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Amorphous silicon carbide coatings grown by low frequency PACVD: Structural and mechanical description

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Abstract

Hard coatings have received considerable attention for many mechanical applications, such as aeronautics, space and high precision mechanics. Material properties, like high hardness, low friction and low wear versus metals, are required for this purpose. Diamondlike carbon films (a-C:H, DLCs) fulfill these requirements. Nevertheless, they are limited in use as their microstructure is strongly changed at high temperature. Doping DLCs with elements such as silicon (up to 30 at.%) should extend their applications to high temperature environments ($T > 675$ K). In this work, hard silicon carbide based films (a-Si:C:H) grown from tetramethylsilane/argon plasma are presented. Such coatings are obtained in a capacitively coupled low frequency ($\nu = 50$ kHz) PACVD device, at surface temperature ranging from 623 to 853 K. The evolution of their microstructure, observed by Infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS) and EDS is described in regard to variations of i) surface reactivity, through substrate temperature, ii) nature of plasma species through gas residence time and TMS content, iii) energy of ions impinging the growing film through surface DC bias. As generally observed, an increase of surface temperature leads to an improvement of film crosslinking (Si–C content increase, H content decrease) as an increase of gas residence time in the reactor leads, through recombinations of gaseous species in the discharge, to a reduction of bonded hydrogen and silicon contents in the deposits. Finally, the energy of impinging ions during growth is of major importance as it limits films growth rate through selective sputtering phenomena. Comparisons between characterizations of films grown at various DC bias in Ar/TMS mixture, and films post-treated in argon plasma without precursor, lead to the fact that an ion energy domain exists which limits silicon and C–Csp^2 contents to the benefit of C–Csp^3 (XPS) and sp^3CH_2 (FTIR) environments. Determination of hardness (H) and Young modulus (E) of those films by nanoindentation technique, shows that exploiting ion bombardment can significantly improve hardness (from 20 to 30 GPa). Corresponding ion energies lead to an improvement of the ratio H^3/E^2, giving rise to low friction coefficients against steel (μ # 0.15).

Keywords: PACVD; Tetramethylsilane; Silicon carbide; Hardness; Friction

1. Introduction

Hard coatings are of interest for many mechanical applications. To attain such functionalities, diamondlike carbon films (DLCs) have been extensively developed during the last ten years. They potentially find application in aeronautics, space and high precision mechanics, but seem to be limited in use as their microstructure, hence tribological and mechanical properties, are strongly changed at high temperature (> 675 K) [1]. In recent years, the effect of doping DLCs with elements such as Si (up to 30 at.%), N, Ti [2] has been studied by several authors. Silicon would be supposed to extend applications to higher temperatures. In this work, amorphous hydrogenated silicon carbide based films (a-Si:C:H) have been prepared by low frequency PACVD of tetramethylsilane ($TMS = Si(CH_3)_4$). They are found to be candidates for mechanical applications, as they can reach a hardness close to 30 GPa and a friction coefficient lower than 0.2 against steel. Those characteristics depend on the growth process, as their composition and microstructure strongly vary ($0.6 < Si/C < 1.5$).

Even if PACVD techniques are commonly employed for a-Si:C:H growth, the plasma chemistry and growth mechanisms

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are not fully apprehended. To get a better knowledge of these phenomena, in the case of low frequency (50 kHz) plasma, a set of coatings has been elaborated, with varying deposition parameters. The selected experimental parameters permit to draw the influence of major factors. On one hand, the role of plasma neutral species, responsible for growth of the films, on the chemical composition of these latter, has been studied by varying gas residence time in the deposition area, and precursor rate in the total gas flow. On the other hand, varying the substrate temperature allows to modify surface reactivity, and explore its influence on the microstructure of films. Moreover, the control of DC bias imposed to the substrate settles the energy of impinging species on the growing surface: argon ions, attracted by the potential difference existing between the plasma and the substrate, hit the surface and cause structure modifications in the material. This set of coatings is analyzed in terms of its chemical bond content by FTIR and XPS, and EDS atomic composition measurement. These analyses are connected to the mechanical and tribological behaviors (nanoindentation, alternative friction).

2. Experimental

2.1. Plasma reactor and deposition procedure

The experimental set-up is described elsewhere [3]. The low frequency generator provided 50 kHz during deposition. Deposition total pressure was set to 93 Pa (0.7 Torr), and kept constant by use of a capacitive gauge connected to an automatic butterfly valve.

The other parameters were varied, in order to explore effects explained above. Hence, the substrate temperature was either 623, 773 or 853 K. The substrate is independently heated so that its temperature can be maintained constant. The total gas flow rate in the reactor, regulated by flowmeters, was varied as to settle gas residence time to either 0.8 or 3 s. The TMS flow rate represented 3% or 12% of the total gas flow rate (%TMS). At last, the negative DC bias was varied from 50 to 300 V. Thick coatings (0.5 to 10 μm, depending on the deposition factors) were elaborated on 38CD4 steel substrates. Thinner films (150 nm) were grown with the same operating conditions, on crystalline (100) silicon substrates, to permit FTIR analysis.

2.2. Material characterization

The microstructure of films was studied using Energy Dispersive Spectroscopy (EDS), Fourier Transform InfraRed Spectroscopy (FTIR) and X-ray Photoelectron Spectroscopy (XPS). The devices used are described elsewhere [4], as well as nanoindentation set-up utilized for hardness and Young modulus measurements. In addition, friction characterization was performed by means of a microscratch-tester CSEM under constant load, to obtain alternate friction coefficients (μ) against steel (100C6 antagonist 6 mm in diameter, normal load = 3 N, track length 5 mm at 10 mm/min, total friction length = 15 m in dry air).

3. Results and discussion

An overview of the results of material analysis on the cited coatings is presented, from which several trends are drawn. Substrate temperature, plasma gas residence time and precursor rate (TMS) effects on the deposited material are considered in regard to the DC bias, thus the energy of impinging ions on the surface of the deposits. Indeed, the surface ratio between the electrodes (substrate holder/grounded inner wall of the reactor) is low enough to allow high ion energies (high DC bias). Ion bombardment can then become prominent over the other studied deposition parameters. A competition may exist between growth mechanisms and etching/sputtering phenomena, which has been highlighted under certain plasma conditions, as described below.

As a general manner, whatever the experimental conditions, FTIR and XPS reveal the complexity of film microstructure. The assignment of absorption bands observed on FTIR spectra of the deposited a-Si:C:H films appears elsewhere [4]. One can observe a broad contribution of Si–C bonds around 760 cm^{-1}, the band corresponding to Si–H bonds around 2100 cm^{-1}, and a large one corresponding to C–H bonding in the 2800–3000 cm^{-1} area. Being broad, this last absorption band contains several contributions due to sp^2 and sp^3 of carbon bonded to hydrogen in CH_2 and CH_3 groups. Another contribution can also be observed around 1000 cm^{-1}, attributed both to Si–CH_3 (970 cm^{-1}) and Si–$(CH_2)_n$–Si (998 cm^{-1}) environments. Si–CH_x presence is confirmed by XPS analysis where a peak located close to 16 eV (C_{2s}) is observed on valence bands. Moreover, C_{1s} core level peak is large, denoting various carbon bondings. It is then decomposed into five contributions [3]: C–Csp^2 at 284.4 eV, [C–Csp^3 + C–H] (structurally bonded and/or contamination) at 285 eV, ordered C(Si_4) at 282.5 eV and disordered C–Si at 283.5 eV to characterize an amorphous form of C–Si bonding. A shoulder corresponding to C–O bonds is observed at 286 eV.

3.1. Influence of substrate temperature

Whatever the other experimental parameters, an increase of the growth temperature (T_S) evidently leads to a better structuration of the material. Indeed, one observes a decrease of Si–H and C–H FTIR contributions with T_S increase: the diminution of hydrogen content favors the formation of Si–C bonds in spite of Si–C–C environments, as revealed by the increase of the absorption band at 765 cm^{-1} relatively to the Si–$(CH_2)_n$–Si (1000 cm^{-1}) and Si–CH_3 (975 cm^{-1}) ones. Corresponding Si/C ratios are then enhanced.

3.2. Influence of plasma neutral species

The effect of the nature of plasma species which react with the growing film has been studied by use of variations of the residence time τ of the gas mixture in the discharge, with substrate temperature and TMS rate respectively fixed to 623 K and 3%. Fig. 1 shows its effect versus DC bias (V_{dc}). An