

# Comparison of H<sub>2</sub>O and D<sub>2</sub>O Oxidation Kinetics of <100> Silicon

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**Abstract**—Recent reports indicate that the incorporation of deuterium in the gate oxide of MOS-transistors can improve the integrity of thin gate oxides. The easiest and most direct means to incorporate the deuterium is to grow the gate oxide using heavy water (D<sub>2</sub>O). In this study the oxidation rate of <100> silicon using H<sub>2</sub>O and D<sub>2</sub>O are compared. The experimental data show that the oxidation rate is lower for D<sub>2</sub>O. The measured oxidation curves can physically not be fitted with the Deal-Grove model. A power law model seems to be more correct. The difference in oxidation rate of silicon using H<sub>2</sub>O and D<sub>2</sub>O might be attributed to a difference in H/D desorption from the silicon interface. This can be an explanation for improved oxide integrity.

**Keywords**— Silicon oxide; H<sub>2</sub>O; D<sub>2</sub>O; oxidation kinetics; Deal-Grove; power law

## I. INTRODUCTION

Recent reports [1][2] indicate that the reliability of thin gate oxides can be improved by incorporating deuterium during some stage in the process. The deuterium can be incorporated in different ways, but the easiest and most direct means is to grow the gate oxide in a D<sub>2</sub>O environment.

To be able to grow an oxide with a controllable thickness, knowledge of the oxidation kinetics is necessary. A lot of data is available for H<sub>2</sub>O, mostly for relative thick oxides. There is no data available in literature for D<sub>2</sub>O. Mitani et al. [3] briefly mention they observed a difference in oxidation rate.

This study compares the oxidation rate of silicon in an H<sub>2</sub>O and a D<sub>2</sub>O ambient for varying oxidation time and temperature. An attempt is made to model the measured oxidation curves with the Deal-Grove model and a power law model. The observed difference in oxidation

rate might provide an explanation for a difference in oxide integrity.

## II. EXPERIMENTAL SETUP

A thin (0-10nm) layer of silicon oxide was grown on 4 inch <100> silicon wafers with a boron concentration of approximately  $6 \cdot 10^{14} \text{cm}^{-3}$ . Prior to oxidation the wafers were dipped in a 1% HF solution until the wafer surface was hydrophobic. The oxidation was performed in a horizontal furnace. Nitrogen flowed at a rate of 4L/min through a small bubbler taking up H<sub>2</sub>O or D<sub>2</sub>O vapour and carried the precursor into the furnace. The resulting oxide thickness was measured with an ellipsometer.

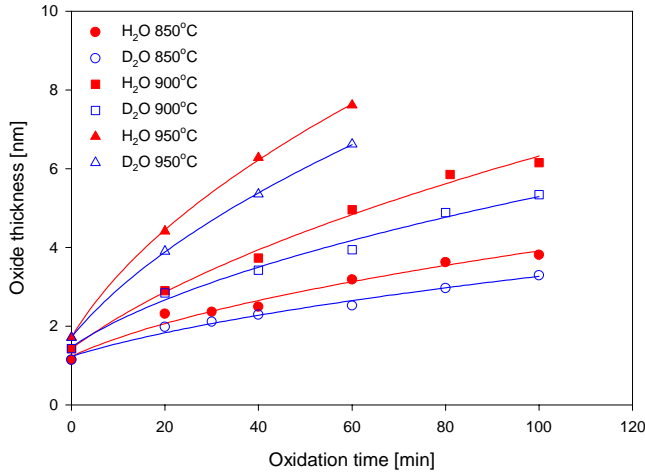
To exclude the influence of H<sub>2</sub>O/D<sub>2</sub>O pressure on the oxidation kinetics, the temperature of the bubbler was set at 17.5°C for H<sub>2</sub>O and at 20°C for D<sub>2</sub>O. These bubbler temperatures set the vapour pressure at 0.02Atm in both cases [4]. To investigate if the difference in bubbler temperature indeed resulted into an equal partial pressure for the two precursors inside the furnace, the mass loss of the bubbler was measured during oxidation.

## III. RESULTS AND DISCUSSION

### A. Oxidation curves

Figure 1 shows the oxide thickness as a function of time, temperature and precursor. The graph indicates that, for the same oxidation time and temperature, the oxide grown in a H<sub>2</sub>O ambient is on average 14% thicker than the oxide grown in a D<sub>2</sub>O ambient.

When going into the furnace, some cleanroom air (containing oxygen) is transported along into the furnace. This gives rise to an initial oxide thickness grown during the ramp-up of temperature as can be seen at  $t = 0$ .



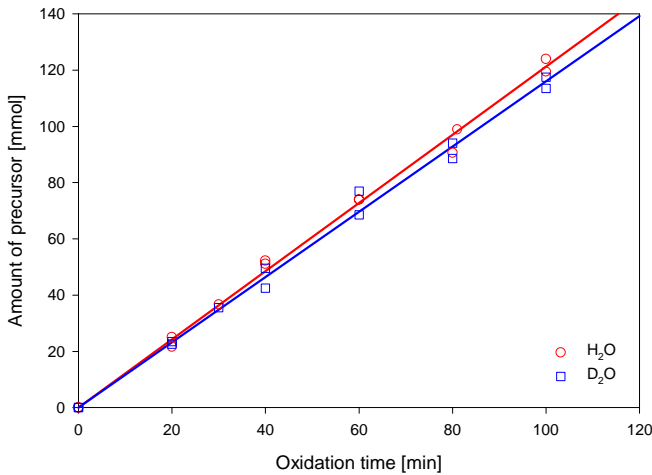
**Figure 1: Oxide thickness as a function of oxidation time, temperature and precursor. The markers indicate the experimental data and the lines the best fit with the Deal-Grove model.**

### B. Partial oxidation pressure

To exclude a possible influence of partial oxidation pressure on the oxide thickness, the mass loss of the bubbler was measured during oxidation. This mass loss is converted to the amount of precursor that was used during oxidation and is shown in figure 2.

The data in the figure indicates that there is a small difference between the amount of precursor introduced in the furnace for H<sub>2</sub>O and for D<sub>2</sub>O. The slope of the linear regression lines is 1.21 mmol/min for H<sub>2</sub>O and 1.16 mmol/min for D<sub>2</sub>O. The difference is only 4% and not enough to explain the difference in oxide thickness.

Taking into account the nitrogen flow of 4L/min, the precursor partial pressure is calculated to be  $7 \cdot 10^{-3}$  Atm.



**Figure 2: Amount of precursor introduced in the furnace as a function of oxidation time.**

### C. Modelling with the Deal-Grove model

The earliest developed model for thermal oxide growth of silicon is the model by Deal and Grove [5]. This model has been quite successful in explaining a large portion of the experimental data available. It is widely used. The model cannot explain the experimental data for thin oxides, especially grown with dry oxygen.

The model assumes the oxide growth occurs at the interface between the silicon and the silicon oxide. The model recognizes two rate-limiting steps. Firstly, the reaction between the precursor and the silicon interface to produce silicon oxide, and secondly the diffusion of the precursor through the already grown oxide towards the interface.

The first step is rate limiting during the initial growth and gives rise to a linear dependence. The second step is rate limiting when the oxide becomes thicker and gives rise to a parabolic dependence. When both processes are taken into account, the oxide thickness  $x$  can be expressed as a function of oxidation time  $t$  with the following equation:

$$x = \frac{A}{2} \left[ \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1 \right] \quad (1)$$

The parameters  $B/A$  and  $B$  are the linear and parabolic rate constants.  $\tau$  is a fitting constant and gives the time needed to grow an initially present oxide. The temperature dependence of the rate constants is described by an Arrhenius expression.

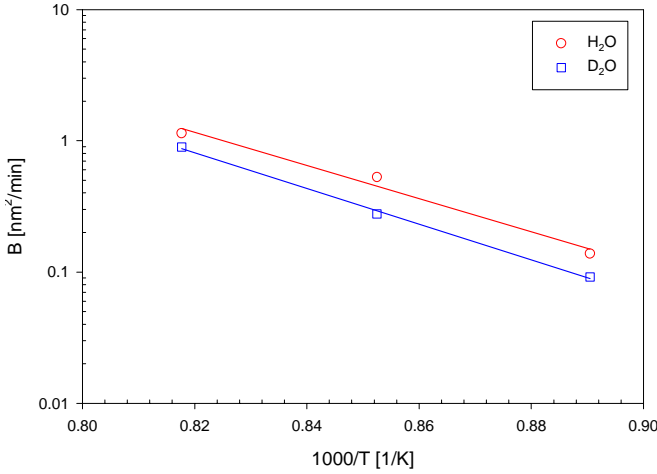
	T	B (g)	B/A (g)	B (f)	B/A (f)	$\tau$ (f)
	°C	nm <sup>2</sup> /min	nm/min	nm <sup>2</sup> /min	nm/min	min
H <sub>2</sub> O	850	14.2	$7.1 \cdot 10^{-3}$	0.14	12.2	11.0
	900	20.1	$1.8 \cdot 10^{-2}$	0.53	0.17	12.0
	950	27.5	$4.0 \cdot 10^{-2}$	1.14	0.52	5.8
D <sub>2</sub> O	850	-	-	0.09	50.6	16.6
	900	-	-	0.28	0.53	10.5
	950	-	-	0.90	0.34	8.4

**Table 1: Comparison of general accepted (g) and best fit (f) parameters for the Deal-Grove model.**

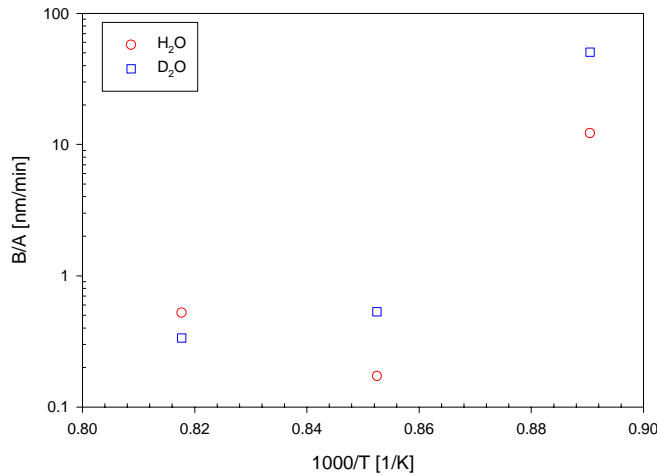
The experimental data in this work is fitted with the Deal-Grove model. Figure 1 compares the experimental data with the model. The figure shows a reasonable fit. The model parameters used, are listed in table 1. These parameters assure the least square error.

Table 1 compares the best fit parameters with the general accepted values [6] for the used temperature and

partial pressure. The extracted linear rate constant ( $B/A$ ) is 10 or for  $850^\circ\text{C}$  even 1000 times higher than the general accepted value. The extracted parabolic rate constant ( $B$ ) is 24 to 100 times smaller than the general accepted value. This questions the physical validity of the model for the experimental window investigated in this study.



**Figure 3: Arrhenius graph of the extracted parabolic rate constant**



**Figure 4: Arrhenius graph of the extracted linear rate constant**

Arrhenius graphs for  $B$  and  $B/A$ , given in figures 2 and 3, further doubt the physical validity of the derived parameters.  $B$  can be described by an Arrhenius expression as expected, but the extracted activation energy of  $2.5\text{eV}$  for  $\text{H}_2\text{O}$  is 3 times the general accepted value of  $0.78\text{eV}$ . It should be possible to describe  $B/A$  by an Arrhenius expression, but as figure 3 shows for the best-fit values, an extracted activation energy would be negative. The Deal-Grove parameters extracted from

the measured data are physically incorrect.

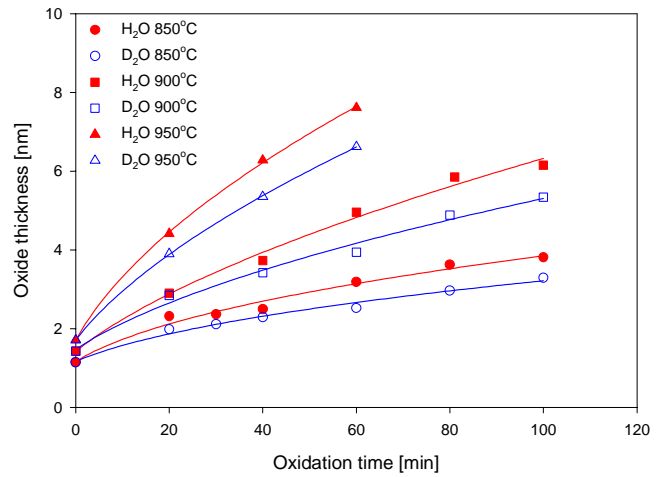
#### D. Modelling with a power law

Reisman et al. [7] show that a simple power law can model a large portion of the available oxidation data:

$$x = a(t + \tau)^b \quad (2)$$

where  $\tau$  serves the same purpose as in the Deal-Grove model. They show that this model is able to model oxide growth for thick and thin oxides.

Nicollian and Reisman give a theoretical foundation for this power law in [8]. They suggest the reaction at the interface is at all times the rate-limiting step. This reaction is retarded by the volume expansion necessary to accommodate the newly formed oxide at the interface. Taking into account a time dependent viscosity for the oxide they arrive at a power law. Furthermore, the authors show that the temperature dependence of the product of the parameters  $a$  and  $b$  can be described by an Arrhenius expression.



**Figure 5: Oxide thickness as a function of oxidation time, temperature and precursor. The markers indicate the experimental data and the lines the best fit with the power law model.**

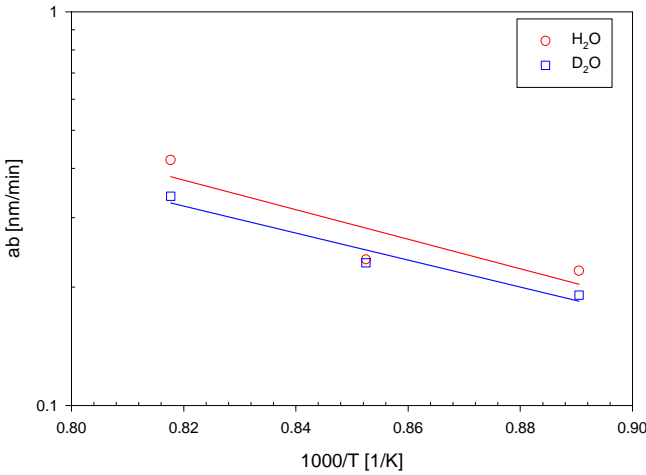
Figure 5 compares the power law model with the experimental data. The figure shows a reasonable fit. The model parameters used, are listed in table 2. These parameters assure the least square error.

There are no values known in literature (at least to the authors of this paper) for  $\text{H}_2\text{O}$  oxidation of silicon. Therefore, the values are compared with the values given in [7] for dry oxidation at  $0.01\text{ Atm}$ . Interestingly, the values for the exponent  $b$  are in close agreement. It has to be noted however that a full comparison is not possible, due to the difference in precursor systems.

	T °C	a (d) nm/min	b (d) -	a (f) nm/min	b (f) -	$\tau$ (f) min
H <sub>2</sub> O	850	0.42	0.40	0.51	0.43	6.6
	900	0.42	0.47	0.40	0.59	8.6
	950	0.47	0.53	0.75	0.56	4.3
D <sub>2</sub> O	850	-	-	0.46	0.41	9.4
	900	-	-	0.43	0.53	10.0
	950	-	-	0.59	0.58	6.4

**Table 2: Comparison of the power law model parameters found for dry oxidation (d) in [7] and the best fit (f) parameters for the experimental data in this work.**

Further confidence in the use of this model is given by the Arrhenius graph of  $a$  times  $b$ , as shown in figure 6. The product can be described by an Arrhenius expression with an activation energy of 0.75eV for H<sub>2</sub>O and 0.68eV for D<sub>2</sub>O. The difference in the activation energy is small and probably within the error of the extraction procedure.



**Figure 6: Arrhenius graph of the product of the power-law parameters.**

#### E. Difference between H<sub>2</sub>O and D<sub>2</sub>O oxidation

The product of  $a$  and  $b$  is slightly higher for H<sub>2</sub>O oxidation than for D<sub>2</sub>O oxidation. According to [8] this product depends on several parameters. One of these parameters is a specific reaction rate constant.

The reaction at the interface can be described as a sequence of H<sub>2</sub>O dissociation into H and OH, forming of Si-H and Si-OH bonds and desorption of H<sub>2</sub>. The same applies for D<sub>2</sub>O.

Lyding et al. [9] have already proven that desorption of deuterium from a Si-D bond is more difficult than desorption of hydrogen from a Si-H bond. Van de Walle

[10] attributed this difference in desorption to a difference in vibration frequency of the two bonds. The bending mode vibration frequency of the Si-D bond lies in the phonon spectrum of the silicon lattice. Thus, this bond is able to loose excess energy to this lattice. This does not apply to the Si-H bond. Therefore, it is easier to break a Si-H bond.

The difference in desorption rate will give a difference in the overall reaction rate. The reaction of H<sub>2</sub>O with the silicon surface will be slightly faster than the reaction of D<sub>2</sub>O with the silicon surface. The already formed silicon oxide will have more time to create the necessary volume expansion in the case of D<sub>2</sub>O oxidation. This extra time can result in a more stable configuration in the oxide (less stress), which will improve the overall integrity of the oxide.

#### IV. CONCLUSIONS

The oxidation of silicon in a D<sub>2</sub>O ambient is slower than in a H<sub>2</sub>O ambient under the same oxidation conditions. The oxidation curves for the oxidation conditions investigated in this work can be modelled with the Deal-Grove model, but the resulting parameters are physically incorrect. A power law model appears to be physically more correct. The difference in oxidation kinetics of silicon with H<sub>2</sub>O and D<sub>2</sub>O might find its origin in the difference of desorption of hydrogen and deuterium from a silicon surface.

#### V. FUTURE WORK

The oxidation curves measured in this work will be used to grow gate oxides and the integrity of the gate oxides will be tested.

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