Paper

Degradation of organic silane monolayers on silicon wafer during XPS measurement

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The degradation of organic materials was often observed during XPS measurement. We have evaluated the degradation of silicon wafers modified with 3,3,3-trifluoropropyltrimethoxysilane (F3PTMS-Si), 3-chloropropyltriethoxysilane (CPTES-Si), 3-bromopropyltrimethoxysilane (BPTMS-Si) and 3-iodopropyl-trimethoxysilane (IPTMS-Si), and gold substrate modified with 1H,1H,2H,2H-perfluorodecanthiol (PFDT-Au) as reference material in order to investigate influence of C-F, C-Cl, C-Br and C-I bonds in the organic silane monolayers. As a result, the order of damaging factor, β, was IPTMS-Si > BPTMS-Si > CPTES-Si > F3PTMS-Si. It was found that the value of β was related to the chemical bond energy of C-X(X=F, Cl, Br, I).

1. Introduction

It is well known that the surface damages have been observed during XPS measurement for many organic materials, such as polymers[1-11], Langmuir-Blodgett films [12-14], and organosilane [15-18] and alkanethiol [18-19] monolayers on solid substrates. Factors for the surface damage are considered to be X-ray irradiation, heat radiation from filament, photoelectrons generated from the sample itself, and so on. In addition, the sample damage also depends on elemental composition and structure of polymer or a thin film. A study on the damages of halogen containing organic materials focused on the effect of halogen atom difference on the damage mechanism and creation of the relevant database will provide fruitful information to XPS users in this field. Additionally, investigation of the mechanism of the damages will contribute to the basic research of XPS.

For the comparison of sample damage, we have proposed the gold substrate modified with 1H,1H,2H,2H-perfluorodecanethiol (PFDT-Au) as reference material [11]. The relative damaging factor, a damaging factor of a sample divided by that of reference material, is practically useful to predict the damage characteristics of the sample and to evaluate data collection time suitable for acquiring sufficiently acceptable XPS spectra. Thus the reference material should be the same material throughout the study and have reproducibility and long-term durability.

In this report, we have studied the degradation of C-F, C-Cl, C-Br and C-I bonds in the organic silane monolayers on silicon wafer surfaces, in order to investigate the difference in damage mechanism on these materials. The samples were the silicon wafers modified with 3,3,3-trifluoropropyltrimethoxysilane (F3PTMS-Si), 3-chloropropyltriethoxysilane (CPTES-Si), 3-bromo-propyltrimethoxysilane (BPTMS-Si) and 3-iodo-propyltrimethoxysilane (IPTMS-Si), and PFDT-Au as reference material.

2. Experimental

2.1 Sample preparation

As the surface modification reagents, PFDT (Sigma-Aldrich), F3PTMS (PCR), CPTES (Tokyo Chemical Ind., TCI) , BPTMS(TCI) and IPTMS (Gelest) were used without further purification. PFDT on Au substrates (PFDT-Au) was prepared as reported by F.Kurayama et al.[11]. Au substrates (higher than 99.95%, 0.5 x 10 x 10 mm) were highly polished with alumina

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lapping film (0.3 μm) and cleaned ultrasonically in isopropyl alcohol. The Au substrate was immersed into 1 mM PFDT ethanol solution for over a day under nitrogen atmosphere. The substrate was rinsed with ethanol, hexane and acetone. The PFDT-Au was stored in a desiccator until used.

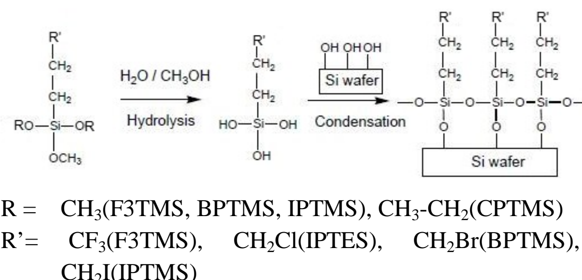
CPTES-treated and BPTMS-treated silicon wafer samples (CPTES-Si and BPTMS-Si) were prepared as reported by M.Sato et al.[18]. F3PTMS-treated and IPTMS-treated silicon wafer samples (F3PTMS-Si and IPTMS-Si) were prepared also by the same method. Before the silane treatment, the wafer was washed with mild detergent (M's one Mild, TSURUHA Co. Ltd.), rinsed with water ultrasonically and dried in vacuum. Thereafter the substrates were placed into the mixed solution (H_2O_2 : NH_4OH : H_2O = 1 : 1: 6) and kept at 80 ºC for 30 min to eliminate any organic contaminants from the surface. The clean substrates were again rinsed with water and dried in vacuum. Organic silane monolayers on the silicon wafer surface were prepared by immersing the clean substrate into the surface-treatment solution of 2 %(v/v) F3PTMS / CPTES / BPTMS / IPTMS in hexane for 6 h, followed by washing with ethanol, hexane and acetone. After drying in a vacuum, the monolayer samples were stored in a desiccator.

2.2 XPS measurement

The XPS measurements of samples were performed by using Shimazu/Kratos AXIS-ULTRA with non-monochromatic Mg Kα X-ray source. The X-ray source was operated at 15 kV 10 mA-emission. The distance between the X-ray anode and the analysis position on the sample was approximately 18 mm. The X-ray incident angle defined by the angle between the center axis of the X-ray gun flange and the sample surface plane was 25 degrees. The photoelectron take-off angle with respect to the sample surface was 90 degrees. XPS measurements were carried out using a depth profile mode without sputtering to obtain the change of peak intensity in each sample. To evaluate the effect of the X-ray dose, the Au 4f peak intensity was measured using Au substrates just after Ar ion etching. The analysis conditions for the sample damage and X-ray dose measurement were exactly the same.

3. Results and Discussions

The reaction schemes of F3PTMS, CPTES, BPTMS and IPTMS film formation on silicon wafer are illustrated in Fig. 1. F3PTMS, CPTES, BPTMS and IPTMS are firstly hydrolyzed by water which has been adsorbed on the substrates, and condensation reaction occurs with surface hydroxyl groups, resulting in the



R = CH_3(F3TMS, BPTMS, IPTMS), CH_3-CH_2(CPTMS)
R'= CF_3(F3TMS), CH_2Cl(IPTES), CH_2Br(BPTMS), CH_2I(IPTMS)

Fig. 1 Schematic illustration of F3PTMS, CPTES, BPTMS and IPTMS monolayer formation on silicon wafer surface.

formation of monolayer strongly combined with the substrate by chemical bond.

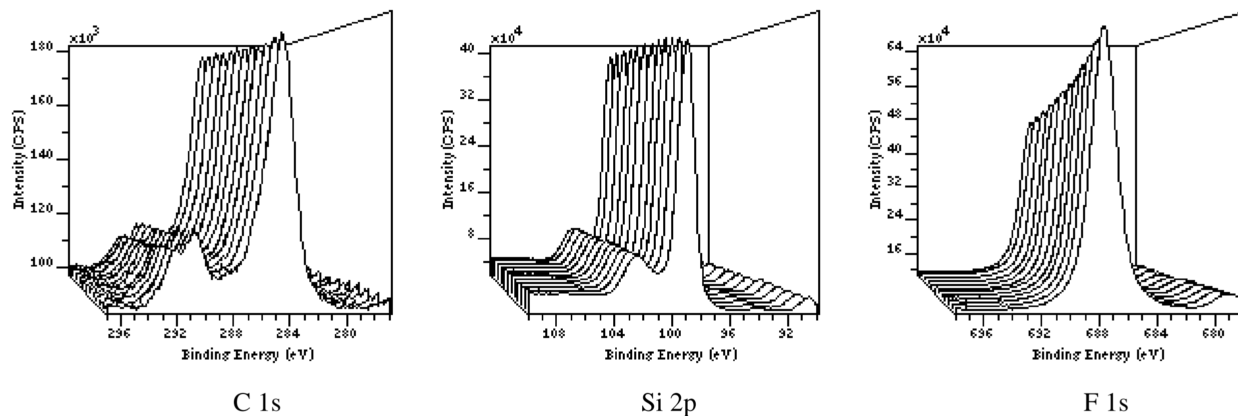
Figure 2 shows the montages of the XPS spectra of F 1s, C 1s and Si 2p of the F3PTMS-Si. The F 1s peak intensity drastically decreases within the measurement cycles. Simultaneously, intensity of the peak at around 292 eV in C 1s region, which is considered to be from the carbon atom connected to fluorine atoms, also decreases. On the other hand, C 1s peak intensity is almost constant, and Si 2p peak intensity slightly increases. These results indicate that the main degradation reaction is the scission of the C-F bond in the trifluoropropyl group. Figure 3 shows the montages of the XPS spectra of I 3d, C 1s and Si 2p of the IPTMS-Si. The tendency of peak intensity within the measurement cycles was the same as that of the F3PTMS-Si shown in Fig.2. Figure 4 shows the change in the particular peaks of CPTES-Si, BPTMS-Si and PFDT-Au with time. The intensity of the Cl 2p peak of CPTES-Si, the Br 3d peak of BPTMS-Si and the F 1s peak of PFDT-Au decreases within the measurement cycles as shown in other studies[18]. These results imply that all prepared organic silane monolayers on silicon wafer were damaged during XPS measurement. The decomposition mechanism of these thin films is considered to be mutually alike.

Figure 5 shows the semi-logarithmic plots obtained

from the Fig. 2 to the Fig.4 according to the following equation:

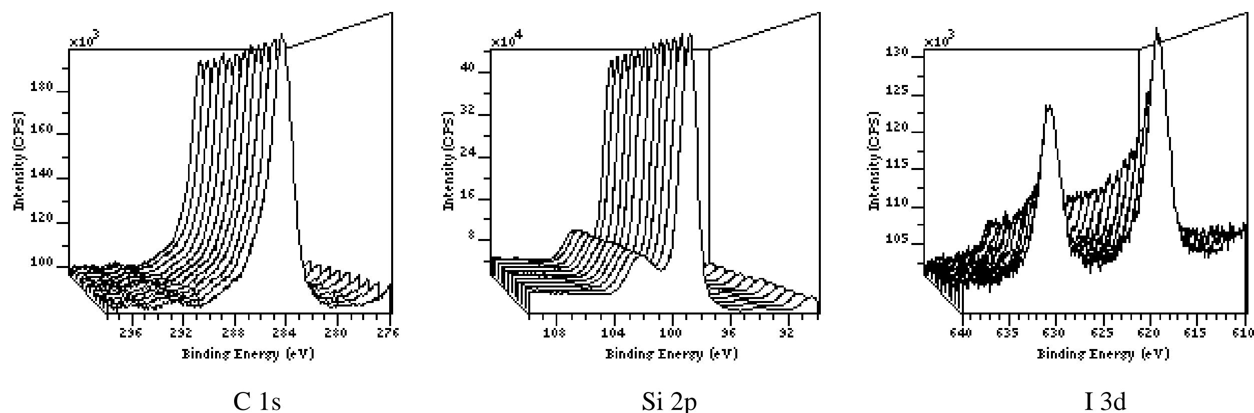
$$\ln(I/I^0) = -\beta D_{\mathrm{Au}} = -\beta I_{\mathrm{Au}}t = -kt \quad (1)$$

where β is the 'damaging factor', D_{Au} is relative X-ray dose, I_{Au} is peak intensity of Au 4f, k is the degradation rate constant, and t is the X-ray irradiation time. For all samples, the relations between $\ln(I/I^0)$ and D_{Au} show almost straight lines in the smaller part of D.



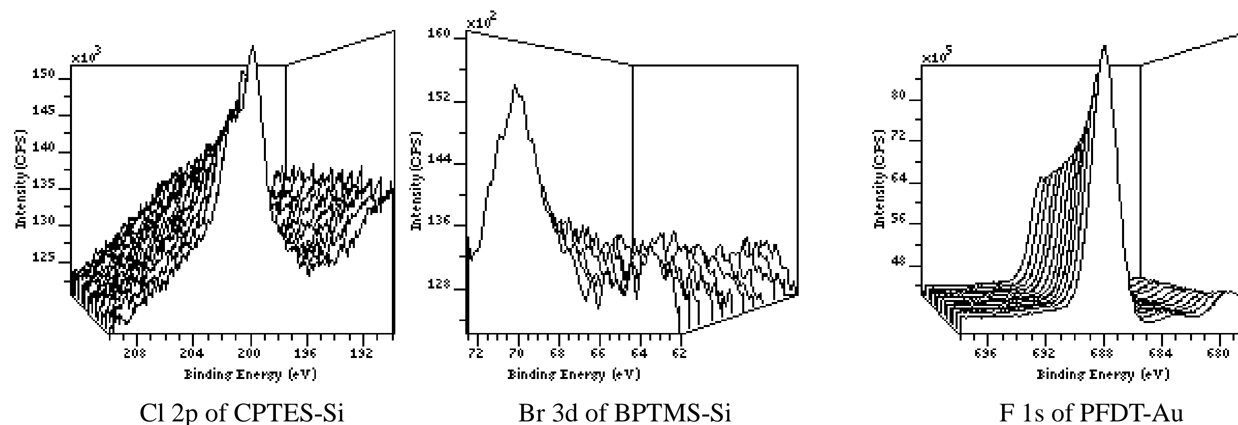
C 1s Si 2p F 1s

Fig. 2 The montages of the XPS spectra of C 1s, Si 2p and F 1s of F3PTMS-Si.



C 1s Si 2p I 3d

Fig. 3 The montages of the XPS spectra of C 1s, Si 2p and I 3d of IPTMS-Si.



Cl 2p of CPTES-Si Br 3d of BPTMS-Si F 1s of PFDT-Au

Fig. 4 The montages of the XPS spectra Cl 2p of CPTES-Si, Br 3d of BPTMS-Si and F 1s of PFDT-Au.

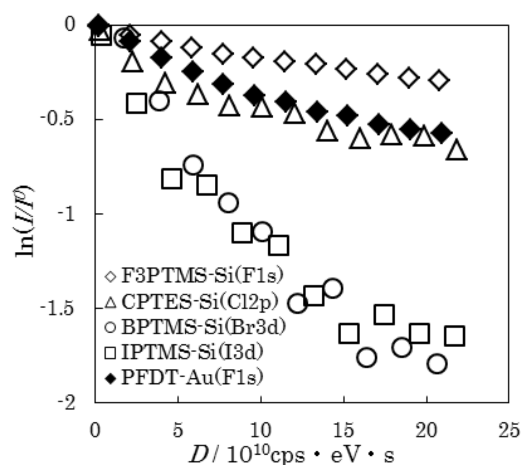


Fig. 5 Plots of $\ln(I/I^0)$ against relative X-ray dose D.

The damaging factor β calculated from Eq.(1) for F3PTMS-Si (F 1s), CPTES-Si (Cl 2p), BPTMS-Si (Br 3d), IPTMS-Si (I 3d) and PFDT-Au (F 1s) are 2.19×10^{12}, 6.56×10^{12}, 11.3×10^{12}, 13.3×10^{12} and 3.86×10^{12} ($cps^{-1}eV^{-1}s^{-1}$), respectively. Thus, the degradation rates are in the order of IPTMS-Si > BPTMS-Si > CPTES-Si > F3PTMS-Si.

However, the values of the damaging factor, β, depend on the analysis conditions. PFDT-Au is regarded as a reference material for damage evaluation, and relative damaging factor, R_β, which is defined as the damaging factor of a sample divided by that of PFDT-Au. The R_β does not depend on the difference of the apparatuses and measurement conditions as shown in recent report[11]. The R_β values for F3PTMS-Si(F 1s), CPTES-Si(Cl 2p), BPTMS-Si(Br 3d), and IPTMS-Si(I 3d) are 0.57, 1.70, 3.03 and 3.45, respectively. Figure 6 shows the relationship between the bond energy of C-X (X=F:F3PTMS, Cl:CPTES, Br:BPTMS, I:IPTMS) in monolayers and relative damaging factor, R_β. The R_β are recognized to decrease with increase in the chemical bond energy. This tendency suggests that the damaging factor is related to the chemical bond energy.

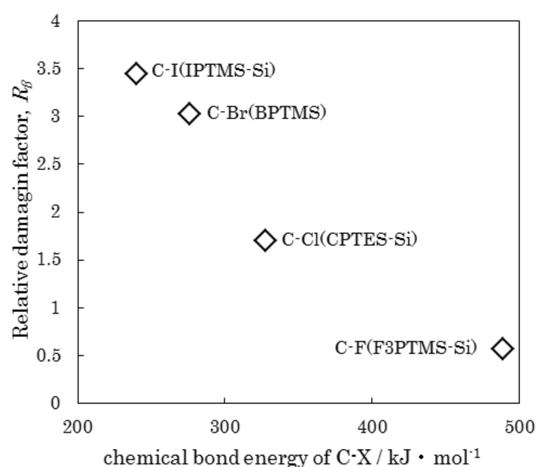


Fig. 6. Relationship between R_β and the chemical bond energy of C-X in monolayers structure.

4. Conclusion

We have evaluated the degradation of F3PTMS, CPTES, BPTMS and IPTMS organic silane monolayers on silicon wafer in order to investigate influence of C-F, C-Cl, C-Br and C-I bonds in the organic silane monolayers on the wafer surfaces during XPS measurements. From the results, the decomposition mechanism of these thin films is considered to be mutually alike and the scission of C-X(X=F, Cl, Br, I) bonds will be the main reaction. The first order reaction mechanism could be applied to the degradation of these films. The order of damaging factor, β, was IPTMS-Si > BPTMS-Si > CPTES-Si > F3PTMS-Si. It was found that the β value decreases with an increase in the chemical bond energy of C-X.

References

[1] D. R. Wheeler and S. V. Pepper, *J. Vac. Sci.Technol.* **20**, 226 (1982).
[2] A. H. K. Fowler, H. S. Munro and D. T. Clark, *Polym. Degrad. Stab.* **11**, 287 (1985).
[3] L. P. Buchwalter and G. Czornyi, *J. Vac. Sci. Technol. A* **8**, 781 (1990).
[4] B. C. Beard, *Appl. Surf. Sci.* **45**, 221 (1990).
[5] G. Beamson and D. Briggs, *Surf. Interface Anal.* **26**, 343 (1998).
[6] G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers*, John Wiley, Chichester (1992).
[7] G. Coullerez, Y. Chevolot, D. Leonard, N. Xanthopoulos and H. J. Mathieu, *J. Surf. Anal.* **5**, 235 (1999).
[8] H. Tohma, K. Miura, and Organic Materials Group of Surface Analysis Society of Japan, *J. Surf. Anal.* **5**, 220 (1999).
[9] N. Suzuki, T. Sakamoto, T. Isano, K. Iimura, T.kato, H. Tohma, T. Maruyama, K. Miura and Organic Materials Group of Surface Analysis Society of Japan, *J. Surf. Anal.* **5**, 224 (1999).
[10] K.Yoshihara and A.Tanaka, *Surf. Interface Anal.* **33**,

252 (2002).

[11] F. Kurayama, N. Suzuki, M. Sato, T. Furusawa, H. Isahara, Y. Kikuchi, S. Fukushima, M. Takano, E. Iwase, R. Inoue, M. Sato and T. Itoh, *J. Surf. Anal.* **16**, 2 (2009).

[12] L. B. Hazell, A. A. Rizvi, I. S. Brown and S. Ainsworth, *Spectrochim. Acta, Part B* **40**, 739 (1985).

[13] L. B. Hazell, I. S. Brown and F. Freisinger, *Surf. Interface Anal.* **8**, 25 (1986).

[14] T. L. Marshbanks, H. K. Jugduth, W. N. Delgass and E. I. Franses, *Thin Solid Films* **232**,126 (1993).

[15] E. Frydman, H. Cohen, R. Maoz and J. Sagiv, *Langmuir* **13**, 5089 (1997).

[16] N. Suzuki, T. Isano, T. Sakamoto, T. Saino, K. Iimura and T. Kato, *Surf. Interface Anal.* **30**, 301 (2000).

[17] M. Sato, H. Watanabe, T. Furusawa and N. Suzuki, *J. Surf. Anal.* **12**, 183 (2005).

[18] M. Sato, T. Furusawa, T. Hotta, H. Watanabe and N. Suzuki, *Surf. Interface Anal.* **38**, 838 (2006).

[19] A. J. Wagner, K. Han, A. L. Vaught and D. H. Fairbrother, *J. Phys. Chem. B* **104**, 3291 (2000).