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 multilayered dielectric 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 outgassing during fabrication processes, which degrades device reliabilities. 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 gassing species from via holes whose total area is 25% are found to be aluminum compound such as AlF and AlC3, 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 gases. 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. 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 NH₃ and CH₄. 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 NH₃ because of the consistency with the fragment pattern of NH₃ (NH₃⁺; NH₂⁺; NH⁺ = 1: 1: 0.1). The amount of NH₃ desorption corresponds to 5-10% of water desorption.

In order to study where the NH₃ 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 NH₃ desorption. A comparison between these spectra shows that significant amounts of NH₃ and H₂O are desorbed from the SOG film. Although the SOG film has been made from materials not including nitrogen, the NH₃ and H₂O 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 NH₃ was desorbed from the SOG film, the nitrogen in the SOG film decreased. The SOG film not including nitrogen indeed provides outgassing of NH₃.

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 NH₃ was desorbed by the TDS. The TDS spectrum for the air exposure shows NH₃ redesorption. It is found that the SOG film occludes molecules including nitrogen from the air. N₂ and NH₃ will be candidates for the molecules including nitrogen in the air. Much larger amount of NH₃ redesorption is observed for the film exposed to NH₃ ambient, compared with N₂ ambient. This indicates that N₂ gas, the main constituent of the air, is not absorbed into the SOG film but a very small amount of NH₃ in the air is absorbed into the SOG film. NH₃ desorption from the via holes originates from NH₃ 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, AIF and SiF₃, 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 AIF and one desorption peak for SiF₃. The desorptions of the higher temperature peaks for HF and AIF and the peak for SiF₃ occur simultaneously. The peak intensity of HF is about a quarter of that of NH₃. Furthermore, the peak intensities of AIF and SiF₃ 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 H₂O, NH₃ and fluorinate gasses such as HF, AIF and SiF₃ 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 H₂O and NH₃ 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

Fig. 1 Schematic diagram of TDS samples.

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

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

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.