

phys. stat. sol. (a) **134**, 447 (1992)

Subject classification: 68.55; 61.16; S10.1

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Silicon Oxidation in the Thin Oxide Regime

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Thermal oxidation of silicon in the thin regime is of vital importance to VLSI device engineers because thin layers of SiO₂ are exclusively used as the gate dielectric for high performance of MOS devices. There exists a number of models to explain this kinetics of oxidation. However there is a considerable variance among the reported rate constants, which are supposed to describe the oxidation process. Rather than arriving at an alternative model, the present study aims at simulation of existing models of oxidation in dry oxygen, with a set of experimental data and arrive at the best possible model and provide accurate rate constants for oxidation in dry oxygen. These experimental data have been obtained, earlier, using high-resolution transmission electron microscopy (HRTEM) and ellipsometry techniques to measure thickness of silicon oxide, grown at 800 °C in dry oxygen, in the thickness range of 2 to 20 nm.

Die thermische Oxydation von Si im dünnen Bereich ist besonders wichtig für VLSI-Device-Ingenieure, weil dünne SiO₂-Schichten ausschließlich als Gate-Dielektrikum für Hochleistungs-MOS-Devices verwendet werden. Es gibt eine Reihe von Modellen zur Erklärung der Oxydationskinetik. Die angegebenen Werte der den Prozeß beschreibenden Konstanten variieren jedoch erheblich. Es wird hier kein neues Modell entwickelt, sondern die existierenden Modelle werden mit experimentellen Daten simuliert, um zum besten Modell und genauen Konstanten für die Oxydation in trockenem Sauerstoff zu gelangen. Die experimentellen Daten stammen von früheren HRTEM und ellipsometrischen Messungen der Dicke des bei 800 °C in trockenem Sauerstoff gewachsenen SiO₂ im Bereich von 2 bis 20 nm.

1. Introduction

The oxidation of silicon is necessary during the entire process of fabricating modern integrated circuits. The production of high-quality ICs requires not only an understanding of the basic oxidation mechanism, but the ability to form in a controlled and reproducible manner a high quality oxide. Thus the growth of SiO₂ by thermal oxidation has been a critical step in semiconductor processing since the very inception of microelectronics industry.

With devices approaching submicron dimensions, production and characterization of highly reliable ultrathin SiO₂ films are assuming major importance in very large-scale integration (VLSI) technology. The thermal oxidation of Si in the thin regime (< 50 nm) is of vital importance to VLSI processing and technology. This is because thin layers of SiO₂ are used exclusively as the gate oxides, requiring a low thermal budget, compatible with the rest of the processing steps involved in silicon technology [1].

The oxidation of single-crystal Si is for the most part actually characterized by Deal and Grove model [2] formalism. The major deviation of this model consists of anomalously rapid initial oxidation for the first 20 to 40 nm of growth in dry O₂. The standard linear-parabolic formulation accounts for the regime especially by the incorporation of a

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time constant τ in the expression for oxide growth. Moreover this model is based on arguable physical assumptions (e.g. steady state is possible in solid state diffusion, and linear and diffusion specific rate constants can be rate limiting at the same time).

Extensive research efforts have been devoted to the study of this initial regime and number of different forms and mechanisms have been suggested. Rather than arriving at a new model, this paper aims at reviewing the current models and arrive at a relationship, which best describes the initial regime during oxidation in dry oxygen, in the light of the present experimental data. The discrepancy between the ellipsometric and high-resolution transmission electron microscopy (HRTEM) measurements is also of particular interest.

2. Experimental Procedure and Data Analyses

The oxides were grown at 800 °C on single-crystal silicon wafers (p-type Czochralski). The wafers were of $\langle 100 \rangle$ orientation and 2 Ωcm resistivity. The wafers were cleaned using conventional RCA technique followed by a dilute hydrofluoric acid dip and a thorough rinsing with deionized (DI) water. Oxides were thermally grown for time durations of 1 to 300 min. Ultra high purity oxygen ($\text{H}_2\text{O} < 0.5$ ppm) was used in the oxidation process. Typically, the oxide thickness used in the measurement of the electrical properties was ≈ 20 nm. This thickness is typical of the present day gate oxides for a 1 μm CMOS process [3].

Oxide thickness measurements were carried out using a carefully aligned Gaertner manual and automatic ellipsometer [1, 4]. The agreement in the thickness obtained from both the ellipsometers was within 0.5 nm. Thickness measurement was carried out at nine positions of the wafer. The mean deviation of the thickness was found to be $\approx 2\%$. For determination of the oxide thickness, a refractive index of 1.465 (at 632.8 nm corresponding to the He-Ne laser) for SiO_2 was used.

The data analyses were performed by using an analysis and graphics program called GENPLOT [5], a product of Computer Graphic Service (CGS). It includes a very powerful set of data fitting routines. Data may be fitted to linear or polynomial functions or to a user specified arbitrary function. This non-linear fit searches the parameter space of the variables to obtain the best squares fit of the data to the analytic function. The best fit estimate and an estimate of the error are returned to each parameter.

3. Results and Discussion

A summary of the oxide thickness measurements is presented in Table 1. As can be seen from the table, the oxide thicknesses obtained by ellipsometry are within ≈ 1 nm of those measured by TEM. Fig. 1 shows the thickness versus time growth kinetics for these samples. Both ellipsometric and HRTEM data are plotted in this figure. Two very thin and two thick samples (A through D, respectively) were chosen for HRTEM studies. From the figure, it can be seen that the oxide growth data obtained from ellipsometry shows a non-linearity, whereas the data obtained from TEM is fairly linear. It may be noted here that the ellipsometry data of the oxide thickness in Table 1 and Fig. 1 represent an average of several nine-point measurements made on each wafer [1, 4]. The mean deviation of the oxide thickness was found to be within 0.3 nm.

Similar measurements of the oxide thickness in the thin oxide regime have been reported by Carim [6]. It is interesting to note that our results of the growth rate behavior obtained from TEM and ellipsometry are similar to those reported by Carim [6] despite the differences in the method of growth of the oxide in the two cases. In this study, the oxides have been

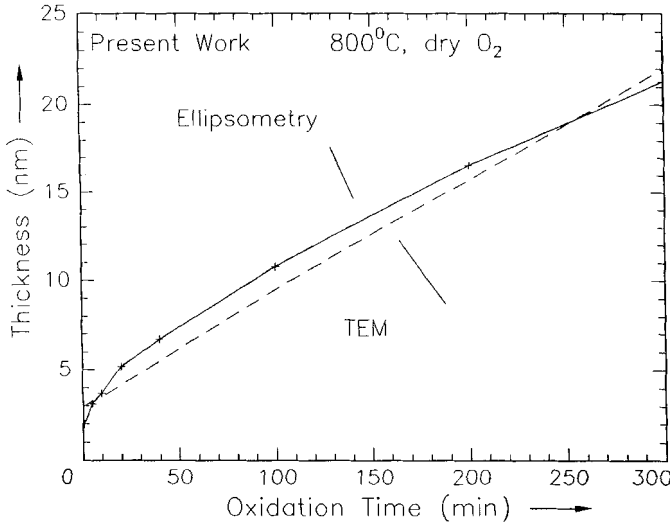


Fig. 1. Oxide thickness vs. time as measured by TEM and ellipsometry

grown at 800 °C in dry O₂, while Carim [6] grew the oxides at 900 °C in an ambient of 10% dry O₂ in Ar.

In this discussion, the various models are categorized by the functional forms, that they give rise to, for the initial oxide regime. Separate linear, parabolic, linear-parabolic, and variable power forms have been used to characterize the initial oxidation preceding the linear-parabolic portion of the curve that is well described by the Deal-Grove equation [2]. The different expressions considered in this work are listed below:

- linear-parabolic $x(t) = A_0 + A_1t + A_2t^2$,
- linear $x(t) = A_0 + A_1t$,
- parabolic $x(t) = A_0 + A_1t^2$,
- variable power $x(t) = A_0t^{A_1}$.

Table 1

Summary of the oxide thickness measurements (all thickness-values represent average values)

sample	oxidation time (t) at 800 °C (min)	oxide thickness (x)	
		ellipsometry (nm)	HRTEM (nm)
A	1	2.0	3.0
	5	3.1	
B	10	3.7	3.5
	20	5.2	
	40	6.7	
C	100	10.8	9.5
	200	16.6	
D	300	21.3	22.0

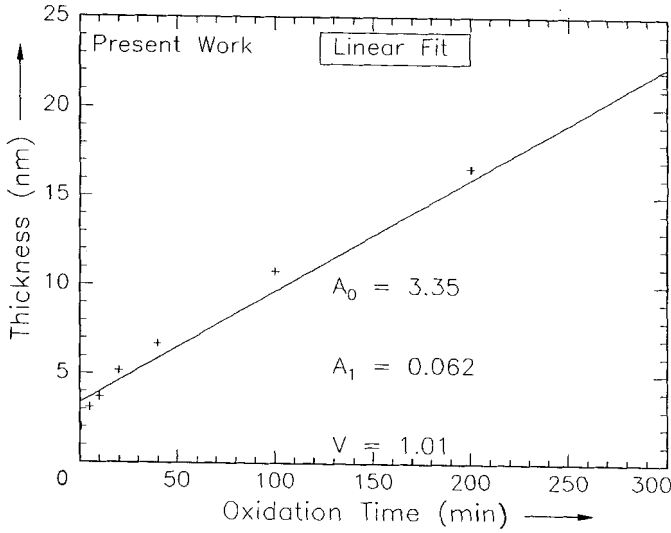


Fig. 2. Linear fit to oxide growth. (V is the variance)

Table 2

Calculated values of coefficients for linear, parabolic, linear-parabolic, and variable power best fits to oxidation data from ellipsometry

linear		parabolic		linear-parabolic			power	
A_0	A_1	A_0	A_1	A_0	A_1	A_2	A_0	A_1
3.35	0.062	-1.128	0.723	2.75	0.0908	-0.98×10^{-4}	1.01	0.52

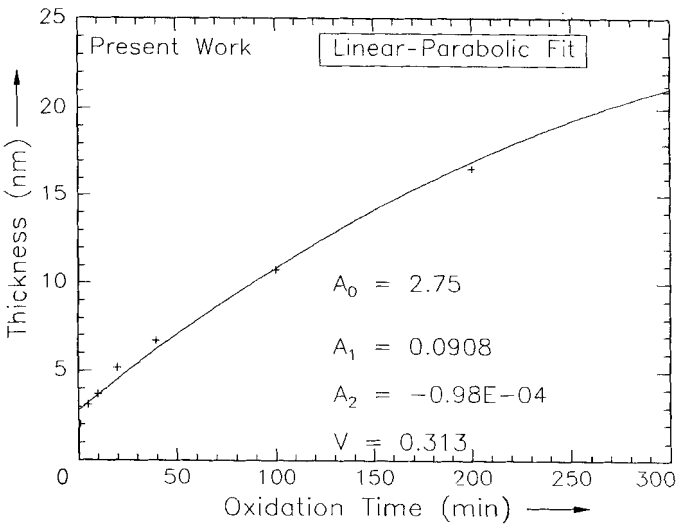


Fig. 3. Linear-parabolic fit to experimental data

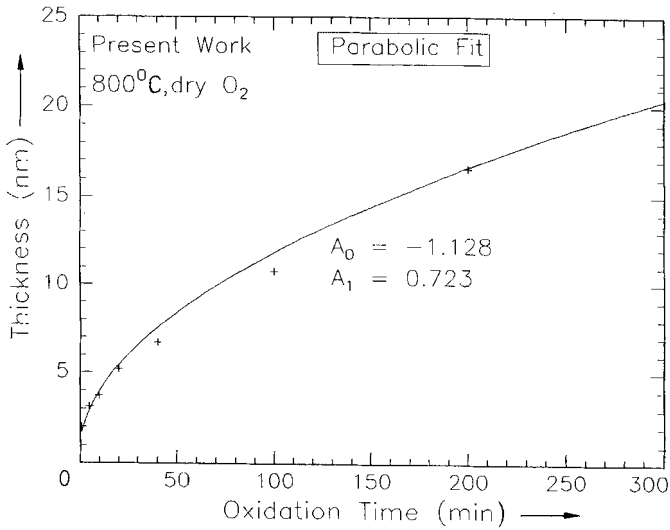


Fig. 4. Parabolic fit to experimental data

To compare possible formulations of the initial oxide growth law, it was assumed that all the oxides examined here were fabricated within the initial regime prior to Deal-Grove linear-parabolic oxidation and that approximation of the initial oxidation by a separate limiting expression is a reasonable simplification. The same thickness versus time data that is presented in Fig. 1 has been fitted to linear, parabolic, linear-parabolic, and variable power equations. Graphs illustrating the best fit of these equations to the data are shown in Fig. 2 to 5. The TEM data is fitted to linear and linear-parabolic expressions in Fig. 6 and 7, respectively. This is because of the fact that the HRTEM data in Fig. 1 shows a

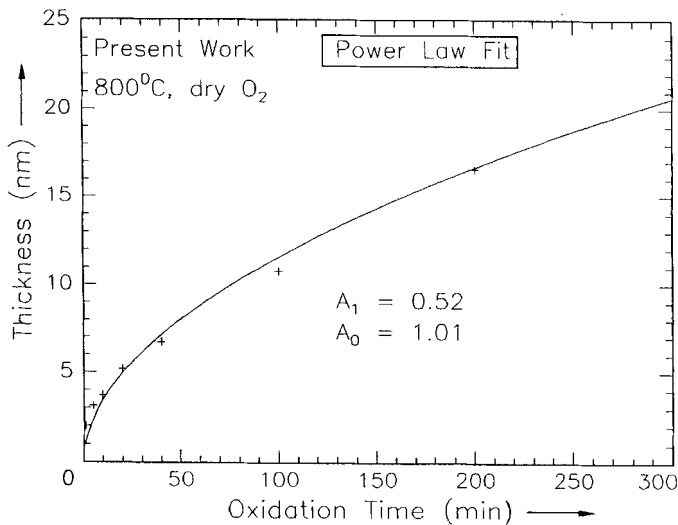


Fig. 5. Power law fit to experimental data

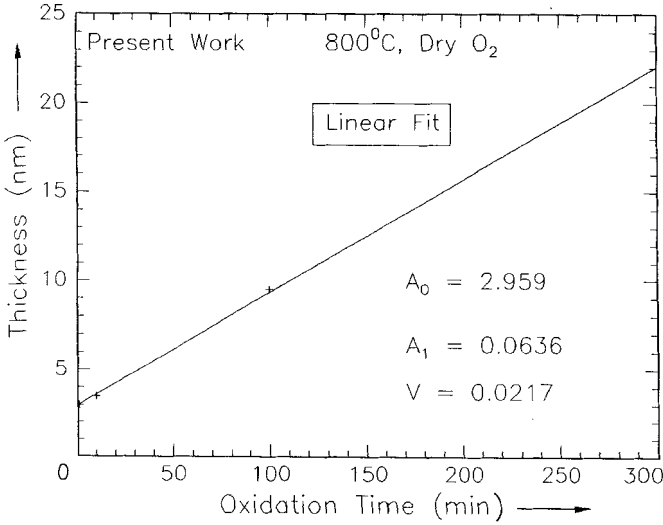


Fig. 6. Linear fit to experimental data

linear trend. The coefficients for the fitted expressions, for both ellipsometry and TEM, are shown in Tables 2 and 3.

It is interesting to note that the linear-parabolic expression gives an excellent fit to the data, as shown in Fig. 3. The existence of the third adjustable parameter will always lead to a better fit for a linear-parabolic formulation, than is possible for either a linear or a parabolic expression. The valid power law form which also provided a reasonable representation of the oxide growth data, is physically unrealistic, since increasing growth rate is obtained.

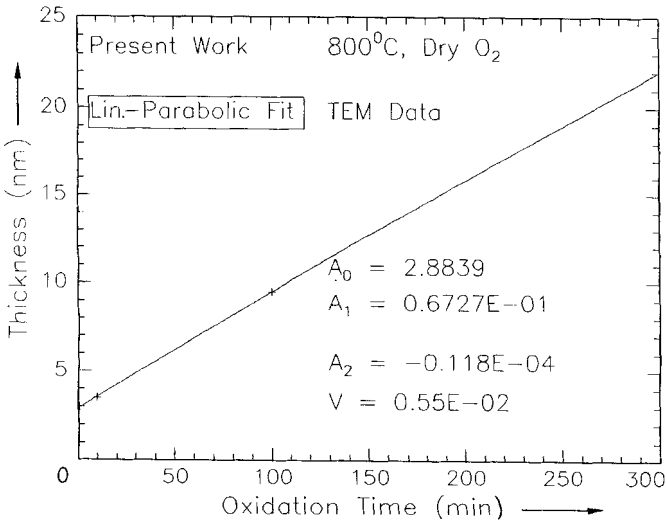


Fig. 7. Linear-parabolic fit to TEM data

Table 3
Calculated values of coefficients for linear and linear–parabolic best fits to TEM data

linear		linear–parabolic		
A_0	A_1	A_0	A_1	A_2
2.96	0.06	2.88	0.067	-0.12×10^{-4}

Several sets of data were then analyzed by the present procedure, and in all cases an excellent fit to linear–parabolic model was observed. The constants obtained from the work of other researchers [6 to 9] are described in Table 4. There is notable difference between the constants, but this phenomenon is well known to workers in this field. This indicates that oxidation data is process dependent. Examples of this phenomenon include pre-oxidation surface cleaning procedures, partial pressures of the chemical species, temperature and its uniformity, orientation, and resistivity of the wafers.

The linear–parabolic fits give an extrapolated “initial” oxide thickness of 2.76 nm prior to oxidation. This initial thickness is similar to the values of 2.7 and 2.5 to 3.0 nm derived by other workers [10, 11], although obtained via different techniques. This is due to the native oxide thickness and the oxide formed during the insertion of wafers into the furnace during ramp up of temperature.

The most striking facet of this work is that although the linear–parabolic expression gives an excellent fit to the ellipsometric data, it is less accurate when applied to the HRTEM data, which clearly shows a linear trend. The implications are that although the optical thickness of the oxide may develop according to a linear–parabolic law, the structural thickness increases linearly with time in the initial region. However, there are uncertainties in both techniques: a) In both single-wavelength and spectroscopic ellipsometry, a prior knowledge of the refractive index and extinction coefficient of SiO_2 is required in order to evaluate thickness. These values are dependent on the wavelength of the incident radiation and the oxide thickness, especially, for very thin films that are a few monolayers thick. b) In HRTEM, the oxide thickness measurements are complicated by the very nature of the

Table 4
Coefficients obtained from linear–parabolic fitting of published experimental data

ref.	A_0	A_1	A_2
present work	2.75	0.0908	0.98×10^{-4}
Carim et al. [6]	2.995	0.0089	-0.16×10^{-5}
Massoud et al. [7]	1.984	0.065	-0.41×10^{-4}
Reisman et al. [8]	7.3	0.487	-0.31×10^{-4}
Lie et al. [9]	15.3	0.26	-0.58×10^{-4}
Deal and Grove [2]	24.21	0.039	-0.20×10^{-5}

interface. Furthermore, as much as the method is destructive, one needs to perform these measurements on many samples from each wafer in order to map thickness as function of position on the wafer.

3. Conclusions

An analysis of the various models, proposed in the literature, for explaining the oxidation kinetics of silicon in the thin oxide regime, has been presented in this study. This analysis considers recently reported measurements of thicknesses of SiO₂ films grown thermally on Si at 800 °C for time durations of 1 to 300 min in dry O₂, using the techniques of HRTEM and ellipsometry. The ellipsometric data obtained from this work as well as from other research, showed an excellent fit to the linear-parabolic formulation of Deal and Grove. However the HRTEM data are somewhat different, and showed an initial linear regime.

Acknowledgements

The financial support of the New Jersey Commission of Science and Technology and the Center for Manufacturing Systems is gratefully acknowledged.

References

- [1] N. M. RAVINDRA, W. N. CARR, O. L. RUSSO, D. FATHY, A. R. HEYD, K. VEDAM, and J. NARAYAN, Proc. of the SPIE Conference on Semiconductors '88 **945**, 84 (1988).
- [2] B. E. DEAL and A. S. GROVE, J. appl. Phys. **36**, 3770 (1965).
- [3] N. M. RAVINDRA, J. NARAYAN, D. FATHY, J. K. SRIVASTAVA, and E. A. IRENE, J. Mater. Res. **2**, 216 (1987).
- [4] N. M. RAVINDRA, O. L. RUSSO, D. FATHY, J. NARAYAN, A. R. HEYD, and K. VEDAM, Proc. Mater. Res. Soc. **105**, 169 (1988).
- [5] GENPLOT, Computer Graphic Services, 1986.
- [6] A. H. CARIM, Ph. D. dissertation, Stanford University, Stanford (CA), 1989.
- [7] H. Z. MASSOUD, JAMES D. PLUMMER, and E. A. IRENE, J. Electrochem. Soc. **132**, 2685 (1985).
- [8] A. REISMAN, E. H. NICOLLIAN, C. K. WILLIAMS, and C. J. MERZ, MCNC Tech. Rep., TR86-04, April (1986).
- [9] L. N. LIE, R. R. RAZOUK, and B. E. DEAL, J. Electrochem. Soc. **129**, 2828 (1982).
- [10] K. K. NG, W. J. POLITO, and J. R. LIGENZA, Appl. Phys. Letters **44**, 626 (1984).
- [11] J. WONG, D. A. JEFFERSON, T. G. SPARROW, J. M. THOMAS, R. H. MILNE, A. HOWIE, and E. F. KOCH, Appl. Phys. Letters **48**, 65 (1986).

(Received July 16, 1992)