Manufacturing of Silica Glass from Silica Powder Consolidated with Tetramethoxysilane Oligomer-derived Binder (II). Role of Tetramethylammonium Hydroxide as a Catalyst for Binder Synthesis

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The role of a catalyst during the synthesis of a binder, which could harden a silica slurry, was investigated. Tetramethoxysilane oligomer was efficiently hydrolyzed and poly-condensed to the binder when tetramethylammonium hydroxide and tetraethylammonium hydroxide, which are both organic bases having bulky groups, were used as catalysts. On the other hand, nitric acid, sodium hydroxide, potassium hydroxide and ammonia were not effective catalysts for binder synthesis. The difference in the role between these catalysts was explained as follows. The bulky organic groups were assumed to have a steric hindrance interaction with methyl groups in tetramethoxysilane oligomer and this steric interaction could successfully produce the binder.

Key Words : Sol-gel Method, Silica Glass, Tetramethylammonium Hydroxide, Tetramethoxysilane

1 Introduction

Silica glass is one of the most important materials for semiconductor manufacturing, because it has a high melting point and a small amount of metallic impurities. The general method to make silica glass is to melt natural quartz. However, natural quartz contains a large amount of metallic impurities such as Al and Ti. Highly purified silica glass has been manufactured by the sol-gel method.^{1, 2)} When using this method, however, the green compact must shrink, which leads to many cracks during the drying process.³⁾ Toki *et al.*⁴⁾ used colloidal silica to prevent the shrinkage. This method was very useful in reducing the shrinkage, however, precipitation of colloidal silica took place when the sol solution stood for a long time, generating many cracks during the drying process.

Previously, the author described a new method⁵⁾ for the effective and inexpensive manufacturing of purified silica glass in which the hardening of a slurry of a purified synthetic silica powder with a binder had been applied to prevent cracking of the silica bulk during the drying process and then the bulk was successfully sintered to produce the silica glass. This method is characterized by the flexibility of the binder. The methoxysilane oligomer (MS-51) used in the binder synthesis was incompletely hydrolyzed and poly-condensed, leaving partial methoxy groups in the binder, which provided flexibility to the binder. Moreover, tetramethylammonium hydroxide (TMAH),⁶⁾ which is an organic base having a bulky group, was a good catalyst for the binder synthesis.

In this paper, the role of TMAH as the catalyst for the synthesis of binder in manufacturing the bulk by hardening a slurry of silica powder was described.

2 Experimental

2. 1 Materials

Methanol and ethanol were both distilled from the extra pure grade reagents (Kanto Chemical Co., Inc.) and stored in polyethylene bottles. Ethylene glycol, nitric acid and ammonia water (special grade reagents both from Kanto Chemical Co., Inc.) were used without further purification. The oligomer of tetramethoxysilane (MS-51; trimer as the mean polymerization degree), tetramethylammonium hydroxide (TMAH) solution and tetraethylammonium hydroxide (TEAH) solution were made by Tama Chemicals Co., Ltd. The silica powder (20 μ m mean diameter) was made by Mitsubishi Rayon Co., Ltd.

2. 2 Measurement of the slurry hardening time

In a 500 ml three-necked glass vessel with a thermometer and a condenser, 218.4 g of MS-51 and 80 g of methanol were added and stirred, and then 21.6 g of an aqueous solution including the catalyst for the binder synthesis was added. The reaction mixture was heated in an oil bath. The silica slurry was made by mixing 64.2 g of the reaction mixture with 22.0 g of ethanol and 20.0 g of ethylene glycol in a polyethylene vessel, and then stirred with 250 g of the silica powder. After 1.7 g of a slurry hardening catalyst was added to the silica slurry which was then stirred for 4 min, it was poured into a polypropylene container which was covered with a polyethylene sheet. The slurry hardening time is defined as the course of reaction time for the slurry to harden enough so that it did not flow when the container was slanted.

2. 3 Influence of acid concentration of the binder on dried bulk synthesis

In the same 500 ml three-necked glass vessel as described above, 218.4 g of MS-51 and 80 g of methanol

Table 1 Measurement of the slurry hardening time on bulk synthesis.

Run	MS-51 g	H ₂ O ^{a)} g	equivalent ^{b)}	Methanol g	Time ^{c)} h	Binder catalyst	Hardening catalyst	Hardening Time
1	218.4	21.6	2.0	80	16	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	>2 h
2	218.4	21.6	2.0	80	16	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	TMAH (1.10×10^{-1} mol dm ⁻³)	>2 h
3	218.4	21.6	2.0	80	16	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	NH ₄ OH (2.86×10^{-1} mol dm ⁻³)	<1 min
4	218.4	21.6	2.0	80	2	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	NH ₄ OH (2.86×10^{-1} mol dm ⁻³)	<1 min
5	218.4	21.6	2.0	80	<0.5	NH ₄ OH (2.86×10^{-2} mol dm ⁻³)	—	gelation
6	218.4	21.6	2.0	80	2	TMAH (1.10×10^{-2} mol dm ⁻³)	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	>2 h
7	218.4	21.6	2.0	80	2	TMAH (1.10×10^{-2} mol dm ⁻³)	TMAH (1.10×10^{-1} mol dm ⁻³)	>2 h
8	218.4	21.6	2.0	80	2	TMAH (1.10×10^{-2} mol dm ⁻³)	NH ₄ OH (2.86×10^{-1} mol dm ⁻³)	15 min

^{a)} Water content in the binder. ^{b)} Mole equivalent to the methoxy groups in MS-51. ^{c)} Refluxing time.

Table 2 Influence of the residual acid concentration of the binder on dried bulk synthesis.

Run	Acid conc. of MS-51 (mg/g) ^{a)}	Binder catalyst	Total acid conc. of binder (mg/g)	Time h	Result ^{b)}
1	0.027	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	0.110	2	Many long cracks
2	0.027	HNO ₃ (3.17×10^{-2} mol dm ⁻³)	0.110	19	Many long cracks
3	0.027	HNO ₃ (1.59×10^{-2} mol dm ⁻³)	0.064	2	Many long cracks
4	0.027	HNO ₃ (1.59×10^{-2} mol dm ⁻³)	0.064	19	Many long cracks
5	0.041	—	0.028	6	One or two short cracks
6	0.041	TMAH (5.48×10^{-3} mol dm ⁻³)	0.013	7	No crack
7	0.041	TMAH (1.10×10^{-2} mol dm ⁻³)	−0.003	2	No crack
8	0.041	TMAH (1.65×10^{-2} mol dm ⁻³)	−0.019	1	One or two short cracks
9	0.041	TMAH (1.65×10^{-2} mol dm ⁻³)	−0.019	2	Many long cracks
10	0.027	NH ₄ OH (1.43×10^{-3} mol dm ⁻³)	0.015	3	One or two short cracks
11	0.027	NH ₄ OH (2.86×10^{-3} mol dm ⁻³)	0.011	2	Many long cracks
12	0.027	NH ₄ OH (5.71×10^{-3} mol dm ⁻³)	0.002	3.5	Gelation after 3 days
13	0.027	NH ₄ OH (1.43×10^{-2} mol dm ⁻³)	−0.022	1.5	Gelation
14	0.027	NH ₄ OH (2.86×10^{-2} mol dm ⁻³)	−0.064	0.5	Gelation

^{a)} The different residual acid concentrations of MS-51 are due to the samples which have different batches of MS-51 preparation. ^{b)} Short crack: less than 10 mm depth, long crack: more than 10 mm depth.

were added and stirred, and then 21.6 g of the catalyst solution was added. The reaction mixture was heated in an oil bath. After cooling, 64.2 g of the reaction mixture was added to ethanol and ethylene glycol in a polyethylene vessel, and then stirred with 250 g of the silica powder. The slurry was mixed with 1.7 g of a NH₄OH (5.71×10^{-1} mol dm⁻³) solution and stirred for 4 min. It was then poured into a 105-mm diameter mold and covered. After 3 h, the hardened wet bulk was removed from the mold and put into a polyvinyl chloride bag. Five small holes of about 5 mm diameter each were made in it every 24 h. The bulk, which was dried this way for 1 week, was then allowed to stand in open air. The presence of cracks was then investigated.

3 Results and Discussion

The slurry, which was mixed with the binder, silica powder and solvents, was poured into the polypropylene container, and the hardening time was measured from the time when its mobility was lost. The results are shown in Table 1. When a NH₄OH (2.86×10^{-2} mol dm⁻³) solution was used as the binder catalyst (Run 5), the binder gelled in the glass vessel. When combinations of the binder catalysts and hardening catalysts were HNO₃ (3.17×10^{-2} mol dm⁻³)/HNO₃ (3.17×10^{-2} mol dm⁻³) (Run 1), HNO₃ (3.17×10^{-2} mol dm⁻³)/TMAH

(1.10×10^{-1} mol dm⁻³) (Run 2), TMAH (1.10×10^{-2} mol dm⁻³)/HNO₃ (3.17×10^{-2} mol dm⁻³) (Run 6) and TMAH (1.10×10^{-2} mol dm⁻³)/TMAH (1.10×10^{-1} mol dm⁻³) (Run 7), the hardening times were over 2 h. On the other hand, when the combination was HNO₃ (3.17×10^{-2} mol dm⁻³)/NH₄OH (2.86×10^{-1} mol dm⁻³) (Runs 3 and 4), the times were too short for handling. The most favorable one was TMAH (1.10×10^{-2} mol dm⁻³) as the binder catalyst and NH₄OH (2.86×10^{-1} mol dm⁻³) as the hardening catalyst (Run 8). The reason why TMAH showed a good result as the binder catalyst is discussed as follows.

MS-51 used here usually contains a small amount of acid (nitric acid). When MS-51 is made from its monomer and water by a poly-condensation reaction, an acid catalyst (nitric acid) is used and consequently a small amount of it remains in MS-51. In this study, when MS-51 is used as the starting material and the acid catalyst is added to the binder synthesis process, the total catalyst concentration in the binder solution is actually more acidic than what is added. When a basic catalyst is used, on the other hand, it is actually less acidic than what is added. The influence of the residual acid significantly appears for a small amount of catalyst. Therefore, the catalyst effect in synthesizing the binder was examined with the consideration of the residual acid in MS-51 (Table 2).

In Table 2, the "acid conc. in MS-51: 0.027 mg/g" shows that 0.027 mg of KOH was consumed for neutralizing the residual acid in 1 g of MS-51. The symbol "—" in the fourth column means that the binder was basic.

When nitric acid was used as the binder catalyst (Runs 1-4), the dry bulk, which had no cracks, was not able to be obtained regardless of the acid concentration. In the case of NH_4OH as the catalyst, the obtained binder immediately gelled when its concentration was high. Only at a very low concentration of $1.43 \times 10^{-3} \text{ mol dm}^{-3}$, the dry bulk had "one or two short cracks" in it. In the case of TMAH as the catalyst, the good results were obtained at concentrations of less than $1.10 \times 10^{-2} \text{ mol dm}^{-3}$ (Runs 6 and 7). This means that better results for all catalyst used here were obtained when the acidities of the binders gradually approached neutral. Among them, the best result was obtained for TMAH which was able to be used over a wider concentration range than the others.

Generally, the catalysts used in the sol-gel method are acids and bases. There is, however, a significant difference between them in the mechanism of hydrolysis and poly-condensation. The difference in the mechanism for them is explained as follows. Steric factors exert the greatest effect on the hydrolytic stability of alkoxy silanes. An alkyl and a hydroxyl groups should increase the stability of the positive and negative charged transition states, respectively (Fig. 1)¹⁾. Under acidic conditions, the hydrolysis rate decreases with each subsequent hy-

drolysis step, whereas under basic conditions, the increased electron withdrawing capabilities of OH (and OSi) compared to OR may establish a condition in which each subsequent hydrolysis step occurs more quickly as the hydrolysis and condensation proceed.

In the case of basic conditions, when compared with the two compounds in Fig. 2 (a) and (b), it shows that the Si atom having an OH (or SiO) group (Fig. 2 (a)) is easily attacked by OH^- rather than one not having it (Fig. 2 (b)) because of their charges on the Si atoms ($\delta a^+ > \delta b^+$). This means that once the Si atom is attacked by OH^- , an RO group is immediately replaced by an OH group which then poly-condensed to siloxane bonds and finally result in a particle which has a highly developed 3-dimensional structure.

In the case of acidic conditions, on the other hand, a hydrolysis reaction begins first by the addition of H^+ to the oxygen atom in the RO group (Fig. 2 (c) and (d)). This means that the Si atom once attacked by OH^- (Fig. 2 (c)) does not receive further attack as there are some other Si atoms which have more RO groups (Fig. 2 (d)). That is, all molecules uniformly undergo the reactions of hydrolysis and poly-condensation. This attack is more favorable for the Si atom which has more RO groups than the others. Therefore, siloxane chains in the binder obtained under acidic conditions produce a thin film of which the microstructure will become more regular than under basic conditions. This is the reason why a thin film or a fiber will be obtained when acidic conditions are used.

This fact shows that acidic conditions are better than basic conditions for a binder catalyst. For this reason, an acid was thought to be better for a catalyst at the beginning of this study. In the case of nitric acid, in fact, good results could not be obtained when its concentrations were high (Table 2, Runs 1-4). When the condition of the binder solution was nearly neutral, "one or two short cracks" were observed in the dried bulk (Table 2, Run 5).

The reason why better results were obtained when the condition of the binder solution was nearly neutral was

Fig. 1 Inductive effects of substituents bond to silicon, R, OR, OH or OSi.¹⁾

Fig. 2 Hydrolysis mechanism of alkoxy silane. (a), (b); basic condition and (c), (d); acidic condition.

Fig. 3 Relative gel time.¹⁾

Table 3 Influence of organic and inorganic catalysts on binder synthesis^{a)}.

Run	MS-51 g	H ₂ O g	equivalent ^{b)}	Methanol g	Time ^{c)} h	Binder catalyst	Result
1	218.4	16.2	1.5	80	7	TMAH (5.5×10^{-3} mol dm ⁻³)	No crack
2	218.4	16.2	1.5	80	7	TEAH (5.5×10^{-3} mol dm ⁻³)	No crack
3	218.4	16.2	1.5	80	7	NaOH (5.5×10^{-3} mol dm ⁻³)	Many cracks
4	218.4	16.2	1.5	80	7	KOH (5.5×10^{-3} mol dm ⁻³)	Many cracks
5	218.4	16.2	1.5	80	1	NH ₄ OH (5.5×10^{-3} mol dm ⁻³)	gelation

^{a)} Bulk was prepared with SiO₂ powder 250 g, the binder 64.2 g, ethanol 22.0 g and ethylene glycol 20.0 g, and was followed by addition of a NH₄OH (5.71×10^{-1} mol dm⁻³) solution 1.7 g. ^{b)} Mole equivalent to the methoxy groups in MS-51. ^{c)} Refluxing time.

Fig. 4 Steric interaction between TMAH and alkoxy silane in hydrolysis.

considered as follows. The relationship between the pH value and the gelation time is shown in Fig. 3.¹⁾ Under acidic conditions, the condensation reaction is dominated by Eq. (1) and Eq. (2). It takes a long time for alkoxy silane to polymerize, because Eq. (2) is a slow reaction.

Under basic conditions, the condensation reaction is dominated by Eq. (3), Eq. (4) and Eq. (5). In a high pH region, the generated polymer decomposes into a low molecule unit according to Eq. (5). Therefore, it also takes a long time for alkoxy silane to polymerize.

On the other hand, at near neutral pH, since Eq. (5) is not accelerated because of lower concentration of ⁻OH than under basic conditions, the polymerization of alkoxy silane takes a short time. Therefore, the binder was obtained for a short reaction time at neutral pH.

TMAH exhibited a higher catalytic ability for binder synthesis than the other catalysts (nitric acid and ammonia) when a binder was synthesized under nearly neutral condition. This fact is explained as follows. When TMAH is used as a catalyst, tetramethylammonium ion (TMA⁺) having an organic property can be assumed to have a steric interaction with alkoxy groups of the alkoxy silane. The hydrolysis reaction of alkoxy silane is a S_N2 mechanism⁷⁾ as shown in Eq. (6).

Because the conjugate acid (TMA⁺) of ⁻OH is bulky compared to NH₄OH, this reaction will be more affected by the steric interaction than using less bulky catalysts such as NH₄OH. This means that the Si atom once attached by Si-O⁻ (Fig. 4 (b)) does not receive a further attack as there are some other Si atoms which have fewer Si groups (Fig. 4 (a)) than it. Namely, TMAH having bulky organic groups uniformly catalyzes the polycondensation reaction the same as the acid type reaction. This interaction also affected the slurry hardening time. When using TMAH as a slurry hardening catalyst, its hardening times were far longer than the NH₄OH catalyst (Table 1, Runs 2 and 3, and Runs 7 and 8).

In order to confirm the efficiency of the bulky organic bases as the catalyst, binders were synthesized with tetraethylammonium hydroxide (TEAH) as the bulky organic base and sodium hydroxide and potassium hydroxide as the less bulky inorganic bases. These results are shown in Table 3. For the organic bases, dried bulks could be obtained without cracks. For the inorganic bases, on the other hand, a bulk with no crack could not be obtained. These results suggest the difference in the catalytic mechanisms between the bulky organic and less bulky inorganic bases.

4 Conclusion

The effectiveness of TMAH as a catalyst of the binder synthesis when manufacturing a dried bulk was described. The bulky organic bases were assumed to exhibit the ability of the binder to make a dried bulk have no cracks during the drying process.

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