

Wear Life Test and Mechanisms of Silicon MEMS Devices under Different Gas Environments

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Abstract: Microelectromechanical systems (MEMS) are usually fragile to wear problems. In this research, a bulk-fabricated side-wall Si-MEMS tribotester with the feature of on-chip buckle loading mechanism was designed and used to study the wear life and the mechanisms of early stage wear of resonant MEMS devices in different gas environments. Two distinguishable wear mechanisms are recognized: (1) in dry N₂ or O₂/N₂ mixture environments, wear exhibited an adhesive feature that the instantaneous wear rate is inversely proportional to the wear depth; (2) if corrosive vapors, such as fatty alcohols, are introduced into the environment, chemical reaction can limit the wear rate as a constant. In more complex situation, such as trifluoroethanol vapor, the rubbing process shows a transition from a short adhesive wear phase to a corrosive wear process. The thermal- and tribo-solvolysis could not give a full explanation of the life-time tests for the tested fatty alcohols. Therefore, there must be derivative reactions of grafting groups at silicon surfaces, which cause the instability of such groups. A mechanochemical mechanism is established to understand the stability of grafting groups in friction situation. Compared with fatty alcohols, fluoroalcohol is much more stable and can be used as vapor lubricant for Si-MEMS devices.

Key words: MEMS, wear, solvolysis, mechanochemistry

1. Introduction

Microelectromechanical systems (MEMS) are a class of IC-compatible sophisticated mechanisms to realize highly controllable precision motions at micro/nano scales. Compared with the failure modes of fracture and fatigue, tribological problems, including adhesion, friction and wear, are the main factors which give rise to device failure at such scales owing to the high surface-to-volume ratios of these devices [1]. Until now the adhesion problem can be solved by lowering down the surface energy using self-assembly monolayers (SAM), such as fluoro-substituted tris(dimethylamino)silane [2]. However, SAM could not provide persistent protection of contacting surfaces from wear to achieve enough life-time [2-4]. To overcome the wear problem, lubricant needs to be able to diffuse onto the moving part continuously. Two instances of vapor phase have been successfully used to lubricate tribo-MEMS devices, one is perfluorodecanoic acid vapor using for protecting the aluminum protrusion in Digital Micromirror DeviceTM [5], and the other is 1-pentanol vapor which is effective to prolong the life-time of silicon micro-tribotester fabricated by Sandia National Laboratory [6]. The possible reasons for the good lubricity of these two lubricants are not exactly the same. For the perfluorodecanoic acid, the competitive adsorption may reduce the corrosion of water on aluminum material, while the 1-pentanol can react with silicon in a soft manner to avoid adhesive wear, which is the most common wear mechanism of silicon materials [7]. In order to expand applications of MEMS, looking for a suitable lubricant and understanding the wear mechanism at micro scales becomes particularly important.

For tribo-MEMS, devices are easy to fail at the early stage of wear, only allowing for blunt rough asperities and a small number of wear debris. To study the early stage of wear, a

bulk-fabricated side-wall micro tribotester is designed to test the wear life of silicon in different vapor environments. In this paper, we first introduce the tribotester and the experimental details. In Section 3, adhesive and corrosive wear are distinguished by the motion mode of the driving shuttle. In Section 4, we analysis the corrosive wear of fatty and fluoro- alcohols, pointing out that the solvolysis can not give a full explanation of tribochemical reactions of fatty alcohols on silicon surfaces. A mechanochemical mechanism is proposed to understand the stability of grafting groups in the presence of friction, helping to explain the stability of fluorocarbon chains on silicon surfaces.

2. Experimental details

Every 50- μm -thick Si-MEMS tribotester consists of a driving shuttle and a pair of loading frames (Fig. 1). The on-chip buckle structure can push the loading frame over a certain displacement to maintain a deflection of the restriction beam to realize 2.7 μN or 5.2 μN normal loads. For each tribotester, a loading frame and its corresponding restriction beam serves as the reference pair working in the ethanol vapor environment, and the opposite pair is used to study the effects of other environments, such as dry nitrogen or fluoroalcohol vapors. The friction pair to be tested is blown by dry nitrogen or the bubbled vapor stream with saturation lower than 20%. This design can be as far as possible to cancel the interference of device fluctuation in fabrication [8] and give more reasonable judgments of anti-wear effect of candidate lubricants.

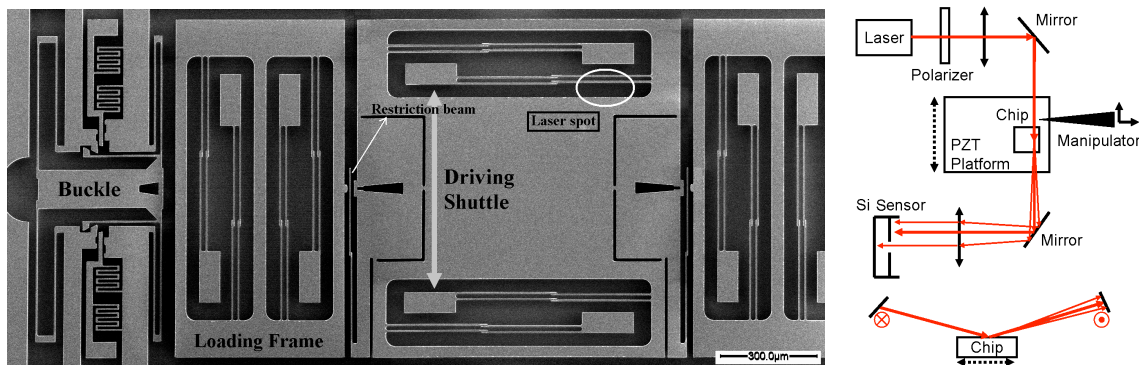


Figure 1. The bulk-fabricated micro- tribotester and the optical path to monitor the vibration of the driving shuttle, top view (up) and side view (down).

To drive the friction pair, the tribotester is stuck to a home-made one dimensional piezoelectric platform to force the shuttle vibrating near its nature frequency. The typical oscillation amplitude of the shuttle is about 4.5 μm at 3850Hz. This method can offer a driving force no more than 10 μN . And the on-chip buckle loading method avoids the necessity of finding the zero-point in a trial-and-error way. Thus this tribotester can be sensitive enough to observe the early stage of wear from its real starting point in MEMS devices.

The vibration of the shuttle can reflect the friction/wear process. A HeNe 633nm laser focuses onto the edge of the shuttle to reflect a speckle field. The light intensity of the carefully chose point in this speckle field denotes the position of the shuttle. Since the air resistance is measured only 1/20 of the average friction force, the vibration degradation ΔC ($\Delta C = C_0 - C$, C_0 is the vibration amplitude under empty load) reflects the real-time friction force ρ , which has a relationship of $\rho \propto \sqrt{\Delta C}$ deduced from the vibration equation under suitable simplifications [9].

3 Adhesive and corrosive wear mechanisms

After a short while vibration, the tribotester would stop owing to the overlarge friction. Figure 2 shows the worn morphologies of loading heads and restriction beams failed in nitrogen and ethanol vapor environments. On restriction beams only the feature of blunt peaks can be found and the bearing area is no more than 6% of the total nominal contact area. Hence these devices failed at the early stage of wear. The reason of blunt peaks can be inferred from the morphologies of the loading heads, where the worn area concentrated in a small region less than $5\mu\text{m}\times 5\mu\text{m}$ with more wear features. For samples in nitrogen atmosphere, scratches and pie-like wear debris distributed on the wear scars, while glass-like materials around bearing spots without scratches were found on samples working in ethanol vapor atmosphere. These glass-like materials can decompose in wet hydrofluoric acid vapor and is considered as the reaction products of silicon and ethanol in rubbing conditions. Therefore wear in nitrogen is attributed to adhesive type while in ethanol vapor it is corrosive type.

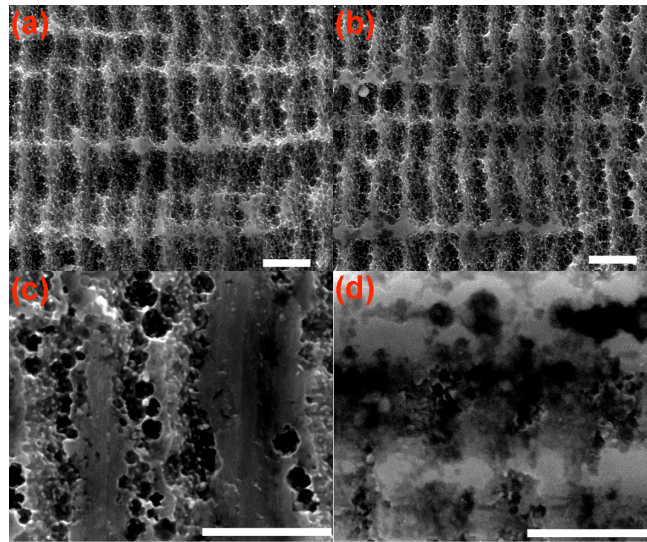


Figure 2. Worn morphologies of driving shuttles (a, b) and loading heads (c, d) after device failure. (a, c) Dry nitrogen atmosphere. (b, d) Ethanol vapor environment. The scale bar is $1\mu\text{m}$.

The two wear mechanisms can be further convinced by the shuttle vibration degradation. Assuming each initial rough peak has a parabolic shape $h = r_0 \cdot r^2$ and the average friction force ρ is proportional to the total bearing area $A = N \cdot A_0 = N(\pi \cdot h / r_0)$. For adhesive wear, combining the classical Archard wear equation [10, 11]

$$\frac{A \cdot \Delta h}{v \cdot \Delta t} = \frac{\Delta V}{\Delta s} = \lambda_1 A_r \quad (1)$$

(V is the wear volume, s is the sliding length, v is the sliding speed, and λ_1 is the wear coefficient) and the simplified relationship between atomic contact area A_r and normal load F_n of $A_r = \lambda_2 \cdot F_n$ [12], the transient wear rate is inversely proportional to the wear depth as

$$\frac{dh}{dt} = \lambda_1 \lambda_2 v \frac{F_n}{A} = \left(\frac{\lambda_1 \lambda_2 v \cdot r_0}{\pi \cdot N} \right) \frac{F_n}{h}, \quad (2)$$

which induces $h \propto \sqrt{t}$ or $\rho \propto \sqrt{t}$. And for corrosive wear in strong media, only the reacted materials

will be worn out and the wear rate is limited by the reaction rate, which depends on the activation energy E_a of silicon and adsorbed small molecules:

$$h_0 = \frac{dh}{dt} = d_a K \cdot f_0 \exp[-(E_a - dE) / k_b T], \quad (3)$$

where d_a is the silicon atom diameter and K is a probability multiplier to express the uniform assignment of multi-contact wear. dE is a modifier for sharp contact between fresh asperities. Since the initial shape can be worn out quickly in bulk-fabricated devices, dE is omitted to prevent redundant discussion [13]. Therefore, the transient wear rate is a time-independent constant, which induces $h = h_0 \cdot t$ or $\rho \propto t$. Therefore, using the relationship of $\rho \propto \sqrt{\Delta C}$, two modes of ΔC should be observed at the beginning of wear.

Figure 3 shows the shuttle vibration degradation in nitrogen and ethanol vapor conditions. The initial degradation can be fitted by the $\Delta C \propto t$ or $\Delta C \propto t^2$ quite well, consistent with the analysis of wear mechanisms from surface morphologies.

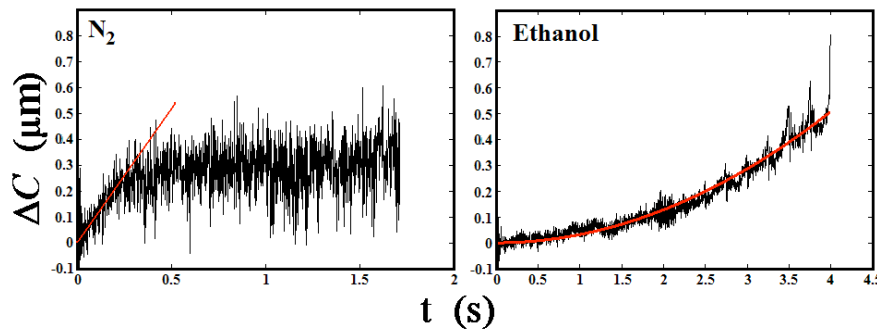


Figure 3. The typical vibration degradation of the driving shuttle in nitrogen and ethanol vapor environments.

$\Delta C = d \cdot t^2$ (red line) is used to fit the data for ethanol vapor condition.

More kinds of gas environments have been tested on our tribotesters. In addition to dry nitrogen, O_2/N_2 mixture, n-hexane vapor and HFE 7100 ($CF_3(CF_2)_3OCH_3$) vapor also exhibit adhesive type. According to the density functional theory (DFT) calculation, n-hexane and HFE 7100 have very limited reactivity with silicon materials. Oxygen is easy to react with silicon in tribo-conditions [14]. However, lacking of inert groups, oxygen can not saturate dangling bonds to avoid atom bridges between couple surfaces. Besides ethanol, typical corrosive wear can be found in short chain fatty alcohols, such as methanol and hexanol, as well as propylene oxide. More complex wear processes are observed in water and fluoroalcohol vapor conditions, where a short linear vibration degradation can usually be found before the time-square degradation. Using the DFT calculation, fluoroalcohols show a weaker reactivity than fatty alcohols (Sec. 4). Hence they can not passivate initial sharp asperities as effectively as fatty alcohols to avoid adhesive wear. The reason for the boundary lubrication behavior of water is not very clear. A possible explanation is that silicon surfaces passivated by $-OH$ groups still has possibilities to form atom bridges like Si-O-Si to cause adhesive wear when the local stress is high enough.

Using the time scaling of $\rho \propto \sqrt{t}$ and $\rho \propto t$, the worn area increases in a manner of $t^{3/4}$ and $t^{3/2}$ for adhesive and corrosive wear, respectively. For conventional macro structures, corrosive wear is usually more harmful since it has a superlinear growth. However, for MEMS devices, the permitted

wear volume is light and the wear process fails at its early stage. Near the initial point, the $t^{3/2}$ curve increases slower than that of $t^{3/4}$. That means if suitable chemical reactions are introduced into micro- tribo-devices, corrosive wear can exhibit a longer life-time than adhesive type (Fig. 4).

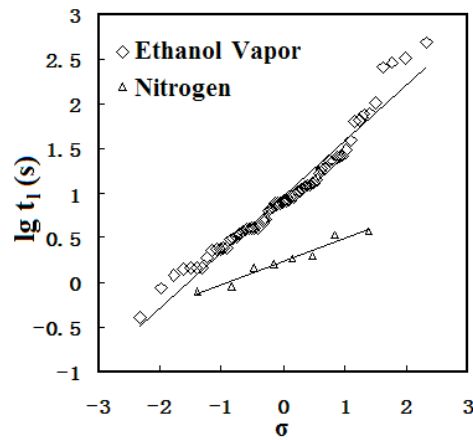


Figure 4. The log-normal distribution of life-time (t_1) in nitrogen and ethanol vapor environments.

4. The life-time test in corrosive vapor environments

Since the initial wear is sensitive to chemical conditions, several vapor environments are tested to study their lubrication effects, including methanol, ethanol, propanol, isopropanol, 2,2,3,3-tetrafluoropropanol, 2,2,2-trifluoroethanol, hexanol, propylene oxide and water. Their life-times compared by the reference pairs in ethanol vapor environments are shown in Fig. 5. According to these results, fluoroalcohols are better lubricant than fatty alcohols.

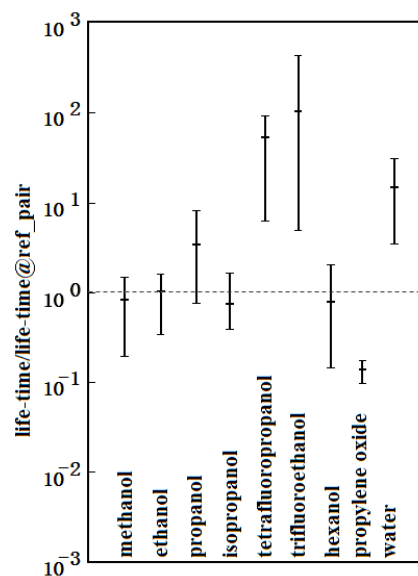
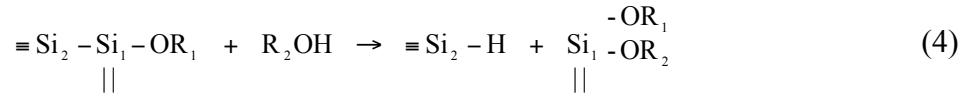


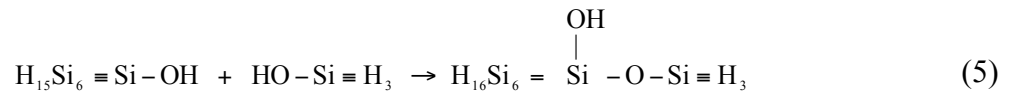
Figure 5. The life-time ratio of different corrosive vapors. The error bars denote the maximum and minimum values for each case.

A basic question is what chemical reactions happen on tribo-surfaces that make fluoroalcohol a better lubricant. For silicon material, especially the silicon dioxide, solvolysis (i.e., hydrolysis for water and alcoholysis for alcohols) is the most important reaction when the environment is filled by

active agents [15-21]. The solvolysis of silicon dioxide with water and fatty alcohols has been studied broadly. In our wear tests, however, the driving frequency is high enough and it is believe that there is not sufficient time to form fully native oxide on tribo-surfaces. Hence the reaction substrate is determined to be silicon instead of silicon dioxide. To compare the solvolysis reactivity of different compounds, the activation energy E_b of reaction



is calculated in the framework of the density functional theory where Si(111) cluster model Si_7H_{16} is used (Fig. 6). The calculation is carried out with the Dmol3 software packaged in Material Studio v5.5, employing the BP functional and the DND basis set. Similar model is also used to calculate the hydrolysis barriers for $\text{SiO}_2(111)$ and $(\text{HO})_3\text{Si}-\text{O}-\text{Si}(\text{OH})_3$, which gives the same transient structures and reaction energies given by Gaussian [22]. The virtual reaction



is used to estimate the upper limit of E_b (149.7kJ/mol) for ROH compounds, where the H-H-H plane in $\text{HO}-\text{Si} \equiv \text{H}_3$ is parallel to the Si(111) surface.

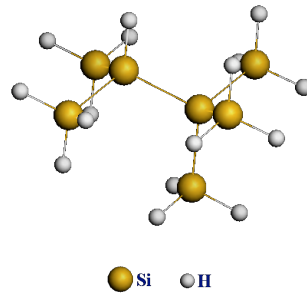
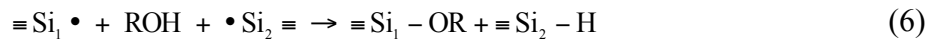


Figure 6. The Si_7H_{16} cluster model used in DFT calculation. H atoms are fully restricted.

Besides the thermal-solvolysis there can be another way to graft carbon chains onto silicon atoms, which depends on the dangling bonds formed in the rubbing process. The friction force in dry nitrogen environment is only several times larger than that in above vapor conditions. Since almost all the driving work in dry nitrogen condition is consumed on the formation of silicon dangling bonds, it is supposed that dangling bonds still forms in vapor conditions. In this paper we ignore the dynamic details in the formation of dangling bonds and use the reaction



to judge the reactivity of dangling bonds with different small molecules and define this reaction in terms of tribo-solvolysis. Two unsaturated Si atoms are used in this reaction to avoid odd number of electrons in DFT calculation. The distance from one Si atom to the other is set to be two times of equilibrium distance to contain the adsorbed small molecules. The energy of $\text{Si} \cdot \cdot \text{Si}$ is 351kJ/mol higher than Si-Si of equilibrium state and the energy change ΔE in Reaction (6) is used as the reactivity of tribo-solvolysis.

Figure 7 shows the DFT calculation results of E_b and ΔE . E_b and ΔE at the reference point are 149.7kJ/mol and -351kJ/mol, respectively. The distance Δ from each compound to the reference

point in kJ/mol can be considered as the activation energy E_a in Eq. (3). Since worn depth of failure devices is about 100-150nm as a constant, the life-time t_1 in each vapor environment is theoretically expressed by

$$\lg(t_1 / t_{1_ethanol}) = (\Delta_{ethanol} - \Delta) \times 0.1744. \quad (7)$$

Figure 8 shows the experimental relationship of t_1 and Δ of vapors in Fig. 4. Two approximate linear regions are found, one consists of water and fluoroalcohols with the slope of 0.05 and the other includes fatty alcohols with the slope of 0.01. The deviation of the slope from 0.1744 to 0.05 in Region II can be expressed by the non-corrosive stage of the initial wear. And for fatty alcohols, the significant deviation from the theoretical expectation suggests that only the thermal- and tribo-solvolysis is not able to give a full explanation of the tribo-reactions.

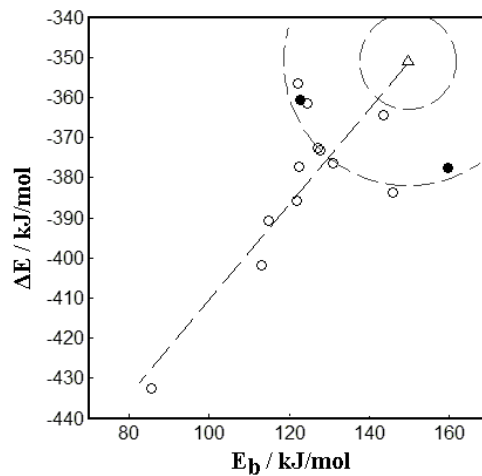


Figure 7. The DFT calculation results of E_b and ΔE . Δ : The reference point, \circ : Volatile solvent, \bullet : Less volatile solvent. Dashed lines are used to guide the sight: along the straight line from top right to bottom left - the reference point, trifluoroethanol, 2-methoxyethanol, propanol, pentanol, hexanol, octanol and propylene oxide, along the arc line from top left to bottom right - tetrafluoropropanol, glycol, isopropanol, ethanol, methanol, 2-methoxyethanol, water and phenol.

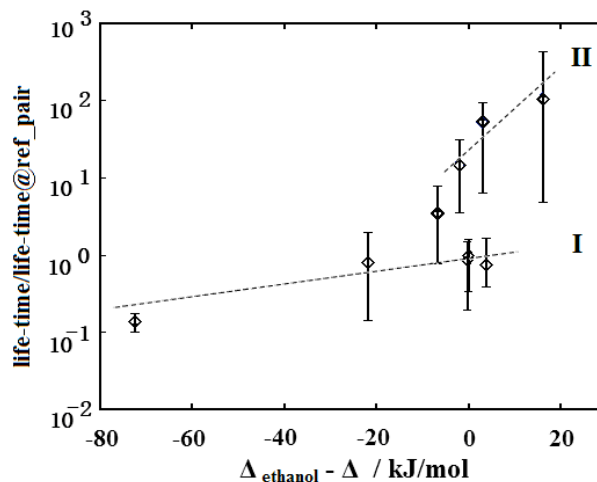


Figure 8. The relationship of life-time test and Δ . From left to right: Region I - propylene oxide, hexanol, propanol, methanol, ethanol and isopropanol, Region II – water, tetrafluoropropanol and trifluoroethanol.

Here we suggest a mechanochemical mechanism to understand the possible degradation routines for grafting groups on silicon surfaces. In tribo-conditions, the dangling bonds may not only form at top silicon atoms but also form by the rupture of grafted carbon groups. Consider the quasi-static vertical stretching of the end carbon atom on hexanol grafted at Si(111) surface in Figure 9. Using the DFT calculation by the Si_7H_{16} model, the chain will break at the end C-C bond, releasing the $\text{CH}_3\cdot$ radical. This character gives an explanation of the “tribochemical polymerization” [23] of short C_xH_y compounds found by TOF-SIMS in pentanol lubricating experiments, including surface-MEMS devices [24] and macro- ball(SiO_2)-on-disc(Si) experiments [23]. Figure 10 shows the rupture details of different grafted alcohols. Before a critical strain of approximately the same, the Si-O-R chain is stretched uniformly. And at the critical strain (about 0.2), the chain “breaks” at the end C-C bond, where the energy increase is about 0.86~1.25 times of forming a $\text{Si}\cdot\text{Si}$ pair. However, different chains have different trends to release carbon radicals. For hexanol, there is a jump at the break point and the CH_3 group is almost fully released to form radical. For ethanol, the jump is not significant and the CH_3 group still has some quantum connection with the main chain when the strain is more than 0.2. The situation of propanol is between ethanol and hexanol. But for fluoroalcohols, the $\text{CH}_x\text{F}_{3-x}$ group can not get rid of the influence of main chain as fatty alcohols since the Si-O-R chain relaxes in a continuum manner. Therefore, the fluoroalcohols is much more stable than fatty alcohols when they are grafted on silicon surfaces and the latter can degrade by local mechanochemical effect. The longer the alcohol, the easier to break. This degradation may be harmful for lubrication and fluoroalcohols are better lubricant than fatty alcohols.

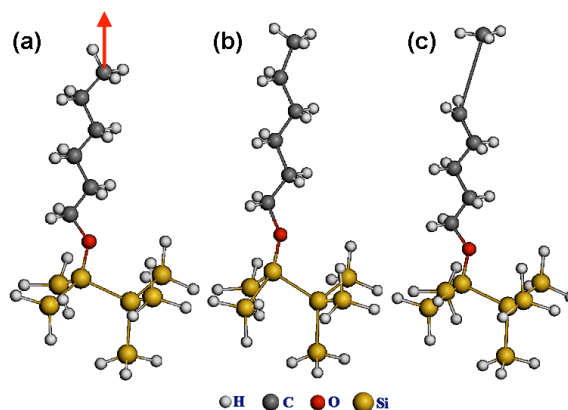


Figure 9. The quasi-static stretching of grafted hexanol on Si_7H_{16} cluster. (a) Initial state, (b) just before C-C break, (c) just after C-C break.

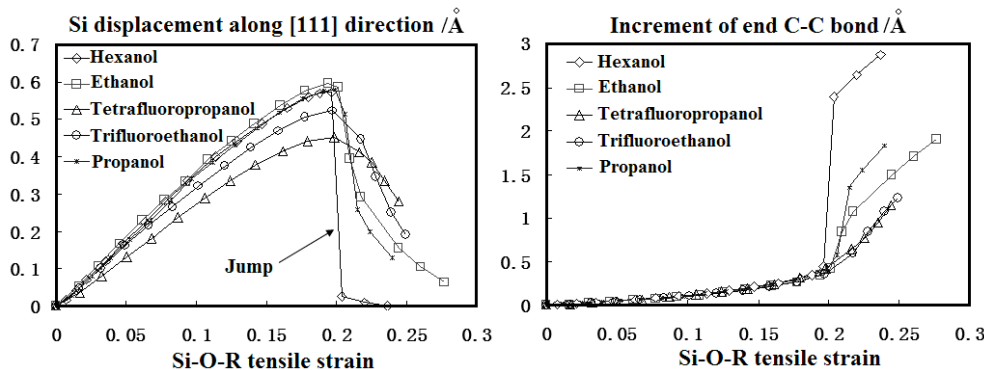


Figure 10. The tensile responses of different grafted alcohols on Si(111) surface.

5. Conclusion

In this research, a bulk-fabricated side-wall Si-MEMS tribotester is fabricated to study the life-time and wear process in different gas environments. By using the on-chip buckle loading method and the resonant driving strategy, the early stage of wear can be studied and classified into adhesive and corrosive types, depending on the gas environment. Since the permitted wear is quite light in MEMS devices, introducing a suitable corrosive vapor, such as alcohol, can relieve the initial wear to prolong the life-time. For fatty alcohols, the thermal- and tribo- solvolysis may not give a full explanation of tribo-reactions. A mechanochemical mechanism is proposed to understand the possible degradation of grafted alcohols on silicon and fluoroalcohols exhibit much more stable than fatty alcohols in the DFT calculation. The average wear life-time ratio in 2,2,2-trifluoroethanol vapor is about 100 times larger than that in ethanol vapor, so trifluoroethanol can give an effective lubrication for silicon devices.

Acknowledgements

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