

Nanotribology of self-assembled monolayers coated on nanostructured materials – Influence of the chain length and the substrate orientation on the frictional behaviour

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Abstract

Micro/nanotribological study of self assembled monolayers (SAMs) derived from *n*-alkyltrichlorosilanes deposited on silicon wafers (100) and (111) has been conducted using a ball-on-disc nanotribometer. The influence of the alkyl chain length, the effect of the substrate crystallographic orientation and its roughness, at various sliding velocities and total sliding distances, on the SAMs tribological performances have been analyzed. Experimental results show that frictional behavior is affected by the chain length but also by the crystallographic orientation of the substrate. A lubricating effect occurs with chain containing more than 8 carbons atoms ($C > 8$) whereas a seizure phenomenon is detected for $C \leq 8$. In the lubrication domain ($C > 8$), friction coefficient is quite independent on the sliding velocity beyond 5 mm.s^{-1} whereas it is velocity-dependent below this value. Results also show that both substrate crystallographic orientation and substrate nanostructure have a great influence on the SAM behavior and more particularly on the seizure resistance. This crystallography-induced anisotropy in friction and wear reported previously for bare silicon still occurs in presence of SAMs whatever the roughness of the substrate.

Keywords: Self-assembled monolayers; Alkylsilanes; Chain length; Nanotribology; MEMS/NEMS.

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1. INTRODUCTION

The rise of nanotechnology has paved the way towards miniaturization of many electronic and mechanical components. At this scale, the surface-to-volume ratio is so large that adhesive and friction forces generally dominate gravitation and inertia [1].

Micromanipulation of micro-mechanical devices (MEMS) requires an accurate control of surfaces interactions in order to adjust adhesion and friction. Hence, self-assembled monolayers (SAMs) are currently used for improving functional surface properties (adsorption, condensation, wetting, lubrication, friction and adhesion) [2]. Due to a better adhesion to the substrates, *n*-alkanethiols are usually deposited on gold substrates whereas *n*-alkyltrichlorosilanes are well suitable on glass or silicon surfaces as met in MEMS devices.

Currently, grafted octadecyltrichlorosilane (OTS) or perfluoroalkyl SAMs allow to obtain good results in terms of friction, adhesion and wear on smooth surfaces [3, 4, 5]. Besides, results carried out with *n*-alkanethiols and *n*-alkyltrichlorosilanes generally reveal that the friction coefficient decreases with increasing *n* – *i.e.*, the chain length [6]. However, these

results are generally carried out without any consideration about the substrate characteristics – as for instance, the surface roughness and/or the crystallographic orientation of the substrate – whereas these latter are known to have a great influence on the capillary effects, and on the seizure occurrence, respectively.

Hence, due to the thin thickness of SAMs coatings, effects of the chain length on the tribological behavior have to be studied in connection with the nanostructure and the crystallographic orientation of the substrates in order to control the transition between the nanostructure's effect of the substrate and the chemical's effect of SAMs.

In this work, the tribological behavior of *n*-alkyltrichlorosilane monolayer films deposited by immersion on silicon substrates is studied by varying respectively: (i) the alkyl chain length, (ii) the sliding parameters (sliding velocity, sliding distance and normal load), and (iii) the roughness and the crystallographic orientation of the silicon substrates – Si (100) and Si(111).

2. EXPERIMENTAL PART

2.1. Nanotribological setup

The experimental device is constituted by a ball-on-disc *nanotribometer* manufactured by *CSM Instruments (Switzerland)*. A pin (Si_3N_4 , Ø 4mm) is mounted on a stiff lever, designed as a frictionless force transducer ($K_x = 295 \text{ Nm}^{-1}$; $K_z = 155.6 \text{ Nm}^{-1}$). The friction force is determined during the test by measuring the deflection of the elastic arm (low load range down to $50 \mu\text{N}$). The ball is loaded onto a flat sample with a precisely known force using closed loop. The load and friction resolutions are about $1 \mu\text{N}$. In this work, tribological tests are carried out in linear reciprocating mode at room temperature (22°C) under ambient air (RH 35%). Normal load (F_N) varies from 10 to 130 mN corresponding to a maximum Hertzian pressures ranging from 0.15 to 0.48 GPa. The sliding speed (v) ranges from $50 \mu\text{m}\cdot\text{s}^{-1}$ to $20 \text{ mm}\cdot\text{s}^{-1}$ to change the frictional dissipated energy in a large range. The amplitude of the sliding length is about 1 mm whether a total distance (d_t) of 0.2 m (corresponding to 100 cycles).

Table 1: Mechanical properties of the samples.

	Substrate		Ball Si_3N_4
	Si(100)	Si(111)	
E (GPa)	129	187	310
v	0.28	0.36	0.22
Roughness (nm) (smooth/rough)	0.311/692	0.244/683	

2.2. Materials

2.2.1 Substrates

Four types of silicon samples (n-type material grown by CZ process and p-doped) were used. They display two different crystallographic orientations and two different nanostructures. Nanostructure is changed by varying the wafer's roughness (**Table 1**). As shown in **Table 1**, a crystallography-induced anisotropy is clearly observed in the mechanical properties of Si (100) and Si (111).

2.2.2 SAM thin coatings

Alkyltrichlorosilanes ($\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$), with $n = 5, 7, 9, 11, 17$, are used to synthesize the SAMs displaying various chain lengths. Characteristics are compiled in **Table 2**. C6 are provided by Aldrich, and C8 to C18 by Alfa Aesar, respectively. Molecules were used without further purification.

2.3. Preparation of SAMs on Silicon wafers

Before immersion in the monomer solution, silicon wafers were, firstly, ultrasonic cleaned in a detergent (GP 17.40 SUP), acetone and ethanol for 5 minutes.

Secondly, they were submitted to an oxygen plasma treatment at 100 W power for 5 minutes, with a flow rate of oxygen of 50 L/h and a processing pressure of 0.4 mbar. Such treatment leads to form a thin silicon oxide film on the surface which facilitates the SAM adhesion on the substrate. Finally, *n*-alkyltrichlorosilane monolayers were grafted by immersing the cleaned substrates in a 25 mM solution of silane in toluene (99.5%, anhydrous) for 20 min. Then the functionalized substrates were rinsed with toluene, absolute ethanol (99.9%) and distilled water to eliminate any possible physically absorbed impurities.

Table 2: Alkylsilane informations.

	Chemical Structure	Purity	Measured contact angles
n-Octadecyltrichlorosilane (C18)	$\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$	95 %	$104.9 \pm 2^\circ$
n-Dodecyltrichlorosilane (C12)	$\text{CH}_3(\text{CH}_2)_{11}\text{SiCl}_3$	96 %	$104.7 \pm 2.4^\circ$
n-Decyltrichlorosilane (C10)	$\text{CH}_3(\text{CH}_2)_9\text{SiCl}_3$	97 %	$103.1 \pm 2^\circ$
n-Octyltrichlorosilane (C8)	$\text{CH}_3(\text{CH}_2)_7\text{SiCl}_3$	97 %	$103.6 \pm 1^\circ$
n-Hexyltrichlorosilane (C6)	$\text{CH}_3(\text{CH}_2)_5\text{SiCl}_3$	97%	$100 \pm 2.3^\circ$

3. RESULTS AND DISCUSSION

3.1. Characterization of SAMs

Hydrophobicity of the alkyltrichlorosilane films is checked by assessing the static water contact angles ($V = 5\mu\text{L}$). As expected [6, 7, 8], values (**Table 2**) are higher than 90° whatever the chain length, the roughness and the orientation of the substrates.

Molecules grafting on silicon is checked by using IR spectra of SAMs in the frequency range of $2750\text{-}3050 \text{ cm}^{-1}$. As shown in **figure 1**, frequencies of their characteristic peaks ($\nu_{\text{asym}}(\text{CH}_2)$ and $\nu_{\text{sym}}(\text{CH}_2)$) are clearly observed. So, monolayers are well grafted on the silicon wafers whatever the type of substrate. It is worth of noting that the coatings homogeneity depends on the time of immersion, as reported by Jung *et al* [9] and Masuko *et al* [10]. Thus, on smooth silicon wafers, SAMs generally grow as small islands to form a discontinuous monolayer. However, when the immersion time increases the islands grow laterally to form a continuous monolayer. The minimum time to obtain this continuity is about 20 min on smooth silicon wafers and 24 h on rough ones. So, films can be then considered as continuous.

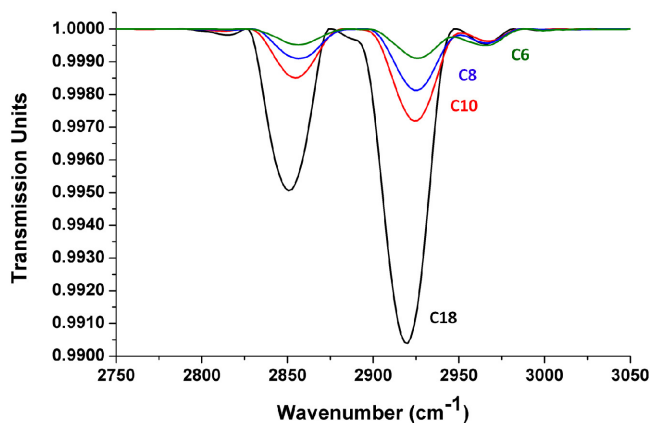


Figure 1: FT-IR spectra of alkyltrichlorosilane films.

3.2. Influence of the normal load and chain length on the frictional behavior

Figures 2a and 2b show the variations of the friction coefficient vs. chain length and normal loads, for smooth silicon wafers (100) and (111), respectively.

On the one hand, a lubricating effect is clearly observed when the chain length of SAMs is higher than 8, whatever the crystallographic orientation of the smooth substrates. Frictional behavior is completely controlled by SAMs properties.

On the other hand, a seizure area appears on SAMs displaying the lowest chain lengths ($C \leq 8$). A high friction coefficient is hence observed connected to a wide standard deviation. This seizure is probably due to the less densely packed and disordered monolayer displaying short alkyl chains [6, 8]. However, the seizure threshold clearly depends on the crystallographic orientation of the smooth substrate: it increases when the crystallographic orientation of the substrate is switched from (100) to (111). Thus, for Si (111) seizure is not observed for the lowest chain length at 10 mN (fig. 2b) in contrast to the same test on Si (100) substrate (fig. 2a).

These results reveal that the crystallography-induced anisotropy in friction and wear still occurs when SAMs – displaying short alkyl chains – is grafted on smooth silicon wafer. However, this anisotropy completely vanishes when the chain length is long enough (ie $C > 8$). In that latter case, their well-ordered and rigid structure provides better tribological behavior leading to a low friction coefficient and no seizure [6, 8]. As shown in figures 2a and 2b, seizure occurrence is completely controlled by the substrate itself, so this threshold increases when the orientation is switched from (100) to (111) according to their difference in mechanical properties (Table 1) [11, 12]. For instance, seizure threshold is 15 mN for C6 monolayers and 30 mN for C8 monolayers on Si (111)

instead of 10 mN for the same molecules for the Si (100). As a consequence, the friction coefficient is clearly dependent of the crystallographic orientation in the seizure area, and on the contrary, is not load-dependent in the lubrication domain. Thus, in this latter, anisotropy completely vanishes for both substrates. So, what is the effect of the sliding velocity within the lubrication domain?

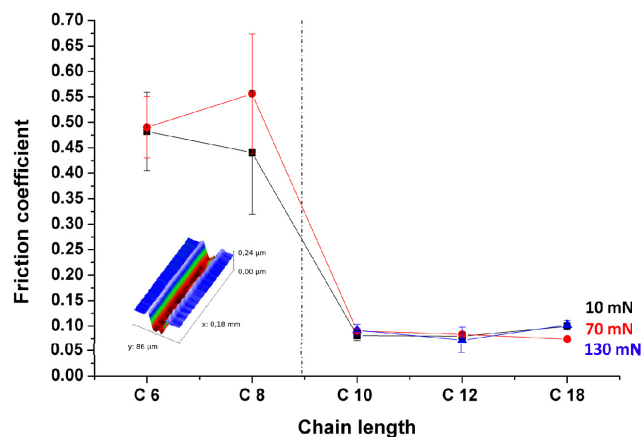


Figure 2a: Variations of the friction coefficient vs. chain length in the case of polished monocrystal Si (100) wafers ($v: 1 \text{ mm.s}^{-1}$, $d_i: 0.2 \text{ m}$).

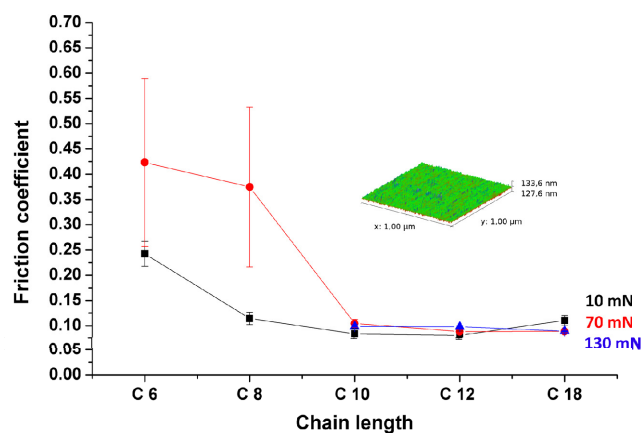


Figure 2b: Variations of the friction coefficient vs. chain length in the case of polished monocrystal Si (111) wafers ($v: 1 \text{ mm.s}^{-1}$, $d_i: 0.2 \text{ m}$).

3.3. Influence of the sliding velocity in the lubrication domain

To study the dissipative mechanisms that occur in the lubrication domain, tribological tests have been conducted at velocities ranged between $50 \mu\text{m.s}^{-1}$ and 20 mm.s^{-1} . As mentioned before, the frictional behavior is quite independent of the crystallographic

orientation. Since, the friction coefficient is not load-dependent either; tests are performed at the medium value (70 mN).

Fig. 3 shows the evolution of the friction coefficient vs. sliding velocity for monolayers displaying chain lengths higher than 8 carbons coated on Si (100). Two different dissipative behaviors are observed, as a function of the sliding velocity:

- a solid-like sliding behavior is observed for the higher sliding velocity. The friction coefficient is quite independent of the sliding velocity when the sliding velocity is higher than $5 \text{ mm}\cdot\text{s}^{-1}$;
- a liquid-like sliding behavior is observed for the sliding velocity lower than $5 \text{ mm}\cdot\text{s}^{-1}$. The friction coefficient is velocity-dependant and drops when the sliding velocity decreases.

This behavior is rather independent as the chain length meaning that the frictional dissipative mechanism is likely to be the same whatever the chain length. As expected, **fig. 4** displays the same variations for the short length chains ($C \leq 8$) deposited on Si (111).

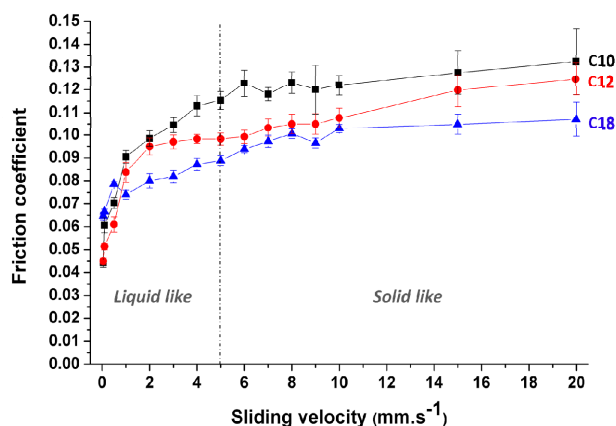


Figure 3: Variations of the friction coefficient vs. sliding velocity chain length in the case of polished monocrystal Si (100) wafers. Identical results were obtained with Si (111) wafers (F_N : 70mN).

The transition between liquid-like and solid-like sliding behavior as a function of the increase of the sliding velocity is also reported by Casoli *et al* [13], who have conducted macrotribometer study on PDMS brushes in a lower range of load. This behavior is also observed by Tambe *et al* on LFM/FFM tests [14], that is, in a lower range of velocities and higher contact pressure. According to them, at low velocity, the grafted molecules reorient themselves under the ball normal load. The monolayers could be compressed and squeezed leading to a change in the molecular orientation, but before the return of the ball, molecules

have time to reorient and recover their original structure. On the contrary, at high velocity (here $5 \text{ mm}\cdot\text{s}^{-1}$), the molecules do not have enough time to recover their initial position, so friction coefficient increases with the velocity until it reaches a critical values (0.13). However due to the high sliding velocities, the behavior could be also attributed to any change of the monolayers' structure connected to either the heating within the contact, as reported by Ren *et al* [15]. It could be also due to the stiffening of the layers by nanoconfinement effect under the slider [16]. What is happening on a higher sliding distance?

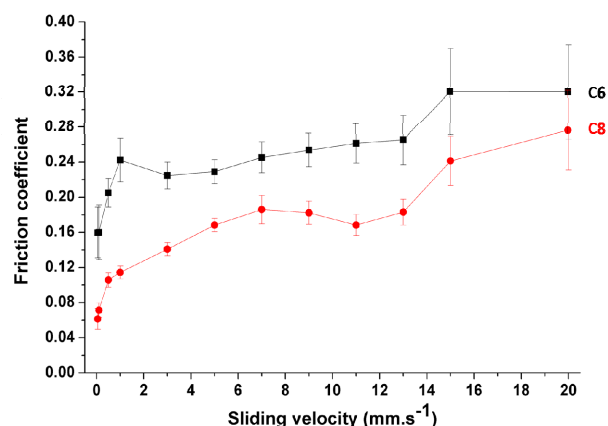


Figure 4: Variations of the friction coefficient vs. sliding velocity chain length in the case of polished monocrystal Si (111) wafers (F_N : 10mN).

3.4. Influence of the sliding distance in the lubrication domain

In the previous section (§ 3.3) results shows that the crystallographic anisotropy in friction and wear does not exist in the lubrication domain for short sliding distance (ie 100 cycles). In order to investigate the tribological evolution for higher sliding distances, tests have been performed during 10 000 cycles at $1 \text{ mm}\cdot\text{s}^{-1}$.

Fig. 5 shows the evolution of the friction coefficient vs. number of cycles for C18 monolayers deposited on polished Si (100) and Si (111), respectively.

On the first thousands cycles, no difference is noticed between the Si (100) and Si (111). This evolution is the same as the one observed during the first hundred cycles (see § 3.2 and **fig. 2**). There is no crystallography-induced anisotropy in friction and wear. But, surprisingly the effect of the substrate appears beyond 1500 cycles. Whereas the friction coefficient remains stable and low ($\mu \sim 0.07$) for the Si (111) substrate along 10 000 cycles, it continuously rises until the seizure for the Si (100) substrate. The seizure occurrence is likely to appear at anytime

beyond this threshold, becoming completely uncontrollable.

Thus, as an unexpected result, the substrate crystallographic orientation has again a great influence on the high chains SAMs frictional behavior, and more particularly on the resistance to the seizure. Indeed, on Si (111) substrate, wear is quite low and hard to detect, even in AFM. Anyway, since seizure occurrence is mainly due to the fracture resistance of the substrate, this behavior can be attributed to the better mechanical and physico-chemical properties of Si (111), as the densest crystallographic plane, compared to the Si (100).

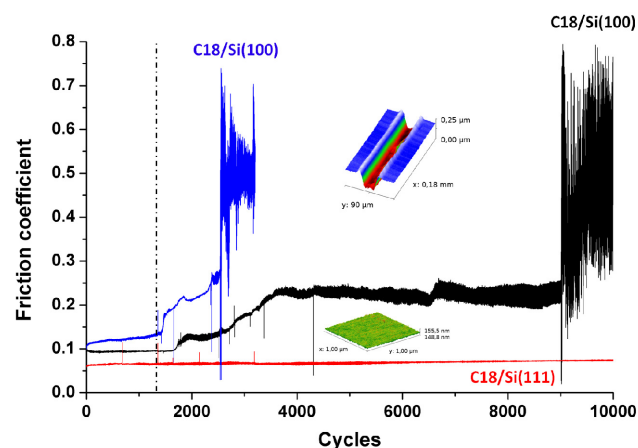


Figure 5: Variations of the friction coefficient vs. sliding distance for C18 SAMs in the case of polished monocrystal Si (100) and Si (111) wafers (F_N : 70mN).

3.5. Influence of the substrate nanostructure on the tribological behavior

The influence of roughness on crystallography-induced anisotropy in friction and wear of bare silicon wafers has been extensively studied in a previous paper [17]. It has been shown that crystallography-induced anisotropy in friction and wear does not exist when the roughness is important (eg, 600 nm), because the tribological behaviour becomes completely controlled by the third body generated by seizure.

In the present study, the effect of the substrate roughness on tribological behavior of SAMs, tests have been conducted in the lubrication domain at a sliding velocity of 1 mm.s^{-1} and a normal applied load of 15 mN.

Fig. 6 shows the variations of the friction coefficient vs. number of cycles for C18 monolayers deposited on rough Si (100) and Si (111), respectively. Whereas rough C18/Si(100) shows a high friction coefficient and suffers seizure, rough C18/Si(111) starts with a low friction coefficient which continuously increases with the number of cycles, but no seizure occurs. So,

the crystallography-induced anisotropy in friction is still observed in spite of the higher roughness. The Si (111) is definitely a better substrate than the Si (100) whatever its surface nanostructure. Nevertheless, when the nanostructure of the substrate is increased the immersion time becomes a key parameter that controls the homogeneity of the films. Indeed, tribological tests on C18 SAMs deposited during 20 min inevitably lead to quick seizure even on Si (111) substrate. A long immersion time is necessary to form a closed-packed and homogeneous monolayer on rough surface, as explained by Masuko et al [10]. In addition stearic considerations probably have to be taken into account when the roughness becomes important.

Hence, effect of nanostructure, design and nanopattern, as a function of the immersion time need to be studied in the future.

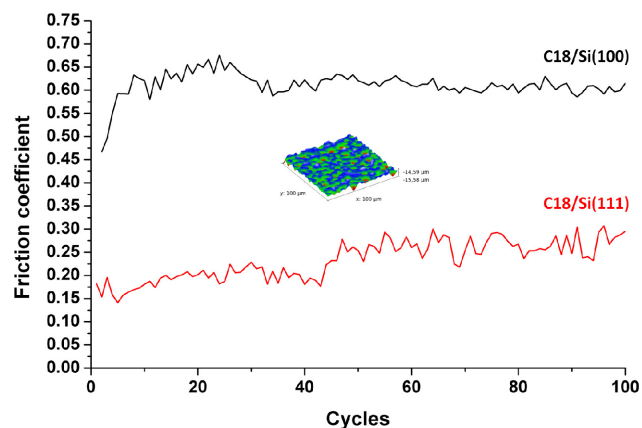


Figure 6: Variations of the friction coefficient vs. sliding distance for C18 SAMs in the case of rough monocrystal Si (100) and Si (111) wafers (v : 1 mm.s^{-1} , F_N : 15mN, immersion time: 24h).

4. CONCLUSIONS

Micro/nanotribological study of self assembled monolayers (SAMs) derived from n-alkyltrichlorosilanes deposited on silicon wafers (100) and (111) with different roughnesses has been conducted against a silicon nitride ball using a ball-on-disc nanotribometer. The effects of the chain length, the substrate crystallographic orientations and roughness and the experimental conditions on the SAMs tribological performances have been analyzed.

The following conclusions may be drawn:

- Films composed of long chains ($C > 8$) show lubricating effect whereas a seizure phenomenon is observed for shorter chains ($C \leq 8$).
- In the seizure domain, crystallography-anisotropy in friction and wear was found whatever the total

sliding distance. On the contrary, in the lubrication domain, crystallography anisotropy appears only after a long sliding distance.

- Tribological performances of SAMs deposited on silicon (111) are always better than those of the film deposited on silicon (100).
- In the lubrication domain, friction coefficient is quite independent on the sliding velocity beyond 5 mm.s^{-1} whereas it is velocity-dependent below this value. This reveals that various dissipative mechanisms occur as a function of the sliding velocity.
- On rough silicon (100) and (111) wafers, the immersion time appears as a key parameter which controls the homogeneity of the films.

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