The Effect of IPA Adsorption on Thin Oxide

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1. Introduction

Contamination control is becoming much important to fabricate sub-micron ultra-large-scale integrated (ULSI) devices. Especially, the atomically clean and flat Si surface is of great importance for the reliability of very thin and high quality gate oxide which form a key element of metal-oxide-silicon (MOS) devices. In recent years, it has been pointed out that the organic molecules degrade the characteristics of thin oxide. The method of isopropyl alcohol(IPA) vapor dry has been widely used in pre-treatment process of the oxidation. However little attention has been given to remained IPA molecules, these might influence to the gate oxide since it is becoming very thin and small. In this study, we introduced IPA contamination compulsorily on the Si surface to clarify the effect of it on the electrical property of the very thin oxide.

2. Experimental

Si wafers are treated in HF solution for H-termination and rinsed in pure water. In order to control the amount of adsorbed IPA molecules, these were managed in IPA vapordryer or dipped in the IPA solution(>99.5%) at room temperature(R.T.) or about 70°C. The Thermal Desorption-Atmospheric Pressure Ionization Mass Spectrometer (TDS-APIMS)¹⁾ (Hitachi Tokyo Electronics Co., Ltd.) was used to measure desociated IPA molecules from the Si surface by heattreatment.

Using similar dry up process (IPA vapor-dry and IPAdipping) during the pre-treatment of oxidation, MOS capacitors were fabricated for the measurement of the electrical characteristics on p-type Si substrate. The 5-10 nm-thick gate oxide were formed by wet oxidation using load lock oxidation system.²⁰ I-V characteristics and time zero dielectric breakdown (TZDB) measurements were performed to evaluate oxide reliability.

2. Results and discussion

Increasing the dipping time and the temperature of IPA, the IPA concentration on the Si surface is turned to be larger, as shown in Fig.1. This indicates that IPA molecules do not physically adsorb but react and chemically remain on the Si surface, in agreement with previously reported FT-IR-ATR and TDS data³⁾.

I-V characteristics were measured as the function of the



Fig. 1 TDS-APIMS measurement of the IPA concentration on the Si surface

amount of the IPA contamination and the oxide thickness. As shown in Fig. 2, with increasing adsorbed IPA molecules, leakage current raised in low electric field region of the 5 nm-thick oxide (see allow in Fig. 2). However, apparent changes were not observed on 8 and 10 nm-thick oxides. Figure 3 shows the distribution of breakdown voltage (gate voltage which causes leakage current of 10^{-5} A/cm²) in TZDB measurement of MOS capacitors with the area 0.019cm². It is clearly shown that the reliability of TZDB is degraded if the amount of IPA adsorption is increased. These results strongly indicate that adsorbed IPA molecules degrade the



Fig. 2 I-V characteristics of MOS capacitors under several IPA concentrations and oxide thickness.



Fig. 3 The breakdown voltage of MOS capacitors dependence on IPA concentration.(t_{ox} =5nm, gate area=0.019cm², leakage current Jg=10⁻⁵A/cm²)

electrical characteristics of the very thin oxide less than 5 nm so that it must be considered as a kind of organic contamination affection. Therefore, as gate oxide become thinner with semiconductor devices become smaller, the effect of IPA adsorption and other organic contamination on thin oxide will be more serious.

To clarify the mechanism of this degradation, XPS measurements were carried out about carbon atoms in the Si wafer surfaces before and after oxidation. As shown in Fig. 4, it was found that C-Si bonds were created during thermal oxidation. It should be noted that these bonds were not observed before oxidation. It is reasonable to suppose that C-Si bonds turn to be weak points or causes the thickness of the oxide not to be uniform. Therefore, it is considered that the electric field is locally enhanced in the thin oxide with C-Si bonds. As a result, the electrical characteristics of the thin



Fig. 4 The C1s XPS core-level spectra in Si wafer obtained before and after thermal oxidation.

oxide are degraded. These effects must be more evident in thinner oxide. Thus, only the 5nm-thick oxide film is influenced by the IPA adsorption.

In order to decrease C-Si bonds introduced by adsorbed organic molecules, we tried pre-annealing treatment (400°C 30sec) just before the rapid thermal oxidation. The XPS data show the amount of C-Si bonds decreased to reference level as shown in Fig. 5.

3. Conclusions

The effect of IPA adsorption on the electrical characteristics of thin oxide of Si MOS capacitor has been investigated. The IPA adsorption degrades the 5 nm-thick thin oxide reliability. This indicates the effect of carbon contamination on thin oxide will be serious as gate oxide become thinner in future. It was found that the heat treatment creates C-Si bonds in oxide, which may prevent uniform oxidation. Pre-annealing treatment was found to be effective to reduced the formation of the C-Si bonds.

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Fig. 5 C-Si bonds concentration of the Si after thermal oxidation.

¹⁾ Y. Mitsui et al., Anal. Chem. 55, 477 (1983).