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Citation	Applied Physics Letters, 75(11), 1562-1564 https://doi.org/10.1063/1.124755
Issue Date	1999
Doc URL	http://hdl.handle.net/2115/5502
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Type	article
File Information	APL75-11.pdf



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Attenuated total reflection Fourier transform infrared spectroscopy study of the adsorption of organic contaminants on a hydrogen-terminated Si(111) surface in air

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(Received 13 May 1999; accepted for publication 14 July 1999)

The adsorption of organic contaminants on a hydrogen-terminated Si(111) surface was investigated using attenuated total reflection Fourier transform infrared spectroscopy. When the hydrogen-terminated Si(111) surface was exposed to dry air, the sharp Si-H monohydride peak became weaker and a broad component became visible in the lower wave-number region. Furthermore, a number of bands within the C-H stretching region were observed. The intensity of the sharp Si-H band was recovered to a certain extent and those of the broad component and the C-H bands decreased after the sample was rinsed in hexane. These results suggest that the contamination by organic adsorbates is not accompanied by a chemical bond formation. © 1999 American Institute of Physics. [S0003-6951(99)01337-6]

Contamination of Si surfaces by organic species significantly deteriorates the reliability of semiconductor device performance in ultra-large-scale integrated circuits (ULSIs).^{1,2} It has been reported that a trace amount of organic contaminants still exists on the Si surface³⁻⁵ even after Si wafers were cleaned using the RCA cleaning procedure.⁶ Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy has been widely applied to investigate the vibration state of organic adsorbates on Si surfaces, especially on the Si(100) surface.⁷⁻⁹ Although the study of the structure of adsorbates on Si(100) is important in view of practical application, quantitative investigation on this surface is difficult since there is no established technique to prepare an atomically flat Si(100) surface. Recently, the preparation of a well-defined Si(111)-(1×1) surface terminated by a monohydride was realized by etching in a concentrated NH₄F solution.¹⁰ This ideal H-Si(111)-(1×1) surface provides an excellent model to study the chemical reaction process on a well-defined Si surface. Furthermore, although it is known that hydrogen termination (Si-H) protects the Si surface from contamination and oxidation, no quantitative study has yet been carried out to clarify its role.

In the present study, ATR-FTIR spectroscopy was employed to monitor the surface contamination process by organic contaminants on a well-defined H-Si(111) surface during exposure to a dry air environment in real time. The nature of the adsorption state of the airborne organic contaminants was discussed based on the intensity and band shape of the bands of the Si-H and C-H stretching vibrations.

Parallelogram ATR prisms (26×20×0.38 mm, 45° bevel angle) were prepared from floating-zone-grown Si(111) wafers (Shin-Etsu Semiconductor, *n*-type, 50–500 Ω cm, both sides polished) by polishing the side portions of the wafers with alumina powder (final size, 0.3 μm). The

internal reflection number within the Si prism was ~70.

A Si(111) ATR prism was cleaned in a sonication bath of acetone and then with Milli-Q water (resistivity>18 M Ω cm), oxidized in a boiling solution of concentrated HCl:H₂O₂:H₂O (1:1:4) for 20 min, etched in 40% NH₄F solution (Morita Chemical Industries, EL grade) for 5 min, sonicated in Milli-Q water for 5 s, and finally, dried in flowing purified nitrogen gas. The sample was mounted on an ATR accessory (Pike Technology) immediately after the preparation process.

ATR-FTIR measurements were performed using a Bio-RAD FTS-30 spectrometer equipped with a HgCdTe (MCT) detector cooled with liquid nitrogen. The dry air was continuously provided to the FTIR chamber by a BioRAD air dryer (type II, dew-point-50 °C) in which a heatless drier (HD-0.5, CKD) containing a molecular sieve 13× and an oil-free compressor (Hitachi 0.4-OP-7S, 45 l/min) were used. The ATR-FTIR spectra were recorded in *p*-polarization with respect to a spectrum of an oxidized Si(111) surface as a function of the time exposed in a dry air environment. All spectra were obtained by integrating 128 interferograms with a resolution of 0.5 cm⁻¹. Deconvolution of the band was carried out using WIN-IR software (version 4.14, Galactic Industries Corporation) with a Lorentz function.

Figure 1(a) shows the ATR-FTIR spectra of a Si(111) surface in the regions of 2300–2000 and 3000–2800 cm⁻¹ after etching in 40% NH₄F solution. A very sharp peak was observed at 2084 cm⁻¹ [full width at half maximum (FWHM) ~1 cm⁻¹]. This peak is attributed to the stretching vibration of the monohydride on the Si(111)-(1×1) surface, whereas no bands related to the dihydride or trihydride were observed. This result is in good agreement with that reported by Higashi *et al.*,¹⁰ demonstrating that an atomically flat Si(111) surface terminated by an extremely homogeneous monolayer of hydrogen was obtained. No band was found in the region of 3000–2800 cm⁻¹.

Figures 1(b)–1(e) show the ATR-FTIR spectra obtained after various exposure times. As the exposure time increased,

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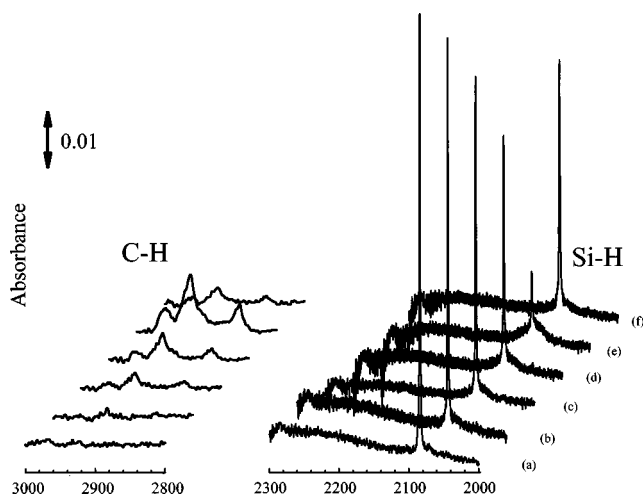


FIG. 1. ATR-FTIR spectra of a hydrogen-terminated Si(111) surface in the regions of 2300–2000 cm^{-1} and 3000–2800 cm^{-1} after the sample was exposed to dry air for (a) 0, (b) 8, (c) 24, (d) 48, and (e) 120 h and (f) was sonicated in hexane after (e).

the peak height of the sharp Si–H band became smaller and a broad component became visible at the bottom of the Si–H peak. At the same time, a number of bands grew in the C–H stretching region of 3000–2800 cm^{-1} . Three pronounced peaks at 2852, 2923, and 2960 cm^{-1} and a small shoulder at 2931 cm^{-1} were observed in this region. These peaks can be assigned to the symmetric (2852 cm^{-1}) and asymmetric (2923 cm^{-1}) stretching of methylene group and asymmetric stretching (2960 cm^{-1}) and Fermi resonance (2931 cm^{-1}) of the methyl group of hydrocarbon species adsorbed on the Si surface.¹¹ The appearance of these bands shows the adsorption of organic contaminants. Similar bands were previously reported^{7–9} and were attributed to organic contaminants introduced during the wafer cleaning process.^{7,8} In the present case, however, since no bands were observed in the C–H region immediately after etching [Fig. 1(a)], contamination during the etching process can be excluded and these C–H-related bands should arise from adsorbed hydrocarbon impurities which were contained in the dry air.

When the Si(111) sample was sonicated in hexane after a 120 h exposure to dry air, the intensities of the C–H bands and the sharp Si–H peak decreased and increased, respectively, as shown in Fig. 1(f). The recovery of the sharp Si–H peak after the sonication shows that the Si–H band was not irreversibly decomposed.

To analyze the results more quantitatively, the intensities of the various bands were plotted as a function of time in Fig. 2. The Si–H band was deconvoluted into two components, i.e., a sharp component at 2084 cm^{-1} with a FWHM of $\sim 1 \text{ cm}^{-1}$ and a broad component that peaked at a slightly lower wave number (2071 cm^{-1}) with a FWHM of $\sim 20 \text{ cm}^{-1}$. These two components were separately plotted. While the former peak decreased with time, the latter increased. The total intensity of these two bands also decreased with time but less significantly than the sharp peak shown in Fig. 2. The exposure time dependence of the intensity of the band due to the C–H asymmetric stretch of the methylene group at 2923 cm^{-1} is also shown in Fig. 2 that represents the amount of adsorbed organic contaminants, which clearly increased with time. It is clear that the increase in the C–H band is

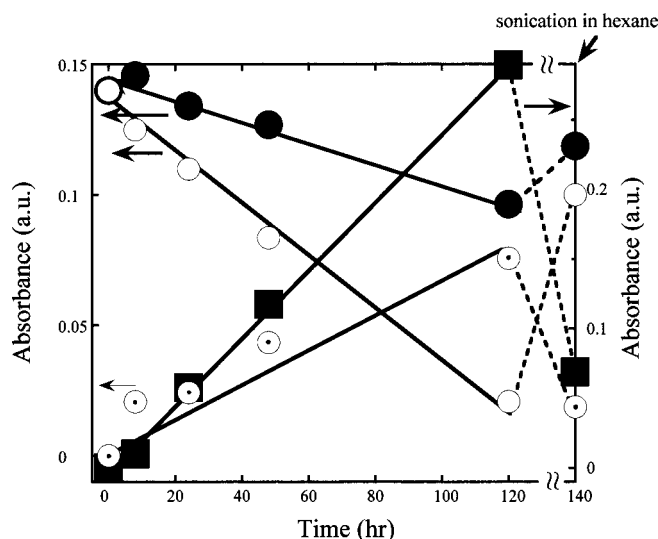


FIG. 2. Intensities of Si–H and C–H bands as a function of time and after the sonication in hexane. White, dotted, and black circles correspond to intensities of deconvoluted sharp, broad, and total Si–H bands, respectively. The black square shows the intensity of the C–H bands represented by the intensity of the band due to the C–H asymmetric stretch of the methylene group at 2923 cm^{-1} .

strongly correlated with the decrease and increase in the sharp and broad Si–H bands, respectively.

The intensities of these bands after the sonication in hexane are also presented in Fig. 2. The recovery of the sharp Si–H band after the sonication seems to be correlated with the decrease in the C–H and broad Si–H bands.

Two possibilities can be considered for the intensity change of the Si–H bands. One is the oxidation of the Si(111) surface during the exposure to air. Niwano *et al.* actually reported the observation of a new band around 2250 cm^{-1} , which was attributed to the formation of $\text{SiH}(\text{O}_3)$ after a hydrogen-terminated Si(111) surface was exposed to air with 10% humidity for longer than $\sim 50 \text{ h}$.¹² In the present study, however, no peak was observed around 2250 cm^{-1} even after a 5 day exposure [Fig. 1(e)], showing that $\text{SiH}(\text{O}_3)$ was not formed on the surface. An x-ray photoelectron spectroscopy measurement also confirmed the absence of silicon oxide after the same exposure time. Thus, the decrease in the sharp Si–H peak should not be due to the oxide formation. Oxide did not grow in the present study possibly because the Si(111) surface was exposed to only dry air. The hydrogen-terminated Si(111) seemed to effectively passivate the surface from oxidation in dry air.

The more likely reason is the adsorption of organic contaminants because there is a good correlation between the changes in the intensities of the Si–H and C–H bands. The effects of organic species on the Si–H band have been investigated by various groups. Linford *et al.* reported that the Si–H bands disappeared irreversibly after a chemically bonded organic monolayer was formed on the Si(111) surface.⁹ Since a significant portion of the sharp Si–H band, which was lost during air exposure, was recovered by sonication in hexane, the loss of the Si–H band was not irreversible in the present case. Dumas *et al.* observed that when C_{60} was deposited on a Si(111) surface, the Si–H band was shifted to a lower wave number (2062 cm^{-1}) and became broader (FWHM: $\sim 10 \text{ cm}^{-1}$) while the total intensity of the

Si-H band did not change. They proposed that the van der Waals interaction between C₆₀ and Si-H caused the peak shift and broadening.¹³ Band broadening phenomena of Si-H were also observed when the hydrogen-terminated Si(111) surface was in contact with aqueous¹⁴⁻¹⁶ and non-aqueous solutions.¹⁷ The fact, observed in the present study, that the peak position of the broad component of the Si-H band shifted only slightly, the broad component grew as the sharp component decreased during the exposure to air, and the broad and sharp components decreased and increased, respectively, by the sonication in hexane, all suggest that the broad component is due to Si-H interacting with some species and these two components are reversibly converted into each other. C-H bands were also observed in the higher wave-number region than those of the chemically bonded monolayer,⁹ indicating a lower order of the organic adsorbate layer than that of the chemically bonded monolayer. Furthermore, the broad component increased in parallel to the increase in the C-H bands. Thus, one can conclude that the broad component is due to the stretching vibration of Si-H that has a strong interaction with physisorbed organic contaminants.

Based on the above results, one can explain the present results as follows. When a hydrogen-terminated Si(111) surface is exposed to air, organic contaminants are adsorbed on the surface because of the strong hydrophobic nature of the hydrogen-terminated Si(111) surface. As a result, the intensities of the C-H bands increase. The organic contaminants seemed to form islands leaving other portions of the hydrogen-terminated surface clean because the position and the width of the sharp Si-H band were not affected by the adsorption of the organic contaminants. Sonication in hexane removed most of the contaminants, leading to the increase in the free Si-H area. As a result, the intensities of the broad and sharp components of the Si-H band decrease and increase, respectively, and that of the C-H related bands decreased.

One should note that the intensity of the sharp Si-H bands did not recover its original value and C-H bands were still observed after the sonication in hexane. One of the reasons for this observation may be that the adsorbed organic contaminants are poorly soluble in hexane. The formation of

a small amount of chemically bonded organic species and/or polymerized species may also contribute to the irreversible behavior of Si-H on the Si(111) surface. Detailed investigations are now in progress.

The ATR-FTIR measurements clearly showed that the hydrogen-terminated Si(111) surface was not oxidized even after 5 days as long as the surface was exposed to only dry air. However, the surface was contaminated with the hydrocarbon impurities contained in dry air. Most of the contaminants can be removed by sonication in hexane.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of "Electrochemistry of Ordered Interfaces" (No. 09237101) from the Ministry of Education, Science, Sports and Culture, Japan. Kitazawa of Shin-Etsu Semiconductor is acknowledged for the donation of the Si wafers.

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