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Growth behavior and surface topography of different silane coupling agents adsorbed on the silicon dioxide substrate (0001) for vapor phase deposition

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Abstract The growth behavior and surface topography of the deposited films formed from silane coupling agents on silicon dioxide substrate (0001) via vapor phase deposition was investigated using atomic force microscopy (AFM). The surface topography of the films adsorbed on the silicon dioxide substrates is dissimilar with different silane coupling agents and different deposition conditions: (1) the films adsorbed on the silicon dioxide substrate become smoother with the increasing temperature of the silicon dioxide substrate; (2) the surface roughness of the films increases with the increasing concentration of the silane coupling agent solutions; (3) with the increasing temperature of the carrier gas, the surface roughness of the films decreases firstly and then increases; (4) with the increasing time of deposition, the surface roughness of the films increases firstly, then decreases and subsequently increases again. In experiments, the films adsorbed on the silicon dioxide substrate was rinsed ultrasonically with toluene, the results indicate that the silane coupling agent adsorbed on the substrate by physisorption and chemisorption: the chemisorbed coupling agents present island morphology and the physisorbed coupling agents are deposited on the substrate between the islands to decrease the surface roughness of the film.

Introduction

Nowadays, surface modification is becoming of great importance in both scientific laboratory experiments and industrial processes with the development of powder technology. Silane coupling agents are often used for the powder surface modification to change the surface property from a hydrophilic one to a hydrophobic one, enhance the compatibility and interface adhesion between the inorganic powder and organic materials, and avoid the aggregation of the powder [1–11]. Because of their widespread applications, there is a lot of research on the underlying reaction mechanisms in the modification process involving silane coupling agent [11–15]. A fundamental understanding of these mechanisms can lead to an improvement of the method for powder surface modification.

The process of powder surface modification can be considered to be the process of self-assembled monolayer (SAM) formation of the coupling agent on powder surface. So, adsorption of the silane coupling agent on silicon dioxide substrate can provide a comparison to the surface modification of the powder. The mechanism of formation and the structure of SAM have been studied by many groups using a variety of characterization methods now, such as infrared spectroscopy, ellipsometry, and surface wettability [16–18]. The development of atomic force microscopy (AFM) provided a new tool to study SAM formation: it can provide real-space film morphology and nanostructure and provide detailed topographical information about surface features in terms of the roughness parameters of the films [18–25]. But more groups research the silane films adsorbed from the solvent solution, few group researches the silane films formed via vapor phase deposition [16, 24, 25], and there is no detailed report on the influence of the deposition conditions on the surface topography of the films.

The aim of this paper is to study the process of the silane coupling agent adsorption on silicon dioxide substrate via vapor phase deposition and study the

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influence of deposition conditions on the growth behavior and surface topography of the films.

Experiment

Experiment materials

Chemicals used in the present investigation include: γ-Aminopropyltriethoxysilane (KH-550), γ-Glycidoxypropyltrimethoxysilane (KH-560), and γ-Methacryloxypropyltrimethoxysilane (KH-570) purchased from Nanjing Shuguang chemical group Co., Ltd., Dodecyltrimethoxysilane (WD-10) purchased from Wuhan university silicone new material Co., Ltd., silicon dioxide wafers (crystal, 0.5 mm thick, ⟨0001⟩ orientation, polished on one side, 1×1 cm^2) purchased from Hefei Kejing materials technology Co., Ltd., ethanol and toluene are analytical reagents purchased from Beijing Beihua fine chemicals Co., Ltd.. All of the chemicals were used as received.

Experiment methods

The schematic diagram of the device for vapor phase deposition is shown in Fig. 1. Silicon dioxide substrate was fixed on the surface of a rectangular-section pipe, in which the constant temperature water flows and the temperature of the silicon dioxide substrate can be controlled from 15 to 90 °C during silane coupling agent deposition. The solution of the modifying agent such as silane coupling agent was sprayed into a chamber from an air atomizing nozzle, and then dispersed by another three air nozzles to reinforce the dispersion performance of the modifying agent. The temperature of the carrier gas for modifying agent dispersion is controllable, from 20 to 500 °C, and the solvent in modifying agent solution can be evaporated. By this way, the modifying agent can be dispersed uniformly into the air flow and deposited on the silicon dioxide substrate via vapor phase deposition. In experiment, deposition parameters can be adjusted, such as the temperature of the substrate, temperature of the carrier gas, deposition time, and the concentration of the modifying agent solution, which will influence the surface topography of the films on the substrate.

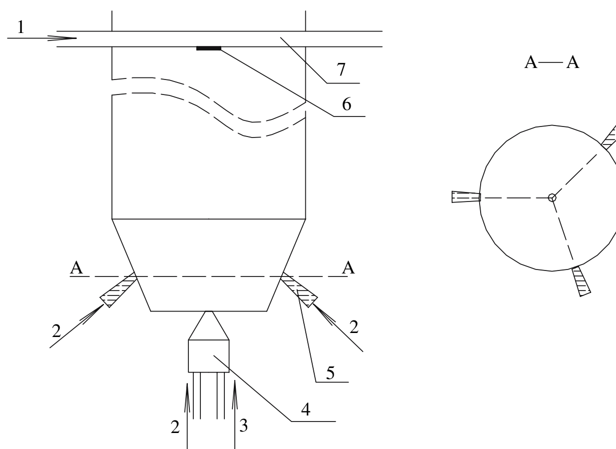

Fig. 1 Schematic diagram of the device for vapor phase deposition: 1, water; 2, high temperature air; 3, modifying agent; 4, air atomizing nozzle; 5, normal air nozzle; 6, substrate; 7, rectangular-section pipe

After silane coupling agent deposition, the silicon dioxide substrate was treated with two processes: (1) the silicon dioxide substrate was dried at 105 °C for 30 min in an oven under ambient pressure directly; (2) the silicon dioxide substrate was rinsed ultrasonically with toluene for 10 min to remove the weakly or physically adsorbed silane molecules, and then rinsed with ethanol 3 times, dried by a stream of air. Finally the substrate was dried at 105 °C for 30 min in an oven under ambient pressure.

In experiment, the silane films were prepared in a normal chemistry laboratory and the silicon dioxide substrates were used as received. The solutions of the silane were prepared by dissolving the silane coupling agent in a solvent mixture of ethanol and distilled water at a proper concentration, the proportion of the silane and distilled water is 1:0.3 in volume.

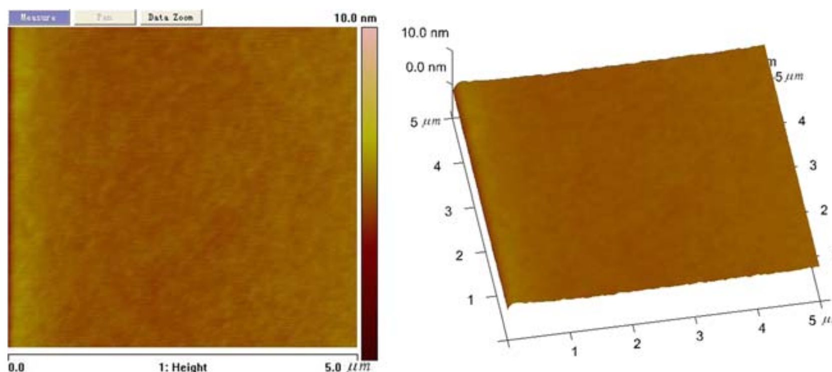

Fig. 2 AFM image of a bare silicon dioxide substrate

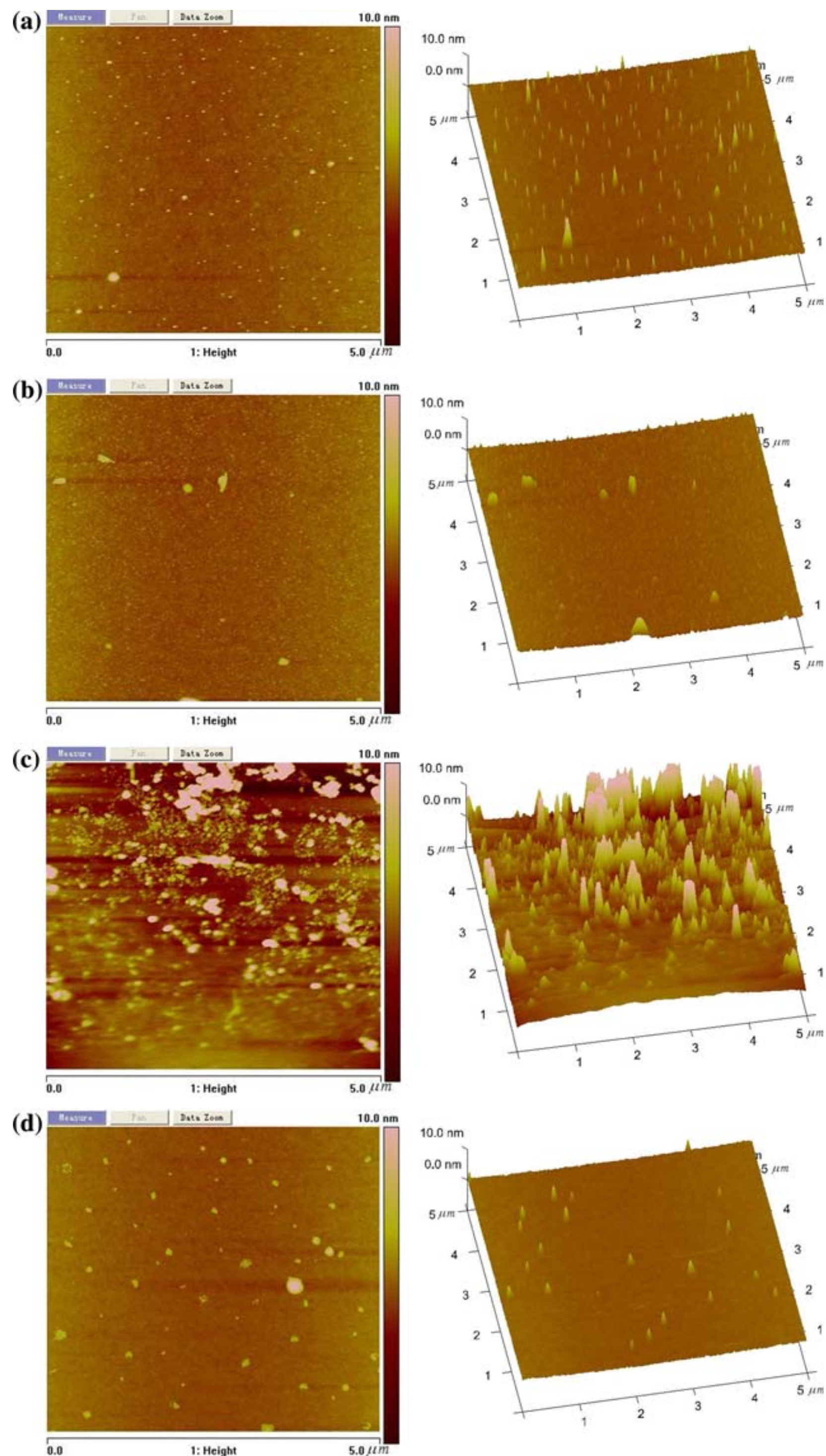

Fig. 3 AFM image of different silane films on the silicon dioxide substrate: (**a**) γ-Aminopropyltriethoxysilane (KH-550); (**b**) γ-Glycidoxypropyltrimethoxysilane (KH-560); (**c**) γ-Methacryloxypropyltrimethoxysilane (KH-570); (**d**) Dodecyltrimethoxysilane (WD-10)

AFM imaging

The surface topography of the silane films on the silicon dioxide substrate was investigated under laboratory ambient conditions with a commercial atomic force microscope (Nano scope IV, Digital Instruments). All the samples were imaged with silicon nitride probes mounted on cantilevers in tapping mode to avoid surface damage, which signifi-

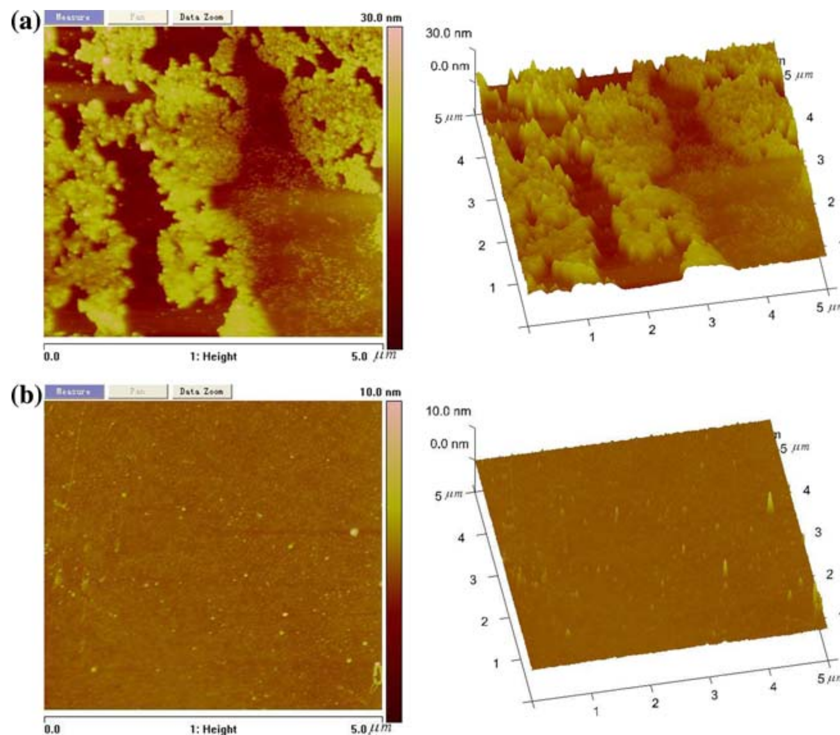

Fig. 4 AFM images of KH-550 film deposited on the substrate with different substrate temperature (60 °C is shown in Fig. 3a): (**a**) the temperature of the substrate is 20 °C; (**b**) the temperature of the substrate is 80 °C

cantly improves lateral resolution on soft surfaces and thin films. All images presented in the paper were acquired on scales ranging 500 × 500 nm^2 and 5 × 5 μm^2.

X-ray photoelectron spectroscopy (XPS)

The surface composition of the silane treated substrate was determined by X-ray photoelectron spectroscopy and the XPS data were performed using a VG ESCALAB MKII spectrometer with an AlK_α X-ray source (1,486.6 eV photons) for sample excitation. A takeoff angle of 45° was used.

Results and discussion

A typical AFM image obtained from a bare silicon dioxide substrate without any deposition is shown in Fig. 2. The image is quite smooth and clean on a submicron scale.

Influence of silane coupling agent kinds

The surface topography of KH-550, KH-560, KH-570, and WD-10 films are shown in Fig. 3, which adsorbed on the silicon dioxide substrate via vapor phase deposition. In the process of deposition, the flux of the silane coupling agent

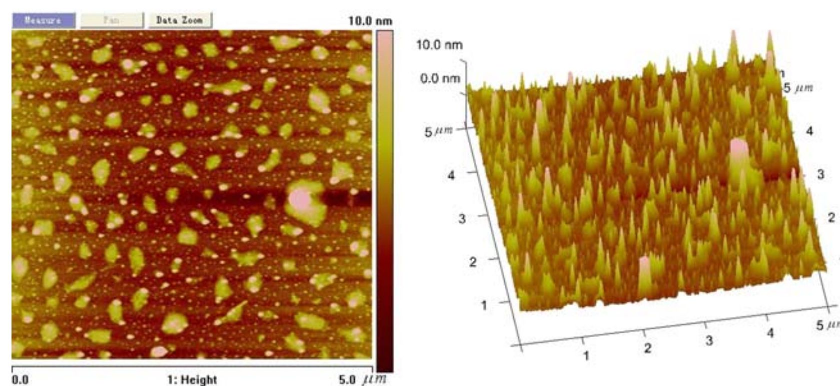

Fig. 5 AFM images of KH-550 films with washing procedure

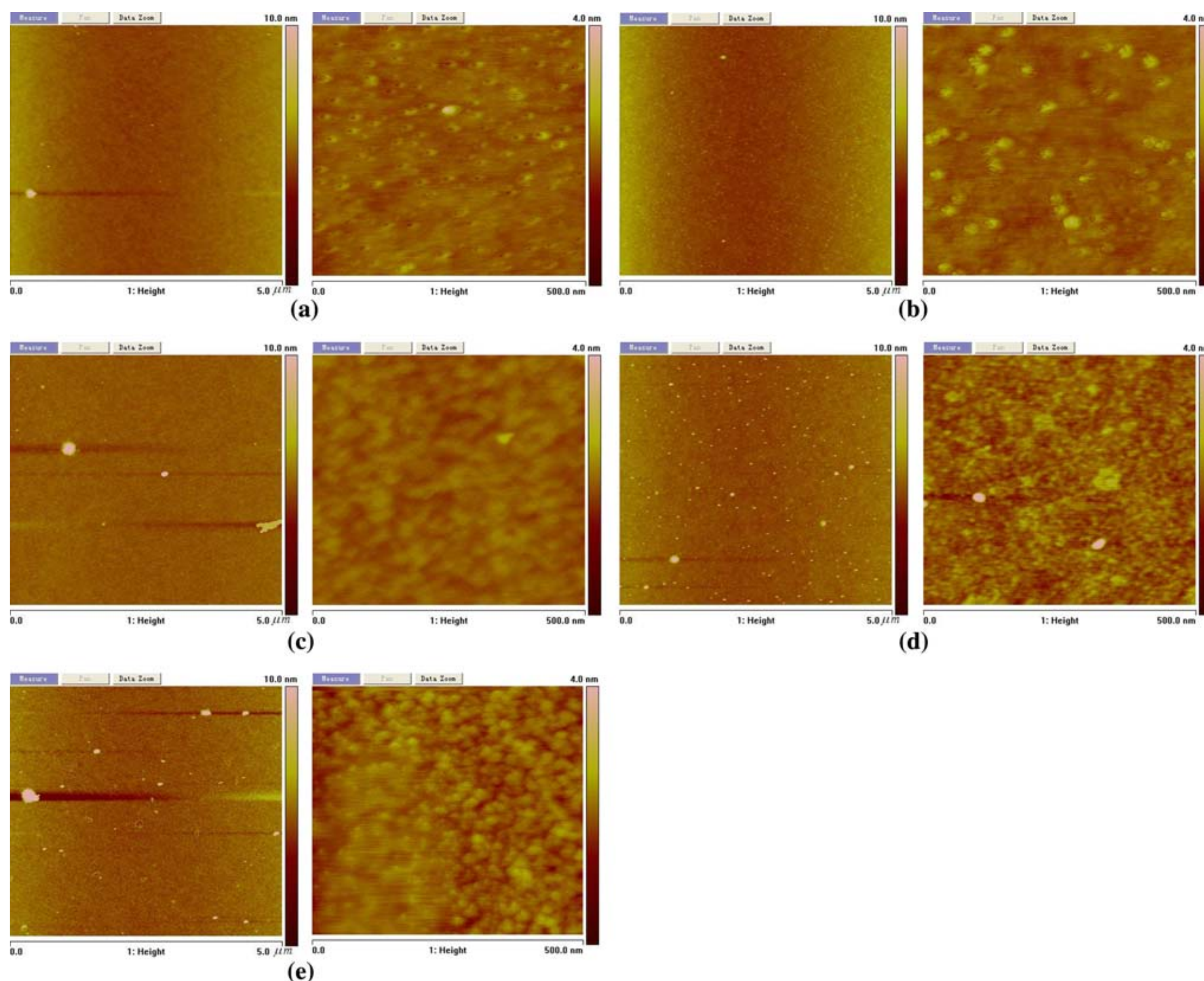

Fig. 6 zAFM images of KH-550 film deposited on the substrate at different deposition time: (**a**) 30s; (**b**) 1 min; (**c**) 5 min; (**d**) 10 min; (**e**) 20 min

solution is 4 ml/min, the temperature of the substrate is 60 °C, the concentration of the solution is 5 wt% in ethanol–water, the time for deposition is 10 min, and the temperature of carrier gas is 110 °C during deposition. The substrates were dried at 105 °C for 30 min in an oven after deposition.

From the figures it can be seen that the topography of different silane films are dissimilar and the roughness of the films are also different. This maybe caused by the different terminal functional groups in different silane molecules and the difference of the molecular chain length.

Influence of the substrate temperature

Figure 4 shows the AFM images of KH-550 films deposited on silicon dioxide substrate with various temperature of the substrate. In the process of deposition, the flux of the KH-550 solution is 4 ml/min, the concentration of the solution is 5 wt% in ethanol–water, the time for deposition is 10 min, the temperature of carrier gas is 110 °C, and the temperature of the substrate is 20 °C, 60 °C (shown in Fig. 3a), and 80 °C. From the figures it can be seen that the surface roughness decreases with an increase in the temperature of the substrate. This maybe caused by the difference between the self-polymerization rate of KH-550 and the adsorption rate of KH-550 to the substrate: at low temperature of the substrate, the self-polymerization rate is greater than the adsorption rate, the KH-550 adsorbed on the substrate at the formation of globules aggregates, and the surface roughness is high. But at high temperature of the substrate, the adsorption rate is greater than the self-polymerization rate, the KH-550 adsorbed on the substrate at the formation of molecule, so the surface roughness of the KH-550 film is low and the surface is smooth.

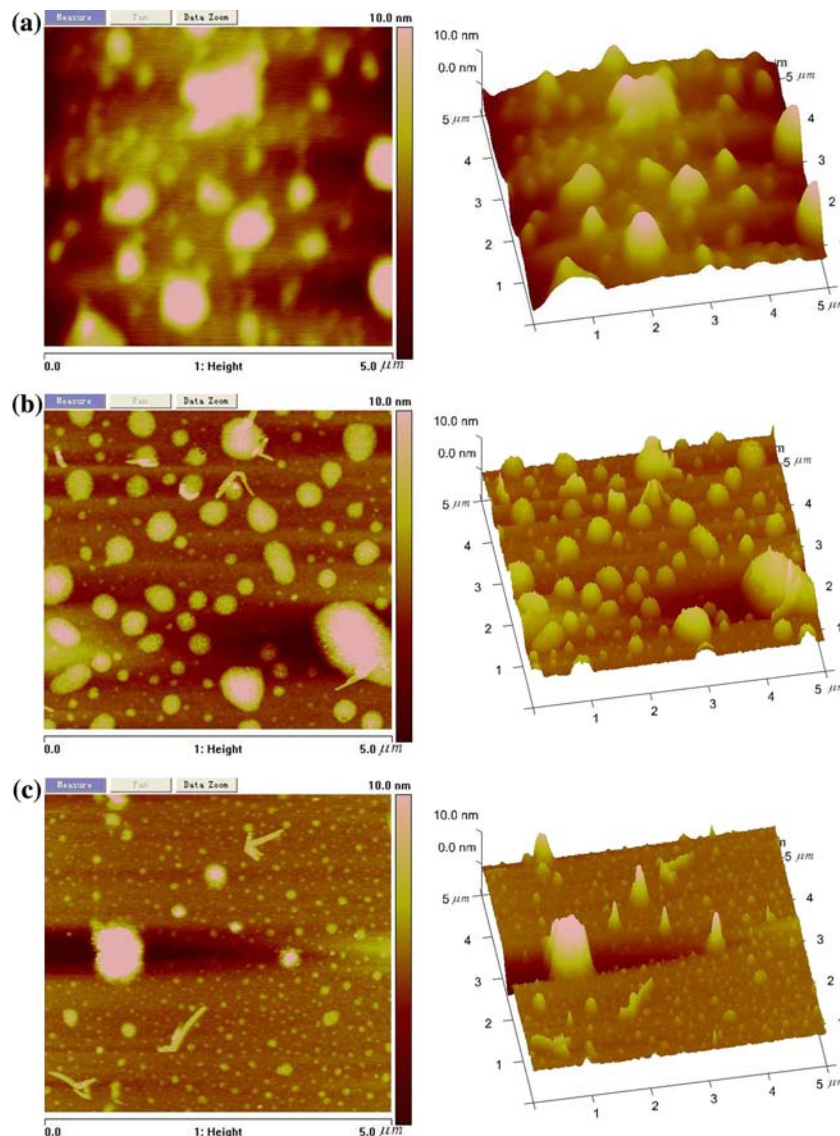

Fig. 7 AFM images of KH-550 film deposited on the substrate with different KH-550 concentration: (**a**) 1 wt%; (**b**) 5 wt%; (**c**) 20 wt%

Influence of toluene washing

After KH-550 deposition (the deposition condition is the same in Fig. 3a), the silicon dioxide substrate was treated with two processes: (1) dried at 105 °C for 30 min directly; (2) rinsed ultrasonically with toluene for 10 min and rinsed with ethanol 3 times, then dried by air blow, and finally dried at 105 °C for 30 min. The surface topography of KH-550 films with washing procedure is shown in Fig. 5 (without washing procedure is shown in Fig. 3a). From the figure it can be seen that the KH-550 film is smooth without washing procedure but present islands morphology with washing procedure. We attribute this difference to the desorption of the physisorbed or weakly adsorbed KH-550 molecules during toluene washing, and only chemisorbed KH-550 molecules remained after toluene washing: the chemisorbed KH-550 molecules adsorbed on the substrate by island growth pattern and the physisorbed KH-550 molecules filled in the place between the islands to decrease the surface roughness of the film.

Influence of the deposition time

Figure 6 shows the AFM images of KH-550 films deposited on silicon dioxide substrate with different deposition time. In the process of deposition, the flux of KH-550 solution is 4 ml/min, the concentration of solution is 5 wt% in ethanol–water, the temperature of carrier gas is 110 °C, the temperature of the substrate is 60 °C, and the time for

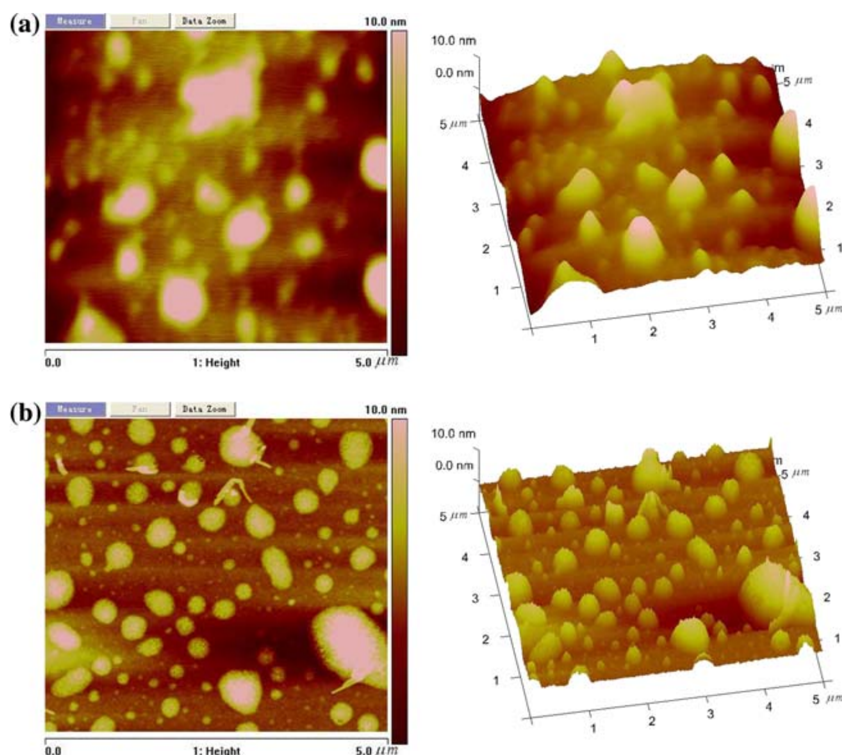

Fig. 8 AFM images of KH-550 film deposited on the substrate at different temperature of the carrier gas: (**a**) 60 °C; (**b**) 150 °C

deposition is 30 s, 1 min, 5 min, 10 min, and 20 min. From the figures it can be seen that the KH-550 molecules were chemically adsorbed on the activated sites on the silicon dioxide substrate firstly (Fig. 6a and b), then deposited on the inactivated sites by physisorption to form a continuous film on the substrate (Fig. 6c) and the surface roughness decreased. With the increase of the deposition time, the KH-550 molecules were deposited on the continuous films and formed the multilayer structure, but the surface roughness of the KH-550 film increased with the increasing time (Fig. 6d and e).

Influence of the concentration of the solution

The surface topography of KH-550 films, deposited with different concentration of the KH-550 solution, is shown in Fig. 7. In the process of deposition, the flux of KH-550 solution is 4 ml/min, the temperature of carrier gas is 110 °C, the temperature of the substrate is 60 °C, the time for deposition is 5 min, and the concentration of KH-550 is 1, 5 and 20 wt% in ethanol–water. From the figure it can be seen that the surface roughness increases with an increase in the concentration of KH-550 solution.

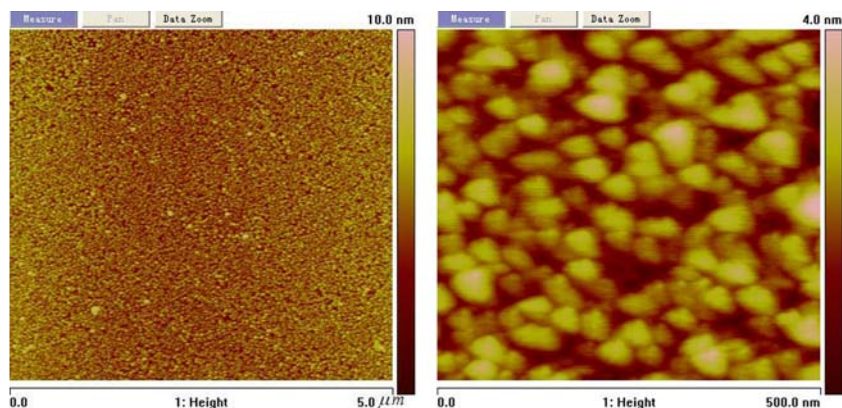

Fig. 9 AFM images of KH-550 film deposited from solvent solution

Influence of the temperature of the carrier gas

In experiment, the silane coupling agent dispersed by an air atomizing nozzle and another three air nozzles, the temperature of the carrier air could be controlled to evaporate the solvent in the solution of silane coupling agent. So, the temperature of the carrier gas will influence the surface topography of silane films. The surface topography of KH-550 films is shown in Fig. 8, deposited with different temperature of the carrier gas. In the process of deposition, the flux of KH-550 solution is 4 ml/min, the temperature of the substrate is 60 °C, the time for deposition is 10 min, the concentration of solution is 5 wt% in ethanol–water, and the temperature of carrier gas is 60 °C, 110 °C (shown in Fig. 3a), and 150 °C. From the figure it can be seen that the KH-550 film is smoother at 110 °C than at 60 and 150 °C. A possible explanation for this is that, the solvent in the solution could not be evaporated completely before KH-550 deposited on the silicon dioxide substrate at low temperature (60 °C) of the carrier gas, many droplets of the concentrated silane solution deposited on the substrate, which is equivalent to the aggregates of the coupling agent deposited on the substrate. So, the KH-550 film is coarse at low temperature of the carrier gas. At high temperature (150 °C) of the carrier gas, the solvent in the solution was evaporated quickly and the KH-550 molecules self-polymerized with each other before the deposition, so, the KH-550 film is also coarse at high temperature of the carrier gas. Only at the proper temperature, KH-550 molecule can be dispersed uniformly into the air flow, deposited on the substrate by the formation of molecule, not by the formation of solution droplets or KH-550 aggregates, for example shown in Fig. 3a.

Comparison of different methods

In order to study the influence of different deposition methods on the film topography, the coupling agent was deposited on the silicon dioxide substrate from solvent solution. The surface topography of the KH-550 films adsorbed from the solvent solution is shown in Fig. 9. In the process of deposition from solvent solution, the silicon dioxide substrate was immersed into the solution of KH-550 in ethanol–water for 10 min under ultrasonic stirring, which is 5 wt% in concentration, and rinsed with ethanol 3 times, dried by air blow, then dried at 105 °C for 30 min in an oven under ambient pressure. From the figure it can be seen that the film deposited via vapor phase deposition (Fig. 6d) is smoother than deposited from solvent solution (Fig. 9). We attribute this difference to the various formations of KH-550 molecules during adsorption: KH-550 adsorbed on the substrate by the formation of molecule during vapor phase deposition but adsorbed on the substrate by the formation of granular aggregates from solvent solution.

XPS analysis of KH-550 treated substrate

The surface composition of the KH-550-treated substrate (in Fig. 3a) was analyzed by the X-ray photoelectron spectroscopy (XPS), and the typical XPS survey spectra of the KH-550 treated substrate and original substrate are shown in Fig. 10. From the figure it can be seen that the N1s peak was presented in the spectra of the KH-550 treated substrate, but was not presented in the spectra of the original substrate. From the XPS results and the molecular formula of the KH-550 ($NH_2(CH_2)_3Si(OC_2H_5)_3$) it can be seen that the KH-550 adsorbed on the substrate after deposition.

Theory of silane deposition

From the results of the experiment, the processes of the silane coupling agent deposition via phase deposition can be proposed and the schematic diagram of deposition is shown in Fig. 11. The silane coupling agent is chemically adsorbed onto the activated sites on the surface of the silicon dioxide substrate firstly, and then, more coupling agent will be adsorbed nearby and form the island morphology, which is shown in Fig. 11b. With the increasing deposition time, the silane coupling agent will be deposited on the place between the islands by physisorption, and then, the continuous silane coupling agent films will be formed on the surface of the substrate until the island edges touch, which is shown in Fig. 11c. In subsequent deposition, the silane molecule will be deposited on the continuous film and form the multilayer film structure.

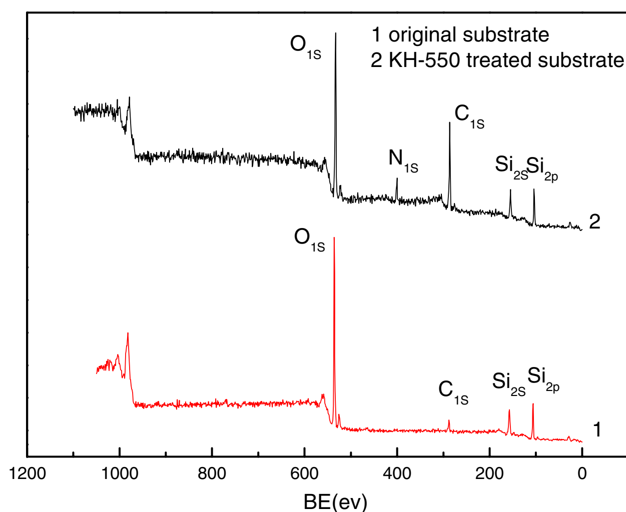

Fig. 10 XPS survey spectra of the original substrate (Fig. 2) and the KH-550 treated substrate (Fig. 3a)

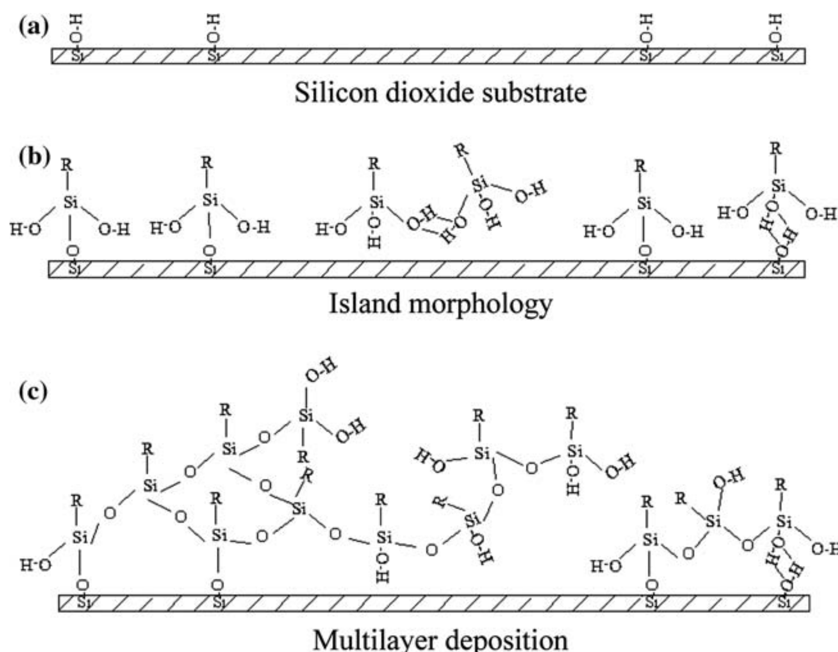

Fig. 11 The schematic diagram of silane deposition via phase deposition: (**a**) silicon dioxide substrate; (**b**) island morphology; (**c**) multilayer deposition

Conclusion

The process of the vapor phase deposition of silane coupling agent on silicon dioxide substrate was studied. With the increasing temperature of the silicon dioxide substrate, the films adsorbed on the silicon dioxide substrate will become smoother. With the increasing concentration of the silane coupling agent solution, the surface roughness of the film will increase. With the increasing temperature of the carrier gas, the surface roughness of the film decreases firstly and then increases. With the increasing time of deposition, the surface roughness of the film increases firstly, then decreases and subsequently increases again. In experiment, the films adsorbed on the silicon dioxide substrate were rinsed ultrasonically with toluene, the results indicate that the silane coupling agent adsorbed on the substrate by physisorption and chemisorption. Compared with the films adsorbed from solvent solution, the films formed via vapor phase deposition are smoother.

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