Preparation and Existing States of La/Al Co-Doped Quartz Powders

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Abstract. The La/Al co-doped quartz powders were prepared by solid-liquid doping method. The structure, morphology and existing states of La/Al co-doped quartz powders were measured and characterized by DSC-TG, XRD, ESEM-EDX and so on. The results show that the solid-liquid doping method can effectively ensure the uniform distribution of dopant elements for La/Al. The doped salt compounds for preparing La/Al co-doped quartz powders can be completely decomposed when calcined at 650 °C. There is a certain degree of fusion between the oxides of La/Al prepared by doping and quartz powders particles, which helps improve the inherent quality of doped quartz glass.

1. Introduction

High-performance silica glass materials are one of the key auxiliary materials in the manufacturing process of semiconductor integrated circuit. This is because silica glass has excellent characteristics, such as high purity, high temperature, low cost, high spectral transmittance, good processability and machinability, and so on. In fields of production of semiconductor or liquid crystal, production apparatuses using plasma are widely used. In recent years, semiconductor integrated circuits have become minute, and hence, a dry-etching step using plasma bears importance. In the dry-etching step, a halogenated gas such as fluorine-containing gas or chlorine-containing gas is used. For example, fluorine-containing gases include such as F₂, HF, C₂F₆, C₃F₈, C₄F₈, CHF₃, SF₆ and NF₃; chlorine-containing gases include such as Cl₂, HCl, BCl₃ and CCl₄. Although the silica glass has good properties, the surface of silica glass member is gradually etched and eroded by a halogenated gas or its plasma at the exposed location [1-2]. This undesirable etching reduces the durability of the silica glass member and sometimes causes abnormal discharge, which is difficult to meet the requirement of continuous etching for semiconductor. Therefore, to remedy the above-mentioned problems, inside the semiconductor silicon chip etching process requires the use of corrosion resistant silica glass materials and products.

Up to now, only a few companies such as Tosoh Corporation, Herseus Quarzglas GmbH & Co. KG, Shin-Etsu Quartz Products Co., Ltd., Applied Materials, INC. have the ability to produce anti-corrosion and durable silica glass, and their products have been widely used in the process of semiconductor etching. Among them, Kazu Arai and the others of Tosoh Corporation [1-2] have developed a high durability silica glass comprising silica having incorporated therein aluminum and at least one element (M) selected from group 2A elements, group 3A elements and group 4A elements of the periodic table. Preferably, the sum of aluminum and element (M) is at least 30 atomic % based on the amount of total metal elements in the silica glass, and the atomic ratio of aluminum to element (M)
is in the range of 0.05 to 20. This silica glass has a high purity, substantially no bubbles inside the glass and cracks, and exhibiting enhanced resistance to a halogenated gas and/or a plasma thereof while good process ability and machinability, and reduced dusting property are kept, and the silica glass is suitable for members of a semiconductor production apparatus or liquid crystal display production apparatus using a halogenated gas and/or its plasma. Tatsuhiro Sato and the others of Herseus Quarzglas GmbH & Co. KG [3-6] have studied a mixed quartz powders contains quartz powders and two or more types of doping element in an amount of from 0.1 to 20 mass %. The aforementioned doped elements include a first dope element selected from the group consisting of N, C and F, and a second dope element selected from the group consisting of Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, Hf, the lanthanides and the actinides. Al as well as the aforementioned doped elements is preferably included in the mixed quartz powders. The quartz glass produced by using the mixed powders are effective as jig materials for the plasma reactions which are used in semiconductor production in that they have excellent plasma erosion resistance, and especially erosion resistance in respect of F-based plasma gas. Juergen Weber and the others of Shin-Etsu Quartz Products Co., Ltd. [7] have investigated an ideal quartz glass for a wafer holder for application in an etching environment, which is characterised both by high purity and also a high dry etching resistance. This quartz glass is doped with nitrogen, at least in a region near the surface, and has an average content of metastable hydroxy groups of less than 30 wt. ppm. The fictive temperature is less than 1250°C and the viscosity at a temperature of 1200 °C is at least $10^{13}$ dPa- s. Jie Yuan and the others of Applied Materials, INC. [8] have carried out the research for fabricating doped quartz component such as a yttrium doped quartz ring configured to support a substrate, a yttrium and aluminum doped cover ring, and a yttrium, aluminum and nitrogen containing cover ring. These doped quartz components are suitable for using in components exposed to a corrosive plasma environment, thereby improving the service lifetime of the chamber component, while reducing maintenance and manufacturing cost.

Despite there have been a lot of researches on highly durable silica glass and some pivotal issues such as “the influence of the method” and “species and concentration of dopants” were solved, the doping mechanism of mixed quartz powders and doped silica glass are still unclear. The team also conducted a study of this kind of durability quartz glass materials, using the method of liquid doping quartz powders to prepare the mixed quartz powders, and then the doped quartz glass was made by vacuum melting process. The doping method can evenly distribute the doped elements, and is suitable for the preparation of block quartz glass. Through a large number of experiments, it was found that the La/Al co-doped quartz powders were prepared by doping 1% La$_2$O$_3$ and Al$_2$O$_3$ in quartz powders, and the corrosion resistance of La/Al was greatly improved by vacuum melting into quartz glass. However, in the preparation process, it is found that the degree of decomposition of the salt compounds doped with oxides, the doping of oxide in the surface of quartz powders, such as the control of the occurrence state of the surface of the quartz powders, will directly affect the internal quality of the subsequent fused silica glass such as air bubble, impurity point defects, and the high temperature viscosity can't be clarified due to the melting system, the doping uniformity depends completely on the uniformity of the doped material. According to the data query, the doping mechanism of this kind of quartz glass is not discussed at home and abroad, especially the occurrence state of doping elements in the doped quartz powders are not reported, so it is difficult to guide the improvement of doping technology and improve the durability of quartz glass. Therefore, the La/Al co-doped quartz powders were prepared by solid-liquid doping method, and the existing state of doping elements in quartz powders were studied to optimize the doping process.

2. Experimental

2.1. Preparation of La/Al Co-doped Quartz Powders

The La/Al co-doped quartz powders were prepared by solid-liquid doping method with high purity chemicals quartz powders (99.99% purity grade, and particle sizes between 60 and 100 mesh), lanthanum nitrate (La(NO$_3$)$_3$$\cdot$6H$_2$O), aluminum hydroxide (Al(OH)$_3$), deionized water and pure nitric
acid. Firstly, the 80g lanthanum nitrate and 220g aluminium hydroxide were dissolved in the mixed solution with 100ml nitric acid and 300ml deionized water, and the desired doping solution was obtained. Then the above mixed solution mainly containing lanthanum and aluminium were added in the 3000g high purity quartz powders, which were mixed in the “Y-type” mixer for about 8 hours (20 rpm/min rotating speed, and Positive inversion every 10 minutes to ensure the uniform distribution of the doped raw materials). Then the mixed quartz powders were taken in the quartz crucible and kept in a high temperature electrical furnace sintering at temperature 650 °C and 1000 °C for about 5 hours, and the La/Al co-doped quartz powders mixture were obtained. Finally, in order to verify the quality of the doped compound, the durability quartz glass was melted at temperature 1850 °C for about 2 hours under the vacuum conditions. This process is depicted as block diagram in Fig. 1.

2.2. Characterization of Performance

The phase analysis of undoped high purity quartz powder and La/Al co-doped quartz powder samples were carried out by using D8 ADVANCE X-ray diffraction (XRD) of German BRUKER company (Cu Kα ray, λ =0.15406 nm and the scanning range of 2θ angle is 15°-85°). The surface morphology of the samples was tested by using Quanta 200 FEG emission scanning electron microscope (ESEM) of American FEI electronics Ltd, and the element analysis of the sample was employed by using X-ray energy dispersive spectrometer (EDX) (the samples were sprayed with gold for 4 min). The DSC-TG curve of La/Al co-doped quartz powders was determined by using STA 449 F3 thermal analyzer of Netzsch (the air atmosphere and 10 °C/min heating rate). The DTA - TG curves of lanthanum nitrate and aluminium hydroxide were determined by using CRY-2P differential thermal analyzer (DTA) and ZRY-2P thermogravimetric analyzer (TG) of Shanghai precision science instruments co., ltd (the air atmosphere and 10 °C/min heating rate). The micro bubbles of the doped quartz glass were observed by using polarizing microscope of Leits.

3. Results and Discussions

3.1. Thermal Analysis of Doped Raw Materials and La/Al Co-doped Quartz Powders

Because the non-calcined La/Al Co-doped quartz powders contains a lot of water, nitrate and hydroxide before, it needs to dehydrate, decompose into doped oxide and attach to quartz powders particles by sintering at high temperature. Fig. 2 is DSC-TG curve of non-calcined La/Al doped quartz powders of containing 1% each of La2O3 and Al2O3. Fig. 3 is DSC-TG curve of undoped high-purity quartz powders. Fig. 2 and Fig. 3 show that the characteristic peak at 575.5°C represents α-quartz converted to β-quartz, the characteristic peak at 1336 °C represents α-tridymite converted to α-christobalite, but the characteristic peak of dehydration and decomposition of doped salts doesn’t appeared. Considering the comprehensive analysis, it is mainly because doped oxide content is too low (only 1%), and the characteristic peak of doped oxide is negligible comparing with high purity quartz
power, so the characteristic peak of dehydration and decomposition of doped salts cannot exert on the thermal analysis curve.

Based on the above reasons, in order to accurately master the key reaction process such as dehydration and decomposition of the salt compounds, it needs to test the DTA-TG thermal analysis of each doped raw material by holding its dehydration and decomposition temperature. Fig. 4 and Fig. 5 are DTA-TG curves of Al(OH)₃ and La(NO₃)₃·6H₂O, respectively. From the diagram, the decomposition temperature of Al(OH)₃ is about 300 °C, the dehydration temperature of La(NO₃)₃·6H₂O is about 250 °C, and the decomposition of nitrate radical begin at 380 °C until 650 °C and completely formed La₂O₃, which is consistent with the thermal decomposition of lanthanum nitrate by S. R. WU [9]. Therefore, in order to ensure the complete decomposition of the salt compounds doped with oxides, the mixture of lanthanum and aluminium must keep at 650 °C for more than 5 h.

3.2. X-ray Diffraction (XRD) Analysis

Fig. 6 is XRD patterns of La/Al co-doped quartz powders under different sintering temperature and undoped quartz powders. Because the content of doped La₂O₃ and Al₂O₃ is only 1 % each of, even if a new phase is formed in the La/Al co-doped quartz powders, the diffraction peak of the XRD is very weak. Therefore, Fig. 6 is the square root of the diffraction peak intensity, in order to weaken the diffraction peak intensity of high purity quartz powers and obviously enhance the diffraction peak intensity of La/Al co-doped quartz powders. Fig. 6(a) and (b) show that the diffraction peaks are basically the same between La/Al co-doped quartz powders sintering at temperature 650 °C and
undoped high purity quartz powders by comparing with the standard card, which indicates that there are no other diffraction peaks of La/Al co-doped quartz powders sintering at temperature 650 °C beside the diffraction peaks of \( \alpha \)-christobalite. Through the analysis, it may not produce new phases in the condition, or create some new phases but not show on the diagram due to the diffraction intensity is too weak. Fig. 6 shows that there are some of the other diffraction peaks beside the diffraction peaks of \( \alpha \)-christobalite for La/Al co-doped quartz powders sintering at temperature 1000 °C. By comparing with the standard card, the new and weak diffraction peaks are La(AlO\(_3\)).

3.3. Scanning Electron Microscopy (SEM) Analysis
Fig. 7(a) and (b) are SEM backscattered electron image photographs of La/Al co-doped and undoped quartz powders, respectively. According to the relationship between the color of backscattered electron image and the size of doped atomic number, by comparing Fig. 7(a) and (b) it shows that the white parts are doped oxide in Fig. 7(a), and the doped oxide is uniformly attached to the surface of the particles of high-purity quartz powders, which fully validates it can ensure the uniform distribution of doped oxide in the high-purity quartz powders by solid-liquid doping method, and improve the consistency and stability of the doped quartz glass performance.

Fig. 8(a) and (b) are SEM backscattered electron image photographs and line scan element distribution of La/Al co-doped quartz powders calcined at 650 °C, respectively. As seen in Fig. 8, the white parts are doped oxide in Fig. 8(a), and there is a clear reaction fusion interface between the high-purity quartz powders particles. As shown in Fig. 8(b), the elements of Si, La, Al and other elements are uniformly distributed, which also shows that there is a certain degree of communion between La/Al doping oxide and quartz powders particles.

Fig. 9(a) and (b) are energy spectral analysis curves of the surface points 1 and 2 of the doped quartz powders particles in Fig. 8 (b) , respectively. It is shown from the graph that position 2 contains both doping elements of La, Al, and also Si, which is consistent with the distribution of line scan elements in Fig. 8(b). It further validates the existence of a certain degree of communion between La/Al doping oxide at temperature 650 °C and quartz powders particles, and verifies the conjecture that it create some new phases but the diffraction peak intensity too weak to appear in Fig. 6(b).
Figure 7. SEM backscattered electron image photographs of La/Al co-doped quartz powders (a) and undoped quartz powders (b).

Figure 8. SEM backscattered electron image photographs (a) and line scan element distribution (b) of La/Al co-doped quartz powders calcined at 650 °C.

Figure 9. EDS spectrum of the position 1 and 2 in Fig. 8(b).

Fig. 10(a) and (b) are SEM backscattered electron image photographs and line scan element distribution of La/Al co-doped quartz powders calcined at 1000 °C, respectively. As seen in Fig. 10, the white parts are doped oxide in Fig. 10(a), and there is a clear reaction fusion interface between the high-purity quartz powders particles. According to the Fig. 10(b), the elements of Si, La, Al and other
elements are uniformly distributed, which also shows that there is a certain degree of communion between La/Al doping oxide and quartz powders particles. But there is a serious exfoliation phenomenon of La/Al co-doped quartz powders calcined at 1000 °C, which is similar to having a violent reaction of doped oxide on the surface of quartz powders particles, and this kind of exfoliation phenomenon is the main cause of bubbles occur in the quartz glass by melting the La/Al co-doped quartz powders calcined at 1000 °C.

Fig. 11(a) and (b) are energy spectral analysis curves of the surface points 1 and 2 of the doped quartz powders particles in Fig. 10 (b), respectively. It is shown from the graph that position 2 contains both doping elements of La, Al, and also Si, which is consistent with the distribution of line scan elements in Fig. 10(b). It further validates the existence of a certain degree of communion between La/Al doping oxide at temperature 1000 °C and quartz powders particles. This result is consistent with the diffraction peaks of the relatively weak for La(AlO_3) new phase in Fig. 6(c), which shows that the weak diffraction peaks of new phase is further enhanced at temperature 1000 °C.

Fig. 12(a) and (b) are doped quartz glass melted at temperature 1850 °C for about 2 hours under the vacuum conditions using La/Al co-doped quartz powders calcined at 650 °C and 1000 °C under, respectively. It can be seen from the Fig. 12 that the doped quartz glass by melting La/Al co-doped quartz powders calcined at 650 °C is transparent and no bubbles, but the doped quartz glass by melting
La/Al co-doped quartz powders calcined at 1000 °C is opaque due to the glass contains a large number of tiny bubbles. Fig. 13 is Polarized optical microscopy of doped quartz glass melted by La/Al co-doped quartz powders calcined at 1000 °C. According to Fig. 13, the micro bubbles of the doped quartz glass by melting La/Al co-doped quartz powders calcined at 1000 °C is about 5 ~ 25 μm, and these bubbles are the main reasons for opaque.

4. conclusion

In this paper, the La/Al co-doped quartz powders were prepared by solid-liquid doping method, using lanthanum nitrate and aluminum hydroxide as doped raw materials, and the durability quartz glass was prepared by melting the La/Al co-doped quartz powders at temperature 1850 °C under the vacuum conditions. Through the performance characterization of La/Al co-doped quartz powders and doped quartz glass, the following conclusions are drawn:

1. It can prepare the La/Al co-doped quartz powders with uniform distribution of doped oxide in the high-purity quartz powders by solid-liquid doping method.

2. The La/Al co-doped quartz powders calcined at 650 °C can completely decompose the doped salt compounds. And there is a certain degree of fusion between La/Al oxide and quartz powders particles, which can effectively improve the internal quality and corrosion resistance of doped quartz glass. When the calcination temperature reaches at 1000 °C, the fusion ability of La/Al oxide and quartz powders particles is more intensive. But there is a serious exfoliation phenomenon of La/Al co-doped quartz powders calcined at 1000 °C, which is the main cause of bubbles occur in the doped quartz glass and will affect corrosion durability of the doped quartz glass.
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