STUDY OF A CORROSION RESISTANT COATING LAYER FOR METAL MAGNETIC CORES USING NEUTRON REFLECTOMETORY

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Abstract

The structure of an SiO_2 layer (SiO_2(PHPS)) synthesized using perhydropolysilazane (PHPS) on an Si substrates was studied by Fourier transform infrared spectroscopy (FT-IR), spectroscopic ellipsometry (SE), and neutron reflectivity (NR) analysis. The FT-IR results confirmed that the molecular structure of the SiO_2(PHPS) layer can be represented as SiO_2. The thickness of the thin SiO_2(PHPS) layer were estimated using both SE and NR analysis methods. The SE and NR analyses revealed that the thin SiO_2(PHPS) layer could be uniformly coated in all samples. In addition, the NR results suggested that the density of the SiO_2(PHPS) layer was altered by varying the thickness of the SiO_2(PHPS) layer. These results indicate that the variation in the density of SiO_2(PHPS) layer depends on the efficiency of cross-linking reaction between the silazane oligomers in the coated PHPS layer.

INTRODUCTION

Silicon based ceramics such as Perhydropolysilazane (PHPS) derived ceramic have been studied as coating materials to protect certain metallic components [1]. PHPS is useful material to be applied for the protection of metallic materials in corrosive environments because PHPS can be easily used to synthesize high-quality SiO_2 layers on metallic materials through the hydrolysis or oxidation of PHPS [1]. We have used the PHPS/*p*-xylene system to synthesize an SiO_2-waterproof layer, denoted as SiO_2(PHPS), for the magnetic alloy core of the accelerator ring in the Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan [2]. Although the waterproofing properties of the SiO_2(PHPS) layer increases with increasing the thickness of the SiO_2 layer (Figure 1), the level of stress in the SiO_2(PHPS) layer also increases, and this can lead to cracking. Therefore, it is important to investigate the structure and synthesis mechanism of the synthesized SiO_2 layer in detail for improving the properties of the SiO_2 layer.

A variety of techniques have been used to study the structure of thin SiO_2 layer, including Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), spectroscopic ellipsometry (SE), and reflectometry [3-4]. In particular, SE and neutron reflectometry (NR) are ideally suited to study thin layer structures on surfaces [5]. In this study, we prepared three kinds of the thin SiO_2(PHPS) layer samples with different thickness and

used them as the model SiO_2(PHPS) layer sample. Using the FT-IR, SE, and NR techniques, we analysed the structure of the samples to investigate the thickness, density, and roughness of the SiO_2(PHPS) layer in detail. And then, we discussed the synthesis mechanism of the synthesized SiO_2(PHPS) layer in detail.
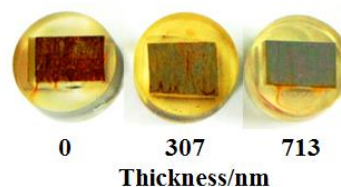

Figure 1: Relationship between SiO_2 layer thickness and corrosion rates under the salt-spray test.

EXPERIMENTAL

Sample Preparation

The Si wafers (diameter = 5.08 cm, thickness = 0.3 mm) and the PHPS polymer (AQUAMICA) were supplied by SEMITEC Co, Ltd. (Tokyo, Japan), and AZ Electronic Materials Co, Ltd. (Tokyo, Japan), respectively, and these compounds were used without further purification. The SiO_2(PHPS) layers were prepared by spin coating 5 % of PHPS/*p*-xylene solution onto Si substrates at a speed of 4500 – 6000 rpm using a spin-coater (MS-A150, Mikasa co. Ltd., Tokyo, Japan). Then, the samples were cured at 60 °C for 1 h and allowed to stand for 48 h at room temperature. The SiO_2(PHPS) samples with different thickness (in this paper, these samples are denoted as sample-A, sample-B, and sample-C) were prepared for the NR measurements. These samples were stored in a box under low humidity and dust-free conditions at room temperature.

FT-IR Measurements

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., Tokyo, Japan). The wavenumber range of the FT-IR spectra was 600 – 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.

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Spectroscopic Ellipsometry Measurements

We measured the SE data by using a variable angle spectroscopic ellipsometer (M-2000U, J. A. Woollam Co., Inc.) system installed at the Industrial Technology Center of Tochigi prefecture. The SE spectra were obtained at three different positions for each sample. The incident angles were 70, 75, and 80°, and the spectral wavelength range was from 245 to 1000 nm. The ellipsometric data were fitted and modelled using the WVASE software package (J.A. Woollam Co., Inc.) to analyse the thickness of the thin SiO_2 layer on the Si substrate. All measurements were performed at room temperature.

Neutron Reflectivity Measurements

The NR measurements were performed on a BL17 SHARAKU reflectometer installed at the Materials and Life Science Experimental Facility (MLF) in J-PARC [6]. The incident beam power of the proton accelerator was 400 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 [6]. The wavelength (λ) range of the incident neutron beam was tuned to approximately $\lambda = 2.2 - 8.4$ 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 0.5 and 1 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 20 mm beam footprint was maintained on the sample surface by using six kinds of incident slits [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, and the thickness, scattering length density (SLD, ρ), and Gaussian roughness were evaluated by using the program.

RESULTS AND DISCUSSION

FT-IR Analysis of the Thin SiO$_2$(PHPS) Layer

Figure 2 shows the FT-IR spectra of the thin SiO_2(PHPS) layer samples in the wavenumber range of $600-4000$ cm^{-1}. 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. This result indicated that the starting PHPS material completely reacted in the curing process. The absorption around 3300 cm^{-1} can be attributed to the O-H stretching of the Si-OH group, and the absorption peak between $1000 - 1100$ cm^{-1} and the shoulder between $1100 - 1200$ cm^{-1} are mainly due to the absorption of the Si-O asymmetric stretching transverse optical (TO) and longitudinal optical (LO) modes, respectively [9]. In addition, the absorption between $1100 - 1200$ cm^{-1} can be assigned to the stretching vibration of the Si-O bond in the SiO_4 tetrahedral terminal group [10]. These results suggest that the synthesized SiO_2(PHPS) material primarily consists of

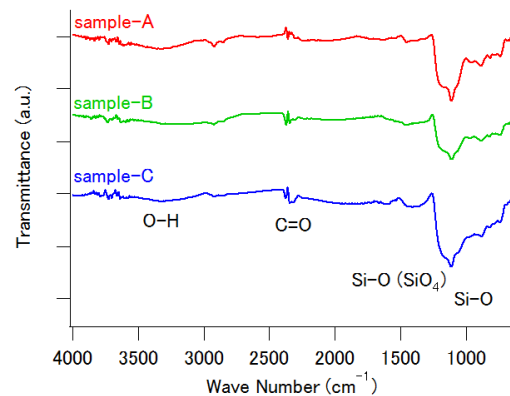SiO_2 and similar compounds as observed from the surface measurement by the FT-IR method.

Figure 2: FT-IR spectra (mean) of the thin SiO_2 layer samples.

Spectroscopic Ellipsometry Analysis

To estimate the thickness of the thin SiO_2(PHPS) layer, we measured and analysed the SE spectra.

Table 1 shows the estimated thickness of each sample. The SE spectra were measured at three different positions for each thin SiO_2(PHPS) layer sample. The thickness of the thin SiO_2(PHPS) layer was estimated to be 682.2, 681.3, 681.2 Å for sample-A, 784.8, 784.5, 783.2 Å for sample-B, and 1493, 1507, 1485 Å for sample-C, respectively. Although the measurement position was changed, the estimated thickness values at three different positions were same. This result revealed that the thin SiO_2(PHPS) layer could be uniformly coated in all samples. Therefore, it was concluded that the equal SiO_2-thickness layer could be synthesized using the PHPS/*p*-xylene coating system.

For the reasons mentioned above, the NR data were analysed by assuming that the equal SiO_2-thickness layer was formed on the Si substrate, and the average thickness values were used as the initial parameter for the fitting analysis of the NR profiles.

Table 1: The Thickness of the Thin SiO_2(PHPS) Layer Estimated by the SE Analysis

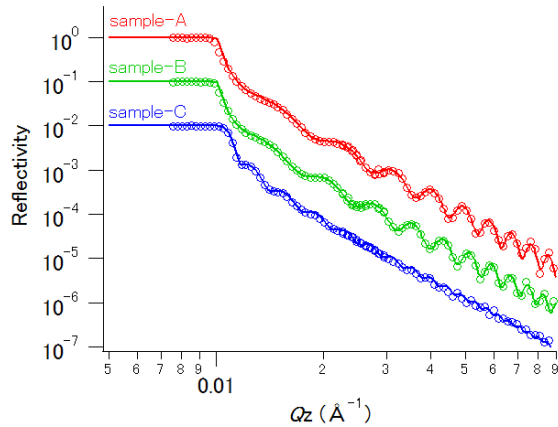|		Thicknss (Å)	Average Thickness (Å)
Sample-A	Position-1	682.2	681.6
	Position-2	681.3	
	Position-3	681.2	
Sample-B	Position-1	784.8	784.2
	Position-2	784.5	
	Position-3	783.2	
Sample-C	Position-1	1493	1495
	Position-2	1507	
	Position-3	1485	

Figure 3: Neutron reflectivity profiles of SiO_2(PHPS) samples. The circles represent the experimental data, and the solid lines represent the best-fit calculated NR profiles.

Neutron Reflectivity Analysis

To investigate the synthesis mechanism of the thin SiO_2(PHPS) layer, the structure of the thin SiO_2(PHPS) layer samples was analysed by the NR analysis method in detail.

The air-solid reflectivity measurements for the SiO_2(PHPS)/Si samples are shown in Figure 3. The NR profiles of the samples were analyzed using the Motofit reflectometry package, and the calculated theoretical reflectivity profiles are shown in Figure 3. The symbols represent the observed NR profiles, while the solid lines represent the calculated NR profiles determined from the structural models. Because actually a naturally oxidized thin SiO_2 layer formed between the SiO_2(PHPS) layer and the Si substrate, a two-layer model, SiO_2(PHPS)/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 SiO_2(PHPS) layer were estimated to be 663 Å and 2.01 ($\times 10^6$ Å^{-2}) for sample-A, 765 Å and 2.01 ($\times 10^6$ Å^{-2}) for sample-B, and 1349 Å and 2.28 ($\times 10^6$ Å^{-2}) for sample-C, respectively. The estimated thickness values were agreed with the results of the SE analysis. The estimated ρ values indicate that the density of the synthesized SiO_2(PHPS) is lower than that of natural SiO_2, since the ρ value of natural SiO_2 is 3.47 ($\times 10^6$ Å^{-2}). The ρ value is defined as $\rho = \rho_{SiO2} \cdot N_A \cdot \Sigma_i b_i / M$ [11], where ρ_{SiO2}, N_A, b_i, and M are the density of SiO_2, Avogadro's number, the coherent scattering length of the element, and molecular weight, respectively. Thus, assuming that the dominant component of the SiO_2(PHPS) layer is SiO_2, the ρ_{SiO2} value of each SiO_2(PHPS) layer was estimated to be 1.17 (sample-A), and 1.28 (sample-B), and 1.45 (sample-C), respectively, as shown in Table 2. The density of the SiO_2(PHPS) layer was altered by varying the thickness of the layer, whereas the condition of the SiO_2 coating did not change. Since the existence of a non-cross-linked precursor will result in a lower ceramic yield [12], the change in the density depending on the thickness would

be attributed to the efficiency of the cross-linking reaction between the silazane oligomers. Therefore, the NR measurements revealed that a uniform SiO_2 layer can be synthesized on a Si substrate by using the PHPS/*p*-xylene system, and the density of the SiO_2(PHPS) layer could increase by increasing the thickness of the layer. It could suggest that if the cross-linking reaction rate is too high (that is, the thickness of the SiO_2(PHPS) layer is too thick), a densified SiO_2(PHPS) layer is formed and it leads to cracking.

Table 2: Best-fit Parameters for the Reflectivity Model Data Shown in Figure 3

		Sample -A	Sample -B	Sample -C
SiO_2(PHPS)	t (Å)	663	765	1349
	ρ ($\times 10^6$ Å^{-2})	2.01	2.02	2.28
	σ (Å)	8.28	6.38	6.56
	ρ_{SiO2} (g/cm^3)	1.27	1.28	1.45
SiO_2(oxidized)	t (Å)	39.2	36.8	22.4
	ρ ($\times 10^6$ Å^{-2})	2.39	2.45	2.41
	σ (Å)	14.1	21.6	2.86
Si substrate	ρ ($\times 10^6$ Å^{-2})	2.07	2.07	2.07
	σ (Å)	1.43	1.09	25.0

t: thickness, ρ: SLD, σ: roughness of the surface or interface, ρ_{SiO2}: density of SiO_2(PHPS) layer calculated from the ρ value.

SUMMARY

In this study, we investigated the structure of the SiO_2-waterproof layer (SiO_2(PHPS)) in detail by using the FT-IR, SE, and NR methods. These analyses revealed that the unreacted PHPS material did not remain in the SiO_2(PHPS) layer, and a uniform SiO_2(PHPS) layer could be formed in all SiO_2(PHPS) layer samples. In addition, the density of the SiO_2(PHPS) layer increases by increasing the thickness of the layer. This suggests that the efficiency of the curing reaction in the PHPS/*p*-xylene system would increase with the thickness of the SiO_2(PHPS) layer.

ACKNOWLEDGMENT

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