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Native Oxide Growth on Silicon Surface in Wet Ambient

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The effects of dopant concentration for n-type dopant (P, As) in silicon (100), temperature, and oxidizing species on native oxide growth in liquid water are described. The oxide growth on phosphorus (P) and arsenic (As) doped n^+-Si surfaces (10^{20} cm^{-3}) in ultrapure water exhibits saturation of oxide thickness, suggesting a field assisted mechanism. In contrast, oxide thickness on n^--Si (10^{15} cm^{-3}) continuously increases with time following a parabolic law. Oxide thickness saturation is also found on n^--Si in hydrogenperoxide (H_2O_2) solution or in H_2O_2 solution in the presence of a platinum (Pt) mesh that creates oxidizing radicals or ions. The oxide growth rate in ultrapure water increases with temperature.

1. Introduction

Native oxide on Si surfaces is one of the major contaminants which degrade device performance.[1,2] Detailed investigations of conditions for native oxide growth is increasingly required by the downscaling of large-scale integrated devices. Because native oxide films on Si surfaces prevent the growth of high-quality epitaxial Si films at low-temperature, increase the contact resistance in via-hole Si-metal contact, and is a source of impurities inducing defects in the silicon substrate. An understanding and control of native oxide growth is therefore of great importance to obtain ultraclean Si wafer surfaces.

Recently, we reported that the coexistence of oxygen and water (or moisture) is required to grow native oxide on Si, both in air and in ultrapure water at room temperature.[3-8] In this paper, we describe the effects of dopants and their concentration in Si, temperature, and oxidizing species on the native oxide growth in liquid water. We also discuss the dissolution of Si in water for n^+-Si.

2. Experiment

The wafers used were P doped n-type Cz(100) wafers with a resistivity of 2-4 Ωcm (10^{15} cm^{-3}), as well as P and As doped n^+-type (10^{20} cm^{-3}) wafers. Highly doped P and As layers were prepared by chemical vapor deposition of phosphosilicate grass (PSG) followed by the thermal diffusion treatments and by ion implantation of As followed by thermal activation annealing, respectively. All wafers were chemically precleaned (H_2SO_4+H_2O_2 followed by a standard RCA clean), etched with diluted (0.5%) HF solution, rinsed with ultrapure water with a dissolved oxygen concentration of 0.6 ppm for 10 minutes, and blow-dried with ultraclean nitrogen.

Native oxide film thickness are determined by x-ray photoelectron spectroscopy (XPS) combined with ellipsometry[8] as follows :(1) The thickness of thermal oxide films (70-140 A) is measured by ellipsometry without the postulation of the refractive index. (2) The Si_{2p} spectra of the same oxide are measured by XPS. (3) The area ratio of the XPS Si_{2p}-

signal from the oxide (SiO_x:x≥0.5) to that from the Si substrate is calibrated with the thickness measured by ellipsometry. The escape depth of electrons for the oxide overlayer and the Si substrate are determined. (4) The thicknesses of the native oxide films are determined from the area ratios of XPS spectra of the native oxide and the above calibration data. The dissolved oxygen level in ultrapure water is monitored by polarography. The amount of the dissolved Si in ultrapure water is measured by atomic absorption.

3. Results and Discussion

We have first investigated the influence of the doping level on native oxide growth. An oxide is grown during overflow rinsing (10 min) with ultrapure water right after etching with diluted HF solution. This water had a dissolved oxygen concentration of 0.6 ppm. The oxide thickness (3.2 A) on n^+-Si is thicker than that (1.9 A) on n^--Si (see Fig. 1 first two data points). This result implies that the initial growth rate of native oxide on n^+-Si in overflow rinsing ultrapure water is very high.

Figure 1 shows the thickness of native oxide on P doped n^-- and n^+-Si wafers as a function of immersion time in ultrapure water with 9 ppm dissolved oxygen concentration at room temperature. This dissolved oxygen concentration in ultrapure water is the value in equilibrium with air at room temperature. The oxide thickness on n^+-Si tends to saturate at value of 10 A in spite of its rapid initial growth. In contrast, the thickness on n^--Si continuously increases with a immersion time following a parabolic law.

The influence of different dopant species (P, As) in n^+-Si on oxide growth is shown in Fig. 2. The thickness is shown as a function of immersion time in ultrapure water with a dissolved oxygen concentration of 9 ppm. The oxide thickness on As-doped n^+-Si saturates at approximately 12 A, while the initial oxide thickness on As-doped n^+-Si is less than that on P-doped n^+-Si. It is seen from Figs. 1 and 2 that the growth

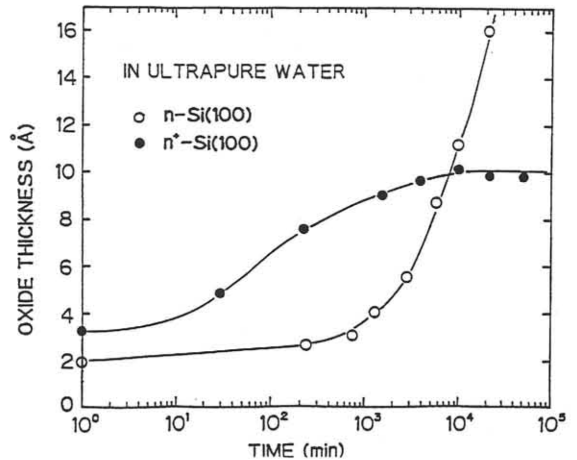

Fig. 1 Thicknesses of native oxide on n^--Si and n^+-Si as a function of immersion time in ultrapure water with 9 ppm dissolved oxygen concentration at room temperature.

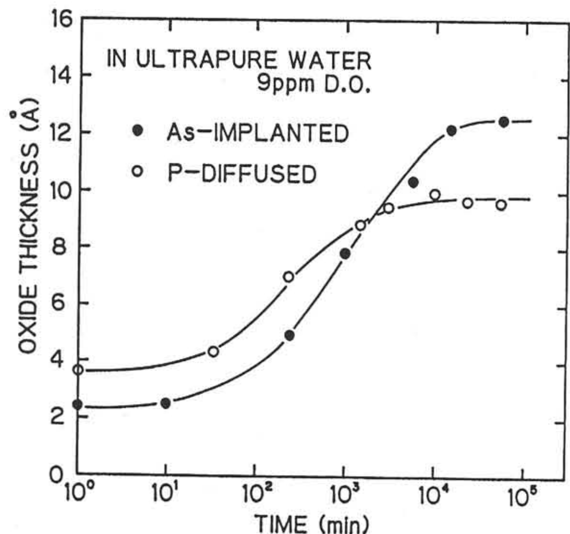

Fig. 2 Thicknesses of native oxide on P- and As-doped n^+-Si as a function of immersion time in ultrapure water.

behavior strongly depends on the electron concentration in Si surface layer, but not on the dopant. These data lead us to conclude that the growth of native oxide on n^+-Si in ultrapure water is dominated by a field assisted mechanism.[9]

Figure 3 shows the Si atoms dissolved into ultrapure water as a function of the immersion time of n^--Si and n^+-Si surface layer at room temperature, with a dissolved oxygen concentration in ultrapure water of 9 ppm. The number of dissolved Si atoms into ultrapure water for n^+-Si wafer is smaller than that for n^--Si wafer at all times. It is worthwhile to notice that the number of dissolved Si atoms into ultrapure water for n^+-Si is smaller than that for n^--Si even in the time region ($>8\times10^3$min) where the oxide thickness on n^+-Si is thinner than that on n^--Si. This indicates that the growth of native oxide on n^+-Si is influenced little by the Si dissolution, while the growth on n^--Si is accompanied by Si dissolution.[8] Moreover, this result indicates that the structure of the native oxide grown on n^+-Si is probably different from that on n^--Si, because the number of Si atoms dissolved

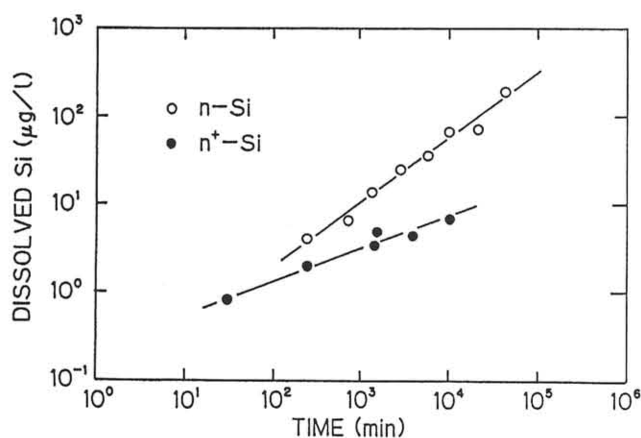

Fig. 3 Dissolved Si atoms in ultrapure water as a function of immersion time of n^--Si and n^+-Si.

into ultrapure water is small for the Si wafer covered with native oxide grown on n^+-Si.

The temperature dependence of oxide thickness grown on n^--Si in ultrapure water is shown in Fig. 4. The growth rate increases with temperature although the dissolved oxygen concentration in ultrapure water becomes low at higher temperatures. The thickness of native oxide grown in ultrapure water decreases with decreasing dissolved oxygen concentration at room temperature.[8] This result indicates that the growth rate is sensitive to the temperature but not to the dissolved oxygen concentration at higher temperatures. However, the growth rate is sensitive to dissolved oxygen concentration at room temperature.

Figure 5 shows the oxide thickness on n^--Si as a function of immersion time in H_2O_2 solution at room temperature. The thickness of oxide formed in H_2O_2 solution saturates at 7 A even on n^--Si.

We used a Pt catalyst to produce oxidant radicals or ions from H_2O_2 to see whether they influence the native oxide growth. The oxide thickness on n^--Si and n^+-Si as a function of immersion time in a solution of H_2O_2 including a mesh of Pt

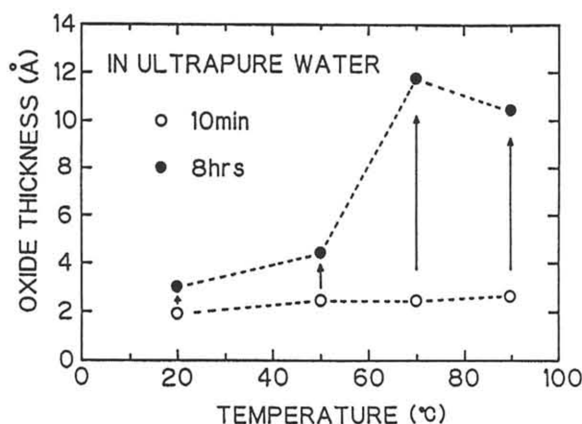

Fig. 4 Temperature dependence of oxide thickness grown in ultrapure water.

catalyst is shown in Fig. 6. The temperature of the solution is also given as a function of the time; the solution is exchanged for a new solution every 60 min. Oxide growth saturation to the same thickness is found on n^--Si and on n^+-Si. These results indicate that the oxide growth in the solution including the oxidant radicals or ions is governed by the field assisted mechanism even on n^--Si.

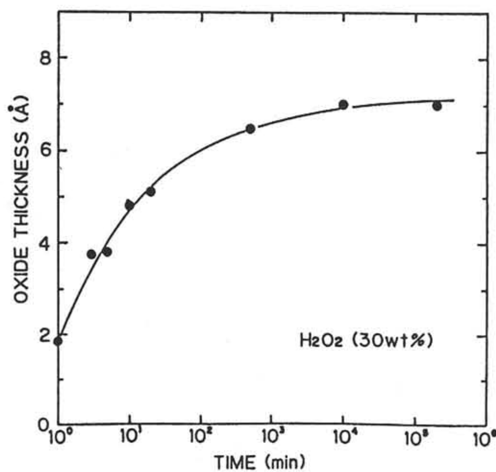

Fig. 5 Oxide thickness on n^--Si as a function of immersion time in H_2O_2 solution at room temperature.

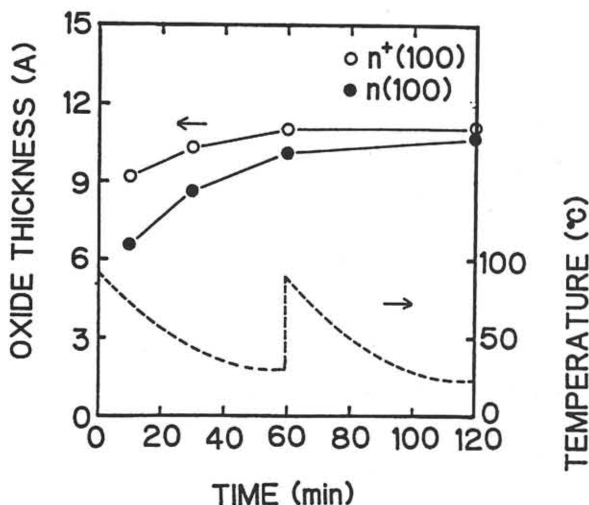

Fig. 6 Oxide thicknesses on n^-- and n^+-Si as a function of immersion time in H_2O_2+Pt solution.

4. Conclusions

We demonstrated that the oxide growth on n^+-Si(100) in ultrapure water and on n^--Si(100) and n^+-Si(100) in a solution with oxidant radicals or ions exhibits a thickness saturation behavior, suggesting a field assisted mechanism. Native oxide growth on n^--Si in ultrapure water depends on the temperature, but not on the dissolved oxygen concentration at higher temperatures. The number of Si atoms dissolved into ultrapure water for n^+-Si is small.

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