Dynamics of solid thin-film dewetting in the silicon-on-insulator system

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Abstract. Using low-energy electron microscopy movies, we have measured the dewetting dynamics of single-crystal Si(001) thin films on SiO\textsubscript{2} substrates. During annealing ($T > 700$\textdegree C), voids open in the Si, exposing the oxide. The voids grow, evolving Si fingers that subsequently break apart into self-organized three-dimensional (3D) Si nanocrystals. A kinetic Monte Carlo model incorporating surface and interfacial free energies reproduces all the salient features of the morphological evolution. The dewetting dynamics is described using an analytic surface-diffusion-based model. We demonstrate quantitatively that Si dewetting from SiO\textsubscript{2} is mediated by surface-diffusion driven by surface free-energy minimization.

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Solid thin films play a variety of vital technological roles, e.g. as catalytic membranes, and are key building-blocks of microelectronics. Numerous thin-film systems are known to be susceptible to dewetting instabilities, wherein the two-dimensional (2D) film spontaneously agglomerates into compact 3D nanostructures—typically during thermal annealing—which may activate mass-transport processes in or on the film [1]–[22]. From one viewpoint, dewetting is a problem that e.g. complicates the fabrication of thin-film-based devices by imposing constraints on the thermal budget during processing [1]. However, thin-film dewetting

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is also an innovative route for producing surface-adsorbed nanocrystals used in catalysis, vapor–liquid–solid nanowire growth and emerging nanoscale devices [2, 3].

To understand solid thin-film dewetting instabilities, a key challenge is to explore the interplay between kinetic processes and thermodynamic forces that transforms the film into 3D structures [19]–[22]. Silicon-on-insulator (SOI), an essential building-block of microelectronics, is an excellent model system to study solid-state dewetting. Our samples are single-crystal Si(001) films, elastically relaxed and dislocation-free, on amorphous SiO\(_2\) substrates. Previous works showed, by post-mortem ex-situ measurements, that < 100 nm thick Si films dewet from SiO\(_2\), producing Si nanocrystals during annealing \((T > 700{\degree}C)\) [5]–[17]. The Si nanocrystals have a relatively high Young’s contact angle of 72–73° [10, 14], implying that dewetting is favorable from a surface free-energy standpoint. It has been suggested that SOI dewetting is driven either by thermal expansion mismatch stress [7, 8], or by surface and interfacial free energies [12, 14], but neither suggestion has been justified by connecting measurements with comprehensive models.

Here, we report on a quantitative characterization of the dewetting dynamics of SOI measured in situ in real time using low-energy electron microscopy (LEEM). Solid-state SOI dewetting occurs in a fluid-like mode, with capillary instabilities decomposing the Si film into 3D finger structures, which in turn decompose into Si nanoislands. We show that the entire complex morphological evolution is reproduced by a kinetic Monte Carlo (KMC) model in which dewetting is driven by surface free energies and mass transport is mediated by surface diffusion. We develop a surface-diffusion-based model of the dynamics. By fitting the model to our data, we show that SOI dewetting is driven by surface free-energy minimization. Our results provide a complete physical picture of one mode of solid thin-film dewetting, definitively resolving the uncertainty about the cause of SOI dewetting.

The experiments are performed in an Elmitec LEEM III at pressures < 10\(^{-9}\) Torr. The LEEM measurements are complemented by ex-situ non-contact atomic force microscopy (AFM; PSIA-XE 100) measurements of the surface morphology at room temperature. Our samples are bonded SOI (CEA-Leti, France) fabricated by the Smart Cut\textsuperscript{TM} process. Each sample is a single-crystal Si(001) film, 6, 11, 14 or 22±2 nm thick, bonded to a 150-nm-thick \(\alpha\)-SiO\(_2\) layer on an Si(001) wafer. Prior to the experiments, the samples are cleaned by a published formula [23]. Dewetting is measured by recording a LEEM image sequence at a fixed rate (0.3–10 Hz) while annealing the sample \((T > 700{\degree}C)\). The images are acquired in a darkfield mode from electrons in a 1/2-order diffraction spot associated with either the Si(001)-2\(\times\)1 or 1\(\times\)2 surface reconstructions [24]. Adjacent terraces have orthogonal (2\(\times\)1 versus 1\(\times\)2) reconstructions, and so they appear alternately bright and dark, allowing us to see the step-terrace structure of the surface with 10 nm resolution. LEEM movies show the nanoscale motion of atomic-height steps on the surface, which is an indication of surface diffusion. We can see the larger-scale evolution of dewetting, e.g. shape and size of the 3D features, and simultaneous local processes, e.g. layer-by-layer nucleation and growth on facets of 3D features.

Figure 1(a) shows several images revealing the key features of the SOI dewetting process in which (i) voids open at defects in the Si, exposing the oxide, (ii) the voids grow, evolving a 3D Si rim, (iii) the rim undergoes a (capillary) instability to form Si fingers and (iv) the fingers break down into Si nanocrystals [12, 14]. A typical movie revealing the complete dewetting sequence (after square-void nucleation) can be found in the supplementary data, available at stacks.iop.org/NJP/13/043017/mmedia. On each sample, numerous voids open simultaneously.
Figure 1. (a) LEEM images of SOI dewetting (SOI, 22 ± 2 nm thick, \( T = 870 \degree \text{C} \), electron energy = 7.8 eV). Bright–dark speckling is due to the \( 2 \times 1 \) Si surface (darkfield conditions). Dewetting voids nucleate at defects (white arrow, \( t = 0 \) s). Si nanocrystals (black arrow) appear distorted owing to electronic charging effects. (b) KMC simulation of dewetting (\( E_s/J = 1.5 \) and \( k_B T/J = 0.4 \), \( 1200 \times 1200 \) lattice, initial film thickness = 3 layers). (c) AFM images of various stages of dewetting along with line profiles through the dewetting rim. The location of the profiles is indicated in the images. (d) Dewetting rim in the KMC model along with a few line profiles near void fingertips.
Figure 2. Large-scale images of dewetting: (a) optical image (field of view 100 × 130 µm²) with several similar square-shaped dewetting zones. (b) AFM image (field of view 30 × 30 µm²). Note that these images have been taken in the latter stages of the dewetting process where the dewetted zones start to coalesce.

at the beginning of the anneal, and undergo the same qualitative evolution exposing similar square-shaped dewetted areas (see figure 2). The qualitative features of the dewetting process are identical for 6–22 nm thick Si films, in agreement with recent experimental results [6, 9], which show that, in this thickness range, dewetting occurs via hole nucleation regardless of the thickness of the film. For thinner films (< 4 nm) hole nucleation is homogeneous, and a different arrangement of islands, with poorer order, is observed (in agreement with KMC simulations of [29]). Here we present results for 11, 14 and 22 nm thick films. Note that since the 2 × 1 and 1 × 2 surface reconstructions are visible during the whole dewetting process, this is a solid-state dewetting mechanism. This behavior is expected since (i) although the melting temperature of nanostructures is size dependent, Wautelet [25] has shown that the melting point reaches $T = 1000 \, ^\circ C$ for 3D Si particles of radius 6 nm, and (ii) there is no surface premelting of the Si(001) surface in this temperature range [26, 27].

A surface-energy-driven KMC model [28, 29] reproduces the key features of the dewetting experiments. In the KMC model, a film of material A is placed on a substrate B, which is flat and frozen. Units of A occupy a simple cubic lattice, bound by energy $-nJ$, where $n$ is the number of in-plane nearest neighbors. Units of A in direct contact with the substrate have an additional energy $E_s$, which is the dewetting driving force. Under the conditions of the model, $E_s = \gamma_A + \gamma_{A-B} - \gamma_B$, where $\gamma_A$ and $\gamma_B$ are surface free energies, and $\gamma_{A-B}$ is the interfacial free energy. $E_s > 0$ enforces dewetting. In a simulation, a hole is made in film A to mimic heterogeneous nucleation; then the system evolves by moving units of A to nearest-neighbor sites at rates $v = v_0 \exp(-nJ - \delta_{ib}E_s)/k_BT)$, where $\delta_{ib}$ is the Kronecker delta ($i = 0, 1, 2, 3, \ldots$ is the layer in which the A unit sits). There are two parameters in the model, $E_s/J$ and $k_BT/J$. Figure 1(b) shows typical simulation results. Owing to computational time limitations, the simulation uses a film three monolayers thick. Comparing figures 1(a) with (b), it is clear that this ‘coarse’ KMC simulation reproduces all the complex features of the experiments, which means that the model contains the correct ingredients.

5 Simulations with $0.5 < E_s/J < 2$ and $k_BT/J = 0.4$ yield the same features. For SOI, we estimate $0.2 < J < 1 \text{ eV atom}^{-1}$, $1 < E_s < 2 \text{ eV atom}^{-1}$ and $k_BT \sim 0.1 \text{ eV}$, so $2 < E_s/J < 7$ and $0.1 < k_BT/J < 0.5$.

6 With only three layers, the formation of new voids must be forbidden to prevent homogeneous dewetting.
Figure 3. Dewetted area versus time in (a) the experiments and (b) the KMC model for the voids shown in figure 1. The unit of time is $v_\circ^{-1}$, the area is in ‘units of A’. Insets: early linear growth. Dotted lines: the results of our analytic model. (c–e) Schematic diagrams of the dewetting dynamics. (c) A square void and rim. (d) The rim grows, and thickens via nucleation on the top facet, as the void grows. (e) Later stages: finger growth.

Let us now compare the qualitative features of the KMC simulations to the SOI dewetting experiments. Owing to the surface-free-energy cost to spontaneously form holes in the crystal surface [14], dewetting starts with void formation at preexisting extrinsic defects, such as pinholes and scratches that expose the oxide (figure 1(a)). In this early time of the dewetting, the voids evolve a square shape with $\langle 110 \rangle$-oriented sides ($\langle 100 \rangle$ in the KMC model). Insets of figures 3(a) and (b) show that the void area grows linearly in time (i.e. $x \propto t^{1/2}$). The material (Si) expelled from a void is conserved in a 3D rim around the void (figure 1(c)). The rim is facetted, e.g. $\{100\}$ and $\{111\}$ in experiments [10, 11] and $\{100\}$ in the KMC model. There is a large (001) top facet on the rim (see the black AFM lineprofile in figure 1(c)). In the LEEM and the KMC model, the rim is directly observed to thicken via layer-by-layer nucleation and growth on the (001) top-facet. A schematic diagram of the void–rim evolution is shown in figures 3(c) and (d).

The shape evolution of the voids is shown in figure 4 in stroboscopic images compiled from LEEM and KMC data. Figure 4 shows that the KMC simulation captures the local dynamics of the void shape evolution observed in the experiments.

As the voids grow, their shape evolves from square to star-like (figure 4(a)). The center of the rim thickens relative to the corners (figures 1(a)–(c)). The thickened regions move outward with $x \propto t^{1/2}$, while the void corners move out at a constant velocity, i.e. $x \propto t$ (figures 4(e) and (f)).

Some Si ($< 2\%$) is lost to a reaction, $\text{Si} + \text{SiO}_2 \rightarrow 2\text{SiO}$, at the triple line. The SiO desorbs into the vacuum.
Figure 4. Stroboscopic images showing the void edge position versus time (color). (a) Early times (11 nm thick SOI, 800 °C). (b) Finger formation (14 nm SOI, 800 °C). (c) Late times (14 nm SOI, 850 °C). (d) Finger formation in the KMC model ($E_s/J = 1$, $k_B T/J = 0.4$, 1200 × 1200 lattice, initial thickness = 3 layers). (e, f) Position of the void-edge-versus-time along lines indicated in the upper panel in (e) experiments and (f) the KMC model. The unit of time is $v_o^{-1}$; the length is in units of Å.

The thickened regions evolve into 3D Si fingers, which can grow to > 10 times the initial film thickness. The finger development in the experiment and the KMC model is qualitatively similar (figures 4(b) and (d)). As the voids continue to open, periodic rim thickening seeds new fingers at a characteristic wavelength along the void edge. The periodic thickening of the rim is similar to the rim-pinching instability modeled in [30, 31]. This instability is driven by surface
free energies (reduction of the surface area at fixed volume). Compact capillary fingers are a common feature of solid and fluid thin-film dewetting systems [18, 30, 32]. The fingers are uniformly oriented with respect to the void edges. In the experiment, the fingers are oriented at 25–45° with respect to the ⟨110⟩-oriented dewetting edge. Previous works claim that the Si finger direction, which is quoted as ⟨130⟩ (~ 27°), is determined by the presence of facets, e.g. {311}, on the sides of the fingers [10, 13, 14]. In the KMC model, the ⟨110⟩-oriented fingers are not bounded by low-free-energy facets, but rather by relatively high-free-energy ⟨110⟩ surfaces. Thus, the fingers in the KMC model are oriented by a balance of surface kinetic processes.

Finally, as the rim retracts, the Si fingers lengthen and then break down at a characteristic wavelength into Si nanocrystals (figure 1). The breakdown, a Plateau–Rayleigh capillary instability, is driven by surface energies (reduction of Si surface area at fixed volume). In the long-time limit (figure 4(c)), straight fingered void edges move at a constant speed set by finger growth, \( x \propto t \), leaving Si islands in their wake.

To connect the void growth rate with the underlying physics, i.e. the thermodynamic driving force and the limiting mass-transport mechanism, governing dewetting, we have built an analytic 2D model. We assume that the rim position, \( x(t) \), moves with a speed determined by an Einstein relation \( \frac{dx}{dt} = -\mu F \), where \( \mu \) is a surface-diffusion-based mobility, and \( F \) is a thermodynamic driving force [33]. In the model geometry in figures 3(c) and (d), the driving force per unit length acting to displace the rim outward a distance \( dx \) is \( F = -E_s + 2\gamma_{Si}(d)h/dx \). Typically, \( E_s \gg 2\gamma_{Si}dh/dx \), so the driving force is \( \approx -E_s \). Using Morgenstern’s method [34], with the approximation that the mobility is limited by diffusion across the width, \( w \), of the rim, we obtain [29] \( \mu = \Omega^2 D_{Sc}/\alpha^2 h^2 w k_B T \), where \( \Omega \) and \( \alpha^2 \) are the volume and surface area of an atom, and \( D_{Sc} \) is the surface self-diffusivity on the rim. So \( dx/dt = -\mu F = (\Omega^2 D_{Sc}/\alpha^2 h^2 w)(E_S/k_B T) \).

To fit void growth, it is necessary to know how the rim grows, i.e. we need to know \( h(t) \) and \( w(t) \). A recent model [29] proposed that the growth of a faceted dewetting rim is controlled by size-dependent nucleation-limited dynamics, which governs the growth of 3D structures in some other crystalline dewetting systems, e.g. ice/Pt(100) [21]. In this regime, the growth of faceted 3D structures is limited by the rate of layer nucleation, which is typically a strong decreasing exponential function of the size of the structure. In our KMC model, the rim thickens obeying size-dependent nucleation-limited dynamics, where the nucleation rate is a strong exponentially decreasing function of the height, i.e. \( dh/dt \propto \exp(-h/k_B T) \) [29]. By contrast, in the experiments there is no distinct evidence of size-dependent nucleation-limited rim growth: new layers nucleate on the top facet at a roughly constant rate independent of its height.

To fit the void growth dynamics in the early times (\( x \propto t^{1/2} \)), we approximate that the rim grows with a fixed aspect ratio, \( (h - h_o)/w = \text{constant} \). The black AFM lineprofile in figure 1(c) shows that \( h - h_o \approx 70 \text{ nm} \) and \( w \approx 600 \text{ nm} \). With a fixed aspect ratio, \( (h - h_o)/w = 1/9 \), and mass conservation, \( xh_o = w(h - h_o) \), we numerically integrate our expression for \( dx/dt \) to determine the void area-versus-time. The surface self-diffusivity, \( D_{Sc} = 7.4 \times 10^6 \text{ nm}^2 \text{s}^{-1} \), of Si(100) at \( T = 870 \text{°C} \) is taken from [35], and \( E_s \) is the fit parameter. The best fit, inset of figure 3(a), is \( E_s = 14 \text{ eV nm}^{-2} \), within the range \( E_s \sim 7–15 \text{ eV nm}^{-2} \) estimated from published values of the Si surface free-energy [36]–[38]. Our calculation shows that a driving force\(^8\)

\(^8\) From [37]–[39]: \( \gamma_{Si} \approx 5–9 \text{ eV nm}^{-2} \) at \( T \sim 800 \text{°C} \). Anisotropy of \( \gamma_{Si} \) is negligible (~10%) [37, 38]. From AFM data: \( \theta_e \approx 50–80 \text{°} \). Using these numbers: \( E_s = \gamma_{Si}(1 + \cos \theta_e) \approx 7–15 \text{ eV nm}^{-2} \).

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consistent with known values of the surface and interfacial free energies for the Si/SiO\(_2\) system can cause dewetting at the rates we measure.

With this fixed aspect-ratio assumption, our analytic model asymptotically obeys \( x \propto t^\beta \), where \( \beta = 2/3 \) in the short-time limit. The exponent \( \beta \) decreases with time, and for large times \( \beta = 2/5 \), which is consistent with the motion of a straight dewetting rim in the isotropic diffusion-limited model of Wong [39], but in disagreement with the \( \beta = 1/4 \) exponent predicted by Srolovitz and Safran [40]. The assumption of a rectangular cross-section with a fixed aspect ratio has two main advantages. Firstly, it accounts for the crystalline anisotropy of Si, with a wide facet on the top of the rim. Secondly, it leads to a simple analytical solution for arbitrary times, even outside the asymptotic large-time limit discussed by Wong [39].

After finger formation, void growth reaches a steady state in which the void area \( \propto t^2 \) (figure 3), i.e. the linear dimensions of the void increase at a constant speed set by the growth of the void fingers (figures 4(b) and (d)). That the void fingertips move outward at a constant speed implies that the rim near the fingertips propagates with a conserved volume and shape, i.e. mass is efficiently shuttled from the film into the Si fingers. In the experiment at \( T = 870^\circ\text{C} \) (figure 3(a)), the void fingers grow at \( 2.2 \pm 0.5 \text{ nm s}^{-1} \). From our expression for \( \text{dx/dt} \), we calculate \( E_s = 10 \text{ eV nm}^{-2} \). We have used \( h = 60 \text{ nm}, w = 250 \text{ nm} \), from the AFM data in figure 1(c). In KMC simulations with \( E_s/J = 1 \) and \( k_B T/J = 0.4 \), the finger velocity is \( \text{dx/dt} = 1.1 \times 10^{-4} v_0 \), where the length unit is the lattice spacing \( a \). Our formula for the speed, with \( h_1 \approx 4 \) and \( w \approx 7 \) observed in the simulations, gives \( \text{dx/dt} = 0.4 \times 10^{-4} v_0 \), in reasonable agreement with the simulations.

To conclude, we have presented measurements of SOI dewetting dynamics. Dewetting begins with the growth of voids surrounded by a thickening Si rim. In the early stage of dewetting, rim growth determines the dynamics and the void area grows linearly with time. In later stages, dewetting is dominated by void finger growth, and the dewetted area grows as \( t^2 \). A surface-energy-driven KMC model reproduces the dewetting morphological evolution. A simple analytic model shows that the void growth rate is consistent with a surface free-energy driving force. Our results show that SOI dewetting is mediated by surface diffusion driven by surface free energies with a driving force \( E_s \sim 10–14 \text{ eV nm}^{-2} \).

Acknowledgments

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