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NOTE

FT-IR/ATR Spectra of Octadecyltrichlorosilane Adsorbed on Germanium Surface

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For the construction of artificial supermolecular organizes with planned structure and properties, the Langmuir-Blodgett (LB) technique is one of the promising method. The monolayer self-assembly created by the spontaneous chemical adsorption of long-chain alkyl-trichlorosilanes dissolved in organic solvent onto fused silica, Si, or glass surfaces is also another strong candidate for constructing more thermally- or mechanically-stable organizes. In a recent paper, Cheng *et al.*¹⁾ have reported the *in situ* observation and kinetics of the self-assembly of a monolayer of n-octadecyltrichlorosilane (OTS) on the surface of Ge. However, since they presented only a limited part (1480-1410 cm^{-1}) of the Fourier transform infrared (FT-IR) spectra, it was not clear for us whether their data come from the chemical adsorption or physical adsorption. In the present study, therefore, we re-investigated the adsorption of OTS on the Ge surface by FT-IR/attenuated total reflection (ATR) spectroscopy. Another motivation originates from the fact that we have once observed the infrared bands due to the surface hydroxyl species of Ge.²⁾

OTS (>85% purity) and bicyclohexyl (BCH, >99% purity) was purchased from Tokyo Chemical Industry Co., Ltd. and cyclohexane (CH) was the Spectrosol™ grade of Dojindo Laboratories. The preparation of the 20 mM BCH solution and 50 or 100 mM CH solution of OTS and their filling into the ATR cell were performed in a globe box filled with dry nitrogen. We used the liquid ATR cell shown in Fig. 1, like our previous FT-IR/ATR studies.^{3,4)} The Ge ATR prism was cleaned by ultrasonication in dichloromethane, acetone, and ethanol for 15 min each. If necessary, a Harrick Model PDC-3XG plasma cleaner was used for complete removal of organic species on the Ge surface. FT-IR/ATR spectra were recorded on a Nicolet 6000C spectrophotometer with the resolution of 4 cm^{-1} . The contact angles were measured under ambient conditions with a Cahn Model DCA322 contact angle goniometer.

Figure 2 shows the FT-IR/ATR spectra of (A) OTS, (B) adsorption of OTS from a BCH solution at 23 °C (difference spectrum between 20 h and 0 h), (C) BCH, and (D) silicone rubber packing. In Fig. 2C and 2D, the absorbance scale was drawn downward, for

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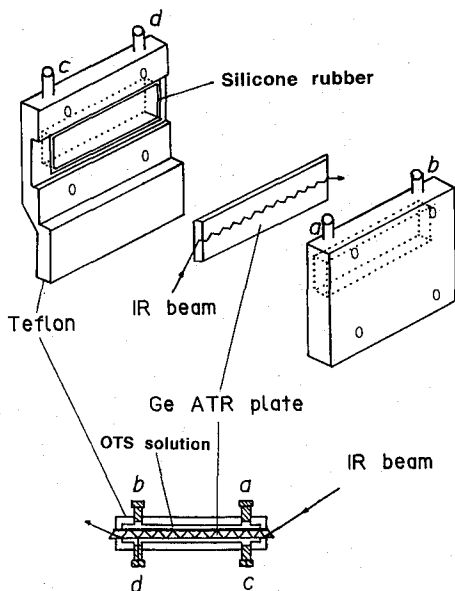


Fig. 1. Liquid ATR cell for adsorption experiments.

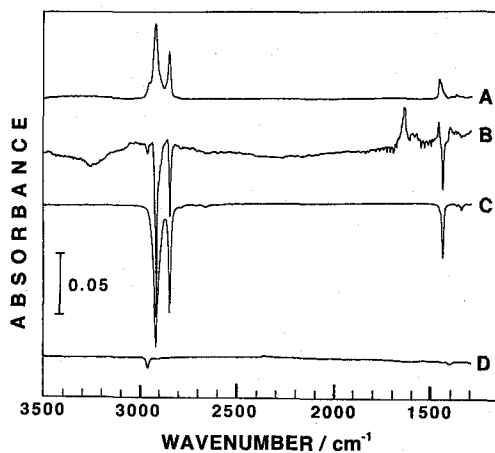


Fig. 2. FT-IR/ATR spectra of (A) OTS, (B) adsorption of OTS from a 20 mM BCH solution at 23 °C (difference spectrum between 20 h and 0 h), (C) BCH, and (D) silicone rubber packing. In (C) and (D), the absorbance scale is drawn downward.

easy comparison with Fig. 2B. The ordinate scale was scaled so that the peaks near 1400 cm^{-1} became equaled, except for that of Fig. 2D where it is scaled with the band at 2920 cm^{-1} . The spectrum of Fig. 2B in the region 1480-1410 cm^{-1} is just the same as reported by

Chen *et al.*¹⁾ The positive band in Fig. 2B indicates that its species near the Ge surface increases with time, and the negative band vice versa. Since the OTS band at 1467 cm^{-1} gives a positive peak and the BCH bands at 2908 , 2851 , and 1448 cm^{-1} give negative peaks in Fig. 2B, it is inferred that the OTS molecules are adsorbed onto the Ge surface in place of BCH molecules. The small negative peak at 2962.5 cm^{-1} originates from silicone rubber used as a seal of the ATR cell (Fig. 1), since it swells by BCH. The broad negative band at ca. 3240 cm^{-1} is due to the ice forming on the surface of the MCT detector with time. A new positive band appears at 1645 cm^{-1} . This frequency corresponds to the stretching mode of the double bond, possibly the C=O or C=C bond. It is appreciably lower than the C=O stretching mode (1733 cm^{-1}) of the $-(\text{C}=\text{O})-\text{O}-\text{Si}$ group formed by the chemical adsorption of OTS to the surface covered by the COOH group.⁵⁾ To check whether the appearance of this band is general or not, we changed the solvent from BCH to CH. The result is shown in Fig. 3. Here, dis-

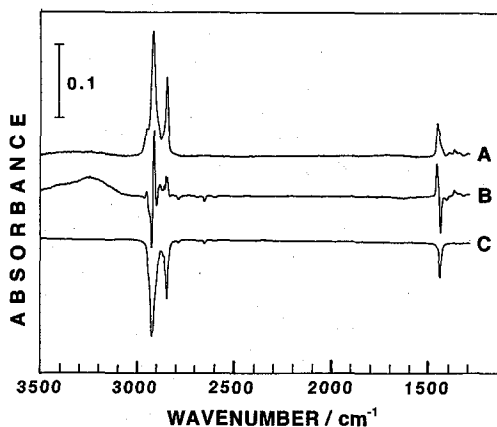


Fig. 3. FT-IR/ATR spectra of (A) OTS, (B) adsorption of OTS from a 50 mM CH solution at $23\text{ }^{\circ}\text{C}$ (difference spectrum between 14 h and 0 h), and (C) CH (absorbance scale is drawn downward).

played are the FT-IR/ATR spectra of (A) OTS, (B) adsorption of OTS from a CH solution at $23\text{ }^{\circ}\text{C}$ (difference spectrum between 14 h and 0 h), and (C) CH (absorbance scale is drawn downward). Apparently, there is no absorption at ca. 1645 cm^{-1} in Fig. 3B. Therefore, the appearance of the peak in Fig. 2B is special for BCH, and awaits further clarification. Other spectral features in Fig. 3B are principally the same with that of Fig. 2B. The positive absorbance of the 2919 cm^{-1} peak (and the negative absorbance of the 2932 cm^{-1} peak) is simply because the frequency of the CH_2 antisymmetric stretching band at 2924 cm^{-1} of OTS is lower than that (2931 cm^{-1}) of CH. (In Fig. 2C, the CH_2 antisymmetric stretching frequency of BCH is 2920 cm^{-1}). Note that the broad ice peak around 3240 cm^{-1} appears upward in this case, while it was downward in Fig. 2B.

Unfortunately, the stretching region ($1000\text{--}1150\text{ cm}^{-1}$) of the siloxane (Si-O-Si) bridge

were obscured by the broad and strong absorption band at 1052 cm^{-1} of the silicone rubber seal (it shifts to higher frequency on swelling), and was not shown in these figures. Thus, the formation of these chemical groups could not be monitored. However, if the chemical adsorption does occur, we may observe the decrease of the absorption intensity of the surface OH groups.^{6,7)} In Fig. 2B and 3B, there is no appreciable decrease in absorbance around the frequencies of the surface OH species of Ge (sharp bands⁸⁾ at 3425, 3210, 3030, and 1428 cm^{-1} which we have observed previously for a plasma treated Ge ATR prism²⁾). Therefore, we are inclined to infer that the observed adsorption of OTS molecules onto the Ge plate is due to physisorption.

In order to ascertain this point, we have measured the contact angle of the Si and Ge plates before and after the treatment with 5% (ca. 100mM) CH solution of OTS for 30 min.

Table 1. Contact angles of H₂O drop on Si and Ge plates before and after OTS adsorption*

Plates	Advancing	Receding
Si before OTS adsorption (clean)	27.1°	0°
after OTS adsorption (rinsed with H ₂ O)	103.0°	54.8°
(ultrasonicated in H ₂ O)	106.0°	60.1°
(ultrasonicated in CH and H ₂ O)	104.0°	53.9°
Ge before OTS adsorption (clean)	44.7°	0°
after OTS adsorption (rinsed with H ₂ O)	68.5°	14.6°
(ultrasonicated in H ₂ O)	102.3°	61.9°
(ultrasonicated in CH and H ₂ O)	100.1°	54.6°

*Rinsing or ultrasonication is for 15 min each.

After the treatment, the plates were either rinsed or ultrasonicated in H₂O for 15 min, or ultrasonicated in CH and H₂O for 15 min each. The results are given in Table 1. Clean plates of both Si and Ge gives small contact angles, indicating that the surfaces are hydrophilic. In the case of Si, it became hydrophobic after OTS treatment by any cleaning process, giving the contact angles of 103°-106° (proceeding) and 54°-60° (receding). In the case of Ge, however, it remained fairly hydrophilic after being rinsed with H₂O. This tendency was almost invariant after 14 h treatment by 50 mM CH solution or 20 mM BCH solution of OTS. These facts indicates that the OTS adsorption is mainly physical in these ambient conditions: the chemical adsorption is slight if it does occur at all. By ultrasonication, however, the temperature increases largely to promote the chemical adsorption. As Maoz and Sagiv have pointed out,⁹⁾ the surface state of Ge is variable according to the different degree of surface oxide films, depending upon the pre-treatment. But, at least we

may conclude that the Ge surface is less reactive with OTS than the Si surface, if the pre-treatment is the same.

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