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Monolayer of Lithocholic Acid by Chemical Reaction on Silicon Crystal Surface

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The reaction of lithocholic acid with silane coupling agent on a Si crystal surface was analyzed with FT-IR(ATR), XPS, and contact angle. The generation of amide bonds within 1nm of the Si surface was confirmed with XPS. The yield of amide was 84%. An abnormal IR absorption was observed in the amide band region.

Organized molecular films have been attracting growing interest, because the anisotropic character of the molecules can appear macroscopically in the aligned film.[1] However, to have a wide choice of functional molecules in these films, a new method which does not depend on self aggregative character[2] of long alkyl chains is necessary. The connection and alignment of the desired molecules on a substrate surface by chemical reaction is promising. We call this *Chemical Reaction Alignment* (CRA). In the course of this study we found an abnormal phenomenon in the IR spectrum of monolayer. Although the IR anomality of monolayers has been reported,[3-4] it has not been fully explained despite its importance to the understanding of monolayer film structures. Many reliable examples are required for the theoretical analysis. In this report, we describe the IR-abnormality due to the amide bond formation within 1 nm of the Si surface and XPS evidence for the existence of the amide bonds which are schematically shown in Scheme 1.

We selected lithocholic acid as a CRA molecule, (N-(2-Aminoethyl)-3-aminopropylmethyldimethoxysilane, TSL8345,[5] as a silane coupling agent, and an Si crystal as a substrate. The Si surface was treated with the silane coupling agent, and then allowed to react with lithocholic acid in the presence of DCC.[6] There are many reports on the treatment of Si surfaces with silane coupling agent,[7] but the reaction of the silane coupling agent with other molecules has not been analyzed intensively. The OH groups, of which density on the Si surface is reported to be 5.0 OH groups/nm^2 after treatment with a strong acid,[8] are believed to react with silane coupling agent in high yield.[2]

The contact angle[9] for H_2O on the Si surface was used as an indicator of the extent of the surface treatment, as shown in Table 1. The same Si prisms, Sample 1, 2 and 3, were treated in a similar manner to examine the degree of reproducibility. The values of contact angle suggest that each

treatment was satisfactory.

Table 1. Contact Angle (deg.) for H_2O on Treated Si Surfaces

Treatment	Sample 1	Sample 2	Sample 3
None(Si)	22	22	23
TSL8345	52	52	52
Lithocholic Acid	59	60	60

Figure 1 shows the ATR spectrum for the treated Si prism(Sample 1), bulk lithocholic acid(KBr) and bulk silane coupling agent(NaCl) for reference. The spectrum of Sample 1 was measured in the ATR mode with eight reflections and the latter two in the transmission mode. For Sample 1, ν (C-H) was observed at 2930 cm^{-1} and 2870 cm^{-1}. These values are the same as those of bulk lithocholic acid. The ν (C-H) bands for the silane coupling agent were overlapped with those of the lithocholic acid. In the lower wave-number region, amide bands I and II[11] are expected to be observed at 1665 cm^{-1} and 1555 cm^{-1}, but the only strong band was observed at 1510 cm^{-1}. This may be a characteristic IR-response for monolayer. Several similar phenomena were reported by Nuzzo et al.[3], who gave some explanation in terms of self-assembled monolayers.

XPS[12] was used to confirm amide bond generation and quantitative analysis of the reaction of the silane coupling agent with lithocholic acid. In order to make assignment easy, TSL8345 with two N atoms in different chemical environment was chosen. The photoelectron detection angle was made 5° to examine the region close to the surface. Two peaks of N1s for NH_2 and NH in TSL8345 were observed in the XPS spectrum, as shown in Fig. 2(a). The peak area ratio was one to one, corresponding to the number of NH_2 and NH in a silane coupling agent attached on the Si surface. The generation of amide bond was confirmed by the generation of a new N1s band, as follows. After the reaction of TSL8345 with lithocholic acid in the presence of DCC, an N1s peak with the lower binding energy than that for NH emerged, and peak of NH_2 and NH decreased to 8% of the total N1s peak area, as shown in Fig. 2(b). The new peak was assigned to -NHCO-. From the area of the peak, the yield of amide was determined to be 84%.

We conclude that bonding between the silicon surface and the bulky rigid lithocholic acid was successfully accomplished through a silane coupling agent, and the reaction within 1 nm of the Si surface gave an 84% yield. We have confirmed the generation of amide bond, and also that an abnormality in the IR spectrum of the monolayer. Efforts to establish the CRA method for molecular alignment are now in progress.

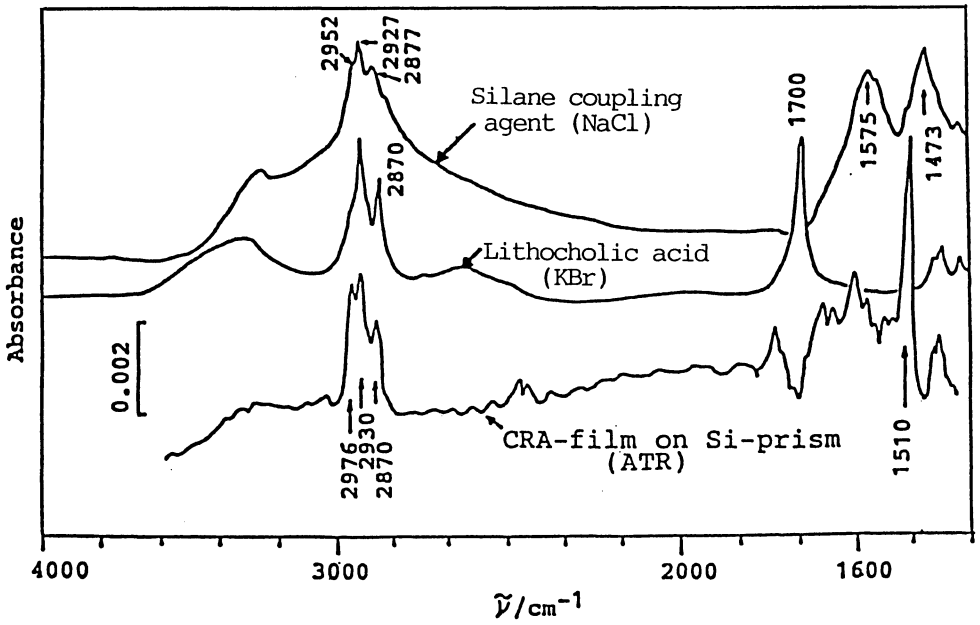
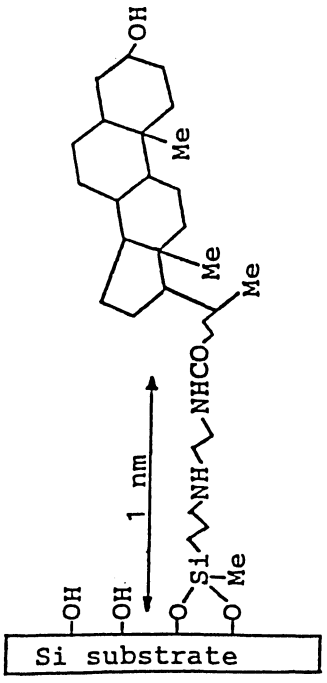


Fig. 1. IR spectra of CRA film and starting materials.



Scheme 1. A model for the modified surface.

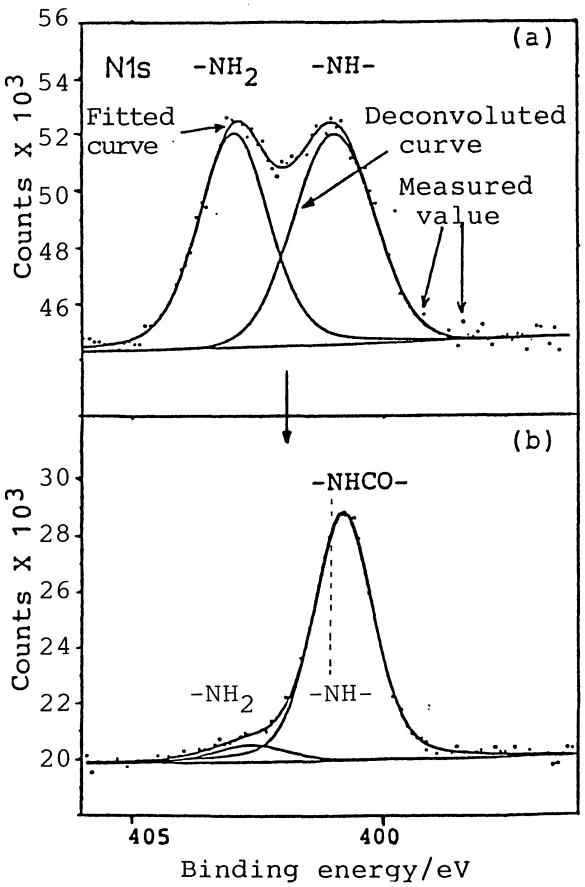


Fig. 2. XPS spectra of Si surface.
(a) Si treated with TSL8345.
(b) After reaction of lithocholic acid with (a).

References

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5) TOSHIBA SILICONE products without further purification.
6) Si substrates (10 x 20 x 2 mm) and Si prisms (28 x 28 x 3 mm, 45° cut for ATR) were polished with 0.25 μm diamond polisher and stored in pH-1-HCl solution. We treated the substrates with the silane coupling agent in acidic water solution of pH 4 at 5 wt % concentration for 24 hours. Lithocholic acid (2 g, 5.4 x 10^{-3} mol) was dissolved in THF (30 ml) with an equivalent amount of DCC (dicyclohexylcarbodiimide) at 0 °C. Then the above Si substrates were immersed in the solution very gently, and left for 24 hours at room temperature. Then the substrates were washed with THF and acetone repeatedly. The Si prisms were treated with both sides.
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9) The contact angles for H_2O were measured with a Model CA-DT A by Kyowa Interface Science.
10) The IR spectra were recorded with a Bio-Rad FTS-60A/896 FTIR spectrometer equipped with an MCT detector. The number of corrected interferograms was 256 with a resolution of 4 cm^{-1}. The ATR spectra were a result of the subtraction of the curves measured with the clean Si prism from those measured after CRA treatment.
11) We confirmed the position of Amide I and II bands using commercially available CHAPS, 3-[(3-Cholamidepropyl)dimethylamino]-1-propanesulfonate, which has the almost same structure as our system.
12) The XPS spectra were recorded with an ESCA-300 of SCIENTA at 10^{-9} Torr. The pass energy was 75 eV, and the X-rays were monochromatized Al-Kα. All treatments were carried out under a pure nitrogen atmosphere. The curve was deconvoluted using a Voight function.

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