Self-Assembled Monolayers Directly Attached to Silicon Substrates Formed from 1-Hexadecene by Thermal, Ultraviolet, and Visible Light Activation Methods

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Abstract

Using 1-hexadecene as a precursor, self-assembled monolayers (SAMs) were fabricated on hydrogen-terminated silicon(111) [H-Si(111)] surfaces without forming an interfacial oxide layer on the basis of thermal (180 ˚C, 2 h), ultraviolet (UV; 500 mW cm^{-2}, 10 h), and visible-light activation (330 mW cm^{-2}, 16 h) processes. As characterized by water contact angle measurements, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and ellipsometry, the hexadecyl SAM fabricated by the visible-light process had a highly-ordered molecular arrangement and a closely-packed methyl-terminated surface similar to the SAMs prepared by the thermal and UV activation processes. The photo-irradiation wavelength dependence of the visible-light activation process was further studied at irradiation wavelengths of 400, 550,

and 700 nm. The SAM formation reaction was certainly promoted at all the wavelengths, even at 700 nm. However, oxidation of the Si surface became apparent due to the slow rate in SAM growth, and thus the monolayer coverage of SAM at 700 nm became smaller. The reaction rate became faster with the decreasing wavelength for activation, probably due to the increase in the light adsorption coefficient of Si. The excitation of Si, namely, the generation of hole/electron pairs at the Si substrate, is assumed to be the rate-controlling step of the visible-light activation process.

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1. Introduction

Organic thin films with a single molecular thickness are known to be formed via self-integration and self-organization of molecules chemisorbing onto solid surfaces. Studies of such self-assembled monolayers (SAMs) have attracted much attention due to fundamental scientific interest and their potential for practical applications. One characteristic feature of the SAMs is that the orientation and arrangement of the molecules are highly ordered.[1] Self-assembly has been recognized as a key for bottom-up nanotechnology to

integrate a set of minute elements and to fabricate novel materials and devices. In particular, SAMs on inorganic semiconductor surfaces[2,3] are of interest for constructing novel micro/nano electronic devices integrating a variety of functions based on organic molecules and semiconductor characteristics. The formation of SAMs on silicon (Si) surfaces is of primary importance considering the utility of Si in semiconductor devices. SAMs have been formed on Si substrates through silane coupling chemistry using a specific organosilane reagent as a precursor.[4,5] In this case, however, the Si substrate must be covered with an oxide layer, that is, an insulating layer, with a thickness of at least 1 - 2 nm. Such an interfacial insulating layer between the SAM and the substrate becomes an electron transport barrier which prevents fusion of the electronic properties of the SAM and Si. Hence, a SAM directly attached to Si without an interfacial insulator is crucial to develop novel electronic materials and devices in which the organic monolayer and Si are effectively integrated.

Since 1993 when Linford *et al.*[6] reported the method to form SAMs on Si substrates without an interfacial insulator, that is, SAMs directly attached to Si, several processes to form such SAMs have been developed.[7] While Linford *et al.* employed 1-alkenes as precursors which reacted with a hydrogen-terminated Si (H-Si) substrate in order to form directly-attached SAMs, alcohols[8] and aldehydes[9] have also been shown to form similar SAMs on a H-Si substrate. In order to promote chemical reactions of a precursor with a H-Si surface, several techniques adopting a reaction initiator, heating, photo irradiation, and

other methods have been reported.[7-11] An accepted scheme of SAM formation from 1-alkenes is as follows: Si radicals, i.e., Si dangling bonds, are first formed by the elimination of hydrogen atoms from a H-Si surface using a reaction initiator or based on photo irradiation. The organic molecules are then covalently immobilized on the Si surface through a reaction with the surface Si radicals. When a 1-alkene molecule reacts with the Si radical, for example, the molecule is bound through a Si-C bond. One radical remains at the beta-position of the bonded molecule and abstracts one H atom from an adjacent Si-H site, resulting in the formation of a Si radical again at the substrate surface. A chain reaction proceeds by repeating these steps.[7,10,12,13] However, the mechanism of the thermal process for SAM formation from 1-alkenes has not yet been satisfactorily elucidated. Although it was first considered to be due to thermal dissociation of Si-H bonds to form Si radicals, it has been pointed out that the temperature of less than 200 $^\circ$C adopted for the thermal SAM formation was too low to dissociate Si-H bonds.[14]

According to the mechanism described above, the formation of Si radicals is the crucial step in the UV activation process to obtain SAM directly attached to Si. Since the bond energy of Si-H is 331 - 351 kJ mol^{-1}, simple arithmetic estimates that UV light with wavelengths shorter than 350 nm is required to perform the efficient homolytic cleavage of a Si-H bond.[15] In 2001, however, Stewart *et al.*[16] reported the formation of 1-dodecene SAMs on hydrogen-terminated porous Si using visible light with wavelengths longer than

400 nm.   Shortly thereafter, in 2004, Sun *et al.*[17,18] reported that 1-hexadecene SAM and related SAMs on H-Si(100) and H-Si(111) were formed using visible light at a wavelength of 447 nm.   In these visible-light excitation methods, the Si radical generation step is unlikely to proceed.   The mechanism for SAM formation must be via a different path without Si radical generation.

In order to activate a H-Si surface thermally for SAM formation, a temperature range of 100 - 200 ˚C is needed in general.   Some precursor molecules may be damaged in this temperature range especially when a SAM consists of molecules with thermally unstable moieties.   UV light also causes damage to some types of precursor molecules, e.g., molecules having an absorption band in the UV region, although the use of UV light has an advantage in that light can selectively illuminate a minute area on the substrate yielding SAMs grown on the selected area.[9]   The use of visible light instead of UV light is expected to reduce such damage and, therefore, detailed studies on the visible light excitation of H-Si substrates for SAM formation are important. However, the information on this topic remains limited to a few reports.[16-20] Furthermore, no report have appeared comparing the surface morphologies of the SAMs prepared by thermal, UV-light, and visible-light activation processes.

The objectives of this study are to compare SAMs formed on H-Si(111) substrates by thermal, UV-light, and visible-light activation processes, to discuss the differences and similarities of these SAMs, and to elucidate the dependence of the formation reaction on wavelength for this type of SAMs.   We have

selected 1-hexadecene as the target substance, since 1-alkenes have been so widely applied as precursors that reference data on such SAMs are available, and the molecule is sufficiently long to allow emergence of intermolecular interactions which promote self-organization of the molecules.

2. Experimental Methods

2.1 *Hydrogen-termination of Si substrates*

A Si wafer [n-type Si(111), P doped, resistivity ρ = 1 - 10 Ω cm, single-side mirror-polished] was used for these experiments. All substrates cut from the wafer were cleaned ultrasonically with ethanol and ultrapure water (> 18.0 Ω cm) and then photochemically cleaned by exposure to vacuum ultraviolet light generated from an excimer lamp [Ushio, UER20-172 (UEM20-172) + UEP20, λ = 172 nm, FWHM = 14 nm, power density = 10 mW cm^{-2}] for 20 min each.[21] H-Si substrates were obtained by etching the cleaned samples in 5% HF solution for 5 min at room temperature and, subsequently, in 40% NH$_4$F solution for 30 s at 80 °C.[22]   During the HF treatment, the experimental set-up was covered with aluminum foil serving as a light shield. Throughout these treatments, the native oxide layer on each sample was removed and, consequently, the underlying Si surface was exposed and terminated with hydrogen. In the second step of the hydrogen-termination (H-termination) treatment, NH$_4$F solution was heated up to 80 °C for oxygen removal.

2.1 *Hydrosilylation*

Hydrosilylation, the reaction of 1-hexadecene with H-Si in this case, was performed under three different conditions as summarized in Table I. The thermal activation system consisted of a three-neck separable glass flask of *ca.* 360 cm^3. About 200 cm^3 of neat 1-hexadecene liquid was put into the flask and heated with a hot plate placed beneath the flask. A thermometer, an Allihn condenser, and a gas inlet were attached to the flask for measuring the liquid temperature, refluxing, and deaeration of the system with a N_2 gas stream, respectively. In order to suppress the H-Si substrate surface oxidation with dissolved oxygen, deaeration was started more than 30 min before the substrate was immersed in the precursor liquid. Heating the liquid was started 30 min after the samples had been put into the liquid; the liquid continued to be deaerated until the sample was removed. The UV activation was conducted as follows. About 200 cm^3 of neat 1-hexadecene liquid was put into a three-neck flask in which two glass tubes used as an inlet and an outlet of a N_2 gas stream were installed. The center neck of the flask was sealed with a polyethylene film with a thickness of about 10 μm which served as a window for UV-irradiation. The liquid was deaerated for more than 30 min, and then a H-Si(111) substrate was immersed in the liquid. The sample was irradiated with UV-light from a high-pressure mercury lamp (Ushio, USH-500D, 500 mW cm^{-2} at the sample surface). The liquid was kept at room temperature and deaerated during irradiation. A custom-made quartz vessel was used for the visible light activation method. The vessel was a rectangular cell with

5-mm-thickness which is attached to one end of cylindrical tube with a diameter of 20 mm. Its capacity was about 100 cm^3. Neat 1-hexadecene liquid (50 cm^3) was put into the vessel. Two glass tubes for purging with N$_2$ gas were attached using a silicone rubber stopper inserted at the open end of the cylinder. The liquid was deaerated with a N$_2$ gas stream for more than 30 min, and then a H-Si(111) substrate was quickly put into the rectangular cell. The substrate was irradiated with a xenon lamp [Asahi Spectra, MAX-1000 (UV-lamp + VIS-mirror)] from the outside of the cell through a long pass filter (> 420 nm) for 16 h or through one of three types of band pass filters (400 nm, 500 nm, 700 nm, FWHM ≈ 10 nm) for 8 - 32 h. Light longer than 850 nm was cut off by the VIS-mirror. The liquid was kept at room temperature and deaerated during irradiation. The intensity of the visible light at the sample surface was controlled at 330 mW cm^{-2} with the long pass filter and at 8 mW cm^{-2} with each of the band pass filters by using a neutral density filter installed inside the xenon lamp source. The power density was measured using a laser power meter (Neoark, PM335), on the light-receiving part of which cardboard with a 1 × 1 cm^2 square hole was attached. All the samples prepared by the three activation methods were subsequently sonicated for 5 - 10 min each in hexane, methanol, and ultrapure water, in that order. The samples prepared by thermal, UV-light, and visible-light activation methods are hereafter referred to as Th-SAM, UV-SAM, and Vis-SAM, respectively.

2.3   *Analytical method*

The static water contact angles of the fabricated samples were measured with a contact angle meter (Kyowa Interface Science, Model CA-D); we fixed the size of the water droplets at about 1.5 mm in diameter.   X-ray photoelectron spectroscopy (XPS) analysis was carried out using an ESCA-3400 system (Kratos Analyical), the background pressure of which was less than 5×10^{-6} Pa. The Mg Kα X-ray source was operated at 10 kV and 10 mA.   The XPS spectra obtained were calibrated so that Si-Si peaks from the Si substrates were referenced to 99.6 eV[23] in order to cancel binding energy shifts due to charging up effects.   To make the chemical state conspicuous, the intensity scales of the Si 2p spectra were standardized so that the main Si-Si peaks became the same intensity.   Topographic images with an area of 1000×1000 nm^2 were acquired by an atomic force microscope (AFM; Seiko Instruments, SPA-300HV + SPI-3800N) with a Si probe (Seiko Instruments, SN-AF01-100, force constant of 0.1 N m^{-1}).   The thicknesses of the fabricated SAMs were measured with a spectroscopic ellipsometer (Otsuka Electronics, FE-5000).   The region measured was 400 - 800 nm in wavelength. The incident angle was set at 70˚. The model of air / organic film / Si was used for the analysis of raw data.   The refractive index of SiO$_2$[24] was adopted as that of the organic film over the measured wavelength range.[21]

3.   Results and Discussion

3.1   *Comparison of the three activation methods*

Table II summarizes water contact angles of the H-Si(111) substrate and the substrates treated by the thermal, UV-light, and visible-light activation processes with 1-hexadecene. The H-Si(111) surface shows a water contact angle of about 84˚, in good agreement with the reported value.[25] The samples treated with 1-hexadecene show water contact angles of around 108˚ irrespective of the activation methods. These values are close to the value of closely-packed methyl terminated surfaces, 110˚,[26] and that of an octadecyl SAMs on Si fabricated by Linford *et al.*,[10] who reported that advancing and receding contact angles of the octadecyl SAMs prepared on a H-Si substrate by a thermal method were 113˚ and 110˚, respectively. Thus, our samples are considered to have a similar methyl-terminated surface. Accordingly, 1-hexadecene molecules have also been successfully attached to the H-Si(111) substrate surfaces resulting in the formation of hexadecyl SAMs.

XPS-Si 2p spectra of the samples are shown in Fig. 1. While the spectrum of a cleaned Si substrate without H-termination has a small side peak centered at 103.8 eV which corresponds to oxidized Si and indicates that the substrate is covered with a surface oxide, the other spectra consist of a single peak centered around 99.6 eV, which corresponds to non-oxidized Si (see the experimental section). These results indicate that there is no interfacial oxide layer on each of the samples and that the SAMs are directly attached to the Si substrates.

Results of quantitative XPS analysis of the samples are summarized in Table III. The surface oxygen concentration decreases greatly from 37 to 4

at.% due to the H-termination process, since the surface oxide layer is removed during the process.   This oxygen concentration value of 4 at.% is due to contamination, most likely adsorbed water molecules, since the H-Si(111) sample surface is not oxidized as shown in Fig. 1.   When focusing on the three SAM-covered samples, the carbon amounts at the surfaces increase greatly up to 34 - 38 at.%, compared with that of the H-Si(111) sample (11 at.%), which is due to contamination during sample handling in air.   These increases in the surface carbon concentration support our conclusion that 1-hexadecene molecules have been fixed on the samples.   Here we should note that the values of 34 - 38 at.% may involve a contribution of carbon contamination of about 11 at.% at most, while the higher water contact angles of the SAM surfaces compared to that of H-Si(111) indicate that the SAM surfaces are not likely to be contaminated.   Considering the similar carbon amounts of the SAM-covered samples, the densities of the fixed organic molecules are almost the same. Furthermore, visible light could excite the SAM formation reaction just as UV light does, although the irradiance of the visible light was relatively weak compared with that of UV light, so that the visible light could not homolytically cleavage a Si-H bond as mentioned in the introductory section.

An AFM image of the H-Si(111) sample is shown in Fig. 2(a).   Its surface morphology shows that a surface consisting of flat terraces and steps has been successfully fabricated.   The step height is estimated to be about 0.3 nm from a cross-sectional view of the AFM image (not shown here).   This value agrees

with the theoretical value of 0.31 nm as a monoatomic step on the Si(111) surface.   The average width of the terraces is about 60 nm, which is consistent with a miss-cut angle of the Si wafer of less than 0.5˚.   AFM images of the SAM-formed substrate surfaces [Figs. 2(b)-2(d)] show very similar surface morphologies to that of the H-Si(111) surface.   The SAM surfaces have terraces with the same widths and monoatomic steps.   These results demonstrate that the prepared SAMs are all uniform and highly-ordered.

The thicknesses of the SAMs were estimated to be 2.0 - 2.3 nm by ellipsometry.   These values are reasonable for the thickness of monolayers, since the precursor molecule of 1-hexadecene has a length of about 2 nm.   The thickness of a monolayer is determined by the density and the tilt angle of the adsorbed molecules.   The SAMs prepared in this study were highly uniform as demonstrated by the AFM images.   In such a situation, a lower density of the adsorbed molecules results in a large molecular tilt angle and a thinner layer. If we know the absolute thicknesses of the SAMs, then their molecular densities and tilt angles can be derived.   However, in our case, the thicknesses estimated by ellipsometry are not absolutely accurate, mainly because of uncertainty about the refractive index data of the SAMs, although the data are sufficiently accurate to compare the relative difference in thickness between SAMs.   We can only conclude here that there is little difference in film thickness, and consequently in molecular density and tilt angle, between Th-, UV-, and Vis-SAMs.   Here we should emphasize again that the organic molecules are arranged with a high

order in these SAMs since monoatomic steps of the H-Si(111) substrates remain without any distortions as demonstrated in the AFM images even though the substrates were coated with a SAM, the thickness of which was more than 7 times greater than the step height.

From the results described above, visible light certainly promoted the SAM formation reaction between H-terminated Si and 1-alkene, as has been reported.[16-20] The Vis-SAM obtained has been proven to have the same features as the Th- and UV-SAMs. The visible light under which the Vis-SAM was formed had a spectrum with wavelengths between 420 nm and 850 nm. But it has not yet been elucidated whether light of any wavelength would result in the same SAMs on Si. We then examined the wavelength dependence of the SAM formation reaction specifically in terms of the uniformity of the SAM.

3.2 *Wavelength dependence*

Figure 3 summarizes (a) the water contact angle, (b) the ellipsometric thickness, and (c) the surface carbon density obtained from quantitative analysis by XPS on each sample fabricated by irradiation of a Xe lamp through each of the band-pass filters with center wavelengths of 400, 550, and 700 nm for 0, 8, 16, and 32 h. As the irradiation wavelength becomes shorter, the water contact angle increases faster. For example, the angle changed from 90° up to 108° with 32 h of irradiation time and approached the value of the closely-packed methyl terminated surfaces (110°)[26]. For 8 h of 550- and 700-nm-light irradiation, exposure of the methylene group to the surface resulted in the

temporary decrease of the water contact angle. The thicknesses of the films grown on the samples estimated by means of ellipsometry also increased as irradiation time increased [Fig. 3(b)]. The growth rate is higher with irradiation at a wavelength of 400 nm than with irradiation at a wavelength of 700 nm. The growth in thickness measured using ellipsometry implies the possibility of molecular adsorbtion as well as H-Si oxidation.

XPS-Si 2p spectra of the samples after 16-h-irradiation at each wavelength are shown in Fig 4. The spectra of the irradiated samples consist of a single peak centered at around 99.6 eV, which corresponds to non-oxidized Si. The spectra have no side peak corresponding to oxidized Si. The surface carbon concentration increases with the increase in irradiation time of the visible light at wavelengths of 400, 550, or 700 nm [Fig. 3(c)]. The carbon amount increases as the irradiation wavelength becomes shorter from 700 to 400 nm. The carbon density saturated at 30 at.% under irradiation with wavelength of 400 nm and at 20 at.% in the case of 400 nm. We discuss this difference later.

These experimental results clearly demonstrate that 1-hexadecene molecules adsorbed on the H-Si substrates gradually and formed SAMs by visible-light irradiation even when the wavelength was 700 nm, and the reaction rate becomes faster as the wavelength of irradiation was shortened. AFM images of the samples in Fig. 5 show very similar surface morphologies to that of the H-Si(111) surface, demonstrating that the prepared SAMs are all uniform and highly-ordered and that the films grow gradually without making domains.

The SAMs formed by photo irradiation for 16 h with each of the selected wavelengths showed lower contact angles, smaller carbon amounts, and smaller thicknesses compared with the Vis-SAM. This is due to the much smaller irradiation intensities of 8 mW cm^{-2} reduced by the band-pass filters than 330 mW cm^{-2} when irradiated with visible light longer than 420 nm. It is suggested that the SAM growth was not completed for 16 h at such low irradiation intensity. Nevertheless, we conclude that the reaction of 1-hexadecene and H-Si was certainly promoted by irradiation at 400, 550, and 700 nm.

Here we discuss on the difference in the saturated surface carbon densities shown in Fig. 3(c). As previously concluded, the SAM formation reaction rate increases as the irradiation wavelength is shortened. During the immersion in the precursor liquid, an oxidation reaction occurs, in which the surface Si atoms bonded to hydrogen atoms react with dissolved oxygen molecules. There are small amounts of oxygen in the liquid in spite of N_2 purging before and during the immersion of the substrates. The SAM formation reaction is slow when light with a long wavelength of 700 nm is irradiated on the surface at a low intensity of 8 mW cm^{-2}, at which point that surface oxidation rate is comparable to SAM formation reaction rate. Surface oxidation decreases the number of reaction sites for 1-hexadecene molecules, so that the number of attached molecules at 700 nm is smaller than the number at 400 nm.

A mechanism to promote the chemical reaction of 1-alkenes with a H-Si surface for SAM formation based on the excitation of the H-Si surface with

visible light has been suggested in several recent papers: Stewart *et al.* suggested an exciton-based mechanism.[16] This mechanism sounds reasonable because SAMs were formed on H-terminated porous Si substrates, which have a direct band gap and, hence, are easily excited by visible light to provide hole/electron pairs. Sun *et al.* proposed that the same mechanism was also adaptable the SAM formation on H-Si(100) surfaces.[17] They have recently suggested another refined mechanism in which Si-Si bonds are cleaved in a concerted manner.[20] In these mechanisms proposed by Sun *et al.*, the generation and separation of hole/electron pairs are hypothesized. First, hole/electron pairs are generated at the H-Si surface due to photo-excitation. The electrons generated temporarily transfer deep into the bulk Si. Finally, only the holes remaining at the surface participate the reaction. However, this hypothesis is not perfect, since photochemical hydrosilylation based on visible light excitation can occur both on n- and p-type Si substrates. On the p-type Si surface, in general, photo-generated holes migrate into the bulk Si and most electrons remain on the surface. In 2006, Coletti *et al.*[27] proposed a new concerted mechanism for thermal hydrosilylation as an alternative to the conventional radical-based mechanism. In this mechanism, the carbon-carbon double bond of a 1-alkene approaches the Si-H bond in a parallel fashion, and they then form a four-membered transition state, resulting in the evolution of a Si-C bond. They have explained using density functional calculations that the activation energy is much lower than that required for the radical-based mechanism. According to

their calculations, the activation energy of this concerted mechanism is about 270 kJ mol^{-1}. Based on a simple arithmetic estimation, light with a wavelength shorter than 441 nm has a photon energy larger than 270 kJ mol^{-1}. However as elucidated in this study, the reaction proceeded even under irradiation with lower photon energies at wavelengths of 550 and 700 nm. UV/vis spectroscopy showed that 1-hexadecene molecules do not absorb light with wavelengths between 300 and 800 nm. This indicates that the visible light used in this experiment was not absorbed by the precursor molecules but excited the Si substrate itself. In addition, the optical absorption coefficient of single crystal Si at 400 nm is about 50 times that at 700 nm.[24] Thus, as the irradiation wavelength becomes shorter, the number of hole/electron pairs generated at the Si substrate surface increases and governs the SAM growth reaction. Therefore, the generation of a hole/electron pair with an excitation photon is plausible as the rate-controlling step in the reaction between H-Si and a 1-alkane. While Coletti *et al.*[27] did not consider hole/electron generation, this process can further reduce the activation energy of the concerted mechanism for Si-C bond formation. The electron-rich vinyl group of the 1-alkene can attack the holes on the surface which migrated to the surface due to the band bending of n-type Si.

4. **Conclusions**

SAMs were fabricated on Si(111) substrates via the chemical reaction of 1-hexadecene with H-Si.   The reaction was promoted by thermal, UV-light, or visible-light activation of the H-Si surface.   The hexadecyl SAM prepared by visible-light activation showed the same chemical and physical properties as were indicated by water contact angle measurements, XPS, ellipsometry, and AFM.   The Vis-SAM had a highly-ordered molecular arrangement and a closely-packed methyl-terminated surface similar to Th-SAM and UV-SAM. Moreover, the dependence of the visible-light activation process on irradiation wavelength was studied at irradiation wavelengths of 400, 550, and 700 nm. We found for the first time that the SAM formation reaction was promoted even at 700 nm, which was a longer wavelength than already reported in the literatures.[16-20]   The first systematic AFM observation of SAMs made by light irradiation at each wavelength including 700 nm elucidated that each SAM was uniform and flat, so that terrace and step structures were easily recognized. The SAM formation at the longest wavelength of 700 nm, which is longer than that employed by Sun *et al.*,[20] clearly indicated that the photo-activation reaction mechanism is related to band excitation in bulk Si.   In addition, the reaction rate increased with decreasing wavelength of activation, probably due to the increase in the light adsorption coefficient of Si.   The rate-controlling step of the visible-light activation process is assumed to be the excitation of Si and subsequent generation of hole/electron pairs.   Since Si-H bond cleavage cannot occur with only the energy gain from visible light irradiation, it should

take place in concert with other covalent bond formation(s). The fact that the thermal activation method produced a SAM similar to the visible light activation method showed that the SAM formation, in this case, involves a thermal band excitation of carriers. The effect of the intensity of light and/or dopant density in bulk Si on SAM formation by the visible light activation method must be elucidated in the future. The visible-light activation process examined in detail is certainly promising as a soft process for the fabrication of SAMs directly attached to Si substrates, because visible light is gentler and causes less damage to organic molecules than the thermal and UV activation processes.

Acknowledgements

6. References

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Table I. Experimental conditions for SAM formation.

Excitation method	Tempreture or irradiance	Reaction time (h)
Heat (thermal)	180 ˚C	2
UV light	500 mW cm^{-2}	10
Visible light (>420 nm)	330 mW cm^{-2}	16
Visible light (400 nm)	8 mW cm^{-2}	8 - 32
Visible light (550 nm)	8 mW cm^{-2}	8 - 32
Visible light (700 nm)	8 mW cm^{-2}	8 - 32

Table II. Water contact angles of the samples (deg).

H-Si	84
Th-SAM	109
UV-SAM	109
Vis-SAM	108

Table III. Surface chemical compositions of the samples as determined by

quantitative analysis by XPS (at.%).

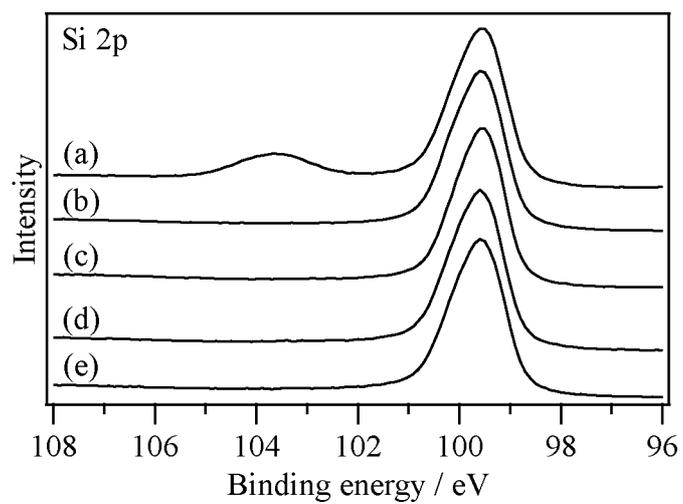|	Si	C	O
Cleaned Si	53	10	37
Si-H	84	11	4
Th-SAM	58	38	3
UV-SAM	59	36	4
Vis-SAM	61	34	5

Fig. 1. XPS-Si2p spectra of (a) photochemically-cleaned and (b) H-Si substrates, and (c) Th-SAM, (d) UV-SAM, and (e) Vis-SAM coated samples.
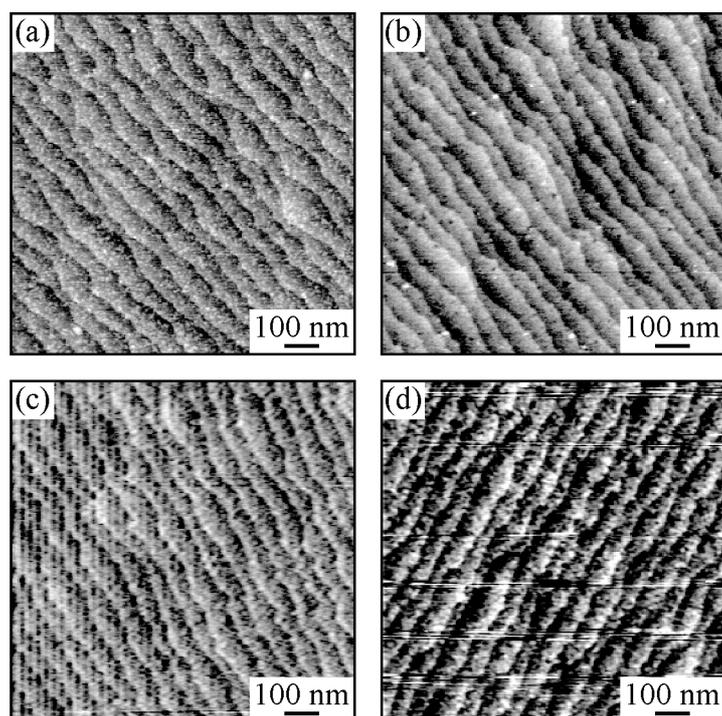
Fig. 2.　AFM topographic images of (a) a H-Si substrate and (b) Th-SAM, (c) UV-SAM, and (d) Vis-SAM coated samples.
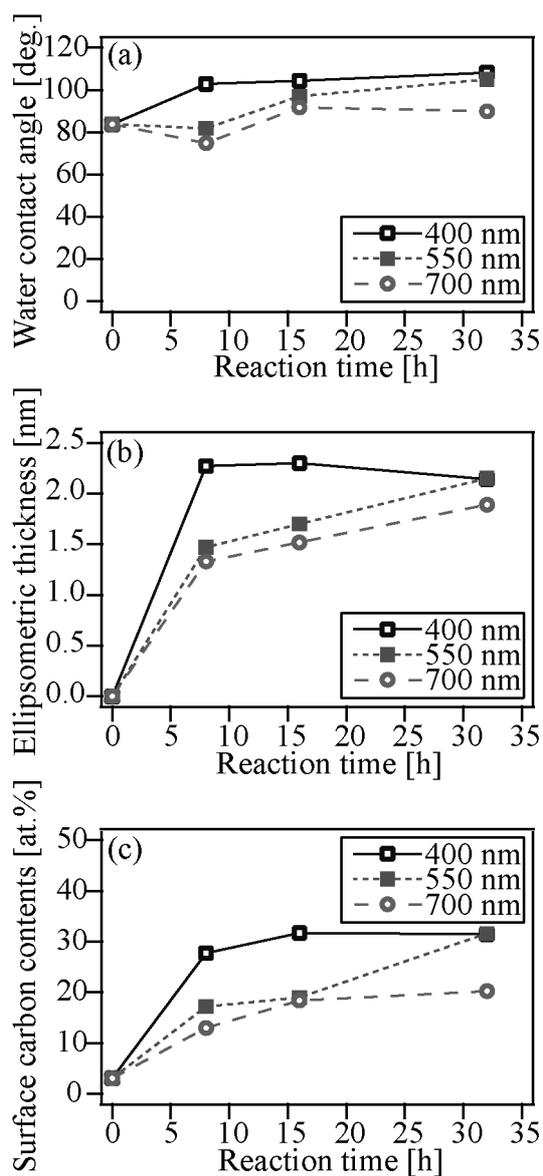
Fig. 3. (a) Water contact angles, (b) ellipsometric thickness, and (c) surface carbon density obtained from quantitative analysis by XPS on each sample immersed in liquid 1-hexadecene for 8 - 32 h with visible light irradiation at 400, 550, and 700 nm in wavelength.
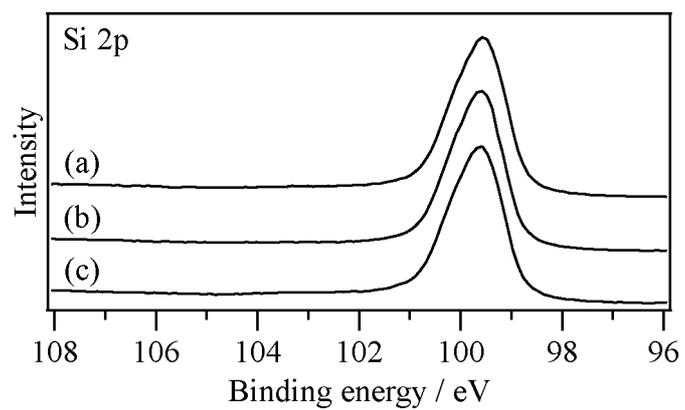
Fig. 4. XPS-Si 2p spectra of SAM-coated samples prepared by visible-light irradiation at (a) 400, (b) 550, and (c) 700 nm in wavelength.
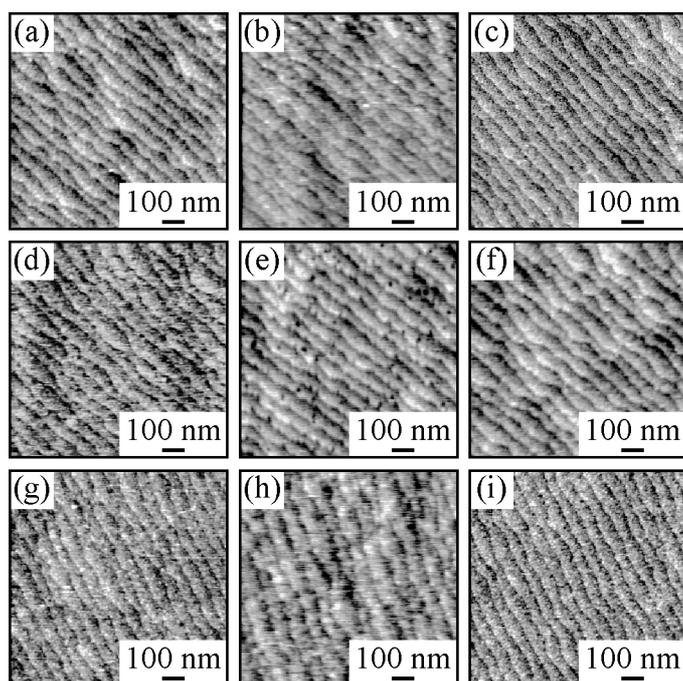
Fig. 5. AFM topographic images of the SAM-coated samples prepared by visible light irradiation at (a,b,c) 400, (d,e,f) 550, and (g,h,i,) 700 nm in wavelength for (a,d,g) 8, (b,e,h) 16, (c,f,i) 32 h.