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FORMATION OF OTS SELF-ASSEMBLED MONOLAYER ON GLASS SURFACE INVESTIGATED BY AFM*

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Abstract: The whole process of octadecyltrichlorosilane (OTS) self-assembled monolayer formation on glass surface was clearly revealed by using Atomic Force Microscope (AFM). The growth regularity pattern of OTS self-assembled monolayer on glass substrate was obtained by analyses of the AFM images and the average surface mean roughness (R_{avg}) of the sample surfaces. The adsorption feature of OTS molecules on the substrate surface during the initial reaction period was probed through a comparison experiment.

Key words: octadecyltrichlorosilane (OTS), self-assembled monolayer, Atomic Force Microscope (AFM)
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INTRODUCTION

Since Sagiv (1980) investigated the reaction of octadecyltrichlorosilane (OTS) molecules with slide glass plates to form self-assembled monolayers in 1980 for the first time, many researches have been conducted to study the formation of OTS monolayers on mica, silicon, silica and glass substrate surfaces by self-assembly of OTS molecules due to its extensive applications in various research fields. Those researches dealt with wide-ranging aspects of the reaction, including the hydrolysis mechanism of OTS molecules (Sagiv, 1980; Angst et al., 1991; Carson et al., 1989; Carson et al., 1990; Kessel et al., 1991; Peanasky et al., 1995), the adsorption feature of OTS molecules on the substrate surfaces (Tripp et al., 1992; Tripp et al., 1995; Hair et al., 1995; Xiao et al., 1995; Maoz et al., 1984), the role of the solvents (Maoz et al., 1984; Gun et al., 1986; McGovern et al., 1994), the influence of the reaction temperature (Silberzan et al., 1991; Brzoska et al., 1992), the influence of the alkylchain length and the terminal function groups (Bierbaum et al., 1995a; Bierbaum et al., 1995b; Tripp et al., 1993), and the substrate materials and its pretreatments (Ulman, 1991; Barrat et al., 1992). But the nature of the reaction of OTS molecules with hydroxylic substrate surfaces to form self-assembled monolayers is still not very clear; different opinions were reported in the literature.

Our use of the Atomic Force Microscope (AFM) in this work clearly revealed the whole process of OTS monolayer formation on glass surface by self-assembly from 1×10^{-3} mol/L OTS-toluene solution at 18℃, and yielded the growth regularity of OTS self-assembled monolayer on the glass surface. We probed the adsorption feature of OTS molecules on the substrate surface during the initial reaction period.

EXPERIMENTAL DETAILS

1. Chemicals.

OTS was purchased from Shin-Etsu Co., Ltd., Japan, and used as received without further treatment. Toluene, chloroform, acetone, nitric acid and sodium hydroxide were all of analysis reagent grade. The deionized water used in AFM experiments was distilled water with further purification by a Milli-Q ion-exchange purification system.

2. Pretreatment of the glass substrate surface.

The 12 mm diameter micro cover glass plates (from Digital Instrument Inc., USA) were

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cleaned by sonication in an ultrasonic cleaning tank with household use detergent solution, concentrated nitric acid, 5×10^{-3} mol/L sodium hydroxide solution, for 10 min, respectively. After each sonication, the glass plates were rinsed with distilled water, and finally sonicated in deionized water again for 10 min, then dried in a stream of nitrogen gas.

3. Preparation of OTS self-assembled monolayer.

The modification reaction of the glass plates was conducted in a 50 mm diameter, 10 mm deep Teflon cup under open air laboratory conditions. The well-cleaned glass plates were rapidly immersed in the freshly prepared 1×10^{-3} mol/L OTS-toluene solution from 20 sec to 2 hr as the experimental requirements, then withdrawn from the solution as quickly as possible. After the reaction, the modified glass plates were rinsed in chloroform, acetone, and chloroform again, to remove excess deposits, then dried in a stream of nitrogen gas. According to Brzoska et al. (1992), a high quality n-alkyltrichlorosilane monolayer could be obtained only when the reaction temperature was below the temperature threshold. For OTS the temperature threshold is about 28 ℃. Because of the AFM image's nanometer resolution, any subtle changes of the reaction conditions were reflected in the AFM images. In this experiment, the reaction temperature was strictly controlled at 18 ± 0.1 ℃.

In the sample preparation, two very important, but usually neglected experimental measures should be emphatically followed:

(1) Sagiv (1980) suggested that the glass slides should be immersed into or withdrawn from the reaction solution at a velocity of 2.7mm/s. We found this velocity prevented the deposition of the undissolved, disordered condensations of OTS hydrolysates on the sample surfaces. It is well known that OTS is easily hydrolyzed. If the OTS solution is exposed in the open air, the OTS molecules will be hydrolyzed into silanol even under the atmospheric humidity, and further form undissolved, 3-dimensional disordered polymerized condensations (Sagiv, 1980). In this experiment, if the 1×10^{-3} mol/L OTS-toluene solution was exposed in the open air for about 30 min, undissolved condensations appeared on the solution surface. If the glass plates were immersed into or withdrawn from the solution not so quickly, the undissolved condensations would deposit on the sample surfaces. Some condensations were too big to be easily removed by the following solvent rinsing, and could be clearly shown in AFM images. So the glass plates should be immersed into or withdrawn from the reaction solution as quickly as possible.

(2) Experiments showed that on the substrate surface, the physisorbed silane or silanol (hydrolysates of silane) molecules could be easily rinsed away by organic solvent (Carson et al., 1989; Carson et al, 1990). We believe that, specially during the initial period of the reaction, the OTS molecules or its hydrolysates may be just physisorbed on the glass surface. But those physisorbed molecules play a very important role in the growth process of the OTS self-assembled monolayer. Unfortunately, this adsorption feature during the initial reaction period is always ignored by researchers. In some experiments (Bierbaum et al., 1995a; Bierbaum et al., 1995b), even after a very short time reaction, the modified samples were so violently rinsed under the strong magnetic stirring, the original structure of the sample surface was destroyed and the information on the surface structure during the initial period of reaction was lost. In our experiments, only the samples with the reaction time longer than 15 min were washed in organic solvents by magnetic stirring for 3 – 5 min. Samples whose reaction time did not exceed 15 min were just dipped in organic solvents for 1 – 2 min and very gently rinsed by hand.

4. AFM analysis.

A Nanoscope III multimode AFM (from Digital Instrument Inc., USA) was employed to study the sample surfaces. A microfabricated Si_4N_3 triangle cantilever with a spring constant of 0.58 N/m was used for surface analysis. All surface images were captured in deionized water by using a liquid cell in contact mode. The height data type was used to collect the image data in this experiment. To ensure the captured images were the typicals, which reflected the real situation of the sample surfaces, each sample was investigated first in a large $10 \times 10\ \mu m^2$ area, then the zoom command was used to select a $5 \times 5\ \mu m^2$ typical area when the image was captured. The surface mean roughness, *Ra*, defined as the mean value of the surface relative to the central plane was analyzed by AFM off-line software.

The AFM analysis of the well-cleaned glass plates indicated that the roughness of the two sides of the glass plates was different. Each glass plate had a smooth surface with *Ra* of about 0.150 nm/25 μm^2 and a rough surface with *Ra* about 0.225 nm/25 μm^2. In our experiments, we used the smooth sides of the glass plates. Usually, the surfaces of the micro cover glass plates were always somewhat wavy. This surface waviness will affect the calculation of *Ra* considerably. Especially when the surface area is larger than 5 μm^2, the influence of the surface waviness on *Ra* must be taken into account. To eliminate the influence of the surface waviness, in this research we presented a concept of the average surface mean roughness, R_{avg}, which was obtained like this: we first measured the respective *Ra* of five 2×2 μm^2 areas covering the four corners and the central section of each image, then used the average value of the five *Ra* to characterize the roughness of the sample surface. For the surface of the smooth side of a well-cleaned glass plate shown in Fig. 1, the R_{avg} is about 0.130 nm/4 μm^2.

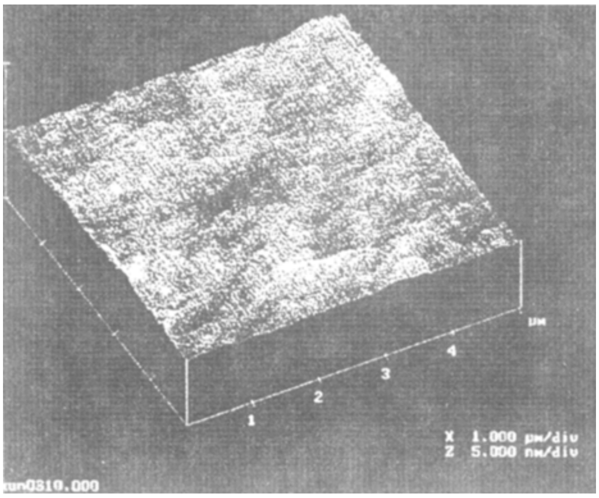


Fig.1 **A typical AFM image of the smooth side of a well-cleaned glass plate surface.**

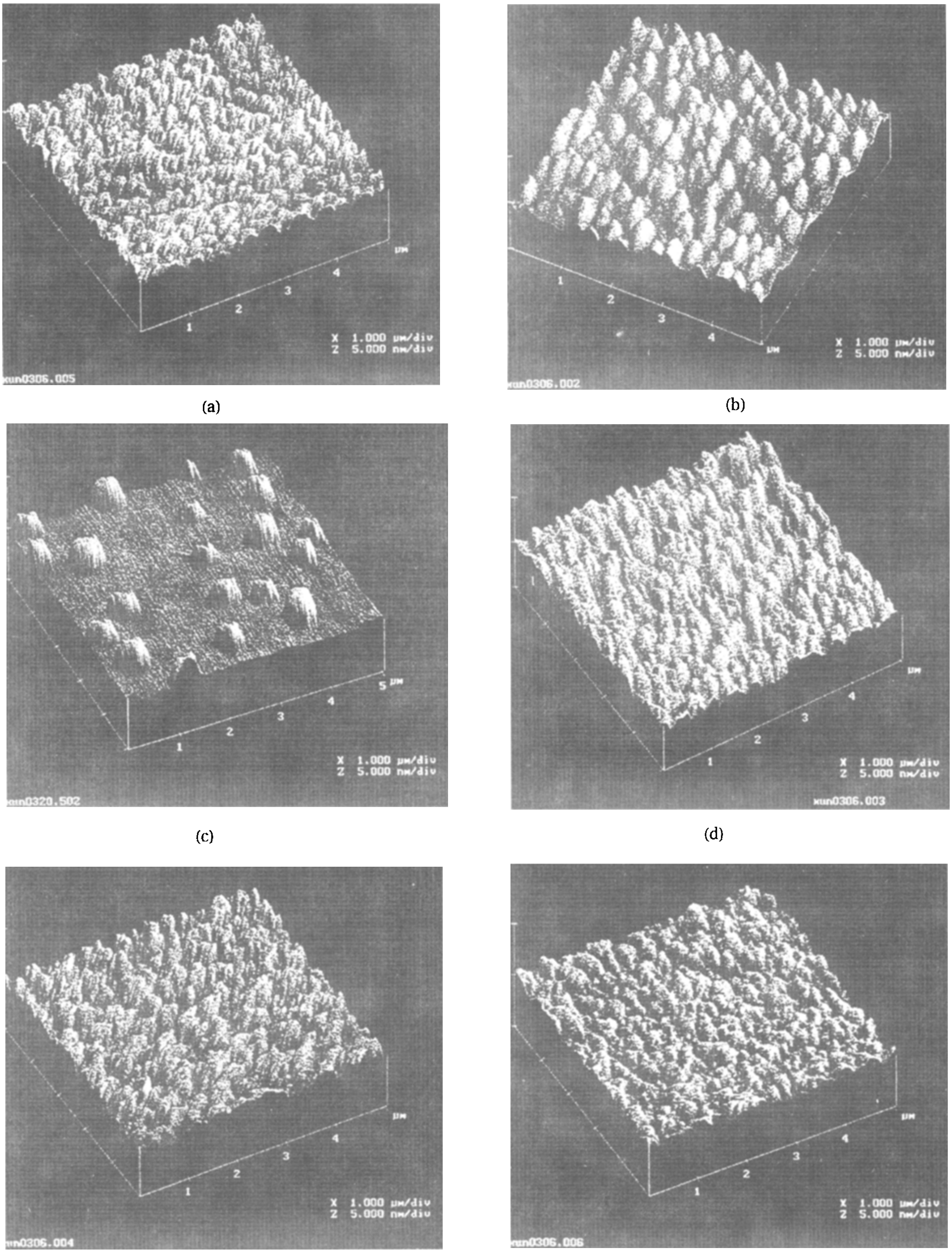
5. Advancing contact angle measurements.

Advancing contact angles were measured by growing small sessile water droplets on sample surfaces by means of a homemade apparatus under open-air conditions at room temperature. A 2.5 µl water droplet was placed on the sample surface and a close-up picture was taken by a camera. The droplet was added every 20 sec and the procedure was repeated 5 times (total 12.5 µl). The contact angles were measured by using the enlarged pictures of the developed film. The mean error of this photographic method was about ± 3 ℃.

RESULTS AND DISCUSSION

1. Kinetics of OTS self-assembled monolayer formation.

Fig. 2 clearly shows the whole process of OTS self-assembled monolayer formation on the surface of the micro cover glass plate. Only after 20 sec reaction were adsorption islands of OTS molecules or its hydrolysates formed on the substrate surface (Fig. 2a). The research showed that OTS molecules might be hydrolyzed by both the trace water dissolved in the solution and the trace water adsorbed on the substrate surface (Sagiv, 1980; Angst et al., 1991; Kessel et al., 1991; Peanasky et al., 1995; Tripp et al., 1992; Tripp et al., 1995; Hair et al., 1995; Xiao et al., 1995; McGovern et al., 1994; Silberzan et al., 1991). So the islands that appeared on the substrate surface might be made up of both the OTS molecules and its hydrolysates. It was also found that the distribution of the islands seemed somewhat uniform. As the reaction proceeded, the numbers of the adsorption islands increased rapidly and the substrate surface was covered quickly with them within 2 min (Fig. 2b – f). After 5 min reaction, the distinguishable adsorption islands on the substrate surface disappeared, and a not well-organized OTS monolayer with a rough surface appeared (Fig. 2g). Fig. 2h shows the surface image of the sample with reaction time of 15 min. It could be found immediately that the OTS monolayer formed after 15 min reaction was the smoothest and had surface shape quite similar to that of the well-cleaned glass plate (Fig. 1). However, when the reaction time exceeded 15 min, the roughness of the sample surfaces increased to an almost constant value as shown in Fig. 3.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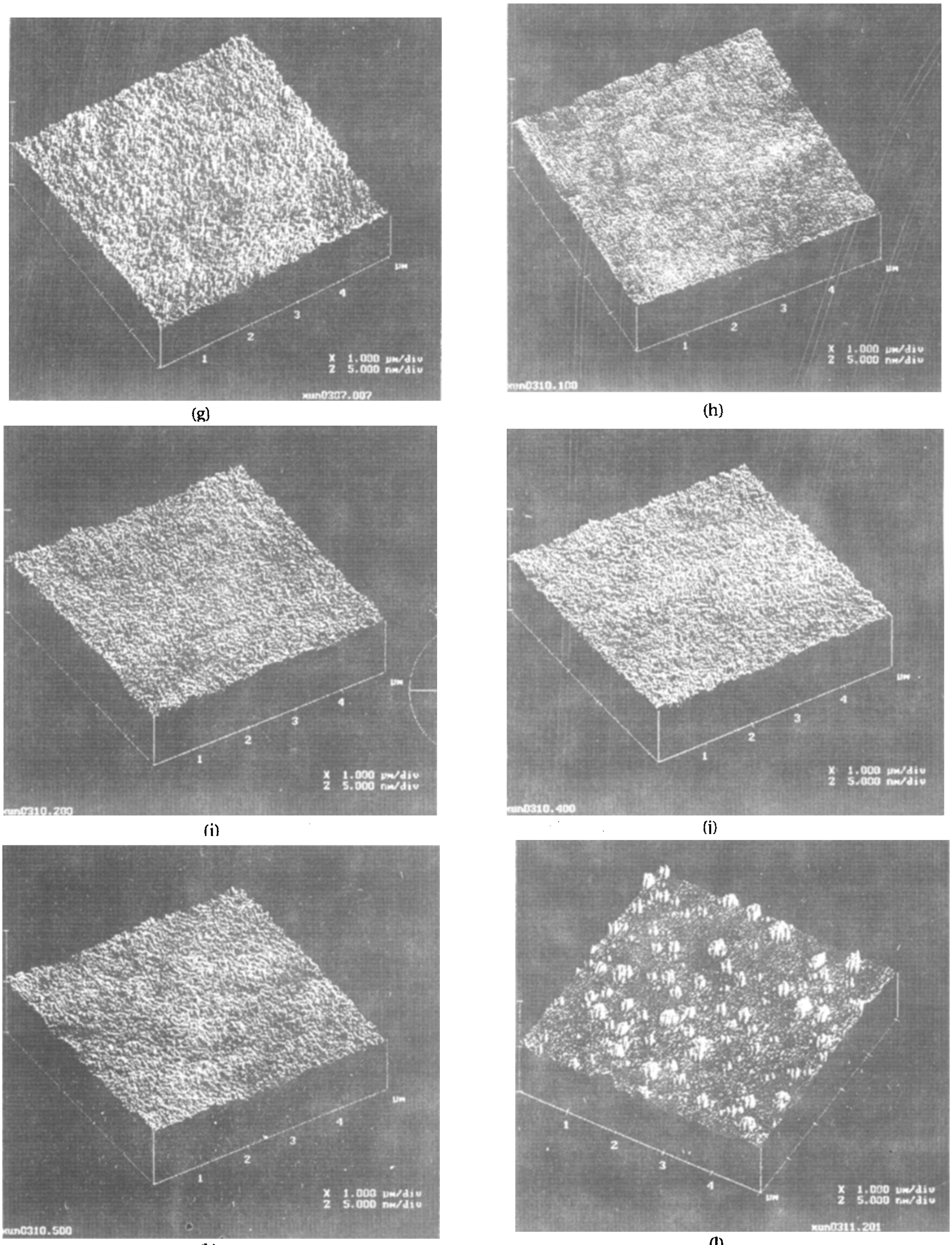
(a) (b)

(c) (d)

(e) (f)



(g) (h)

(i) (i)

(k) (l)

Fig. 2 AFM images of the modified sample surfaces with reaction time of (a) 20 sec; (b) 40 sec; (c) 60 sec; (d) 80 sec; (e) 100 sec; (f) 2 min; (g) 5 min; (h) 15 min; (i) 30 min; (j) 60 min; (k) 90 min; (l) 40 sec (rinsed under strong magnetic stirring).

Fig.3 shows the changes of the average surface mean roughness with reaction time. The analysis of sample R_{avg} indicated the existence of a minimum R_{avg} in the process of OTS self-assembled monolayer formation. Consistent with the AFM images, R_{avg} of the OTS monolayer reached its minimum value, 0.156 nm/4 μm^2, at the reaction time of 15 min. After that, R_{avg} was slightly increased within the succeeding 15 min and seemed approach to a stable value of 0.170 nm/4 μm^2 without remarkable change even for a long time reaction. If the difference, (0.02 nm/4 μm^2, was considered as resulting from the changes of some influencing factors, such as experimental error or changes in surface waviness, it seemed that after 15 min reaction, the OTS monolayer had formed completely without further essential changes. In our large number of experiments, this minimum R_{avg} was always observed.

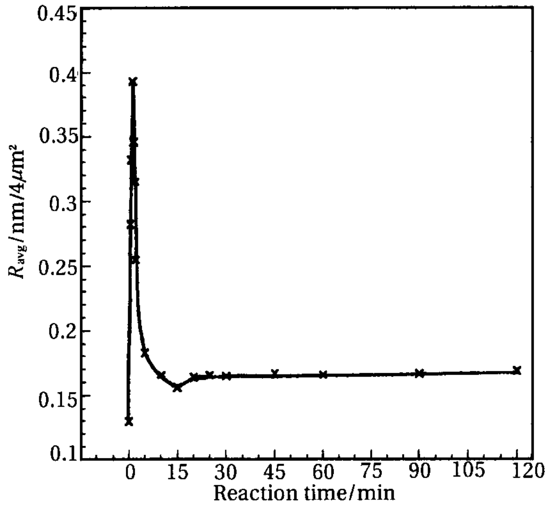


Fig.3 **Average surface mean roughness of sample vs reaction time.**

Being limited by the function of the AFM, we do not know the reason for the slightly increasing of R_{avg}. Brzoska et al. (1992) inferred that there might exist a lateral rearrangement within the monolayer, following physisorption onto the substrate and preceding chemical grafting. On the basis of the analyses of AFM images and the sample R_{avg} presented in this paper, it is reasonable to assume that the freshly formed OTS self-assembled monolayer after 15 min reaction is metastable; and that perhaps some kind of structural rearrangements or chemical bonding occurs inside the monolayer.

Banga et al. (1995a; 1995b) investigated the formation of OTS self-assembled monolayer on the surface of industrial float glass at room temperature by means of AFM and FTIR-ATR and reported that, an OTS self-assembled monolayer could be obtained on the glass surface after 90 min reaction. This conclusion was supported and corroborated by many researchers (Kallury et al., 1992). We agree with Bierbaum et al. (1995a; 1995b) and Barrat et al. (1992) that the growth rate as well as the growth mode of OTS self-assembled monolayers on substrate surfaces are greatly influenced by the materials of the solid substrate and its pretreatment method, as well as the reaction conditions. Different experiments yielded different conclusions (Sagiv, 1980; Gun et al., 1986; Silberzan et al., 1991; Brzoska et al., 1992; Banga et al., 1995a; Banga et al., 1995b; Kallury et al., 1992). But after carefully studying the AFM images and other experimental data offered by Banga et al. (1995a; 1995b), we believe their conclusion is not convincing.

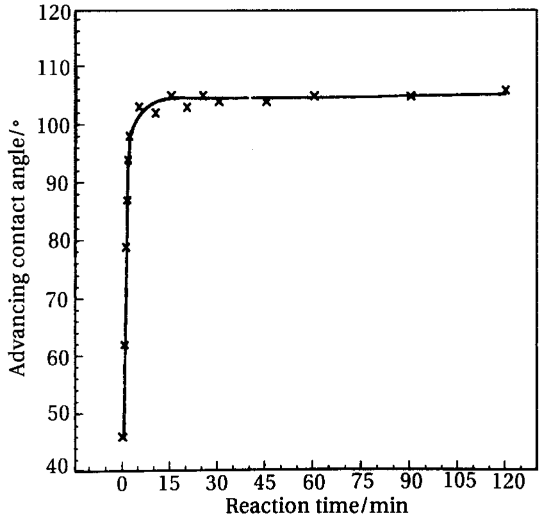


Fig.4 **Advancing contact angles vs reaction time.**

The variation of the advancing contact angles on the modified glass surfaces with reaction time also indicated that after 15 min reaction, the modified glass surface became hydrophobic completely. As Fig.4 shows, the advancing contact angles were increased rapidly during the initial 2 min reaction, after which, the advancing contact angle of the modified glass surface was increased to 98°; then the increasing of the advancing contact angles was not remarkable. After 15 min reaction, the advancing contact angle of the modified glass surface reached the value of 105°, and was around 105° without further large changes even for 2 hr reaction. The variation regularity of the hydrophobicity of the sample surfaces obtained from the advancing contact angle measurements was consistent with that from AFM. It is noteworthy that the value of 105° is lower than the reported 110° – 120° for water droplet on OTS monolayers (Angst et al., 1991; Carson et al., 1989; Carson et al., 1990; Kessel et al., 1991; Xiao et al., 1995; McGovern et al., 1994; Bierbaum et al., 1995b). We attribute this difference to the limited measurement precision of the photographic method and the influence of the surface roughness of samples. It is well known that if the contact angle is greater than 90°, it is increased by the surface roughness. We would like to point out that our sample surface was atomically smooth. However, a contact angle of 105° indicates the solid surface is completely hydrophobic.

2. The adsorption feature of the molecules on the substrate surface during the initial reaction period: Do $Si_{substrate}$-O-Si_{silane} covalent bonds form?

Generally, it is believed that the formation of $Si_{substrate}$-O-Si_{silane} covalent bonds between the monolayer and the solid substrate surface is crucial for the formation of high quality OTS monolayers (Sagiv, 1980; Angst et al., 1991; Carson et al., 1989; Carson et al; 1990; Kessel et al., 1991; Tripp et al., 1992; Tripp et al., 1995; Hair et al., 1995; Xiao et al., 1995; Maoz et al., 1984). The formation of $Si_{substrate}$-O-Si_{silane} covalent bonds can firmly bind the monolayer onto the substrate surface, and improve the mechanical strength and stability of the monolayer. Do $Si_{substrate}$-O-Si_{silane} covalent bonds form? It is a very important but still under controversy problem. According to Tripp and Hair (Tripp et al., 1992; Tripp et al., 1995; Hair et al., 1995), there was no direct evidence of the reaction between OTS molecules and the surface hydroxyl groups. Also the experiments conducted by Xiao et al. (1995) showed that the mechanical strength and stability of the monolayer arose mainly from the cross-linked siloxane network formed among molecules inside the monolayer by chemical or hydrogen bonding.

Fig.2i shows the effects of the strong magnetic stirrer rinsing on a sample with reaction time of 40 sec. After being pulled out from the OTS solution, this sample was rinsed in chloroform for 5 min under strong magnetic stirring, and then washed in acetone and chloroform for several minutes respectively, finally dried in a stream of nitrogen gas. Comparison of Fig. 2l with Fig.2b showed that after the strong magnetic stirrer rinsing, almost all the adsorption molecules were rinsed away, which gave the direct evidence that during the initial reaction period, almost all the adsorption molecules just adsorbed on the substrate surface physically without strong relationship or covalent bonding with the neighboring molecules or the hydroxyl groups on the substrate surface. It was also noted that although the strong rinsing washed away almost all adsorbed molecules, a few molecules still remained firmly stuck on the substrate surface, and were quite difficult to be pulled out. What caused the remaining OTS molecules to bind so strongly to the substrate surface? Is it the $Si_{substrate}$-O-Si_{silane} covalent bond? To draw such a kind of conclusion needs the support of direct experimental evidence. In experiments of Bierbaum et al. (1995b), all the modified samples were rinsed under magnetic stirring in chloroform for several minutes. Comparing the AFM image of Fig.2l in this paper with that offered by Bierbaum et al. (1995b), we can find some common characteristics. It can be confirmed that, during the initial period of the reaction, almost all the OTS molecules or its hydrolysates adsorbed on the substrate surface physically; but some very strong combinations (much stronger than the physical adsorption) between a few of the adsorption molecules and the substrate surface were established. Although the numbers of this combinations were limited, they should be crucial for the formation of the adsorption islands and the formation of a robust, well-organized OTS self-assembled monolayer.

The comparison experiments presented in this paper revealed the adsorption feature of the OTS molecules on the glass surface during the initial reaction period. We have no direct experimental evidence to prove the force sticking the remained adsorption molecules onto the substrate surface is the covalent bond, but the experiments showed that this force is obviously much stronger than the physical interaction, and was entirely possible the $Si_{substrate}$-O-Si_{silane} covalent bond.

CONCLUSIONS

By using AFM, we completely revealed the whole process of the OTS monolayer formation on the glass surface by self-assembly from 1×10^{-3} mol/L OTS-toluene solution at 18 ℃. The analyses of the presented AFM images as well as the average surface mean roughness, R_{avg}, of the sample surfaces indicated that, after 15 min reaction a smooth OTS monolayer with an R_{avg} of 0.156 nm/4 μm^2 could be obtained on the sample glass surface. However, this freshly formed OTS monolayer was metastable. With longer reaction time, the R_{avg} of the monolayer surface was slightly increased within the succeeding 15 min, then kept to a constant value of about 0.170 nm/4 μm^2 even for 2 h reaction. This slightly increasing of R_{avg} perhaps implies possible structural rearrangements or chemical bonding inside the monolayer. The advancing contact angle measurements showed that after 15 min reaction, a completely hydrophobic surface with advancing contact angle of 105° was formed. Our results also showed that during the initial reaction period, most of the adsorption molecules just adsorbed on the substrate surface physically, but some kind of very strong combination between a few adsorption molecules and the substrate surface was established which was much stronger than physical interaction.

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