

***In Situ* Detection of Surface SiH_n in Synchrotron-Radiation-Induced Chemical Vapor Deposition of *a*-Si on an SiO₂ Substrate**

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The sensitivity and linearity of infrared reflection absorption spectroscopy (IRAS) has been significantly improved by using a buried-metal-layer (BML) substrate having an SiO₂(15 nm)/Al(200 nm)/Si(100) structure, instead of a plain Si(100) substrate. By applying this BML-IRAS technique to the *in situ* observation of synchrotron-radiation-induced chemical vapor deposition of amorphous Si (*a*-Si) on an SiO₂ surface using Si₂H₆ gas, the vibrational spectra of surface SiH_n species in this reaction system have been observed for the first time with sufficient sensitivity for submonolayer coverage. The main silicon hydride species after deposition at 423 K are surface SiH₂ and SiH. Surface SiH₃ and SiH₂ are observed to be easily decomposed by synchrotron radiation irradiation. The decomposition rate of SiH by synchrotron radiation irradiation is much slower than those of SiH₂ and SiH₃.

Keywords: silicon hydrides; chemical vapor deposition; infrared reflection absorption spectroscopy; surface reactions; disilane; amorphous silicon.

1. Introduction

Studies with synchrotron-radiation-induced processes have been carried out actively over the last ten years, mainly with a view to applying them to semiconductor processes such as etching (Urisu & Kyuragi, 1987), chemical vapor deposition (CVD) (Kyuragi & Urisu, 1987; Inoue, Okuyama & Hamakawa, 1988), and molecular beam epitaxy (Urisu, Takahashi, Utsumi, Akutsu & Kuchitsu, 1994). Several interesting phenomena such as material selectivity have been found (Takahashi, Utsumi & Urisu, 1991), but the reaction mechanisms are not sufficiently clear. In the deposition of amorphous Si (*a*-Si) or crystalline Si by synchrotron radiation-CVD, the detection of surface SiH_n is an important means of analyzing the reaction mechanisms and deposited film qualities, since the growth rate and the film quality or crystallinity are significantly influenced by surface and bulk hydrogen atoms (Urisu, Takahashi, Utsumi, Akutsu & Kuchitsu, 1994). But *in situ* observation of SiH_n species has not yet been attained in the synchrotron-radiation-induced processes.

Infrared reflection absorption spectroscopy (IRAS) (Chabal, 1988; Greenler, 1975) is suitable for monitoring surface reactions for several reasons: (1) *in situ* observations can be made nondestructively, (2) the vibrational spectra

of molecules adsorbed on the surface can be observed with high sensitivity and high resolution, and (3) its cut-off frequency does not depend on the absorption of the substrate material, so that the optical arrangements can be easily constructed even in a vacuum chamber. Despite these characteristics, the application of IRAS to semiconductor process monitoring is severely limited, because when the adsorbate is on a semiconductor or an insulator surface, its sensitivity is low and the band shape is significantly distorted depending on the incident angle, the wavelength, and the anomalous dispersion of the adsorbate. To overcome these disadvantages, several authors have proposed the use of a buried-metal-layer (BML) substrate (Bermudez & Prokes, 1991; Ehrley, Butz & Mantl, 1991), which has a metal layer buried under a thin film of semiconductor or insulator material (buffer layer) that is thinner than the wavelength of the infrared radiation. Such a substrate exhibits the characteristics of the buffer layer for surface chemical reactions, while it behaves as a metal for the infrared radiation. However, in spite of its potential, few efforts have been made to apply BML substrates to monitoring semiconductor surface reactions.

In the present work, the sensitivity and linearity of the BML-IRAS method has been evaluated by using Langmuir-Blodgett (LB) films of barium stearate deposited on BML substrates with SiO₂/Al/Si(100) structure, then the

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BML-IRAS technique has been used to monitor the surface SiH_n *in situ* in synchrotron radiation-CVD using Si_2

2. Experimental

n-Type Si(100) substrates with a 200 nm-thick Al layer buried under a 15 nm-thick SiO_2 thin film were used as BML substrate. The Al layer was deposited by plasma sputtering on the surface of an *n*-type Si(100) substrate covered by thermal oxide, and the SiO_2 layer was deposited on the Al layer by electron cyclotron resonance plasma CVD. The surface roughness of the SiO_2 layer was evaluated by atomic force microscopy. The unevenness was about 1 nm (root-mean-square value) and the average lateral period of the roughness was about 160 nm. Thus, the surface of the SiO_2 layer can be assumed to be almost flat. LB films were deposited on the surface of an SiO_2 BML substrate and an *n*-type Si(100) substrate of resistivity larger than $1 \Omega \text{ cm}$, without removing the surface native oxide, by a conventional method using a solution of stearic acid in benzene spread on the surface of purified water containing $5 \times 10^{-4} \text{ M}$ BaCl_2 . By comparing the transmission spectra of LB films deposited on the Si(100) substrate and the IRAS spectrum of the BML substrate, it is concluded that LB films are deposited with their hydrocarbon chain axis almost perpendicular to the substrate surface (Umemura, Kamata, Kawai & Takenaka, 1990). The spectra with the LB films were measured by using a Fourier-transformed infrared (FTIR) spectrometer (Perkin-Elmer model 1600) and a TGS detector (4 cm^{-1} resolution and 100 scans). Spectra with *a*-Si deposited by the synchrotron-radiation-stimulated process were measured by using an FTIR spectrometer (JEOL model JIR7000) and an HgCdTe (MCT) detector (4 cm^{-1} resolution and 1000 scans). The *p* polarization of

the infrared beam was selected by a wire-grid polarizer using a barium fluoride substrate. The optical path was purged with dry N_2 . The spectra were recorded as $\Delta R/R_0$ ($\Delta R = R' - R_0$) where R' and R_0 are the reflectances of the substrate with and without the deposited layer, respectively. The *a*-Si was deposited on the surface of the SiO_2 BML substrate by synchrotron radiation beam irradiation at 423 K under an Si_2H_6 gas pressure of 1×10^{-3} Torr. The substrate was set with a synchrotron radiation beam incidence angle of 45° in an ultra-high-vacuum chamber (base pressure = 4×10^{-10} Torr) equipped with an IRAS optical system, as shown in Fig. 1. The infrared beam was introduced through the ZnSe viewing port. The IRAS was measured *in situ* with an incidence angle of 85° after pumping out the reaction gas. The synchrotron radiation beam from beamline 4B of the 0.75 GeV storage ring at the Institute for Molecular Science was used without monochromatization. The calculated photon wavelengths ranged from 1 nm to more than 100 nm with a peak at 10 nm, and the flux was 1.6×10^{16} photons s^{-1} (0.47 W) for a 100 mA ring current on the 15 mm^2 sample surface.

3. Results and discussion

Fig. 2 compares the IRAS spectra of LB films deposited on the BML and Si(100) substrates for various infrared beam incident angles. The LB film thickness was five monolayers. The observed peaks are assigned to asymmetric CH_3 stretching (2957.7 cm^{-1}), asymmetric CH_2 stretching (2917.3 cm^{-1}), symmetric CH_3 stretching (2872.4 cm^{-1}), symmetric CH_2 stretching (2850.0 cm^{-1}), asymmetric COO^- stretching (1512.8 cm^{-1}), and symmetric COO^- stretching (1446.2 cm^{-1}) modes (Umemura, Kamata, Kawai & Takenaka, 1990). The improved performance of BML

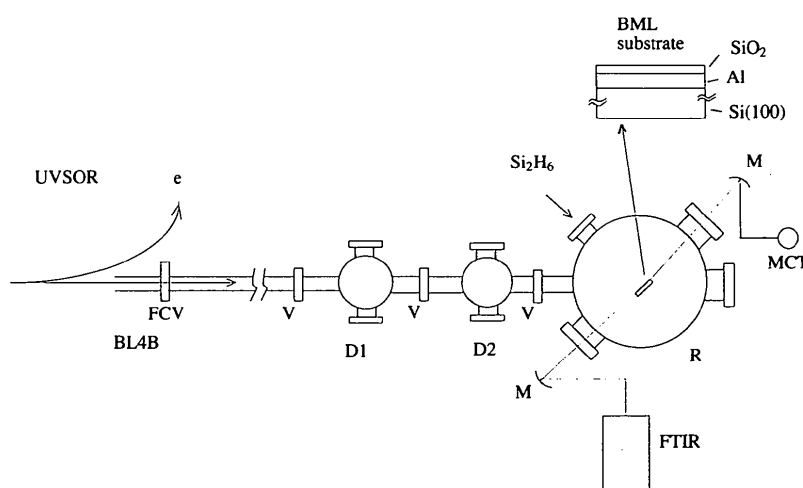


Figure 1

Schematic diagram of the experimental system and the $\text{SiO}_2(15 \text{ nm})/\text{Al}(200 \text{ nm})/\text{Si}(100)$ BML substrate used in the experiments. The ultra-high-vacuum reaction chamber (R) and differential vacuum pumping chambers D1 and D2, which are pumped by turbo molecular pumps ($500, 150, 300 \text{ l s}^{-1}$, respectively) are set at the end of beamline 4B of the synchrotron radiation storage ring at the Institute for Molecular Science (UVSOR). The surface reaction is monitored *in situ* by BML-IRAS using a Fourier-transformed infrared spectrometer (FTIR). MCT is an HgCdTe detector. M is an Au-coated mirror. The ZnSe windows are used for infrared beam introduction. FCV is a fast closing valve and V is a pneumatic valve.

substrates can be clearly seen: the peaks in the BML spectra all increase gradually with increasing incident angle, and have sufficient sensitivity for one-monolayer film thickness. The dependence of the peak intensity on the LB film thickness was almost linear in the range from 1 to 15 monolayers. On the other hand, in the case of the Si substrate, the signal distortion is significant and depends on the wavelength and the incident angle as already mentioned.

Fig. 3 shows the IRAS spectra of *a*-Si observed *in situ* after deposition with several different doses (= storage ring current × exposure time). An SiO₂ BML substrate was washed in acetone and deionized water, and placed on the sample holder in the ultra-high-vacuum chamber. Its infrared reflectivity R_0 was measured for the *p* polarization, and then, after deposition of *a*-Si by synchrotron radiation irradiation of a certain dose, the reflectivity R' was measured. The deposition rate was found to be about 0.3 Å (100 mA)⁻¹ min⁻¹ using a step profile meter. Assuming the deposition rate to be constant throughout the deposition, and by extending the interpretation of 'film thickness' to submonolayer adsorbates, the spectra shown in Fig. 4 correspond to thin films of 0.1–1 Å thickness. This indicates that the present BML-IRAS technique has sufficient sensitivity to detect submonolayer adsorbates of SiH_n. The peaks at around 2109, 908 and 860 cm⁻¹ are assigned to SiH_n vibrations by referring to the reported value of the peak position (Chabal, Higashi, Raghavachari & Burrows, 1989; Lucovsky, Nemanich & Knights, 1979) as shown in Table 1. The peaks observed in the range 1400–1700 cm⁻¹ are ascribed to atmospheric water fluctuations. It is known that the peak position of the Si—O—Si stretching vibrations shifts with a decrease of O-atom concentration from 1075 cm⁻¹ in the case of the stoichiometric amorphous SiO₂ to 940 cm⁻¹ in O-doped amorphous silicon (Pai, Chao, Takagi & Lucovsky, 1986). Therefore, the 950 cm⁻¹ peak is

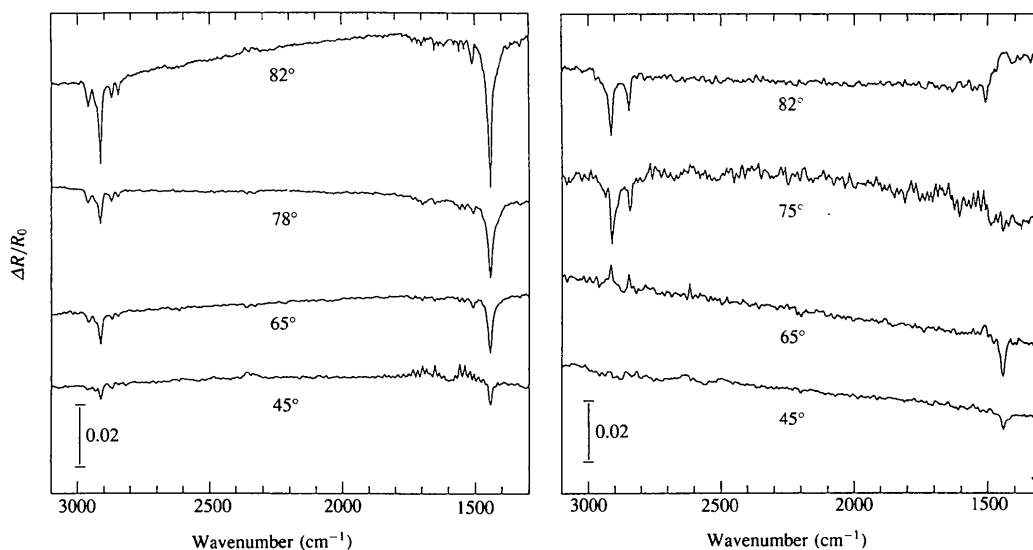
Table 1Absorption frequency of Si hydride vibrations (cm⁻¹).

Vibrational mode	Reported values*			
	I	II	This work	
SiH ₃	Symmetric stretching	2130	2150	2140
	Asymmetric stretching	2141	2150	Not clear
	Degenerate deformation		900	Not clear
	Symmetric deformation		850	860
SiH ₂	Symmetric stretching	2108	2100	2113
	Asymmetric stretching	2118	2100	Not clear
	Bending scissor		900	908
	Wagging		850	Not clear
	Twisting		820	Not observed
SiH(surface)† (bulk)†		2089		2100
			2000	Not observed

* Reported values are I (Chabal, Higashi, Raghavachari & Burrows, 1989) and II (Lucovsky, Nemanich & Knights, 1979). † Two kinds of SiH vibrational peaks assigned to surface SiH and bulk SiH are reported.

assigned to Si—O—Si stretching vibrations in the O-doped amorphous Si, which probably appear due to synchrotron radiation-induced reactions between the surface SiO₂ and Si₂H₆.

To make the assignment of the SiH_n species in more detail, the structure of the 2109 cm⁻¹ band is shown on an expanded scale in Fig. 4. Furthermore, the change of the IRAS spectra by synchrotron radiation irradiation of the SiH_n species after deposition was measured as shown in Figs. 5 and 6. For the spectra (a), (b) and (b) – (a) in Fig. 6, curve resolution analysis was examined assuming three peaks with Lorentzian forms for SiH₃, SiH₂ and SiH. The results are shown in Fig. 6 (broken lines) to clarify the change of each vibrational band on synchrotron radiation irradiation. IRAS can only detect the perpendicular component of the transition dipole moments

**Figure 2**

Observed IRAS spectra of five monolayers of barium stearate Langmuir-Blodgett film deposited on the SiO₂ BML substrate (left) and on the Si(100) substrate (right) for various infrared beam incident angles.

(surface selection rule) (Chabal, 1988; Greenler, 1975). In the present case, the SiO_2 surface is almost flat, and the thickness of the deposited film is less than one monolayer in the IRAS measurement. Thus, it can be assumed that SiH_2 and SiH_3 adsorb on the surface with their symmetry axis (C_{2v} and C_{3v}) perpendicular to the surface, although the deposited film is amorphous. This assumption predicts that the vibrational modes of asymmetric stretching, degenerate deformation, wagging and twisting are not observed according to the surface selection rule. Experimental results broadly agree with this prediction as shown in Table 1.

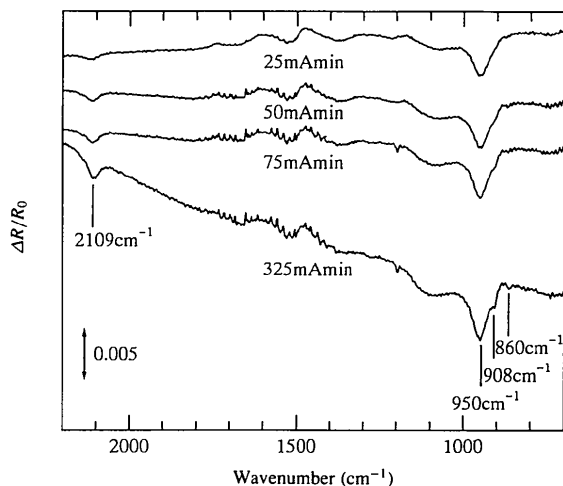


Figure 3

The IRAS spectra of the *in situ* observation with the *a*-Si deposited by synchrotron radiation-CVD on the SiO_2 BML substrate. The dose (synchrotron radiation beam current \times irradiation time) dependence is shown. The substrate temperature was 423 K. The Si_2H_6 gas pressure was 1×10^{-3} Torr.

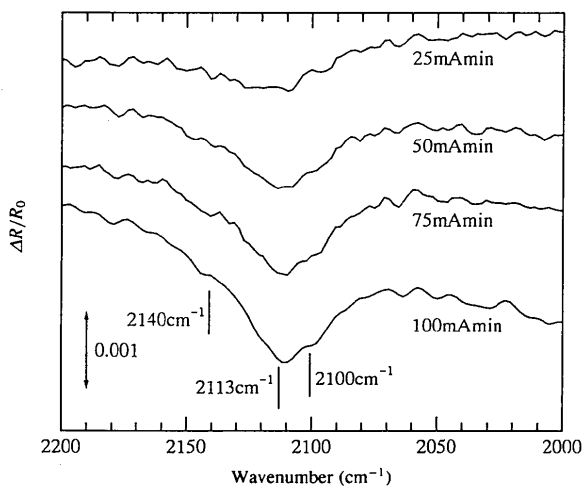


Figure 4

The IRAS spectra of the *in situ* observation with the *a*-Si deposited by synchrotron radiation-CVD on the SiO_2 BML substrate. The dose (synchrotron radiation beam current \times irradiation time) dependence is shown. The substrate temperature was 423 K. The Si_2H_6 gas pressure was 1×10^{-3} Torr. The 2000–2200 cm^{-1} region in Fig. 3 is expanded. Peak positions for SiH_n vibrations shown in Table 1 are indicated by solid lines.

The 860 and 908 cm^{-1} peaks are assigned to SiH_3 symmetric deformation and SiH_2 bending scissor vibrations, respectively, while the contribution of degenerate deformation of SiH_3 and wagging of SiH_2 may not be ignored completely. Both peaks decrease on synchrotron radiation irradiation as shown in Fig. 5. Therefore, the observed peaks at 2113 and 2140 cm^{-1} in Fig. 6, which decrease on synchrotron radiation irradiation, are assigned to SiH_2 and SiH_3 symmetric stretching vibrations, respectively. The

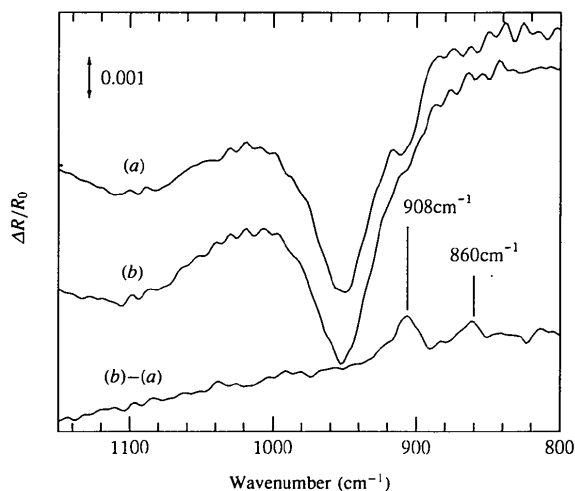


Figure 5

Changes of the IRAS spectra on synchrotron radiation irradiation after deposition for the 800–1150 cm^{-1} region: (a) just after deposition with an Si_2H_6 gas pressure of 1×10^{-3} Torr, a substrate temperature of 423 K and a dose of 515 mA min, (b) after a synchrotron radiation irradiation of 278 mA min, and (b) - (a) the difference spectrum between (b) and (a).

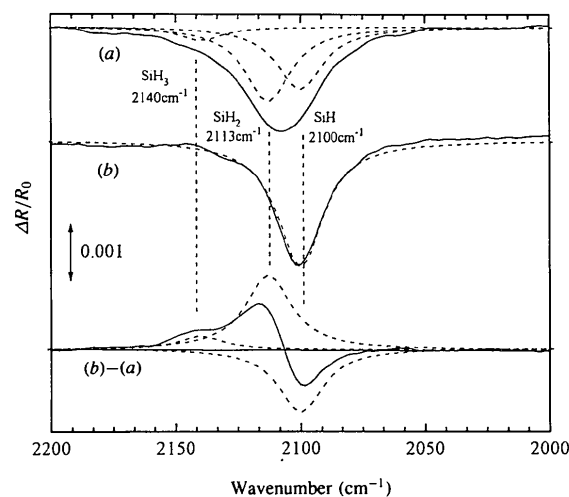


Figure 6

Changes of the IRAS spectra on synchrotron radiation irradiation after deposition for the 2000–2200 cm^{-1} region: (a) just after deposition with an Si_2H_6 gas pressure of 1×10^{-3} Torr, a substrate temperature of 423 K and a dose of 515 mA min, (b) after a synchrotron radiation irradiation of 278 mA min, and (b) - (a) the difference spectrum between (b) and (a). Results of the curve resolution assuming three peaks with Lorentzian form are shown by broken lines.

2100 cm⁻¹ peak, which was observed (Fig. 6) to increase on synchrotron radiation irradiation, is assigned to surface SiH stretching vibration, as shown in Table 1. The change of the spectra shown in Figs. 5 and 6 indicates that surface SiH₃ and SiH₂ are easily decomposed by synchrotron radiation irradiation, but SiH is not.

The 2109 cm⁻¹ band in Fig. 3 appears to consist mainly of surface SiH₂ stretching (2113 cm⁻¹) and surface SiH stretching (2100 cm⁻¹) vibrational modes. The vibration of the SiH contained in the bulk network, which was reported at 2000 cm⁻¹ (Toyoshima, Arai, Matsuda & Tanaka, 1990; Lucovsky, Nemanich & Knights 1979), was not observed, as shown in Fig. 3. It is worth mentioning that surface SiH₃, which was observed only weakly in the present case, is often observed strongly in such experiments as an Hg lamp (Wadayama, Suetaka, Sekiguchi, 1988) or metastable Ar-induced CVD of *a*-Si (Toyoshima, Arai, Matsuda & Tanaka, 1990) and hydrogen termination of Si(100) surfaces (Chabal, Higashi, Raghavachari & Burrows, 1989). The transition dipole moment of the SiH₃ symmetric stretching vibration is parallel to the C_{3v} symmetry axis, which is almost perpendicular to the substrate surface as already mentioned. The observed data thus indicate that the number of SiH₃ molecules is small on the surface. This may be due to the easy decomposition of SiH₃ by synchrotron radiation irradiation, as shown in Figs. 5 and 6. SiH may also be decomposed by synchrotron radiation irradiation (Niwano, Takeda, Takakuwa & Miyamoto, 1992), but our results indicate that its decomposition rate is extremely slow compared with SiH₂ or SiH₃. The differences between the decomposition rates for SiH, SiH₂ and SiH₃ may be due to differences in the electronic excited-state lifetimes. We intend to study this point in more detail in subsequent experiments.

4. Conclusions

The performance of IRAS for adsorbates on semiconductor or insulator substrates has been significantly improved using BML substrates. BML-IRAS is suitable for the *in situ* observation of surface reactions on semiconductor or

insulator substrates. SiH_n adsorbates in the deposition of *a*-Si by synchrotron radiation-CVD using Si₂H₆ have been observed for the first time by IRAS. SiH₂ and SiH₃ are the main adsorbates in the deposition at a substrate temperature of 423 K. Surface SiH₂ and SiH₃ are easily decomposed by synchrotron radiation irradiation. The decomposition rate of SiH is much slower than those of SiH₂ and SiH₃.

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