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Thermo-Oxidative Stability of SiO_x-doped Diamondlike Carbon Studied via Environmental XPS and AFM

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A broad array of carbon-based thin films, such as diamond, diamond-like carbon (DLC), and others, have been developed over the last several years [1]. These materials exhibit high strength and stiffness, low friction and wear, tolerance to withstand harsh physical and chemical conditions, and can form smooth, continuous, conformal coatings. This has resulted in their use in a wide range of applications. However, the strong environmental dependence of the tribological properties of DLC coatings limits their widespread use. For example, hydrogenated amorphous carbon (a-C:H) rapidly degrades above 150°C due to evolution of hydrogen followed by conversion of C from sp^3- to sp^2-hybridization [2, 3]. Thus, several variants of DLC have been developed. Among these, silicon oxide-doped DLC (SiO_x-DLC) is of interest as it exhibits very good tribological properties across a range of environments [4]. SiO_x-DLCs are fully amorphous coatings supposedly consisting of two interpenetrating, interbonded networks, one being a hydrogenated amorphous carbon network and the other a silica glass (SiO_x) network [5]. SiO_x-DLC are thus attractive candidates as advanced solid lubricants, including as candidates for next-generation hard-disk storage devices, which require superior thermal stability [6].

This work aims to understand the origins of the superior thermal stability of SiO_x-DLC, and to determine the decomposition pathway, and the influence of the environment on the degradation kinetics. Furthermore, the temperature dependence of the tribological properties of SiO_x-DLC is being investigated. The experimental methodology takes advantage of an advanced surface science apparatus [7], which includes an environmental X-ray photoelectron spectrometer (E-XPS) able to acquire XPS spectra at pressures up to 0.4 Torr while heating the sample *in situ* up to 1000°C. XPS and X-ray induced Auger electron spectroscopy (XAES) were performed to determine surface composition, oxidation state, and the carbon hybridization state of the near-surface region of the films. High-resolution XPS and XAES spectra of SiO_x-DLC suggested that the amorphous carbon and silica networks in the material are interbonded to a small extent. Furthermore, silicon is present in different oxidation states (from +1 to +4). Angle-resolved XPS (AR-XPS) analysis indicated compositional uniformity as a function of depth.

Molecular dynamics (MD) simulations were performed using the ReaxFF potential to visualize the atomic structure of SiO_x-DLC (Figure 1). The composition was matched to experiments, and the resulting structures relaxed to the measured density (1.75 g/cm^3). The simulations show that SiO_x-DLC is composed of a single, amorphous phase with neither phase segregation nor gaps or pores.

To assess the thermal stability of SiO_x-DLC, heating experiments were carried out inside the XPS chamber under high vacuum conditions. Changes in the surface chemistry could be then accessed *in situ,* thus avoiding drawbacks associated with exposing the specimen to air. XPS characterization showed a slight, progressive increase in the relative concentration of silicon with higher oxidation states (+3 and +4) with the annealing temperature (Figure 1a and 1c). The XPS data indicated a small decrease in the carbon concentration and an increase in the oxygen concentration upon heating (Figure 1d). The vacuum results were compared with the results obtained under aerobic conditions. In this case, a much

larger increase in the relative concentration of silicon in high oxidation states was detected in SiO_x-DLC (Figure 1b and 1c), suggesting the formation of a silicon oxide layer.

Subsequent *ex situ* atomic force microscopy (AFM) measurements investigated sample morphology and nanoscale tribological properties. No change in surface topography occurred after annealing up to 450°C both under vacuum and aerobic conditions. Compared to as-received samples, a slight increase in adhesion and friction forces measured for positive loads was observed in the case of the vacuum-annealed sample. This might be due to the higher hydrophilicity of its surface induced by surface reactions with water. The air-annealed sample showed a slight increase in adhesion and a decrease in friction forces measured for positive loads. This may be due to the formation of a hydrophobic silicon dioxide layer. We also see that thermal AFM probes are able to locally degrade the films at the nanometer scale.

These new insights into the surface phenomena occurring for SiO_x-DLC exposed to elevated temperatures and in the presence of different gas environments provide guidance for designing modified solid lubricants able to meet the ever-increasing performance requirements of advanced applications.

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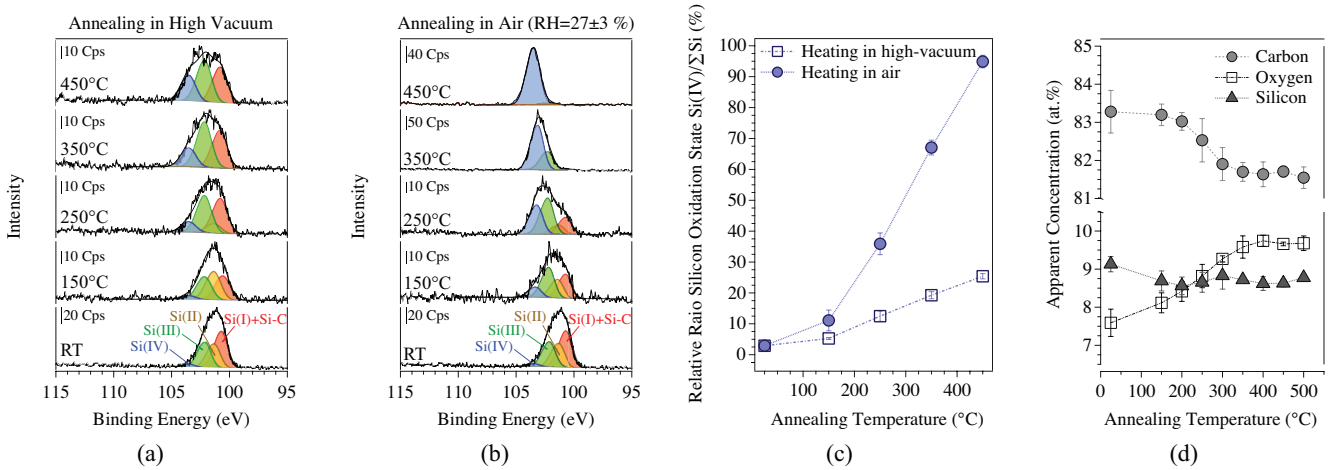

Figure 1. XPS Si 2p spectra (the Si $2p_{3/2}$ and Si $2p_{1/2}$ contributions were summed up into a single envelope corresponding to a certain oxidation state) acquired after annealing for 1 hr at different temperatures under high vacuum conditions (a) or in aerobic conditions (relative humidity: 27±3 %) (b); (c) relative concentration of silicon in oxidation state +4 as a function of the annealing temperature; (d) apparent composition of SiO_x-DLC as a function of the annealing temperature under high vacuum conditions.

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