

# In-Situ Observation of a Self-Assembled Monolayer Formation of Octadecyltrimethoxysilane on a Silicon Oxide Surface Using a High-Speed Atomic Force Microscope

*Junji Iwasa,<sup>1</sup> Kazuhisa Kumazawa,<sup>1</sup> Kazumasa Aoyama,<sup>1</sup> Hiroshi Suzuki,<sup>1</sup> Shingo Norimoto,<sup>2</sup>  
Takafumi Shimoaka<sup>2</sup> and Takeshi Hasegawa<sup>2\*</sup>*

<sup>1</sup>Nippon Soda Co. Ltd., Chiba Research Center, Goi-minamikaigan, Ichihara, Chiba 290-0045,  
Japan

<sup>2</sup>Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

**ABSTRACT:** The formation mechanism of a self-assembled monolayer (SAM) of octadecyltrimethoxysilane on a silicon oxide surface in reaction is studied *in situ* by using a high-speed atomic-force microscope that has a time resolution of 2 sec per a frame. The SAM formation of a silane coupling reagent on silicon is known to comprise three development stages of nucleation, growth and coalescence. In the present study, the first nucleation stage is found to have dynamical processes: a molecular cluster attached to the substrate swings largely, which keeps reactive molecules off in an early stage, during which the cluster needs many minutes to develop in diameter. Once a domain of ca. 30 nm in diameter is formed, the reaction rate is dominated by the rim length of the domain, which implies that the weakly-adsorbing limit approximation can be employed. Another important point is that the molecular domains generate a SAM like an occupied sheet of tiles, and each tile is connected to the substrate by few feet. In fact, a molecular tile can easily be removed by applying soft air plasma leaving the rest tiles of highly packed molecules, which is confirmed by infrared p-polarized external-reflection spectroscopy.

**KEYWORDS:** high-speed AFM, self-assembled monolayer, silicon, formation dynamics

The self-assembled monolayer (SAM)<sup>1,2</sup> technique is one of the promising surface coverage techniques, which provides an ultrathin layer with the monolayer thickness over a wide area of a solid surface. SAM is outstanding for the chemical stable character due to the covalent bond to the substrate. This extremely thin and stable coating technique is quite suitable for protection of a precision processed product such as an optical lens and an electronic device. Another benefit of SAM is that the preparation procedure is relatively easy, which can be done in a wet process. A wet process is quite suitable for industrial applications in terms of a mass production.

The concept of SAM dates back to the first report of adsorption of oleophobic films from a solution on a glass flask by Zisman et al.,<sup>3</sup> followed by a famous report of thiol chemisorption on a gold surface, which was characterized in detail by Nuzzo and Allara using infrared (IR) spectroscopy.<sup>4</sup> The formation of SAM on a glass or silicon oxide was first comprehensively studied by using IR spectroscopy by Maoz and Sagiv.<sup>5</sup> In this first IR analysis on a nonmetallic surface, the generated SAM of *n*-octadecyltrichlorosilane on silicon had inferior molecular packing to that made on zinc selenide or germanium. The problem of SAM preparation on silicon was, however, thoroughly overcome later by the same research group,<sup>6,7</sup> and the monolayer coating technology is ready for many applications in basic science as well as the industrial purposes. Recently, a long-term stable chemical reagent that lasts for two months is commercialized to make a defect-free SAM in ten minutes on silicon, glass and alumina with a great reproducibility.<sup>8,9</sup>

Although the preparation technique has thus already been accomplished, the chemical formation mechanism of a SAM on silicon is not fully revealed yet. In the case of the thiol chemisorption on gold, the mechanism is relatively easy to understand,<sup>2,4</sup> since the thiol molecule diffused in the reactive solution attains a gold atom of the surface to make a chemical

bond. In fact, the molecular arrangement and orientation of a thiol SAM on gold depends on the surface orientation of gold.<sup>10</sup> On the other hand, the SAM formation on silicon is highly complicated especially when a silane coupling reagent is employed.<sup>11</sup>

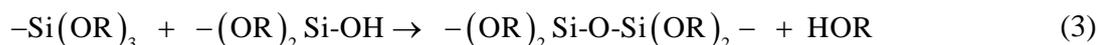
The chemical bond of Si-O-R (R: hydrocarbon residue) in a silane coupling reagent is weak and ready for cleavage on an attack by a nucleophilic reagent such as an anionic species, water or an alcohol; whereas the siloxane bond (Si-O-Si) is chemically stable.<sup>12</sup> With the chemical characteristics, a silane coupling reagent is designed to have a reactive terminal having  $-\text{Si}(\text{OR})_3$ . When the group is reacted with a dissociated substrate surface (the surface is denoted by “||” in Eq. (1)), the acid dissociated group on the surface ( $^-\text{O}-\text{Si}||$ ) works as a nucleophilic reagent to replace the  $\text{OR}^-$  group to make a siloxane bond as:



When the terminal group reacts with another silane coupling reagent in the solution with an aid of water or an alcohol, on the other hand, the following reaction occurs.



The generated intermediate product reacts again with the terminal group to form a siloxane bond.



In short, the reaction of Eq. (1) and other reactions represented by Eqs. (2) and (3) should occur in a competitive manner. In the present study, this competition is discussed via a time-resolved observation of the surface topography.

To reveal the surface topography with time of reaction, atomic-force microscope (AFM) is a powerful tool. The development of SAM with time was first studied by Zasadzinski et al.,<sup>13</sup> although it was an *ex-situ* analysis. They focused on the shape of the developing monolayers, and it was readily discussed via the fractal dimension. As for *in-situ* measurements in a reaction

solution, the first AFM study was carried out by Woodward and Schwartz.<sup>14</sup> They point out that dense two-dimensional (2D) monolayer islands are formed “in solution” in an early reaction stage, followed by nucleation, growth and coalescence, which is a core image of the SAM formation on silicon.

To reveal the dynamics of molecular motion during the SAM formation, a time-resolved measurement technique is needed, and the high-speed AFM (HS-AFM) technique<sup>15</sup> meets the expectation. HS-AFM with a rapid scanning speed (shortest: 80 ms per frame) yields a series of AFM images having a wide scan area (micrometer order). In this manner, HS-AFM provides dynamic images like an animation, which is used in biochemistry<sup>16</sup> and material chemistry fields.<sup>17</sup>

In the present study, HS-AFM is employed to study the reaction dynamics of SAM formation of octadecyltrimethoxysilane (OTS) on a silicon oxide. As a result, accomplishment of the nucleation step is found to require long time, during which a molecular cluster swings largely, which works as a barrier to receive additional molecules. Once the cluster develops to be a molecular domain, the reaction rate becomes linear with time, which implies that the SAM formation is dominated by lateral (2D) polymerization to generate molecular tiles, and the surface reaction with the silicon oxide surface is very minor.

This molecular scheme is examined by molecular quench by applying soft air plasma to the SAM on silicon. As a result of the quench of the SAM, some molecular tiles (not individual molecules) are removed to leave a highly dense tiles even after three fourth of the SAM was removed, which is confirmed by IR spectroscopy. This study also supports that only a part of each molecular tile is chemically connected with the substrate surface, and the foot area of SAM on silicon is sparse in comparison to that of thiol on gold.

## RESULTS AND DISCUSSION

**Nucleus generation in the initial stage:** Figure 1 presents snap shots of AFM images in the initial time course (0.5~15 min) of SAM generation on the Si(100) surface. The HS-AFM system has a time resolution of 2 sec per frame with the size of  $3 \times 3 \mu\text{m}^2$ . In the series of images, small spots are figured out gradually, and the number of the spots increases monotonously over the time scale. Since the spatial resolution of the AFM system is insufficient for observation of a molecule, the spot involves at least tens of OTS molecules, i.e., a molecular cluster.

On a closer inspection, however, each spot is found to exhibit “blinking” with time keeping its position (Figure 2 or ‘Video 1’ in Supporting Information). The “fixed position” indicates that a molecular cluster is generated as a nucleus, and the cluster stays without desorption, which further implies that the molecules are at least partly bound to the silicon oxide surface. Since a topographic image by AFM visualizes the height change, the blinking of a cluster chemically-bound to the Si substrate suggests that the molecules in the cluster swing largely in the solution (Figure 3a). This may be because each molecular domain generated in this time range is spatially isolated, which has no support to keep the molecular orientation. The orientation fluctuation is a repeating reversible phenomenon, and the bright spot during the blinking should be attributed to the perpendicular molecular orientation in a molecular domain. Since the blinking is observed with a time scale of 10 sec, the time constant of the molecular swing is expected to be in a several sec range.

This “molecular swing model” is supported by a fact that the diameter of each cluster does not develop in this time region, although the number of clusters increases. If the molecules are rigidly aggregated without swing, the nucleus should attract additional molecules via the van der Waals interaction and a condensation reaction, which makes the diameter of the ‘cluster’

larger to be a ‘domain.’ Therefore, an appearance of a “rigid domain” is a key to generate the SAM layer. In other words, the direct chemical reaction between the Si surface and the monomeric OTS is not significant; whereas two-dimensional molecular assembling takes place about a rigid domain (nucleus) in the parallel direction to the surface. In this manner, the development of the diameter of nucleus needs much time, and the development is not observed in this time range.

**Development of the domains:** On a further observation, the domains begin to develop in diameter (17 min or later). Figure 4 presents a series of HS-AFM images of an identical area. Although the frame position is a little bit shifted with time due to a convection flow induced by the solvent volatilization, an identical spot can be pursued and the development of the diameter is apparently found. In this time range, blinking is no longer found, which suggests that the molecular swing halts to receive additional molecules on the domain with time. Once a domain is formed, the domain begins to develop two dimensionally in size. The critical size of a domain for the irreversible size-development is found to be ca. 30 nm in diameter.

To make the 2D polymerization reaction of the Si-O-Si formation proceed smoothly parallel to the substrate surface, as discussed in the previous section, the molecules in the domain should have a perpendicular stance to the surface (Figure 3b), so that the outer rim of the domain would be clear to receive the reacting molecules. Now, the siloxane formation reaction is a competitive reaction on the domain rim to that on the substrate surface.

The reaction kinetics on the ‘substrate surface’ is relatively simple: the reaction is governed by the ‘diffusion’ of the reactant,  $D$ , which is expressed by  $D \propto t^{-1/2}$ . Once reactant molecules are provided on the surface, the number of reacted molecules on the surface,  $n_s$ , increases linearly to  $t$ . The entire reaction involving the diffusion thus becomes  $n_s \propto Dt = t^{1/2}$ .<sup>14</sup>

In a similar manner, the number of reacted molecules on the rim,  $n_R$ , is  $n_R \propto t^{1/2}$ . Since  $n_R$  is proportional to the rim length,  $l$ ,  $n_R$  can be a function of the radius of the domain,  $r$ , via  $l = 2\pi r$  (i.e.,  $r \propto n_R \propto t^{1/2}$ ). As a result, the number of reacted molecules,  $n_A$ , contributes to the domain area,  $\pi r^2$ , such as  $n_A \propto \pi r^2 \propto t$ . In short, if the reaction is driven by the “on-rim” reaction, the domain *area* should be *linear to the reaction time*. In this manner, the reactions on the substrate surface and on a domain rim can be discriminated.

The height of each domain was 3 nm keeping the monolayer thickness, which implies that the reaction occurred two-dimensionally as expected. Since the domain area can be calculated by an image analysis thanks to the stable domains, the areas of the domains were read from Figure 5, and they are summarized in Figure 6. As discussed above, each domain exhibits a linear change once a stable domain is generated. This result straightforwardly implies that the rate-determination step is governed by the rim length of a domain, and the reaction on the substrate surface is minor. This is named the “on-rim aggregation mechanism.” Woodward and Schwartz state that the reaction rate should be linear with time when the weakly-adsorbing limit holds on the substrate surface,<sup>14</sup> which agrees with our schematic image.

On a further observation by using HS-AFM, creation of a new domain and a merge of largely developed domains were both observed as presented in Figure 7. In the panel with the time stamp of 2'00'' (of ‘Video 2’ in Supporting Information), a large domain is close to another small domain indicated by a blue arrow. Four minutes later (at 6'00''), these domains begin are merged, and similar merges and increases of size are found here and there to occupy the surface in a few minutes. This surface reaction continued and the surface was fully covered in additional time of about 8 min.

**Removal of domains using soft plasma:** If the “on-rim aggregation mechanism” dominantly works in the SAM formation, the chemical bonds between the molecules and the silicon-oxide surface can be imperfect as illustrated in Figure 3b, which results in sparse space about the molecular foot region near the substrate surface. To experimentally confirm this schematic model, the SAM was subjected to soft plasma. Air plasma comprises electronically charged small gas molecules, and a direct contact of plasma with a molecule can cut a chemical bond. In the present case, the charged small molecules are expected to penetrate into the sparse room, and some chemical bonds connecting the SAM and the Si oxide surface would be broken. If an individual molecule is removed after cutting the bonds, the molecular density of the SAM would homogeneously be decreased, which should be monitored by checking the molecular conformational disorder using IR spectroscopy.

Figure 8 presents four IR p-polarized external-reflection (ER) spectra<sup>16-21</sup> of the SAM on silicon as a function of the exposure time in 11 sec to the soft air plasma. Since the angle of incidence was chosen to be  $60^\circ$  that is less than Brewster’s angle, the surface selection rule (SSR)<sup>16-21</sup> is summarized as follows: the surface-parallel component of a normal mode yields a negative absorption band; whereas the surface-perpendicular component appears as a positive band. The strong negative bands of the anti-symmetric  $\text{CH}_2$  stretching vibration ( $\nu_a\text{CH}_2$ ) mode and symmetric ( $\nu_s\text{CH}_2$ ) one thus indicate that molecular axis is nearly perpendicular to the surface.<sup>21</sup> In this manner, the band intensity is influenced by the molecular orientation as well as the molecular density. The spectrum at  $t = 0$  sec of the present study quantitatively reproduces the spectra reported in a former study,<sup>8</sup> which confirms that the reproducibility of the SAM on silicon is very high. The band positions of the two modes ( $2917$  and  $2850\text{ cm}^{-1}$ ) tell us that the

molecules have the all-trans zigzag conformation.<sup>21</sup> In other words, the molecular packing is quite high.

The methyl group, on the other hand, yields three bands: the asymmetric  $\text{CH}_3$  stretching vibrations ( $\nu_a\text{CH}_3$ ) at  $2966\text{ cm}^{-1}$  (in-skeleton; “is”),  $2958\text{ cm}^{-1}$  (out-of-skeleton; “os”) and the symmetric  $\text{CH}_3$  one ( $\nu_s\text{CH}_3$ ) at  $2879\text{ cm}^{-1}$ . Reflecting the perpendicular stance of the molecule, the  $\nu_a\text{CH}_3$ -is and  $\nu_s\text{CH}_3$  modes appear as positive bands while the  $\nu_a\text{CH}_3$ -os mode appears as a negative band, which perfectly consistent with the image of the perpendicular stance when considering the SSR. Of note here is that the methyl-related bands are from both the terminal end of the main chain and a part of the methoxy group near the molecular foot. The unusually high wavenumber position of the  $\nu_a\text{CH}_3$ -is band at  $2966\text{ cm}^{-1}$  indicates that the molecular feet are highly crowded.<sup>22</sup>

When the SAM is exposed to the plasma, the band intensities soon exhibit an apparent decrease, which is found even at  $t=1$  sec (Figure 8). Since the decrease is found nearly proportional for each band, the methyl group at the terminal of the hydrocarbon chain is concluded to remain without break although the terminal methyl groups are faced to the air plasma. In this manner, fortunately, the molecules are readily removed from the Si substrate by the soft plasma. Of particular importance is that both  $\nu_a\text{CH}_2$  and  $\nu_s\text{CH}_2$  bands keep the wavenumber positions of the all-trans zigzag conformation during the exposure time up to 11 sec. As mentioned above, if the molecules are removed individually, the monolayer would soon be loosed resulting in a higher wavenumber shift in the IR spectra. Therefore, “no shift” paradoxically indicates that “molecular domains” are removed from the monolayer by breaking the sparse feet. In other words, the monolayer is packed with molecular domains like tiles, and

some tiles are removed by breaking the connecting feet to the substrate. This molecular scheme is consistent with the “on-rim aggregation mechanism.”

Of another interest is that the  $\nu_a\text{CH}_3$ -is band at  $2966\text{ cm}^{-1}$  (crowded molecules) is shifted down to  $2964\text{ cm}^{-1}$  (normal packing) when the plasma was irradiated for 11 sec. Since nearly 75% of the monolayer is removed at this time, many rims of tiles would be free, which should yield a normal position of the  $\nu_a\text{CH}_3$ -is band (ca.  $2963\text{ cm}^{-1}$ ). In this manner, the schematic of “a sheet of molecular tiles” is readily confirmed by IR ER spectroscopy.

**CONCLUSION:** The SAM formation mechanism of OTS on a silicon oxide surface was pursued by using a HS-AFM. In an early stage of reaction, small molecular clusters appeared with blinking with a time constant of a few seconds, but the size increase was not recognized, which implies that molecules are not tightly packed and they are swinging in the reaction solution. Once the molecular cluster is stabilized to be a 2D domain, the rim of the domain works as the reaction front to receive reacting molecules. In fact, the reaction rate is found linear with time in this time region. This implies that molecular aggregation is an important factor to help the condensation reaction between the silane coupling reagents; whereas the reaction with the silicon oxide surface is much slower. As a result, the SAM is generated by paving the 2D molecular domain until the surface is fully covered. In this manner, the direct chemical reaction between the molecule and the silicon-oxide surface is not a dominant factor to control the SAM generation. The connection between the monolayer and the substrate by the sparse feet was readily confirmed by IR spectroscopy after an exposure to soft air plasma. The dynamic molecular covering process on silicon has thus been revealed for OTS.

## METHODS

**Materials:** Octadecyl trimethoxy silane (OTS) was a product of Nippon Soda Co., Ltd. (Tokyo, Japan), which was provided as a 0.5% methylethylbenzene solution (SAMLAY<sup>®</sup>-A). The organic solvents used were all guaranteed reagents purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The water was obtained by using a Millipore (Molsheim, France) Elix UV-3 pure-water generator and a Yamato (Tokyo, Japan) Autopure WT100U water purifier, which is a compatible model with Milli-Q. The electric resistivity of the final product was higher than 18.2 M $\Omega$  cm and the surface tension was 72.8 mN m<sup>-1</sup> at 25 °C measured by using a Kyowa (Saitama, Japan) DropMaster DM-501Hy contact angle meter, which guaranteed that the water was free from organic contaminants.

Single-side polished Si(100) substrates with a thickness of 725 $\pm$ 25  $\mu$ m were purchased from Valqua FFT Inc. (Tokyo, Japan) for infrared external-reflection (IR ER) measurements. A piece (20 x 40 mm<sup>2</sup>) of the wafer was cleaned by sonications in pure water, ethanol, acetone, dichloroethane (1 min each) and 2-propanol (10 min) successively.

**Preparation of SAM on silicon for IR studies:** After a Si(100) surface was oxidized under an ozone atmosphere to have hydroxyl groups on the surface,<sup>8</sup> the oxidized silicon was dipped in the SAMLAY<sup>®</sup>-A solution for 10 min, and the substrate is washed by the solvent, NS clean 100. The reaction goes rapidly within a few minutes,<sup>16</sup> and 10 min is enough to complete the reaction.

To remove the unreacted compounds and contamination on the surface, an organic solvent, NS Clean 100, made by JX Nippon Oil and Energy (Tokyo, Japan) was used to wash the SAM. For the detail of the solvent, the reader is referred to the literature.<sup>8</sup> For the background measurements of the IR spectra, a hydrogen-terminated silicon wafer was prepared by using a standard technique described in the same literature.

**High-speed AFM measurements:** High-speed AFM measurements were performed on a Research Institute of Biomolecule Metrology (Tsukuba, Ibaraki, Japan) Nano Explorer High-speed Atomic Force Microscope with an Olympus (Tokyo, Japan) BL-AC10FS cantilever. A Si(100) substrate was cut into 2x2 mm<sup>2</sup> pieces, and the surface of each piece was oxidized by using a UV ozone cleaner. After the substrate was immersed in SAMLAY<sup>®</sup>-A with a volume of 120 μL, topographical images were collected every 2 sec with a frame size of 3x3 μm<sup>2</sup> by the AC mode.

**IR ER spectroscopy:** IR p-polarized external-reflection (ER) measurements<sup>167-21</sup> were performed on a Thermo Fischer Scientific (Madison, WI, USA) Magna 550 FT-IR spectrometer equipped with a Harrick (Pleasantville, NY, USA) VR1-NIC Variable Angle Reflection Accessory. The p-polarized IR ray was obtained by using a Harrick PWG-U1R Wire-Grid Polarizer. The modulation frequency of FT-IR was 60 kHz, and the detector was a liquid-N<sub>2</sub> cooled MCT detector. The wavenumber resolution was 4 cm<sup>-1</sup> and the interferogram was accumulated 2000 times.

## **AUTHOR INFORMATION**

### **Corresponding Author**

\*E-mail: htakeshi@scl.kyoto-u.ac.jp

The present address:

Shingo Norimoto: JASCO Co. Ltd., Ishikawa-machi, Hachioji-shi, Tokyo 192-8537, Japan

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**Supporting Information Available:** Videos 1 and 2 are available in Supporting Information.

These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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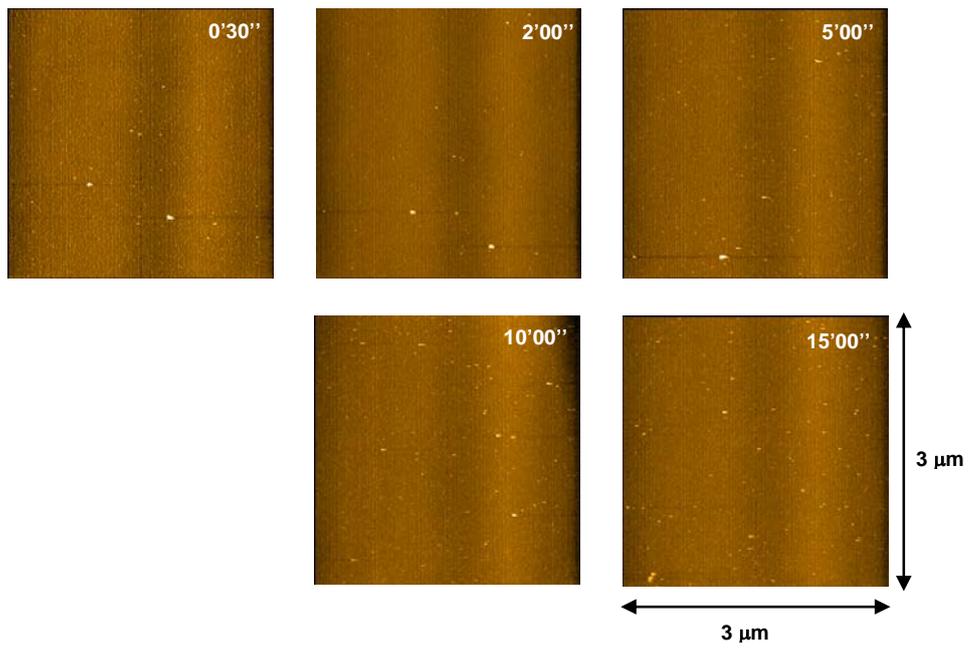
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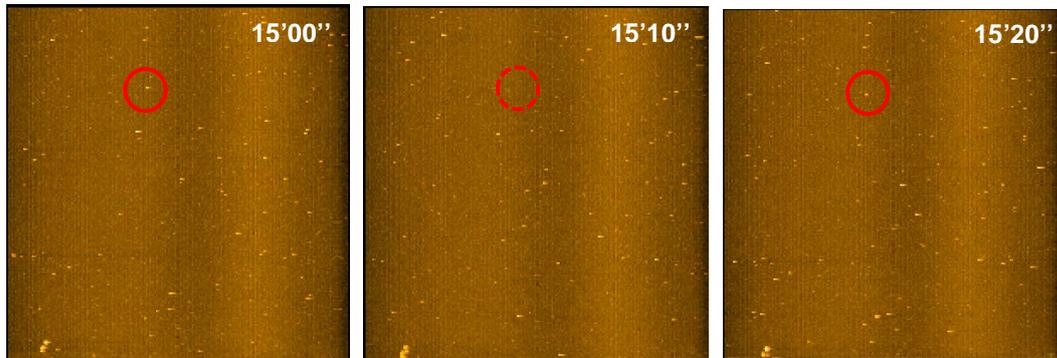
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## FIGURE CAPTIONS

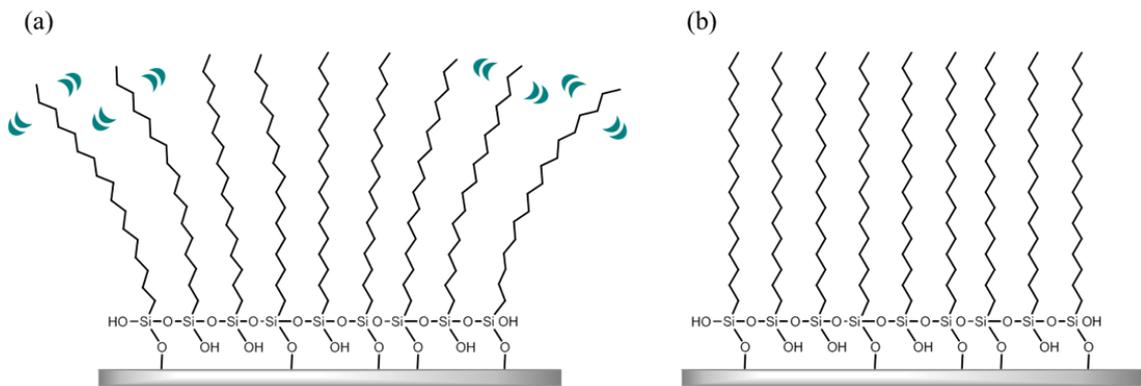
- Figure 1.** Snap shots of a HS-AFM movie measured in the first stage of the SAM formation reaction on a silicon oxide from  $t = 0.5$  min to  $t = 30$  min.
- Figure 2.** Blinking of a bright spot at a fixed position.
- Figure 3.** Schematic images of a swing of a molecular cluster having a) a tilted orientation and b) surface normal orientation.
- Figure 4.** Snap shots of HS-AFM showing a development of a molecular cluster to be a molecular domain measured from  $t = 17.0$  min to  $t = 19.5$  min.
- Figure 5.** Once the diameter of a molecular domain reaches 30 nm, the reaction is accelerated. The domains marked by a~k are used to pursue the reaction with time (see Figure 6).
- Figure 6.** Relationship between the domain area and the reaction time after 20.5 min. The domains used for the measurements are presented in Figure 5.
- Figure 7.** Snap shots of HS-AFM showing an appearance of a new domain and their merge.
- Figure 8.** IR p-polarized ER spectra of an OTS SAM on silicon oxide as a function of the exposure time to a soft air plasma from 1 to 11 sec. The angle of incidence was  $60^\circ$ .



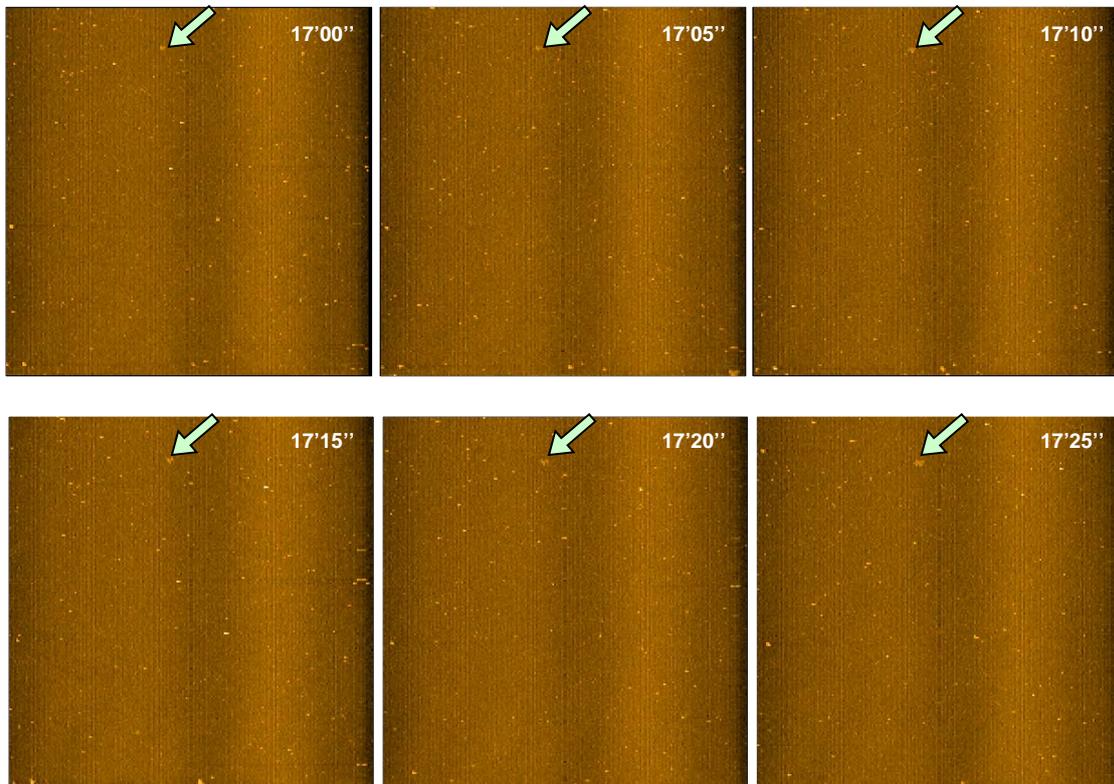
**Figure 1.** J. Iwasa et al.



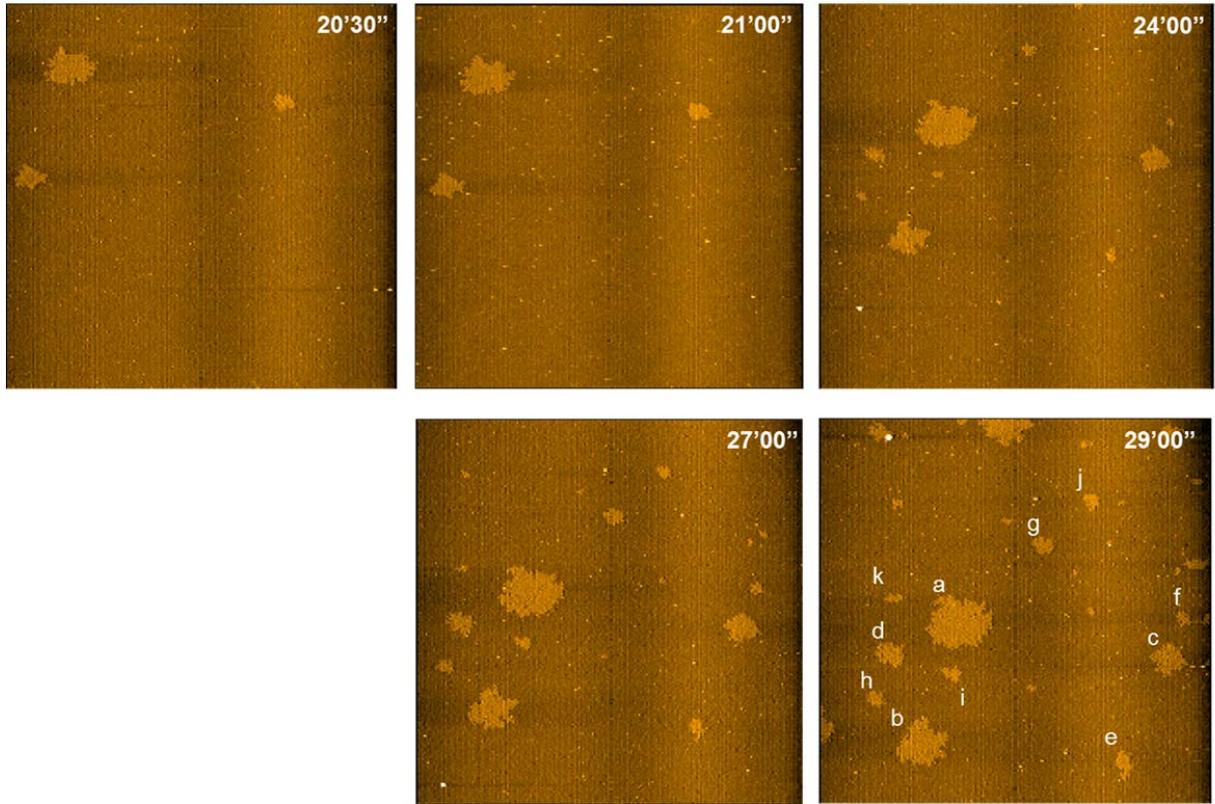
**Figure 2** J. Iwasa et al.



**Figure 3** J. Iwasa et al.



**Figure 4** J. Iwasa et al.



**Figure 5** J. Iwasa et al.

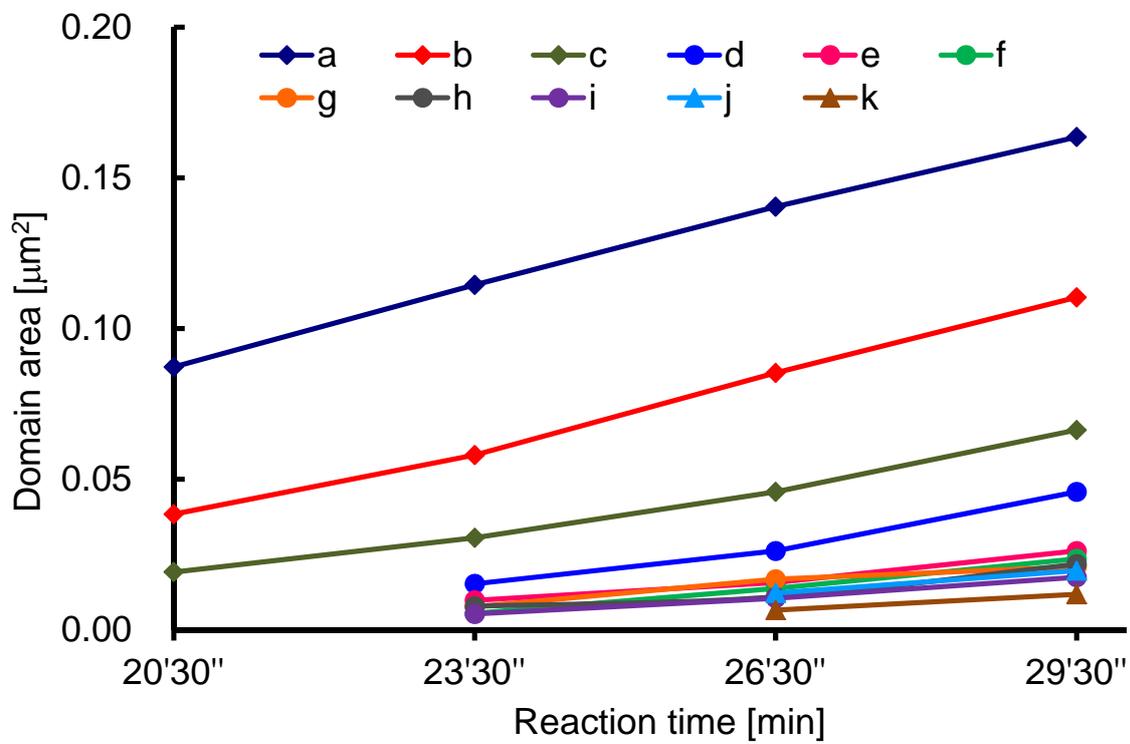
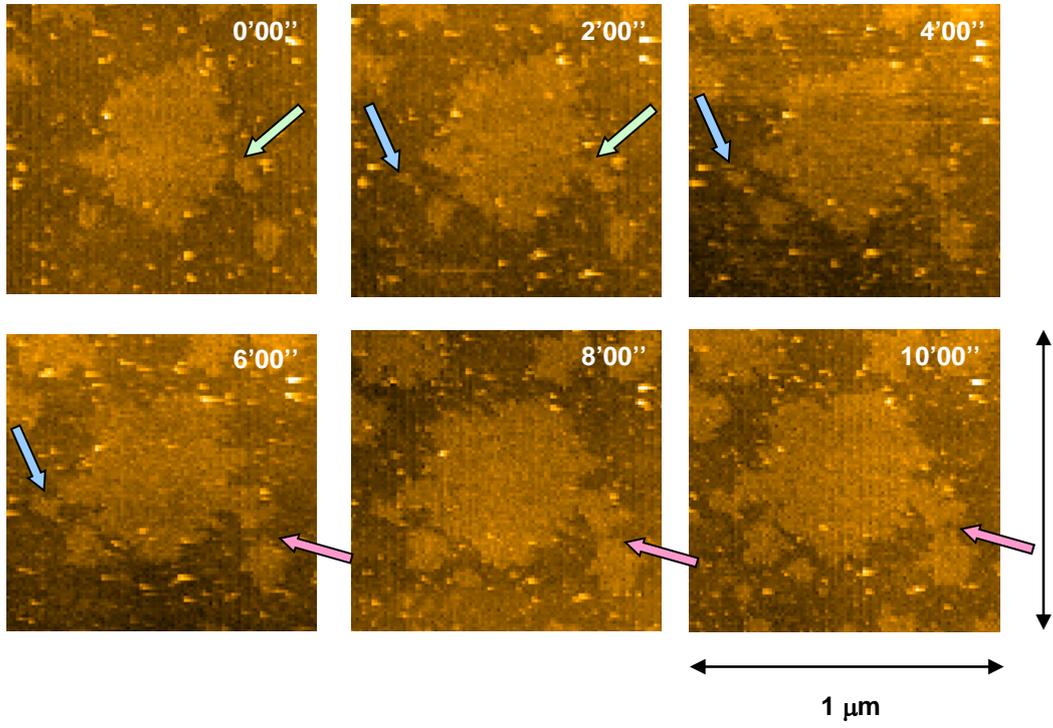


Figure 6 J. Iwasa et al.



**Figure 7** J. Iwasa et al.

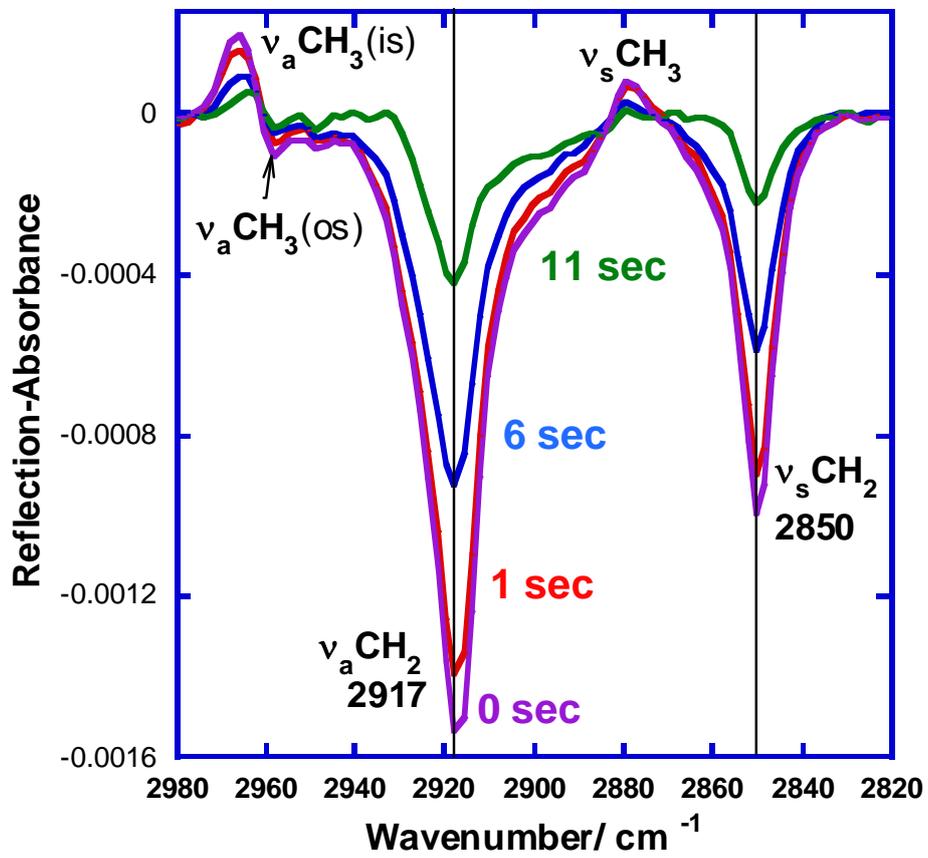


Figure 8 J. Iwasa et al.

### TOC Graphics

