In Situ Detection of Surface SiH\textsubscript{n} in Synchrotron-Radiation-Induced Chemical Vapor Deposition of a-Si on an SiO\textsubscript{2} 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 SiO\textsubscript{2}(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 SiO\textsubscript{2} surface using Si\textsubscript{2}H\textsubscript{6} gas, the vibrational spectra of surface SiH\textsubscript{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 SiH\textsubscript{2} and SiH. Surface SiH\textsubscript{3} and SiH\textsubscript{2} 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 SiH\textsubscript{2} and SiH\textsubscript{3}.

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\textsubscript{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\textsubscript{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 SiO\textsubscript{2}/Al/Si(100) structure, then the
BML–IRAS technique has been used to monitor the surface SiH$_4$ 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 $\Omega$ 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 $5 \times 10^{-4}$ 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 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 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).

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...
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 x 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 R₀ 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 SiH₃.

The peaks at around 2109, 908 and 860 cm⁻¹ are assigned to SiH₃ 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 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 SiH₃ 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 SiH₃ 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

**Table 1**

<table>
<thead>
<tr>
<th>Vibrational mode</th>
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<th>This work</th>
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<tr>
<td>SiH₃</td>
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<tr>
<td>Symmetric stretching</td>
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<td>Asymmetric stretching</td>
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<td>2150</td>
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<td>Degenerate deformation</td>
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<td>860</td>
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<tr>
<td>SiH₂</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>2108</td>
<td>2100</td>
</tr>
<tr>
<td>Asymmetric stretching</td>
<td>2118</td>
<td>2100</td>
</tr>
<tr>
<td>Bending scissor</td>
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<td>908</td>
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<tr>
<td>Wagging</td>
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<tr>
<td>Twisting</td>
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</tr>
<tr>
<td>SiH(surface)†</td>
<td>2089</td>
<td>2100</td>
</tr>
<tr>
<td>(bulk)†</td>
<td>2000</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

* 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.

*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.
In the present case, the SiO₂ 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 SiH₂ and SiH₃ adsorb on the surface with their symmetry axis (C₂ᵥ and C₃ᵥ) 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.

The 860 and 908 cm⁻¹ peaks are assigned to SiH₃ symmetric deformation and SiH₂ bending scissor vibrations, respectively, while the contribution of degenerate deformation of SiH₃ and wagging of SiH₂ 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 SiH₂ and SiH₃ symmetric stretching vibrations, respectively. The

![Figure 3](image-url)

**Figure 3**
The IRAS spectra of the in situ observation with the a-Si deposited by synchrotron radiation-CVD on the SiO₂ BML substrate. The dose (synchrotron radiation beam current × irradiation time) dependence is shown. The substrate temperature was 423 K. The Si₂H₆ gas pressure was 1 × 10⁻³ Torr.

![Figure 4](image-url)

**Figure 4**
The IRAS spectra of the in situ observation with the a-Si deposited by synchrotron radiation-CVD on the SiO₂ BML substrate. The dose (synchrotron radiation beam current × irradiation time) dependence is shown. The substrate temperature was 423 K. The Si₂H₆ gas pressure was 1 × 10⁻³ Torr. The 2000-2200 cm⁻¹ region in Fig. 3 is expanded. Peak positions for SiH₆ vibrations shown in Table 1 are indicated by solid lines.

![Figure 5](image-url)

**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 Si₂H₆ 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](image-url)

**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 Si₂H₆ 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.
In situ detection of surface SiHₙ

A 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 SiHₓ and SiHᵧ 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 SiHₓ, 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 C₃ᵥ 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 SiHₓ. The differences between the decomposition rates for SiHₓ, SiHᵧ and SiH 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. SiHₓ adsorbates in the deposition of α-Si by synchrotron radiation-CVD using Si₂H₆ have been observed for the first time by IRAS. SiH₂ and SiHₓ are the main adsorbates in the deposition at a substrate temperature of 423 K. Surface SiHₓ and SiHᵧ are easily decomposed by synchrotron radiation irradiation. The decomposition rate of SiH is much slower than those of SiH₂ and SiHₓ.

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References