Shape transition in nano-pits after solid-phase etching of SiO₂ by Si islands

F. Leroy, Y. Saito, S. Curiotto, F. Cheynis, Olivier Pierre-Louis, Pierre Müller

► To cite this version:

F. Leroy, Y. Saito, S. Curiotto, F. Cheynis, Olivier Pierre-Louis, et al.. Shape transition in nano-pits after solid-phase etching of SiO₂ by Si islands. *Applied Physics Letters*, 2015, 106, pp.191601. 10.1063/1.4921091 . hal-01151207

HAL Id: hal-01151207

<https://hal.science/hal-01151207>

Submitted on 4 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Shape transition in nano-pits after solid-phase etching of SiO₂ by Si islands

F. Leroy, Y. Saito, S. Curiotto, F. Cheynis, O. Pierre-Louis, and P. Müller

Citation: *Applied Physics Letters* **106**, 191601 (2015); doi: 10.1063/1.4921091

View online: <http://dx.doi.org/10.1063/1.4921091>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/106/19?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Interfacial reaction of Si islands on SiO₂ during high-temperature annealing](#)

J. Appl. Phys. **108**, 083520 (2010); 10.1063/1.3500506

[Nanoscale structural change in a sputter-deposited SiO₂/a-Si/SiO₂ sandwich](#)

J. Appl. Phys. **95**, 1600 (2004); 10.1063/1.1636523

[Thermal decomposition behavior of the HfO₂/SiO₂/Si system](#)

J. Appl. Phys. **94**, 928 (2003); 10.1063/1.1578525

[Effect of Si lattice strain on the reliability characteristics of ultrathin SiO₂ on a 4° tilted wafer](#)

Appl. Phys. Lett. **80**, 386 (2002); 10.1063/1.1435404

[Octadecyltrichlorosilane self-assembled-monolayer islands as a self-patterned-mask for HF etching of SiO₂ on Si](#)

J. Vac. Sci. Technol. A **16**, 1680 (1998); 10.1116/1.581142

Frustrated by old technology?

Is your AFM dead and can't be repaired?

Sick of bad customer support?

It is time to upgrade your AFM

Minimum \$20,000 trade-in discount for purchases before August 31st

Asylum Research is today's technology leader in AFM

dropmyoldAFM@oxinst.com

The Business of Science®

Shape transition in nano-pits after solid-phase etching of SiO₂ by Si islands

F. Leroy,¹ Y. Saito,² S. Curietto,¹ F. Cheynis,¹ O. Pierre-Louis,³ and P. Müller¹

¹Aix Marseille Université CNRS, CINaM UMR 7325, 13288 Marseille, France

²Department of Physics, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Japan

³Institut Lumière Matière, UMR 5306 Université Lyon-1-CNRS, 69622 Villeurbanne, France

(Received 9 March 2015; accepted 2 May 2015; published online 11 May 2015)

We study the nano-pits formed during the etching of a SiO₂ film by reactive Si islands at $T \approx 1000^\circ\text{C}$. Combining low energy electron microscopy, atomic force microscopy, kinetic Monte Carlo simulations, and an analytic model based on reaction and diffusion at the solid interface, we show that the shape of the nanopits depend on the ratio R/x_s with R the Si island radius and x_s the oxygen diffusion-length at the Si/SiO₂ interface. For small R/x_s , nanopits exhibit a single-well V-shape, while a double-well W-shape is found for larger R/x_s . The analysis of the transition reveals that $x_s \sim 60$ nm at $T \approx 1000^\circ\text{C}$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4921091>]

Due to its great importance in modern micro- and nano-electronics, the Si/SiO₂ interface is one of the most studied solid-on-solid interface, especially with the recent development of Silicon-on-Insulator (SOI) devices that are based on thin single crystalline Si film bounded to a SiO₂ substrate. The thermal stability of such Si/SiO₂ film has been extensively studied^{1–8} because the fabrication of microelectronics devices requires several annealing steps. In this context, it has been recently shown that the interface between three dimensional Si islands and SiO₂ is much more reactive than the interface of a two dimensional Si film on SiO₂.⁹ Indeed, in that case, the interfacial reaction is expected to proceed in three steps: (i) SiO₂ decomposition at the interface, (ii) oxygen diffusion along the interface, and finally, (iii) production of volatiles SiO species at the island edge.⁹ The kinetics of the interfacial reaction should thus depend on the quantity L/x_s , where L is the island diameter and x_s the O diffusion length at the interface.

In this paper we study the formation of nano-pits drilled in a SiO₂ film by the thermally activated reaction between Si islands and an underlying SiO₂ substrate. We show that a careful analysis of the island motion and the shape of the pits left by the reactive islands validates the above mentioned 3-step scenario. More precisely we show that, depending on the experimental conditions, two types of pit morphologies can be found: single-well profiles or ring-shaped profiles (which means V- or W-shaped radial profiles). Furthermore, using an analytical model based on reaction and diffusion at the solid interface and kinetic Monte Carlo simulations, we show that the V-W shape transition occurs when L/x_s is of the order of unity.

We use SOI wafers fabricated by the Smart-cut process of CEA-Leti (Grenoble, France). More precisely, we have used two SOI wafers, thin SOI-20 (20-nm thick Si film bonded to a 150-nm thick amorphous SiO₂ on a Si wafer) and thick SOI-145 (145-nm thick Si film bonded to a 1000-nm thick amorphous SiO₂ on a Si wafer). The SOI samples have been prepared in ultrahigh-vacuum conditions following the recipe described previously.¹⁰ The samples have been studied *in-situ* by Low Energy Electron Microscopy (LEEM) and characterized *ex-situ* by Atomic Force

Microscopy (AFM). The instruments, as well as the experimental conditions, have been described elsewhere.¹³

The pits in the SiO₂ layer have been generated in two steps. In the first step, the SOI sample is annealed close to 800 °C. Due to its metastable nature, the Si film dewets and agglomerates into an assembly of Si islands, as discussed in details in Refs. 7, 8, and 12. In Fig. 1(a), a LEEM image of a dewetting film is reported. During dewetting, the Si edge recedes forming periodic elongated Si structures (called Si fingers) that spontaneously break into small Si islands (dots in Fig. 1(a)). In Fig. 1(b), we show an AFM image of the final dewetted state in which the Si 3D crystals can be seen. As already reported¹¹ for a given temperature, the size of the resulting 3D Si crystals increases when the initial film thickness increases.

In Fig. 1(b), one may observe that a track is left by the Si fingers before they break into 3D islands. These tracks originate from the chemical reaction that occurs at the Si/SiO₂ interface under the Si fingers and are all the more deep when the dewetting temperature is high and the reaction time is long. For the lowest dewetting temperatures, tracks are not observed.

In the second step, increasing further the temperature (>900 °C) of the dewetted SOI sample activates the chemical reaction of Si islands with underlying SiO₂ layers. In

FIG. 1. (a): LEEM image ($E=9\text{ eV}$) of a 22-nm thick dewetting SOI film (dark:Si, bright: SiO₂). A dewetting front recedes and leaves behind it small 3D islands (white line: mean position of a receding $\langle 100 \rangle$ front, blue arrows: direction of motion of the front). (b): AFM image of the dewetted film.

Fig. 2, we show several sequences of LEEM images of reacting Si islands. Figs. 2(a)–2(d) have been obtained from the SOI-145 dewetted sample. In this case, the dewetted state shows an assembly of islands with a quite large distribution of sizes (island radius 800 ± 200 nm). When the interfacial reaction is thermally activated the Si islands (dark zones on the bright silicon dioxide in Fig. 2) move, shrink, and drill pits in the SiO_2 film by chemical reaction (a typical movie is given in supplementary material¹⁴).

In Fig. 2(a), all pits still contain a 3D island. The smallest islands (dark arrows) continuously move until complete disappearance (Fig. 2(c)). The largest islands (orange arrows in Fig. 2(a)) exhibit a quite different behaviour since at the beginning of the reaction they stay more or less immobile, shrink on place then abruptly shift towards the edge of the pit they have drilled (Fig. 2(c)). After this event, the islands move continuously until complete disappearance. Notice that these moving islands may split into two smaller islands (Fig. 2(d)) that continue to move and shrink until complete disappearance.

To be more quantitative, we have recorded the square displacements of the center of mass of many Si islands. We can thus distinguish two behaviors: the islands whose position continuously and randomly fluctuates (one can thus define the mean square displacement (MSD) of an assembly of such islands), and the islands whose motion is characterized by a lag time before moving. This lag time varies from one island to the other so that it is no more possible to define a meaningful mean square displacement. In Fig. 2(e) are reported the mean square displacement of small islands (Brownian motion) as well as the simple square displacement of four large islands characterized by four different lag times. The lag time corresponds to the time the island needs to depin and move at the periphery of the ring it has drilled in the SiO_2 substrate. In Fig. 2(f) is reported the size distribution of both populations (motion with or without any lag time). It clearly appears that the island motion depends on the island size and that two populations of islands may be defined: a population of small islands characterized by a Brownian motion and a population of large islands characterized by a lag time. From Fig. 2(f), we evaluate the transition to occur for an island radius of 450 ± 25 nm.

Fig. 3 shows the SiO_2 film morphology resulting from complete disappearance of the Si islands. Since the mean island size depends on the initial thickness of the Si film and since the interfacial reaction ends when the Si islands have been completely consumed, the depth of the etched pits depends on the initial thickness of the film. Thus for SOI-20, where the average diameter of the 3D Si islands is 300 ± 100 nm, the mean depth of the pits is 100 nm whereas for SOI-145 where the average diameter of the islands is 800 ± 200 nm the mean depth of the pits is 300 nm. Moreover, the shape of the pits clearly depends on the initial island size. More precisely small islands (Brownian motion during etching) have drilled single wells with a shape similar to an asymmetric cone characterized by a V-shape along an island diameter (Figs. 3(a) and 3(c)) whereas large islands (with a lag time at the beginning of the etching) form ring-shaped wells characterized by a W-shape along an island diameter (Figs. 3(b) and 3(d)). Finally notice that, as reported in our previous work,¹¹ while the 3D islands shrink and form pits, their mean projected area decreases linearly with time. This observation indicates that the global consumption rate of Si is proportional to the linear dimension of the islands, and therefore to the length of the triple-line. Hence, the limiting kinetic process in the reaction is probably localized at the periphery of the island. However, in the framework of the 3-step model depicted in the introduction, the width of the etched zone should depend on the ratio L/x_s .

In order to discuss the experimental results in more details, we use KMC simulations with a Solid-on-Solid (SOS) model with two height variables on a two-dimensional square lattice. This model was already successful in describing some of the features of the random motion of nano-islands in the same system.¹¹ Here, we show that it also reproduces the main features of the V-W nano-pit shape transition.

In the x direction, the lattice has a finite extension L_x with periodic boundary conditions. The lattice constant a is set unity. In the y direction, the system is infinite. We denote an adsorbate as atom A instead of Si, and a substrate unit as S instead of SiO_2 . At a site x , the A-S interface has a height $y = h_I(x, t)$, on which is an A island with a height $h_A(x, t)$.

FIG. 2. LEEM sequences showing pit formation at $T \approx 1000^\circ\text{C}$. Images (a)–(d): time sequence for SOI-145. The dark (red) arrows indicate the smallest (largest) islands. (e): linear MSD of small islands that move continuously (population 1) and SD of four islands that form a ring before moving (population 2) and are thus characterized by different lag times. (f): size distribution of both populations.

FIG. 3. AFM images of SOI-20 (a) and SOI-145 (b). Corresponding characteristic profiles are given in (c) for SOI-20 and (d) for SOI-145.

For simplicity, we assume first and second nearest neighbor interactions between two adatoms, $J_{AA1} = J$ and $J_{AA2} = \zeta J$, respectively. The ratio $\zeta = J_{AA2}/J_{AA1}$ controls the anisotropy of the crystal shape.¹¹ An adatom A also interacts with the first and the second nearest neighbor substrate units S with interaction strengths, J_{AS1} and J_{AS2} , respectively, with $J_{AS2}/J_{AS1} = \zeta$ to reduce the number of free parameters. The dimensionless number $\chi = J_{AS1}/J_{AA1}$ defines the wettability of the adsorbate to the substrate. For $0 < \chi < 1$, the adsorbate partially wets the substrate surface and forms an island.

Surface diffusion of adatoms is implemented via the hopping of the topmost A atom to neighboring columns. The adatom hopping rate is

$$W_A = \nu_A \exp\left(-\sum_i n_i J_i / k_B T\right), \quad (1)$$

where ν_A is an attempt frequency, summation runs over $i = AA1, AA2, AS1$, and $AS2$, n_i is the number of i -th bonds before hopping, T is the temperature, and k_B denotes the Boltzmann factor. In contrast, substrate atoms are assumed to be frozen.

The presence of the reaction-diffusion process at the interface is accounted for by means of four additional microscopic processes. First, a S unit at the interface decomposes in an A atom and emits two O atoms with a rate

$$W_{DC} = \nu_{DC} e^{-m\phi/k_B T}, \quad (2)$$

where ν_{DC} is a constant, m is the number of lateral S-S bonds before decomposition, and ϕ represents the associated energy change per bond. Second, the reverse oxidation rate is $W_{OX} = \nu_{DC}$. Remaining rates of oxygen diffusion along the A-S interface and of evaporation of A and O atoms from an island edge site are assumed constant for simplicity, and set as $W_O = \nu_O$, and $W_E = \nu_E$, respectively.

In the following simulations, we choose $k_B T = 0.4J$, $\zeta = 0.8$, and $\chi = 1/2$, so that the island is almost isotropic, and its equilibrium shape is a semicircle. The interface energy ϕ is chosen to be rather large as $\phi = 1.5J$ to keep the A-S interface smooth during the dynamics. In the following,

our reference time-scale will be the time τ_A of hopping of an adatom at a surface kink site

$$\tau_A = \nu_A^{-1} e^{2(1+\zeta)J/k_B T}. \quad (3)$$

Using this time-scale, the interface decomposition frequency, and the evaporation rate are chosen to be small $\nu_{DC} = \nu_E = 0.1/\tau_A$, and oxygen interface diffusion $\nu_O = 10/\tau_A$ is large.

We have performed simulations starting from a semi-circular island on a flat substrate. The initial radius is varied from $R_0 = 40a$ to $R_0 = 100a$. We observe a transition from a V-shape with a single minimum for pits produced by small islands, to a W-shape with two minima for pits produced by large islands. The V-W transition is obtained around $R_0 \sim 80a$.

Such a transition is similar to experimental observations. However, in most KMC simulations, the islands do not split in two small islands in the final of the process as observed in experiments. This difference could be a consequence of the two-dimensional nature of the KMC model.

In order to gain a better understanding of the origin of the V-W transition, we use a simple analytical model based on oxygen reaction-diffusion dynamics at the interface. Following the same lines as in the KMC model, the evolution equation of oxygen concentration C_O at the interface follows:

$$\partial_t C_O = D_O \partial_{xx} C_O + K_0 - K_1 C_O^2, \quad (4)$$

where D_O is an oxygen diffusion constant along the interface, K_0 is a rate of oxygen creation, which is twice the SiO_2 decomposition rate, K_1 is the kinetic coefficient for the reaction of Si oxidation. These coefficients can be related to the KMC model as follows: $K_0 = 2W_{DC}$, $K_1 = W_{OX}$, and $D_O = a^2 W_O / 2$.

Since two oxygen atoms are emitted by SiO_2 decomposition which decreases the interface height h_I , whereas two O's are consumed by the Si oxidation which increases h_I , the interface height profile h_I is determined by the reaction as

$$\partial_t h_I(x, t) = \frac{1}{2} (-K_0 + K_1 C_O^2). \quad (5)$$

When O atoms reach the triple line at $x = L_{\pm}$, they combine with Si to form SiO , which evaporates. In order to describe this process, we use the condition

$$J_{\pm} = \mp D_O \partial_x C_O = \nu_E C_O(x = L_{\pm}), \quad (6)$$

where ν_E is the evaporation kinetic coefficient defined above, and $J_{\pm}$ is the O flux to the triple lines.

Finally, global mass conservation reads

$$\frac{dN}{dt} = -\frac{1}{2}(J_+ + J_-), \quad (7)$$

where N is the total number of Si atoms in the island. The factor $1/2$ accounts for a fact that the evaporation of one SiO corresponds to a decrease of $1/2$ Si atom in the island; $\frac{1}{2}$ Si + $\frac{1}{2}$ SiO₂ → SiO ↑.

We now wish to grasp the main qualitative behavior of the solutions of the model by making some additional assumptions. First, we assume the $x \rightarrow -x$ symmetry, with $L_+ = -L_- = L/2$. In addition, we make the following simplification: we assume that the interface profile exhibits small slopes as compared to the island shape. Moreover, we assume that the island profile stays close to the Wulff-Kaishew equilibrium profile with a fixed contact angle θ , and we have $N = L^2 f(\theta)/\Omega$. If the surface is isotropic, the contact angle is simply related to the KMC model parameters via $\cos \theta = 2\chi - 1$, and the equilibrium shape is a portion of circle, leading to

$$f(\theta) = \frac{\theta - \sin \theta \cos \theta}{4 \sin^2 \theta}. \quad (8)$$

Finally, we assume that the O concentration is close to the equilibrium concentration of oxygen at the interface $C_{eq} = (K_0/K_1)^{1/2}$. We therefore linearize the model for small concentration deviations $\delta C_O = C_O - C_{eq}$. The linearized diffusion equation (4) can then be solved exactly. The interface shape under the island for $|x| < L(t)/2$ reads

$$h_I(x, t) = -\frac{f(\theta)}{2x_s} \cosh\left(\frac{x}{x_s}\right) \int_{L_0}^{L(t)} \frac{LdL}{\sinh(L/2x_s)}, \quad (9)$$

where L_0 is the initial extent of the island-substrate interface. Once the island edge passes the position x , the interface

height $h_I(x)$ is frozen. Therefore, the final frozen surface profile $h_S(x)$ of the nanopit when $|x| > L(t)/2$ in the presence of the island, and for all x once the island has completely disappeared is

$$h_S(x) = -\frac{f(\theta)}{2x_s} \cosh\left(\frac{x}{x_s}\right) \int_{L_0}^{2x} \frac{LdL}{\sinh(L/2x_s)}. \quad (10)$$

As in the KMC simulations and in the experiments, two types of a final nano-pit profiles can be identified. First, for small initial island sizes, when $L_0 \ll x_s$, a pit has a conical V-shape profile

$$h_S(x) = f(\theta)(L_0/2 - |x|). \quad (11)$$

In the opposite limit of large islands, where $L_0 \gg x_s$, a pit has a W-shaped profile

$$h_S(x) = 2f(\theta) \left[\left(\frac{L_0}{2} + x_s \right) e^{(|x| - L_0/2)/x_s} - (|x| + x_s) \right], \quad (12)$$

with two minima close to the triple-line at

$$|x_{min}| = \frac{L_0}{2} - x_s \ln \left(1 + \frac{L_0}{2x_s} \right). \quad (13)$$

This leads to one of the main conclusion of our analysis: the pits exhibit a transition from a V-shape to a W shape profile when increasing the initial island size L_0 .¹⁵

We have compared these results with the KMC simulations. The island profile is reconstructed by adding the island height to the substrate profile. The morphologies are strikingly similar, with a V-W transition observed in both cases as the island size increases, as shown in Fig. 4. However, the simulations indicate an asymmetric island shape in the late stages, which is not accounted for in the reaction-diffusion model.

The numerical solution of the reaction-diffusion model with $\theta = \pi/2$ indicates a crossover for $L_0/2x_s \approx 5.6$ in Fig. 4(b). This is not in quantitative, but in good qualitative

FIG. 4. (a) Superimposed snapshots of KMC simulations of the island (red line) and nano-pit (green line) profiles for various values of the Si island radius. Model parameters $L_x = 256$, $\nu_0 = 10/\tau_A$, $\nu_E = 0.1\tau_A$, $\phi = 1.5$ J, and $k_B T = 0.4$ J, leading to $x_s \approx 27$. The V-W transition appears for $R_0/x_s \approx 2.9$. (b) Reaction-diffusion model for different island sizes (from top to bottom $R_0 = 2, 4, 8$ (arbitrary units)). The shaded (orange) area represents the Si island at different times, and the lower curve is the final corresponding nano-pit shape. Reaction-diffusion model parameters: $K_0 = 1$, $K_1 = 1$, $D_O = 1$, and $\theta = \pi/2$, leading to $x_s = 2^{-1/2} \approx 0.707$. The transition is observed for $R_0 \approx 4$, i.e., $R_0/x_s \approx 5.6$.

agreement with the simulations in Fig. 4(a), which indicate a crossover at $L_0/2x_s \approx 2.9$.

As a conclusion, in spite of crude assumptions, the good qualitative agreement between the models and the experimental results validate the 3-steps scenario of interfacial reaction between a 3D Si island and its underlying SiO₂ substrate. As initially suggested, the quantity L_0/x_s plays a great role on the kinetics of the reaction and thus on the pits the Si islands etched in the underlying SiO₂ substrate. Moreover, the experimental V-W pit shape transition is recovered in both models and enables to estimate that the transition roughly takes place for $L_0/2x_s \sim 3$ to 6 (at least in a 1D scheme). Extrapolating this result to our 3D experimental case we can estimate that, at $T \approx 1000$ °C, $x_s \sim 40$ to 80 nm.

The work was supported by ANR-13-BS04-0004-02 Grant. We thank O. Kononchuk (SOITEC company) and J. C. Barbé (LETI-Grenoble) for providing us SOI samples.

¹S. Ogawa and Y. Takakuwa, *Jpn. J. Appl. Phys., Part 1* **45**, 7063 (2006).

²D. Danielson, D. Sparacin, J. Michel, and L. Kimerling, *J. Appl. Phys.* **100**, 083507 (2006).

- ³R. Nuryadi, Y. Ishikawa, and P. Tabe, *Appl. Surf. Sci.* **159–160**, 121 (2000).
- ⁴B. Yang, P. Zhang, D. Savage, M. Lagally, G. Lu, M. Huang, and F. Liu, *Phys. Rev. B* **72**, 235413 (2005).
- ⁵E. Dornel, J.-C. Barbé, F. de Crecy, G. Lacolle, and J. Eymery, *Phys. Rev. B* **73**, 115427 (2006).
- ⁶F. Cheynis, E. Bussmann, F. Leroy, T. Passanante, and P. Müller, *Phys. Rev. B* **84**, 245439 (2011).
- ⁷E. Bussmann, F. Cheynis, F. Leroy, P. Müller, and O. Pierre-Louis, *New J. Phys.* **13**, 043017 (2011).
- ⁸F. Leroy, F. Cheynis, T. Passanante, and P. Müller, *Phys. Rev. B* **85**, 195414 (2012).
- ⁹K. Sudoh and M. Naito, *J. Appl. Phys.* **108**, 083520 (2010).
- ¹⁰E. Bussmann, F. Cheynis, F. Leroy, and P. Müller, *IOP Conf. Ser./Mater. Sci. Eng.* **12**, 012016 (2010).
- ¹¹F. Leroy, Y. Saito, F. Cheynis, E. Bussmann, O. Pierre-Louis, and P. Müller, *Phys. Rev. B* **89**, 235406 (2014).
- ¹²M. Dufay and O. Pierre-Louis, *Phys. Rev. Lett.* **106**, 105506 (2011).
- ¹³F. Cheynis, F. Leroy, A. Ranguis, B. Demailleur, P. Bindzi, C. Velt, W. Bon, and P. Müller, *Rev. Sci. Instr.* **85**, 043705 (2014).
- ¹⁴See supplementary material at <http://dx.doi.org/10.1063/1.4921091> for LEEM movie of the islands motion induced by the interfacial reaction.
- ¹⁵Notice that the final pit profile, Eq. (10), does not depend on the kinetic coefficient ν_E , so that the crossover does not depend on ν_E in the reaction-diffusion model.