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Deposition of 10-undecenoic acid self-assembled layers on H–Si(1 1 1) surfaces studied with AFM and FT-IR

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Abstract

Self-assembling layers of 10-undecenoic acid (UA) were deposited on H-terminated Si(1 1 1) surfaces and characterized with atomic force microscopy (AFM) and Fourier-transform infrared (FT-IR) spectroscopy measurements for the first time. The unique island structures are deposited by layer-by-layer growth mechanism. The IR spectra suggest that the multilayers grown over the first monolayer are deposited by weak intermolecular interactions such as Van der Waals force and hydrogen bonding.

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1. Introduction

A large number of studies have been conducted on self-assembled monolayers (SAMs) from the points of view of structure, formation process, and physical properties. This is because SAMs are promising materials that have been widely applied to adhesion promotion, surface modification, surface protective film deposition, and fabrication of devices such as field effect transistors [1–5]. Recently, in the research of alkyl SAMs on Si substrates, the deposition of SAMs with a reactive group especially –COOH is becoming more and more interesting [6–8]. Because of the ease of applying successive chemical treatments to SAMs, they show potential to be used to control hydrophobicity and surface charge, and area selective immobilization of many kinds of bio-functional materials such as DNA and proteins. This is expected to become one of the key technologies in bioelectronics device fabrication. Although deposition of SAMs with –COOH group on Au [6], SiO_2 [7], and Si [8] surfaces has been investigated previously, this was done mainly with infrared (IR) absorption spectroscopy that gives strong peaks of CH_2 (∼2900 cm^{-1}) and –C=O (∼1700 cm^{-1}) stretching vibration bands. However, much less is known about the morphology of these –COOH functionalized surfaces despite its great importance.

In the present work, we will show the kind of structure that appears after UA deposition on an H-terminated Si(1 1 1) surface, and how these results were investigated with atomic force microscopy

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(AFM) together with Fourier-transform infrared (FT-IR) spectroscopy measurements. In this work, we observed unique island structures and self-assembled multilayers deposited by layer-by-layer growth. Furthermore, the IR spectra that we obtained suggest that the multilayers assembled over the first monolayer are formed by weak intermolecular interactions.

2. Experimental procedures

We cleaned B-doped p-type Si(1 1 1) ($0 \pm 0.1^\circ$ off) wafers with a resistivity in the range of 8.4–8.9 Ωcm and obtained H-terminated surfaces with the following processes: (1) dipping them into H_2O_2:H_2SO_4 (1:4), NH_4OH:H_2O_2:H_2O (1:4:20), and diluted (2.5%) HF solutions; (2) dipping them into HCl:H_2O_2:H_2O (1:1:6) and diluted (2.5%) HF solutions; (3) forming thermal oxidation at 1000 °C for 1 h; (4) removal of this thermal oxide layer by dipping them into a diluted HF (2%) solution until the appearance of a hydrophobic surface; and (5) etching of the Si sample with a solution of NH_4F:NH_4OH (pH 8) for 5 min.

Reaction of UA with the H-terminated Si surfaces was conducted through these processes: (1) distillation of UA, (2) bubbling of distilled UA by N_2 gas for 30 min at room temperature (RT), (3) immersing the Si sample into neat UA with continuous N_2 bubbling for 30 min at RT, (4) heating of UA at 200 °C or 150 °C for requesting time during continuous N_2 bubbling, (5) cooling the sample down to RT naturally, and (6) rinsing the sample with methanol and propanol.

We investigated the surface morphology of the sample by using the tapping mode of an AFM (SPA400-AFM, Seiko Instruments Inc.), and measured the transmission IR spectra with a FT-IR spectrometer (JR7000, JEOL Inc.).

3. Results and discussion

Fig. 1a is a typical AFM contact mode images of the H–Si(1 1 1) surface after the cleaning process. Uniform steps with a single bilayer height (3.1 Å) are distributed on the H–Si(1 1 1) surface. Fig. 1b is an AFM image after UA deposition at 200 °C for 20 min. Large terraces and the step edges can be clearly observed. In general, an H–Si(1 1 1) surface treated with HF solution is always atomically rough. However, the surface treated with a slightly basic fluoride solution NH_4F:NH_4OH (pH 8) consistently showed an atomically flat H–Si(1 1 1) surface [9–12].

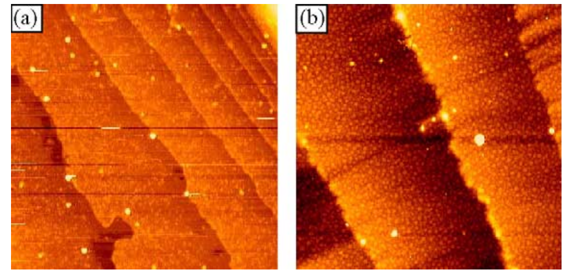

Fig. 1. AFM contact mode images of the H–Si(1 1 1) surface (a) just after cleaning (800 nm × 800 nm) and (b) after undecenoic acid deposition at 200 °C for 20 min (6 μm × 6 μm).

Fig. 2 provides AFM images after the deposition of UA on the H–Si(1 1 1) surface at 200 °C for different deposition times. In the case of 5 min deposition

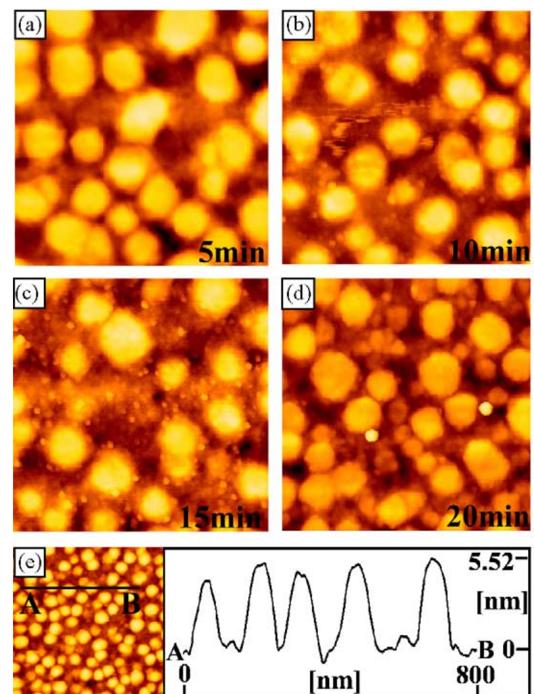

Fig. 2. AFM images (600 nm × 600 nm) of UA self-assembled layers deposited on H–Si(1 1 1) surface at 200 °C for (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) AFM image (1 μm × 1 μm) at 5 min and line profile.

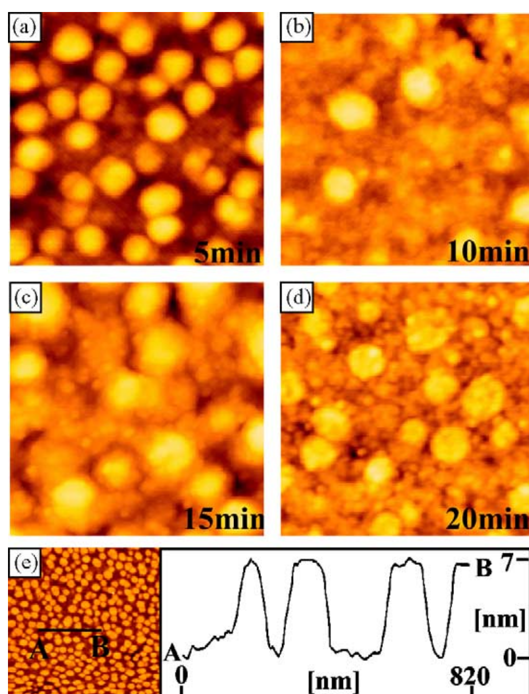

Fig. 3. AFM images (600 nm × 600 nm) of UA self-assembled layers deposited on H–Si(1 1 1) surface at 150 °C for (a) 5 min; (b) 10 min; (c) 15 min; (d) 20 min; (e) AFM image (2 μm × 2 μm) for 5 min and line profile.

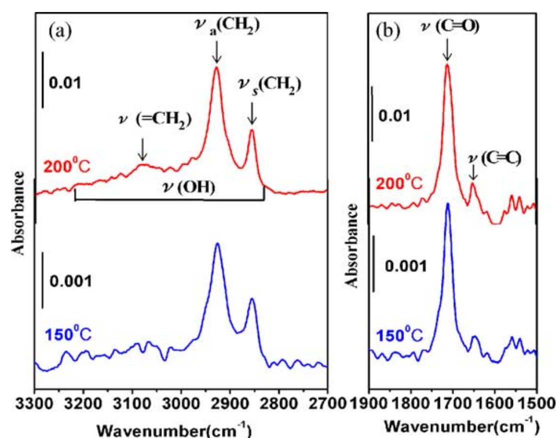

Fig. 4. Transmission FT-IR spectra of the UA self-assembled multilayers deposited on H–Si(1 1 1) surface for 15 min at 200 °C (upper line) and 150 °C (lower line): (a) C–H stretching region and (b) C=O and C=C stretching region.

(Fig. 2a), growth of many large islands was observed. At 10 min (Fig. 2b), a few small islands started to grow between large islands, and the number of these increased at 15 min (Fig. 2c), and at 20 min (Fig. 2d), the growth of the small islands became clearer. Interestingly, the number of small islands between large islands increased and their size grew with increased reaction time, while the size of the large islands remained almost the same.

Fig. 3a–d are AFM images after the deposition of UA at 150 °C for 5, 10, 15 and 20 min deposition times, respectively. The tendency of the morphological change on the surfaces with increased deposition time was roughly the same as that at 200 °C. Compared with 200 °C, however, the large islands at 150 °C were slightly smaller and they became larger gradually as deposition time was increased.

Fig. 4a and b show the IR absorption spectra of UA films deposited at 200 and 150 °C for 15 min. Interestingly, we found that although the height and the density of the large islands were not so different between the 200 and the 150 °C depositions, as shown in Figs. 2 and 3, the intensity of the IR spectra at 200 °C was almost one order of magnitude larger than that at 150 °C. This indicated that the island structures were on the flat UA self-assembled multilayers. Furthermore, detailed investigation showed that the heights of the islands were almost uniform in the whole wafer and the height values were distributed over about 1 nm intervals, suggesting layer-by-layer growth mechanism. In the C–H stretching region, shown in Fig. 4a, two strong peaks observed at 2928 and 2856 cm^{-1} are assigned to the CH_2 asymmetric and symmetric stretching vibration, respectively [13]. The broad band observed in the range of 2900–3200 cm^{-1} is assigned to the –O–H stretching vibration restricted by the hydrogen bond interaction [13]. Two clear peaks observed in Fig. 4b, 1712 and 1650 cm^{-1} are assigned to C=O and C=C stretching vibration [13]. From these IR data, several important conclusions about the structure and the deposition mechanisms were obtained. The very strong intensity of CH_2 stretching vibration peaks compared with reported SAMs (for example $\sim 1 \times 10^{-3}$ of dodecene [3], 2×10^{-3} of octadecyltrichlorosilane [14]) indicates that the multilayers are deposited even at 150 °C for 15 min as mentioned earlier. Furthermore, to consider that the multilayers were formed by very

weak intermolecular interactions such as the Van der Waals force and hydrogen bonding is reasonable because the peak position and the intensity ratio of C=O and C=C stretching vibration were almost same as those of the neat UA liquid. Existence of the hydrogen bonding interaction in the deposited multilayers is certified by the observed broad –O–H stretching vibration at 2900–3200 cm^{-1} in Fig. 4a. Here, we must note that self-assembled multilayers with island structure formed on the first monolayers combined by Si–C bonds to the Si(1 1 1) surface [15]. Since the multilayers are formed due to the weak intermolecular interactions, the possibility exists that the multilayers deposition can be suppressed at higher temperatures. Furthermore, we considered that the multilayers deposition occurred during the cooling down process after we stopped the heating. Therefore, an interesting trial would be to examine the deposition experiments at higher temperatures than the boiling point (187 °C) of 10-undecenoic acid. We are going to examine this higher temperature deposition in succeeding experiments.

4. Conclusion

Self-assembled multilayers of UA were deposited on an H–Si(1 1 1) surface and their surface morphology was investigated with AFM for the first time. The characteristic structure of islands with almost the same height that formed on the surface was observed. The AFM images and transmission IR spectra confirmed that the multilayers deposition occurs easily via layer-by-layer mechanism through weak intermolecular interactions such as Van der Waals force and the hydrogen bonding.

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