

Nano-tribological characteristics of TiO₂ films on 3-mercaptopropyl trimethoxysilane sulfonated self-assembled monolayer

J LI[†] and X H SHENG*

Shanghai Zhuzong Company, Shanghai 200032, P.R. China

[†]School of Mechanical & Electronic Engineering, Shanghai Second Polytechnic University, Shanghai 201209, P.R. China

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Abstract. Silane coupling reagent (3-mercaptopropyl trimethoxysilane (MPTS)) was used to prepare two-dimensional self-assembled monolayer (SAM) on silicon substrate. The terminal –SH group was *in situ* oxidized to –SO₃H group to endow the film with good chemisorption ability. Then TiO₂ thin films were deposited on the oxidized MPTS–SAM to form composite thin films, making use of the chemisorption ability of the –SO₃H group. Atomic force microscope (AFM) and contact angle measurements were used to characterize TiO₂ films. Adhesive force and friction force of TiO₂ thin films and silicon substrate were measured under various applied normal loads and scanning speed of AFM tip. Results showed that the friction force increased with applied normal loads and scanning speed of AFM tip. In order to study the effect of capillary force, tests were performed in various relative humidities. Results showed that the adhesive force of silicon substrate increases with relative humidities and the adhesive force of TiO₂ thin films only increases slightly with relative humidity. Research showed that surfaces with more hydrophobic property revealed the lower adhesive and friction forces.

Keywords. SAM; AFM; nano-tribological characteristics.

1. Introduction

Microelectromechanical systems (MEMS) offer great promise for integration of sensors, signal processing, and communications. Miniature smart systems that interact with the physical world perform computations, and communications with other systems are the goals of MEMS technology (Eappen *et al* 2002; Yoon *et al* 2003; Patton and Zabinski 2005). A major hurdle towards wider application of these micro devices is the tribological issues associated with them. A variety of surface modification techniques including deposition of self-assembled monolayers (SAMs) which have advantageous characteristics of well-defined structure, strong head group-substrate binding and dense packing of hydrocarbon chains have been employed to improve the tribological behaviour of MEMS devices, and have provided varying degrees of success (Maboudian *et al* 2000; Ashurst and Yau 2001; Cha and Kim 2001).

Numerous studies have been conducted in order to understand the applications of TiO₂ in many fields such as optics, medicine, magnetism, tribology and so on (Sidebottom *et al* 1997; Konishi *et al* 1998; Yu *et al* 1998; Cheng and Bai 2006). A number of studies have been

done on the nano-tribological properties of different SAMs (Cha and Kim 2001; Bhushan 2005), but the study of TiO₂ films on the nano-tribological behaviour is much lacking.

3-Mercaptopropyl trimethoxysilane (MPTS) can be obtained expediently and have been previously used to make functional monolayers (Xiao *et al* 1998; Alessandro *et al* 2004; Wang *et al* 2004). And the thiol groups (–SH) can be oxidized into sulfonic acid groups (–SO₃H) easily, which can provide both a high degree of surface acidity and net negative charge to deposited TiO₂ thin films. In this paper, MPTS was deposited by self-assembly technique, providing modestly hydrophobic monolayer films as substrates for the deposition of TiO₂ thin films from aqueous solutions. Many means, such as X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), etc had been applied to characterize the structure and nano-tribological properties of self-assembled TiO₂ thin films on MPTS SAM substrates.

2. Experimental

2.1 Materials

Silicon plates were used as substrates for SAM film transfer. The silicon plates were cut into pieces of

*Author for correspondence (shengxiaohong2@sina.com)

~1.0 cm by 1.0 cm before cleaning and modifying. MPTS were purchased from Sigma Aldrich (Deisenhofen, Germany) and used as received. All other chemicals used in chemical manipulations were of reagent grade. Deionized water was obtained from a Barnstead Nanopure apparatus.

2.2 Preparation of film

Firstly, the preparation of MPTS SAM was performed according to the literature (Xiao *et al* 1998). With proper prehydration, the hydroxide substrates were capable of covalent bonding to the hydrolyzed silane molecules via condensation reaction of silanol groups. Glass substrates were immersed for 30 min in Piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 7/3$ (V/V)) at 90°C to make hydroxy radicals on the surfaces. Then the substrates were carefully rinsed with deionized water and dried. After that the hydroxide substrates were dipped into the dehydrated benzene solution containing 0.5 mM of MPTS solution for 12 h, to allow the formation of MPTS SAM. At last the substrates were cleaned ultrasonically with chloroform, acetone and deionized water in turn to remove the other physisorbed ions or molecules and dried for 1 h at 120°C , then cooled in a desiccator. The oxidation of the $-\text{SH}$ groups to the desired $-\text{SO}_3\text{H}$ groups was carried out by dipping the substrates into the solution of 30% nitric acid at 80°C for 1 h, followed by washing with distilled water and dried in nitrogen.

The titanate solution was prepared as follows: TiO_2 and ethylenediamine tetra-acetic acid (EDTA) etc were mixed with alcohol, followed by stirring at room temperature for 1 h. And its pH was adjusted to 4–5 using nitric acid. Then the substrates deposited with the sulfonated MPTS-SAM were immersed in the resulting mixed solution at 90°C for 12 h, to allow the adherence of the TiO_2 thin films on the sulfonated MPTS-SAM. At last the substrates were cleaned ultrasonically with deionized water to remove other physisorbed ions or molecules and dried for 2 h at 120°C , then cooled in a desiccator.

2.3 Experimental apparatus and measurements

The microscopic study was conducted on a NanoScope IIIa atomic force microscopy (Digital Instruments Inc.) in the contact mode. All measurements were performed in air at 23°C and 37% relative humidity (RH). Contact angles of water were measured by the sessile drop method using the OCA-20 measurement apparatus (DataPhysics Instruments GmbH) under ambient laboratory conditions (24°C , 40% RH). Measurements were made at a minimum of five different spots on each sample. The results stated below are averages of all these measurements.

During the adhesion measurements, SPM tips were pushed to the flat surface until the normal load reached to

a fixed value, and then it was pulled off from the surface until release. The maximum pull-off force was calculated from the force-displacement curve and defined as the adhesive force. In order to investigate the nano-tribological characteristics of SAM-coated surface, an AFM was used for friction measurements. Friction tests were performed using a V-shaped cantilever (radius ~ 15 nm, normal stiffness ~ 0.12 N/m). Adhesion and friction tests were carried out with Si_3N_4 tip under ambient condition of $20\text{--}22^\circ\text{C}$ and $28\text{--}35\%$ RH, unless otherwise specified. For each sample, adhesive and friction were measured at more than 5 times and 5 different locations.

3. Results and discussion

3.1 Characterization of MPTS SAM and the deposited TiO_2 thin film on sulfonated MPTS-SAM

Figure 1 shows the AFM images of hydroxide substrates, MPTS SAM, oxidized MPTS SAM, and the TiO_2 thin films by contact mode. The mean roughness (R_a) were 0.159 nm, 0.527 nm, 0.2 nm and 4.464 nm, respectively.

MPTS film had been successfully obtained in our work as shown in figure 2. When the terminal groups ($-\text{SH}$) of self-assembly monolayers were oxidized into sulfonate ones ($-\text{SO}_3\text{H}$) by dipping in a solution of 30% HNO_3 , the contact angle of samples decreased from $70\text{--}31^\circ$ (Xiao *et al* 1998). The increase of contact angles from 31° to 64° indicated that the TiO_2 film had been successfully obtained in our work which led to the reduction of the surface energy.

3.2 Nano-tribological properties of TiO_2 thin film

3.2a Influence of relative humidity on adhesive and friction forces: The influence of relative humidity on the adhesive force was studied at 25°C . Figure 3 shows that the adhesive force of silicon substrate increases with relative humidity and the adhesive force of TiO_2 thin films increases slightly with relative humidity. The adhesive force is related to the work of adhesion of the surface which is related to the polarity of the surface terminal (Liu and Bhushan 2002). The TiO_2 thin films were deposited on the oxidized MPTS-SAM, making use of the chemisorption ability of the $-\text{SO}_3\text{H}$ group. The TiO_2 thin films have non-polar surface terminal and a very small work of adhesion; thus the adhesive force is not sensitive to the change of humidity. The $-\text{Si-O-H}$ group was regarded as one terminal of silicon substrate. The electronegativity of Si and H are 1.9 and 2.1, respectively. This suggests that the silicon substrate has polar surface terminal and larger adhesive force in higher relative humidity, which in turn increases the friction force.

The influence of relative humidity on the friction force was presented in figure 4. Figure 4 shows that the friction

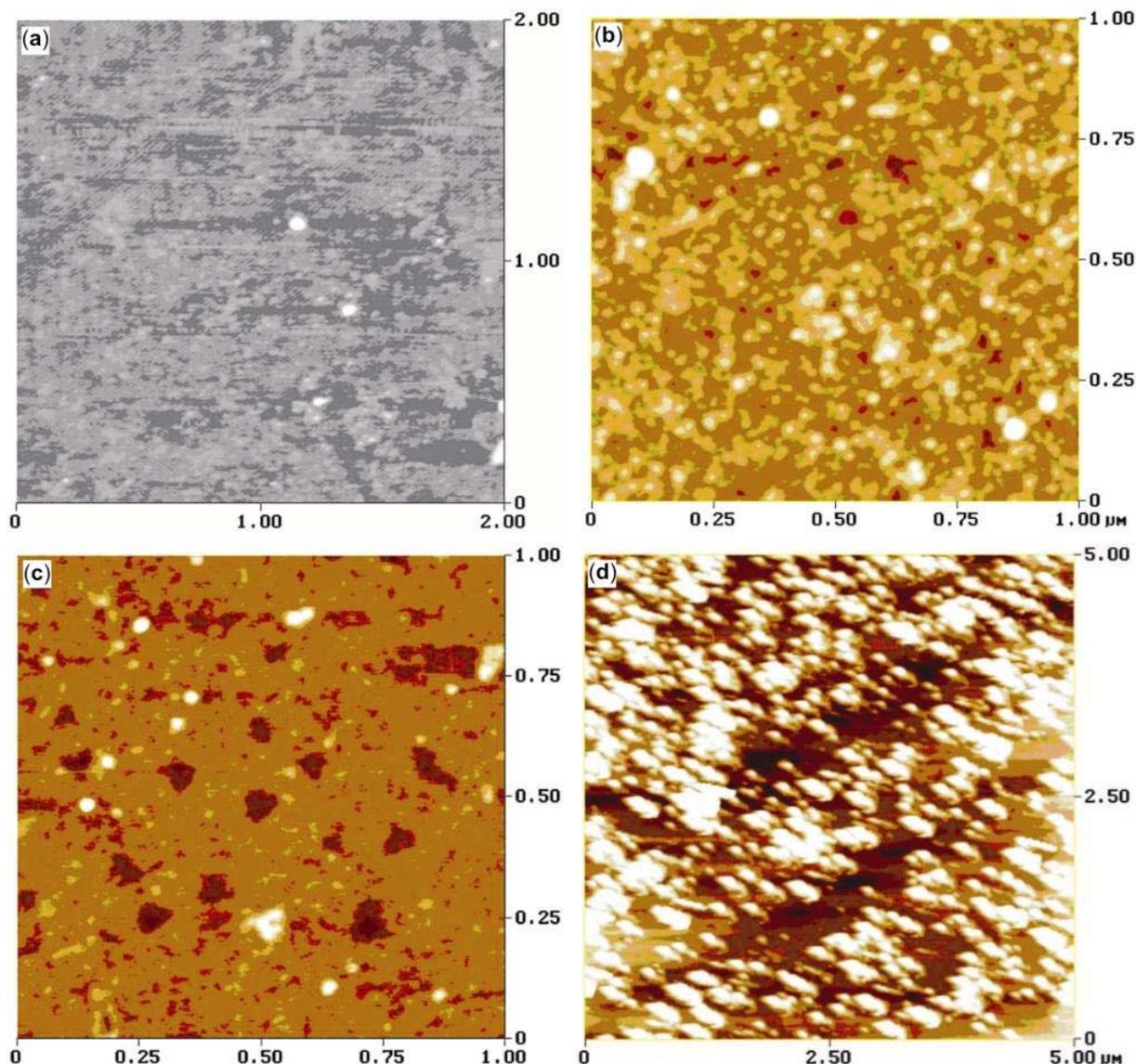


Figure 1. AFM images of (a) hydroxide substrate, (b) MPTS SAM, (c) oxidized MPTS SAM and (d) TiO_2 thin films.

force of TiO_2 thin films is lower than that of silicon substrate at the same relative humidity. It can also be seen that the friction force of silicon substrate decreases with relative humidity and the friction force of TiO_2 thin films is not sensitive to the change of humidity. The thin adsorbed water layer on sample surface can produce capillary force and with thickness of water layer capillary force became larger in moist condition. The normal force becomes larger with the increase of capillary force because the direction of capillary force is consistent with the direction of load. From the above studies, it was found that the adhesive force of TiO_2 thin films was smaller than that of silicon substrate, which indicated that water layer was not easy to adsorb on the TiO_2 thin films. According to the above discussion, the normal force of

TiO_2 thin films was smaller than that of silicon substrate and friction force of TiO_2 thin films did not change with the increase of humidity. The fact that silicon substrate showed lower friction force at high RH suggested that a thin adsorbed water layer can act as a lubricant. It may be related to the thickness of the adsorbed layer. When the adsorbed layer was thick enough, it can act as a kind of liquid lubricant rather than forming water capillary.

3.2b Influence of scanning speed on adhesive and friction forces: The effect of sliding velocity on the adhesive forces of silicon substrate and TiO_2 thin films is shown in figure 5. It can be seen that the adhesive forces of silicon substrate and TiO_2 thin films do not change with the increase of sliding velocity. The adhesive force

of sample surface is mostly affected by van der Waals force and capillary force. The change of sliding velocity did not affect van der Waals force and capillary force. So the adhesive force did not depend on the sliding velocity of tip.

The effect of scanning speed on the frictional force of silicon substrate and TiO₂ thin films was observed using a Si₃N₄ tip. Scan area was set to 2 × 2 μm and normal load was set to 10 nN. The influence of sliding velocity on the friction force is studied as shown in figure 6. It was shown that for a silicon substrate, cleaned by Piranha solution just before the friction test, the friction force increased with the increase of velocity. For TiO₂ thin film, the friction force also increased with velocity. But the friction force of silicon substrate was higher than that of TiO₂ thin films at lower velocity. And the increase in friction force with velocity was large for silicon substrate

as compared to TiO₂ thin films. This difference was caused by the difference of the high stiffness and the viscoelastic properties of substrates. The quick increase in friction force at high velocities was the result of asperity impacts and the corresponding high frictional energy dissipation at the sliding interface.

The SAM molecules reorient under the tip normal load. As the tip proceeds along the scan direction, the molecules are ‘relieved’ from the tip load and reorient to their initial position. For our experiments, the underlayer of TiO₂ thin films was the MPTS SAM. MPTS molecules whose chain is short and rigid responds anelastically to mechanical deformation under the tip normal load with recovery after load release having a short relaxation time. When more time was available for reorientation before the tip reached the same location on the sample surface again, most of molecules in the wake of the tip scan

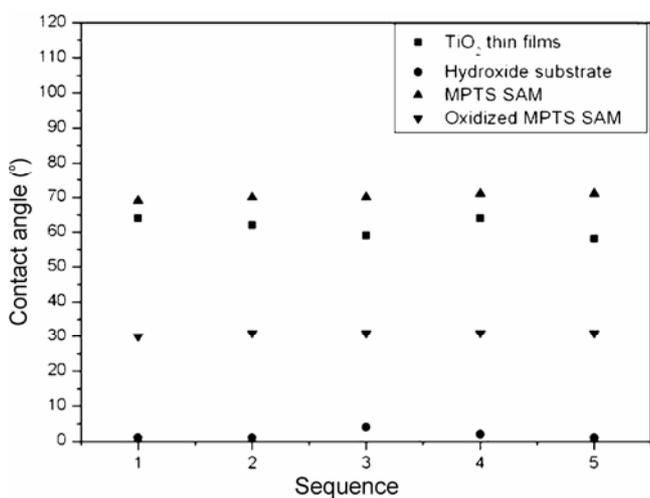


Figure 2. Contact angle of hydroxide substrate and different SAMs.

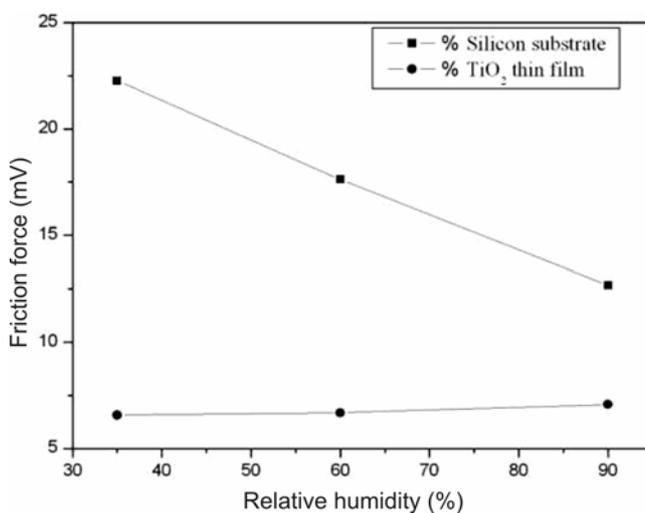


Figure 4. Variation of friction forces with humidity.

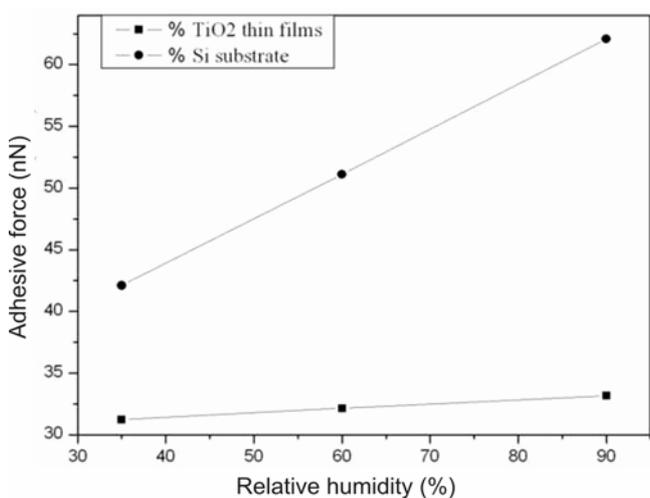


Figure 3. Variation of adhesive forces under various humidity.

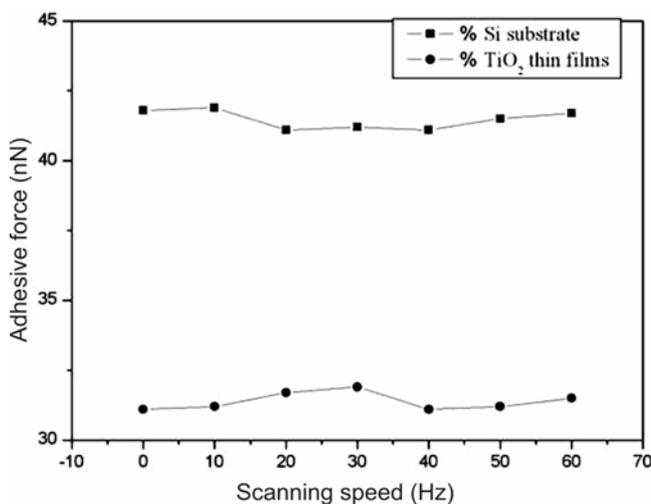


Figure 5. Variation of adhesive forces with scanning speed.

direction will spring back. The results above suggested that the friction force of TiO₂ thin films changes slightly with increasing velocity.

3.2c Influence of load on adhesive and friction forces:

The average values of adhesive force measured by contact mode AFM were presented in figure 7. It showed the adhesive forces between the SPM tip and sample at various applied normal loads in 35% relative humidity. Figure 7 showed that the adhesive force of TiO₂ thin films is lower than that of silicon substrate. As the applied normal load increased from 0 to 70 nN, the adhesive force did not change. It was noted that the contact angles of the hydroxide silicon substrate and the TiO₂ thin films are 1° and 64°, respectively which indicated that surface energy of the substrate can be obviously reduced when TiO₂ thin films was coated on the silicon substrate. The result implied that the wetting characteristics are important factors that affected the adhesion. The adhesive force of sample

surface is mostly affected by van der Waals force and capillary force. The capillary force of sample surface is related with water layer on the surface. When the relative humidity of condition did not change, capillary force of sample surface did not change. The van der Waals force of sample surface is related with the distance between the AFM tip and sample surface. Therefore, the change of load did not affect van der Waals force and capillary force.

Figure 8 shows the influence of normal load on the friction of TiO₂ thin films and silicon substrate. Friction force signals were obtained by scanning a 2 × 2 μm area at speed, 5 Hz, using an AFM. From the results, it was found that for TiO₂ thin films and silicon substrate, the friction force increased with increasing load. And the TiO₂ thin films showed lower friction than silicon substrate in the testing range of the loads. The difference in the frictional behaviour of TiO₂ thin films and substrate may be due to the difference of the surface energy values and surface roughness. From the results above, it was noted that the silicon substrate had a lower surface roughness but a higher surface energy value than the TiO₂ thin films. The normal force is the sum of load and adhesive force. From the above research, the adhesive force of TiO₂ thin films was smaller than that of silicon substrate. Therefore, the normal force of TiO₂ thin films was smaller than that of silicon substrate, and friction force of TiO₂ thin films was smaller than that of silicon substrate in same load. From our studies, it could be found that the water wetting characteristics played an important role on the nano-friction. The strong bonding between the film and surface can withstand the shear due to frictional force at light loads. Figure 8 also shows that the friction force increased linearly with the applied normal loads while friction force existed even at a zero applied normal load. It was thought that the adhesive force caused by a capillary action was mainly responsible for this friction force.

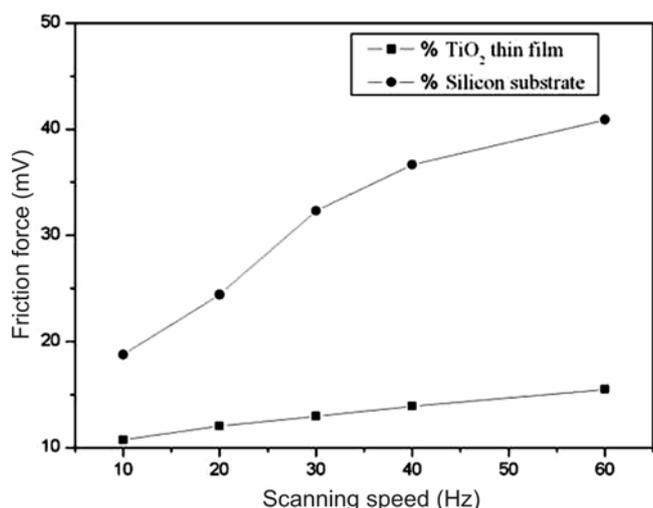


Figure 6. Variation of friction forces with scanning speed.

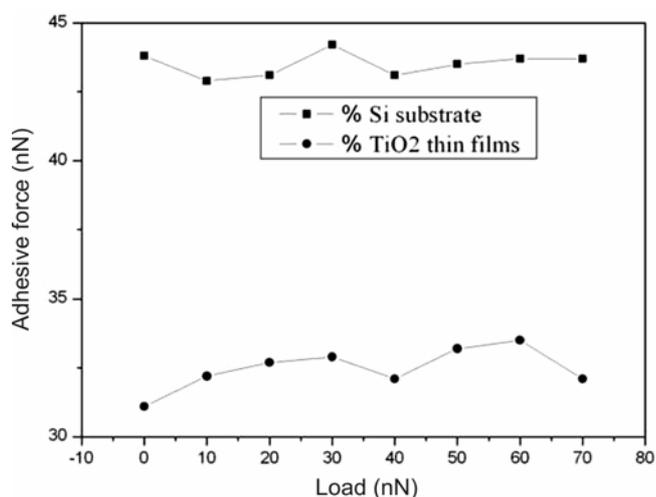


Figure 7. Variation of adhesive forces with loads.

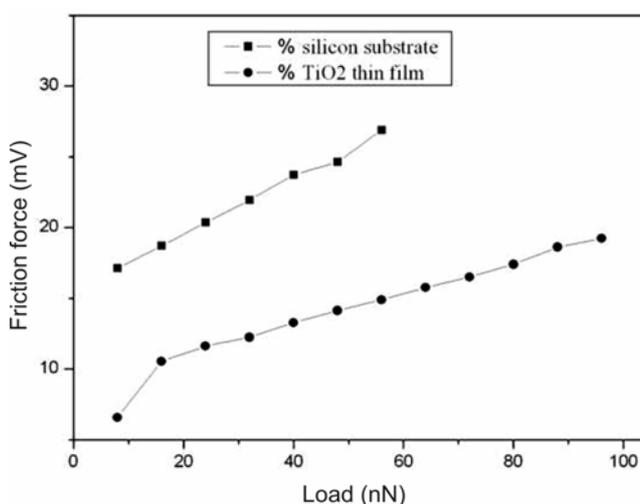


Figure 8. Variation of friction forces with loads.

4. Conclusions

(I) TiO₂ thin film was obtained using the self-assembly technique on MPTS SAM. Compared with bare silicon substrate, the adhesive force of TiO₂ thin films coated silicon was much less sensitive to relative humidity conditions, applied load, and scanning speed of tip.

(II) For TiO₂ thin film, the friction force increased slightly with the increase of relative humidity, applied load, and scanning speed of tip. And the TiO₂ thin films showed lower friction than silicon substrate in the same test condition.

(III) The adhesive force of sample surface is mostly affected by van der Waals force and capillary force. The influence of van der Waals force on the adhesive force is not affected by environment. The lower adhesive force of TiO₂ thin films was attributed to non-polar surface terminal. The lower friction of TiO₂ thin films is dominated by the lower adhesive force of TiO₂ thin films.

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