

## Reduction of Water in Inorganic SOG by Plasma Treatment

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**Abstract** The water absorption characteristics of an inorganic SOG is investigated. Absorbed water constitutes a higher percentage of the water in 450°C-baked SOG. It can be removed by evacuation and is not harmful to poisoned via <sup>1)</sup>. Chemisorbed water, on the other hand, can be harmful to the poisoned via because it can not be removed completely by heating below 450°C and evolves by the exposure of SOG to the Al sputtering plasma. A plasma treatment using a parallel-electrode reactor with C susceptor is found to be very effective in reducing both the absorbed water and the chemisorbed water.

### Introduction

Inorganic spin-on-glass (SOG) has been the most widely used dielectric for ULSI multilevel interconnections because of its good planarizing characteristics and its low processing cost. However, a serious problem with SOG has been that the water evolving from it degrades the Al alloy in vias, resulting in a high contact resistance or open circuit between the upper and lower level metal lines (poisoned via <sup>1)</sup>). This problem becomes more severe as via size is reduced. Thus, the reduction of water in SOG films is indispensable for future SOG submicron interconnection applications. This paper describes the water absorption characteristics of SOG during ULSI fabrication processes and a method to reduce absorbed and chemisorbed water.

### Experimental

Water retained in SOG exists in three different states: absorbed, physically adsorbed, and chemically adsorbed (chemisorbed). The adsorbed water and

other gases were measured by mass spectrometry (MS); here, the SOGs were heated in a vacuum. The absorbed water, which is removed by the evacuation at room temperature and is not detected by MS, was measured by weight. FTIR and AES were also carried out to study the chemical structure of the SOG.

Baking at 200°C and 450°C, O<sub>2</sub> ashing, and immersion in resist stripper, methanol, and water were carried out to simulate the ULSI fabrication processes. Then the effect of these treatments on the water in SOG was investigated.

Oxygen plasma treatments using a parallel-electrode reactor were also carried out to reduce the water absorption of SOG. The plasma treatment, named reactive glass stabilization (RGS) <sup>2)</sup>, was originally developed to achieve crack-free organic SOG during O<sub>2</sub> ashing. Carbon (C) and SiO<sub>2</sub> susceptors were used in this work. RGS(C) means RGS with C susceptor.

### Result and Discussion

The absorbed water is removed from

the SOG by evacuating at room temperature or by heating in dry ambient. However, the SOG quickly absorbs water again from moisture when it is exposed to the atmosphere after baking.

The effectiveness of RGS(C) in reducing absorbed water was evaluated by weight measurement and compared with the following processes: baking at 450°C, ashing, and RGS(SiO<sub>2</sub>) (Fig.1). Si-O band absorption by IR measurement is also shown in Fig. 1, which indicates the variations of SOG matrix. About an 8 % reduction of the Si-O band was observed in RGS(C)-treated film. Thus the water reduction is actually about 35 % (=43-8). No reduction in Si-O absorption was observed in the other treatments. RGS plasma, which contains many energetic ions, was very effective in removing the absorbed water. On the other hand, ashing plasma which contains less energetic ions removed very little water from the 450°C-baked film. In addition, baking at 450°C reduced the film weight by ~15%. Assuming that the 200°C-baked film contains exactly 35% water by weight, it is concluded that the 200°C+450°C-baked film contains about 20% water.

The adsorbed water in SOG was measured by mass spectrometry. Figure 2 shows water evolved from SOGs which underwent (a) baking, (b) +a plasma treatment, and (c) +the immersion process in series when they were heated in a vacuum. Two peaks at 100°C and 500°C in lines (b) and (c) can be divided at 300°C into the lower physically adsorbed water and the higher chemically adsorbed water. The peaks at 100°C were found only in the films which underwent plasma treatment (RGS or ashing), so the water

may be physically adsorbed on the SOG surface that is distorted by the plasma (plasma damage). Physically adsorbed water, which is removed from SOG by heating below 300°C, can not be the cause of the poisoned via because it is lost during preheating in the vacuum chamber for Al deposition. In the case of line (a) with no plasma process, it is better to consider that the water evolved below 300°C is not the physically adsorbed water but the tail of the chemisorbed water.

The chemisorbed water can be harmful because it evolves from SOG heated above 400°C or exposed to plasmas such as that used in Al alloy sputtering deposition. If only heating is applied, it is necessary to heat the SOG up to 800°C in a vacuum to completely remove the chemisorbed water as shown in Fig. 2. Figure 3 shows FTIR data of SOG films which underwent baking at 200°C, baking at 200°C and 450°C, and baking at 200°C +RGS(C) +baking at 450°C, respectively. The baking at 200°C and 450°C did not remove the Si-OH absorption completely. However, the addition of the RGS(C) between bakings removed the Si-OH absorption almost completely implying that the chemisorbed water detected by mass spectrometry is from the Si-OH bond.

Figure 4 shows the water retention characteristics of the inorganic SOG that underwent various processes, including immersion in water and organic solutions, as measured by mass spectrometry. Plasma processes decreased the Si-OH (chemisorbed water) but increased the physically adsorbed water in general. However, addition of RGS(C) reduced the Si-OH and slightly increased the physically adsorbed water. Note that the

absorbed water evolved from the sample during evacuation at room temperature is not detected using this method.

Addition of RGS(C) removed most of the absorbed water as shown in Fig. 1, and removed most of the chemisorbed water and minimized the new absorption and adsorption of water as shown in Fig. 4. Addition of RGS(SiO<sub>2</sub>) removed the absorbed water but increased significantly the physically adsorbed water.

Figure 5 shows the depth profile of oxygen and carbon in the SOG normalized to the Si concentration. The figure indicates that the carbon atoms incorporated by RGS(C) were bound so tightly to the SOG that baking at 450°C and ashing could not remove them completely. It is thought that the incorporation of the carbon compound results in the water repellency of the SOG film. Some pin holes that reached the Si substrate raised the Si signal, which is the main reason why oxygen concentrations are low in the samples (b) and (c).

The organic SOG is generally water repellent<sup>2)</sup> and it does not admit much water when it is immersed in water. The organic side groups in the siloxane, which is a typical material of the organic SOG, are less ionic and less hydrophilic than -OH groups.

The incorporation of C probably made the inorganic SOG have a large number of organic side groups resulting in water repellency.

## Conclusion

The inorganic SOG film baked at 200°C and 450°C contains water about 20% its weight. Most of this water is absorbed water and a small portion is chemisorbed water. The chemisorbed water can be

harmful to the poisoned via because it can not be removed by pre-heating; it is evolved by heating at a temperature above 300°C or by plasma irradiation in the Al sputtering chamber.

The chemisorbed water is originated from a Si-OH bond and can be removed by addition of RGS(C) between the bakings. RGS(C) can also reduce absorption and physical adsorption of water during immersion in water and organic solutions.

Carbon which is incorporated by RGS(C) plays an important role in making the SOG water repellent.

## Reference

- (1) C. Ching, N. Lam, J. Chu, N. Cox, D. Fraser, J. Bozarth, and B. Mumtord: IEEE V-MIC (1987) 404.
- (2) S. Ito, Y. Homma, E. Sasaki, S. Uchimura, and H. Morishima: J. Electrochem. Soc. **137** (1990) 1212.

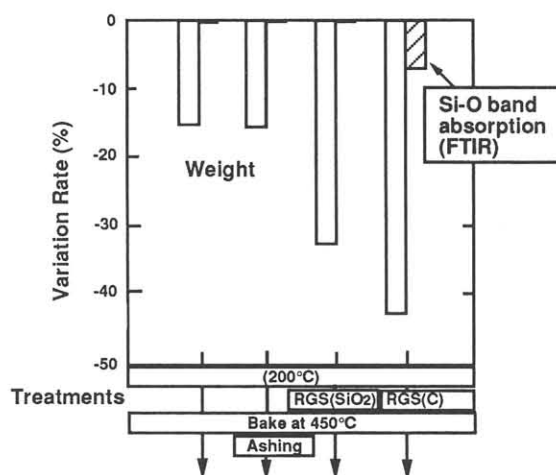


Fig.1 Percentage of weight loss and Si-O band absorption (FTIR) in SOG films after various treatments, with the data of 200°C-baked film as reference

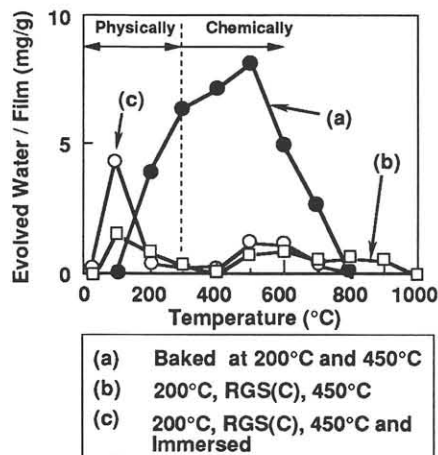


Fig.2 Reduction of water content of SOG film by RGS(C) (Mass Spectrometry)

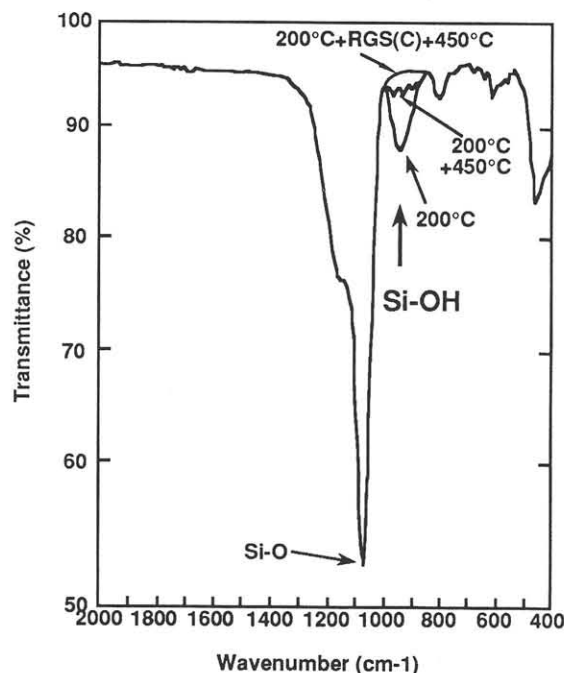


Fig.3 Change in Si-OH band absorption of SOG film by RGS(C) (FTIR)

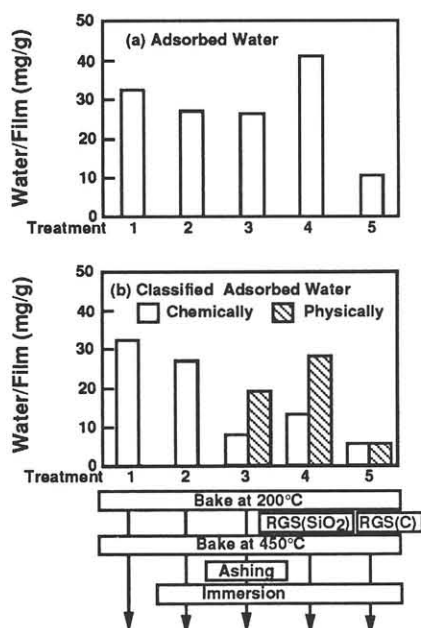


Fig.4 Change in the film components by plasma treatment + immersion in water and other solutions

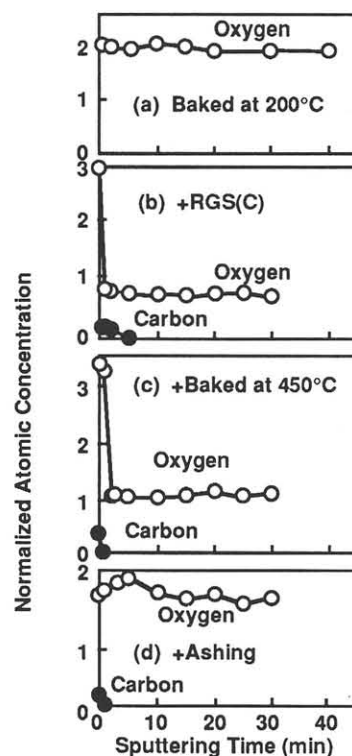


Fig.5 Depth profile of oxygen and carbon concentration normalized to that of Si (AES)