In-situ Study of SAMs Growth Process by Cross Analysis of AFM Height and Lateral Deflection

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ABSTRACT

This paper introduces a novel way to investigate SAMs growth process by cross analysis of the information of AFM height and lateral deflection scanning results. The traditional ways by analysis of AFM height and histogram data can not differentiate the molecular growth detail behavior of alkylsinae SAMs because the images captured by AFM are static and lack molecular level information. Thus, this paper proposes to employ the standard deviation of AFM data to analyze the in-situ growth behaviors of alkylsinae SAMs in comparison with the local height and lateral deflection data. The analysis results demonstrated close correlation of the SAMs growth process among the aforementioned data analysis methods.

Keywords: *In-Situ, AFM, growth, self assembly monolayer, lateral deflection*

1. INTRODUCTION

Self assembly monolayers (SAMs) has been studied since 1945 [1], and play an important role in the modification of nano-properties for micro devices, owning to their easy preparation, capability of the design of functional groups on the molecule head and tail, chain length and specie selection, and simple fixing method on substrate, thus extensively applied to biotechnology, nanotechnogy, nanopattern [2], material science and Microelectronmechanical System (MEMS)[3].

Among different SAMs' systems, the growth mechanism of alkanethiol SAMs on gold substrate were most studied [4,5], partially due to the more regular gold crystalline surface for AFM and conductive substrate ready for STM studies. However in alkylsinae SAMs, they are usually applied on surfaces with oxides, not a surface with regular crystal structures and conductive. As a result, the surface roughness of oxides, usually close to the height of SAMs, will greatly affect AFM measurement. Yet alkylsinae SAMs are commonly applied to silicon or glass substrate based micro devices. Therefore, this study focus on the investigation of the in-situ self-assembly processes of alkylsinae SAMs, including nucleation, growth and integration processes by AFM techniques and new data analysis methods.

There have been many progresses in characterization of SAMs growth process in the past 15 years [6] owing to the invention of new tools, such as Atomic Force Microscope (AFM), XPS, ellipometry, etc. However most of those methods measuring the average properties such as morphology or height of sample in at least μm^2 area, can not bring out detail information about nucleation, clustering, growth progress, and their molecular behaviors in nano scale. Although Brewer had investigated SAM phase separation by chemical force microscopy at 2004 [7], the histograms of pull-off forces still can't explain molecular dynamic behaviors. In this research, we propose a novel method that can carry out more nano scale information on SAM growth mechanism by cross analysis of AFM height and lateral deflection in raw data and standard deviation at same time for different SAMs growth stages.

2. MATERIALS AND METHODS

2.1 Sample 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 10min. After the substrates have been allowed to cool 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 10^{-3}(v/v) solution of OTMS (Octadecyltrimethoxysilane, Fluka 74763) in dried ethanol at room temperature (25^{o}C).

2.2 Measurement

In situ AFM measurement were performed using JPK NanoWizard AFM (Germany). The AFM operated in contact mode by ultrashap silicon cantilever (CSC38/AIBS of Micromash, Russia). In-situ image were continuously captured in a 256-second period, and the whole experiment acquired 67 images within 17152 seconds. Scan size was 5um x 5um with a x-y resolution of 256x 256 pixels. All the information measured by height mode and lateral deflection mode were obtained at the same time. (Fig.1)

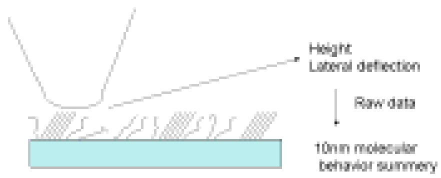

Fig.1 Schematic of multiple-channel AFM image analysis: height and lateral deflection analyzed at one time.

2.3 Data Process and Analysis

All images have been adjusted by linear leveling, and transferd into to 256x 256 raw data. Because the height and lateral deflection are not under the same reference, the analysis of standard deviation (STD) of the whole raw data provides the distribution of SAMs status on the measured area and information of integral molecular behavior in stead. On the other hand, the analysis of the relative height and lateral defection variation in each pixel can indicate molecular status at the local region for comparasion. The analysis flowchart is shown in Fig.2.

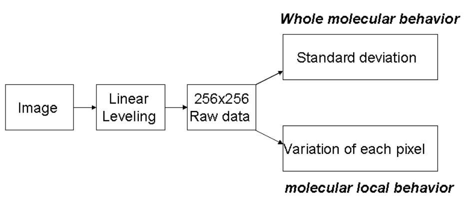

Fig.2 The flowchart of data process and analysis.

3 RESULT AND DISCUSSION

By analyzing the raw data of the whole image, the standard deviation (STD) increases very fast then decreases to the initial one in both height mode and deflection mode scanning results, as shown in Fig. 3 and 4. The higher standard deviation mean the larger variation resulted from molecular random distribution on substrates. On the contrary, when the SAMs grow into a complete nano-film and fill up the substrates, the STD decreases into that of the initial stage, meaning the surface properties, including roughness (from the height data) and friction forces (from the lateral deflection data), become very uniform as those on the bare substrate surface. Therefore, the growth process in Fig. 3 can be classified into 4 stages based on the cross correlation between the STD of height and lateral deflection data. In the growth process, the STD of height appears rapid increasing stage (A-B), decreasing stage (B-C), standing stage (C-D) and decreasing stage (D-F), in Fig 3, meaning that group SAMs molecular nucleated first (A-B), partially leaving (B-C), forming cluster (C-D) and filling up substrate (D-F). The lateral deflection in Fig. 4 means fluctuated friction forces on surfaces with high roughness and low stability at the stage of A-C, the friction forces are then rapidly reduced owning to more stable cluster formation on the surface at the stages of B-D, and then the friction further reduce into lower level than that of the bare silicon dioxide surface owning to complete and flat film formation as well as lower friction on OTMS film than that of silicon surface because of more hydrophobic functional group on the tip of OTMS. The process is schematically shown in Fig. 5.

To better verify this point of view, in addition to the average STD throughout the whole chip, the relative heights and lateral deflections of individual pixels in nano scale are also analyzed and the results are shown from Fig. 6 to Fig. 10. The local height information in Fig. 6 shows that molecules stack firstly in group, leave, then gradually stack again, and eventually form complete films on the substrate. This process is schematically shown in Fig. 7, and demonstrates a similarity to that in Fig. 5.

The height of SAMs gradually increasing in Fig. 6 and 8 shows molecule standing-up from lying and scattering status, and gradually form complete film when time goes by. The existing of Multiple layers can also be verified form the height variation couple times of molecular length. All those individual behavior have been averaged out in the overall behavior in Fig. 3 and 4.

Not like the height one, local lateral deflection information does not reveal large variation versus time in Fig. 9 and 10, yet the local fiction forces are lower than that of bare silicon dioxide surface (decreases from 0.04 to -0.08), consistent with the surface properties for silicon dioxide and OTMS and the data analysis in Fig. 4.

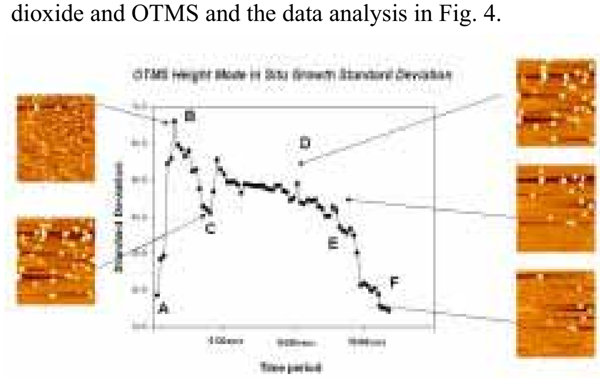

Fig.3 The standard deviation of height mode AFM scanning data at different time stages of SAMs growth.

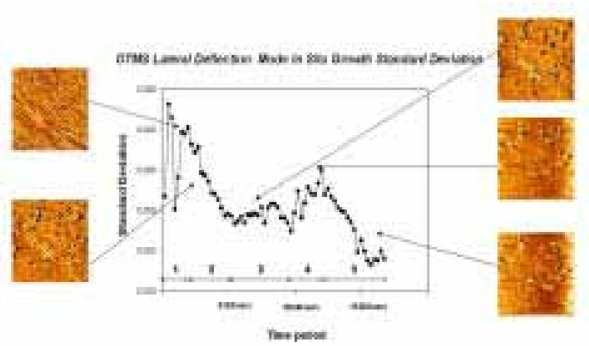

Fig.4 The standard deviation of lateral deflection mode AFM scanning data at different time stages of SMAs growth.

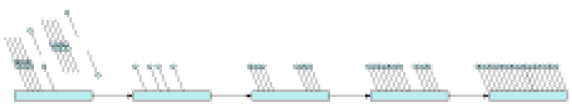

Fig.5 Schematic Diagram of SAMs growth process.

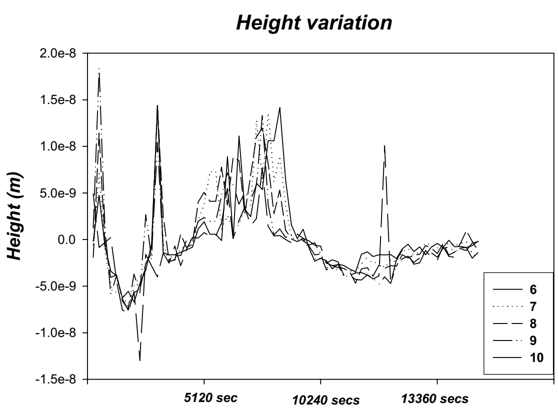

Fig.6 The height variation data of SAMs growth in an area containing 6th-10th pixel that were captured randomly from 65536 pixels at different time.

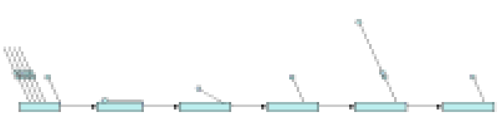

Fig.7 Schematic diagram shows the local behaviors of molecules.

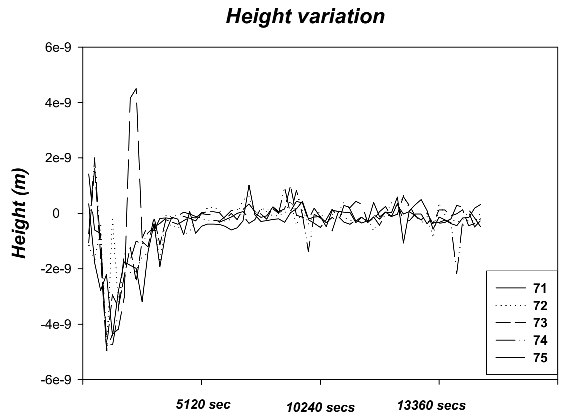

Fig.8 The height variation data of SAMs growth in an area containing 71th-75th pixel that been captured randomly from 65536 pixels at different time

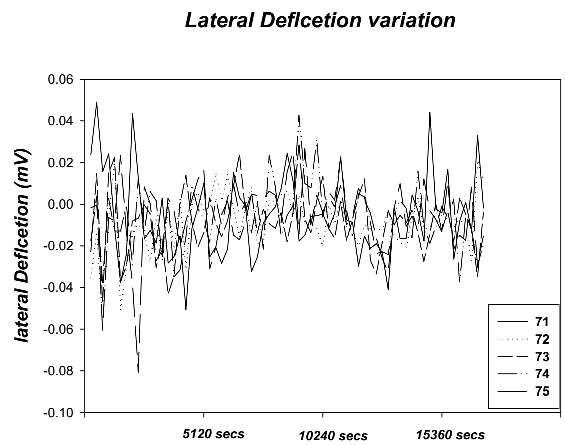

Fig.9 The lateral deflection variation data of SAMs growth in an area containing 6th-10th pixel that been captured randomly from 65536 pixels at different time.

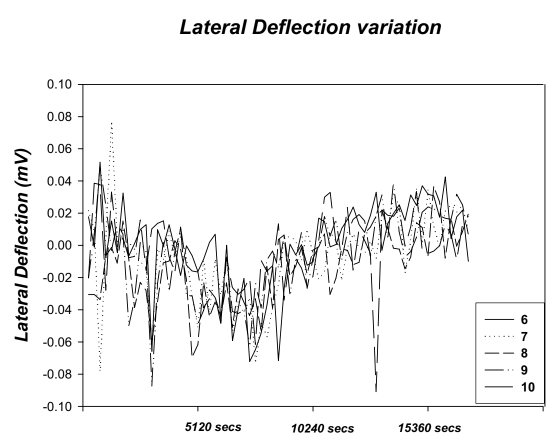

Fig.10 The lateral deflection variation data of SAMs growth in an area containing 71th-75th pixel that been captured randomly from 65536 pixels at different time.

4 CONCLUSION

This paper introduces a novel way to investigate SAMs growth process by cross analysis the information of AFM height and lateral deflection scanning results. The analysis results show that the growth of alkylsinae SAMs have 4 different stages including group SAMs molecular nucleated, partially leaving, forming cluster and filling up substrate. Those results are also verified by the local height and lateral deflection data. This method provide an alternative to the traditional AFM analysis ways on only morphology and histogram of scanned image, carrying out more meaningful information on the explanation of SAMs growth process.

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