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Atomic scale flattening of organosilane self-assembled monolayer and patterned tin hydroxide thin films

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Abstract

We have succeeded in fabricating an atomic flattening surface of organosilane self-assembled monolayers (SAMs) on a Si substrate. In the present process, the octadecyltrichlorosilane (OTS) compound was selected as the starting material for the SAM. The OTS–SAM was formed by the reaction between the OTS molecules and the substrates, which were hydrogen terminated Si(001) (H:Si) and silica covered on Si(001) (SiO_2/Si), at room temperature in a N_2 atmosphere. The formation rate of the OTS–SAM onto H:Si was smaller than that on SiO_2/Si. Interestingly, the hydrophobicity of the OTS–SAM was observed to increase the amount formed on H:Si in comparison with that on SiO_2/Si. The photo reactivity of the SAMs formed on each substrate was also investigated by using ultraviolet (UV) irradiation in ambient air. Tin hydroxide thin films were site-selectively deposited on the patterned OTS–SAM/Si substrate in order to clarify the cleavage of the OTS–SAM by the UV irradiation.

Keywords: Films; Functional applications; Organosilane self-assembled monolayer; Surfaces

1. Introduction

Recently, great attention has been focused on the ''Direct Productive Approach'', which is a technique for site-selective arrangement of functional materials at desired sites on a Si substrate, in order to realize a smart process for fabrication of advanced devices.[1] For this purpose, the use of the patterned organosilane self-assembled monolayer (SAM) as the template on a Si substrate is one of the advanced lithography techniques without traditional photoresist (or resist) for recording the pattern on the semiconductor following exposure to the energy source (e.g. a light). Two processes in particular have been investigated to obtain a patterned organosilane SAM template: one is the 'Soft Lithography'[2] process, and the other is the patterning process by any energy source thorough the photomask.[3] As a result of the processes, two regions within and without the organosilane SAM should exist on the Si substrate, and are available as templates for site-selective arrangement and/or deposition of particles, molecules, and films, respectively. Saito et al.,[4] have succeeded in the low-temperature fabrication of ZnO micropatterns, which show patterned cathodoluminescence images, through the use of a patterned SAM with a phenyl/OH surface.[4] The visible light luminescence is observed only at the ZnO-deposited regions on the phenyl surfaces in the patterned phenyltrichlorosilane (PTCS) SAM/SiO_2/Si substrate. Dressick et al.,[5] have also reported site-selective electroless Ni, Co and Cu metallization using a patterned PTCS film and a colloidal Pd/Sn catalyst, and clarified that metal films deposit only on the phenyl regions of phenyl/OH surfaces. In contrast, Masuda, et al.,[6] have succeeded in TiO_2 thin film micropattern site-selectively on the silanol region in the patterned octadecyltrichlorosilane (OTS) SAM/SiO_2/Si substrate, for both the silanol and methyl regions, prepared by ultraviolet (UV) irradiation. Also, it has been known that the film growth rate on sulfonate SAM/SiO_2/Si substrate is different from that on a SiO_2/Si substrate without SAM.[7,8]

To further develop the patterning process, an atomic flattening of the organosilane SAM surface is required, because of its role as a template for the arrangement and deposition of numerous kinds of particles and films. However, it is difficult to form such a flat organosilane SAM surface on a Si substrate, because of the roughness of the SiO_2 existing between the organosilane SAM and the Si.

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In the present study, we suggest a novel process of organosilane SAM formation on an Si substrate by the reaction of OTS and an hydrogen terminated Si(001) substrate (H:Si). In addition, the role as a template for site-selective deposition of metal hydroxide thin film was also investigated.

2. Experimental procedure

A P-type Si (001) wafer with resistivity in the range 5–1Ωcm was used as the substrate. The substrates were first degreased ultrasonically in toluene, ethanol, and deionized water (resistivity = 18.3 MΩcm). They were then exposed for 2 h to UV light (184.9 nm) from Hg lamps in ambient air in order to remove any contamination existing on their surfaces. The native oxide films covering the Si substrates were removed by immersing the cleaned substrate into a 1.0 vol.% HF solution for 1.5 min. The water drop contact angles of the cleaned and the hydrogen terminated surfaces were measured to be <5 and 81°, respectively. Two types of substrates were prepared for the formation of the OTS–SAMs: one was a H:Si substrate, and the other was a chemical oxide thin film covering a Si substrate. The chemical oxide was grown by placing the H:Si (SiO_2/Si) substrate in the RCA standard clean 2, or SC-2 solution, which is composed of the usual volume ratios of 6 H_2O:1 H_2O_2:1 HCl, at 75–80 °C for 10 min.[9] The substrate was rinsed several times in deionized water and then wiped off. The water drop contact angles at the chemical oxide surface were also measured to be $<5°$. The OTS–SAMs were formed by placing the H:Si and the SiO_2/Si substrates in a 1.0 vol.% solution of the OTS precursor dissolved in anhydrous toluene 99.8%, water <0.002%, Aldrich) for a duration of between 0 and 30 min in a N_2 atmosphere (water vapor pressure <0.1 hPa). After immersion, the OTS–SAM substrate was carefully rinsed several times in new anhydrous toluene, blown dry using N_2, heated at 120 °C for 5 min to remove residual solvent and to promote chemisorption of the SAM, and ultrasonicated in ethanol for 5 min for removal of the physically adsorbed molecules on the monolayer surfaces,[10] and before being then wiped off.

The patterned SAM substrate was prepared using UV (184.9 nm) irradiation through a photomask for the desired time in ambient air. Tin chloride (TC) was used as a starting material for site-selective deposition of a tin hydroxide thin film. The patterned OTS–SAM substrates were immersed in an anhydrous toluene solution containing the precursor (0.05 mol/l) at room temperature for a soaking time of 10 min in a N_2 atmosphere. After the desired soaking time, the residual solvent on

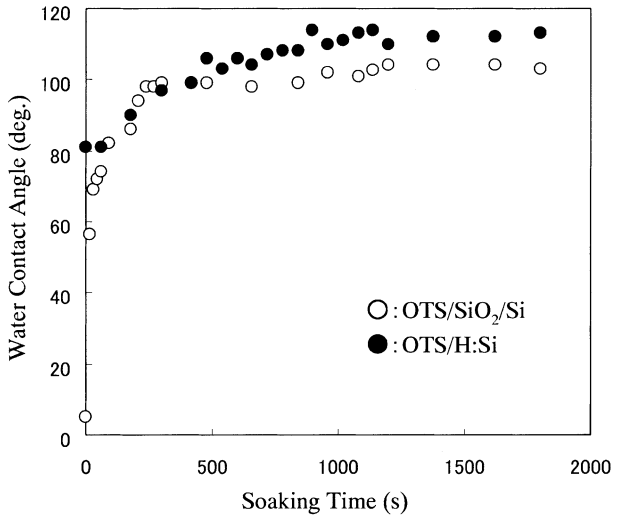

Fig. 1. Soaking time dependence of the water drop contact angles at the OTS–SAM surfaces formed onto SiO_2/Si (○) and H:Si substrates (●), respectively.

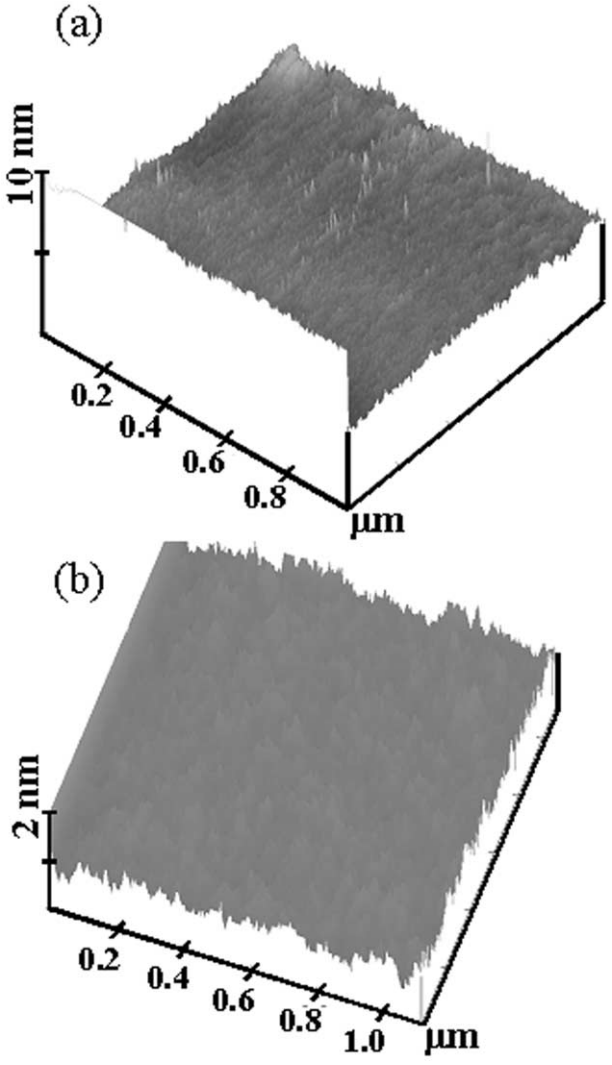

Fig. 2. AFM images showing the typical surface morphologies of OTS–SAMs formed onto (a) SiO_2/Si and (b) H:Si substrates, respectively.

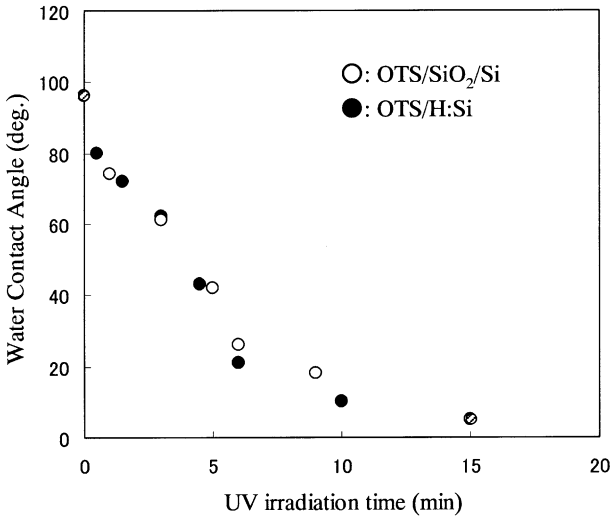

Fig. 3. Ultraviolet (UV) irradiation time dependence of the water drop contact angles at the OTS–SAM surfaces formed onto SiO_2/Si (○) and H:Si substrates (●), respectively.

the surface of the samples was immediately rinsed away using new toluene and then blown dry using N_2.

The changes of the functional groups in the OTS precursors in anhydrous toluene solution at the soaking time were detected using a Fourier transform-infrared spectrometer (FT-IR; Hitachi, 270-30) using the KBr disc method under a N_2 stream. Three samples were prepared using this method. The samples were the anhydrous toluene solution containing 1.0 vol.% OTS precursors after the soaking time of 0, 10, and 15 min in a N_2 atmosphere, respectively. The surface roughness of the OTS–SAMs on different substrates was measured using an atomic force microscope (AFM, Nanoscope E, Digital Instruments). The surface roughness, as evaluated by the root mean square (RMS), can be expressed as:

$$\text{RMS (standard deviation)} = [\Sigma_i(Z_i - Z_{ave})/n] \quad (1)$$

where Z_i is the height at point I, Z_{ave} is the average of Z, and n is the number of data points. A scanning electronic microscope (SEM, Hitachi, S-3000N) was used to observe the surface morphologies of the selectively deposited films on the patterned OTS–SAMs at an accelerating voltage of 20 kV. X-ray photoelectron spectroscopy (XPS; Mg$K\alpha$) operated at 15 kV and 18 mA under high vacuum (1.0×10^{-10} Pa) conditions in order to research the Sn 3d, O 1s, and Cl 2p region of the deposited films. The correct charge of 284.6 eV, was performed by C 1s spectra, and included in the contamination on the as-deposited film surface.

3. Results

Fig. 1 shows the soaking time dependence of the water drop contact angle (θc) at the surfaces of the SiO_2/Si and H:Si substrates in toluene solution including an OTS precursors of 1.0 vol.% in a N_2 atmosphere. The fact that the θc enormously increased within several seconds at the surface of the SiO_2/Si substrate showed the modification of its surface from a hydrophilic plane to a hydrophobic one by an immediate formation of the OTS–SAM on the substrate. The coverage of the OTS–SAM on the SiO_2/Si substrate gradually increased with time ($\theta c = 99^\circ$), and then nearly saturated after 5 min with the θc ranging between 99 and 103°, which was in good agreement with the values reported in our previous paper.[11] Interestingly, however, no changes in θc were observed at the surface of the H:Si substrate for the initial 1 min. The θc increased with the soaking time from 3 ($\theta c = 90^\circ$) to 15 min ($\theta c = 114^\circ$), and then saturated while keeping the θc above 110° after 15 min. Although similar hydrophobicity was observed at the surfaces of both substrates for soaking times from 4 to 7 min, the θc on the H:Si substrate further increased after 7 min. Fig. 2 shows AFM images of OTS–SAMs

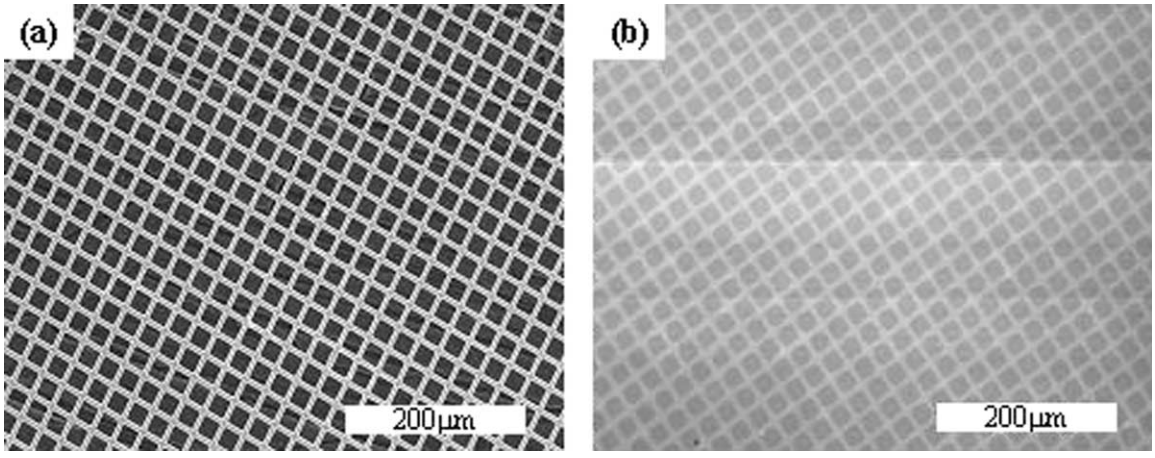

Fig. 4. SEM images of (a) the photomask used for obtaining the patterned OTS–SAM substrate and (b) tin hydroxide thin film selectively deposited on silanol region in the patterned OTS–SAM formed on H:Si substrate.

formed on (a) SiO_2/Si and on (b) H:Si substrate, respectively. Each sample was prepared for the soaking times of (a) 5 min and (b) 15 min. The RMS value at the OTS–SAM surface on the SiO_2/Si was measured to be 0.88 ± 0.38 nm, which was much larger than that on the H:Si (0.42 ± 0.12 nm). The RMS value of the OTS–SAM surface formed on the H:Si substrate was closer to the value of the H:Si surface (0.19 ± 0.03 nm) rather than that of the OTS–SAM on SiO_2/Si.

Fig. 3 shows the photoreactivity of OTS–SAMs formed on the H:Si and SiO_2/Si substrates, respectively. Samples with the same values for θc were selected for the precise evaluation of the photoreactivity of each SAM. In this figure, two slash circles mean the same θc

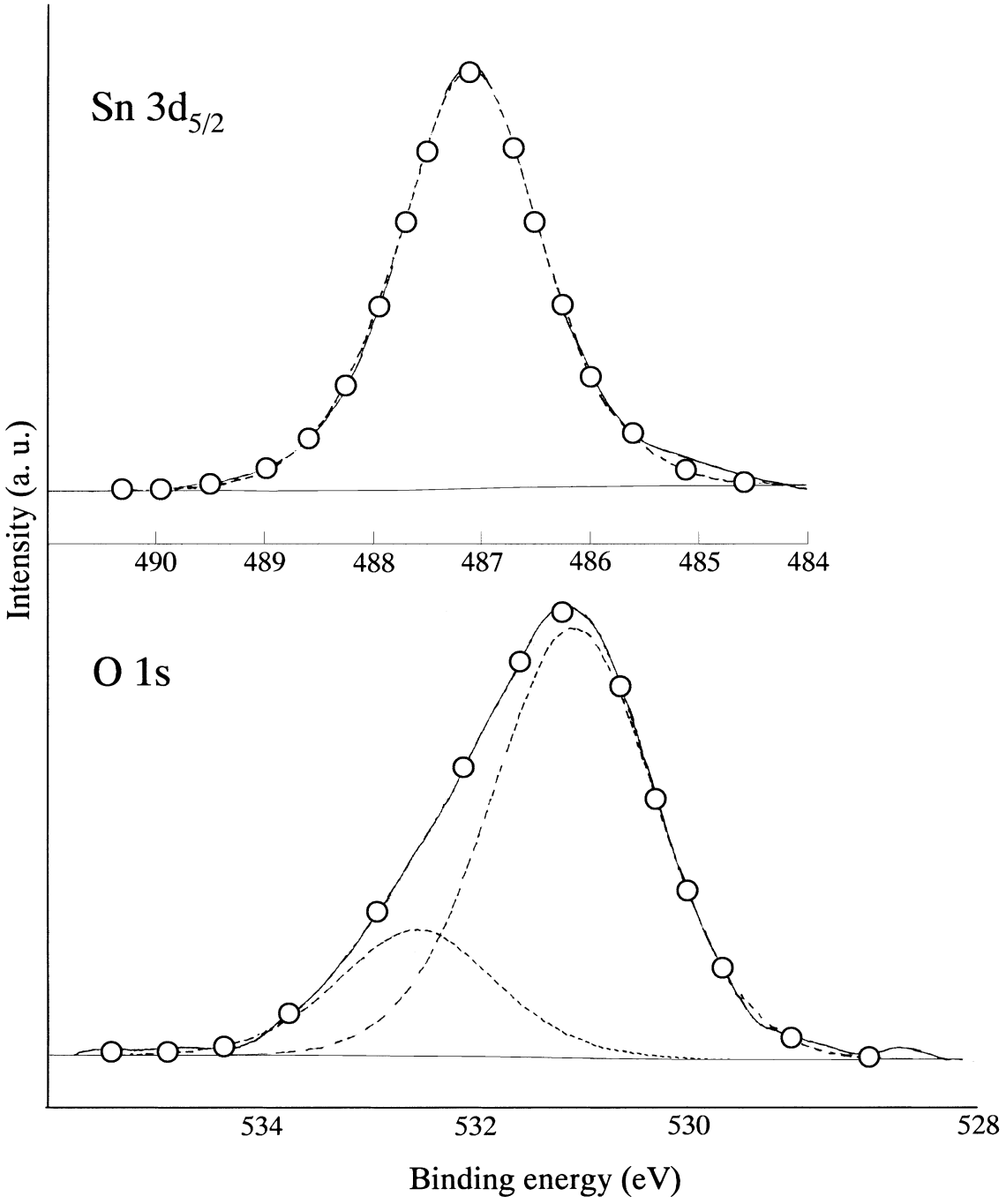

Fig. 5. XPS spectra of the thin film, formed on silanol region in the patterned OTS–SAM formed onto H:Si substrate, heated at 600 °C for 3 h in ambient air. The solid lines are the experimental data, the dashed lines are the deconvolutions, and the open circles are the resulting fits to the spectra.

at the OTS–SAM surfaces formed on the H:Si and SiO_2/Si substrates. At both OTS–SAM surfaces, the θc decreased with the UV irradiation time, and the similar behavior in the θc decrease at both surfaces was observed. After 15 min, the θc at the surfaces of both samples were measured to be $<5^\circ$, which indicated elimination of the SAMs on both substrates. The OTS–SAM with the θc of 114° was also cleaved within 15 min by UV irradiation in ambient air.

Fig. 4 shows micropatterned thin films selectively deposited on silanol regions in the patterned OTS–SAM, formed on the H:Si substrate, prepared by UV irradiation for 15 min through the photomask. Comparing both SEM images, a high quality resolution pattern of the thin films with a thickness of about 30 nm could be obtained. In addition, the straight line and any kinds of curves could be described at the desirable sites on the substrate. Fig. 5 shows Sn $3d_{5/2}$ and O 1s XPS spectra for the thin film, which was site-selectively deposited on the silanol region in the patterned OTS–SAM formed on the H:Si substrate, oxidized at 600 °C for 3 h in ambient air. Both spectra could be completely fitted by the pseudo-Voigt functional curve, as shown in Fig. 5. The observed binding energy of 487.1 eV is very close to Sn $3d_{5/2}$ data confirmed in SnO_2 thin film.[13] The O 1s spectrum was verified to be composed of two

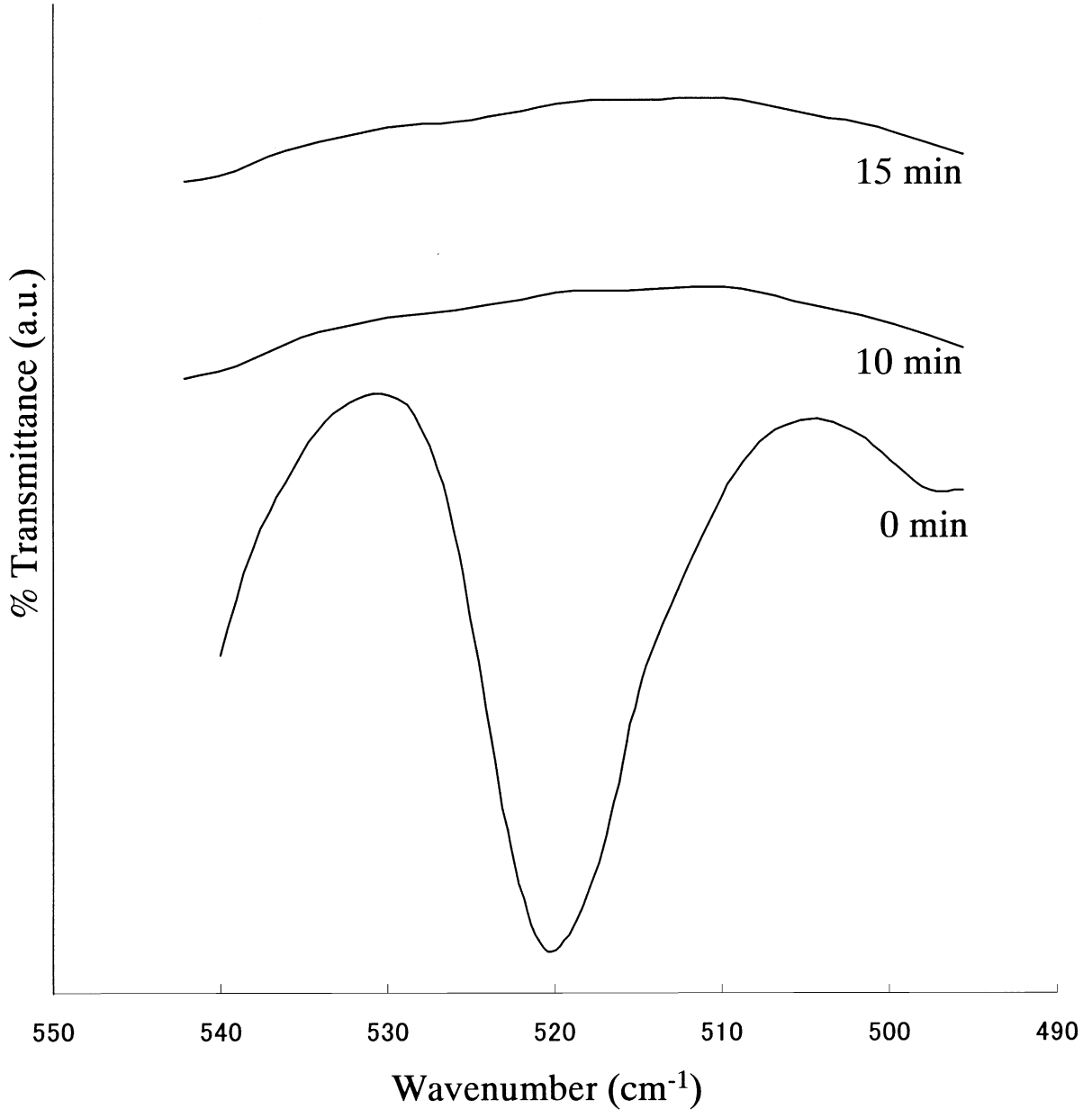

Fig. 6. FT-IR spectra of the anhydrous toluene solution included OTS precursor of 1.0 vol.% for the soaking time of 0, 10, 15 min, respectively.

components positioned at around 531.1 and 532.5 eV, respectively. The peak observed at 531.1 eV is probably attributed to O in the SnO_2 phase and the other to adsorbed molecular oxygen from an atmosphere on the SnO_2 thin film as a charged oxygen species, i.e. O^{2-} and O^{-}.[14] The different peak positions of the two O 1s components are due to the difference in the electronegativity between oxygen and tin.[15]

4. Discussion

Sagiv[16] has first found that OTS molecules covalently bond to the inorganic solid surface and form a well ordered and oriented surface of monolayers, which is similar to Langmuir–Blogett film, by the dehydration–condensation reaction between the hydrolyzed OTS molecules [$C_{18}H_{17}Si(OH)_3$] and the hydroxyl groups at

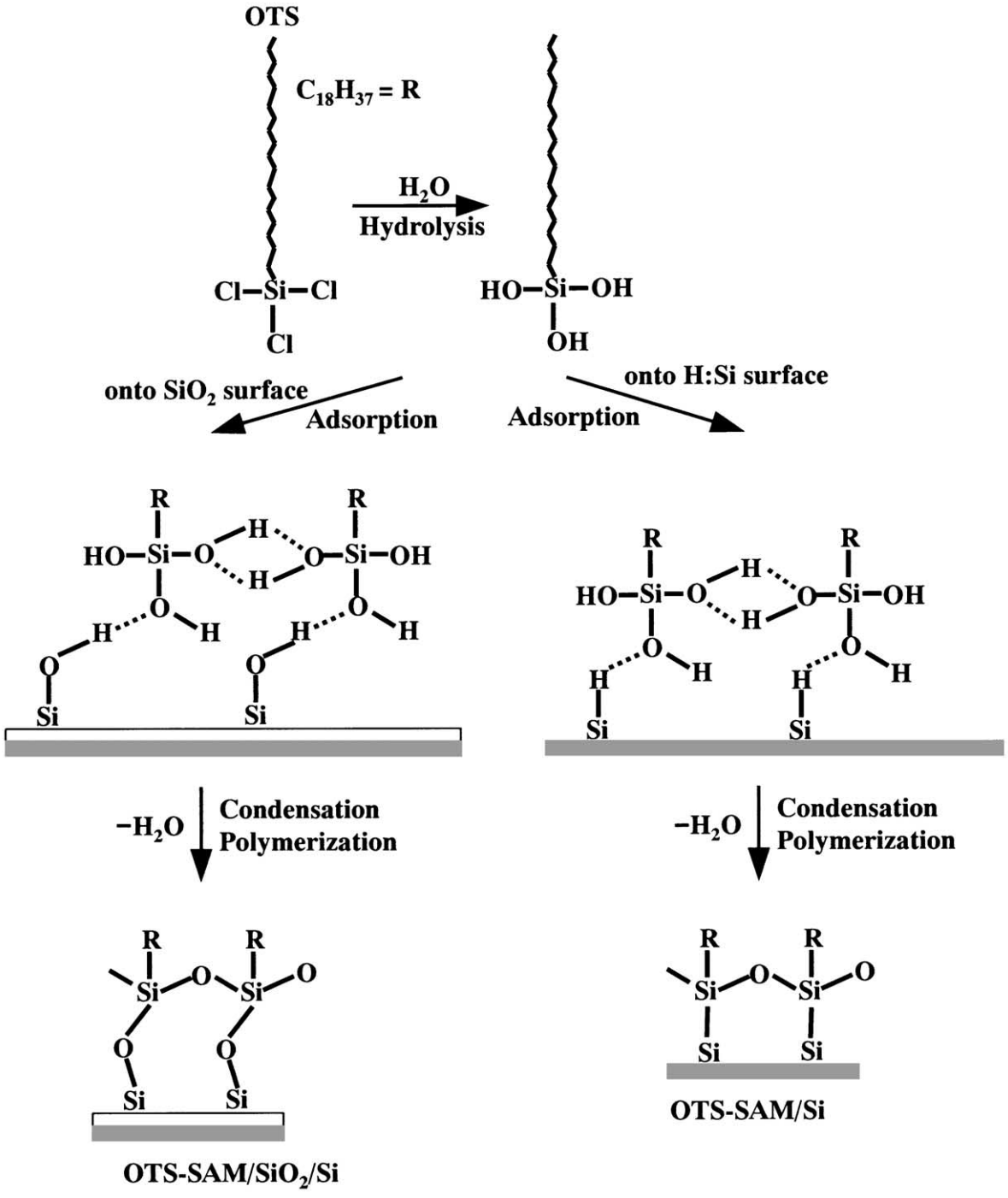

Fig. 7. Illustration for the formation of the OTS–SAM on the SiO_2/Si and the H:Si substrates.

the surface of the inorganic substrate. It is well known that the organosilane compounds, such as alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes require hydroxylated surfaces as substrates for their formation.[17] The driving force for this self-assembly is the in-situ formation of polysiloxane, which is connected to the surface by silanol groups, and therefore, the organosilane–SAM formations have been successfully formed only on SiO_2, Al_2O_3, quartz, mica, GeO_2, glass, ZnSe, and Au.[17]

However, OTS molecules densely formed on a H:Si substrate, as shown in Fig. 1. Fig. 6 shows the FT-IR spectra measured using the KBr method. The peak detected at around 520 cm^{-1} shows that the molecules with the Si–Cl bonds[18] initially presented in the sample. From this figure, it can be seen that the OTS molecules were imperfectly hydrolyzed initially but, gradually hydrolyzed with soaking time, and then perfectly hydrolyzed by small amounts of H_2O molecules dissolved into an anhydrous toluene solution after 10 min soaking. This behavior obeys the general rule for the formation of OTS–SAM, as mentioned above. In contrast, surprisingly, none of the θc changes at the H:Si surfaces were observed with the soaking time ranging from 0 to 30 min in an anhydrous toluene solution containing OTS molecules of 1.0 vol.%.

Fig. 7 shows the possible scheme for the formation mechanisms of the OTS–SAMs on a SiO_2/Si and a H:Si substrates. In the case of the SAM formation on a SiO_2/Si, the OTS molecules are hydrolyzed by water existing only as a layer adsorbed on the surface of the solid substrate, i.e. adsorbed to silanol groups.[16] The covalently bound silane monolayers were formed by the dehydration–condensation at the interface between adsorbed molecules and the substrate.[16] The heat treatment of the as-formed OTS–SAM plays an important role in monolayer formation, because of the promotion of their perfect polymerisation.[17]

Based on the earlier mechanism of the SAM formation on SiO_2/Si, the mechanism for the formation of the OTS–SAM on H:Si substrate would be considered as follows. Firstly, the fact that the θc at the surface of the OTS–SAM formed on H:Si was made $<5^\circ$ by UV irradiation for 15 min as shown in Fig. 3 would imply no or little existence of H–Si bonds in the OTS–SAM substrate, because of the photoreactivity of H–Si was extremely low even in ambient air. Indeed, H–Si bonds were imperfectly cleaved by UV irradiation, judging from the observation that the θc was kept above 28° even at the surface of the H:Si substrate exposed by UV for 3 h in ambient air. In addition, no changes in the θc at the OTS–SAM surfaces formed on the H:Si were observed by ultrasonication in H_2O for several hours. This implies that the OTS molecules do not adsorb not but covalently bond to the H–Si bonds at H:Si surface, because of the removal of the adsorbed molecules by ultrasonication for 1 h in ethanol.[10] Furthermore, the θc at the SAM surface on the H:Si, which was measured to be above 110°, was larger than that on the SiO_2/Si as shown in Fig. 1. This θc was close to the value at the surface of the alkyl monolayers directly bonded to the Si surface.[19]

These experimental facts would imply the direct bonding between OTS–SAM and the surface of the Si substrate. Therefore, the OTS molecules are considered to bond directly to the Si substrate, which means formation of an "OTS–SAM/Si substrate", by the dehydration and condensation mechanism through the heat treatment as shown in Fig. 7. As shown in Fig. 2(b), the formation of OTS–SAM directly bonded on Si is also considered to cause atomic flattening of the OTS–SAM surface.

Tin hydroxide thin films were selectively deposited only on the silanol region in the patterned OTS–SAM/Si substrate. Masuda et al.[12] have succeeded in fabricating a micropatterned TiO_2 thin film only on the silanol regions in the patterned OTS–SAM/SiO_2/Si substrate, through the use of hydrolysis between the titanium (IV) chloride precursors and Si–OH groups at the silanol region. From this mechanism, the cleaved area of the OTS–SAM/Si could be made a hydrophilic surface through photoxidation by UV irradiation in ambient air.

5. Conclusion

An atomic scale flat OTS–SAM surface was formed on a Si substrate by the reaction between the OTS molecules and the H:Si substrate. The hydrophobicity at the surface of the OTS–SAM formed on the H:Si substrate was larger than that formed on the SiO_2/Si substrate. Similar photoreactivity was observed in both the OTS–SAMs formed on the H:Si and SiO_2/Si substrates. Tin hydroxide thin films were site-selectively deposited on the silanol region in the patterned OTS–SAM substrates.

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