

Degradation of SiO₂/Si Interface Characteristics by Aluminum Contamination

T. Itoga, H. Kojima and A. Hiraiwa
Central Research Laboratory, Hitachi Ltd.,
Kokubunji, Tokyo 185, Japan

This paper discusses the effects of Al contamination on SiO₂/Si interface characteristics. The interface state density increases as the Al contamination level increases, and the influence is greater when the oxide layer becomes thinner. This is because contaminating Al is segregated in the oxide layer and remains very close to the oxide surface. Since Al is, and will continue to be, the most widely used material for process equipments, Al contamination control might become one of the key issues in achieving future giga-scale ULSIs.

1. Introduction

Contamination control, as well as particle control, have become one of key technologies in ULSI fabrication. Transition metals such as Fe and Cu are known to lead to device failures^{1,2}). Thus, ULSI manufacturing equipment is mainly made of Al-alloys, since it is believed that Al only serve as an acceptor. Although it is well known that Al atoms in the oxide layer behave only as a negative charge center, the influence of Al on device characteristics is still not clear. One report has shown the possibility of heavy Al contamination during high energy ion implantation³). In this paper, we first show that an Al contamination of a higher concentration than previously reported occurs during the ion implantation and then discuss its influence on SiO₂/Si interface characteristics.

2. Al contamination induced by ion implantation

During ion implantation, a large amount of Al can be introduced into a Si wafer (Fig. 1). In this figure, the concentration of Al atoms in a P⁺ implanted Si wafer is plotted against the implanted P⁺ dose. Al concentration on the Si wafer was measured using inductively coupled argon plasma spectrometry (ICPS). The results show that, the Al contamination level can be as high as one tenth of the implanted dose. This Al is believed to be incident dopant ions.

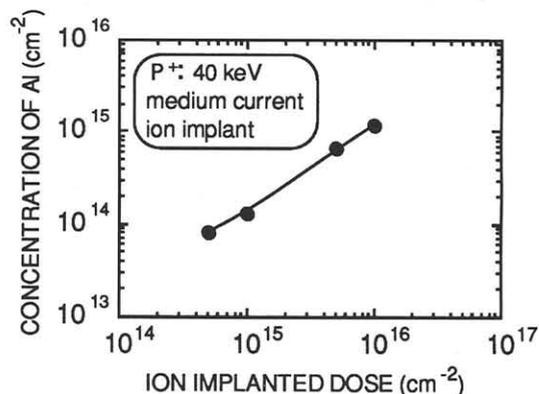


Fig. 1 Al contamination of P⁺ implanted Si wafers.

3. Investigation of Al contaminated SiO₂ and SiO₂/Si interface

The effects of Al contamination to device characteristics are investigated.

3.1 Sample Preparation

A controlled amount of Al was deposited on CZ (100) p-type 10 Ω-cm Si wafers using an aqueous NH₄OH and H₂O₂ solution containing dissolved Al. The amount of deposited Al was measured by flameless atomic absorption spectrometry and ICPS. The wafers were subsequently oxidized at 1000°C in wet oxygen ambient (H₂O:1%, O₂:99%) using a rapid thermal process. After removing the backside SiO₂, metallization for C-V measurement followed. The SiO₂/Si interface state density at the Si mid gap

(D_{it}) was calculated from high-frequency and quasi-static C-V data⁴). The depth profile of the Al concentration was measured using angle resolved x-ray photoelectron spectroscopy (XPS) and precise etching rate measurement of the SiO_2 in dilute HF solution.

3.2 Electrical Characteristics

The SiO_2/Si interface state density at the Si mid gap is plotted as a function of the amount of Al deposited (Fig. 2). As the Al concentration increases to $1 \times 10^{14} \text{ cm}^{-2}$, D_{it} increases up to $5 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$. There are two probable reasons for the increase in D_{it} . One is that the interface state density has increased due to structural changes in the oxide layer or due to stress induced by Al incorporation. Another is that Al that exists near the interface directly generates the interface state.

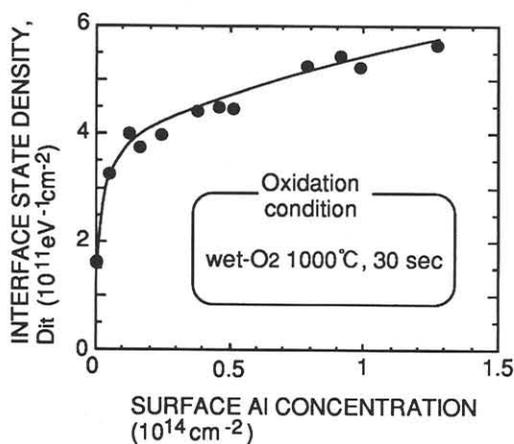


Fig. 2 Interface state density at Si mid gap versus surface Al concentration before oxidation.

The dependence of D_{it} with a fixed concentration of $1.4 \times 10^{14} \text{ cm}^{-2}$ on the oxide thickness is shown in figure 3. Oxidation time varied from 30 seconds to 300 seconds. It can be seen that the D_{it} decreases as the oxide thickness increased which indicates that the interface of the thinner oxides is more sensitive to Al contamination. This effect will be discussed later.

The flat band voltage (V_{fb}) shift to a positive voltage was also observed in the Al-contaminated oxide. The V_{fb} shift might have originated from the D_{it} increase or the negative charge induced by Al contamination. The other characteristics of SiO_2 films, such as breakdown voltage or infrared absorption were not changed by Al contamination.

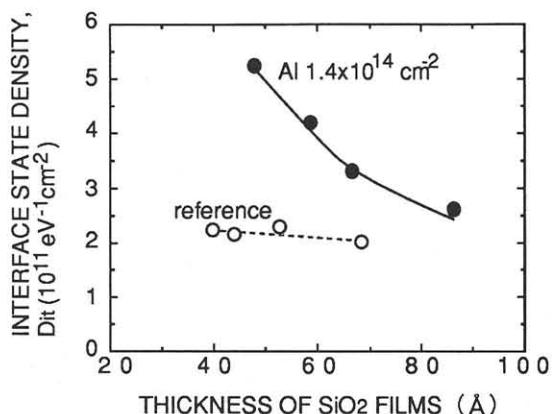


Fig. 3 On oxide thickness dependence of the interface state density. The surface Al concentration was fixed at $1.4 \times 10^{14} \text{ cm}^{-2}$ before oxidation.

3.3 The depth profile of Al concentration in SiO_2

The total amount of Al within the oxide layer did not change and was independent of the oxidation time or oxide thickness, as shown in Fig. 4. In order to investigate the dependence of Al on the oxide thickness, the Al depth profile

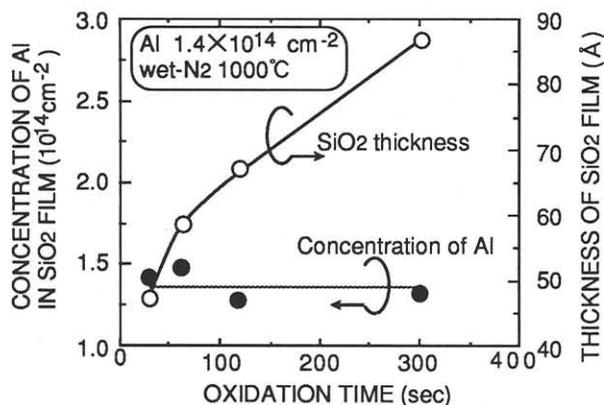


Fig. 4 Al concentration in oxide and SiO_2 film thickness as a function of oxidation time. The surface Al concentration was fixed at $1.4 \times 10^{14} \text{ cm}^{-2}$ before oxidation.

was measured using angle resolved XPS. Figure 5 shows Al-2p photoelectron spectra of Al deposited in oxides of two different thicknesses (46 Å and 87 Å) with a fixed amount ($1.4 \times 10^{14} \text{ cm}^{-2}$) of deposited Al. Intensities are normalized using oxide Si-2p peak intensities as a standard.

Therefore, the intensity of Al-2p peak is a fairly good indicator of the Al to Si atomic ratio within the region of escape depth (less than 46 Å for oxide at a detection angle of 25°). It can be seen from the figure that the intensities are almost identical for both samples, and higher for the shallow detection angle (25°) compared with that of the normal detection angle (90°) for each oxide thickness. These results indicate that Al is distributed near the surface of the oxide layer (less than 46 Å from the surface, with a peak concentration of greater than $3 \times 10^{20} \text{ cm}^{-3}$) regardless of thermal treatment or oxide thickness.

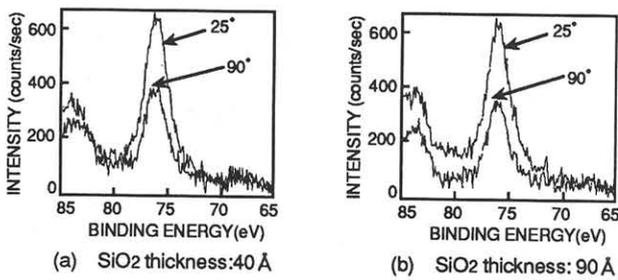


Fig.5 The results of angle resolved XPS. The spectra have Al 2p peaks.

This concentration of Al, which corresponds to about 1% of the Si concentration in SiO₂, can affect the HF etching rate of the oxide, due to the existence of Al-O bonds. Therefore, the etching rate of the Al-contaminated oxide in a 0.5% HF solution was measured. Figure 6 shows the etching rate of the Al contaminated and reference oxide layers as a function of the depth from the surface. The etching rate of the Al-contaminated oxide is small compared with that of the reference oxide in the surface re-

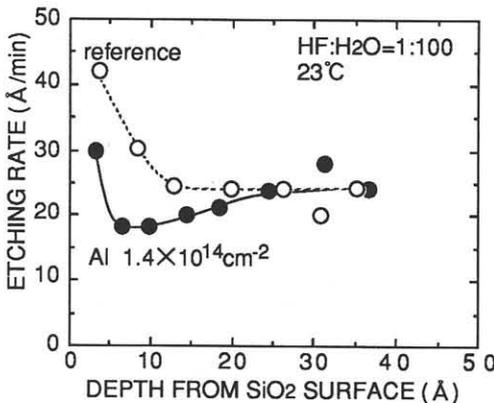


Fig. 6 Depth profile of oxide etching rate in 0.5% HF solution.

gion down to a depth of 20 Å. This suggests that most Al atoms exist within 20 Å of the oxide surface. Thus, we can conclude that Al contaminants on a Si wafer are incorporated into the oxide in the early stages of oxidation process and remain there during the oxidation process.

3.4 Oxide/Si interface state density dependence on oxide thickness

We previously mentioned two possible mechanisms to explain the D_{it} increase caused by Al contamination. D_{it} dependence on oxide thickness can be explained by both mechanisms. If the D_{it} increase is caused by structural changes in the surface region of the oxide layer or by stress induced by incorporating of Al, there must only be slight change in interface characteristics in thicker oxide layers. Even if the D_{it} increase is caused by the Al contamination itself, its dependence on oxide thickness can be explained. In the oxide layer, Al cannot easily diffuse toward the interface during oxidation. As the oxide thickness increases, the amount of Al near the interface decreases. Thus, D_{it} may decrease as the oxide thickness increases. However, further investigation is required to clarify which mechanism is dominant.

4. Summary

Al contamination is found to degrade the SiO₂/Si interface. This phenomenon is more pronounced in thinner SiO₂ layer. Thus, Al contamination control will be a key technology in future ULSI fabrication.

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