

## Temperature Dependence of the Structure of Alkyl Monolayers on Si(111) Surface via Si–C Bond by ATR-FT-IR Spectroscopy

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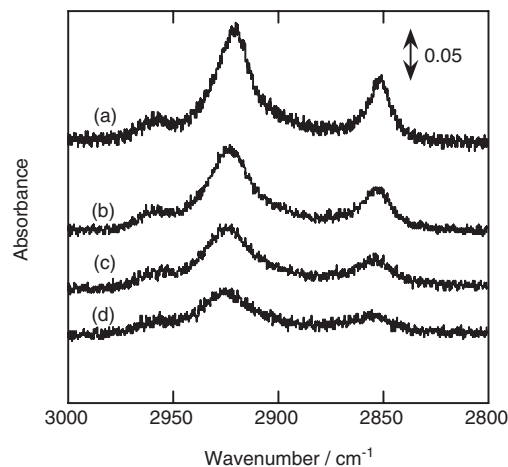
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The temperature dependence of C–H stretching modes of alkyl monolayer formed on Si(111) surface was investigated by an attenuated total reflection Fourier transform infrared spectroscopy from room temperature up to 540 K. Continuous disordering of the monolayer was indicated from the gradual peak shifts toward higher frequency in C–H stretch modes upon heating. The irreversible conformational disorder was introduced in the monolayer above 440 K.

Self-assembled monolayers (SAMs) have been widely studied because they can be potentially used for many applications such as wetting control, surface protection, chemical sensing, ultrathin resist layer, and control of electron transfer reactions at surfaces.<sup>1</sup> While most of studies on SAMs are carried out on gold surface, SAMs on semiconductors are of great interest.<sup>2</sup> It is reported that monolayers are formed by reacting 1-alkene with a hydrogen-terminated Si surface<sup>3</sup> via Si–C bond and we have also reported that the SAMs formed by this method can be used as the resist layer for lithography in nm scale.<sup>4</sup> It is essential to investigate the thermal phase behavior of the SAMs to understand the difference among the SAMs with different anchoring head groups such as alkanethiols and alkylsiloxanes and to use the SAMs for various processing steps. Sung et al. reported that the alkyl monolayer formed on Si surface via Si–C bond was stable up to 615 K.<sup>5</sup> The thermal phase behavior, however, has not been reported on the monolayer on Si surface via Si–C bond. It is well established that the careful investigation of C–H stretch modes gives fruitful information on the conformational order of the alkyl chains.<sup>6</sup> In this study, we report the temperature dependence of the structure of the alkyl-monolayer formed on the Si(111) surface by an attenuated total reflection Fourier transform infra-red (ATR-FT-IR) spectroscopy.

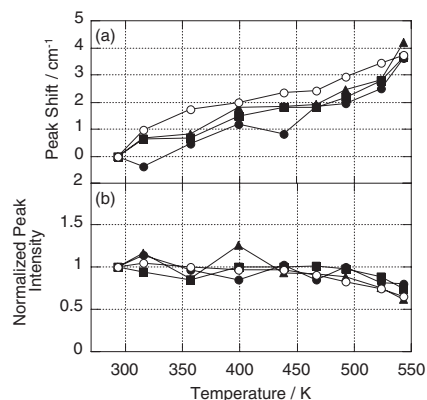
Substrates ( $20 \times 50 \times 0.5$  mm<sup>3</sup>) were cut from double sided polished *n*-type Si(111) wafers with a resistivity of 1–10  $\Omega$  cm (Furuuchi-Kagaku). The edge of the substrate was polished to give a trapezoidal shape with a bevel angle of 45°. 100 times internal reflections were estimated from the geometry. The monolayer formation was carried out by immersing the hydrogen terminated Si(111) substrate in neat alkene (C<sub>*n*</sub>H<sub>2*n*</sub>; *n* = 12, 14, 16, and 18) at 200 °C with Ar bubbling and circulation over 2 h.<sup>3,7,8</sup> The substrate was rinsed with hexane and ethanol and then dried in air. ATR-FT-IR spectra were recorded using FT620plus spectrometer (JASCO) equipped with a HgCdTe (MCT) detector and an ATR accessory (Specac 11000) with a home-made sample holder. The sample chamber was kept under vacuum (ca. 10 Pa) by an oil rotally pump with a liquid nitrogen trap. Tem-



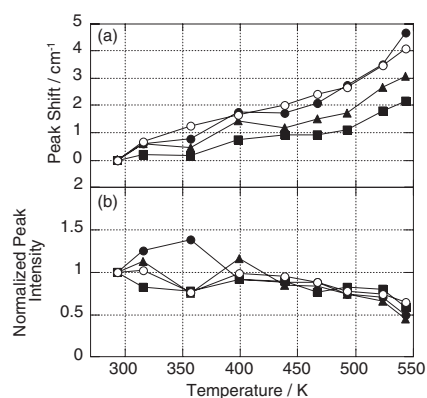
**Figure 1.** ATR-FT-IR spectrum of the Si(111) surface modified with octadecene taken at (a) r.t., (b) 360 K, (c) 440 K and (d) 540 K.

perature of the substrate was raised by using resistive ceramic heater which was in contact with the sample holder. All spectra were obtained with a resolution of 0.5 cm<sup>-1</sup> and by integrating 100–256 spectrum dependent on the total beam intensity with *p* polarization. It took 10 to 30 min to complete measurements at each temperature. The spectra of the chemically oxidized Si(111) substrate at each temperature was used for the references.

Figure 1 shows an ATR-FT-IR spectra of the Si(111) surface covered with octadecane monolayer at (a) room temperature (r.t.), (b) 360 K (c) 440 K and (d) 540 K in the region of C–H stretching modes. Three peaks seen around 2960, 2920, and 2850 cm<sup>-1</sup> were assigned to the asymmetric CH<sub>3</sub> stretching, the asymmetric CH<sub>2</sub> stretching and the symmetric CH<sub>2</sub> stretching mode, respectively.<sup>3</sup> No significant difference was observed among the spectrum of the Si(111) surface covered with dodecene, tetradecene and hexadecane monolayer except the peak intensity. The peaks became broader and the position of the peaks shifted to the higher frequencies as the temperature raised. Figures 2(a) and (b) show the peak shift of the asymmetric CH<sub>2</sub> mode (2920 cm<sup>-1</sup>) and its normalized peak intensity, respectively, for dodecene, hexadecane, and octadecene monolayers as a function of the substrate temperature. It was shown that the peak position was continuously shifted to higher frequency. The peak intensity began to decrease from 490 K regardless of the chain length. The full-width and half-maximum value of the each peak was monotonically increased as the temperature was increased. The position and intensity of the peak did not return to the orig-



**Figure 2.** (a) peak shift and (b) normalized peak intensity of *asym*-CH<sub>2</sub> mode as a function of the temperature. Marker assignment; filled circle: dodecene, filled square: tetradecene, filled triangle: hexadecane and open circle: octadecene monolayer.



**Figure 3.** (a) peak shift and (b) normalized peak intensity of *sym*-CH<sub>2</sub> mode as a function of the temperature. Marker assignment is the same with that in Figure 2.

inal values completely when the substrate was once heated above 440 K, indicating that the irreversible change took place. Basically, the similar result was obtained in the region of the symmetric CH<sub>2</sub> mode as shown in Figure 3 while the decrease in the peak intensity began around 440 K where irreversible process took place as mentioned above.

It is well known that the peak positions of the C–H stretch modes are shifted to higher frequency as the conformational disorder of the alkyl chains increases.<sup>6,9,10</sup> Therefore, the continuous increase of the frequency of the C–H stretch modes observed in this study indicates that the disordering of alkyl monolayer formed on Si via Si–C bond continuously proceeds as a function of the temperature of the substrate. The similar phase transition behavior was reported on the SAM of alkanethiols on gold<sup>9,10</sup> in which strong anchoring is expected as is the present case. The decrease in the peak intensity upon heating observed in the present study was also reported in bulk alkane crystals, polyethylene,<sup>6</sup> and the SAMs of alkanethiols.<sup>9,10</sup> It should be noted that the peak intensity decreases at higher temperature not only when molecules are disappeared but also when the molecules in the monolayer are untilted<sup>9</sup> and the coupling between lower and higher frequency modes takes place.<sup>6</sup> We suppose that the desorption of the molecules are not a major reason for the decrease

in the peak intensity because hydrophobic surface was maintained after the heating at 540 K and previous reports showed the existence of the monolayer up to 615 K.<sup>5</sup> Thus, untilting of the molecules in the monolayer and the coupling between lower and higher frequency modes are possible major reasons to explain the decrease of the peak intensity because the molecules have a tilting angle of 30 degree at r.t.<sup>14</sup>

Bensebaa et al. reported that the peak intensity of the C–H stretching modes of the SAMs of alkanethiols on the Au surface increased upon heating above 350 K while the peak intensity decreased upon heating up to 350 K.<sup>9</sup> Their result should be related to the phase transition of the alkanethiol monolayer on the Au surface from  $c(4 \times 2)$  of  $\sqrt{3} \times \sqrt{3}$  to  $p \times \sqrt{3}$  structure around 350 K.<sup>11</sup> During this phase transition, the desorption of the alkanethiol molecules took place<sup>11–13</sup> and the orientation of the molecular axis with respect to the surface plane is changed from perpendicular to parallel. The present study, in which peak intensity did not increase upon heating at any temperature, confirms high stability of the monolayer formed via Si–C bond. However, the irreversible behavior upon heating over 440 K indicates that strong conformational disorder which cannot be healed by cooling was introduced and/or that partial desorption of the molecule took place.

In conclusion, the phase behavior of the alkyl monolayer formed on Si(111) surface via Si–C bond was investigated from the C–H stretching vibrational modes. The continuous disordering of alkyl chain upon heating was observed from r.t. to 540 K. The irreversible conformational disorder was introduced in the monolayer above 440 K.

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