Gas desorption during friction of amorphous carbon films

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Abstract. Gas desorption induced by friction of solids, i.e. tribodesorption, is one of the numerous physical and chemical phenomena, which arise during friction as result of thermal and structural activation of material in a friction zone. Tribodesorption of carbon oxides, hydrocarbons, and water vapours may lead to significant deterioration of ultra high vacuum conditions in modern technological equipment in electronic, optoelectronic industries. Therefore, knowledge of tribodesorption is crucial for the performance and lifetime of vacuum tribosystems. Diamond-like carbon (DLC) coatings are interesting materials for vacuum tribological systems due to their high wear resistance and low friction. Highly hydrogenated amorphous carbon (a-C:H) films are known to exhibit extremely low friction coefficient under high vacuum or inert environment, known as “superlubricity” or “superlow friction”. However, the superlow friction period is not always stable and then tends to spontaneous transition to high friction. It is supposed that hydrogen supply from the bulk to the surface is crucial for establishing and maintaining superlow friction. Thus, tribodesorption can serve also as a new technique to determine the role of gases in superlow friction mechanisms. Desorption of various a-C:H films, deposited by PECVD, ion-beam deposition and deposition using diode system, has been studied by means of ultra-high vacuum tribometer equipped with a mass spectrometer. It was found that in superlow friction period desorption rate was below the detection limit in the 0-85 mass range. However, transition from superlow friction to high friction was accompanied by desorption of various gases, mainly of H₂ and CH₄. During friction transition, surfaces were heavily damaged. In experiments with DLC films with low hydrogen content tribodesorption was significant during the whole experiment, while low friction was not observed. From estimation of maximum surface temperature during sliding contact it was found that temperature rise during friction is short-term and not significant. The number of desorbed molecules due to frictional heating was calculated.

1. Introduction
DLC (diamond-like carbon) contain numerous forms of amorphous carbon, mainly, in the form of coatings obtained by methods of physical or chemical vapor deposition. DLC can be divided into four categories by Robertson’s classification [1]: a-C – amorphous carbon, a-C:H – amorphous hydrogenated carbon with a predominance of sp² bonds (like graphite) and ta-C – tetragonal...
amorphous carbon, ta-C:H – hydrogenated tetragonal amorphous carbon with a predominance of sp\(^3\) bonds (like diamond).

DLC have found their application due to their combination of superior properties: low friction coefficient, extremely low wear rate, great hardness, high thermal conductivity, chemical inertness, high stiffness, etc. These applications includes: diamond loudspeakers, diamond X-ray windows, diamond bonders, diamond cutting tools, and heads for magnetic disks coated with diamond-like carbon.

Desorption of gases from tribological coatings is almost inevitable source of deterioration of ultra high vacuum and pollution of the system with inadmissible gases like carbon oxides and hydrocarbons. The properties of the DLC films are strongly dependent on the deposition process and its parameters. Especially, hydrogen content is critical for friction behavior of DLC [2]. It is supposed that hydrogen supply from the bulk to the surface is crucial for establishing and maintaining superlow friction. Tribodesorption can serve as a new technique to determine the role of gases in superlow friction mechanisms.

### 2. Experimental

The hydrogenated diamond-like carbon films were deposited onto silicon substrates by using different methods of deposition and its parameters. In this study, two a-C:H films deposited by PECVD method from acetylene were tested. The difference between films was various substrate biases used during deposition process: -800 V and -500 V. By varying biases different hydrogen contents and bonds were obtained. The detailed deposition conditions [3] and the friction tests with previous results [2] have been described elsewhere [2,3]. Some properties of these films deduced from forward recoil elastic scattering, \(^{13}\)C nuclear magnetic resonance spectroscopy, Fourier transform infrared and ellipsometry investigations [3,4] are presented in table 1.

|                           | AC8  | AC5  |
|---------------------------|------|------|
| dc bias during deposition (V) | -800 | -500 |
| Hydrogen content (at\%)   | 34   | 40   |
| Relative fraction of hydrogen bonded to carbon | 0.57 | 0.73 |
| Quaternary C sp\(^2\) (%) | 61   | 54   |
| Quaternary C sp\(^3\) (%) | 2    | 2    |
| Index of refraction       | 2.15 | 1.83 |

Friction tests have been performed using UHV tribometer (10\(^{-10}\) mbar) with type of the contact pin-on-flat, reciprocating motion with length 4 mm, sliding speeds 0.5-2 mm/s. Gas desorption during friction was measured by quadrupole mass-spectrometer which was situated in the vacuum chamber near the contact area.

### 3. Results and discussion

The results of the experiment for the sample AC8 are presented in the figure 1. Conditions of this experiment was the following: velocity of the friction – 2 mm/s; length of the trace – 4 mm; normal force – 3 N; time of one friction cycle – 4 s; time between two scans of mass-spectrometer – 10.8 s. For the sample AC5 there was no visible gas desorption during friction.
We can see pressure rise on the graphics with partial pressure in torr when there is no longer super low friction period, while during super low friction there is no visible change of pressure observed. The mass-spectrometer was working in the mass range 0-85, but for this film pressure has increased.
until mass number \(m/e = 16\). The most significant pressure raise was observed for the mass number \(m/e = 15\) (more than one order of the value).

Maximum surface temperature during sliding contact was estimated using approximate solution of Tian and Kennedy [5]. Special mechanical and thermal properties for a-C:H film are taken from [6,7]. The values of maximum surface temperatures are: for superlow friction period – \(1.6 \times 10^{-4}\) K; for high friction period – \(2.7 \times 10^{-2}\) K. Temperature rise during friction is short-term and not significant.

Calculation of the number of desorbed molecules due to frictional heating was performed. For hydrogen this number is equal 0.2 molecule for superlow friction period and 3.4 molecule for high friction period. The values for activation energy for desorption (88 kJ/mole) and for surface density of adsorbed molecules in a monolayer \((1.57 \times 10^{15} \text{ m}^{-2})\) used in calculations are taken for hydrogen on a C(001)-(1×1) surface from [8].

Because of very small temperature rise, the number of desorbed molecules due to frictional heating is not significant.

4. Conclusions
The superlow friction period of DLC films is not always stable and then tends to spontaneous transition to high friction. During super-low friction period there was no visible gas desorption while when we loose super-low friction different gases desorbe from the surface. Thus, tribodesorption can serve as a new technique to determine the role of gases in superlow friction mechanisms.

It was shown, that gas desorption has strong correlation with friction period. Thus, tribodesorption can be used as a method for diagnostics of the failure of mechanism using control of the pressure.

From flash temperature estimation it was found that surface temperature rise during sliding contact is very small, therefore the number of desorbed molecules due to frictional heating obtained in the calculation is not significant. Thus, we can conclude that there are some different desorption mechanisms of athermic nature, which can be related with the structural modification of the material in friction zone.

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