

## Invited

**Silicon Oxidation Kinetics in the Thin-Film Regime**

Hisham Z. Massoud

Department of Electrical Engineering, Duke University,  
Durham, North Carolina 27706, U.S.A.

The present status of silicon oxidation in the thin-film regime is reviewed with emphasis on experimental results and modeling approaches. The effects of temperature, orientation, and dopant concentration in the substrate on the oxidation kinetics are discussed. The observation of a delay in the onset of oxidation at temperatures in the 800-1000°C range is also presented.

**INTRODUCTION**

The investigation of silicon oxidation kinetics in the thin-film regime for oxides thinner than 300Å is becoming increasingly more important with the continuous shrinkage of VLSI and ULSI device dimensions. Oxide thicknesses smaller than 120Å are used in submicron channel-length MOSFETs as the gate-dielectric material. Understanding the oxidation kinetics in this thickness range is not only important for the technological purposes of controlling the growth process and the oxide quality, but also in optimizing the multitude of other phenomena influenced by oxidation such as point-defect diffusion and recombination, dopant diffusion, gettering, and damage annealing.

In this paper, some experimental and modeling investigations of SiO<sub>2</sub> growth in the thin-film regime will be highlighted, the oxidation of heavily doped silicon in the thin-film regime and its modeling will be discussed, and experimental observations of a delay in SiO<sub>2</sub> growth at the onset of the oxidation process will be presented.

**ULTRATHIN OXIDATION KINETICS**

It has long been established that the oxidation of lightly doped silicon in dry oxygen and in steam can be modeled by the transport of oxidizing species through the existing oxide and their reaction with silicon atoms at the Si-SiO<sub>2</sub> interface to form

SiO<sub>2</sub>, as described by the Deal-Grove model.<sup>[1]</sup> This model yields linear-parabolic growth kinetics where the oxidation rate is expressed as

$$\frac{dX_{ox}}{dt} = \frac{B}{2X_{ox} + A}, \quad (1)$$

where  $X_{ox}$  is the oxide thickness,  $B$  the parabolic rate constant, and  $B/A$  the linear rate constant. In early studies of SiO<sub>2</sub> growth kinetics, it was also observed that, for oxides thinner than 250Å, oxidation proceeds at a rate larger than predicted by linear-parabolic kinetics.<sup>[1]</sup> The use of high-temperature *in situ* automated ellipsometry has provided a detailed characterization of SiO<sub>2</sub> growth kinetics in the thin-film regime on (100),<sup>[2]</sup> (111),<sup>[3]</sup> and (110) silicon in the 800-1000°C range in dry-O<sub>2</sub>/Ar mixtures ranging from pure O<sub>2</sub> to 1% O<sub>2</sub> in Ar. Figure 1 shows the oxidation kinetics of (110) silicon in dry oxygen.

The oxidation rate enhancement in the thin-film regime was analyzed as a function of the oxide thickness,<sup>[2]</sup> and the oxidation time.<sup>[3]</sup> As a function of the oxide thickness, the oxidation rate was found to best fit a growth rate expression of the form

$$\frac{dX_{ox}}{dt} = \frac{B}{2X_{ox} + A} + C \exp(-X_{ox}/L), \quad (2)$$

where  $C$  and  $L$  are constants. The parameter  $C$  was found to be both temperature- and orientation-dependent while the parameter  $L$  was found, in a

first-order analysis, to be independent of temperature and orientation.<sup>[2]</sup> When analyzed as a function of time, it was found that the oxidation rate best fit an expression of the form<sup>[3]</sup>

$$\frac{dX_{ox}}{dt} = \frac{B + K_1 \exp(-t/\tau_1) + K_2 \exp(-t/\tau_2)}{2X_{ox} + A}, \quad (3)$$

where  $K_1$ ,  $K_2$ ,  $\tau_1$ , and  $\tau_2$  are well behaved parameters that depend on both the silicon orientation and the oxidation temperature. The oxidation rate expression in Eq. (3) can be integrated analytically in the form<sup>[3]</sup>

$$X_{ox}(t) = \left\{ (A/2)^2 + Bt + M_1[1 - \exp(-t/\tau_1)] + M_2[1 - \exp(-t/\tau_2)] + M_0 \right\}^{1/2} - A/2, \quad (4)$$

where  $M_1 = K_1\tau_1$ ,  $M_2 = K_2\tau_2$ ,  $M_0 = X_n^2 + AX_n$ , and  $X_n$  is the native oxide thickness. A typical fit to the experimental data is shown in Fig. 2, for (100) silicon oxidized in dry oxygen at 900°C.<sup>[3]</sup> Among other approaches that are successful in fitting the oxidation data in the thin-film regime, two fitted the data over a wide range of experimental conditions. In the first, the oxidation rate was assumed to consist of two Deal-Grove terms with different rate constants,<sup>[4]</sup> and in the second, a power-law fit was used.<sup>[5]</sup>

It has been experimentally established that the kinetics of silicon oxidation in the thin-film regime depends on the pre-oxidation chemical cleaning,<sup>[6]</sup> the concentration of interstitial oxygen dissolved in the substrate,<sup>[7]</sup> the substrate orientation resulting in kinetics cross-over at small thicknesses,<sup>[8]</sup> the partial pressure of oxygen in the oxidizing ambient,<sup>[9]</sup> the formation of SiO as an intermediate in the oxidation process,<sup>[10]</sup> and the presence of chlorinated species.<sup>[11]</sup> The models of silicon oxidation in the thin-film regime have been reviewed, analyzed, and revised.<sup>[12-21]</sup> These models were based on chemical transport effects in the oxide,<sup>[3,22,23]</sup> oxidant solubility in the oxide,<sup>[19]</sup> carrier tunneling and space-charge effects in the oxide,<sup>[24-28]</sup> stress and viscosity effects in the oxide,<sup>[29-31]</sup> oxidant effects at the interface,<sup>[32]</sup> oxidant effects in the substrate,<sup>[3,33]</sup> and substrate effects.<sup>[12]</sup>

It was proposed<sup>[12]</sup> that the oxidation rate enhancement in the thin-film regime is likely caused by additional oxidation sites near the surface by virtue of being the surface of an unoxidized silicon substrate. Some departure in the silicon surface from bulk properties could be in the form of damage, disorder, bond breaking, bond stretching, surface re-

construction, or vacancies. This departure from bulk conditions is an inherent property and would exist on any oxide-free surface. The concentration of these sites has a profile which decays exponentially with a characteristic length of  $\sim 30\text{\AA}$ .<sup>[12]</sup> It was also proposed that the presence of hydrogen generated when silicon is oxidized in steam would be responsible for the reordering of the silicon surface layer and the absence of oxidation-rate enhancement in the thin-film regime in steam oxidations.<sup>[12]</sup>

## OXIDATION OF HEAVILY DOPED SILICON

Silicon heavily doped with B, P, or As has long been characterized by an oxidation rate larger than that of lightly doped silicon.<sup>[34]</sup> This behavior was explained by the influence of the concentration of the electrically active dopant at the oxidizing interface on the surface Fermi level.<sup>[34]</sup> Additional unexpected observations of heavily arsenic-implanted silicon oxidizing faster at lower temperatures<sup>[35]</sup> and heavily doped silicon oxidizing more slowly after  $\sim 300\text{\AA}$  grown in a first oxidation were etched prior to the second oxidation<sup>[36]</sup> were reported. These observations indicated that phosphorus depletion takes place at the onset of oxidation, which is in agreement with previously reported phosphorus pile-up at the Si-SiO<sub>2</sub> interface obtained by Auger electron spectroscopy (AES) profiling.<sup>[37]</sup> The nature of the pile-up region at the interface was identified by Haggmann *et al.*<sup>[38]</sup> for heavily arsenic-implanted silicon oxidized in wet oxygen with transmission electron microscopy (TEM) and secondary-ion mass spectrometry (SIMS) as a silicide phase AsSi formed at the interface.

A three-stage model was proposed to describe SiO<sub>2</sub> growth kinetics and the behavior of high concentrations of phosphorus in silicon during oxidation in dry oxygen in the thin-film regime.<sup>[39]</sup> In the first stage, the formation of a silicide phase at the interface depletes the dopants near the surface lowering the concentration of electrically active species. In the second stage, the flux of dopant atoms to the interface stops and the concentration of electrically active phosphorus increases at the interface from concentrations smaller than that in the bulk value to higher values. In the third stage, a steady-state concentration of electrically active phosphorus is reached at the interface. The time dependence of the concentration of electrically active phosphorus at the interface results is reflected in the oxidation kinetics. The redistribution of dopants in the initial stages of the oxidation of heavily doped substrates

can be modeled by considering that a third phase, in this case the silicide layer, is present between the bulk phases of the substrates and that of the oxide, as described by Orlowski.<sup>[40]</sup>

### THE ONSET OF THE OXIDATION PROCESS

Monitoring the thermal growth of SiO<sub>2</sub> layers on silicon in the thin-film regime *in-situ* using a high-temperature automated ellipsometer allowed for a closer examination of the kinetics in the early stages of the oxidation process in the 800°C–1000°C range.<sup>[2]</sup> The wafers were introduced into the oxidation furnace and allowed to reach the oxidation temperature while idling in argon. The native oxide thickness was measured and the system was then switched to dry oxygen. The oxide thickness was monitored as soon as oxygen was allowed in the oxidation chamber. From the geometry of the oxidation furnace and the oxygen flow rate, it was estimated that a complete volume change would necessitate less than 1 sec. It was observed for all orientations that SiO<sub>2</sub> growth only starts after a delay period  $T_D$ .<sup>[41]</sup> Figure 3 shows the temperature and orientation dependence of  $T_D$  for (100), (111), and (110) wafers. The oxidation of silicon at room temperature was also observed to exhibit a delay period  $T_D$  that depends on the substrate orientation and dopant concentration, and on the chemical nature of the pre-oxidation treatment.<sup>[42]</sup>

The time needed for O<sub>2</sub> molecules to diffuse through the thickness of the native oxide is much shorter than that observed for the delay time  $T_D$ . It is therefore concluded that the delay in the onset of SiO<sub>2</sub> growth is due to the presence or the formation of a layer that blocks the oxidation at the Si–SiO<sub>2</sub> interface in the initial stages of oxidation. The nature of this blocking mechanism has not been identified. It is proposed here that the presence of a surface film on the wafer following the pre-oxidation cleaning could be responsible for the delay  $T_D$ . Further investigations are needed to define the nature of the delay mechanism. A possible example of a blocking layer that forms at the onset of oxidation is to assume that the concentration of oxygen at the silicon/native-oxide interface is initially so low that the formation of SiO is favored. It then is assumed that all oxygen reaching that interface is consumed in the formation of SiO and that the diffusivity of SiO molecules in the native oxide is so low, especially at low temperatures, that they hardly leave the interface region. These SiO molecules, being slightly larger than O<sub>2</sub> molecules, block oxidation

sites and prevent the formation of SiO<sub>2</sub>. When the entire surface of silicon is covered with a monolayer of SiO, this blocking layer at the interface then becomes a perfect reflecting boundary for incoming oxygen whose concentration increases rapidly and reaches quickly the condition where SiO<sub>2</sub> formation is favored. At that point, the oxide forms with a large growth rate which reflects the transformation of both Si and SiO into SiO<sub>2</sub>. This process could be repeated after each step and a staircase growth curve would be obtained as was observed experimentally by Ohmi *et al.*<sup>[42]</sup> Calculated times for the formation of a monolayer of SiO is on the same order of magnitude as the observed delay times.<sup>[41]</sup>

### CONCLUSIONS

The oxidation kinetics of silicon in the thin-film regime was reviewed and found to be different from thick-film kinetics as a result of the presence of the oxide-free surface at the onset of the oxidation process. This presence affects the onset of SiO<sub>2</sub> formation, the nature of the oxidation mechanism, and the behavior of dopants in the initial stages of oxidation.

### REFERENCES

1. B. E. Deal and A. S. Grove, *J. Appl. Phys.* **36**, 3770 (1965).
2. H. Z. Massoud, J. D. Plummer, and E. A. Irene, *J. Electrochem. Soc.* **132**, 1745 and 2685 (1985).
3. H. Z. Massoud and J. D. Plummer, *J. Appl. Phys.* **62**, 3416 (1987).
4. C. J. Han and C. R. Helms, *J. Electrochem. Soc.* **134**, 1297 (1987).
5. A. Reisman, E. H. Nicollian, C. K. Williams, and C. J. Merz, *J. Electron. Mat.* **16**, 45 (1987).
6. See for example: D. B. Kao, B. E. Deal, J. M. de Larios, and C. R. Helms, in *The Physics and Chemistry of SiO<sub>2</sub> and the Si–SiO<sub>2</sub> Interface*, C. R. Helms and B. E. Deal, Eds., Plenum Press, New York, N.Y., p. 421, 1988.
7. V. Murali and S. P. Murarka, *J. Appl. Phys.* **60**, 4327 (1986).
8. E. A. Irene, H. Z. Massoud, and E. Tierney, *J. Electrochem. Soc.* **133**, 1253 (1986).
9. Y. J. van der Meulen, *J. Electrochem. Soc.* **119**, 530 (1972).
10. S. I. Raider, Ref. 6, p. 35.
11. Z.-M. Ling, L. H. Dupas, and K. M. De Meyer, Ref. 6, p. 53.
12. H. Z. Massoud, J. D. Plummer, and E. A. Irene, *J. Electrochem. Soc.* **132**, 2693 (1985).
13. B. E. Deal, Ref. 6, p. 5.

14. E. A. Irene, *Crit. Rev. Sol. State and Mat. Sci.* **14**, 175 (1988).
15. E. A. Irene, *J. Electrochem. Soc.* **125**, 1708 (1978).
16. A. Fargeix, G. Ghibaudo and G. Kamarinos, *J. Appl. Phys.* **54**, 2878 (1983).
17. W. A. Tiller, *J. Electrochem. Soc.* **127**, 619 (1980), **127**, 625 (1980), **128**, 689 (1981), and **130**, 501 (1983).
18. N. F. Mott, S. Rigo, F. Rochet, and A. M. Stoneham, *Phil. Mag.* **B60**, 189 (1989).
19. M. Orlowski and V. Pless, *Appl. Phys.* **A46**, 67 (1988).
20. F. Rochet, S. Rigo, M. Froment, C. D'Anterrosches, C. Maillot, H. Roulet, and G. Dufour, *Adv. in Phys.* **35**, 237 (1986).
21. E. A. Lewis and E. A. Irene, *J. Vac. Sci. Technol.* **A4**, 916 (1986).
22. E. A. Irene, *Appl. Phys. Lett.* **40**, 74 (1982).
23. V. K. Samalam, *Appl. Phys. Lett.* **47**, 736 (1985).
24. Y. Z. Lu and Y. C. Cheng, *J. Appl. Phys.* **56**, 1608 (1984).
25. S. M. Hu, *Appl. Phys. Lett.* **42**, 872 (1983).
26. D. R. Wolters and A. T. A. Zegers van Duyhoven, *J. App. Phys.* **65**, 5126 (1989).
27. S. A. Schafer and S. A. Lyon, *Appl. Phys. Lett.* **47**, 154 (1985).
28. E. A. Irene and E. A. Lewis, *Appl. Phys. Lett.* **51**, 767 (1987).
29. E. A. Irene, *J. Appl. Phys.* **54**, 5416 (1983).
30. G. Ghibaudo, *Phil. Mag.* **B55**, 147 (1987).
31. E. H. Nicollian and A. Reisman, *J. Electron. Mat.* **17**, 263 (1988).
32. R. Ghez and Y. J. van der Meulen, *J. Electrochem. Soc.* **119**, 1100 (1972).
33. V. Murali and S. P. Murarka, *J. Appl. Phys.* **60**, 2106 (1986).
34. See for example: C. P. Ho and J. D. Plummer, *J. Electrochem. Soc.* **126**, 1516 and 1523 (1979).
35. S. S. Choi, M. Z. Numan, W. K. Chu, and E. A. Irene, *Appl. Phys. Lett.* **51**, 1001 (1987).
36. H. Z. Massoud, *Appl. Phys. Lett.* **53**, 497 (1988).
37. S. A. Schwarz, R. W. Barton, C. P. Ho, and C. R. Helms, *J. Electrochem. Soc.* **128**, 1101 (1981).
38. D. Hagmann, W. Euen, G. Schörer, and G. Metzger, *J. Electron. Mat.* **18**, 561 (1989).
39. R. R. Ward, H. Z. Massoud, and R. B. Fair, in *Semiconductor Silicon 1990*, H. R. Huff *et al.*, Eds., the Electrochemical Society, Pennington, New Jersey, **PV90-7**, 405 (1990).
40. M. Orlowski, *Appl. Phys. Lett.* **55**, 1762 (1989).
41. H. Z. Massoud, *Appl. Phys. Lett.* submitted for publication.
42. See for example: T. Ohmi, M. Morita, E. Hasegawa, M. Kawakami, and K. Suma, in *ULSI Science and Technology 1989*, the Electrochemical Society, Pennington, New Jersey, **PV89-9**, 327 (1989).

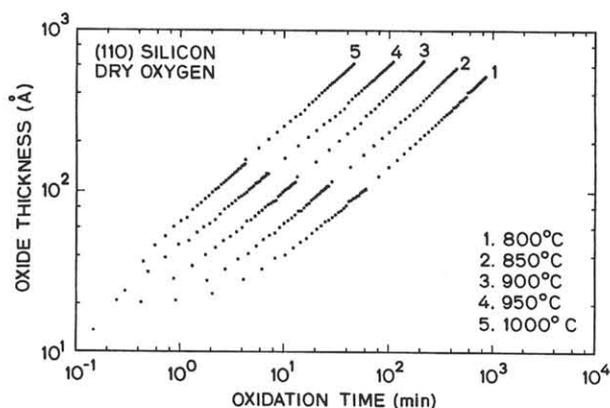


Fig. 1. Silicon oxidation kinetics on lightly doped (110) silicon oxidized in dry  $O_2$  in the 800–1000°C range.

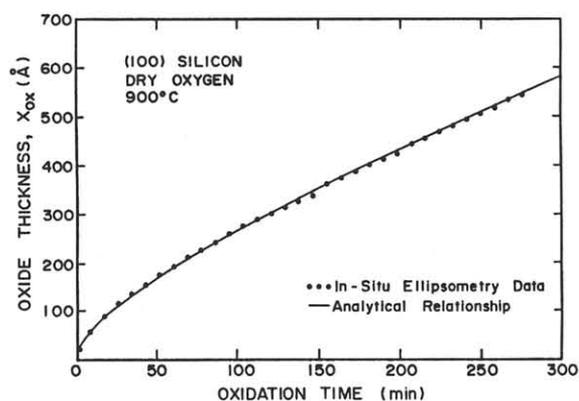


Fig. 2. Fitting the oxidation kinetics of (100) silicon oxidized at 900°C in dry oxygen using the analytical expression in Eq. (4).<sup>[3]</sup>

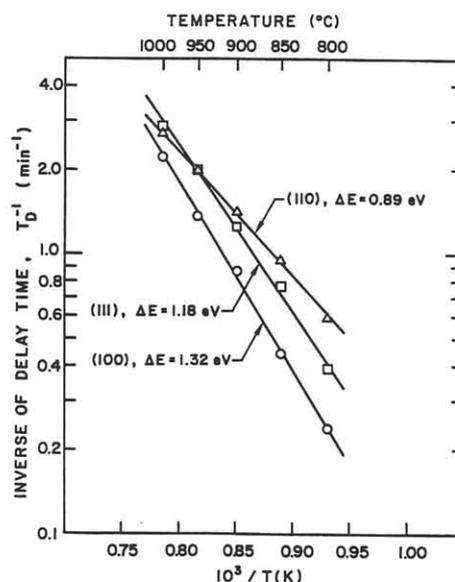


Fig. 3. Orientation and temperature dependence of the delay time  $T_D$  in the oxidation of (100), (111), and (110) silicon in dry  $O_2$ .<sup>[41]</sup>