Investigation of Molecular Rearrangement by AFM Analysis of SAMs Annealing Process

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ABSTRACT

Self assembly monolayers (SAMs) are easily prepared nano-film, and have been widely applied to improve device surface properties and biomaterial conjugation on substrates. Among various steps, annealing is one of the general processes for the improvement of SAMs formation quality. However, there have been not many methods developed to investigate the effects of this parameter quantitatively. This paper proposes to quantitatively investigate the effects of annealing on SAMs by both contact angle and interaction force measurement by AFM. Results demonstrate the quality of nano-film would been greatly improved by annealing process, and the film properties are also functions of temperature. The results demonstrated molecular rearrangement under thermal factor.

Keywords: *AFM, annealing, self-assembly monolayer, adhesion,*

1 INTRODCUTION

The structure stability of self assembly monolayers (SAMs) has been extensively studied in recent years, because they have wide applications for electrode modifications[1], biosensors [2], and reduction of surface adhesion[3]. The most studied SAMs system is alkanethiol group which can be adsorbed on Au surface, and the thermal stability of this type SAMs is very important for many applications. There have been several reports about thermal influence on the disorder of the films [4-7]. The most employed investigation methods are scanning tunneling microscopy (STM), infrared spectroscopy, or X-ray diffraction. Due to the film is fast adsorbed on substrates and VDW interaction increase chain disorder[8], so annealing process after self assembly monolayers preparation is a general treatment mean. However, there are few efforts on the investigation of structure variation of alkylsilane SAMs after annealing or thermal treatment, because silicon oxide, on which alkylsilane SAMs are asorbed, is a amorphous material with neither organized structure nor conductive property for STM study. Therefore, in this paper, we study alkylsilane SAMs' structure variation after annealing and thermal process by both contact angle and interaction force measurement by AFM. The multiple channel information of AFM, including height mode scanning, lateral deflection mode scanning, and adhesion mapping, will be employed for the analysis to investigate the molecule rearrangement process under different temperature conditions, and the principle is schematically shown in Fig. 1.

2 MATERIAL AND METHOD

2.1 Sample preparation

SAMs preparation : commercially available Si(100) wafers were cut into pieces of 1.5x1.5cm^2 and subsequently cleaned and oxidized in a freshly prepared 4:1 mixture of 96% sulfuric acid and 30% hydrogen peroxide (piranha solution) at 100°C for 10 minutes. After the substrates cooled to room temperature, the samples were rinsed with DI water and dried in N_2 gas. After drying the oxidized silicon samples were immediately immersed into a freshly prepared 0.5% APTS (3-aminoproplytrimethoxysilane, Fluka,) in dried ethanol at room temperature (25^{o}C) for 65 minutes at room temperature.

Annealing : The APTS chips were annealed at 80^{o}C under N_2 gas for 2hr.

Temperature conditions: The prepared APTS chips been annealed at 20^{o}C, 40^{o}C, 60^{o}C, 80^{o}C, 100^{o}C, 120^{o}C, 200^{o}C under N2 gas for 2hr, respectively.

2.2 Measurement

In situ AFM measurement were performed using JPK NanoWizard AFM (Germany). The AFM operated on contact mode, and the employed cantilevers are ultrashap silicon cantilevers CSC38/AIBS of Micromash. Scan size is 5um x 5um, x-y resolution is 512x512 pixels. All height mode and lateral deflection mode were captured at the same time. Force mapping was also performed by AFM to obtain information on molecular interactions. (Fig.1,2)

Adhesion force were measured by JPK NanoWizard AFM (Germany). Adhesion forces were Mapped within 5umx5um 64x64 grids, each grid was measured for 256times for adhesion force calculation.

The contact angle of surface was measured with DI water by FTA 200 at room temperature. Each chip was measured five times at different area.

2.3 Data Process and Analysis

All AFM images were adjusted by linear leveling, and transferred to 256x 256 raw data. Because AFM can't get absolute height and lateral deflection without correct reference in this study, so the analysis of standard deviation (STD) of the whole raw data was employed for indicating SAMs behavior under different conditions. Yet the local height and lateral deflection information of each pixel were used to understand in-situ relative height and lateral defection variation for the explanation of molecular behavior, as the data analysis flow chart shown in Fig.3.

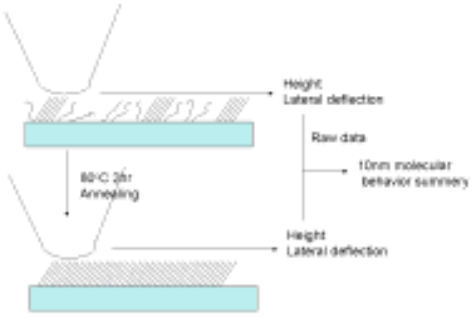

Fig.1 Schematics of height and lateral deflection mode by AFM for the characterization of molecular behavior.

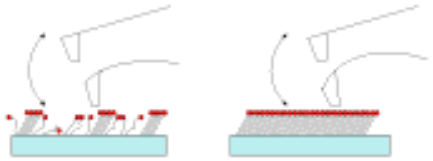

Fig.2 By mapping adhesion force of substrate, the molecule status can be obtained.

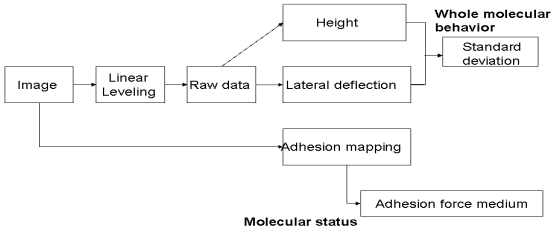

Fig.3 Data analysis process flow chart.

3 RESULT AND DISCUSSION

To reveal molecular-level rearrangement of alkylsilane SAMs immobilized on silicon dioxide surface under different annealing conditions, AFM investigation including height scanning, lateral deflection scanning, and adhesion mapping were utilized.

From the macro phenomenon of contact angle variation shown in Fig. 4 for SAMs before and after annealing, suggested that the molecule structures of SAMs might be rearranged during the process. Through the exploration of lateral deflection and adhesion force of AFM on SAMs, the increment of adhesion between SAMs and cantilever can be verified. On the other hand, the STD of height and lateral deflection of AFM on SAMs after annealing may reveal the random status of SAMs. Fig.5 and 6 demonstrate the STD of both values after annealing are reduced and close to those of substrate original surface. Lower STD means the more uniform, homogeneous and organized SAMs structure obtained. Besides, adhesion force can provide the information of the vertical interaction force between cantilever and SAMs molecules. In Fig. 7, stronger adhesion force between cantilever and SAMs is obtained after annealing process, due to more organized SAMs molecules leading to denser NH_2 group which may keep water thin film on surface to increase adhesion force. When the NH_2 group turning out, the adhesion force increase significantly. During the annealing process, the thermal energy causes molecules to swing or rearrange providing opportunity for random distributed SAMs to form a homogeneous or closer arranged film. According to Wenzel model developed in 1936 [9], and gave the following equation [10]

$$\cos \theta \text{ rough} = r \cos \theta \text{ true} \qquad (1)$$

Where the $\cos \theta$ rough is the apparent contact angle of the rough surface, $\cos \theta$ true is the contact angle of a flat identical surface, and r is the ratio of actual to project surface area. This equation means the roughness of a hydrophilic surface would reduce the contact angle of the same material with flat surface. The contact angle measurement results in Fig. 4 demonstrated the same trend.

In the temperature dependency, the contact angles of annealed SAMs seem to increase mildly with a increasing of annealing temperature, as shown in Fig. 8. The effects of annealing start to happen even at a low temperature of 20 °C. This suggests that the film would slowly rearrange under room temperature, yet higher temperatures provide more thermal energy that can cause the molecular rearrange more effectively.

On the other hand, as annealing temperature increases, the force between cantilever and molecules become lager, implying the more organized film formation providing stronger interaction between surface functional group of

SAMs and cantilever, as shown in Fig. 9. The maximum adhesion force appears at 120 °C with a value almost 60 times higher than that at 20°C. However this tendency can not be applied for the case of 200 °C because of the damage of the film from high temperature. The evidence of film damage can be observed from Fig. 10, the histogram of the adhesion properties of different cases. If the film is in a well organized status, the histogram of the adhesion force would be concentrated into a peak with small STD, as the histograms for the cases of 20°C to 120 °C in Fig. 10. On the contrary, the histogram of the 200 °C is scattered without a significant peak value in Fig. 10, implying very unorganized film structures.

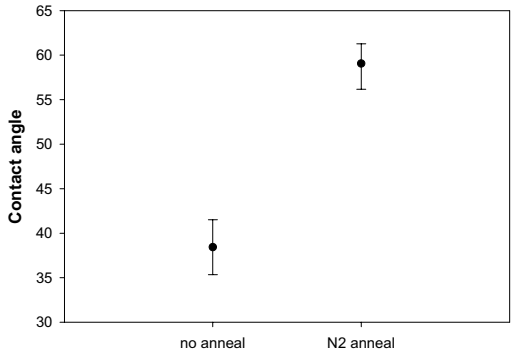

Fig.4 Contact angle measurement on APTS coated chip before and after annealed at 80oC for 2hr under nitrogen environment.

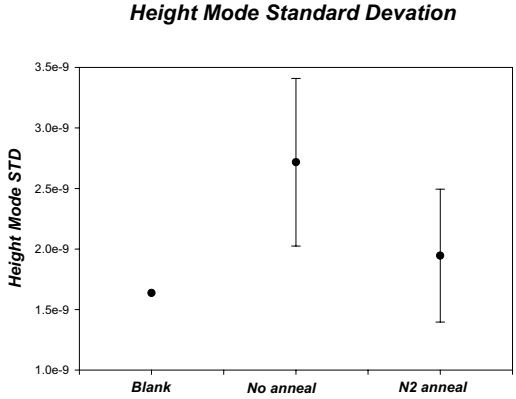

Fig. 5 The STD of height mode scanning for substrate with different APTS annealing conditions.

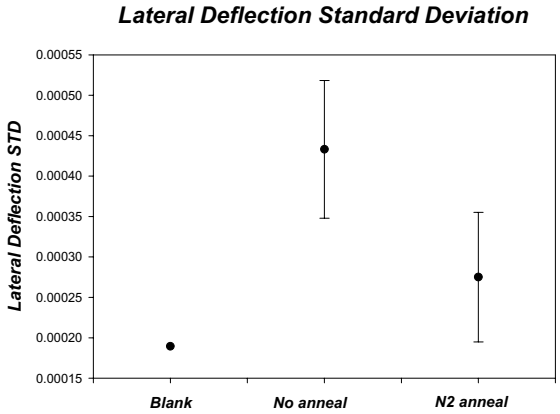

Fig.6 The STD of lateral deflection mode scanning for substrate with different APTS annealing conditions.

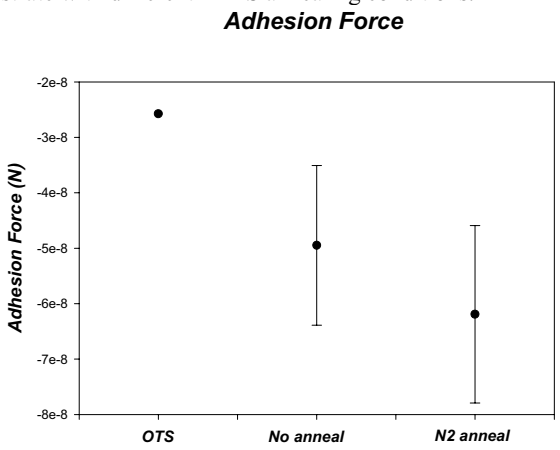

Fig.7 Adhesion force measurement by directly taping AFM cantilever on APTS surface for different annealing conditions. APTS with NH_2 group show stronger adhesion force than OTS that only contain alkyl group. After anneal process, the surface has even stronger adhesion than that of the non-annealed one.

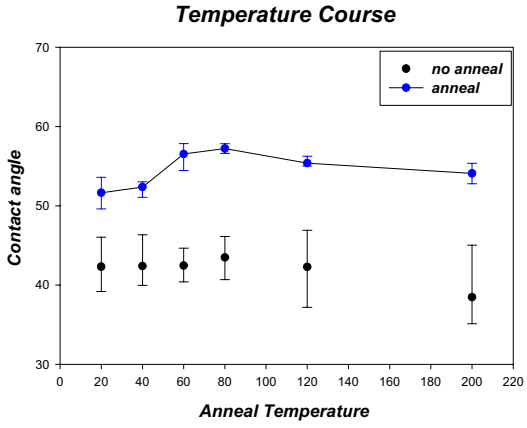

Fig.8 The surface contact angle of DI water on different annealing temperature condition. The black spots represent the contact angles of APTS before annealing process, while blue ones represent the contact angles after annealing under different temperature conditions.

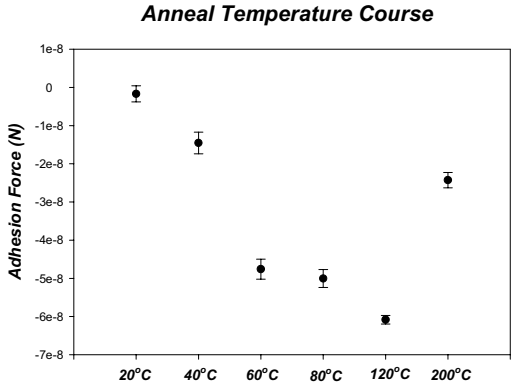

Fig.9 The measured adhesion forces between AFM cantilever and SAMs (APTS) under different annealing temperatures.

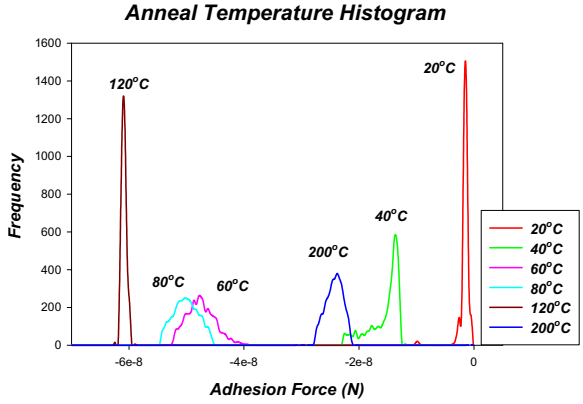

Fig.10 The histograms of adhesion forces between AFM cantilever and SAMs (APTS) under different annealing temperatures.

4 CONCLUSION

In this research, we have studied the temperature influence on the surface properties and orders of APTS SAMs immobilized on silicon oxide by AFM. In height mode observation, the film carried out smoother profile after annealing process. For lateral deflection, friction force decreased owing to surface roughness reduction after annealing. Both of the results also consistently indicate the SAMs molecules becoming a more homogeneous and organized film after annealing. In the vertical interaction force measurement, the adhesion forces obviously increase as the annealing temperature increases. This reveals the hydrophilic group that can hold water thin film turns outside and attracts cantilever. According to above evidence, we can prove that the SAMs molecules rearrange after annealing process and the rearrangement would be strongly influenced by temperature variation. At different temperature, the adhesion force would make 6-10 fold improvement. The contact angle of non-annealed film also appear a lower value owning to larger wetting area from more random molecule distribution compared to that of the annealed one. The variation of contact angle on SAMs surface only have mild effect when the annealing temperature changed from 20-120 °C. This analysis can be applied to many different SAMs system for characterizing their nano scale properties.

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