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Interfacial Silicon Emission in Dry Oxidation -the Effect of H and Cl

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1. Introduction

Silicon oxidation is a key process for the fabrication of silicon devices, and elucidating the oxidation mechanism is of vital importance. Deal-Grove (D-G) theory is widely used for Si oxidation processes, however, the theory takes only the oxidant species into account [1]. On the other hand, recent studies on oxidation have revealed that Si species are emitted from the Si/oxide interface during oxidation and that these Si species play an important role in oxidation [2-4].

We have proposed the interfacial Si emission model based on the following concepts [3,4]: A large number of Si species (~1 % of the oxidized Si atoms) are emitted from the interface to release the oxidation-induced strain, and most of them diffuse into the oxide and are oxidized there. In addition, the emitted Si species in the oxide govern the oxidation rate. Based on the model, we have simulated the whole range of oxide thickness, including the thin film regime, in a wide range of oxidation conditions [5]. Moreover, we have shown [6] that the strain release by the Si emission can explain Si layer-by-layer oxidation.

In this study, in order to further study the effectiveness of the interfacial Si emission model, we simulate dry oxidation containing small amounts ($\leq 10\%$) of water and chlorine based on the model. From the simulation results for the effect of H and Cl on the interfacial Si emission, we show the effectiveness of the interfacial Si emission model.

2. Models and Simulation

We simulate the oxidation in the addition of water and chlorine [7] according to the Si emission model mentioned above, which leads to a set of coupled partial differential equations described in ref. 5. The equations are solved numerically by the partial differential equation solver ZOMBIE [8] using the following set of parameters:

$$\begin{aligned} C_{Si}^0 &: 3.60 \times 10^{24} \exp(-1.07 \text{ eV}/k_B T) \text{ cm}^{-3} \\ C_O^* &: 5.5 \times 10^{16} \text{ cm}^{-3} \\ D_{Si}^{SD} &: 1.3 \times 10^1 \exp(-4.5 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1} \\ D_O^{SD} &: 3.20 \times 10^{-8} \exp(-1.64 \text{ eV}/k_B T) \text{ cm}^2 \text{ s}^{-1} \\ \nu &: 9.44 \times 10^4 \exp(-1.76 \text{ eV}/k_B T) \quad [T \leq 1000 \text{ }^\circ\text{C}] \\ & \quad 2.78 \times 10^2 \exp(-1.12 \text{ eV}/k_B T) \quad [T \geq 1000 \text{ }^\circ\text{C}] \\ \nu(111) &= 0.4 \times \nu(100) \\ \kappa_1 &: 1.46 \times 10^{-14} \exp(-1.55 \text{ eV}/k_B T) \text{ cm}^3 \text{ s}^{-1} \\ \kappa_2 &: 1.46 \times 10^{-31} \exp(-1.55 \text{ eV}/k_B T) \text{ cm}^6 \text{ s}^{-1}, \end{aligned}$$

where C_{Si}^0 is the maximum concentration of Si interstitials in the oxide, C_O^* is the equilibrium concentration of the oxidant in the oxide, D_{Si}^{SD} and D_O^{SD} are the self-diffusivities of Si atom and of the oxidant in the oxide, ν is the emission rate of Si

atoms from the interface, and κ_1 and κ_2 are the oxidation rates of Si atoms in the oxide. The values of C_O^* , C_{Si}^0 and D_{Si}^{SD} from literature were used, and D_O^{SD} , ν , κ_1 and κ_2 were deduced from the simulation to fit the experimental data for dry oxidation [5].

H and Cl atoms may terminate the dangling bonds of Si and O to ease the reconstruction of Si-O bonds. Therefore, the addition of H and Cl could increase the fluidity of the grown oxide, which may decrease ν and increase C_O^* , C_{Si}^0 , κ_1 , and κ_2 . In order to investigate the effect of H and Cl on these parameters, we simulate dry oxidation in the addition of H and Cl. In our model, the decrease of ν cannot be distinguished from the increase of C_{Si}^0 , κ_1 , and κ_2 [4]. In the present simulation, the ν value is tentatively reduced according to the addition of H and Cl, which is found to be reasonable in Sec. 3. The oxidation rates at short oxidation times (reaction-limited regime) are mainly determined by ν , while those at long times (diffusion-limited regime) are determined by D_O^{SD} (and therefore C_O^*). Therefore, the values of ν and C_O^* can be uniquely determined.

3. Results and Discussion

The oxide thickness for Cl_2/O_2 and $\text{H}_2\text{O}/\text{O}_2$ mixtures simulated in this study (solid lines) and that from experiments (symbols) [7] are shown in Figs. 1(a) and (b) for Si (100) substrates at 1000 °C. The simulation gives close fits to the experimental oxide thickness when the ν values shown in Fig. 2 are used [$\nu = 1.0\%$ without Cl_2 and H_2O]. In addition, C_O^* increases in proportion to the concentration of Cl_2 and H_2O . We mention that the oxide thickness for (111) substrates under the same oxidation conditions were also fitted by $\nu(111) = 0.4 \times \nu(100)$, with other parameters being fixed. This is quite reasonable because the transport process and the oxidation in the oxide should be independent of the orientation of underlying substrates [5].

The ν value deduced from the simulation decreases by the Cl additions to one-half that for the case without Cl and levels off at a Cl_2 concentration smaller than 1 %. Similarly, the ν value for the H additions decreases to 65 % that for the case without H and levels off at a concentration smaller than 2 %. These trends have also been seen in the linear rate constant of D-G theory [7]. In addition, the tendency for Cl is consistent with the Si emission to the substrates estimated from oxidation-enhanced diffusion (OED) [9].

The leveling-off of ν seems to suggest that H and Cl mainly contribute to interfacial phenomena and their effect to the oxide bulk properties (C_{Si}^0 , κ_1 , and κ_2) is minor, assuming that more H and Cl atoms than the Si interface

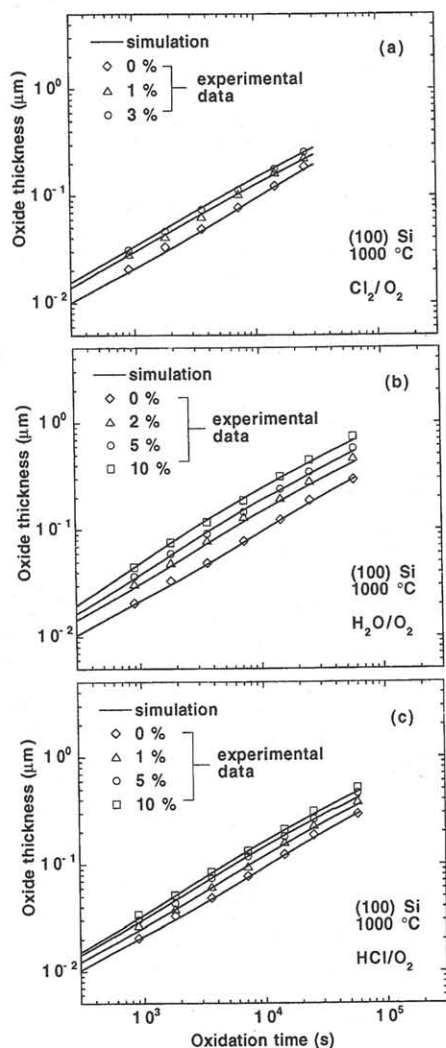


Fig. 1 Simulated (solid lines) and experimental (symbols: ref. 7) oxide thickness for dry oxidation of Si (100) substrates in various mixtures of (a) Cl₂, (b) H₂O, and (c) HCl at 1000 °C.

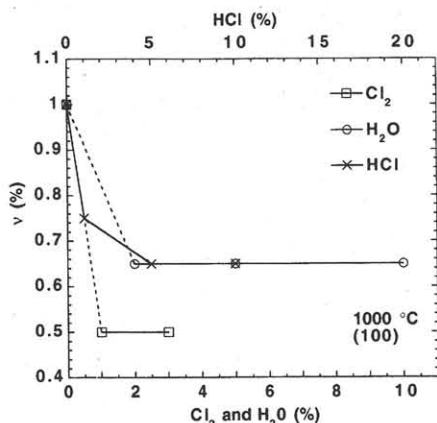


Fig. 2 The ν values deduced from the simulations in Fig. 1.

density do not effectively work. The reduction of OED by Cl has been explained by assuming a direct reaction between Cl and emitted Si atoms [9]. However, we showed that not only Cl but also H reduce the interfacial Si emission. This may suggest that H and Cl could play an important role at the interface in reducing the oxidation-induced strain because the Si emission releases the strain [3]. The mechanism of the strain reduction is not yet clear, and further atomic-level studies by first-principles calculations are required to clarify the effect of H and Cl on the strain reduction at the interface.

Based on the results for Cl₂ and H₂O, we also simulate the oxidation in the addition of HCl [Fig. 1(e)], which produces Cl₂ and H₂O at the interface by the reaction with O₂ [7]. The ν values deduced are shown in Fig. 2, where the 2:1 ratio for (HCl):(Cl₂ and H₂O) is predicted by the reaction $4\text{HCl} + \text{O}_2 \Rightarrow 2\text{Cl}_2 + 2\text{H}_2\text{O}$ [7]. The ν value decreases to 65 % that for the case without HCl and levels off at a HCl concentration between 1 and 5 %. The results in Fig. 2 seem to suggest that H is more likely to occupy the interface than Cl, although Cl can more effectively reduce the interfacial strain.

4. Conclusion

The effect of H and Cl on the interfacial Si emission has been investigated by the simulation of dry oxidation in the addition of Cl₂, H₂O, and HCl. The ν value decreases and the C_0 value increases by the addition of these species, as expected from the interfacial Si emission model. From these results, we showed that the interfacial Si emission model is effective to describe oxidation processes.

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References

- [1] B. E. Deal and A. S. Grove: *J. Appl. Phys.* **36** (1965) 3770.
- [2] S. T. Dunham and J. D. Plummer: *J. Appl. Phys.* **59** (1986) 2541; K. Taniguchi, Y. Shibata and C. Hamaguchi: *J. Appl. Phys.* **65** (1989) 2723; Y. Takakuwa, M. Nihei and N. Miyamoto: *Appl. Surf. Sci.* **117/118** (1997) 141.
- [3] H. Kageshima and K. Shiraishi: *Phys. Rev. Lett.* **81** (1998) 5936.
- [4] H. Kageshima, K. Shiraishi and M. Uematsu: *Jpn. J. Appl. Phys.* **38** (1999) L971.
- [5] M. Uematsu, H. Kageshima and K. Shiraishi: *Jpn. J. Appl. Phys.* **39** (2000) L699; L952; L1153; *J. Appl. Phys.* **89** (2001) 1948.
- [6] K. Shiraishi, H. Kageshima and M. Uematsu: *Jpn. J. Appl. Phys.* **39** (2000) L1263.
- [7] D. W. Hess and B. E. Deal: *J. Electrochem. Soc.* **124** (1977) 735; B. E. Deal, D. W. Hess, J. D. Plummer and C. P. Ho: *J. Electrochem. Soc.* **125** (1978) 339.
- [8] W. Jüngling, P. Pichler, S. Selberherr, E. Guerrero and H. W. Pötzel: *IEEE Trans. ED-32* (1985) 156.
- [9] S. Solmi and P. Negrini: *Appl. Phys. Lett.* **45** (1984) 157.