Oxidation of Silicon in TCA/O_2 Ambients

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Abstract

In this work, we investigate chlorine incorporation, film growth kinetics and oxidation enhanced diffusion of phosphorus during oxidation in TCA (1,1,1-Trichloroethane)/O_2 ambients. Silicon wafers were oxidized at 900 and 1000°C in dry O_2 and TCA/O_2 with 1-4% equivalent HCl. SIMS measurements used to characterize the chlorine incorporation in the films show strong incorporation near the Si/SiO_2 interface. This incorporation increases for longer oxidation times, but is nearly independent of TCA percentage. Parabolic and linear rate constants were extracted from the oxide thickness as a function of time. A nonlinear dependence on partial pressure of TCA was observed, with the greatest change for small percentages of TCA. Oxidation enhanced diffusion of phosphorus was also characterized in TCA/O_2 ambients. Spreading resistance measurements show a reduction in the supersaturation of interstitials relative to oxidation in dry O_2. Like the oxide growth kinetics, the reduction has a nonlinear dependence on partial pressure of TCA.

1 Introduction

One of the techniques routinely used to form thin and highly reliable oxides is addition of chlorine species to the oxidizing ambient. The benefits that have been reported include passivation of mobile ions, improvement of the oxide dielectric breakdown strength and improved threshold stabilities [1]. Inspection of SIMS (Secondary Ion Mass Spectroscopy) profiles shows that a significant amount of Cl is distributed in the oxide, with increasing concentration towards the SiO_2/Si interface [2]. This incorporation changes the structure of the oxide and affects oxidation kinetics and point defect interactions in the silicon bulk.

When Cl species are used during the oxidation of Si, an enhanced oxidation rate is observed [3]. This increase is reflected in both parabolic and linear rate constants. It has been suggested that incorporated Cl provides an alternative path for oxidation [2]. It has also been reported that the Cl species (HCl, TCA, etc.) decompose in the gas phase with reaction products that are known to affect the oxide growth rate [4]. In addition the presence of chlorine in an oxidizing ambient causes a reduction in oxidation enhanced diffusion (OED) of impurities in silicon [5]. The goal of the present experiments is to obtain a consistent set of data that includes Cl incorporation, oxidation kinetics and OED measurements in order to better understand these processes.

2 Experimental Procedures

The starting material for the experiments was ⟨100⟩ n-type 3-inch Czochralski-grown silicon wafers with resistivity of 10-20 Ω–cm. These wafers were oxidized in dry O_2 or O_2 with varying partial pressures of TCA ($C_2H_3Cl_3$). Oxidations were performed at 900 and 1000°C

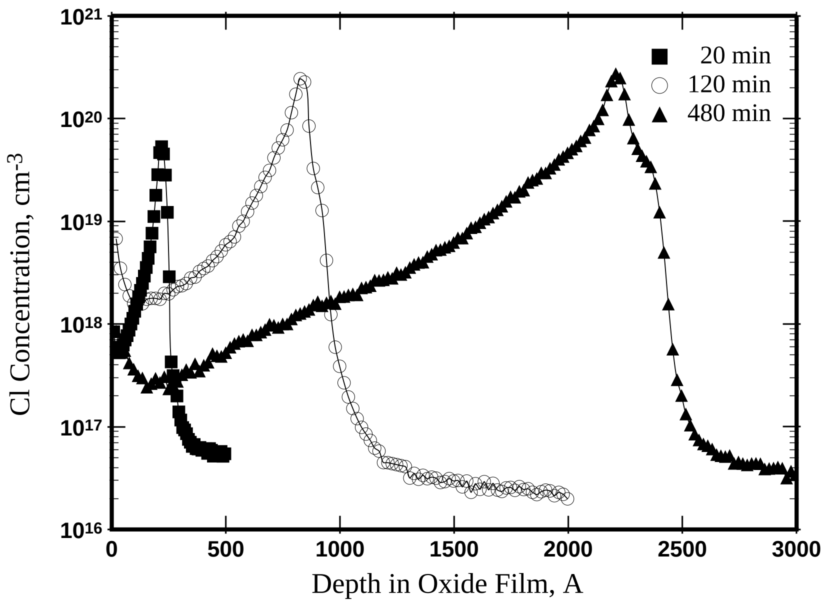


Figure 1: Chlorine incorporation in SiO_2 after 20, 120 and 480min oxidation at 1000°C in TCA/O_2 with 2% equivalent HCl.

for times varying from 20 min to 20 h, and oxide thicknesses were measured using Nanospec and ellipsometry. To understand the relation between the oxide growth conditions and the incorporated Cl in the oxide, a set of Cl profiles were measured by SIMS.[1] The primary bombarding species was Cs^+ with ion energy of 5 keV.

TCA is a liquid source and is supplied via a bubbler with N_2 as the carrier gas. The bubbler temperature used was 25°C, and equivalent HCl partial pressures were calculated using the conversion graphs of J.C. Schumacher [6]. At furnace temperatures, TCA reacts fully with O_2 where each mole of TCA is equivalent to three moles of HCl [7]. In order for our results to be comparable with other work, throughout the paper we will describe the TCA concentrations in terms of equivalent HCl partial pressure.

To investigate the effect of chlorine on dopant diffusion in the bulk, additional experiments were done on n-type 4-inch float-zone ⟨100⟩ silicon wafers with resistivity of 500-1000 Ω–cm. Float-zone wafers were used to avoid interstitial generation during oxygen precipitation in Czochralski silicon. The wafers were first oxidized in dry O_2 at 1000°C for 390 minutes to grow a pad oxide of 1000 Å. Wafers were then implanted with a phosphorus dose of $2{\times}10^{13}$cm^{-2} at 400keV and annealed at 900°C for 30 minutes. Next, a nitride layer of 1500 Å was deposited by low pressure chemical vapor deposition. The nitride layer covering the pad oxide was used as a diffusion barrier to oxidant species so that diffusion under oxidizing and non-oxidizing conditions could be carried out simultaneously. The wafers were patterned with a stripe mask to produce alternating 3mm wide stripes of bare silicon and the oxide-nitride combination. The nitride was removed via plasma etching and then the wafers were immersed in buffered-oxide-etch (BOE) to remove the pad oxide. Finally the

[1]Performed by Evans East, Plainsboro, NJ.

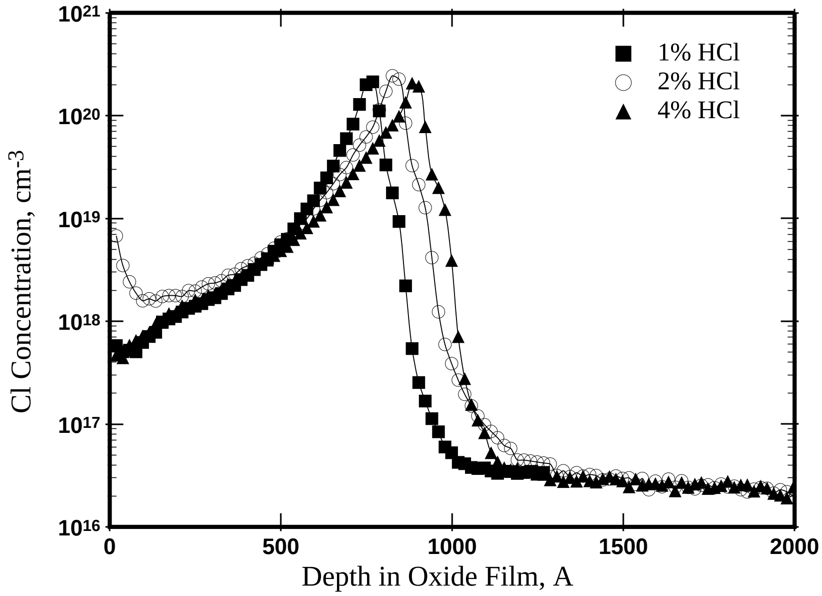


Figure 2: SIMS measurement of incorporated chlorine in oxides grown in TCA/O_2 with 1, 2 and 4% equivalent HCl at 1000°C.

wafers were oxidized in dry O_2 or TCA/O_2 ambients at 1000°C for 8 h.

The phosphorus doping profiles were measured using spreading resistance. The spreading resistance profiles from samples which saw only the initial anneal and ramp up/down were converted to concentration profiles using the software SERAPES [8]. These concentrations were used in SUPREM IV [9] as initial profiles. Simulation of diffusion under oxidizing and nonoxidizing conditions were performed with phosphorus diffusion coefficient as an input parameter. The resulting simulated doping profiles were converted back to spreading resistance data using SERAPES and compared to the data taken on the diffused wafer sections. A nonlinear optimization program PROFILE [10] was used to extract the diffusivity which best matched each of the experimental profiles.

3 Results and Discussion

3.1 Incorporated Chlorine

Samples were chosen for SIMS measurements to illustrate the change in chlorine incorporation with changing time and chlorine concentrations in the gas. All measurements show strong incorporation of chlorine near the Si/SiO_2 interface, with the level of chlorine decreasing with distance from the interface (Figs. 1 and 2). We conclude, in agreement with previous work [2], that the chlorine species must diffuse through the oxide and react with Si at the interface. The knee which appears in the substrate portion of the chlorine profiles may indicate diffusion of chlorine into the silicon, although the effect could also be a result of transient and normalization effects in the SIMS measurement due to crossing a material

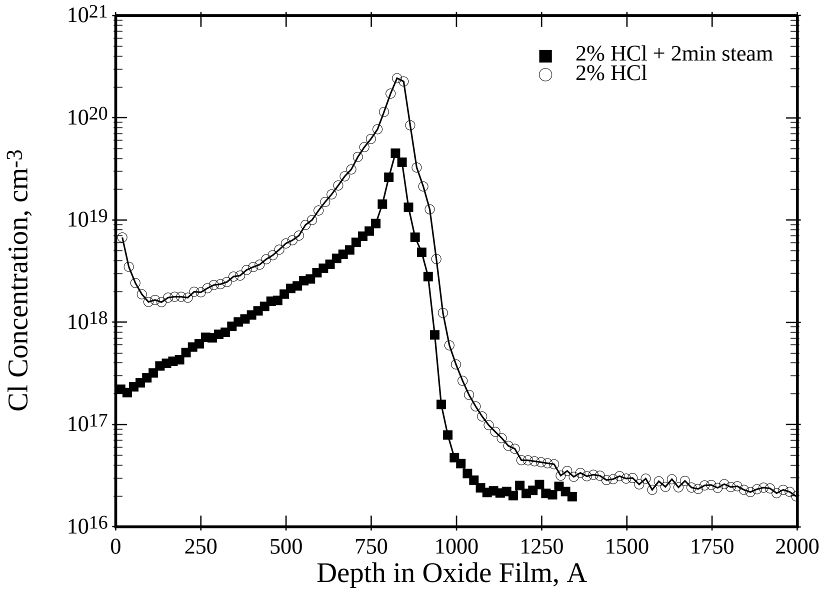


Figure 3: Comparison of chlorine incorporation in oxides grown at 1000°C in TCA/O_2 with equivalent 2% HCl and 2% HCl + 2min in steam after a subsequent 2 min oxidation in a steam ambient.

interface.

The fact that the distribution of incorporated chlorine in the oxide drops strongly with distance from the interface suggests that oxidizing species react to displace incorporated chlorine. It has been assumed in previous work [4] that steam generated by the gas phase reaction of HCl with O_2,

$$4\mathrm{HCl} + \mathrm{O_2} \Leftrightarrow 2\mathrm{H_2O} + 2\mathrm{Cl_2} \tag{1}$$

dominates the replacement reaction. The central role of H_2O in displacing chlorine is further supported by the observation that the chlorine distribution is significantly different in oxides grown in O_2/Cl_2 ambients [2], for which the chlorine concentration drops much more slowly with distance from the interface compared to oxides grown in HCl/O_2.

In order to quantify the rate of the chlorine replacement reaction, one of the wafers oxidized in 2% equivalent HCl/O_2 ambient for 2h at 1000°C, was further oxidized in 100% steam at 1000°C for 2 minutes. SIMS measurements were done on wafers both with and without the additional steam oxidation. Results are shown in Figure 3. It is evident that oxidation for just 2 minutes in a steam ambient causes the concentration of incorporated chlorine to be reduced dramatically. If we consider a first-order replacement reaction (≡SiCl + H_2O → ≡SiOH +HCl),

$$\frac{\partial C_{\mathrm{SiCl}}(x,t)}{\partial t} = -k\, C_{\mathrm{H_2O}}(x,t)\, C_{\mathrm{SiCl}}(x,t) \tag{2}$$

the resulting chlorine incorporation is expected to be

$$C_{\mathrm{SiCl}}(x,t) = C_{\mathrm{SiCl}}(x,0)\, \exp\left[-t/\tau\right], \tag{3}$$

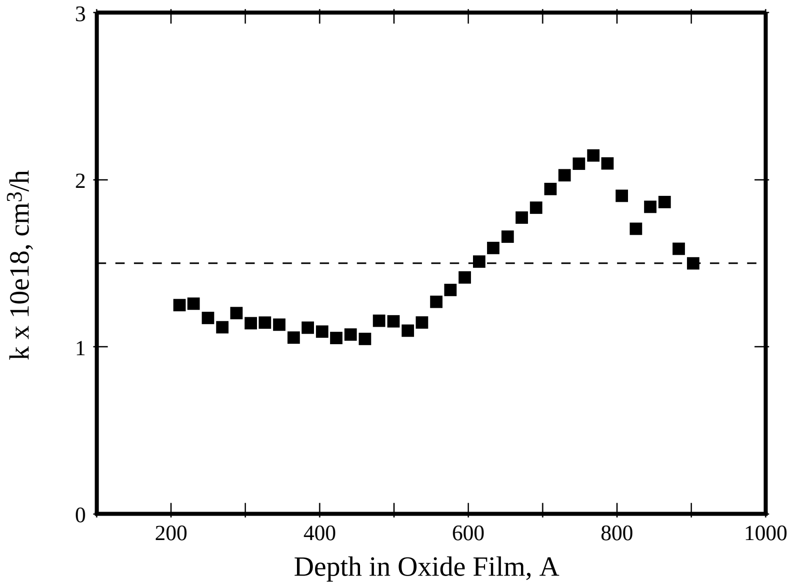


Figure 4: Calculated rate of replacement reaction as a function of location in oxide film from change in chlorine profiles due to 2 min oxidation in steam.

where t is the time in the 100% steam ambient, $C_{\rm SiCl}(x,0)$ is the incorporated chlorine prior to the steam oxidation and $\tau = 1/kC_{\rm H_2O}$ is the time constant for the replacement reaction. An oxidation kinetics calculation for this oxide thickness ($\approx$ 850Å) shows that we are still in the linear regime, which suggests that the concentration of H_2O ($C_{\rm H_2O}$) is approximately constant across the film.

Figure 4 shows the value of k as a function of oxide thickness calculated from Eq. 3 and the data of Figure 3. An average value of $k = 1.5 \times 10^{-18}$ cm^3/h was calculated. The larger calculated reaction rate near the interface may reflect some of the chlorine being incorporated into less stable configurations, resulting in faster replacement kinetics in recently formed regions of the film. If we assume that the incorporated chlorine is immobile [2] and the reduction of chlorine in the film with distance from the interface is mainly due to the reaction of H_2O with incorporated chlorine, then for a constant value of oxidation rate, the steady state dependence of the chlorine incorporation on distance from the oxidizing interface ($x = x_{\rm o}$) would be

$$C_{\rm SiCl}(x) = C_{\rm SiCl}(x_{\rm o})\exp(-\frac{x - x_{\rm o}}{\rm L_{SiCl}}), \tag{4}$$

where

$$L_{\rm SiCl} = \frac{\frac{dx_{\rm o}}{dt}}{kC_{\rm H_2O}(0)} \tag{5}$$

and dx_o/dt is the oxidation rate. The decay length calculated from Equation 5 is much larger than what is experimentally observed. This comparison shows that the reaction of H_2O alone cannot account for the nonuniformity that is observed.

Assuming that chlorine incorporation depends solely on the concentration of chlorine

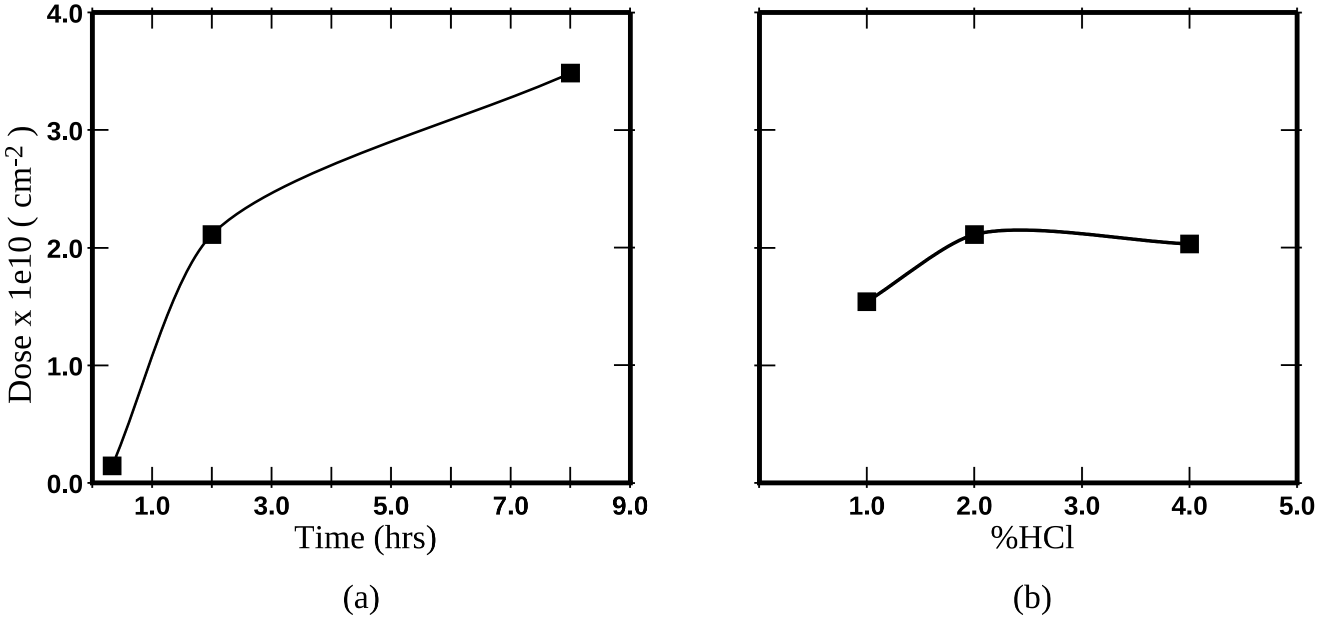


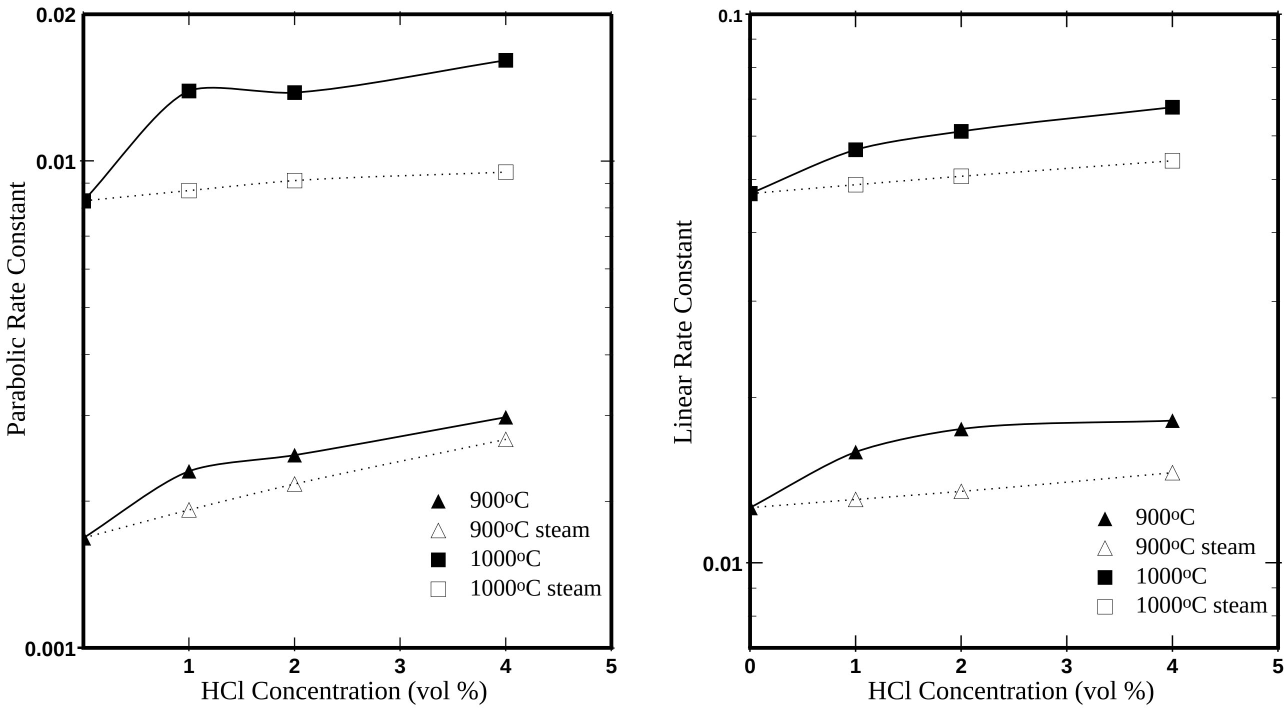
Figure 5: Incorporated chlorine dose versus time (a) and equivalent HCl partial pressure (b) for oxides grown at 1000°C in TCA/O_2 with 2% equivalent HCl.

species one might conclude that chlorine incorporation has to increase as a function of time and partial pressure. However, as depicted in Figure 5, although the incorporated chlorine increases for larger oxidation time, the incorporated dose is independent of partial pressure.

These observation suggests that the determining factor for chlorine incorporation is the ratio of chlorine species to steam at the oxidizing interface. In this scenario, both chlorine and H_2O diffuse rapidly to the interface. Chlorine species react with the interface resulting in incorporation, while H_2O reacts with incorporated chlorine at the interface releasing chlorine, as well as directly oxidizing silicon. Since the concentrations of H_2O and both chlorine species (HCl and Cl2) scale linearly with TCA (or HCl) partial pressure, the incorporated chlorine is independent of partial pressure. As the oxide thickness grows, the H_2O concentration drops near the interface as diffusion across the growing film can no longer keep up with the interface reaction. Thus, the chlorine incorporated at the interface increases with time (or oxide thickness). This rise in the amount of interface chlorine incorporated is also reflected in the distribution of chlorine in the bulk. The chlorine was initially incorporated into regions further from the interface when the oxide thickness was thinner and thus the incorporation smaller. Both initial incorporation and the bulk replacement contribute to the fall off of the profile away from the interface, but the calculation above suggests that the initial incorporation is the dominant effect.

3.2 Kinetics of Oxide Growth

Oxide thickness versus time were obtained for 0-4% equivalent HCl and oxidation temperatures of 900 and 1000°C. Oxide thicknesses were measured using both Nanospec and ellipsometry. The strongest effect on the oxide thickness upon varying the HCl concentration



(b) (a)

Figure 6: Linear (a) and parabolic (b) rate constants versus equivalent HCl concentration (volume percentage in gas).

is the difference between dry O_2 and 1% HCl/O_2. Subsequent additions of HCl have a smaller effect, but the overall rate is systematically increased.

Figure 6 shows the result of extracting the effective parabolic and linear oxidation rate constants (B and B/A) for the Deal-Grove model [11] using PROFILE [10]. Also shown for comparison are the change in the linear and parabolic rate constants due to the presence of steam in the gas phase [11]. Inspection of these plots reveals a strong nonlinear dependence of linear and parabolic rate constants on partial pressure of HCl. Steam alone cannot account for the initial rapid increase in the rate constants which must be due to the effect of chlorine. However, for partial pressure above 1%, parallel oxidation due to steam appears to accurately account for the differences in oxidation kinetics. This observation is fully consistent with the observation that chlorine incorporation is nearly independent of equivalent HCl partial pressure between 1% and 4% (Figs 2 and 5).

The change in the parabolic rate upon chlorine addition is most likely due to an increase in the effective diffusivity of the oxidizing species. This effect can be attributed to chlorine incorporation leading to more complete relaxation of the oxide, as the chlorine may act as a network terminator (similar to OH for steam oxidation). The increase in the linear rate may be attributed to at least two factors. First, the reaction of chlorine at the interface and subsequent replacement by H_2O provides an additional interface reaction. Moreover, increased diffusivity in a region of fixed thickness (as opposed to throughout the film) appears as an increase in the linear rather than the parabolic rate constant.

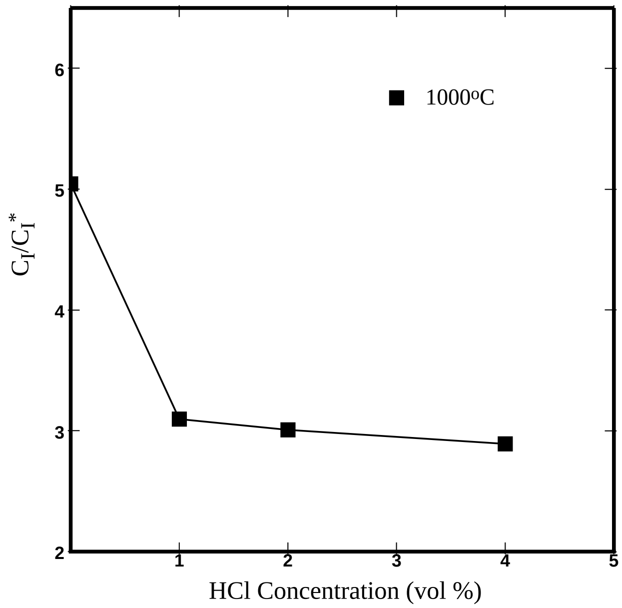


Figure 7: Supersaturation of interstitials versus equivalent HCl concentration at 900 and 1000°C.

3.3 Enhanced Diffusion of Phosphorus

The enhanced diffusivity of phosphorus is plotted as a function of HCl concentration in Figure 7. The inert diffusivity calculated in this work agreed with previously reported values [12]. The by now familiar trend of the chlorine incorporation and oxidation kinetics is seen in this data as well. For addition of a small amount of HCl, there is a large reduction in the supersaturation of interstitials, but further increases result in little change. Again, these results can be interpreted in light of the chlorine incorporation observations. Due to incorporation of chlorine at the interface, the structure of the oxide can be expected to differ from the standard oxide. The presence of Si-Cl, rather than bridging Si-O-Si bonds, can act as a network terminators and result in a less rigid oxide. Thus, chlorine incorporation can reduce the stress near the interface by allowing greater viscous flow of the oxide, providing more of the free volume required at the interface. In addition, the reaction of chlorine at the interface forming $\equiv$Si $-$ Cl may result in a volume reduction and/or an increase in the compressibility of the oxide. All these factors can cause a reduction in the generation of interstitials and thus reduce the OED of phosphorus for increasing HCl concentration. The fact that chlorine incorporation in the film is nearly independent of the HCl concentration in the gas, leads naturally to the observed saturation effect in OED.

4 Conclusions

Incorporation of chlorine in the oxide film plays a key role in the processes occurring during oxidation in chlorine-containing ambients. To illuminate the interactions between chlorine incorporation, oxidation kinetics and oxidation enhanced diffusion, we conducted a set of experiments to characterize these three phenomena under a consistent set of conditions.

SIMS data shows a nonuniform distribution of chlorine in the oxide, with strongest incorporation near the oxidizing interface. The chlorine incorporation increases with time, but is nearly independent of chlorine concentration for the conditions studied. We were able to estimate the rate of the chlorine replacement reaction in the film. and found that the H_2O replacement reaction alone cannot account for the chlorine profiles. These results suggest that distribution of incorporated chlorine depends significantly on the increasing chlorine incorporation with time.

To characterize the oxidation kinetics, a series of oxide thickness measurements were performed for different partial pressures of equivalent HCl at 900 and 1000°C. The oxidation rate for all cases increases with increasing equivalent HCl concentration. We found a nonlinear dependence of the linear and parabolic rate constants on partial pressure of HCl, with the greatest change for small percentages. To account for nonlinear behavior of the parabolic rate constant, we suggest that the effective diffusivity of oxidizing species is enhanced due to chlorine incorporation. The nonlinear increase in the linear rate can be attributed to the chlorine incorporation at the interface providing an alternative path for the interface reaction and increase in diffusivity near the oxidizing interface.

Finally, we examined OED during chlorine oxidation. We observed that for addition of a small amount of chlorine, there is a large reduction of supersaturation of interstitials, but increasing the HCl partial pressure results in an apparent saturation. This observation can be explained by the incorporation of chlorine facilitating viscous flow and providing free volume at the interface.

References

[1] R. S. Ronen and P.H. Robinson. *J. Electrochem. Soc.* **119**, 747 (1972).

[2] Y. D. Sheu, S. R. Butler, and F. J. Feigl. *J. Electrochem. Soc.* **133**, 2136 (1986).

[3] D. W. Hess and B. E. Deal. *J. Electrochem. Soc.* **12**, 735 (1977).

[4] B. Deal, D. Hess, J. Plummer, and C. Ho. *J. Electrochem. Soc.* **125**, 339 (1978).

[5] R. Subrahmanyan, H. Massoud, and R. Fair. *Appl. Phys. Lett.* **61**, 4804 (1987).

[6] E. Tierney. In **TCA Process Calculation for Process Engineers**,. J.C. Shumacher.

[7] E. J. Janssens and G. J. Declerck. *J. Electrochem. Soc.* **125**, 1696 (197x8).

[8] S. Dunham, N. Collins, and N. Jeng. *J. Vac. Sci. Technol. B* **12**, 283 (1994).

[9] M. E. Law, C. Rafferty, and R. W. Dutton. In **SUPREM IV Users Manual**, (1986). Stanford University.

[10] G. L. Ouwerling. In **Profile/Prof2d User's Manual**, (1989). Delft University of Technology, Electrical Materials Lab.

[11] B. E. Deal and A. S. Grove. *J. Electrochem. Soc.* **36**, 3770 (1965).

[12] A. Lin, D. A. Antoniadis, and R. W. Dutton. *J. Electrochem. Soc.* **128**, 1131 (1981).