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# Spherical SiO<sub>2</sub> Filler for Semiconductor Sealing Materials

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# Abstract

Spherical silica particles are mainly used as the filler for semiconductor sealing material. Nippon Steel & Sumikin Materials Co., Ltd. sells spherical silica fillers produced by the thermal spraying method. High fluidity is required for the sealants, in which resin is filled with spherical silica with high volume fraction, with the downsizing and thinning of semiconductor packages. Controlling the roundness and particle size distribution is important for improving the fluidity of silica particles and resin compound. In this report, we focused on the ultrafine submicron particles included in the spherical silica particles by the thermal spraying method and investigated the effects of ultrafine particles on the fluidity of the resin compound. As a result, the ultrafine particles increased the viscosity of the resin and reduced the fluidity. However, it is confirmed that the fluidity of the compounds increases with an appropriate quantity of ultrafine particles. We also report the development of spherical cristobalite particles, which are crystalline silica materials, having a higher thermal expansion coefficient than general amorphous spherical silica particles. It was clarified that Al is effective for the crystallization of amorphous silica particles and spherical cristobalite particles were successfully obtained.

## 1. Introduction

Spherical silica (SiO<sub>2</sub>) particles are used as the filler for semiconductor sealing material (sealant).<sup>1)</sup> Sealants for semiconductors are used to protect IC chips and wirings from heat and moisture, and a resin compound consisting of a mixture of the resin and filler is used. Conventionally, crushed silica has been used as the filler for sealants. However, in recent years, with down-sizing and enhancement of the performance of semiconductors, spherical fillers are used to improve the fluidity of sealants so that gaps can be filled in properly by the compound consisting of a mixture of the resin and filler.

Presently, the spherical silica particles used for sealants are mainly produced by the thermal spraying method. In the thermal spraying method, spherical silica particles are obtained by feeding the crushed silica into the high temperature flame of 2000°C or above and melting, and by quenching the molten silica that is spheroidized by surface tension. As the molten silica is quenched, the obtained spherical silica particles are amorphous and the thermal expansion coefficient is as small as about 0.5 ppm/K. Therefore, the effect of lowering the thermal expansion coefficient of a sealant is obtained by mixing the silica particles with resin that has a high thermal expansion coefficient. With this, the thermal expansion coefficient of a sealant close to that of the Si of semiconductors can be obtained, and the deformation that develops when sealing semiconductor chips can be suppressed.

Additionally, the filling rate of the filler to resin can be enhanced by using spherical silica particles, and the effect of enhancing the strength of the sealant is also obtained. Furthermore, as the sealant with high fluidity is obtained by using spherical silica particles, even the highly integrated parts of semiconductor packages can be sealed without leaving gaps. Due to the advantages previously described, most semiconductor packages currently employ spherical silica particles as the filler for sealants.

Thus spherical silica particles are indispensable in enhancing the reliability of semiconductor packages. However, with the progress of down-sizing and growth in circuit integration of IC chips, re-

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quirements raised by the semiconductor technologies are growing evermore diversified. Particularly, to comply with the down-sizing and thinning of IC chips and refinement of wirings, the requirements for high fluidity of sealant filler are growing.<sup>1–3)</sup>

For the sealant, a resin compound highly filled with spherical silica particles of 85 wt% or above is used. This is equivalent to the high volume fraction of 75 vol% or above, and is the filling rate that exceeds 74% of the hexagonal closest packing structure (hcp), and the cubic closest packing structure (ccp). To obtain fluidity of the resin compound mixed with silica particles at such a high filling rate, not only is the high roundness of particles needed but also, to avoid deterioration in fluidity due to mutual contacts of particles, securing proper inter-particle distance by mixing the particles of different sizes (particle size distribution) is required. This concept is based on the idea that the filling rate can be improved by arranging small-sized particles have been conducted on the improvement of the filling rate through particle size distribution.<sup>4, 5)</sup>

The study to improve fluidity based on the above concept of the filling rate focused on the particle size distribution within the range of several  $\mu$ m to several tens of  $\mu$ m. However, the spherical silica particles produced by the thermal spraying method contain ultrafine particles that have been produced from silica portions being evaporated during thermal spraying and solidified. The ultrafine particles are generally termed as fume and are extremely fine with a particle size of around 0.1 $\mu$ m. The ultrafine particles are considered to influence fluidity when mixed with resin. Therefore, the influence of the content of the ultrafine particles that were generated during thermal spraying was studied.

Additionally, with the down-sizing of semiconductor chips, the needs for filler with a particle size smaller than that of the conventional filler are growing. Meanwhile, a problem of deformation of packages such as warp that is caused by the difference in the thermal expansion coefficient between semiconductor chips or substrates and sealants is also becoming apparent with the thinning of semiconductor packages. To solve the problem, it is necessary to control the thermal expansion coefficient of sealants more precisely. In the conventional sealants, the thermal expansion coefficient of the resin compound has been lowered by filling the resin with the low thermal-expansion amorphous silica particles at a high filling rate. However, in order to control the thermal expansion more precisely while maintaining a high filling rate, a method of filling resin with a mixture of amorphous silica and spherical particles having a thermal expansion coefficient higher than that of the amorphous silica is sought. As materials having higher thermal expansion, crystalline silica and alumina are listed, among which crystalline silica is regarded as preferable as it has already been applied in the form of crushed particles to sealants as a filler. Then, spherical crystalline silica particles were developed by the heat treatment of amorphous spherical silica particles produced by the thermal spraying method.

#### 2. Main Subject

## 2.1 Influence of ultrafine particles on fluidity of sealant

As **Fig. 1** shows, spherical silica particles produced by the thermal spraying method contain extremely ultrafine particles of around  $0.1\,\mu\text{m}$ . These ultrafine particles are produced from silica in the high temperature thermal spraying method, and it is difficult to separate them in the production stage. When the spherical silica particles containing such ultrafine particles are mixed with resin, the ultrafine particles may cause lowering of the fluidity of the sealant. In fact, in



Fig. 1 Scanning electron micrograph of ultrafine particles on spherical SiO, particles



Fig. 2 Scanning electron micrograph of ultrafine particles in semiconductor sealing material

the sealant made of the mixture of resin and the spherical silica particles containing such ultrafine particles, ultrafine particles exist in the resin in a dispersed state (**Fig. 2**).

To examine the influence of the ultrafine particles on the fluidity of a sealant, only the ultrafine particles were mixed with resin, and the change in the viscosity of the resin when the addition of ultrafine particles was changed was evaluated. As the method of evaluation, the mixture of epoxy resin and ultrafine particles was put in between two disc plates of 20mm in diameter placed in parallel to each other, and the viscosity of the resin at 120°C was measured by the Rheometer DAR-50 of Reologica Instruments AB. The result of the measurement of the viscosity is shown in Fig. 3. With the addition of the ultrafine particles by 10-30 vol%, although the resin exhibits viscosity higher than that of the one without the addition of ultrafine particles, the viscosity is relatively low. On the other hand, the viscosity of the resin with the addition of the ultrafine particles by 40 vol% and 50 vol% rises remarkably as the addition is increased. It is considered that, as opposed to the cases of the addition below 30 vol% wherein the contacts among particles scarcely take place, in the cases of 40-50 vol%, contacts take place frequently, and accordingly the viscosity of the resin compound rises.

Furthermore, in order to examine the influence of the ultrafine particles at the mixture rate of silica particles that is the same as those of conventional sealants, the spherical silica particles with an average diameter of  $30\mu$ m and those of  $9\mu$ m were mixed at the rate of 75 vs. 25 vol%, and then mixed with resin and the ultrafine particles so that the filling rate as a whole of silica containing the ultrafine particles was maintained at 85 wt% (75 vol%), and the influence of the ultrafine particles on fluidity was examined. The influence of the change in the amount of ultrafine particles on spiral-flow fluidity is shown in **Fig. 4**. The result shows that the fluidity drops in the





Fig. 4 Effects of amounts of ultrafine particles on fluidity of semiconductor sealing agent

range of 40 vol% or above wherein the viscosity of the mixture of the resin and the ultrafine particles sharply rises. From these results, in the case of a sealant wherein resin and particles are mixed, the viscosity of the portion consisting of ultrafine particles and resin is considered to influence fluidity.

Additionally, the result of the measurement of fluidity shown in Fig. 4 indicates that fluidity becomes high in the vicinity of 20 vol% of the ultrafine particle vs. resin rate. The fluidity of the mixture of resin and silica particles is considered to lower when particles contact with others, and/or when the viscosity of resin in between particles becomes high. This experiment was conducted maintaining the constant addition of silica particles that contain ultrafine particles. When the addition of ultrafine particles is increased, the rate of particles of several  $\mu$ m-several tens of  $\mu$ m in size relatively decreases. Accordingly, the frequency of contacts with others of large size particles is considered to lower. While fluidity rises as collisions of large diameter particles are reduced, the viscosity of the resin part rises where the amount of ultrafine particles increases. When ultrafine particles are thus increased, the lowering of fluidity due to the rise in viscosity of the resin part and the rise in fluidity due to the decreased contact chance of large diameter particles take place concurrently, and the entire fluidity changes depending on which of the two factors becomes dominant. In the case of this experiment, 20 vol% of the rate of ultrafine particles is considered to be the condition wherein the two factors are balanced, and allows high fluidity. 2.2 Development of crystalline spherical silica particles

Crystallization by the heat treatment of amorphous spherical silica particles was studied, aiming at increasing the thermal expansion



(b) Al<sub>2</sub>O<sub>3</sub> content: 4635 ppm

Fig. 5 X-ray diffraction patterns of spherical  ${\rm SiO}_2$  particles before and after heat treatment

of spherical silica particles. A number of crystalline silica structures exists such as those of quartz, tridymite and cristobalite, which are of the stabilized phases under a normal pressure, and that of coesite that is of the stabilized phase under a high pressure.<sup>6)</sup> In the equilibrium diagram, quartz is considered to be of the phase that is most stabilized at a normal temperature under a normal pressure.<sup>7,8)</sup> In the meantime, in the crystallization of amorphous silica, cristobalite is formed through devitrification behavior at a high temperature. On the other hand it is reported that crystallization of amorphous silica starts at around 700°C with the addition of alkali metals. They are crystallized in quartz, tridymite and cristobalite and the crystalline forms depend on the heat treatment temperature, components and additions of alkali metals.9) However, in the crystallization with the addition of alkali metals, sintering and/or softening of particles occur even at a low temperature, and crystallization while maintaining sphericity is very difficult. Furthermore, as alkali metals inhibit the curing of resin and cause the corrosion of IC wiring, they are the components to be avoided for sealants. Then, crystallization of amorphous spherical silica particles by the addition of metal components other than alkali metals was investigated.

Figure 5 shows the X-ray diffraction patterns before and after the heat treatment (HT) of spherical silica particles with low  $Al_2O_3$ content of 133 ppm and high  $Al_2O_3$  content of 4635 ppm. The silica particles were heat-treated at 900–1300°C for 6 hours. Particles with low  $Al_2O_3$  content remained as amorphous even after the heat treatment at 1300°C. While particles with high  $Al_2O_3$  content exhibited a remarkable crystallinity peak at 1200°C heat treatment, and the amorphous phase disappeared at 1300°C heat treatment while the cristobalite phase appeared. In the heat treatment at 1300°C, particles with low Al<sub>2</sub>O<sub>3</sub> content are agglomerated and become a lump. The shape before and after the heat treatment was observed by SEM (scanning electron micrograph). As shown in **Fig. 6**, the particles are beginning to be combined with each other with low Al<sub>2</sub>O<sub>3</sub> content particles. On the other hand, the particles with high Al<sub>2</sub>O<sub>3</sub> content did not agglomerate even after the heat treatment of 1300°C and maintained their spherical shape.

From this result,  $Al_2O_3$  is considered to influence the crystallization of amorphous silica to cristobalite, and spherical silica particles with various  $Al_2O_3$  contents were heat-treated in the same manner. As shown in **Table 1** as a result, particles with an  $Al_2O_3$  content of above 1 000 ppm are crystallized to cristobalite. The specific weights of samples uncrystallized after heat treatment are almost unchanged from 2.21 of amorphous silica. On the other hand, the specific weights of samples crystallized to cristobalite are almost the same as 2.33 g/cm<sup>3</sup> of cristobalite, and all the particles are considered to have been crystallized.

From these results, Al is assumed to significantly influence the crystallization of amorphous silica. The crystallization of amorphous silica progressing under the existence of Al is attributed to the Si of amorphous silica forming a network structure that is replaced by Al. As the ionic radius of Al in tetracoordination is 39 nm, and is close to the ionic radius 26 nm of Si in tetracordination,<sup>10</sup> Si in the SiO<sub>4</sub> tetrahedron structure formed by amorphous silica is replaced by Al.<sup>11,12</sup> This is termed as isomorphous substitution of Si by Al, and with Al<sup>3+</sup> at the position Si<sup>4+</sup>, extra atomic bonding of the adjacent Si activates the structure. It is considered that the rearrangement of SiO<sub>4</sub> tetrahedron structure is triggered in the heat treatment by the portion activated by the replacement, and the crystallization to cristobalite is promoted.

To study the high-temperature behavior of the spherical cristo-



(a) Al<sub>2</sub>O<sub>3</sub> content: 133 ppm



(b) Al<sub>2</sub>O<sub>3</sub> content: 4635 ppm

Fig. 6 Scanning electron micrograph of spherical SiO<sub>2</sub> particles after heat treatment

balite particles thus obtained, thermal differential analysis (DTA) was conducted for particles heat-treated at 1300°C. As a result, an endothermic change starting at 240°C is observed as shown in **Fig.** 7. The cristobalite crystal develops a phase transition from  $\alpha$ -cristobalite to  $\beta$ -cristobalite between 200°C and 250°C, and this endothermic peak is considered to be developed by the phase transition of cristobalite.<sup>13–18</sup>

Additionally, the result of measurement before and after heat treatment of thermal expansion of the compounds obtained by mixing epoxy-resin and particles and cured at 200°C is shown in **Fig. 8**. In the case of the compound with amorphous silica particles, the

Table 1 Results of heat treatment of sperical SiO<sub>2</sub> particles with different contents of Al<sub>2</sub>O<sub>2</sub>

Sample			A	В	С	D	E	F	G	Н
Al <sub>2</sub> O <sub>3</sub> (p		(ppm)	133	148	232	1040	1720	2074	4635	7385
Crystallization to cristbalite		×	×	×	0	0	0	0	0	
Specific	Before heat treatment		2.21	2.22	2.22	2.21	2.21	2.22	2.22	2.23
gravity	After heat treatment		2.20	2.21	2.22	2.33	2.29	2.32	2.32	2.33



Fig. 7 Thermal differential analysis of spherical cristobalite particles



Fig. 8 Thermal expansion of resin and spherical cristobalite particles compound

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thermal expansion increases approximately in a linear manner in the range from room temperature to 300°C, and as a whole, the thermal expansion coefficient is low. Conversely, in the after-heat-treatment case of the compound with cristobalite particles, the thermal expansion coefficient is higher than that of amorphous particles, and furthermore, a sharp rise in thermal expansion is observed at 240°C. The temperature at this change in the thermal expansion agrees with the temperature of the endothermic reaction observed in the DTA. Therefore, it is considered that the thermal expansion has occurred due to the change in the crystalline structure developed by the phase transition of cristobalite from the  $\alpha$ -phase to  $\beta$ -phase.

As mentioned above, by heat-treating the amorphous silica containing Al, the spherical cristobalite particles could be obtained. Additionally, it is confirmed that the cristobalite particles so obtained have a higher thermal expansion coefficient than that of spherical amorphous silica.

#### 3. Conclusion

Spherical silica particles are expected to be used widely as the filler for semiconductor sealants, and requirements are also considered to be diversified. With the sophistication, growing integration of semiconductor chips, and down-sizing and thinning of semiconductor packages, the needs for refined fillers are growing. To cope with these, it is necessary to realize high fluidity of the filler that consists of particles with a diameter of several  $\mu$ m or below. The studied control of ultrafine particles will become a far more important technology in the future as it is considered that the smaller the constituent particles of filler become, the larger their influence on fluidity.

Furthermore, since cristobalite particles of crystalline silica have a thermal expansion coefficient higher than that of the conventional amorphous silica spherical particles, with the combined use with amorphous silica, cristobalite particles are considered to be an effective filler in controlling the thermal expansion of sealants. Furthermore, since cristobalite particles are crystalline and have higher thermal conductivity as compared with that of amorphous silica, its effect of enhancing the heat transfer capability of semiconductor chips is also expected. We will promote further the evaluation of cristobalite spherical particles when they are mixed with resin, and promote study on application technologies.

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