Using VICTORY Process to Model Thermal Oxidation of Silicon in O\(_2\)/HCl Mixtures

Introduction
The addition of a chlorine species during thermal oxidation of silicon results in improved threshold stability, higher and more uniform oxide dielectric strength and improved junction properties due to lower leakage [1-3]. The effect of HCl addition is to increase the oxidation rate relative to the oxidation rate in dry oxidation ambient (O\(_2\)), whilst no influence of HCl on the oxidation rate is seen for wet oxidation ambient (H\(_2\)O). The observed increase in oxidation rate is due to:

- Water generation within the dry oxidation ambient from the reaction of O\(_2\) and HCl
  \[4\text{HCl} + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 2\text{Cl}_2\]
  which increases the solubility of oxidant in the oxide
- A straining of the SiO\(_2\) lattice induced by the presence of chlorine [4].

This paper demonstrates the ability of VICTORY Process to accurately model the effect of chlorine addition to the dry oxidation ambient. The 3D process simulation software VICTORY Process uses the same physical model as the one implemented in ATHENA (2D process simulation software). The model is briefly outlined and simulation results are compared with experimental analysis [4] and the good agreement is demonstrated.

2. Physical Model
The main parameters that describe the kinetics of silicon oxidation are:

- Linear rate, B/A and
- Parabolic rate B.

These rates are normally measured and specified when there is no chlorine addition to the oxidation system [5]. To describe the effect of adding HCl to the ambient, VICTORY Process uses an empirical model according to which the linear and parabolic rates are multiplied by temperature dependent and HCl concentration dependent enhancement factors such that the resulting rates become:

\[
\frac{B}{A} = \left(\frac{B}{A}\right)_0(n, T)
\]

\[B = B_0 \cdot B_{\text{hcl}}(n, T)\]

where

\(n\) being the HCl concentration and
\(T\) being the temperature.

The functional form of the enhancement factors \(B/A\)\(_{\text{hcl}}\)(n, T) and \(B_0(n, T)\) is represented by means of an empirical look-up table. This table specifies the factors for a set of concentrations of HCl and temperatures. Within VICTORY Process for an arbitrary HCl concentration and temperature the factors are determined using linear interpolation between the tabulated points and linear extrapolation outside of the table range.

3. Modelling Parameters and the Open Material Database
Although the material database of VICTORY Process provides a well calibrated table of enhancement factors, a user can adjust this table. The material database is open.

Continued on page 2...
and can therefore be modified, or a local small experiment specific material database can be used to override certain data extracted from a specific experiment.

To demonstrate this, we use experimental data extracted from [4] instead of the data provided with VIC-TORY Process version 3.12.1 to simulate the effect of HCl on the oxidation rate at two temperatures 900C and 1000C.

Within the open material database, the table for the linear rate coefficient enhancement factor for the dry oxidation ambient corresponds to the material database table:

\[
\text{<silicon><bulk><oxidation><dry><hcl\_lin>}
\]

The position data points of this two-dimensional table are defined by the material database tables:

\[
\text{<silicon><bulk><oxidation><dry><hclP>}
\]

and

\[
\text{<silicon><bulk><oxidation><dry><temp>}\]

which specify the HCl percentages and the temperatures where the enhancement factors were measured.

According to [4] we want to use the following experimental values for the enhancement factor of the linear rate

\[
\text{<hclP data=“/d/0.0/1.0/3.0/5.0/7.0/10.0” unit=“:percent”/ >}
\text{<temp data=“/d/900/1000” unit=“:Celsius”/ >}
\text{<hcl\_lin data=“/d/1.0 /1.0 /1.77 /1.11 /1.77 /1.33 /1.77 /1.23 /1.63 /1.33 /1.77 /1.33” unit=:1”/ >}
\]

This means that the enhancement factor is defined for:

- 6 HCl concentration percentages (rows in the table) (first row corresponds to 0.0% HCl) and
- 2 temperatures (columns in the table) (first column corresponds to T=900C).

The format for the parabolic enhancement factor is the same and it is stored by means of the material database table:

\[
\text{<silicon><bulk><oxidation><dry><hcl\_par>}
\]

for the dry oxidation ambient. The data points of this two-dimensional table are also defined by the material database tables:

\[
\text{<silicon><bulk><oxidation><dry><hclP>}
\]

and

\[
\text{<silicon><bulk><oxidation><dry><temp>}\]

This means that for any data point defined by

\[
\text{<silicon><bulk><oxidation><dry><hclP>}
\]

and

\[
\text{<silicon><bulk><oxidation><dry><temp>}
\]

the linear as well as the parabolic enhancement factors are given. Figure 1 and Figure 2 show the graphical representations of the enhancement factor tables.

Datafile 1. Modified oxidation parameters according to [4].
Besides the enhancement factors, linear and parabolic rates in the absence of HCl are also provided for the experiment in [4]. There the following values are used:

\[(B/A) = 1.3595 \times 10^{-3}, \ \text{µm/min}\]
\[B = 1.6163 \times 10^{-4} \ \text{µm}^2/\text{min}\]
for \(T = 1000^\circ\text{C}\) and

\[(B/A) = 3.01 \times 10^{-4}, \ \text{µm/min}\]
\[B = 16.435 \times 10^{-5} \ \text{µm}^2/\text{min}\]
for \(T = 900^\circ\text{C}\).

Note: When VICTORY Process simulates physical oxidation, it converts those empirical parameters into microscopical parameters like diffusion and reaction coefficients which are used in 3D mathematical model.

The linear rate coefficient for the dry oxidation ambient in the open material database corresponds to the material database function (temperature dependent function):

\(<\text{silicon}><\text{bulk}><\text{oxidation}><\text{dry}><\text{lin}>\)
and the parabolic rate coefficient for the dry oxidation ambient corresponds to the material database function (temperature dependent function):

\(<\text{silicon}><\text{bulk}><\text{oxidation}><\text{dry}><\text{par}>\)

For the simulation analysis shown in this paper we have set all this data by creating a small local experiment specific material database which overloads the data in the global material database. Therefore we have created two folders

\text{smdb/material}

in the folder where the experiment is running. The latter folder contains a file

\text{silicon}

with the content shown in Datafile 1.

Running Physical Oxidation with the Locally Defined Material Data

In order to make the local material database which we have created accessible by VICTORY Process, we have to define a multi-folder material database path by means of the environment variable:

\text{SILVACO_SMDB}

It must contain all material database folders which shall be used for the simulation. The order of the folders determines the priorities of the data. For the analysis shown in this paper we want to use the local material database and the global material database, whereby the data in the local material database shall override the data in the global material database. Therefore the local material database must be listed first in the \text{SILVACO_SMDB} environment variable, followed by the global material database, like:

\text{SILVACO_SMDB}=#$PWD/smdb:$SILVACO/lib/victoryp/3.12.1.R/common/smdb

Figure 1. Oxidation linear rate enhancement factors as a function of HCL concentration. The data are extracted from the experiment [4].

Figure 2. Oxidation parabolic rate enhancement factors as a function of HCL concentration. The data are extracted from the experiment [4].

Figure 3. Oxide thickness vs. oxidation time (exp: experiment and vp: simulation) for the oxidation of \(<111>\) oriented silicon at \(T=1000^\circ\text{C}\) in three \(\text{O}_2/\text{HCl}\) mixtures: HCL = (0%, 1% and 10%).
In order to simulate the physical oxidation step, we have used the `Diffuse` statement. To introduce the effect of HCl one needs to set the value of chlorine concentration within the `Diffuse` statement by specifying the parameter `F.HCL` (if other fluxes are provided) or the parameter `HCL.PC`. The first one gives the flux of chlorine, whereas the second parameter gives the percentage of HCl present in the oxidation ambient. For the simulations shown in this paper we have used the second parameter and hence the following `Diffuse` statement

```
Diffuse dryo2 time=1 hour temperature=1000 hcl.pc=10.0
```

has been applied.

5. Comparison of Numerical and Experimental Results

To compare our results with the experimental ones, we have simulated oxidation of plane silicon at the conditions chosen in the experiment, namely, at two different temperatures 900°C and 1000°C and at three values of chlorine concentration (0%, 1%, 10%). Experimental and numerical results are compared in Figure 3 (T=1000°C) and Figure 4 (T=900°C). One can see that the simulation reproduces the experimental results with reasonable accuracy. The shown discrepancy can be explained by:

- The limited accuracy in measurements
- Some uncertainty in experimental conditions (e.g. initial oxide thickness and ambient pressure)
- Errors made during the extraction of the enhancement coefficients.

Conclusion

In this paper we have demonstrated that VICTORY Process is able to accurately simulate thermal oxidation of silicon in the presence of chlorine in an oxidizing atmosphere. We have also shown how to incorporate user’s empirical data into simulation by setting-up a calibration material database in order to override the relevant sections of the material database which is distributed with VICTORY Process.

References