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Manufacturing of Silica Glass from Silica Power Consolidated with Tetramethoxysilane Oligomer-derived Binder

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A sol-gel method was used for manufacturing silica glass. A new method involved making a bulk by hardening a slurry of silica powder with a methoxysilane-derived binder. The bulk manufactured by this method was successfully dried and sintered to produce the silica glass. The significant results of this method are as follows: (1) the amount of reaction water in synthesizing the binder was less than the amount with which the methoxy group in the methoxysilane was completely hydrolyzed and poly-condensed, (2) the methoxy group partially survived in the binder and (3) this survival caused the binder to be flexible. When an oligomer of tetramethoxysilane was used as a starting material, the optimum amount of water for the bulk manufacturing is 2.3 equivalents. The bulk manufactured by this method was dried and sintered to form the purified silica glass without the generation of cracks.

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. In general, the silica glass used for manufacturing a large size wafer is synthesized by melting a natural one which has a large amount of metallic impurities such as Al and Ti. The sol-gel method^{1, 2)} has been widely applied to the manufacturing of silica glass but has been mostly unsuccessful, because the green compact must shrink and therefore produce many cracks during the drying process.³⁾ Many methods were tried to reduce the shrinkage, in which colloidal silica was mixed in the sol solution as an anti-shrinkage agent.⁴⁾ This method was much useful to reduce the shrinkage, however, a precipitation of colloidal silica took place when the sol solution was stood for a long time, and this made the gel generate many cracks during the drying process.

In this paper, a new method for the effective and inexpensive manufacturing of purified silica glass is described. The sol-gel method of hardening a slurry of a purified synthetic silica powder with a binder has 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. The synthetic silica powder is purer than a natural one. To prevent cracking during the drying process, the binder must be flexible. In this paper, a synthetic method for the binder to be flexible enough and a hardening method for the slurry of a silica powder with the binder without the generation of cracks are 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 a polyethylene bottle. Ethylene glycol and ammonia water (the 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) and tetramethylammonium hydroxide (TMAH) solution were both made by Tama Chemicals Co., Ltd. The silica powder (20 μm mean diameter) was made by Mitsubishi Rayon Co., Ltd.

2.2 Decomposition temperature of methoxy group measured by the differential thermal analysis method

The sample was prepared as follows. In a 500 ml three-necked glass vessel equipped with a condenser and a thermometer, 218.4 g of MS-51 and 80 g of methanol were added and stirred, and then 16.2 g of a 0.05%-TMAH aqueous solution was added as the reaction water and catalyst. The reaction mixture was heated in an oil bath at 72°C for 2 h. After cooling, 64.5 g of the reaction mixture was mixed with 22.0 g of ethanol and 20.0 g of ethylene glycol in a polyethylene vessel, and then stirred with 1.7 g of a 2%-NH₄OH solution for 4 min, forming a gel without stirring after 10 min at room temperature. The decomposition temperature of the gel was measured by the differential thermal analysis method.

2.3 Synthesis of the bulk

In a 500 ml three-necked quartz vessel equipped with a condenser and a thermometer, 218.4 g of MS-51 and 80 g of methanol were added and stirred, and then a 0.05%-TMAH aqueous solution was added as the reaction water and catalyst. The reaction mixture was heated in an oil

The starting material was the oligomer of tetramethoxysilane (9) (MS-51: trimer as the mean polymerization degree). A catalyst for synthesizing the binder was tetramethylammonium hydroxide (TMAH),⁶⁾ which is an organic base as strong as NaOH or KOH and decomposes at 135~140°C,⁷⁾ leaving no decomposition residue and inorganic ions. As MS-51 used here is a trimer as the mean polymerization degree, 4 equivalents of water is consumed for complete hydrolysis and polycondensation to generate siloxane bonds (Eq. (6)).

Table 1 Influence of water content on binder and bulk syntheses.

Run	MS-51 g	H ₂ O ^a		Methanol g	Time ^c h	Binder catalyst ^d	H ₂ O ^e Equivalent ^b	Result ^f
		g	Equivalent ^b					
1	218.4	21.6	2.0	80	3	TMAH	2.8	Two short cracks
2	218.4	16.2	1.5	80	7	TMAH	2.3	No cracks
3	218.4	10.8	1.0	80	7	TMAH	1.8	One short crack
4	218.4	8.6	0.8	80	14	TMAH	1.6	Many long cracks

^aWater content in the binder. ^bMole equivalent to the methoxy group in MS-51. ^cRefluxing time. ^d0.05% solution. ^eWater content in the slurry after addition of a 2%-NH₄OH soln. 1.7 g. ^fShort crack: less than 10 mm depth, long crack: more than 10 mm depth.

Table 2 Composition of the silica slurry.

Component	Weight (g)
Silica powder	250
Binder	64.2
Ethanol	22.0
Ethylene glycol	20.0
2%-NH ₄ OH solution	1.7

The binders synthesized with less amount of water are shown in Table 1. The slurry was mixed with the binder and silica powder as shown in Table 2 and Fig. 2. The binder synthesized with 1.5 equivalents of water exhibited better result than the others (see run 2 in Table 1), and the total amount of water in the slurry is 2.3 equivalents, which included the water of the hardening catalyst (2%-NH₄OH solution).

When the amount of water in the slurry is 1 equivalent, the generated siloxane polymer results in a linear type polymer, and 2 equivalent water results in the planar type polymer. More than 2 equivalent water generates three dimensional network of siloxane bonds. Little methoxy groups remain in the formed gel for the water above 3 equivalents and the synthesized binder reduced its flexibility. This indicates why 2.3 equivalent water amount is better than the others. The role of TMAH as a catalyst is under investigation. The bulk thus obtained by this method was dried at room temperature and then sintered to silica glass without cracks at about 1800°C (see Fig. 3). X-ray diffraction analysis indicated that the sintered silica glass contained no crystalline phase (see Fig. 4). The metallic impurities in the synthesized binder and the silica glass were shown in Table 3, which indicates that the silica glass synthesized by this new method has a higher purify than a natural quartz.

Fig. 2 Preparation procedure of wet bulk. **Fig. 3** Sintered bulk without generation of cracks.

4 Conclusion

A new method in which the silica powder slurry was hardened by the binder, was applied to manufacturing silica glass as follows: (1) the amount of reaction water

Fig. 4 X-ray diffraction of the sintered glass.

Table 3 Impurities of the binder, the sinterd glass and natural quartz.

Metal ppm	Binder	Sinterd glass	Natural quartz ^{a)}
Na	<0.1	0.2	1.0
K	<0.1	0.1	0.6
Fe	<0.1	0.7	0.7
Al	<0.5	0.3	17.7
Ti	<0.5	<0.5	1.1

a) Natural quartz is produced by Unimin Corp.

for synthesizing the binder was less than the amount for the complete hydrolysis and condensation of methoxy groups of methoxysilane, (2) the remaining methoxy groups gave the flexibility to the binder. The dried bulk was sintered to high purity silica glass without the formation of cracks.

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