

Studies of Corrosive Outgasses from Via Holes Using Thermal Desorption Spectroscopy

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This work reveals the presence of corrosive outgassing from via holes in multiinterdielectric structures with inorganic spin-on-glass (SOG) films by using thermal desorption spectroscopy. Main species of the corrosive outgassing are found to be H₂O, NH₃ and HF. The amount of NH₃ desorption reaches to 5-10% of water desorption. The desorption of H₂O and NH₃ results from occlusion of both species into the SOG film through the via holes.

1. Introduction

Multilevel metalization is a key technology of the down-scaling of current VLSI devices. It requires planarization technology of interdielectric films. Almost all of the films to achieve the planarization have been reported to provide a significant quantity of outgassing¹⁾ during fabrication processes, which degrades device reliabilities.²⁻⁴⁾ The outgassing from via holes are also believed to cause the increase in resistances of via holes and aluminum corrosion. The most essential subject for realizing low resistivity and high reliability of via holes is the elimination of outgassing from via holes. Although it has been reported that outgassing species from via holes whose total area is 25% are found to be aluminum compound such as AlF and AlC,⁵⁾ little has been reported for corrosive outgassing.

This work reveals, for the first time, the presence of corrosive outgassing from via holes in multi-interlayer dielectric structures with inorganic spin-on-glass (SOG) films by using thermal desorption spectroscopy (TDS). Main species of the corrosive outgassing are found to be H₂O, NH₃ and HF. Especially, the NH₃ is found to reach to 5-10% of water desorption from the via holes due to occlusion into SOG films. Desorption of AlF and SiF₃ which originate from via-hole processes is also observed. This paper presents the detailed study of corrosive outgassing from via holes.

2. Experimental

Figure 1 shows the schematic structures of the five types of samples used in this study. Plasma CVD silicon oxide (SiH₄ P-SiO) was deposited at 380°C using SiH₄ and N₂O gasses. Inorganic spin-on-glass (SOG) was

spun and cured at 300°C. The phosphorus concentration in the SOG film is 9 weight %. The SOG film was sandwiched between SiH₄ P-SiO layers on the Al layer. In sample B, sub-micron via holes were patterned by reactive ion etching (RIE) with CF₄ and CHF₃ mixture gasses. The occupancy ratio of total via holes to be etched was approximately 9% of the samples.

TDS measurements were employed to study outgassing from the samples. The TDS apparatus and procedure of the measurements were described elsewhere in detail.¹⁾ We compare desorption gasses from sample A and sample B to study outgassing from via holes. The sample heating was controlled by the W/Re thermocouple in the sample stage. Samples are directly heated from the back through a quartz rod with an external infrared lamp. Gas species were detected by a quadrupole mass spectrometer. Secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) were also employed to detect nitrogen and fluorine in the dielectric films, respectively.

3. Results and Discussion

Figure 2 shows TDS spectra of mass numbers of 18, 17 and 16, obtained from sample A (without via holes) and sample B (with via holes). TDS spectra of sample A show that the outgassing is hardly observed. Sample B exhibits much larger amount of desorption gasses than sample A, so that these gasses are almost desorbed from the via holes.

The TDS spectra of the mass number of 18 represent water desorption. It is considered that water is desorbed through the via holes from the SOG film, as discussed later. The spectra of the mass numbers of 17 and 16, obtained from sample B, are different from the spectrum of

the mass number of 18, indicating the additional outgassing other than water. The spectra of the mass numbers of 17 and 16 consist of not only fragment ions of water (OH^+ and O^+) but also other gas species such as NH_3 and CH_4 . The spectra of fragment ions of water can be estimated by multiplying the spectrum of the mass number of 18 by fragment factors of water and hence the spectra of the additional gasses can be separated. Figure 3 shows the estimated spectra of the fragment ions of water and the TDS spectra of mass numbers of 17 and 16. The spectra of the shaded regions represent the desorption of the additional gasses. The spectra of two shaded regions exhibit similar shapes, similar peak temperatures and similar peak intensities. In the spectrum of mass number of 15 the peak was also found to be similar to those of the two spectra but the peak intensity was about 1/10 of that of the mass number of 16. Therefore, the additional gas is considered to be NH_3 because of the consistency with the fragment pattern of NH_3 ($\text{NH}_3^+ : \text{NH}_2^+ : \text{NH}^+ = 1 : 1 : 0.1$). The amount of NH_3 desorption corresponds to 5-10% of water desorption.

In order to study where the NH_3 desorbs from, we examined the individual films which are the components of the via hole's surface. Figure 4 presents the TDS spectra of the mass number of 17 and the fragment ion of water (OH^+), obtained from the individual films of sample B. The shaded regions correspond to NH_3 desorption. A comparison between these spectra shows that significant amounts of NH_3 and H_2O are desorbed from the SOG film. Although the SOG film has been made from materials not including nitrogen, the NH_3 and H_2O from the via holes are desorbed from the SOG film. We measured nitrogen depth profiles in the SOG film using SIMS. Nitrogen was detected in the SOG film. After NH_3 was desorbed from the SOG film, the nitrogen in the SOG film decreased. The SOG film not including nitrogen indeed provides outgassing of NH_3 .

In order to study where nitrogen in the SOG comes from, we examined the SOG film exposed to various ambience. Figure 5 shows the TDS spectra of the SOG film exposed to various environments for 6.5 hours after NH_3 was desorbed by the TDS. The TDS spectrum for the air exposure shows NH_3 redesorption. It is found that the SOG film occludes molecules including nitrogen from the air. N_2 and NH_3 will be candidates for the molecules including nitrogen in the air. Much larger amount of NH_3 redesorption is observed for the film exposed to NH_3 ambient, compared with N_2 ambient. This indicates that N_2 gas, the main constituent of the air, is not absorbed into the SOG film but a very small amount of NH_3 in the air is absorbed into the SOG film. NH_3 desorption from the via holes originates from NH_3 gasses which are occluded from the air through the via holes to the SOG film.

Also, fluoride of other corrosive outgasses was examined using TDS. Figure 6 shows the TDS spectra of mass numbers of 20, 46 and 85 for sample B. The TDS spectra of mass numbers of 20, 46 and 85 represent HF, AlF and

SiF_3 , respectively, as a consequence of considering the combination of elements of the sample's materials and the fluoride's etching gasses. The spectra show at least two desorption peaks for HF and AlF and one desorption peak for SiF_3 . The desorptions of the higher temperature peaks for HF and AlF and the peak for SiF_3 occur simultaneously. The peak intensity of HF is about a quarter of that of NH_3 . Furthermore, the peak intensities of AlF and SiF_3 are only 1/10 of that of HF. All desorption of fluoride are caused by usage of fluoride gasses for etching of via holes. The fluoride in the via holes was confirmed by AES analysis. Figure 7 shows the Auger line profiles of F, Al and Si on cleaved via hole of sample B before and after the fluoride desorption. Fluorine and aluminum are especially observed on the sidewall of the via holes and the amount of those on the sidewall decrease after the fluoride desorption. After the fluoride desorption, the amount of silicon on the side wall increase a little because the dielectric appears on the surface of side wall instead of fluorine and aluminum.

The amount of the outgassing which collodes metals was found to depend on the fabrication environments and processes. The TDS measurement is important to decrease the desorption of collosive gasses from the via holes.

4. Conclusion

We investigated desorption of corrosive outgassing due to formation of via holes. The amounts of corrosive outgassing are found to be in order of H_2O , NH_3 and fluorinate gasses such as HF, AlF and SiF_3 from the largest. Nitrogen in the SOG film is observed by SIMS, though the SOG film has been made from materials not including nitrogen. Fluorine in the via holes is observed on the sidewall using AES. We conclude that the desorption of H_2O and NH_3 from the via holes results from occlusion of those into the SOG film through the via holes from the air. Desorption of fluoride is caused by usage of fluoride gasses for etching of via holes. The study of corrosive outgassing from via holes using TDS will be necessary for improving the reliability of multilevel metalization.

5. Reference

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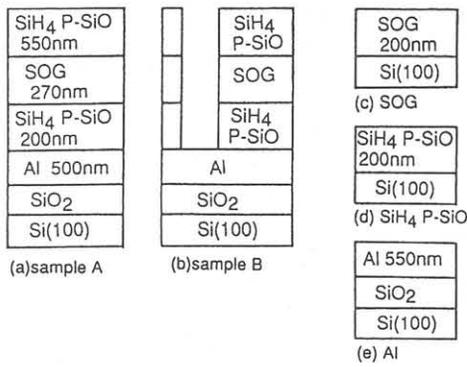


Fig.1 Schematic diagram of TDS samples.

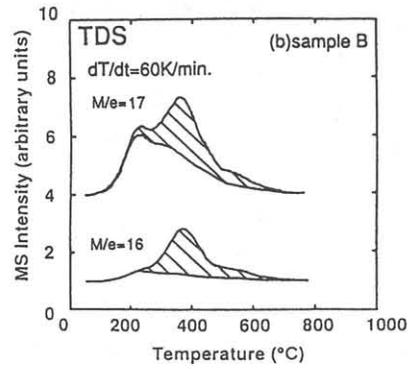


Fig.3 TDS spectra of mass numbers of 17 and 16 for sample B. Shaded regions present NH₃ desorption.

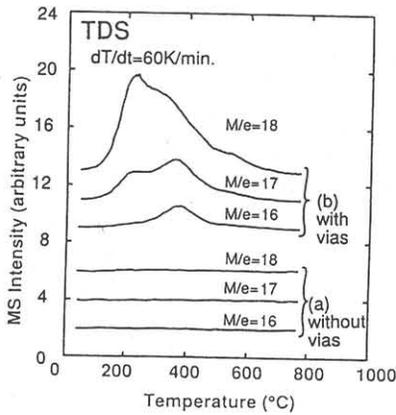


Fig.2 TDS spectra of mass numbers of 18, 17 and 16 for (a) sample A (without via holes) and (b) sample B (with via holes).

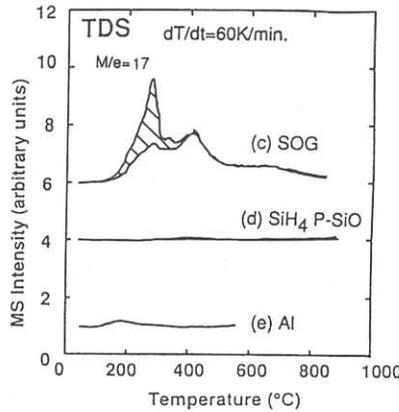


Fig.4 TDS spectra of mass number of 17 for (c) inorganic SOG, (d) SiH₄ P-SiO and (e) Al. Shaded regions present NH₃ desorption.

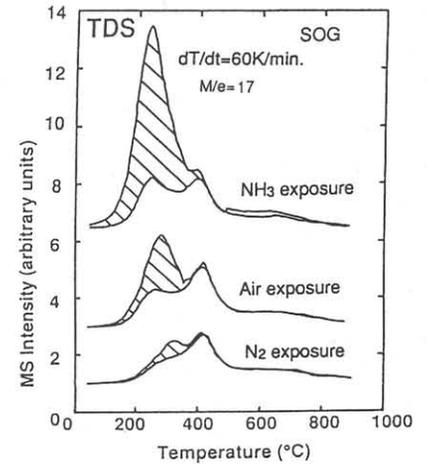


Fig.5 TDS spectra of mass number of 17 for the SOG film exposed to air, N₂ or NH₃ ambient for 6.5 hours after NH₃ desorption. Shaded regions present NH₃ desorption.

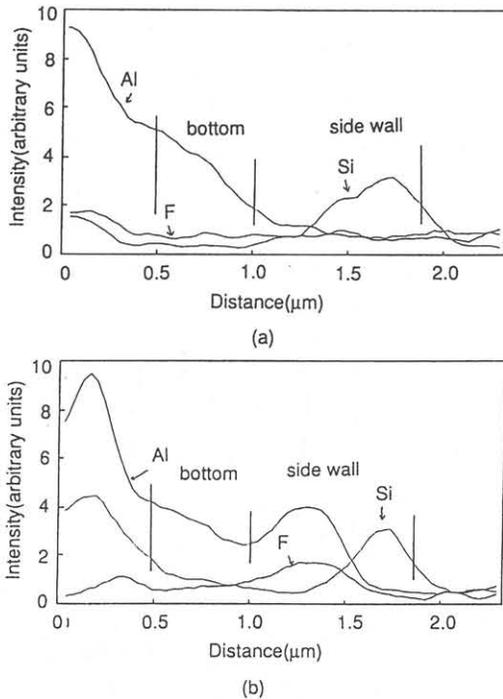


Fig.7 Auger line profiles of F, Al and Si on a cleaved via hole of sample B before (b) and after (a) fluoride desorption.

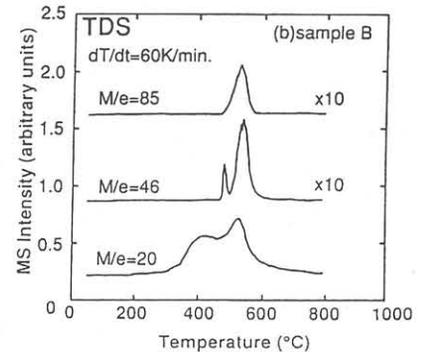


Fig.6 TDS spectra of mass numbers of 20 (HF), 46(AlF) and 85(SiF₃) for sample B.