Formation of Organic Monolayer on a Hydrogen Terminated Si(111) Surface *via* Silicon-Carbon Bond Monitored by ATR FT-IR and SFG Spectroscopy: Effect of Orientational Order on the Reaction Rate

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The formation of an octadecyl monolayer on a hydrogen terminated Si(111) surface in neat octadecene at 200 °C was followed by attenuated total reflectance Fourier transform infrared (ATR FT-IR) and sum frequency generation (SFG) spectroscopy and ellipsometry. Until ca. 60% of the monolayer was formed, the monolayer formation proceeded with simple first-order reaction kinetics and the monolayer was disordered. As the coverage steadily increased, the order of the monolayer became very high and the rate of the monolayer formation became significantly slower.

Construction of organic layers on solid surfaces is one of the most important subjects not only for fundamental science but also for a wide range of applications such as wetting control, corrosion inhibition, molecular and bio-electronic devices. A self-assembly (SA) technique in solution has been extensively employed to construct organic layers because a molecularly well-ordered structure can be prepared very easily without expensive equipment, which is essential for the organic layer formation in ultra high vacuum (UHV).[1]

The most studied SA system is the self-assembled monolayers (SAMs) of alkanethiols on various metals especially gold. SAMs with a wide variety of functionalities have been constructed and the formation process and the structure of the SAMs on gold have been investigated in detail by many research groups including ours.

It may be more important, however, to construct ordered molecular layers with various functionalities on a semiconductor surface as far as technological applications are concerned. Although several attempts have made to use GaAs[2,3] and InP[4] as a substrate, silicon should be the most important substrate for organic layer formation because of the possible applications for molecular and biomolecular devices in conjunction with advanced silicon technology. There are two major methods to form an organic layer on silicon. One is *via* the Si-O-Si bond using silane coupling reactions on a pre-oxidized Si surface. The other is *via* the Si-C bond using various thermal,[5–7] photochemical,[8,9] and electrochemical[10,11] reactions and using a reaction with a radical initiator[5,11–13] on a hydrogen terminated Si(111) surface.[14] The latter method is more attractive for the following reasons: 1. the Si-C bond is expected to be stronger than the Si-O-Si bond, 2. a higher structural order is expected for the monolayer prepared by the latter method as an organic molecule directly bonds to the Si atom of the surface of a single crystal, 3. the thickness control of the oxide is difficult in the former method. Both gas phase[15,16] and liquid phase[5–13] reactions have been proposed to form organic layers *via* the Si-C bond but the latter is more useful for practical applications because the former requires expensive UHV equipment to prepare and maintain the reconstructed, clean surface. Although an understanding of the monolayer formation mechanism is essential for the preparation of a well-ordered layer in a controlled manner, a detailed investigation has not yet been carried out.

Here, we monitored the formation kinetics and development of the molecular order of the octadecyl monolayer on a hydrogen terminated Si(111) surface by attenuated total reflectance Fourier transform infrared (ATR FT-IR) and sum frequency generation (SFG) spectroscopy and ellipsometry.

After a freshly prepared hydrogen terminated Si(111) substrate (Shin-Etsu Semiconductor: P-doped, 8–10 Ωcm)[14,17] was kept in deaerated octadecene (Wako) at 200 °C in an Ar (Pure Water, 99.95%) atmosphere for a certain duration, it was rinsed with and cooled down in deaerated hexadecane (Wako) and then further rinsed with deaerated diethyl ether (Wako), ethanol (Wako), and dichloromethane (Wako). After being dried with a stream of Ar, XPS (Rigaku, XPS7000), ATR FT-IR (Biorad, FTS30),[17] ellipsometry (SOPRA, GESP-5),[18] and SFG[19] measurements were carried out.

XP spectra of the Si(111) surface after the reaction were essentially the same as those reported before.[6,12] A single peak around 100 eV corresponding to Si^0 was observed in Si2p region, showing that no oxide was formed. Three peaks at 283.9, 284.7, and 285.9 eV corresponding to methylene C directly bounded to Si, methylene C bonded to other C, and methyl C, respectively, were observed in C1s region with the ratio of about 1 : 16 : 1. These results confirm the monolayer formation *via* Si-C bond.

Figure 1 shows the ATR FT-IR spectra of the hydrogen terminated Si(111) substrate treated in a deaerated octadecene at 200 °C for (a) 10, (b) 30, (c) 60, (d) 600, and (e) 7200 s in the region of 2800–3000 cm^{-1}. Three dominant peaks were observed around 2960, 2920 and 2850 cm^{-1}, corresponding to the asymmetric CH_3 stretching, the asymmetric CH_2 stretching, and the symmetric CH_2, respectively.[5,20] These peaks grew with time up to 2 h and reached constant intensities. By assuming that a monolayer of full coverage was formed after 2 h and the total integrated intensity of the peaks due to the CH_2 and CH_3 vibrations, I, is proportional to the amount of the monolayer on the surface, the coverage, θ, can be obtained by dividing I at a given time by I of the sample prepared in 2 h. The obtained time dependence of θ is shown in Figure 2(a). If the monolayer formation follows the simple Langmuir kinetics, the rate equation can be described as

$$\ln(1 - \theta) = -kt \qquad (1)$$

where k is the first-order rate constant. Figure 3 shows the relation between $\ln(1 - \theta)$ and time. Until ca. 60% coverage was reached at 60 s, a linear relation between $\ln(1 - \theta)$ and time was observed. The rate constant in this region is determined to be ca. 0.02 s^{-1}. The rate became significantly slower and deviation from the linear relation was observed at longer reaction time.

The ATR-IR spectra also showed that the positions of these peaks shifted with time. Figures 2(b) and 2(c) show the positions of the peaks due to symmetric and asymmetric CH_2 vibrations, respectively, as a
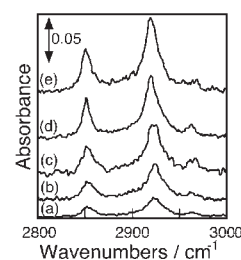

Figure 1. ATR FT-IR spectra of the sample treated in octadecene at 200 °C for (a) 10, (b) 30, (c) 60, (d) 600, and (e) 7200 s.
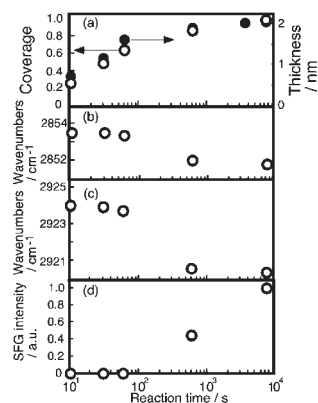
Figure 2. Time dependencies of coverage (open circle) and the thickness (closed circle) (a), the peak positions of CH_2 symmetric (b) and asymmetric (c) modes, and the integrated SFG peak intensity due to CH_3 Fermi resonance (d).
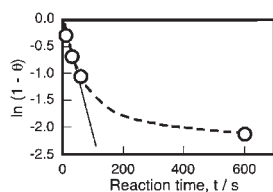

Figure 3. Relation between $\ln(1 - \theta)$ and time.

Figure 4. Schematic model for octadecyl monolayer formation process on a hydrogen terminated Si(111) surface *via* Si-C covalent bond.

function of time. The positions of these peaks were almost constant up to 60 s, i.e., 60% coverage, but shifted to significantly lower wavenumbers between 60 s and 600 s. They were almost constant after 600 s. It is well-known that the solid like or highly ordered alkyl chain gives peaks due to the CH_2 vibration at lower wavenumbers.[20] Actually, the peak positions at 2 h for the symmetric and asymmetric CH_2 vibrations, i.e., 2851.8 and 2920.4 cm^{-1}, respectively, are in good agreement with those observed for the highly ordered octadecanethiol SAM on gold.[20] Thus, the present result shows that a highly ordered monolayer was formed between 60 s and 600 s.

The order of the monolayer can be also evaluated by SFG. If the alkyl chain of the monolayer is well-ordered, i.e., in the all-trans conformation, only the SFG peaks of the CH_3 vibration can be observed in the region of 2800–3000 cm^{-1}, because no SFG signal is expected from the media of inversion symmetry and CH_2 groups are in inversion symmetry.[19,21] Peaks due to the CH_2 vibration were not observed in all the samples and peaks due to the CH_3 symmetric stretch, asymmetric stretch, and Fermi resonance were observed but only in the samples prepared for longer than 600 s. Figure 2(d) shows the integrated SFG peak intensity due to the CH_3 Fermi resonance as a function of time. Up to 60 s, the SFG intensity was zero, showing that the monolayer is in a random orientation. It increased with time after 600 s, reflecting the order of the methyl group. Thus, this result confirms that the well-ordered monolayer on Si(111) started to form between 60 s and 600 s.

The thickness of the monolayer determined by ellipsometry showed a similar time dependent behavior as also shown in Figure 2(a). The thickness rapidly increased at the beginning, then the slowly up to 2 h after which it became constant (ca. 2.1 nm). The final thickness is in good agreement with the expected thickness of the octadecyl monolayer in the all-trans configuration.[5]

By taking all the above mentioned results into account, the formation of the organic monolayer on the hydrogen terminated Si(111) surface seems to proceed as follows. Until ca. 60% of the monolayer was formed, the monolayer formation followed a simple first-order reaction kinetics and the monolayer was in disorder. As the coverage increased,
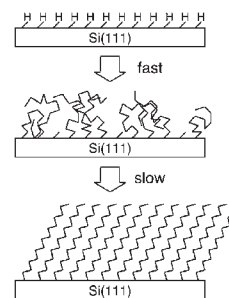
the very high order monolayer with an all-trans conformation is formed and the rate of the monolayer formation became significantly slower, showing that the existence of the highly ordered monolayer hinders further monolayer formation. The monolayer formation process is schematically shown in Figure 4. The results of the present system are essentially the same as the formation of the thiol monolayer on Au(111), which was reported to proceed with a fast adsorption step followed by a slower ordering process,[22,23] although the detailed mechanism must be different as the mobilities of the atoms and attached molecules of the present system must be much lower than those of thiol on gold.

References and Notes
1   A. Ulman, "An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly," Academic Press, New York (1991).
2   T. Baum, S. Ye, and K. Uosaki, *Langmuir*, **15**, 8577 (1999).
3   C. W. Sheen, J.-X. Shi, J. Märtensson, A. N. Parikh, and D. Allara, *J. Am. Chem. Soc.*, **114**, 1514 (1992).
4   Y. Gu, Z. Lin, R. A. Butera, V. S. Smentkowski, and D. H. Waldeck, *Langmuir*, **11**, 1849 (1995).
5   M. R. Linford, P. Fenter, P. M. Eisenverger, and C. E. D. Chidsey, *J. Am. Chem. Soc.*, **117**, 3145 (1995).
6   R. Boukherroub, S. Morin, F. Bensebaa, and D. D. M. Wayner, *Langmuir*, **15**, 3831 (1999).
7   H.-Z. Yu, S. Morin, D. D. M. Wayner, P. Allongue, and C. H. de Villeneuve, *J. Phys. Chem. B*, **104**, 11157 (2000).
8   J. Terry, M. R. Linford, C. Wigren, R. Cao, P. Pianetta, and C. E. D. Chidsey, *Appl. Phys. Lett.*, **71**, 1056 (1997).
9   F. Effenberger, G. Götz, B. Bidlingmaier, and M. Wezstein, *Angew. Chem., Int. Ed.*, **37**, 2462 (1998).
10 C. H. de Villeneuve, J. Pinson, M. C. Bernard, and P. Allongue, *J. Phys. Chem. B*, **101**, 2415 (1997).
11 A. Fidélis, F. Ozanam, and J.-N. Chazalviel, *Surf. Sci.*, **444**, L7 (2000).
12 A. Bansal, X. Li, I. Lauermann, N. S. Lewis, S. I. Yi, and W. H. Weinberg, *J. Am. Chem. Soc.*, **118**, 7225 (1996).
13 A. Bansal and N. S. Lewis, *J. Phys. Chem. B*, **102**, 1067 (1998).
14 G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.*, **56**, 656 (1990).
15 M. J. Bozack, P. A. Taylor, W. J. Choyke, and J. T. Yates, Jr., *Surf. Sci.*, **177**, L933 (1986).
16 G. P. Lopinski, D. D. M. Wayner, and R. A. Wolkow, *Nature*, **406**, 48 (2000).
17 S. Ye, T. Ichihara, and K. Uosaki, *Appl. Phys. Lett.*, **75**, 1562 (1999).
18 Ellipsometric data were collected in the wavelength region of 300–800 nm and refractive index and the thickness were obtained by processing the data using the WinElli software.
19 S. Ye, S. Nihonyanagi, and K. Uosaki, *Phys. Chem. Chem. Phys.*, **3**, 3463 (2001).
20 Y. Sato, B. L. Frey, R. M. Corn, and K. Uosaki, *Bull. Chem. Soc. Jpn.*, **67**, 21 (1994).
21 Y. R. Shen, *Proc. Natl. Acad. Sci. U.S.A.*, **93**, 12104 (1996).
22 K. Shimazu, I. Yagi, Y. Sato, and K. Uosaki, *Langmuir*, **8**, 1385 (1992).
23 R. Yamada and K. Uosaki, *Langmuir*, **14**, 855 (1998).