SUPPLEMENTARY INFORMATION FOR THE PAPER

# Environmental influence on the surface chemistry of ionic-liquid-mediated lubrication in a silica / silicon tribopair

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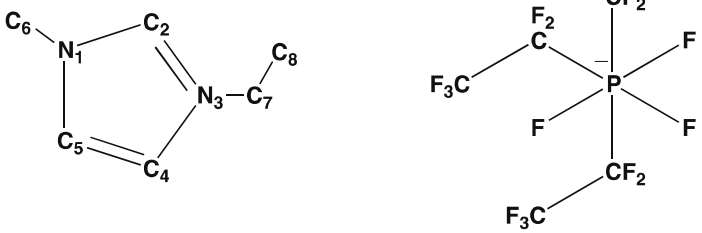
The peak-**fitting** parameters for the high-resolution XP-spectra of tribostressed samples are reported in Tables S1-S2. A list of the binding energies of the compounds considered for the chemical-state analysis of the tribostressed wafer is reported in Table S3. Three replicas of a tribological test carried out in the presence of humid air with [HMIM] FAP as a lubricant, applying a load of 0.5 N are reported in Figure S1. Replicas of the tribological tests carried out applying a load of 4.5 N are reported in Figure S2, S3, S4, and S5. The survey and high-resolution spectra of tribostressed silicon disks lubricated with [EMIM] FAP, applying a load of 4.5 N, are reported in Figures S6-S8. Optical and scanning electron micrographs of tribostressed disks lubricated with [EMIM] FAP are reported in Figures S9 and S10.

**Ionic Liquids used in the present study:**

[EMIM] FAP




[HMIM] FAP

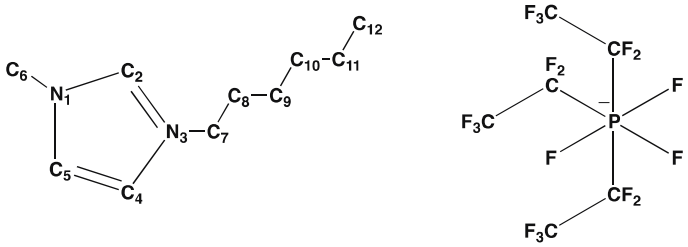


**Table S1:** Peak-fitting parameters for the XP-spectra of silicon samples tribostressed with [EMIM] FAP or [HMIM] FAP ionic liquids in the presence of a nitrogen atmosphere. Normal load: 4.5 N, sliding speed: 50 mm/min, number of cycles: 200, radius: 3.2 mm. The uncertainty in the binding energies (BE) and in the full widths at half-maximum (FWHM) is 0.2 eV.

| | | ***Line shape*** | ***Contact area*** | | ***Non-contact area*** | |
|---|---|---|---|---|---|---|
| | | | ***BE (eV)*** | ***FWHM (eV)*** | ***BE (eV)*** | ***FWHM (eV)*** |
| C1s* | $SiC_xO_y$ | GL(30) | 283.8 | 1.4 | - | - |
| | *C-C* | GL(30) | 285.0 | 1.4 | 285.0 | 1.4 |
| | *C-O* | GL(30) | 286.3 | 1.4 | 286.3 | 1.4 |
| | *C=O* | GL(30) | 287.6 | 1.4 | 286.6 | 1.4 |
| N1s | $SiN_xO_y$ | GL(30) | 398.2 | 1.8 | - | - |
| F1s | *F-Si* | GL(30) | 686.8 | 1.8 | - | - |
| | $SiO_xF_y$ | GL(30) | 687.9 | 1.8 | 687.9 | 1.7 |
| O1s | *O-Si* | GL(50) | 532.9 | 1.9 | 533.1 | 1.7 |
| $Si2p_{3/2}$** | $Si^0$ | LA(1.5,1.8,65) | 99.3 | 0.6 | 99.3 | 0.6 |
| | $Si^+$ | GL(30) | 100.3 | 0.9 | 100.3 | 0.9 |
| | $Si^{2+}$ | GL(30) | 101.2 | 0.9 | 101.2 | 0.9 |
| | $Si^{3+}$ | GL(30) | 101.8 | 0.9 | 101.8 | 0.9 |
| | $Si^{4+}$ | GL(30) | 103.2 | 1.8 | 103.6 | 1.5 |

*The position of the C-O and COOX components are constrained at a distance of +1.3 and +1.6 eV from the C-C signal. The FWHM of the C1s components is constrained at 1.4 eV.

** The position of the components having intermediate oxidation states are constrained according to Seah et al. [1]

**Table S2:** Peak-fitting parameters for the XP-spectra of silicon samples tribostressed with [EMIM] FAP or [HMIM] FAP ionic liquids in the presence of a humid air (45% - 55% RH). Normal load: 4.5 N, sliding speed: 50 mm/min, number of cycles: 200, radius: 3.2 mm. The uncertainty of the binding energies (BE) and of the full widths at half-maximum (FWHM) is 0.2 eV.

| | | ***Line shape*** | ***Contact area*** | | ***Non contact area*** | |
|---|---|---|---|---|---|---|
| | | | ***BE (eV)*** | ***FWHM (eV)*** | ***BE (eV)*** | ***FWHM (eV)*** |
| C1s | $SiC_xO_y$ | GL(30) | 284.0 | 1.4 | - | - |
| | *C-C* | GL(30) | 285.0 | 1.4 | 285.0 | 1.4 |
| | *C-O* | GL(30) | 286.3 | 1.4 | 286.3 | 1.4 |
| | *C=O* | GL(30) | 287.6 | 1.4 | 286.6 | 1.4 |
| N1s | $SiN_xO_y$ | GL(30) | - | - | - | - |
| F1s | *F-Si* | GL(30) | 686.8 | 1.8 | - | - |
| | $SiO_xF_y$ | GL(30) | 687.9 | 1.8 | 687.9 | 1.8 |
| O1s | *O-Si* | GL(50) | 533.1 | 2.0 | 533.1 | 1.7 |
| $Si2p_{3/2}$ | $Si^0$ | LA(1.5,1.8,65) | 93.0 | 0.6 | 93.0 | 0.6 |
| | $Si^+$ | GL(30) | 100.3 | 0.9 | 100.3 | 0.9 |
| | $Si^{2+}$ | GL(30) | 101.2 | 0.9 | 101.2 | 0.9 |
| | $Si^{3+}$ | GL(30) | 101.8 | 0.9 | 101.8 | 0.9 |
| | $Si^{4+}$ | GL(30) | 103.6 | 1.8 | 103.6 | 1.5 |

*The positions of the C-O and COOX components are constrained at a distance of +1.3 and +1.6 eV from the C-C signal. The FWHM of the C1s components is constrained at 1.4 eV.

** The position of the components having intermediate oxidation states is constrained according to Seah et al. [1]

**Table S3:** Binding energies of the compounds considered for the chemical-state analysis of the tribostressed silicon disks.

| | ***Chemical state*** | ***Binding energy (eV)*** |
|---|---|---|
| Si2p | Silicon [2] | 99.3 |
| | Silicon carbide [3] | 100.2 |
| | Silicon oxycarbide [3] | 100.6-101.4 |
| | $SiO_x$ ($Si^{+1}$) [1] | 100.3 |
| | $SiO_x$ ($Si^{+2}$) [1] | 101.2 |
| | $SiO_x$ ($Si^{+3}$) [1] | 101.8 |
| | $SiO_x$ ($Si^{4+}$) [1] | 102.6 – 104.1 |
| | Si-F ($Si^{+1}$) [4] | 100.3 – 100.5 |
| | S-F ($Si^{+2}$) [4] | 101.3 – 100.8 |
| | Si-F ($Si^{+3}$) [4] | 102.4 – 102.8 |
| C1s | Silicon carbide [5] | 283.0 |
| | Silicon oxycarbide [3] | 283.6 |
| | Graphitic [6] | 284.4 |
| | Organic bonded to Si [7] | 283.9 |
| | Aliphatic [8] | 285.0 |
| | Carbon bound to oxygen [8] | 286.1-286.6 |
| | | 287.8 |
| N1s | Silicon oxynitride [9] | 398.3 |
| F1s | Silicon oxyfluoride [10] | 686.4 |
| | Si-F [10] | 687.8 – 688.0 |

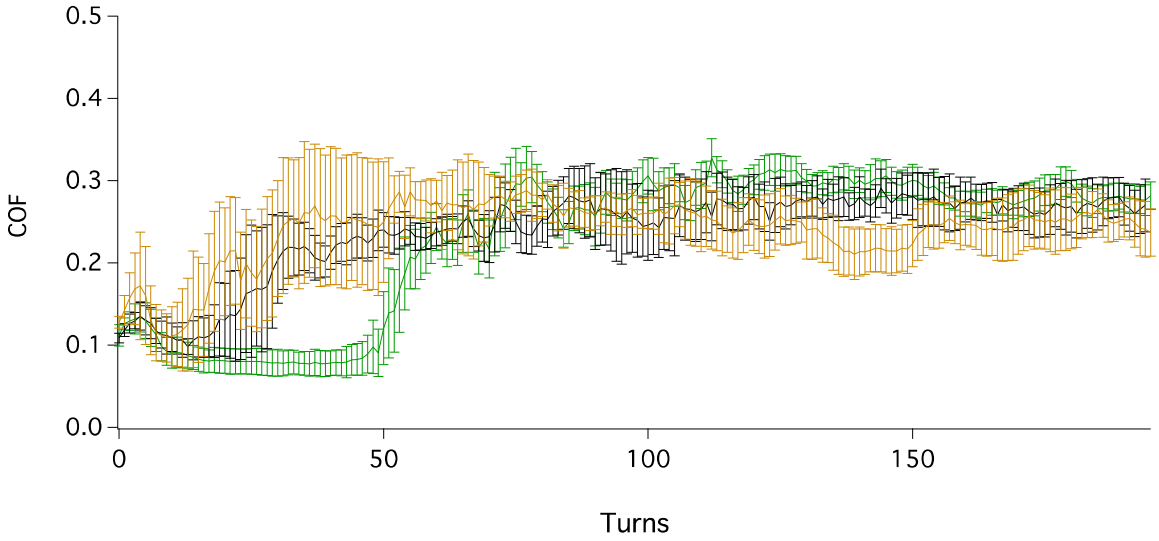



**Figure S1**: Coefficient of friction versus number of cycles (sliding time) during three tribological tests (normal load: 0.5 N sliding speed: 50 mm/min, radius: 3.2 mm) carried out in the presence of [HMIM] FAP at room temperature (296 ± 2 K) and humid air (45% - 55% RH). Error bars express the standard deviation of friction data over a single cycle.

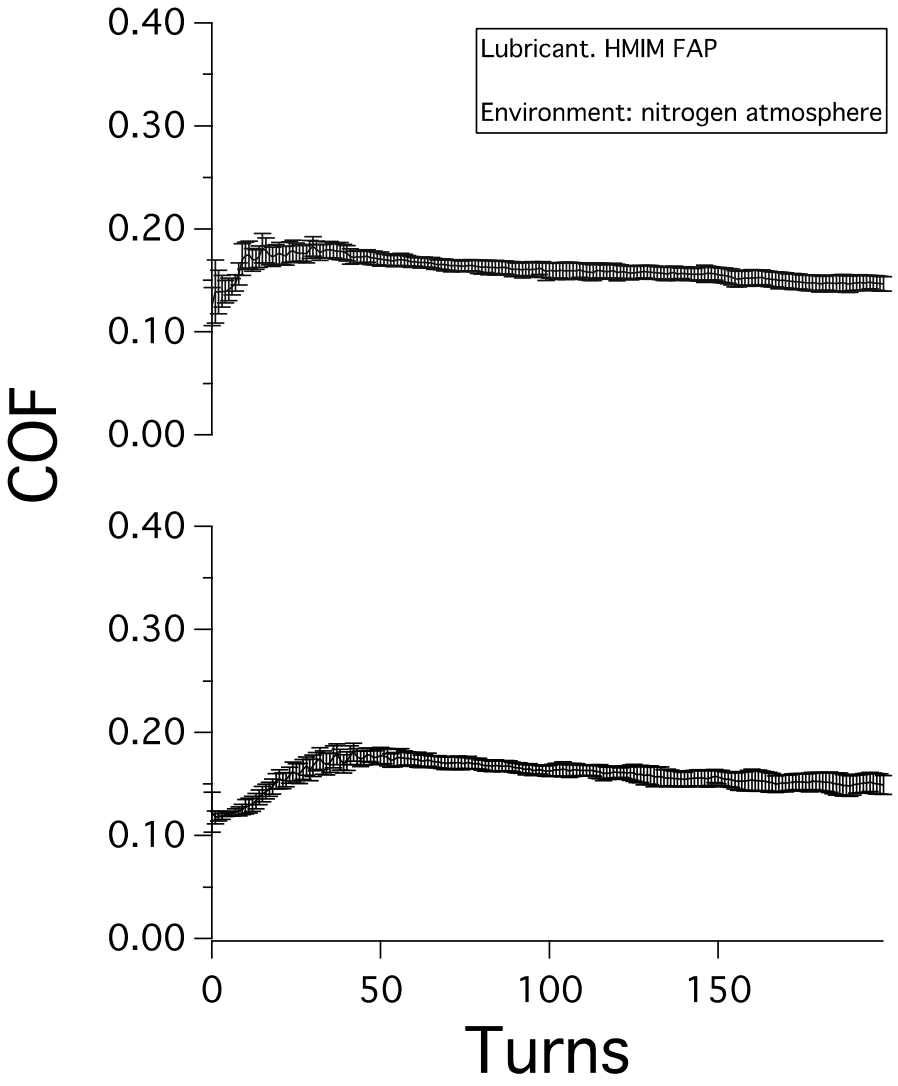



**Figure S2**: Coefficient of friction versus number of cycles (sliding time) during two tribological tests (normal load: 0.5 N sliding speed: 50 mm/min, radius: 3.2 mm) carried out in the presence of [HMIM] FAP at room temperature (296 ± 2 K) and under nitrogen. Error bars express the standard deviation of friction data over a single cycle.

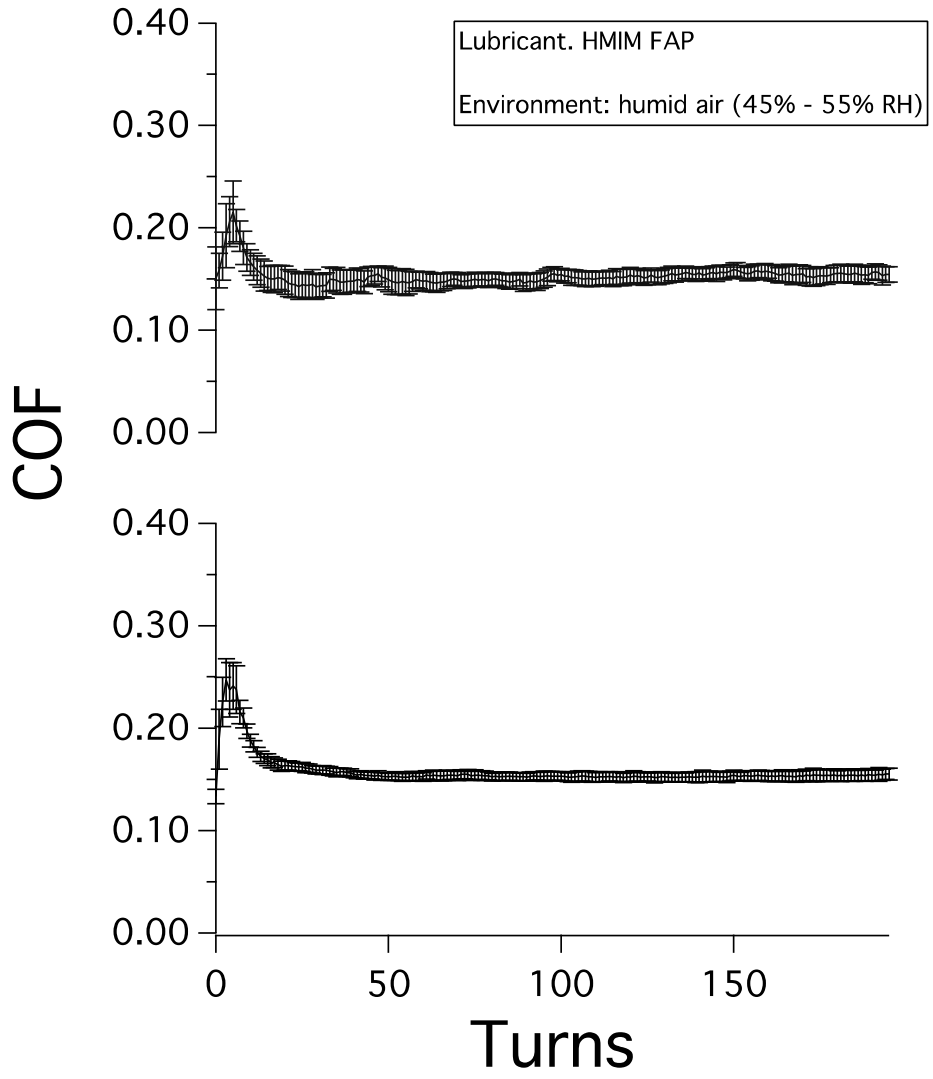



**Figure S3**: Coefficient of friction versus number of cycles (sliding time) during two tribological tests (normal load: 0.5 N sliding speed: 50 mm/min, radius: 3.2 mm) carried out in the presence of [HMIM] FAP at room temperature (296 ± 2 K) and humid air (45% - 55% RH). Error bars express the standard deviation of friction data over a single cycle.

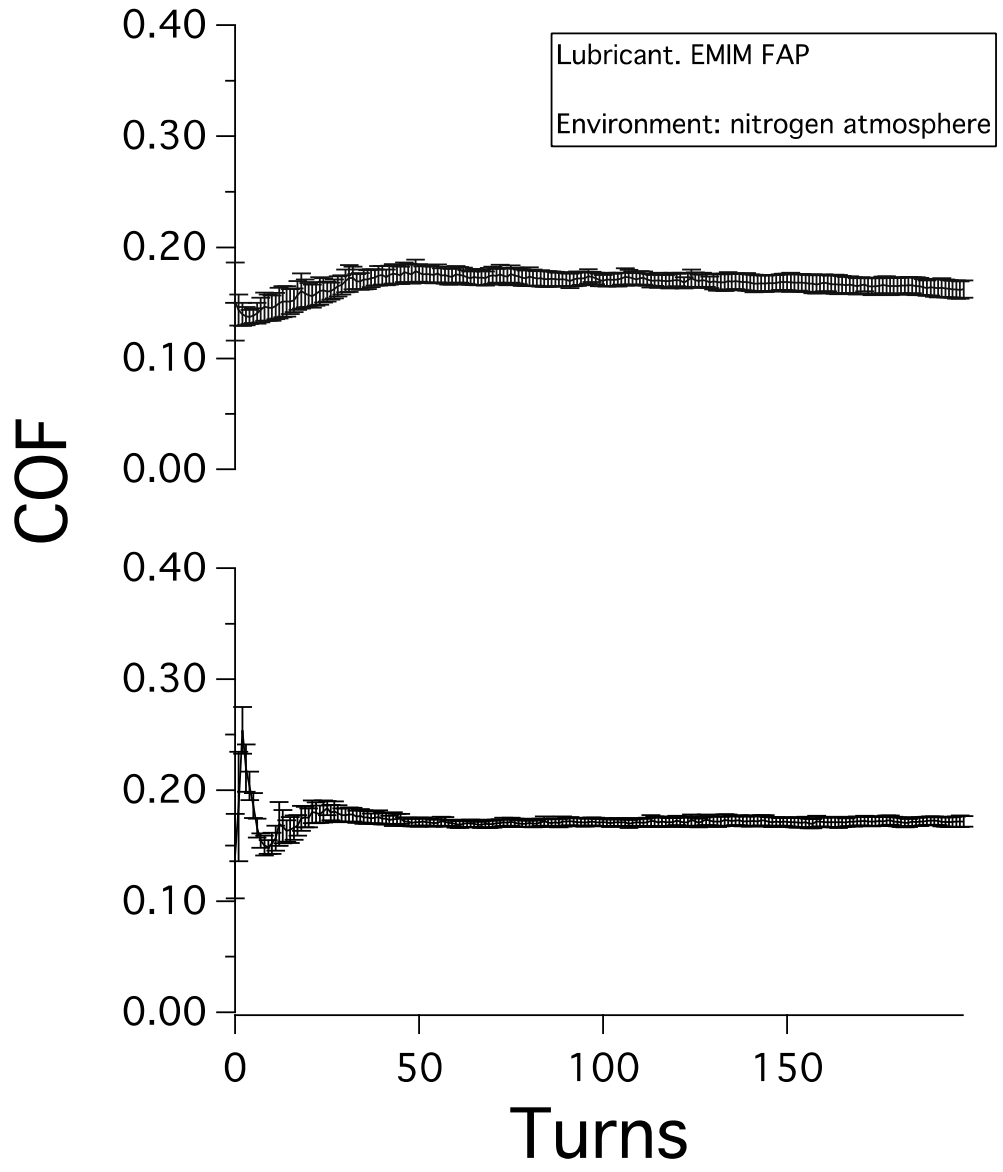



**Figure S4**: Coefficient of friction versus number of cycles (sliding time) during two tribological tests (normal load: 0.5 N sliding speed: 50 mm/min, radius: 3.2 mm) carried out in the presence of [EMIM] FAP at room temperature (296 ± 2 K) and under nitrogen. Error bars express the standard deviation of friction data over a single cycle.

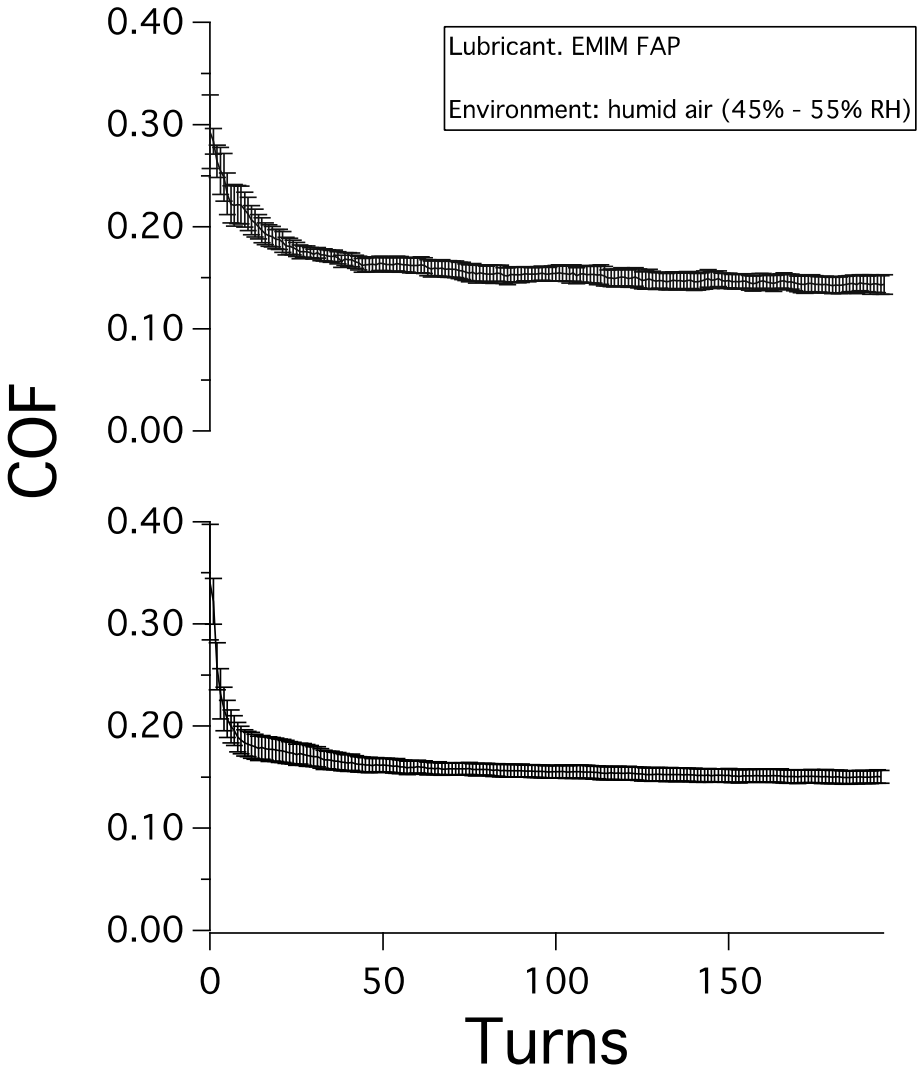



**Figure S5**: Coefficient of friction versus number of cycles (sliding time) during two tribological tests (normal load: 0.5 N sliding speed: 50 mm/min, radius: 3.2 mm) carried out in the presence of [EMIM] FAP at room temperature (296 ± 2 K) and humid air (45% - 55% RH). Error bars express the standard deviation of friction data over a single cycle.

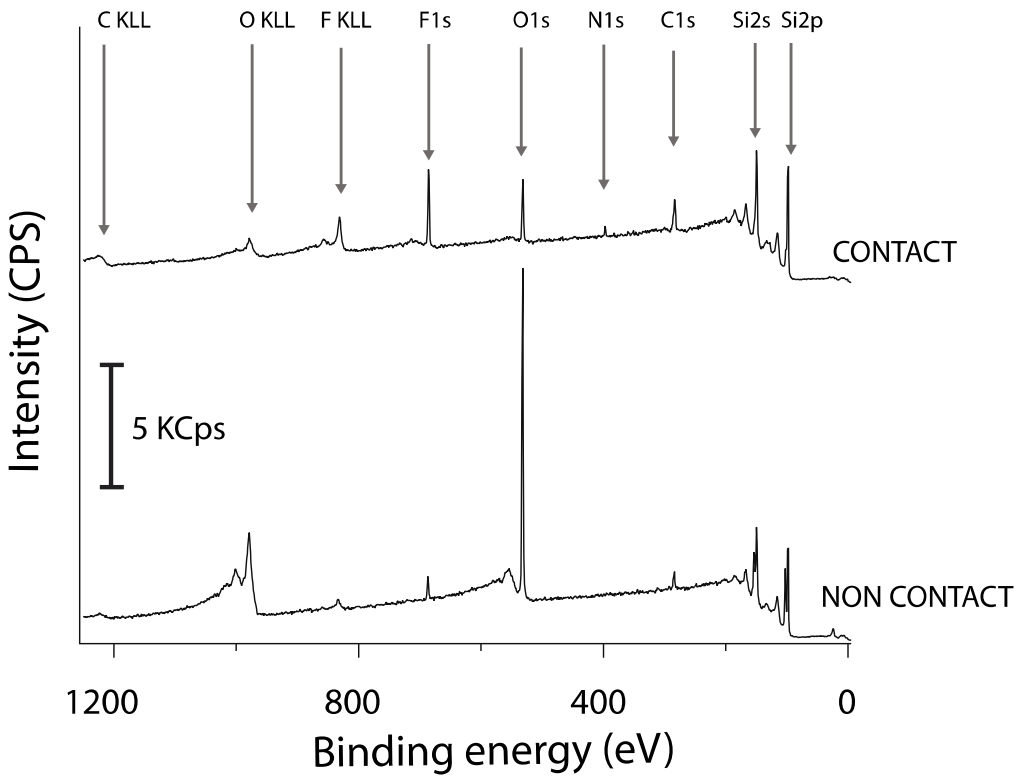



**Figure S6:** Survey XP-spectra of a silicon disk lubricated with [EMIM] FAP under a nitrogen atmosphere. Normal load: 4.5 N, sliding speed: 50 mm/min, number of cycles: 200, radius: 3.2 mm.

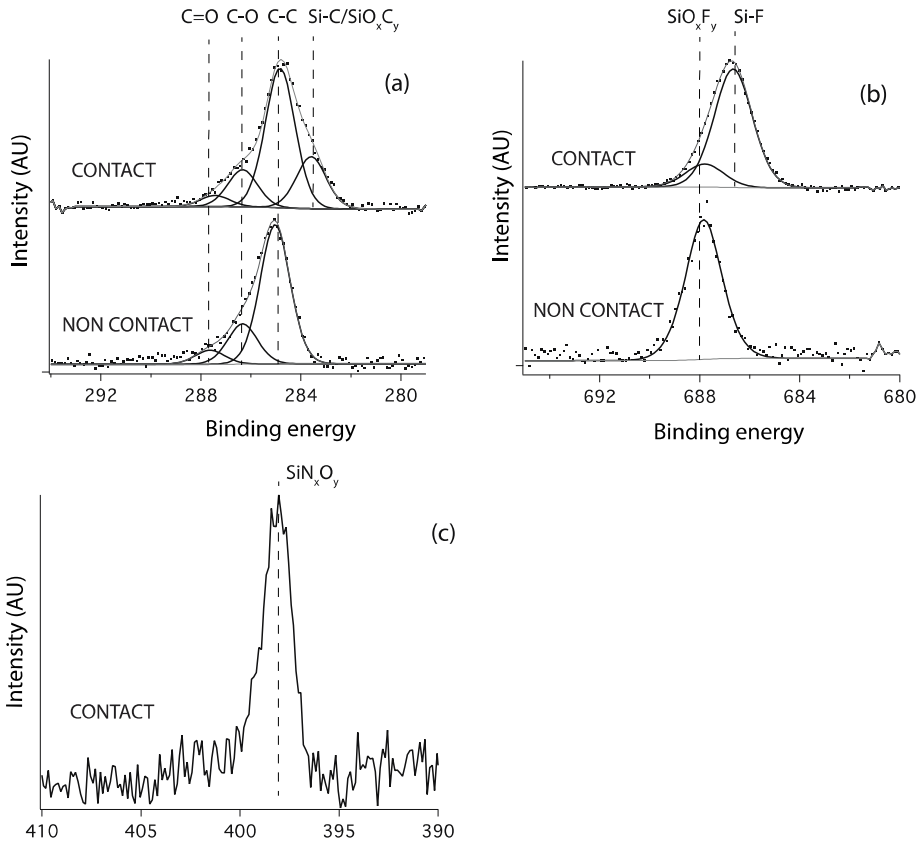



**Figure S7:** C1s (a), F1s (b) and N1s (c) regions of the XP- spectra of a silicon disk lubricated with [EMIM] FAP in the presence of a nitrogen atmosphere. Normal load: 4.5 N, sliding speed: 50 mm/min, number of cycles: 200, radius: 3.2 mm.

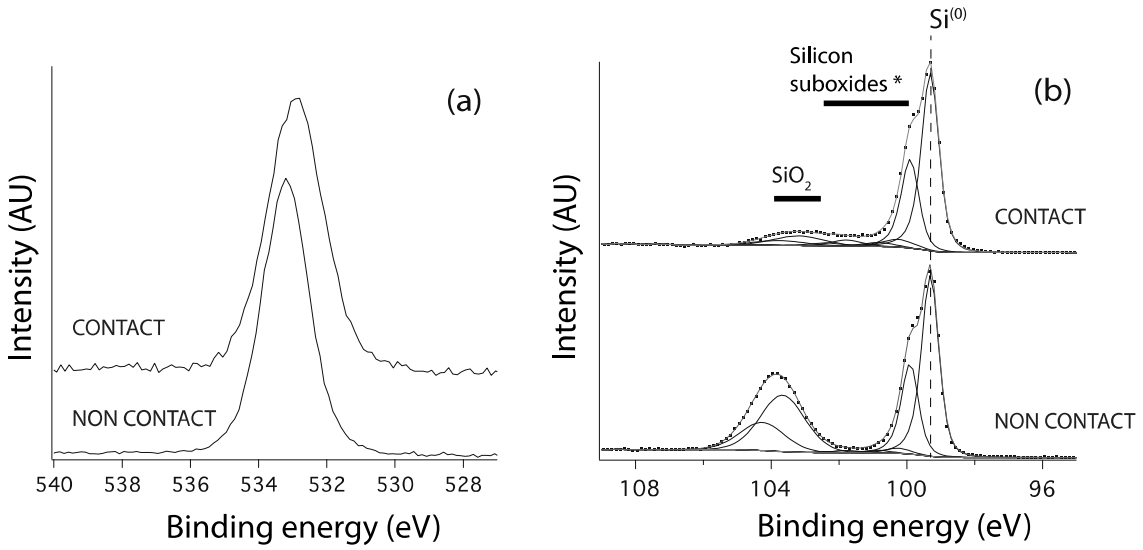



**Figure S8:** O1s (a) and Si2p (b) XP-spectra of a silicon disk lubricated with [EMIM] FAP in the presence of a nitrogen atmosphere. Each Si signal is fitted with two components due to spin-orbit coupling ($2p_{3/2}$ and $2p_{1/2}$). The region labeled as "Silicon suboxides" could also contain contributions from $SiO_xF_y$, $SiC_xO_y$, $SiN_xO_y$. Normal load: 4.5 N sliding speed: 50 mm/min, Normal load: 4.5 N, sliding speed: 50 mm/min, number of cycles: 200, radius: 3.2 mm.

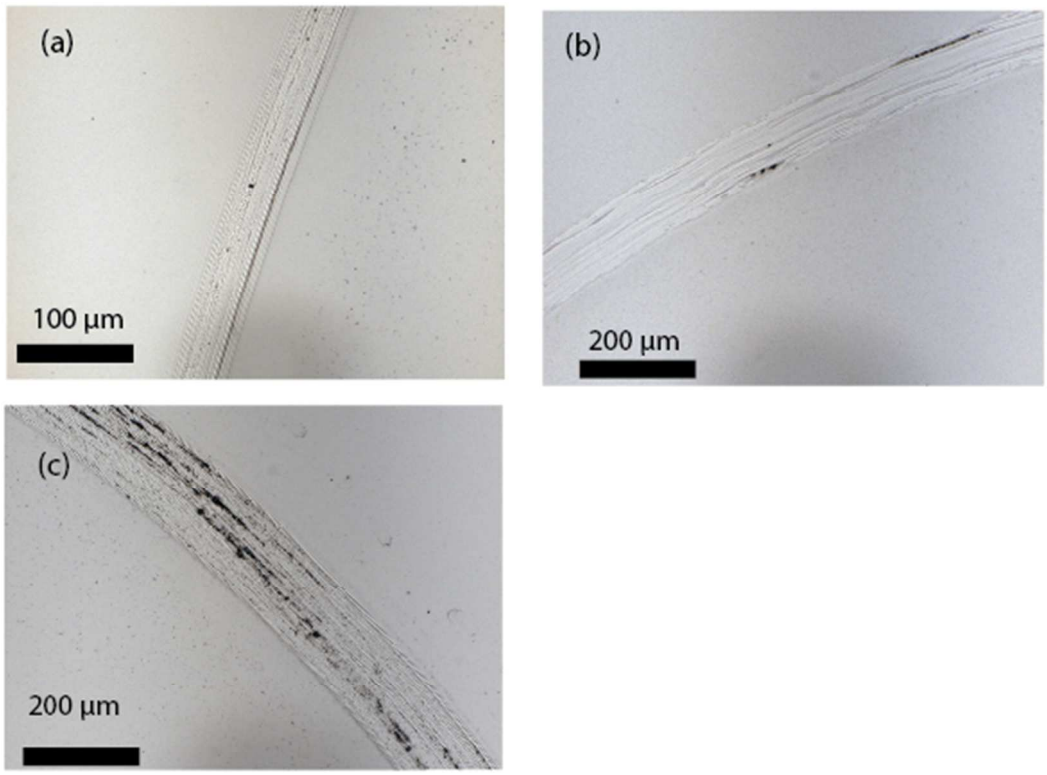



**Figure S9:** Optical micrographs of the contact area of silicon wafers lubricated with [EMIM] FAP; (a) normal load: 0.5 N, environment: humid air (45%-55% RH); (b) normal load: 4.5 N, environment: nitrogen atmosphere; (c) normal load: 4.5 N, environment: humid air (45%-55% RH). All the tests were performed at a sliding speed of 50 mm/min and a duration of 200 cycles (radius: 3.2 mm)

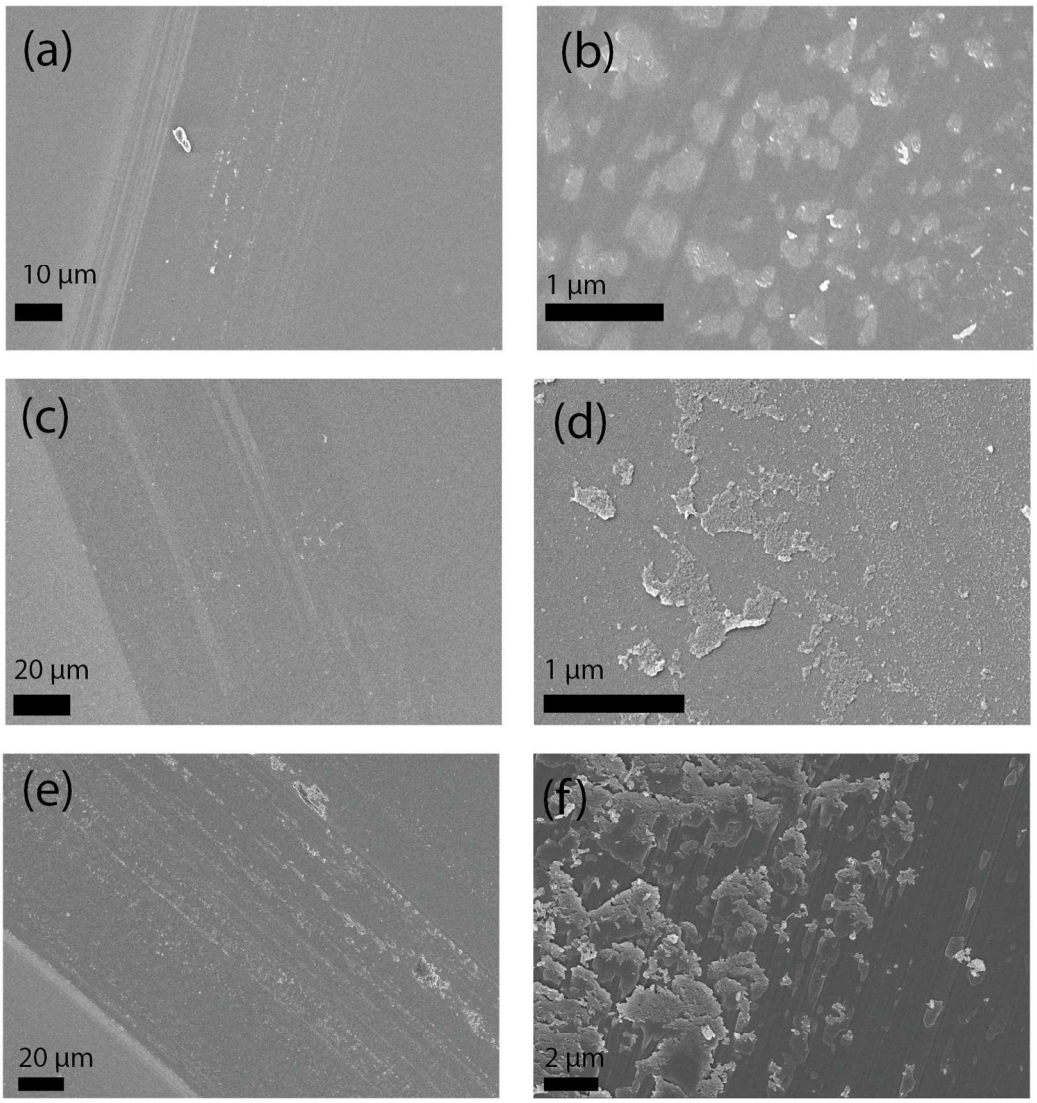



**Figure S10:** SEM images of the contact area of silicon wafers lubricated with [EMIM] FAP; (a) and (b) normal load: 0.5 N, environment: humid air (45%-55% RH); (c) and (d) normal load: 4.5 N, environment: nitrogen atmosphere; (e) and (f) normal load: 4.5 N, environment: humid air (45%-55% RH). All the tests were performed at a sliding speed of 50 mm/min and for a duration of 200 cycles (radius: 3.2 mm).

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