



# Origin of temperature-induced low friction of sputtered Si-containing amorphous carbon coatings

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**Abstract**—This work reports on a tribological study of magnetron-sputtered silicon-containing amorphous carbon thin films vs. their alumina counterparts. Temperature cycling during ball-on-disk tests in humid air revealed a decrease in the coefficient of friction from 0.3 to <0.02 beyond  $240 \pm 15$  °C. Systematic variation of the environment confirmed oxygen to be responsible for the low friction. X-ray photoelectron spectroscopy of the wear tracks indicates oxidation of Si–C bonds and formation of Si–O–C bonds, followed by further oxidation to SiO<sub>2</sub> above 450 °C. Ab initio molecular dynamics simulations of gas interactions with the a-C surface revealed dissociation of O<sub>2</sub> and the formation of oxides. Additional density functional theory calculations of Si incorporation into a graphene layer, resembling the surface of the film, showed preferential attraction of gaseous species (H, O, –OH, H<sub>2</sub>O), to Si-sites as compared to C-sites. Hence, the temperature- and atmosphere-induced changes in friction coefficient can be understood based on correlative X-ray photoelectron spectroscopy and ab initio data: the formation of Si–O–C bonds stemming from a reaction of the as-deposited coating with atmosphere in the tribological contact is observed by theory and experiment.

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## 1. Introduction

The chemical processes occurring in a tribological system strongly affect its performance, characterized by friction and wear. It is well known that the tribological performance of a system critically depends on the testing parameters and surrounding environmental conditions. For diamond-like carbon (DLC, in particular amorphous hydrogenated carbon (a-C:H)) thin films, a phenomenon known as super-low friction (i.e. coefficient of friction (COF) <0.01) at room temperature (RT) in vacuum or inert environments has been reported [1–3]. Under such ideal conditions, the covalent bonds of the film are saturated by hydrogen, and thus—combined with the inert environment—the film surface is efficiently separated from the counterpart [4–6]. This resembles an example of low friction without external lubrication by minimization of the adhesive wear component. However, in reactive

environments (i.e. containing oxygen or moisture), the C–H bonds deteriorate, leading to increased COF values [7–10]. In contrast, solid lubrication of non-hydrogenated carbon is a consequence of graphitization of the disordered matrix by sp<sup>3</sup>–sp<sup>2</sup> transition [11–16] under thermal or mechanical loads, followed by shearing of the weakly  $\pi$ -bonded graphite planes. A surface freshly generated in a tribological contact will be covered by surrounding reactive species within a few nanoseconds, hence leading to saturation of the free “dangling” carbon bonds [8]. This saturation thus strongly depends on the environmental conditions, since these highly reactive bonds are forced to react with surrounding species (O, –OH, H<sub>2</sub>O), in competition with C–C sp<sup>2</sup> bond formation (i.e. graphitization) [17–19]. This explains the decreased performance of carbon films at elevated temperatures, where oxidation and decomposition make their applications difficult [15,20,21]. To enhance the thermal stability of DLC materials, silicon was reported to be a promising candidate, because it promotes stabilization of the disordered carbon structure by forming strong, thermally stable Si–C sp<sup>3</sup> interlinks [22]. This was confirmed by several studies investigating

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structural ( $sp^3$ – $sp^2$  transition) and mechanical changes during thermal annealing [23–25]. Besides this structure stabilization, Si addition affects the film surface chemistry, in particular the surface energy [26], and consequently tribological characteristics [27,28]. Previously published experimental findings [29] showed that less than 5 at.% Si [30] added to hydrogen-free ( $H < 2$  at.%) amorphous carbon thin films significantly improves their tribological properties at temperatures above 200 °C. Here, the Si-induced changes in friction coefficient are investigated as the temperature and the atmosphere is varied by correlative chemical analysis of the wear tracks, and modeling of the resulting surface chemistry. The obtained results can be seen as a basis for establishing a deeper understanding of temperature-induced gas molecule dissociation and adatom formation on solid surfaces. Further, with respect to Si-doped DLC surfaces they illustrate the resulting beneficial effect on their tribological properties at elevated temperatures, where hydrogen is no longer able to passivate and thus protect the surface accurately.

## 2. Experimental and theoretical details

### 2.1. Experimental details

#### 2.1.1. Coating deposition

Coatings were deposited on AISI M2 high-speed steel disks (DIN 1.3343), using a Teer UDP-650 closed field unbalanced magnetron sputtering device (as illustrated in Ref. [31]). This device's chamber has four rectangular magnetrons, 145 × 345 mm in size, where two pyrolytic carbon, one chromium (purity 99.5%) and one silicon (purity 99.999%) targets were mounted. The carousel enabled one axis substrate rotation with a speed between 5 and 10 rpm where the substrates face the each target in turn. The steel disks were quenched and tempered to a hardness of  $64 \pm 1$  HRC and ground to a surface roughness of  $R_a = 0.06 \mu\text{m}$ . Prior to deposition, all substrates were cleaned in acetone in an ultrasonic bath for 15 min. After removal from the acetone, the samples were dried with a hot air dryer. The substrates were mounted on a pre-cleaned substrate holder and fixed on the carousel in the deposition chamber. The chamber was pumped down to an initial pressure of  $< 0.004$  Pa. Argon was then admitted to the chamber to a pressure of 0.1–0.2 Pa. In a preliminary step, plasma etching at  $-400$  V pulsed bias was used to further clean the substrate surfaces, using an Ar plasma with all targets operating. Coating synthesis was started at a pressure between 0.1 and 0.2 Pa with a Cr interlayer to improve the coating adhesion, followed by a gradient layer from 100% Cr to 100% of the final elemental composition, which was deposited with an applied substrate bias between  $-40$  and  $-80$  V. No substrate heating was applied; the substrate temperatures during deposition were below 200 °C. Then, using the same conditions, a-C:Si top layers with a thickness of about  $2 \mu\text{m}$  were grown. The growth rate of the top layer was  $400$ – $550 \text{ nm h}^{-1}$ , depending on the current set for the Si target to achieve Si contents between 0 and 5 at.%.

#### 2.1.2. Tribology

The tribological tests (temperature cycling and gas variation) of the DLC coatings were performed using a CSM

Instruments ball-on-disk (BOD) tribometer against  $\text{Al}_2\text{O}_3$  balls with 6 mm diameter keeping the normal load of 10 N, the sliding speed of  $10 \text{ cm s}^{-1}$  and the wear track radius of 9 mm constant. Temperature cycling between 180 and 350 °C was done over a sliding distance of 22500 laps (636 m) by manually switching the heater on and off. For the gas variation tests, a cover was mounted on the tribometer to allow for a systematic variation of the gas environment at constant temperature of 250 °C over 22500 laps (636 m) in the following sequence: (1) synthetic air (80%  $\text{N}_2$ , 20%  $\text{O}_2$ , relative humidity RH  $< 1\%$ ); (2) humid air (RH  $25 \pm 5\%$ ); (3) dry nitrogen (RH  $< 1\%$ ); and (4) dry argon (RH  $< 1\%$ ). To provide sufficient temperature and gas homogenization, the tests were started after a heating/gas rinsing period of 60 min. Wear tracks for XPS analysis were generated by ball-on-disk tests in humid air (RH  $25 \pm 5\%$ ) at (1) RT (sliding distance 5000 laps, corresponding to 141 m), (2) 300 °C (sliding distance 5000 laps) and (3) 500 °C (sliding distance 250 laps, corresponding to 7 m) against  $\text{Al}_2\text{O}_3$  balls with a normal load of 10 N and a sliding speed of  $10 \text{ cm s}^{-1}$ .

#### 2.1.3. Surface chemistry

Bonding states within the carbon matrix as well as element quantification were identified by means of X-ray photoelectron spectroscopy (XPS) in an Omicron Nanotechnology Multiprobe system with a monochromized Al  $K\alpha$  beam (1486.7 eV) with a step size of 0.02 eV and a resolution  $< 0.5$  eV. No heating or  $\text{Ar}^+$  sputter cleaning of the surface was conducted prior to measurement in order to identify the original surface chemistry, after exposure to air at elevated temperatures. When measuring strongly oxidized coating surfaces, a charge correction was applied to balance the shift of binding energies due to electric charging.

### 2.2. Theoretical methods

#### 2.2.1. Ab initio molecular dynamics simulations of surface chemistry

DLC surfaces with and without Si interacting with  $\text{O}_2$  and  $\text{H}_2\text{O}$  were probed by ab initio molecular dynamics (MD) simulations using the OpenMX code [32], based on the density functional theory [33] and basis functions in the form of a linear combination of localized pseudoatomic orbitals [34]. The electronic potentials were fully relativistic with partial core corrections [35,36] and the generalized gradient approximation was employed [37]. The basis functions were generated by a confinement scheme [34,38] and specified in the following manner: C4.5-s2p1, Si6.0-s2p1d1, H4.5-s2 and O4.5-s2p1. C, Si, H and O designate the chemical name, followed by the cutoff radius (Bohr radius units) and the last symbols define the primitive orbitals. The energy cutoff of 150Ry and the  $75 \times 75 \times 295$  grid within the real space grid technique [39] were adjusted to achieve an accuracy of  $10^{-6}$  Ha/atom ( $1 \text{ Ha} = 2 \text{ Ry} = 4.359 \times 10^{-18} \text{ J}$ ). All ab initio MD analysis was carried out using the ASAP code [40]. Amorphous DLC cells optimized in a previous work [29] with 128 atoms were used to form the DLC surfaces within a slab configuration with a vacuum layer thickness of 20 Å. Canonical ensembles at 300 and 600 K were employed to simulate the DLC surface interactions (surface area approximately  $99 \text{ \AA}^2$ ) with: (i) 1  $\text{O}_2$  molecule, (ii) 3  $\text{O}_2$  molecules (only for pure DLC at

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