STUDY OF WATERPROOF THIN-LAYERS FOR THE MAGNETIC ALLOY CORE BY NEUTRON REFLECTIVITY

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Abstract

The mechanism of the waterproof property of SiO_2(PHPS) and SiO_2(Me-PHPS) (CH_3 modified PHPS) thin layers was revealed by FT-IR and neutron reflectivity analysis. FT-IR results revealed that the SiO_2(Me-PHPS) thin layer undergoes considerable C-H and N-H bond absorption. This result suggests that the synthesized thin SiO_2(Me-PHPS) layer contains large amount of methyl group as well as ammonium compound. The general SiO_2 network structure would be presented in the SiO_2(PHPS) and SiO_2(Me-PHPS) thin layers because both thin layers have clear Si-O absorption peaks. NR analysis revealed that the thickness of the SiO_2(PHPS) and SiO_2(Me-PHPS) thin layers was 38 nm and 52 nm, respectively. In addition, the penetration depth of water into the SiO_2(PHPS) and SiO_2(Me-PHPS) thin layers were estimated to be 38 nm and 17nm, respectively. These results suggest that the SiO_2(Me-PHPS) thin layer is more hydrophobic than the SiO_2(PHPS) thin layer, a consequence of the modification of the SiO_2 thin layer by introduction of the hydrophobic methyl group.

INTRODUCTION

Silicon based ceramics such as perhydropolysilazane (PHPS) derived ceramics have been studied as coating materials to protect certain metallic components [1]. PHPS is a useful material for the protection of metallic materials in corrosive environments. This is due to the fact that PHPS can be easily used to synthesize high-quality SiO_2 layers on metallic materials through hydrolysis or oxidation of PHPS [1]. We have used the PHPS/xylene system to synthesize a SiO_2-waterproof layer, denoted as SiO_2(PHPS), for use in the magnetic alloy core of the accelerator ring in the Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan [2]. The structure of the SiO_2(PHPS) thin layer was studied by neutron reflectivity (NR), Fourier-transform infrared spectroscopy (FT-IR), and spectroscopic ellipsometry (SE) analysis [4, 5]. As a result, detailed SiO_2(PHPS) thin layer structures and their cracking mechanism were elucidated. However, the structural change of the SiO_2(PHPS) thin layer dipped in water have not yet been investigated in detail.

To obtain a thorough understanding of their waterproof properties, the structural change of the SiO_2(PHPS) thin layer dipped in water was studied using FT-IR and NR analysis methods. In addition, an improved SiO_2(PHPS) thin layer, which was modified by the hydrophobic methyl group (denoted as SiO_2(Me-PHPS)), was prepared and its thin layer structure was also studied. Since the SiO_2(Me-PHPS) thin layer contains about 25 % of hydrophobic methyl group, it is predicted that the hydrophobicity of the modified thin layer is higher than that of the normal one. In this paper, we report the results of the FT-IR and NR analysis. The waterproof behaviour and mechanism of these thin layers are also discussed.

EXPERIMENTAL

Sample Preparation

The Si wafers (diameter = 5.08 cm, thickness = 0.3 mm) were supplied by SEMITEC Co., Ltd., Tokyo, Japan. The PHPS polymer was supplied by AZ Electronic Materials Co., Ltd., Tokyo, Japan. Methyltrichlorosilane, and dimethyldichlorosilane were supplied by Shin-Etsu Chemical Co., Ltd., Tokyo, Japan. The Me-PHPS polymer was synthesized using the following procedures: methyltrichlorosilane and dimethyldichlorosilane were mixed in the ratio of 1:1 in toluene with bubbling of NH_3 (200 ml/min)/N_2(50 ml/min) mixed gas for 7.5 h at -60°C. The obtained toluene solution was concentrated at 200°C and the Me-PHPS polymer was obtained as high viscosity liquid. The thin SiO_2(PHPS) layer was prepared by spin coating 3.3 % of PHPS polymer/xylene solution onto Si substrates at a speed of 4500 – 6000 rpm using a spin-coater (MS-A150, Mikasa Co., Ltd., Tokyo, Japan). The thin SiO_2(Me-PHPS) layer was prepared by spin coating a mixed solution, 3.2% of PHPS and 1.1 % of Me-PHPS polymers in xylene, onto Si substrates at a speed of 4500 – 6000 rpm using a spin-coater. These samples were then cured at 60 °C for 1 h and allowed to stand for 48 h at room temperature. These samples were stored in pure water for 7 days, and dried in air for 3 h before the NR experiment to remove the non-adsorbed water molecules.

FT-IR Measurement

The samples for the FT-IR spectroscopy analysis were prepared by removing a section from each samples prepared for the NR measurements.

The FT-IR spectra were measured with an FT/IR-4100ST (Nihon Bunko Co. Ltd., Tokyo, Japan) equipped with an ATR unit (PRO670H-S, Nihon Bunko Co. Ltd.,

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Tokyo, Japan). The wavenumber range of the FT-IR spectra was 700 – 4000 cm^{-1} and the resolution was 4 cm^{-1}. Each spectrum was determined from the average result of 64 scans. All the measurements were performed at room temperature.

Neutron Reflectivity Measurements

The NR measurements were performed using a BL17 SHARAKU polarized neutron reflectometer installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC [3, 6]. The incident beam power of the proton accelerator was 200 kW for all the measurements. Pulsed neutron beams were generated in mercury target at 25 Hz, and the NR data were measured using the time-of-flight (TOF) technique [3, 6]. The wavelength (λ) range of the incident neutron beam was tuned to approximately $\lambda =$ 2.2 – 8.8 Å by a disk chopper. The incident angle was varied from 0.3° to 0.9°, and the exposure times for measurements at incident angles of 0.3° and 0.9° were 1 and 3 h, respectively. The covered Q_z range was $Q_z =$ 0.008 – 0.09 Å^{-1}, where $Q_z = (4\pi/\lambda)\sin\theta$ (θ represents the incident angle). A 25 mm beam footprint was maintained on the sample surface by using six different kinds of incident slits [3, 6]. All the measurements were performed at room temperature. The data reduction, normalization, and subtraction were performed using a program installed in BL17 SHARAKU. The Motofit program [7] was used to fit the NR profiles with a least-squares approach to minimize the deviation of the fit. The thickness, scattering length density (SLD, ρ), and Gaussian roughness were also evaluated by using the Motofit program.

RESULTS AND DISCUSSION

FT-IR Analysis of the Thin SiO$_2$-waterproof Layer

The FT-IR samples were dried in air and ambient conditions about a month before the measurement of the data.

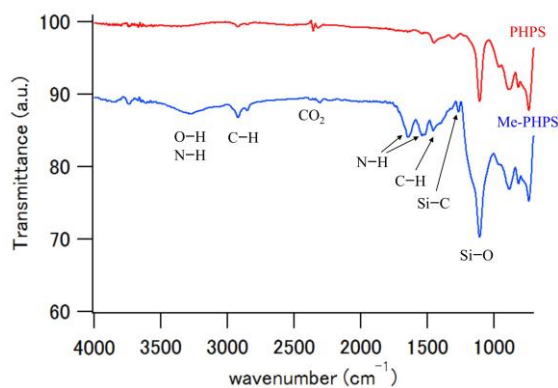Figure 1: FT-IR spectra (mean) of the thin SiO$_2$ layer samples.

Figure 1 shows the FT-IR spectra of the SiO$_2$(PHPS) and SiO$_2$(Me-PHPS) thin layer samples in the wavenumber range of 700−4000 cm^{-1}. In both samples, the strongest absorption peak of Si-O (1100 cm^{-1}) and O-H (3300 cm^{-1}) were observed. This indicated that the

general SiO$_2$ network structure would be presented in these thin layers. In addition, the absorption of N-H (3400 cm^{-1}) and Si-H (2200 cm^{-1}), which are attributed to the unreacted PHPS [8], were not observed in the spectra of the SiO$_2$(PHPS) thin layer sample. This result indicated that the starting PHPS material completely reacted during the curing process. In contrast, the absorption of N-H (1520, 1640, 3400 cm^{-1}), Si-C (1260 cm^{-1}), and C-H (1450, 2850, 2910 cm^{-1}) were observed in the spectra of the SiO$_2$(Me-PHPS) thin layer sample. However, the absorption of Si-H was not observed. These results indicated that the Si-H parts of PHPS were completely reacted in the curing reaction, while the unreacted Si-NH parts or ammonium salt were retained in the layer. Therefore, although the SiO$_2$(PHPS) and SiO$_2$(Me-PHPS) thin layer samples form a general SiO$_2$ like network, the purity of the SiO$_2$(Me-PHPS) thin layer sample is not as high as that of the SiO$_2$(PHPS) thin layer sample.

Neutron Reflectivity Analysis

To investigate the effect of water penetration into the thin SiO$_2$ layer samples, the structure of the thin layer samples, which were stored in pure water, were studied by the NR analysis method in detail.

The air-solid reflectivity measurements for the thin SiO$_2$(PHPS) and SiO$_2$(Me-PHPS) layer samples are shown in Figure 2. The NR profiles of the samples were analyzed using the Motofit reflectometry package, and the calculated theoretical reflectivity profiles are also shown in Figure 2. The NR data of the dry thin SiO$_2$(PHPS) layer sample (gray line and circles) is also shown in Figure 2 [3]. The circles represent the observed NR profiles, while the solid lines represent the calculated NR profiles determined from the structural models. The NR profiles of the wet thin SiO$_2$(PHPS) layer sample were drastically different from those of the dry sample. It implied that water molecules were penetrated deeper into the SiO$_2$ layer. In addition, a naturally oxidized thin SiO$_2$ layer formed between the SiO$_2$(PHPS) layer and the Si substrate, a four-layer model, SiO$_2$(PHPS) water rich/SiO$_2$(PHPS) medium/ SiO$_2$(PHPS) water poor/SiO$_2$(oxidized)/Si, was applied to fit the obtained NR profiles. The theoretical reflectivity profiles reproduced the experimental NR profiles in the all Q_z-range. Table 2 shows the structural parameters obtained from this analysis. The thickness and SLD values of the thin SiO$_2$(PHPS) layer sample were estimated to be 73.9 Å and 0.18 ($\times 10^6$ Å^{-2}) for H$_2$O rich layer, 261 Å and 0.31 ($\times 10^6$ Å^{-2}) for medium layer, 41.5 Å and 1.12 ($\times 10^{-6}$ Å^{-2}) for H$_2$O poor layer, and 21.9 Å and 3.28 ($\times 10^{-6}$ Å^{-2}) for SiO$_2$(oxidized) layer, respectively. The SLD value of the thin SiO$_2$(PHPS) layer and H$_2$O are ~2.0 ($\times 10^{-6}$ Å^{-2}) [3, 9] and -0.56 [10], respectively. Because lower SLD values indicate penetration of H$_2$O molecules into the layers, these obtained low SLD values (0.18, 0.31, and 1.12) clearly indicate that a large amount of water is present in each layer. Depth profile of the thin SiO$_2$(PHPS) layer sample drawn in Figure 2 also indicates that the water
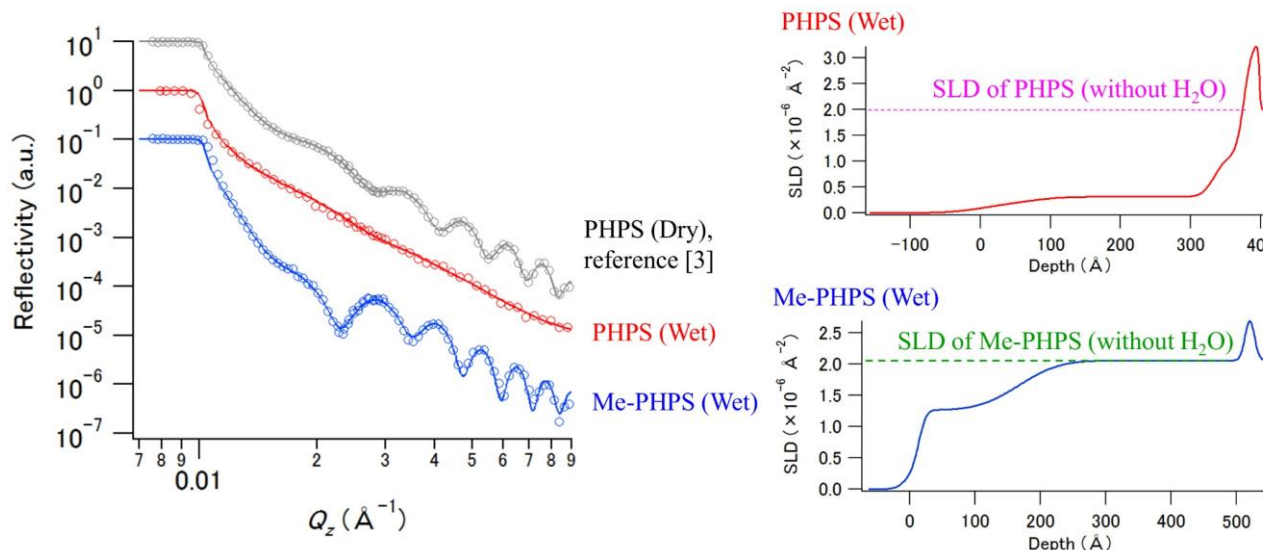
Figure 2: (Left) NR profiles of the thin SiO_2 layer samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles. Gray line and circles are the NR data of dry thin SiO_2(PHPS) layer sample [3]. (Right) Depth profiles of the thin SiO_2 layer samples calculated by obtained structural parameters.

penetration amount increases with decreasing depth from the surface. On the other hand, the thickness and SLD values of the thin SiO_2(Me-PHPS) layer sample were estimated to be 14.3 Å and 0.49 ($\times 10^{-6}$ Å^{-2}) for H_2O rich layer, 153 Å and 1.26 ($\times 10^{6}$ Å^{-2}) for medium layer, 349 Å and 2.06 ($\times 10^{-6}$ Å^{-2}) for H_2O poor layer, and 9.78 Å and 3.22 ($\times 10^{-6}$ Å^{-2}) for SiO_2(oxidized) layer, respectively.

Table 1: Best-fit Parameters for the Reflectivity Model Data Shown in Figure 2

		PHPS	Me-PHPS
SiO_2(PHPS) (H$_2$O rich layer)	t (Å)	73.9	14.3
	ρ ($\times 10^{-6}$ Å^{-2})	0.18	0.49
	σ (Å)	38.1	14.5
SiO_2(PHPS) (Medium layer)	t (Å)	261	153
	ρ ($\times 10^{-6}$ Å^{-2})	0.31	1.26
	σ (Å)	37.0	8.63
SiO_2(PHPS) (H$_2$O poor layer)	t (Å)	41.5	349
	ρ ($\times 10^{-6}$ Å^{-2})	1.12	2.06
	σ (Å)	14.3	48.9
SiO_2(oxidized)	t (Å)	21.9	9.78
	ρ ($\times 10^{-6}$ Å^{-2})	3.28	3.22
	σ (Å)	9.01	6.83
Si substrate	ρ ($\times 10^{-6}$ Å^{-2})	2.01	2.07
	σ (Å)	1.70	6.28

t: thickness, ρ: SLD, σ: roughness of the surface or interface.

The obtained low SLD value, 0.49 (H_2O rich layer) and 1.26 (medium layer), clearly indicate that a large amount of water is present in the layers. Depth profile of the thin SiO_2(Me-PHPS) layer sample drawn in Figure 2 also indicates that the water penetration amount increases with decreasing the depth from the surface. However, in contrast to the thin SiO_2(PHPS) layer sample, water penetration into the thin SiO_2(Me-PHPS) layer sample was limited to approximately 20 nm from the surface. Since the water penetration condition is same, the difference of water penetration behaviour of the thin SiO_2 layer samples simply reflects their waterproof properties. Therefore, it can be concluded that the waterproof property of the thin SiO_2 layer would be improved by the modification of PHPS molecule by addition of the hydrophobic methyl group.

SUMMARY

In this study, the structure of the SiO_2-waterproof layer, SiO_2(PHPS) and SiO_2(Me-PHPS), was investigated in detail by the FT-IR and NR analysis methods. The analyses revealed that the general SiO_2 network structure is present in the thin SiO_2(PHPS) and SiO_2(Me-PHPS) thin layers. Additionally, the penetration depth of water into the SiO_2(PHPS) and SiO_2(Me-PHPS) thin layers was estimated to be 38 nm and 17 nm, respectively. Under service conditions, the magnetic alloy core is covered with 1 μm of SiO_2(PHPS) waterproofing layer. This indicates that water penetration can be sufficiently prevented in the service condition. It therefore can be suggested that the improved PHPS, Me-PHPS, has a potential for utilization as an effective and thinner waterproof SiO_2 coating material.

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