasma flow.

From a mechanical point of view, it appears that hydrogen and (CCsp3 + SiC) contents in the film modify the film hardness in opposite ways: high hydrogen contents are responsible for low hardness values, and high (CCsp3 + SiC) contents promote high hardness values. Tribological properties seem to be mainly related to the bond ratio %[C-H] / %[C-C] in the film.

A friction coefficient as low as 0.06 has been obtained at a wear rate close to 6.10-6 mm3/N.m (versus steel at a Hertz pressure equal to 500 MPa in room atmosphere).