CHEMISTRY LETTERS, pp. 1271-1274, 1994.

2-Step Chemical Vapor Surface Modification of Porous Glass with Fluoroalkyl-functional Silanes

Hiroaki TADA
Central Research Laboratory, Nippon Sheet Glass Co. Ltd., 1, Kaidoshita, Konoike, Itami, Hyogo 664

Surface porous glass substrates were exposed to heptadecafluorodecyltrichlorosilane (HFTS) vapor followed by the treatment with trifluoropropyltrichlorosilane (TFTS). The resistance of the monolayer to liquid H_2O was found to be better than those of the samples treated with the respective reagents, i.e., HFTS or TFTS. The coverage with the molecules in the pores were estimated from the analyses of the reflection spectra having a minimum in the visible range. These results reasonably explain the superior resistance to H_2O of the sample treated with HFTS (1st step) and TFTS (2nd step).

Organic monolayers on solid supports have wide potential for applications in sensors,1) tribology 2) and water-repellent glass.3) Recently, highly oriented monolayers of functional silanes have been shown spectroscopically to form on glass substrates with rough surface 4) as well as smooth surface 5) by the chemical vapor surface modification (CVSM) method. The understanding of the mechanism on formation of the monolayer increasingly becomes clear,6) however, little attention has been drawn to the deterioration process in spite of its delicate structure. In the previous paper, the resistance of fluoroalkylsilane (FAS) monolayers on surface porous glass (SPG) substrates prepared by the CVSM method was examined and hydrolysis was indicated to proceed from the internal surface of the pores incompletely covered with FAS molecules.7) This letter reports characterization and H_2O-resistance of the SPG substrates subjected to CVSM with FAS having a longer fluoroalkyl chain followed by the treatment with one having a shorter chain.

SPG (Anti-Reflection (AR) glass, Nippon Sheet Glass Co.) and smooth surface glass (SSG) substrates were cleaned by irradiation of UV light under O_2 atmosphere. In order to minimize the influence of alkali metal ions on the H_2O-resistivity of the FAS layer, a SiO_2 film with a thickness of about 50 nm was coated on soda-lime-silicate glass substrates (SiO_2 : B_2O_3 : Al_2O_3 : CaO : MgO : Na_2O = 72.6 : 0.8 : 1.7 : 4.6 : 3.6 : 15.2) in the SSG sample by means of a liquid phase deposition method 8) and most of alkali metal ions are leached out by an H_2SiF_6 acid solution in the SPG sample.9) The surface compositions (O : Si : Na : F) of SSG and SPG were semiquantified by the XPS analyses to be 61.7 : 34.8 : 1.5 : 2.0 and 63.8 : 33.9 : 1.5 : 0.9, respectively. The pore size of SPG was determined by the Cranston and Inkley method to be distributed in a wide range between 1.8 and 10 nm around a main peak of ca. 3.5 nm.4) After the substrates (38 mm x 40 mm) had been set in a vacuum chamber (2.83 L), it was evacuated till the pressure reached ca. 10 Torr and heated to a temperature of 80 °C. FAS of ca. 50 μL was dosed and allowed to react with the substrates for 1 h. Then the temperature was raised up to 99 °C, evacuating for additional 1 h to remove the physically adsorbed FAS.

Present address: Nippon Sheet Glass Techno-Research Co. Ltd., 1, Kaidoshita, Konoike, Itami, Hyogo 664.

TFTS ($CF_3CH_2CH_2SiCl_3$, >98 %, Shin-Etsu Chem.) and HFTS ($CF_3(CF_2)_7CH_2CH_2SiCl_3$, >98 %, Toshiba Silicone) were used as fluoroalkylsilane adsorbates. The samples treated singly with HFTS and TFTS are referred to as A and B, respectively. Sample C is one firstly treated with HFTS and followed by exposure of TFTS. Static contact angles (CA) were measured by using a contact angle meter (Model CA-D, Kyowa Interface Science Co.) at room temperature (20±1 °C). H_2O droplets with a diameter of approximately 2 mm were placed at six positions for one sample and the average was adopted as the CA value (reproducibility within ±2.5%). X-ray photoelectron spectra (XPS) were measured with a Shimadzu Electron Spectrometer (Model ESCA 7000) using a Mg Kα X-ray source (hν=1253.6 eV). The X-ray source was operated at 30 mA and 8 kV. The residual gas pressure in the spectrometer chamber during data acquisition was less than 10^{-7} Torr. Incident and detected angles were fixed at 90 ° and irradiation area was ca.19.6 mm^2. The binding energy scales for the fluorocarbon samples were referenced by setting the hydrocarbon (CH_x) peak maxima in the C_{1s} spectra to 284.6 eV. The precision of the binding energy determined with respect to this standard value was within ±0.3 eV.

Figure 1 shows variations of CA with immersion time in boil H_2O for various samples. The initial value of CA is in the order of sample C (117.9 °)>sample A (116.4 °)>>sample B (92.4 °). The remarkable difference in CA between samples A and B seems to be due to that in the molecular orientation; the larger the molecular size is, the smaller the tilt angle from the normal to the surface becomes.10) The excessive increase of CA in sample A over that in the SSG substrate treated with HFTS (107 °) was theoretically accounted for by the surface asperity.4)

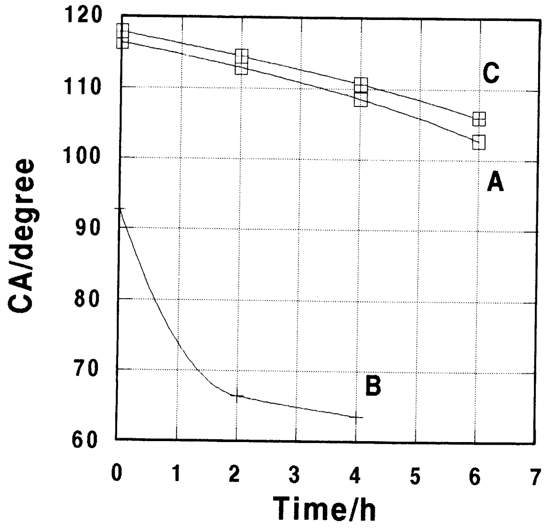

Fig.1. Plots of CA vs. immersion time: A, sample A; B, sample B; C, sample C.

Noticeably, the CA value of sample C is further larger than that of sample A. There exist many micropores with diameters smaller than 2 nm on the surface of SPG. In sample A, its internal surface can not completely be covered with HFTS molecules whose lengths are estimated to be 1.83 nm from the Corey-Pauling-Koltun (CPK) model. Since the size of TFTS is approximately 0.89 nm, TFTS molecules are thought to occupy a part of the pores not covered with HFTS molecules in the 2nd step (vide post); this may be responsible for the increase of CA in sample C compared to the value in sample A. In each case, the CA value monotonously decreases with an increase in immersion time. It was previously revealed that this is mainly caused by hydrolysis of the interfacial Si-O-Si bonds, which had been formed by the reaction of HFTS (or TFTS) and the

Table 1. C_{1s}-XPS signal intensity ratios

Signal intensity ratio / Sample	CF_3/CF_2	CF_3/Si_{2p}	CF_2/Si_{2p}
A	0.195	0.220	1.132
C	0.245	0.342	1.396

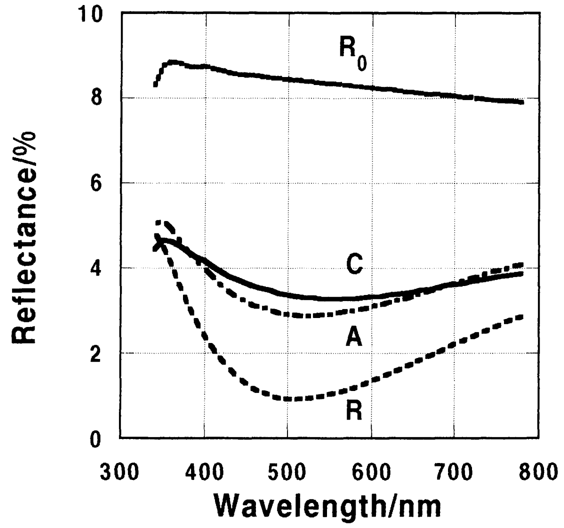

Fig.2. Reflection spectra: R_0, SSG substrate; R, sample R; A, sample A; C, sample C.

isolated Si-OH groups on the surface of SPG.[7] The decreasing rate of CA is in the order of sample B>>sample A>sample C, which is opposite to the order of the initial value. The curve of CA vs. immersion time for the sample subjected to the HFTS treatment (1st step) and post-annealing (80 °C-1 h and 100 °C-1 h) in the absence of TFTS (2nd step) is in good agreement with that of sample A. Also, the H_2O-resistance of the sample treated with TFTS (1st step) and HFTS (2nd step) molecules was only comparable to that of sample B. It was found that the 2-step CVSM with HFTS (1st step) and TFTS (2nd step) molecules increase not only the initial value of CA but the resistance to H_2O, compared to those for the samples treated with the respective reagents.

Table 1 lists C_{1s}-XPS signal intensities for samples A and C. Si_{2p}-signals mainly result from the SPG substrate. In comparison with the values of CF_3/CF_2, CF_3/Si and CF_2/Si for sample A, all the ratios of sample C significantly increase. Evidently, the chemical adsorption of TFTS occurs in the 2nd step, however, the information on its site is not obtained from this.

Figure 2 shows visible reflection spectra of various samples. The reflectance of the SSG substrate (sample R_0) monotonously decreases from 8.85% (360 nm) to 7.9% (780 nm). On the other hand, that of the SPG substrate (sample R) drastically decreases in the whole visible range, having a minimum of 0.93% at 500 nm. The reflectance at 500 nm of sample R rises to 2.91% by the HFTS treatment and further up to 3.34% by the subsequent TFTS treatment. Also, it is noteworthy that the minimum reflectance wavelength (λ_{min}) is red-shifted with the surface treatment, i.e., sample R, 500 nm; sample A, 520 nm; sample C, 560 nm. The refractive indices of the skeleton layers (n_c) in these samples can be calculated from their thicknesses (t=90 nm) and λ_{min} to be 1.33 (sample R), 1.35 (sample A) and 1.46 (sample C) ($n_c=\lambda_{min}/4t$). The porosity of sample R (p) is also obtained to be 41.3% using the n_c value and the refractive index of glass (n_g=1.52).[11] Since, in the surface treated sample, the skeleton layer is regarded as a composite consisting of glass, air and FAS, it may be assumed that the value of n_c is expressed as a linear function of the volume fractions of the three phases.

$$n_c = (1 - p)n_g + p\{(1 - x)n_a + xn_f)\}, \qquad (1)$$

where n_a, n_f and x are the refractive indices of air (~1) and the FAS layer (~1.347), and the volume fraction of FAS in the pores. Substitution of the n_c values for the samples subjected to CVSM into Eq.(1) yields the values of x of ca. 0.3 for sample A and ca. 1 for sample C.

It was quantitatively revealed that most of the internal surface incompletely covered with HFTS in the 1st step is covered with TFTS in the 2nd step. The improvement of the resistance to H_2O in sample C is further explained in terms of the result of this analysis.

The author expresses their sincere gratitude to Dr. S.Tsuchihashi, H.Nagayama, K.Mitani, H.Yamamoto, K.Kinugawa (Nippon Sheet Glass Co.) and K.Shimoda (Nippon Sheet Glass Techno-Research Co.) for helpful discussions and experimental supports.

References

1) G.G.Roberts, K.P.Pande and W.A.Barlow, *Proc. IEE Part 1*, **2**, 169 (1978).
2) V.Novotny, J.D.Swalen and J.P.Rabe, *Langmuir*, **5**, 485 (1989).
3) H.Tada and H.Nagayama, *J. Electrochem. Soc.* **140**, L140 (1993).
4) H.Tada and H.Nagayama, *Langmuir*, in press.
5) H.Tada and H.Nagayama, *J. Phys. Chem.*, in contribution.
6) C.P.Tripp and M.L.Hair, *Langmuir*, **8**, 1120 (1992).
7) H.Tada and H.Nagayama, *Langmuir*, in contribution.
8) H.Nagayama, H.Honda and H.Kawahara, *J. Electrochem. Soc.*, **135**, 2013 (1988).
9) S.M.Thomsem, *RCA Rev.*, **X**, 143 (1951).
10) B.E.Yoldas, *Appl. Opt.*, **19**, 1425 (1980).
11) Y.T.Tao, *J. Am. Chem. Soc.*, **115**, 4350 (1993).

(Received April 6, 1994)