Effect of CaF₂ on fluorocarbon plasma resistance and thermal properties of CaO-Al₂O₃-SiO₂ glasses

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ABSTRACT

The effect of CaF₂ addition on plasma resistance and thermal properties of CaO-Al₂O₃-SiO₂ (CAS) glasses was investigated. The amount of SiO₂ and Al₂O₃ was fixed to 42.9 and 9.1 (in mol %), respectively, while total amount of CaO and CaF₂ was 48 mol% and the ratios of CaO:CaF₂ were changed from 10:1 to 8:2.

As the amount of CaF₂ of CAS glass increased, CF₄/O₂/Ar plasma etch rate of glass decreased proportionally. In case of sample with CaO:CaF₂ = 8:2, its etch rate had 5.04 ± 0.14 nm/min, which was about 20 times lower than that of quartz glass and was improved by more than 25% compared to the glass without CaF₂. All glass samples maintained the initial surface and roughness even after plasma etching. In addition, the glass transition (T_g), crystallization (T_c), and the first melting temperature (T_m) temperatures decreased with the amount of increased CaF₂. F⁻ ion in CAS glasses not only enhances the plasma resistance but also facilitates glass melting and forming operations.

1. Introduction

In the manufacture of various semiconductors devices such as 3D NAND flash, FinFET, and devices of less than or equal to 10 nm, plasma etching process is applied [1,2]. As the nano-process is applied, the etching difficulty increases, and oxide ceramics such as alumina (Al₂O₃) and yttria (Y₂O₃) that show corrosion resistance are usually used for the internal components of the semiconductor process chamber as exposed to a high-density plasma environment [3]. Kim et al. [4] reported that as a polycrystalline material is exposed to a high-density plasma environment that uses fluorinated gas over a long period, the particles fall off due to local erosion, and, accordingly, the probability of contaminated particles may increase. This produces defects in semiconductor devices and has adverse effects on the production yield of semiconductors.

In previous the plasma-resistant glasses (PRG) studies [5–9], they confirmed that the resistance to plasma etching improves as the metal fluoride contains more oxides of high boiling point (T_b). In addition, it has been reported that glass is uniformly etched due to the amorphous structure, thus inhibiting the occurrence of particle contamination. Lee et al. [5] studied R₂ O₃-SiO₂-Al₂O₃ (R: Gd, La, Y) glasses and reported that as they are exposed to plasma, the addition of rare-earth element oxides to form a fluorine compound with a high T_b on the glass surface contributes to a low etching rate.

According to S. HM et al. [10], many different processes take place during the plasma polymerization such as cross-linking and polymerization. So, polymers based on carbon and fluorine element exist as various forms unbound with glass on the surface. The higher T_b showed the lower plasma etching rate. CAS glass had the best plasma resistance in their study. Na et al. [9] reported that the etching rate decreased as the CaO content increased in CAS glass. However, in their plasma resistant glass experiment had some problems as crystallization and glass stability and high melt temperatures.

Against the background of the above study, we considered a method to enhance the plasma resistance and melting workability of CAS glass. It is known that addition of F⁻ ion to the oxide glass lowers its viscosity at the melting as flux. It is also expected that the plasma resistant properties in CAS glass could be improved by adding a CaF₂ in glass. CaF₂ with high T_b could prevent chemical reaction between CF₄ plasma and CaF₂ in glass. We tried to verify the practical effect of introducing CaF₂ into CAS glass, which is expected to improve the plasma resistance and melting of CAS glass at the same time.

2. Experimental

2.1. Glass fabrication

The composition of the base glass was 42.9SiO₂ 9.1Al₂O₃ (48-x)CaO-xCaF₂ (in mol%) (CASF) and the glass was fabricated by melt-quench method. The ratios of CaO:CaF₂ were changed from 10:0 to 8:2 (in mol%) as shown in Table 1. And this is a nominal composition.
The batched powders were uniformly mixed using a 3D mixer for 3 h. The mixed materials were placed into a platinum crucible and glass melting was performed using an electric heating furnace at 1400°C for 2 h. The melts were poured into a graphite plate, it was maintained for 2 h at 50°C higher temperature than the glass transition temperature to remove the internal stress and then was slowly cooled at room temperature. The crystal phase of the fabricated glass was measured with an X-ray diffractometer (DMAX-2500, Rigaku, Japan). Figure 1 shows the appearance and X-ray diffraction patterns of glass samples. As can be seen in the figure, it shows a typical glass appearance and amorphous diffraction patterns.

**2.2. Thermal properties**

Thermal expansion coefficient ($\alpha_{1500-300}$) and glass transition temperature ($T_g$) were measured at a heating rate of 10°C/min under a N$_2$-4 wt% H$_2$ mixture ambiance and carbon rod using a dilatometer (DIL 402 C, NETZSCH, Germany). The crystallization ($T_c$) and the first melting ($T_m$) temperatures were measured at a heating rate of 10°C/min under an argon ambiance using differential thermal analyzer (DTA, Labsys Evo, SETARAM, France).

**2.3. Plasma etching**

For the plasma etching test, glass samples of 10 x 10 x 2 (mm) were mirror-polished on both sides and the glass side was masked with 5 layers of ketone tape, except for the side to be exposed to the plasma of 2 mm width. The plasma etching test used a polymer etcher (TCP-9400DFM, Lam Research, USA). The gas proportion based on fluorocarbon was designed to form more fluorine radicals by adding oxygen and the detailed conditions are shown in Table 2. The test was conducted for 1 h and excessive etching was prevented by pausing the process for 5 min after every 10 min of etching. In addition, to compare the etching rate with the reference materials, the test was conducted by sintered alumina (AES-11, Sumitomo Chemical Co., Japan), single crystal sapphire having a (0001) plane (Sapphire Tech., Korea), and quartz glasses (N Series, Tosoh, Japan) together on the wafers.

**2.4. Plasma resistance**

Plasma resistance is expressed by the etching rate and roughness. The etching rate was calculated by measuring the step difference between the etched and non-etched portions of the glass using α-step (Surfcomm, ET3000, Kosaka Laboratory Ltd., Japan).

A surface roughness was measured using roughness meter (Surfcomm, SJ-411, Mitutoyo, Japan). In addition, the microstructures were observed using scanning electron microscopy (JEOL, JSM-6701 F, Japan) to confirm the surface reactions, and the component analysis was performed using energy dispersive spectroscopy (EDS, AZtecOne, Oxford Instruments, UK).

**Table 1.** Chemical compositions of the glass samples with different CaF$_2$ content (in mol%).

| Glass code | SiO$_2$ | Al$_2$O$_3$ | CaO | CaF$_2$ | CaO:CaF$_2$ |
|------------|---------|-------------|-----|---------|--------------|
| G1000      | 42.9    | 9.1         | 48  | -       | 10.0         |
| G9505      | 42.9    | 9.1         | 45.6| 2.4     | 9.0:5.5      |
| G9010      | 42.9    | 9.1         | 43.2| 4.8     | 9.1          |
| G8515      | 42.9    | 9.1         | 40.8| 7.2     | 8.5:1.5      |
| G8020      | 42.9    | 9.1         | 38.4| 9.6     | 8.2          |

**Table 2.** Conditions of the high-density plasma etch test.

| Parameter | Condition | |
|-----------|-----------|---|
| RF power, W | 600       |   |
| PF power (bias), W | 200      |   |
| CS$_2$, SCCM | 30        |   |
| Ar, SCCM   | 5         |   |
| O$_2$, SCCM | 10        |   |
| Pressure, mTorr | 30        |   |
| Time, min  | 60        |   |
3. Results and discussion

Because of the reactions between the etching materials (glasses and references) and CF$_4$ plasma, reaction products are formed on the surface. In addition, a fall-off reaction (etching) occurs on a substrate because of physical sputtering [11].

**Figure 2** shows the changes in etching rate by plasma based on the addition and content of CaF$_2$ in the glass composition. The etching rate showed a decreasing trend as CaO was substituted with CaF$_2$ in the composition. This meant that the plasma resistance improved. In particular, as the CaF$_2$ content increased to 9.6 mol%, the etching rate was 5.04 ± 0.14 nm/min, which was the lowest; compared to the quartz glass, sintered alumina, and sapphire, it was at 4%, 11%, and 26% levels, respectively. When the CaF$_2$ content was 4.8 mol% or higher in CAS glasses, the etching rate was decreased. This can be made statistically clearer. Two sample-t tests were performed on the etching rate between the glasses with a CaF$_2$ content of 2.4 mol% and 4.8 mol%. The null hypothesis assumes that the average of the two etching rates is the same, and the alternative hypothesis assumes that the etching rate of glass with a CaF$_2$ content of 2.4 mol% is fast. The obtained p-value is 0.002, which makes it possible to adopt the null hypothesis. In other words, there is no statistical difference in the etching rate by plasma gas for glass with 7.2 mol% CaF$_2$ than glass with 4.8 mol%. In other words, it means that the glass containing 7.2 mol% of CaF$_2$ did not improve plasma durability than the glass containing 4.8 mol% of CaF$_2$. That is, in CAS glass, it is effective to replace CaO with CaF$_2$ in order to enhance the durability of plasma gas, but it could be confirmed that there is a limit that improves beyond a certain amount.

Glass containing metal oxides capable of forming fluorine compounds with high $T_b$ during CF$_4$ plasma etching was found to have high plasma resistance [5–8]. Table 3 shows the $T_b$ of a fluorine compound for the reference materials and glass composition elements [12]. $T_b$ of AlF$_3$ and CaF$_2$ was 1275°C and 2533°C, respectively, and these compounds exist as stable solids at room temperature, so even if they are fluorinated on the material surface, their volatility is very low and they are only physically etched only by accelerated Ar$^+$ ions. In addition, when CaF$_2$ is added to CAS glass, fluorine in the glass can be expected to inhibit the chemical reaction between the metal in the glass and the fluorine radicals in the CF$_4$ plasma. Therefore, the decrease in the etch rate when CaF$_2$ is added to CAS glass is believed to be due to the high plasma resistance of metal oxides constituting the glass and the effect of inhibiting reaction with CF$_4$ plasma as fluorine participates in the glass surface structure.

The changes in surface roughness of every glass before and after plasma etching were compared with those of the three reference materials, as shown in Figure 3. After etching, the surface roughness of the quartz glass and sintered alumina increased 26.1% and 24.2%, respectively. By contrast, the sapphire and CASF glasses maintained very low surface roughness values of $R_a = 0.014 \mu m$ or less, even after etching. This meant that uniform etching was accomplished as plasma etching was performed.

**Figure 2.** Etch rate of the glass samples as a function of the molar ratio of [CaF$_2$]/([CaF$_2$]+[CaO]) compared with polycrystalline alumina, single-crystalline sapphire and quartz glass.

| Fluorine compound | Boiling temperature ($T_b$, °C) |
|-------------------|-------------------------------|
| SiF$_4$           | 86                            |
| AlF$_3$           | 1275                          |
| CaF$_2$           | 2533                          |

**Table 3.** Boiling temperature ($T_b$) of fluorine compound formed by CF$_4$ plasma reaction [12].
provide points at which the erosion can be focused, it is thought that contaminated particles will be induced during the etching process, contributing to structural defects. By contrast, the sapphire of a single crystal and the CASF glasses without pores and grain boundaries can prevent differences in etching rate by in certain directions and local etching by the interface and pores. After the etching of sapphire and CASF glasses, the microstructure was not different from the initial state so that it could not be distinguished by an electron microscope. There is no difference in the surface microstructure before and after the CF₄ plasma etching is consistent with the change in surface roughness (Figure 3). Therefore, it was determined that maintaining a low surface roughness and uniform microstructure.

The change in the surface composition of the reference materials and the CASF glasses after plasma etching can be confirmed by the EDS results in Figure 4 and Table 4. All specimens were coated with platinum for specific detection and EDS data were 100% normalized. The quantitative values of the EDS analysis are not completely reliable, but it was checked for trends. In etching process, the surface was accompanied by a chemical reaction with the fluorine component. Fluorine and carbon were detected along with other components. But it is not obvious if they remain bond to the glass components or just exist as polymer on the surface.

**Figure 3.** Surface roughness (Rₐ) of all samples before and after plasma etching.

**Figure 4.** Microstructure and element analysis, which were before and after plasma etching: (a) Quartz glass, (b) Sapphire, (c) Sintered alumina, (d) G1000, (e) G8020. Of the glass samples, the G1000 had the highest etch rate and the G8020 had the lowest etch rate.
surface. Choi et al. [8] reported that fluorine radicals in plasma and R, Si and Al contents formed of oxide glasses were partially bonded on the surface as a result of XPS analysis. Furthermore, it was roughly suggested that CF₄ plasma sintered ceramics and glasses react with the above formula [7,13,14].

\[
\text{SiO}_2 + \text{CF}_4 \rightarrow \text{SiF}_4 + \text{CO}_2 \quad (1)
\]

\[
\text{Al}_2\text{O}_3 + 3\text{CF}_4 \rightarrow 2\text{AlF}_3 + 3\text{CO} + 3\text{F}_2 \quad (2)
\]

\[
\text{CaO} + \text{CF}_4 \rightarrow \text{CaF}_2 + \text{CO}_2 \quad (3)
\]

Figure 5 shows the glass transition temperature (T_g) in terms of its relationship to the [CaF₂]/[(CaF₂) + (CaO)] contents. For all glass species, as the CaF₂ content increased, not only T_g but also T_c decreased, which can be confirmed in Figure 7. This is because fluorine atoms exist in a single valence state in an entirely oxide network, breaking oxygen bridging of glass. Furthermore, this phenomenon can also be confirmed in the same paper [15].

Glass stability, a term that refers to the ability of glass to resist crystallization as heated, can be evaluated using the correlations between characteristic temperatures such as T_g, T_c, and T_r. Hrubý parameter (K_H), which is one of the glass stability indices, is shown in the following equation [16].

\[
K_H = \frac{T_c - T_g}{T_c - T_r}
\]

Because an inverse linear relationship exists between the parameter K_H and the critical cooling rate, the stability of glass increases as K_H increases, and this can serve as a yardstick for the glass forming ability (GFA) of molten material as cooling [17,18]. All glass K_H and specific temperature values are listed in Table 5. As CaO was substituted with CaF₂, the stability of glass increased and reached the maximum at CaF₂ = 7.2 mol %. However, as the CaF₂ content was 9.6 mol %, K_H = 2.18, and the GFA was the lowest among the glasses containing CaF₂.

Table 5. Glass transition temperature (T_g), crystallization temperature (T_r), first melting temperature (T_m), and the value of K_H for glass samples with different CaF₂ content.

| Glass code | T_g(°C) | T_c(°C) | T_r(°C) | K_H |
|------------|---------|---------|---------|-----|
| G1000      | 794.0   | 1103.7  | 1283.7  | 1.72|
| G9505      | 748.5   | 1086.3  | 1196.9  | 3.05|
| G9401      | 724.0   | 1086.2  | 1199.8  | 3.19|
| G8515      | 709.8   | 1085.2  | 1200.0  | 3.27|
| G8020      | 688.4   | 1041.0  | 1202.7  | 2.18|

Figure 5. The glass transition temperature (T_g) from dilatometer of the glass as a function of the molar ratio of [CaF₂] / ([CaF₂] + [CaO]).

Figure 6. Coefficient of thermal expansion (α) of the glass samples as a function of the molar ratio of [CaF₂] / ([CaF₂] + [CaO]). (α 100–300 °C).
systematic changes in $\alpha$ by the extent of fluorine substitution in the composition did not appear.

Figure 7 illustrates the DTA profile of glass based on compositional change. The crystallization temperature ($T_c$) decreased as CaO was substituted with CaF$_2$. The first melting temperature ($T_m$) decreased from 1283°C to approximately 1200°C as CaO was substituted with CaF$_2$. In the four glasses containing CaF$_2$, $T_m$ was similar at about 1200°C regardless of the amount of CaF$_2$ added.

According to a study by Brauer et al., which studied bioactive glasses (SiO$_2$-P2O$_5$-CaO-Na2O-CaF$_2$), it was confirmed that fluorine inhibited spontaneous crystallization [19]. In the CAS glass of this study, as the CaF$_2$ content increases, the crystallization temperature decreases and its peak intensity decreases. They also confirmed that even when fluorine was added to the glass, the average oxygen bridging per network formation remained constant, but the phenomenon of a decrease in temperature related to the glass viscosity with fluorine addition was related to weak ionic cross-linking between the modifier cations and non-crosslinked oxygen. And they thought that CaF$^+$ species with weaker ionic cross-links than Ca$^{2+}$ ions were formed. Therefore, it is reckoned that the decrease in the transition temperature due to the increase of CaF$_2$ content in this study is due to similar reasons. However, for more accurate glass structure analysis, we think that a study on only a separate glass structure is necessary. R. Casasola et al. [20] reported that the addition of fluorine to the oxide glass increase in glass forming ability and, consequently, cause a decrease in the critical cooling rate. This is a similar result to the lower $T_m$ by adding CaF$_2$ to CAS glass in this study. Therefore, it was confirmed that the addition of CaF$_2$ to CAS glass stabilizes and facilitates melting of the glass at high temperatures and has the effect of lowering the viscosity of the glass at low temperatures.

4. Conclusions

This study verified the effect of CaF$_2$ on improving CF$_4$ plasma resistance and decreasing temperatures related to viscosity of 42.9SiO$_2$ 9.1Al$_2$O$_3$ (48-x)CaO-xCaF$_2$ (in mol%) glasses. The etching rate of glass was decreased to 5.04 nm/min by increasing the content of CaF$_2$. The surface microstructure and roughness of the glass were not significantly different after plasma etching. The plasma resistant enhancement when CaF$_2$ is added to CAS glass is thought to be due to the high plasma resistance of the metal oxides constituting the glass and the effect of inhibiting the reaction with CF$_4$ plasma as fluorine participates in the glass surface structure. The addition of CaF$_2$ decreases the glass transition temperature and the degree of crystallization and increases glass stability of CAS glasses.

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Disclosure statement

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