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Study on Recycling of Scraps from Process of Silicon-single-crystal for Semiconductor

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Abstract

So far, the quartz-glassy crucible wastes which was used for pulling up silicon-single-crystal ingot have simply reused for refractory raw-materials, or exhausted. This study is concerned on the advanced recycling-technology that is obtained by the proper micro-particle preparation process in order to fabricate fine amorphous silica filler for EMC (Epoxy Molding Compound). Therefore, this paper will deal with the physical, chemical and thermal pre-treatment process for efficient impurity removal and with the proper micro-particle process for producing the amorphous silica-filler.

In view of the results, if the chemical, physical and thermal pre-treatment process for effective elimination of impurity was passed, the purity of wasted fused glassy crucible is almost equal to the its of first anhydrous quartz glass. Thus, it was understood that this wasted fused glassy crucible was sufficient value of recycling, though it was damaged. When the ingot was fabricated, Phase transformation of crystallization by heat treatment (heat hysteresis phenomenon) was not changed. So, it was understood that as fused silica in the amorphous state, as it is, recycling possibility was very high.

1. Introduction

This paper is intended to investigate of the recycling of waste quartz glass crucible used for drawing silicon single crystal ingot. Generally, these wastes were fallen into disuse by simply reclamation, or just reused cheap additive materials for refractory.

The purpose of this study is to develop economical and effective techniques in order to recycle for fine amorphous silica filler to EMC (Epoxy Molding Compound) through some processes such as waste collection process, effective pre-treatment process to remove impurities, and proper powder preparation process.

This paper discusses techniques of physical, chemical, thermal pre-treatment process in order to eliminate impurities (including ultrasonic cleaning process) and establishes techniques of appropriate powder preparation process in order to fabricate fine amorphous silica filler for EMC.

In this study, technical fields and effects of recycling were following : Crucible of drawing silicon single crystal ingot was made generally with quartz glass crucible because quartz glass has stable thermal properties and identical element component with silicon, and oxygen from quartz glass fix crucible metal impurities during thermal treatment process. The degree of purity of quartz glass is different with manufacturing company. But nevertheless the degree of purity of quartz glass is possible to fabricate silicon ingot with high purity due to control with [ppb] unit in the most companies. Generally, quartz glasses are classified into first fused anhydrous quartz glass, second fused hydrous quartz glass, third synthesized hydrous quartz glass, fourth synthesized anhydrous quartz glass. First fused anhydrous quartz glass was used as crucible of drawing silicon single crystal ingot. While manufacturing method of quartz glass was not wholly opened, only schematic methods are introduced. The waste crucibles of drawing silicon single crystal ingot are considered to be first fused anhydrous quartz glass and are very pure products. But waste crucibles could not be reused in the field due to impurities of poly-silicon on the surface of crucible and thermal hysteresis, and then were fallen into disuse by reclamation.

However, according to data of accurate analysis and systematic investigation, waste fused glass crucible could be used as first fused anhydrous quartz glass with original high purity in spite of broken condition through physical, chemical, thermal pre-treatment process in order to eliminate impurities effectively. Therefore waste fused glass crucible might be worth recycling because purity of SiO_2 contents is similar to that of SiO_2 contents in a new crucible. It is found that waste fused glass crucible is possible to recycle as amorphous fused silica because of no phase transition (thermal hysteresis) of crystallization by thermal treatment of manufacturing company.

From the summary of the above present situation connected with technology field of recycling waste glass crucible, we can find out that waste quartz glass crucible used for drawing silicon single crystal ingot and quartz glass grip parts used as supporting wafers in the process of silicon wafer treatment can not be used as crucible of drawing silicon single crystal as original use through any processes or any treatments, but those can be used as functional filler of EMC through proper pre-treatment technology and effective powder preparation technology.

Consequently, the purpose of the present investigation is to solve problems of above technology field and recycle crucible of drawing silicon single crystal ingot as powder materials of functional filler. Therefore, the aims of technical problems which will be solved by this investigation are to develop proper processing techniques to remove impurities of wastes, and to provide functional powder with improved characteristic which has high value.

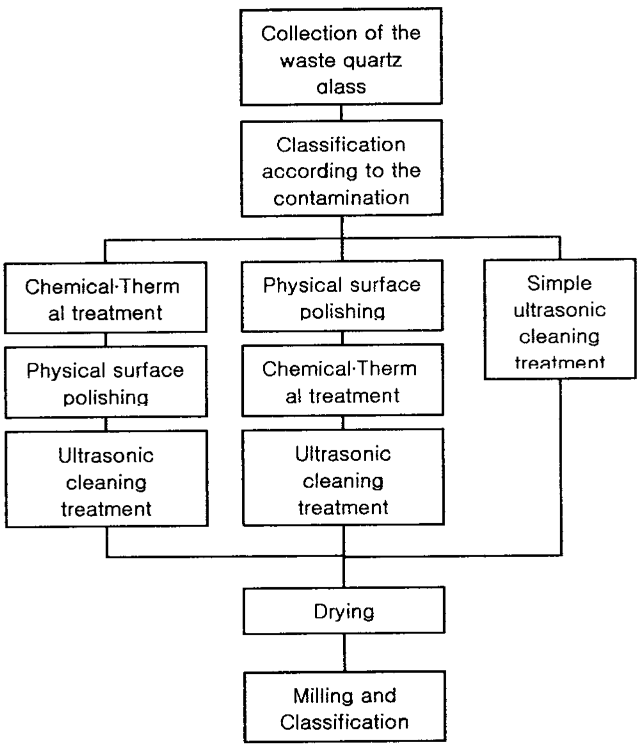
2. Experimental Procedure

2.1 Pre-treatment process

Intermediate products were fabricated by following process as shown in Fig. 1 in order to remove impurities adhered on the surface.

In case of chemical · thermal treatment, waste quartz glass fragment which was located in water soluble are heated over 80℃ for many hours. And then residual poly silicon which is adhered on the surface gradually desorped and removed by oxidation of silicon such as gaseous SiO_2. These pre-treatments processes were used only when it is necessary to classify according to degree of contamination. In case of these pre-treatments, it was not give bad impact on recycling of final filler, even though it is not cleaned completely in the next cleaning process because it existed in the form of not metal silicon but crystalline silica.

Physical Polishing process has a difficulty in collecting large fragments, but it was selected as pre-treatment process in this study because it is most effective and perfect method for eliminating impurities.



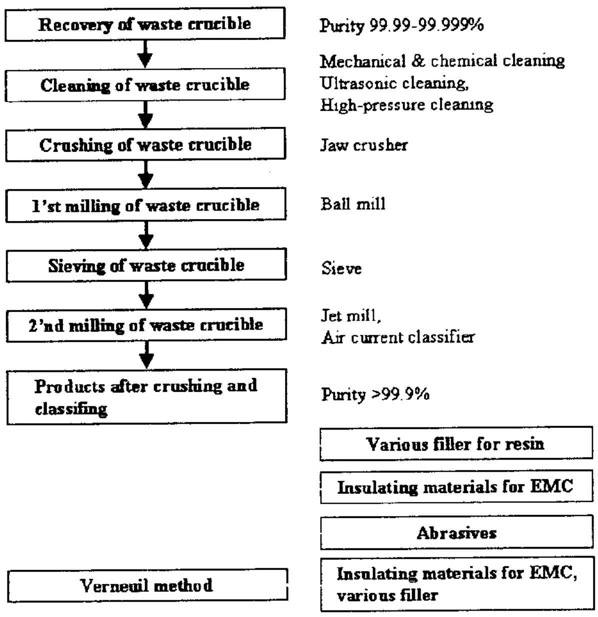
<Fig.-1> Flow chart of pre-treatment process of waste quartz glass fragments

Ultrasonic cleaning process can be used when the dust was adhered lightly on the surface of classified fused wastes during collecting, or when waste parts from semiconductor fabrication process (wafer supporting grip of silicon wafer treatment process). Ultrasonic cleaning process was used as final treatment process can be washed simply after physical, chemical, and thermal pre-treatment process.

A large-sized ultrasonic cleaning device which was manufactured for present study was used in order to consider properties of wastes.

2.2 Powder preparation process

Waste quartz glass fragments which were formed through above described pre-treatment process became fine powder by generally crushing, first milling and second milling as shown in Fig. 2. The accurately controlled selection liner of each device and the other process are needed to in order to prevent impurities from mixing during milling. After parts fixing techniques such as magnetic purification, particle size distribution was controlled by dry-type classifier

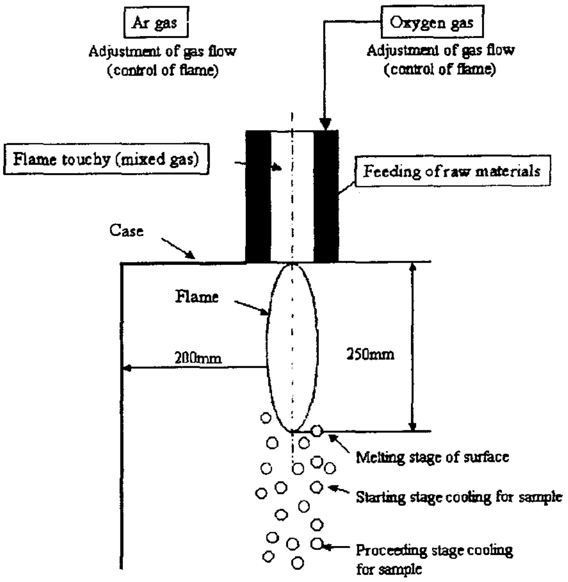


<Fig.-2> Flow chart of manufacturing amorphous silica filler from waste fused silica crucible scraps

Fig. 3 shows schematic illustration of Verneuil method. The experiment of forming into spheres was carried out by Verneuil method with using Ar-O_2 gas, in order to establish processing technology to fabricate high value-added low-α sphere filler from quartz glass powder which was through milling process.

3. Results and Discussion

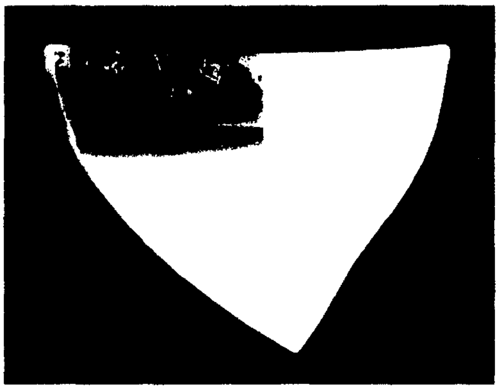
The following results of characteristic analysis of fine amorphous silica powder filler prepared by present technical development were obtained :



<Fig.-3> Schematic illustration of Verneuil method

3.1 Results of process for cleaning

When pre-treatment process was introduced in order to remove and clean impurities adhered on the surface of poly silicon, photographies compared with before and after surface condition of specimen which was most contaminated were showed in Fig. 4. According to observation of the photograph or the naked eyes, it was found that perfectly cleaned surface of specimens was likely to that of before single crystal growth process. But, it is considered that it was required more accurate control of process in order to satisfy inspection ·such as low-α filler which was managed basically ppb unit.



<Fig.-4> Surface of waste crucible scrap before and after cleaning process

3.2 Results of study on fabrication fine amorphous silica filler

The sample powder of waste quartz glass fragments which were cleaned through pre-treatment process was made from fine powder formed by crushing, first milling and second milling process. After accurate dry classification as next process, sharp-edged fused silica filler was divided into six classes as particle size reduction. These classified samples was named 20A, 12B, 11C, 9D, 7E, 4F for convenience. The spherical fused silica filler sample which was fabricated with 20A sample by Verneuil method was named S20A. These results and the discussions will be described later.

O Chemical properties

Wet type chemical analysis for main components was carried out according to KS L 2101. And then, extraction ion concentrations were measured by IC and ICP from 10wt% solution with ultra pure water, after exuding for 5 days.

U and Th composition which are important to judge low-α products was analysed by comparison the results of neutron analysis (NAA) and ICP-MS analysis method. These analytical results of chemical compositions of each sharp-edged samples were showed in Table 1.

<Table-1> Chemical compositions of each sharp-edged sample

Sample	SiO_2 (%)	Trace components(ppm)							
		Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	U(ppb)	Th(ppb)
20A	99.9	300	0	4	3	0.02	0.05	7.2	15
12B	99.9	400	0	2	1	0.01	0.03	-	-
11C	99.9	400	0	2	1	0.02	0.09	-	-
9D	99.9	500	0	3	1	0	0.01	-	-
7E	99.7	1500	0	2	2	0.02	0.01	-	-
4F	99.7	1300	0	2	2	0.05	0.06	15	24

Sample	Extraction Ions(ppm)					
	Fe^{2+}	Na^+	Cl^-	F^-	SO_4^{2-}	NH_4^+
20A	ND	0.04	0.16	1.03	0.50	1.09
12B	ND	0.03	0.44	1.10	0.40	1.26
11C	ND	0.07	0.21	0.21	0.20	0.71
9D	ND	0.01	0.13	0.29	ND	1.19
7E	ND	0.01	0.15	0.13	0.40	1.21
4F	ND	0.05	0.23	0.20	0.40	1.28

It is found that the content of SiO_2 as main composition of each sample is high purity siliceous materials more than 99.7%, and the content of Al_2O_3 as main impurities was included relatively high at 1500ppm. A content of Al_2O_3 in 20A sample at short milling time is 300ppm and increases as milling time goes on. This phenomenon was caused by contamination of processing due to alumina ball mill liner and alumina ball. But this phenomenon can be solved by introducing low-α zirconia equipment. In case of sharp-edged fused silica filler for commercial EMC packaging, the contents of alumina were controled in region of 1400 - 1500 ppm, and it is expected to improve effect of this technique.

It can be considered that there is no effect of impurities such as Fe_2O_3, CaO, MgO, K_2O, Na_2O owing to less or no detection. For analytical results of exudation concentration of main ions, most ions were detected less than 1ppm. Compared with existing products, it is found that there is no problem.

From analytical results of U and Th composition measured by NAA and ICP-MS. The content of U is about 7 - 8 ppb and the content of Th is about 20 ppb. This phenomenon was caused by contamination of processing due to alumina ball mill liner and alumina ball. So, the sharp-edged or spherical filler of low-α for high purity EMC can be manufactured by low-α zirconia equipment.

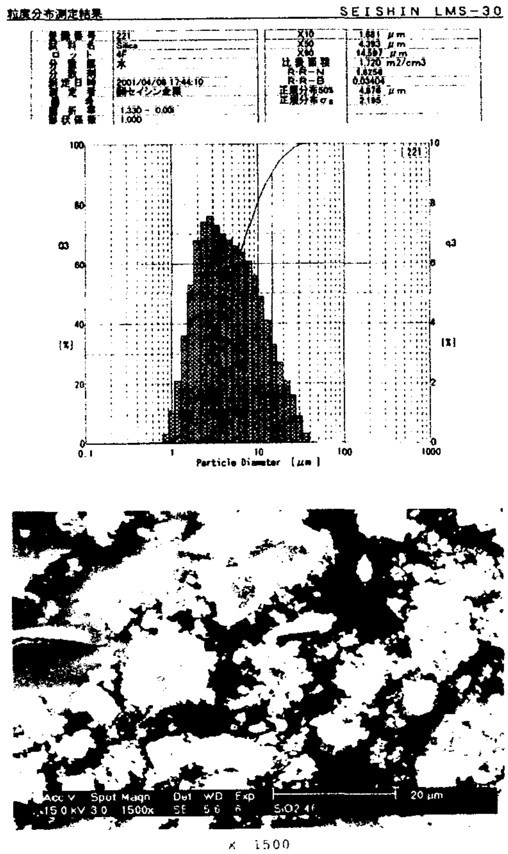
○ **Results of X-ray diffraction analysis**

If thermal treatment was carried out at 1100℃ in the condition of rich oxygen gas or high moisture atmosphere, crystallization called 'devitrification' was occurred in quartz glass. To investigate crystallization of waste quartz glass fragments, X-ray diffraction patterns were obtained with 20A sample as representative sharp-edged powder as shown in Fig. 5. From the result of X-ray diffraction pattern, it was observed that Halo peaks of typical amorphous glass was showed but specific peaks of crystalline phase such as poly silicon was not showed. Therefore, it was found that these waste fragments are the fused silica which have been quartz glass and impurities which was contaminated on the surface during cleaning pre-treatment process was perfectly removed.

<Fig.-5> XRD pattern of the sharp-edged 20A sample

○ **Results of particle size distribution and scanning electron microscopic photographies**

In order to confirm the possibility of reusing waste quartz glass crucible fragments as functional filler of each sharp-edged powder sample which was obtained by powder treatment, particle size distribution and scanning electron microscopic analysis was carried out. These analytical results of 4F sample was shown in Fig. 6.



<Fig.-6> Particle size distribution and SEM photograph of 4F

According to summary of above data results, it was found that the fragments of each sample shows typical clam shell marking of glass and particle size distribution of these sample was relatively broad.

As particle size distribution for EMC packaging filler was broad, high mobility and high mixing are possible. Hence, from the advantages of crack resistance of packing materials, it is considered that recycled silica filler can substitute EMC filler for memory. In the respect of economic market price of filler and the case of different requirements of particle size distribution even between many EMC manufactors, the accurate adjustment of particle size and control of classifying process will be mattered in the future.

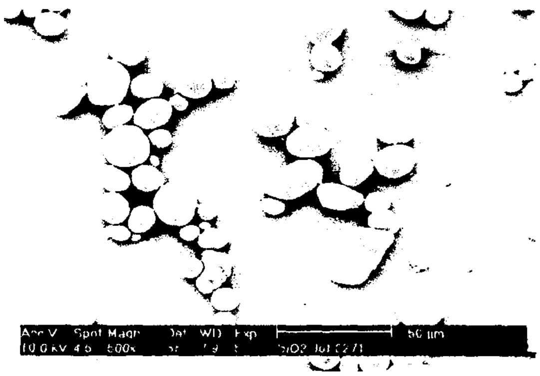
As reference, Table 2 shows results of particle size distribution of amorphous filler for EMC application compared with each six samples.

Scanning electron microgaphies of spherical fused silica filler (sample S20A) which was fabricated with 20A powder by Verneuil method were shown in Fig. 7. From these micrographies, we can get very successful results for forming into spheres, regardless of particle size of 20A sample before treatment. So, it is possible to substitute this spherical fused silica for commercial EMC filler. But this spherical powder sample was prepared by small lab scale with little several tens grams, study on development of the effective spherical process and improvement of treatment condition was necessary to progress continuously.

<Table-2> Comparison commercial sample and testing sample in particle size distribution and shape

Commercial Sample	Particle size (d50,㎛)	Particle size (d100,㎛)	Shape	Preparation process
A	19.73	151.86	sharp -edged	size reduction process
B	11.99	128.07	sharp -edged	size reduction process
C	10.71	128.07	sharp -edged	size reduction process
D	8.82	128.07	sharp -edged	size reduction process
E	10.3	64.79	sharp -edged	size reduction process
F	4.42	38.86	sharp -edged	size reduction process

Testing Sample	粒度分布 (d50,㎛)	粒度分布 (d100,㎛)	Shape	Preparation process
20A	19.93	151.86	sharp -edged	size reduction process
12B	12.16	151.86	sharp -edged	size reduction process
11C	10.72	128.07	sharp -edged	size reduction process
9D	8.65	108.01	sharp -edged	size reduction process
7E	6.28	54.64	sharp -edged	size reduction process
4F	4.39	38.86	sharp -edged	size reduction process



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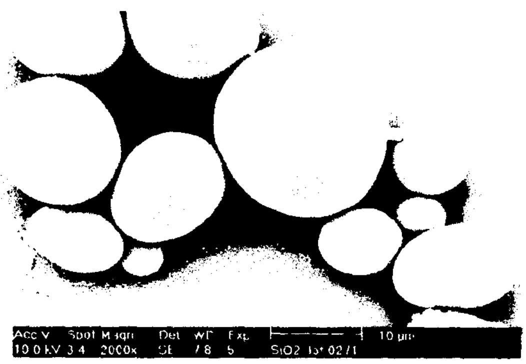

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<Fig.-7> SEM photograph of the spherical S20A sample

○ **physical properties**

Compared with commercial sample and testing sample in physical properties such as specific surface area, electric conductivity, moisture content, pH etc. were showed in Table 3.

Specific surface area of each sample was obtained by BET method. The electrical conductivity and pH value were measured from 10wt% solution with ultra pure water n fabricated in the same condition of extraction ion concentration analysis method. The moisture content value was measured to a little humidity by infrared moisture valance.

According to summary of above data results, it is found that results of each sample was similar to that of EMC filler products which was used on commercial use. Since technical innovation of electric and electronic field was developed, properties of materials for packaging were required strictly in order to use them as improved filler materials. Therefore, filler material with low hygroscopic degree, low stress, high tamping and small viscosity in case of indeed high packing condition was required. In the case of very thin packaging with thickness (less than 1 mm), package crack was occurred at 260℃. From now on, development of special filler by functional providing technology will be needed to satisfy requirements.

<Table-3> Comparison commercial sample and testing sample in physical properties

Commercial Sample	Specific surface area (㎡/g)	Electric conductivity (㎲/㎝)	pH	Moisture contents (%)
A	-	0.3	5.5	0.01
B	1.19	0.6	5.4	0.03
C	2.56	2.1	5.4	0.03
D	1.36	0.7	5.8	0.28
E	-	1.23	6.0	0.04
F	6.9	3.0	-	0.14

Testing Sample	Specific surface area (㎡/g)	Electric conductivity (㎲/㎝)	pH	Moisture contents (%)
20A	0.89	0.3	5.4	0.01
12B	1.08	0.8	5.2	0.01
11C	1.20	0.7	5.5	0.01
9D	1.40	0.2	5.3	0.02
7E	4.30	0.4	5.2	0.01
4F	7.20	0.5	5.7	0.01

4. Conclusion

This paper is intended as an investigation of the recycling of waste quartz glass crucible used for drawing silicon single crystal. The results of this study on development of economical and effective techniques in order to recycle fine amorphous silica filler to EMC (Epoxy Molding Compound) through some process such as waste collection process, effective pre-treatment process to remove impurities, and proper powder preparation process were as follows:

① From the results, the waste crucible was estimated to first anhydrous quartz glass. The waste crucible was worth recycling as high purity materials because the purity of SiO_2 in the waste crucible, which was treated in order to eliminate effectively impurities contaminated on the surface by cleaning process, was silimar to that of un-used new crucible. It is possible to recycle the waste crucible as the fused silica because phase transition of crystalline does not occurred after using crucible.

② The waste quartz glass fragments that were treated by cleaning pre-treatment process became sharp-edged fused silica filler sample by generally crushing, first milling and second milling. According to the results of physical or chemical characteristics analysis, it is possible to substitute the fused silica filler sample with commercially used EMC filler.

③ From the results of scanning electron micrographies of spherical fused silica filler samples which were fabricated by Vereuil method, the spherical fused silica filler sample was successfully formed regardless of particle size of original sample. Therefore, it is considered that spherical powder can be substitute with spherical fused silica for EMC.

④ The composition of U and Th was analyzed in order to consider low-α that could have high value. The content of U component was about 7-8 ppb, and the content of Th was about 20 ppb. This phenomenon was caused by contamination of processing due to alumina ball mill liner and alumina ball. The sharp-edged or spherical filler of low-α for high purity EMC can be manufactured by low-α zirconia equipment.

Referance

[1] Iler. R. K : "The chemistry of silica" , john Wiley & sons,NY(1979)
[2] Bergna,H,E : "The colloid chemistry of silica", ACS,Washington
[3] Toshiro Kagami, Akira Hayashi., Application Technolgy of High-Purity Silica, 1991
[4] P. W. Harben. The Industrial Minerals Handybook Third Edition warwick printing Co. 1995.
[5] Brinker,C.J. and Scherer, G.W : "sol-gel science", Academic, san diego(1990)
[6] Legramd, A.P. et al : Avd, colloid interface sci, 33,91(1990)
[7] "Chemical economics handbook, silicates and silica report", SRI, palo alto(1990)