Characterization of Surface Structure of Silica Thin Films by Auger Parameter

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Si Auger parameter of silica films obtained under different hydrolysis conditions was calculated in order to determine SiOH concentration. It was found that the Auger parameter increased with increasing silicate molecular. Silica films with a large Auger parameter were observed by transmission electron microscope (TEM) to consists of a large diameter particle than films with a small Auger parameter. Increased silica particle diameter demonstrates that the condensation reaction proceeds to an extent that the concentration of OH groups has decreased. It has been concluded that silica film surfaces with a large Auger parameter had few OH groups per Si atom.

An oligomer silicate of tetraalkoxysilane form SiOH groups by a hydrolysis reaction, and the SiOH groups further form Si–O–Si bonding by a condensation reaction.[1] Coatings of silica films have been prepared by using above mentioned reactions.[2] This silica film has improved mechanical strength, and has been used for chemical protection, etc.[3] Recently, the hydrophilic function of the film surface has attracted attention,[4] however, it's mechanism is not yet clear. An elucidation of the mechanism that causes a hydrophilic function is very interesting from the viewpoint of the surface structure design of the coating film. Generally, surface analysis of a silica film is performed by secondary ion mass spectroscopy analysis (SIMS),[5] however, quantitative analysis is difficult. Surface analysis of silicon materials is also performed by X-ray photoelectron spectroscopy (XPS), and the determining method of the oxidation numbers of silicon[6] or SiOR group[7] is reported. However, SiOH group or Si–O–Si bonding has been not determined quantitatively. In the present study, we report the quantification of the surface structure of a silica film using XPS.

The silica films were obtained by coating the hydrolysis products of silicates on aluminum foil. Hydrolysis products of silicates that have different SiOH group concentration were prepared by hydrolysis in a heterogeneous system or a homogeneous system and consisted of only SiOH groups and Si–O–Si bonding. Since solubility of silicates in water is low, water was used as a solvent for the heterogeneous system, and a mixture of water and alcohol was used as a solvent for the homogeneous system. Three methylsilicates having different molecular weight were used. The absence of a methoxy group in the hydrolysis product was confirmed by XPS and FT-IR measurements. The typical conditions of hydrolysis are shown in Table 1. The procedure is as follows: a 0.1 mL of solution of hydrolyzed silicate was uniformly coated on aluminum foil and dried at room temperature. The obtained film was transparent and colorless with a thickness of about 100 nm.

XPS spectra of obtained silica films were measured and the results are shown in Table 1. The statistical error of binding or kinetic energy was ± 0.1 eV. Binding energy of the Si 2p spectrum became small as molecular weight increased, and kinetic energy of the Si KLL spectrum became large. In addition, the Auger parameter, which is expressed as the sum of kinetic energy of Si KLL spectrum and the binding energy of Si 2p spectrum[8,9], became large as the molecular weight increased (Entry 1–3). Since there are two kind of substituent group on Si atom, OH group and SiO group, these results have suggested that the component ratio of OH group and SiO group, which indicates the number of OH group on Si atom, changed with the molecular weight of silicate. As silicate with high molecular weight has a greater number of methoxy groups and OH groups as a functional group for condensation reaction than the silicate with the low molecular weight, it is assumed that the intermolecular crosslinking tends to occur in the condensation reaction. Consequently, the number of OH groups per Si atom is considered to decrease. Therefore, it is presumed that as the number of OH groups per Si atom decreases, the Auger parameter increases. The relation between the Auger parameter and the binding energy of Si 2p spectrum is shown in Figure 1(a). The relation between the Auger parameter and the kinetic energy of Si KLL spectrum is shown in Figure 1(b). Good correlation was obtained in each case. This result indicates that the difference in the surface structure of a silica film can be characterized by using any energy value or parameter. As the Auger parameter does not include the error of energy correction by C 1*s* reference, it is the most suitable value used for characterization. Therefore, the following characterization was carried out using the Auger parameter.

Next, the influence of hydrolysis conditions was investigated. The Auger parameter of a silica film (Entry 5) derived from the homogeneous system was larger than that of a silica film (Entry 3) derived from the heterogeneous system. This tendency was also observed by comparison between Entry 1 and Entry 4.

Table 1. The influence of molecular weight and hydrolysis conditions on XPS spectra and Auger parameter

Entry	M_w [a]	Hydrolysis conditions				Results of XPS		
		C[b]	Solv.[c]	Temp.[d]	T[e]	Si 2p	Si KLL	P[f]
		%		℃	h	eV	eV	eV
1[g]	744	1	W[h]	100	1	103.53	1605.74	1709.27
2[g]	1050	1	W	100	1	103.44	1606.04	1709.48
3[g]	2300	1	W	100	1	103.32	1606.49	1709.81
4	744	1.3	W/E[i]	20	8	103.43	1605.99	1709.42
5	2300	1.3	W/E	20	8	103.21	1606.78	1709.99

[a]Weight-average molecular weight of silicate. [b]Silicate concentration. [c]Solvent. [d]Reaction temperature. [e]Reaction time. [f]Auger parameter. [g]Using after filtration of paper. [h]Water. [i]Water/ethanol=58.3/41.7(weight %) mixture.

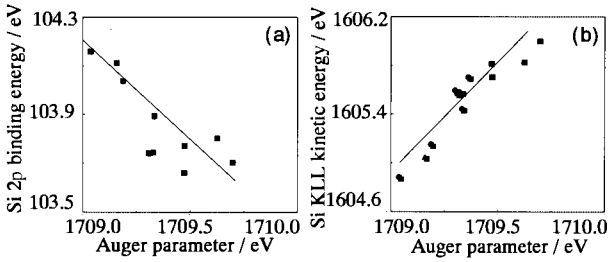

Figure 1. Relationship between Auger parameter and XPS spectrum.

These results have suggested that the number of OH groups per Si atom changed with the conditions of hydrolysis. It was assumed that the condensation reaction was difficult to proceed by hydrolysis in the homogeneous system, so the molecular weight of a hydrolysis product was small compared with that of heterogeneous system. However, since there is low steric hindrance of the hydrolysis product, a condensation reaction during drying tends to progress and it is thought that the number of OH group per Si atom decreases as a result.

It was found that the Auger parameter of a silica film is dependent on molecular weight of silicate and condition of hydrolysis. These estimates were confirmed by TEM observation of silica films. The collodion film was attached to a copper mesh and sputtered with the gold. A 0.01 mL solution of hydrolyzed silicate was dropped on the film and solvent was removed using filter paper. The treated specimen was observed by TEM and typical images of silica films are shown in Figure 2. It was observed that the silica films obtained from the heterogeneous system is comprised of aggregate particles (Figure 2(a)). A continuous film was observed in the silica film obtained from the homogeneous system (Figure 2(c)). This indicates that the condensation reaction is advancing further in a homogeneous system than in a heterogeneous system. The silica film derived from a hetrogeneous hydrolysis system with a low molecular weight silicate was observed to contain an aggregated matrix comprised of particles with a diameter of about 5 nm (Figure 2(a)). However, with a high molecular weight silicate, an agglomerated matrix comprised of particles with a diameter of about 20 nm was observed in the silica film (Figure 2(b)). Generally, it is known that particle size increases with the progress of a condensation reaction in the sol–gel reaction of tetraalkoxysilane,[10] or conversely, the difference in particle size expresses the degree of a condensation reaction. It is known that in the case of small diameter particles, secondary particles produced form voids during the drying step of the hydrosol system; on the contrary, in the case of large diameter particles, a minutely filled structure is produced.[11] The silica film derived from the silicate with high molecular weight has a high Si–O–Si content, which means the condensation has proceeded further.

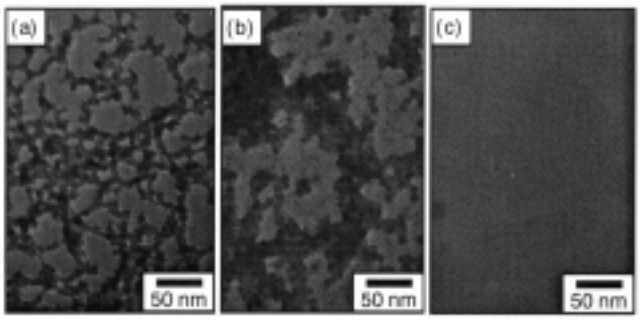

Figure 2. TEM image of silica films; (a)Entry 1, (b)Entry 3, (c)Entry 5.

The result of this TEM observation supports the abovementioned consideration. Therefore, the value of Auger parameter is well correlated with the number of OH groups per Si atom.

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