Understanding of the retarded oxidation effects in silicon nanostructures

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In-depth understanding of the retarded oxidation phenomenon observed during the oxidation of silicon nanostructures is proposed. The wet thermal oxidation of various silicon nanostructures such as nanobeams, concave/convex nanorings, and nanowires exhibits an extremely different and complex behavior. Such effects have been investigated by the modeling of the mechanical stress generated during the oxidation process explaining the retarded regime. The model describes the oxidation kinetics of silicon nanowires while predicting reasonable and physical stress levels at the silicon/silicon dioxide interface by correctly taking into account the relaxation effects in silicon oxide through plastic flow. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4729410]

Retarded oxidation where the oxide growth slows down very rapidly with oxidation time or with the silicon nano-object dimension is still a puzzling physical effect.¹–³ This physical effect can be viewed as a technological nanoscale tool which enables to control the nano-object shape, size distribution interface properties and hence could be used in many applications.⁴ However, only very few studies have been dedicated to the understanding of the phenomenon which remains fragmented and limited.⁵–² In this work, oxidation kinetics have been investigated both on the experimental and theoretical counterparts in order to improve the understanding of retarded mechanisms and to quantify the amount of stress generated at the Si/SiO₂ interface in silicon nanostructures.

With the current top-down fabrication capabilities, etched silicon nanostructures including nanobeams, nanorings, and nanowires have been fabricated with a high resolution² and then wet oxidized at 850 °C. The nano-patterns are realized using electron beam lithography (Vistec EBPG 5000+ system) with a negative-tone resist, namely, hydrogen silesquioxane (HSQ). After exposure, the HSQ resist is developed by immersion in 25% tetramethylammonium hydroxide (TMAH) for 1 min at 20 °C. Nano patterns were transferred to (100) Si substrate by reactive ion etching (Oxford Plasma100 system) in Cl₂ plasma under optimized process parameters³ in order to obtain an anisotropic profile. After the etching step, the remaining HSQ resist was stripped in 10% HF solution. Si nanostructures were thermally oxidized at 850 °C in wet ambiance using a conventional tubular furnace (TEMPRESS) at atmospheric pressure and under a flow of 1.5 l/min of O₂, 2.5 l/min of H₂.⁴ Fig. 1(a) summarizes the evolution of the oxide thickness as a function of the oxidation time in the case of convex Si nanowires (SiNWs) and concave Si nanoring structures. The oxide growth rate is strongly limited by the oxidation time but is faster in a convex structure than in a concave one. The influence of the geometrical effect is stronger with smaller inner radius (i.e., 70 nm compared to 430 nm). For the convex case, a higher oxide growth rate is related to the larger radii. Then, in order to investigate experimentally the influence of silicon nanostructure dimension, nanobeams and nanowires of 240 nm height have been oxidized for 10 and 20 min. As shown in the inset of Fig. 1(b), a non-uniform oxide growth is classically observed along the sidewall of the beam due to the great influence of the top and bottom corners corresponding to a convex and concave structure, respectively. An oxidized one-dimensional nanostructure with diameters from 40 to 140 nm demonstrated completely different shapes as shown in the inset of Fig. 1(b) with the presence of a pinching effect at the bottom of silicon nanobeams (SiNBs) structures. The oxidation behavior between SiNBs and SiNWs kinetics is under comparison in Fig. 1(b). The oxide growth on SiNBs of width L is clearly thinner than SiNWs with the diameter d = L. A size dependent oxidation kinetic was not observed in these structures for any of the considered SiNBs width. These experimental results illustrate that the silicon oxidation retarded mechanism is strongly dependent on the nano-object (i) dimension, (ii) size, and (iii) shape.

These dependencies cannot be explained by the standard Deal and Grove oxidation model¹⁰ since a larger oxidant concentration for the smallest particles should, in principle, lead to a higher oxidation rate. Two main theories have been put forward to explain the retarded/self-limiting kinetics factor. The first one is the “stress limited reaction rate” assumption⁶ with a radial stress increase at the Si/SiO₂ interface up to a critical stress estimated to a few GPa where the oxidation rate would be completely negligible. The second theory proposed is the “diffusion limited mechanism” with a significant increase in the activation energy of the oxidant diffusivity in the highly stressed region.² In this case, the origin of self-limited effects would be the oxidant species supply at the interface. However, despite the fact that an unknown and uncontrolled amount of strain is introduced, no quantitative determination of the mechanical stress build-up is undertaken in the two approaches.

In order to model the oxidation of cylinder nano-objects, the extended Deal and Grove model in cylindrical coordinates has been used.¹¹ The wet oxidation rate v at the Si/SiO₂ interface is given by (Eq. (1))
where \( k_B \) is the Boltzmann constant, \( T \) is the oxidation temperature, and \( V_k \) (15 Å\(^2\)) corresponds to the activation volume. A compressive radial stress \( (\sigma_r < 0) \) slows down the linear oxidation rate. The term \((B/A)_{110}(T)\) takes into account the influence of the [110] crystalline orientation and the factor taking into account orientation effects has been calibrated with planar bulk oxidation experiments. Next the oxidant diffusivity, \( D_{SiO_2}^0 \),

\[
D_{SiO_2}^0 = \frac{N}{2C^0} \cdot B(T) = \frac{N}{2C^0} \cdot B_0(T) \cdot \exp \left( -\frac{PV_d}{k_BT} \right)
\]  

(3)

is linearly dependent on the initial parabolic constant \( B_0(T) \) (2.68 \( 10^{-15} \text{ nm}^2/\text{s} \) at 850°C) and is limited by a compressive (\( P > 0 \)) hydrostatic pressure \( P = -0.5 \cdot (\sigma_r + \sigma_\theta) \) in the silicon oxide \( (V_d = 45 \text{ Å}^3) \). These assumptions are often estimated to be equivalent to a diffusivity dependence with oxide density.\(^{12}\)

A major issue in oxidation modelling is a proper description of the mechanical behavior of silicon dioxide as shown in Fig. 2 and its ability to store or to dissipate mechanical energy. A shortcoming is also observed for the viscous standard approach\(^{11,13}\) since the compressive radial stress at the interface is inversely proportional to the curvature radius of the nano-object and strongly overestimates the stress level.\(^{14}\) The main reason is that the irreversible atomic rearrangements occurring with large shearing forces\(^{15}\) are neglected. This plastic flow is described by a shear dependent viscosity\(^{16}\)

\[
\eta(\tau) = \eta_0(T) \cdot \frac{\tau/\sigma_r}{\sinh(\tau/\sigma_r)}
\]  

(4)

where \( \eta_0(T) \) is the low stress viscosity, \( \tau \) is the critical resolved shear stress, and \( \sigma_r \) is the critical stress threshold where plasticity flow should appear (1 GPa). The low stress viscosity value (1.4 \( 10^{18} \) Poisse at 850°C) considered is

![FIG. 1. (a) Comparison between concave and convex nanostructure oxidation behavior. Inset images: (1) 70 nm convex nanostucture (2) 70 nm concave nanostructure. (b) Oxide thickness as function of the SiNB widths or SiNW diameters for 10 and 20 min oxidation. The experimental trend is described by the dashed lines. Inset SEM images: (1) the SiNBs (cross-section view), (2) SiNWs (tilted view) after oxidation. The images have been obtained with a high resolution SEM (ZEISS ULTRA 55 system at 10 kV, and WD ~4 mm). In the case of NWs, diameters of oxidized Si NWs (d\(_{NW}\)) and after stripping SiO\(_2\) layer (d\(_{SiO2}\)) were measured at the NW mid-height by tilted view (\( \phi = 82^\circ \)). The grown SiO\(_2\) layer thickness (t\(_{SiO2}\)) is estimated as following\(^{9}\):]

\[
t_{SiO2} = d_{SiO2} - d_{Si}/2
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In the case of silicon nanorings, the SiO\(_2\) layer thickness for 10 and 20 min oxidation. The experimental trend is described by the dashed lines. Inset SEM images: (1) 70 nm convex nanostructure (2) 70 nm concave nanostructure. (b) Oxide thickness as function of the SiNB widths or SiNW diameters for 10 and 20 min oxidation. The experimental trend is described by the dashed lines. Inset SEM images: (1) the SiNBs (cross-section view), (2) SiNWs (tilted view) after oxidation. The images have been obtained with a high resolution SEM (ZEISS ULTRA 55 system at 10 kV, and WD ~4 mm). In the case of NWs, diameters of oxidized Si NWs (d\(_{NW}\)) and after stripping SiO\(_2\) layer (d\(_{SiO2}\)) were measured at the NW mid-height by tilted view (\( \phi = 82^\circ \)). The grown SiO\(_2\) layer thickness (t\(_{SiO2}\)) is estimated as following\(^{9}\):

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with \( a \) and \( b \), respectively, the inner and outer radius, \( x \) the volume expansion factor of silicon to oxide conversion (2.25), \( N \) the number of oxidant molecules incorporated into a unit volume of silicon oxide, and + and − signs denote, respectively, the convex and concave surface. This equation classically takes into account that the surface curvature influences the oxidant concentration and in the convex (concave) configuration, the concentration increases (decreases). In our approach, both the reaction rate \( k_{Si}^x \) at the Si/SiO\(_2\) interface and the diffusivity in the silicon oxide \( D_{SiO_2} \) are stress dependent. The reaction rate \( k_{Si}^x \) is directly proportional to the linear rate constant \((B/A)_{110}(T)\) (5.18 \( 10^{-09} \text{ nm}^2/\text{s} \) at 850°C) defined in the Deal and Grove approach by introducing \( C^x \) the oxidant solubility in the silicon dioxide and is strongly dependent on the radial stress component \( \sigma_r \) at the Si/SiO\(_2\) interface

\[
k_{Si}^x = \frac{N}{C^x} \cdot (B/A)_{110}(T) \exp \left( \frac{\sigma_r V_k}{k_BT} \right)
\]  

(2)

where \( k_B \) is the Boltzmann constant, \( T \) is the oxidation temperature, and \( V_k \) (15 Å\(^2\)) corresponds to the activation volume. A compressive radial stress \( (\sigma_r < 0) \) slows down the linear oxidation rate. The term \((B/A)_{110}(T)\) takes into account the influence of the [110] crystalline orientation and the factor taking into account orientation effects has been calibrated with planar bulk oxidation experiments. Next the oxidant diffusivity, \( D_{SiO_2}^0 \),

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![FIG. 2. Schematics of the concave and convex cylinder nanostructure oxidation and resulting stress field in the silicon oxide. The strain in the oxide could be divided into two components the deviatoric part associated to shape modification and the dilatational part often neglected.]

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characteristic of a wet oxide with a high viscosity induced by the presence of hydroxyl content. Following the expression of the critical resolved shear stress \( \tau(\sigma) = \frac{2\mu}{\eta_{\text{crit}}} \), it can be underlined that the oxidation growth rate (Eq. (1)), the shear dependent viscosity (Eq. (2)), and finally the critical shear stress are coupled to each other. The fact that all these equations must be self-consistently solved is often overlooked or not exactly taken into account. Following Rafferty et al., the radial (\( \sigma_r \)) and tangential (\( \sigma_\theta \)) stress field component in the silicon dioxide of a cylinder structure (see Fig. 2) can be expressed as

\[
\begin{align*}
\sigma_r(r) &= \pm \frac{1}{2} \sigma_c \left[ \left( \ln \frac{R}{b} \right)^2 - \left( \ln \frac{R}{b_0} \right)^2 \right], \\
\sigma_\theta(r) &= \sigma_r(r) - 2\tau(r)
\end{align*}
\]

with the reduced parameter \( R = \frac{\sqrt{4\ln(b/c)}}{\sigma_r} \). Compared to a standard viscous approach with a constant viscosity, the radial stress build-up has a logarithmic dependence on the curvature radius which gives us the opportunity to model the oxidation of cylinder shape nanostructures.

Fig. 3(a) shows that the influence of the concave or convex character on the oxidation kinetics can be well predicted by the model. As shown in Fig. 3(b), a substantial non-linear increase is observed for the compressive radial stress component at the interface up to a few GPa, coupled with an initial tensile hydrostatic pressure (inset of Fig. 3(b)). The radial stress build-up is not linear with time as assumed in a previous study. These elements clearly indicate that a reaction limited process takes place in the convex configuration. The

<table>
<thead>
<tr>
<th>Character</th>
<th>( \sigma_r )</th>
<th>( P )</th>
<th>Origin</th>
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<tbody>
<tr>
<td>Convex</td>
<td>/</td>
<td>( \ll )</td>
<td>Limited reaction rate</td>
</tr>
<tr>
<td>Concave</td>
<td>( \ll )</td>
<td>/</td>
<td>Limited diffusion mechanism</td>
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FIG. 3. (a) Modelling of the convex/concave oxidation kinetics using the plastic model (symbols correspond to experimental points). (b) Evolution of the theoretical radial stress \( \sigma_r \) at the Si/SiO\(_2\) interface. Inset provides the hydrostatic pressure evolution during the oxidation for the different nanostructures.

FIG. 4. (a) Linear rate variation with SiNW diameters showing the impact of the radial stress in the initial oxidation regime as the main limiting factor. (b) Highlight of the diffusion limited regime which takes place only when a sufficient oxide thickness has been grown. (c) Compressive radial stress build-up with decreasing SiNW diameters. Inset: tangential stress relaxation.
situation is totally different in the concave case where a radial compressive stress build-up remains limited whereas the compressive hydrostatic pressure clearly impacts the oxidant diffusivity. In that case, the major limiting factor is the diffusion mechanism which reduces the oxidant supply. A quasi self-limited oxidation for 70 nm concave structure is observed and can be correlated to the occurrence of both a diffusion and reaction limited regime. As summarized by Table I, the dominant retardation mechanism is strongly dependent on the surface shape but can be explained by the variation of the stress field component at the Si/SiO₂ in agreement with previous results.¹¹

Fig. 4(a) presents the linear rate modeling with oxidation time and SiNW diameters reported in Fig. 1(b). A strong decrease in the reaction rate with radial stress build-up as a function of SiNW diameters is predicted which could be directly correlated to the large radial stress build up depicted in Fig. 4(c). Large non-linear build-up as a function of the oxidation time and SiNW diameters for the compressive radial stress down to 4 GPa which remains compatible with interfacial stress estimated using contact-resonance atomic force microscopy.¹⁹ This effect causes the initial retarded effects observed in the oxidation of convex nanostructures. The difference in terms of behavior between the SiNBs and the SiNWs can be explained since finite elements simulations estimate a much lower compressive stress build-up for the SiNBs. Fig. 4(b) presents the evolution of the parabolic rate with SiNW diameters. A decrease in the parabolic rate is observed after a significant delay which can be correlated to the tangential stress relaxation as shown in inset of Fig. 4(c). This diffusion limited effect generated by a compressive hydrostatic pressure is probably much more difficult to control as both time and diameter dependences are observed in Fig. 4(b).

In summary, retarded oxidation kinetics have been investigated at the nanoscale level for different silicon nano-objects. The dependence of the nano-object dimension, shape, and size on the oxidation behaviour has been validated. These effects have been correlated to the interfacial stress build-up during oxidation. Modelling aspects show that plastic relaxation needs to be considered in order to estimate (i) a physical mechanical stress build-up at the interface and (ii) the interface velocity. Reaction or diffusion limited mechanisms must be considered to describe retarded oxidation effects in silicon nanostructures.

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