Influence of Ambient Oxygen and Moisture on the Growth of Native Oxides on Silicon Surfaces

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Introduction

As semiconductor devices continue to be highly integrated and their geometries also continue to shrink, thin native oxides grown on silicon surfaces have been shown to be able to cause incubation before film growth during low-pressure chemical vapor deposition[1], and to hinder silicidation reaction[2], as well as epitaxial growth .

A silicided shallow junction in the low resistance source/drain of MOS transistors has been required to produce high-speed and low power transistors. Hence, a silicon surface in the source/drain is heavily implanted with dopants such as arsenic before formation of a metal silicide. It is known that a native oxide grows extremely faster on the heavily doped surface than a normal silicon surface. Therefore, the growth of a native oxide on such surfaces should be stringently controlled.

Meanwhile, a native oxide grows on the surface of silicon wafers during wafer transport from the wafer-cleaning equipment to the film deposition equipment. Hence, silicon wafers must be isolated from the cleanroom air during wafer transport.

It is known that the growth of a native oxide on a normal silicon surface is prevented by wafer-storage in nitrogen with no more than 0.1 ppm of moisture concentration[3]. However, it will not be feasible to maintain the concentration and it has not been reported that the effect of the wafer-storage in nitrogen on the native oxide growth on the heavily doped surface. In this study, we have investigated the relationship between the thickness of native oxide and elapsed time or environment during wafer-storage, such as oxygen and moisture to examine inhibition of the native oxide growth from a practical point of view.

Results and Discussion

Figure 1 shows the change in the concentration of oxygen and moisture in a conventional SMIF pod or in a closed pod (a hermetically sealed pod) we have developed[2] after these pods are purged with nitrogen. The concentration of oxygen and moisture in the pods increases with elapsed time. This increase is considered to be due to the emission of absorbed water from inner wall of pods and permeation of oxygen from exterior to interior of pods through a gap between a flange and a lid of pods.

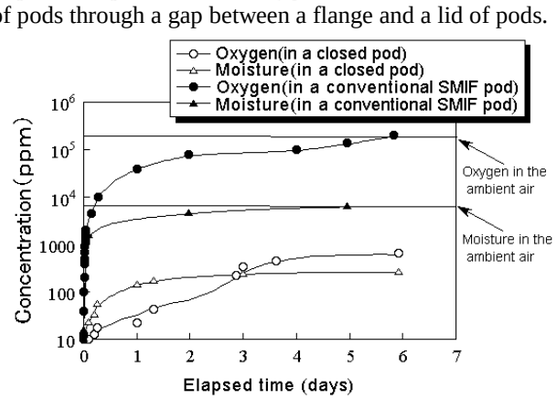
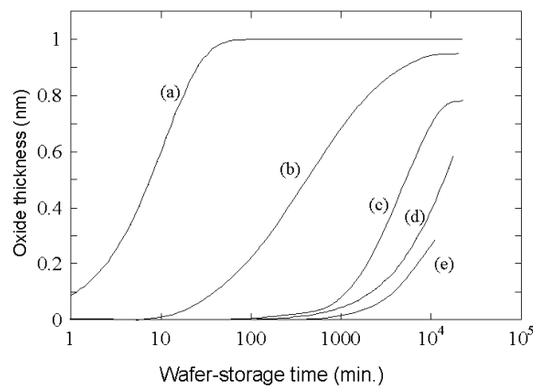


Fig. 1 Time dependence of oxygen and moisture concentrations in pods.



The concentrations in a conventional SMIF pod quickly increase close to the ambient air. In contrast, the concentrations in the closed pod slowly increase and seem to saturate below both concentrations of 1000 ppm. In order to determine the critical concentration and elapsed time which should be controlled to inhibit the growth of a native oxide, the thickness of native oxides grown on the surface heavily implanted with arsenic during wafer storage in environments with different kinds of constant concentrations of oxygen and moisture was measured using X-ray photoelectron spectrometry (XPS).

Fig. 2 Time dependence of the thickness of native oxide grown in various environments: (a)ambient air, (b)1000ppm oxygen and 1000ppm moisture, (c) 1000ppm oxygen and 100ppm moisture, (d) 100ppm oxygen and 1000ppm Moisture, and (e) 100ppm oxygen and 100ppm moisture in nitrogen.

Figure 2 shows time dependence of the thickness of native oxides on the surface of silicon wafers stored in the various environment. The growth of a native oxide is inhibited less than 0.3nm on two-hour or shorter storage time even if both the concentrations of oxygen and moisture are kept at 1000 ppm, in contrast, a native oxide grows up to 1.0 nm to saturate within two hours in the ambient air. The growth rate of a native oxide depends both on the concentrations of oxygen and moisture and on surface- exposure time. In other words, rate constant of the growth of a native oxide is a function of the concentration of oxygen and moisture. Particularly, oxygen concentration will be predominant in the growth of an oxide, compared with moisture concentration. It suggests that even plastic materials can be used as pod materials by choosing materials with a low water absorption rate and by developing adequate sealing methods to isolate silicon surfaces from oxygen.

Equations to determine rate constant in kinetics of the native oxide growth in nitrogen will be discussed.

Summary

The influence of oxygen and moisture concentrations as well as wafer-storage time in nitrogen ambient in wafer-storage pods on the growth of native oxide has been clarified. It has been found that the rate constant of the growth of a native oxide is a function of the concentration of oxygen and moisture. The growth of native oxides as well as the adsorption of organic contaminants on the silicon surfaces has been successfully inhibited by storing silicon wafers in a closed pod purged with nitrogen.

References

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