The kinetics of dewetting ultra-thin Si layers from silicon dioxide

M Aouassa¹,², L Favre¹, A Ronda¹, H Maaref² and I Berbezier¹,³

¹ IM2NP, CNRS—Uni. Aix Marseille, Campus St Jérôme, Case 142, 13397 Marseille Cedex 20, France
² LMON, Faculté des Sciences de Monastir, Avenue de l’environnement 5019 Monastir, Uni. Monastir, Tunisia
E-mail: isabelle.berbezier@im2np.fr

New Journal of Physics 14 (2012) 063038 (16pp)
Received 22 December 2011
Published 27 June 2012
Online at http://www.njp.org/
doi:10.1088/1367-2630/14/6/063038

Abstract. In this study, we investigate the kinetically driven dewetting of ultra-thin silicon films on silicon oxide substrate under ultra-high vacuum, at temperatures where oxide desorption and silicon lost could be ruled out. We show that in ultra-clean experimental conditions, the three different regimes of dewetting, namely (i) nucleation of holes, (ii) film retraction and (iii) coalescence of holes, can be quantitatively measured as a function of temperature, time and thickness. For a nominal flat clean sample these three regimes co-exist during the film retraction until complete dewetting. To discriminate their roles in the kinetics of dewetting, we have compared the dewetting evolution of flat unpatterned crystalline silicon layers (homogeneous dewetting), patterned crystalline silicon layers (heterogeneous dewetting) and amorphous silicon layers (crystallization-induced dewetting). The first regime (nucleation) is described by a breaking time which follows an exponential evolution with temperature with an activation energy $E_H \sim 3.2$ eV. The second regime (retraction) is controlled by surface diffusion of matter from the edges of the holes. It involves a very fast redistribution of matter onto the flat Si layer, which prevents the formation of a rim on the edges of the holes during both heterogeneous and homogeneous dewetting. The time evolution of the linear dewetting front measured during heterogeneous dewetting follows a characteristic power law $x \sim t^{0.45}$ consistent with a surface diffusion-limited
mechanism. It also evolves as $x \sim h^{-1}$ as expected from mass conservation in the absence of thickened rim. When the surface energy is isotropic (during dewetting of amorphous Si) the dynamics of dewetting is considerably modified: firstly, there is no measurable breaking time; secondly, the speed of dewetting is two orders of magnitude larger than for crystalline Si; and thirdly, the activation energy of dewetting is much smaller due to the different driving force, which is based on the crystallization and redistribution of matter around the crystalline nuclei. The third regime (coalescence) corresponds to the merging of the dewetted fronts and of the islands positioned along the edges of the holes. The dynamics of this regime is much slower since it requires overcoming an additional nucleation barrier, while the surface energy reduction is quite low (low decrease of the covered surface area).

Contents

1. Introduction .......................... 2
2. Materials and methods .......... 5
3. Results ................................ 6
4. Conclusion ......................... 14
References ............................ 15

1. Introduction

Research on self-organization at the atomic scale is constantly expanding, covering a wide range of materials and as such it constitutes an intensive field of research. Self-organized Si and Ge nanocrystals on SiO$_2$ have been widely investigated due to their potential applications in many microelectronic devices including nanocrystal memories [1–4]. For these applications, a major scientific bottleneck lies in the islands size dispersion and random lateral distribution as these two parameters alter the charge carrier storage [5–8]. It was shown recently that ultra-small homogeneous Ge and Si nanocrystals could be produced and ordered by dewetting of an ultra-thin Ge or Si film on SiO$_2$ (crystalline or amorphous) [9–11]. The nanocrystals ordering and their size homogeneity were addressed using focused ion beam (FIB) Si(001)-patterned substrates [12]. In the case of amorphous Si and Ge thin films on SiO$_2$ substrate (nominal and patterned), the morphological transformation into self-assembled nanocrystals by dewetting is controlled by crystallization and redistribution of matter around the nuclei [13].

Similar dewetting behaviour has been observed in many different systems with various materials [14–19]. Experimental studies reported that under annealing, holes form in the nominal planar thin films; they propagate to the substrate through grain boundaries or other defects. When the voids grow, they break up the film into isolated islands [20–24]. Analysis of the energetics showed that planar thin films are stable against small perturbations until these perturbations touch the substrate. When the free surface touches the substrate, the film becomes unstable and it breaks up into a discontinuous array of islands [25]. Morphological evolution of the cracks by surface diffusion was simulated numerically [26, 27]. The results evidenced complex dynamical dewetting behaviour, with a wide variety of regimes and instabilities [25–30].
To better quantify the break-up process, silicon on insulator (SOI) thin films of various thicknesses were used as a model system to determine the kinetics of retraction of a thin crystalline film [31–35]. SOI thin films exhibit specific dewetting dynamics, where mass transport is limited by surface diffusion [33]. It was shown that any planar SOI thin films under ultra-high vacuum (UHV) conditions are morphologically unstable against annealing at temperatures $T > 700$ °C from a thermodynamic standpoint due to surface energy effects alone. For these stress-free SOI films, the relative interfacial and surface energies of the system dictate the transformation of the two-dimensional (2D) thin film into semi-spherical droplets with a contact angle between the edges of the Si droplets and the underlying SiO$_2$ layer of 73°. This relatively large equilibrium contact angle produces a surface-energy-related thermodynamic driving force which imposes the top Si film in SOI to dewet and agglomerate [32]. This behaviour was observed in many experimental conditions even if the quantitative evolution of the dewetted areas varied significantly from one to another investigation depending on the experimental conditions [35–38].

In the case of high-temperature dewetting, when oxide desorption is promoted, phenomenological analysis showed that dewetting could involve two rate-limiting laws governing hole opening: (a) the reaction at the periphery, providing a time evolution of the void area $A$ with: $\frac{dA}{dt} \propto \sqrt{A}$ yielding a void-radius evolution $r(t) = kt$; (b) the monomer creation providing an evolution: $\frac{dA}{dt} \propto A$ yielding $r(t) = \exp kt$ [35]. In these conditions, the void-opening proceeded by: (i) Si adatom creation inside the void, (ii) Si adatom diffusion towards the void periphery, (iii) Si + SiO$_2$ → 2SiO chemical reaction at the periphery, and (iv) SiO desorption at the void edge. During the reaction, removal of O atoms from the SiO$_2$ side of the interface occurs, resulting in depression of the Si island/SiO$_2$ interface. Transmission electron microscopy (TEM) observations indicated that the interfacial reaction advances via O out-diffusion from SiO$_2$ into the Si island, O lateral diffusion along the interface, SiO formation at the edge of the Si island and SiO desorption from the surface [36]. The kinetic evolution in the presence of SiO desorption during annealing evidenced evolution of the radii of voids obeying $r(t) \propto t^{1/3}$ at a temperature of 790 °C, which was attributed to the void growth limited by SiO diffusion on the oxide outside the voids [35].

A modelling of the kinetic retraction of SOI thin films considering a kinetics-driven surface diffusion was performed to address the presence of surface energy anisotropy. The contact line between the film and the substrate was defined by its energy, and the contact angle resulted from local equilibrium conditions. The investigations evidenced that the anisotropy of surface energy $(\frac{\partial \gamma}{\partial \theta})$ could considerably change the phenomenology and the breaking time of thin films [9]. It was shown for instance that the breaking time could be three orders of magnitude larger in the case of a cusp point introducing a reduction of 7% of the surface energy [33]. From the mass detachment point of view, the simulations showed that the stability domain can be extended thanks to $(\frac{\partial \gamma}{\partial \theta})$ with a pinch-off phenomenology, which could even be annihilated at cusp points, while the contact line retraction speed is not affected [33].

Recent models have expanded the results of the Mullins model, where two instabilities were supposed to take place: (i) the formation of a rim followed by a valley; the latter eventually touches the substrate to produce the separation of the thickened edge from the rest of the film. In this schema, the edge of the film is expected to retract with constant speed over a long period of time. (ii) The break-up of the rim via a Rayleigh-plateau-like pinching that is at the origin of the formation of ‘fingers’. These fingers are supposed to pinch off to form isolated islands through a periodic mass-shedding mechanism. This mechanism not only yields a constant retraction
speed, but also evidences an inverse cubic dependence on the film thickness \([28]\). This approach also predicts the formation of a smooth dewetting rim at the edge of the film, with scaling laws for the increase of the radius of a hole \(x \approx t^{1/4}\) and for the position of straight fronts \(x \approx t^{2/5}\) \([15]\). Kinetic Monte Carlo (KMC) simulations were carried out to address the presence of facets on the edges of the holes \([33, 34]\). The KMC simulations carried out in the frame of nucleation theory and surface-diffusion-limited dynamics have shown that the thin films dewet with a faceted rim \([39]\). The faceting of the rims leads to a characteristic \(x \approx t^{0.5}\) power law for the motion of dewetting fronts. A layer-by-layer dewetting regime was found to occur only for heterogeneous dewetting and small distances between the pre-existing holes, while a multilayer rim was always found for homogeneous dewetting when the film thickness \(h > 1\) ML \([39]\).

This study focuses on the early stage of the dewetting of ultra-thin silicon films \((h_{\text{Si}} < 20\) nm\) on silicon oxide substrate under a UHV atmosphere and at temperatures for which there is no oxide desorption and no reaction with silicon. In this work, we distinguish three different regimes of dewetting: firstly, the nucleation of holes, which is defined by a breaking time; secondly, the film retraction, which is limited by surface diffusion kinetics, and thirdly, the coalescence of the dewetted areas. For homogeneous dewetting, these three regimes coexist after the nucleation of holes until a complete dewetting has occurred. In order to discriminate the effect of these three regimes on the dynamics of dewetting, we compare the evolution of dewetting for three different model systems: nominally flat unpatterned crystalline SOI films (c-Si), patterned crystalline SOI films (pa-Si) and flat amorphous silicon films (am-Si) deposited on SiO\(_2\). The dynamics of these three model systems are determined as a function of temperature, time and film thickness to provide new insights into the three regimes of dewetting. The dewetting of c-Si and pa-Si are called homogeneous and heterogeneous dewetting, respectively, following the denomination given in \([31]\). The regime I (hole nucleation) is described by an activation energy \(E_H \sim 3, 2\) eV measured during homogeneous dewetting of crystalline silicon. The nucleation of holes at the c-Si/SiO\(_2\) interface is attributed to the enhanced silicon self-diffusion due to the injection of O\(_2\) interstitials at this interface during thermal oxidation.

During regime II (film retraction), the dynamics of a linear dewetted front measured during heterogeneous dewetting is described by a power law \(x \sim t^{0.45}\), which is limited by surface diffusion kinetics. The dynamics of this regime is slightly slower than during homogeneous dewetting (when considering only the slope of regime II), which follows: \(x \sim t^{0.5}\). The slightly larger power exponent in the latter situation is explained by a combination of surface diffusion and hole nucleation. For both homogeneous and heterogeneous dewetting, there is no rim formation on the edges of the holes. Moreover, we did not observe the onset of facets on the edges of the holes, before the final stage of nanocrystal stabilization. The effect of surface energy anisotropy was also investigated by comparing the dewetting of amorphous and crystalline Si. The results show that in the absence of surface energy anisotropy, there is no measurable breaking time. Moreover, the retraction speed of am-Si is almost two orders of magnitude larger than those of c-Si. We also determined a lower activation energy of dewetting for am-Si than for c-Si, in agreement with the kinetics of matter crystallization and redistribution around the nuclei \([11]\) which controls the dewetting of am-Si.

Regime III (coalescence of the dewetted areas), which corresponds to the merging of the dewetted fronts of holes that come close to each other, presents a slower dynamics than regime II. This result is explained by the additional nucleation barrier to overcome when the islands positioned on the dewetted fronts merge, while the surface energy decrease resulting from the reduction of the covered surface area is quite low.
2. Materials and methods

The samples investigated are: (i) ultra-thin crystalline SOI layers (c-Si); (ii) amorphous silicon layers deposited by solid phase epitaxy (SPE) on SiO$_2$ thermal oxide substrate (am-Si) and (iii) patterned ultra-thin crystalline SOI (pa-Si). The SOI samples (CEA-Leti, France) were fabricated by the Smart CutTM process. They are single-crystal Si(001) films, with thickness between 5 and 20 nm, bonded to a 150 nm thick SiO$_2$ layer on a standard Si(001) wafer. The am-Si layers, with thickness between 0.5 and 15 nm, were deposited on an SiO$_2$ thermal oxide layer, using a RIBER Solid Source Molecular Beam Epitaxy (SSMBE) system with a background pressure in the $\sim 10^{-11}$ torr range. Si was evaporated from an electron gun evaporator with beam flux calibrated in situ by reflection high-energy electron diffraction (RHEED) oscillations and resulting in a growth rate $\sim 1 \text{ nm min}^{-1}$.

Prior to loading in the growth chamber, the samples are chemically cleaned using a Shriraki modified process adapted to SOI samples. After cleaning, the samples are immediately transferred under a clean room atmosphere into the MBE chamber (transient time below 15 s). In the growth chamber, a second cleaning step was performed. It consisted of a low temperature heating at 600°C for 30 min to remove the contaminants at the Si surface.

We preliminarily investigated the cleaning procedure, which is of crucial importance to obtain reproducible and accurate measurements of the dewetting areas [35]. The first difficulty concerns the cleaning steps, which should be performed at low temperature to avoid any SiO$_2$ desorption, which should also provide a perfectly flat Si surface, free of contaminants. We obtained perfectly reproducible results when the native oxide is fully removed during a first chemical cleaning step. Moreover, we also observed that the time between this chemical step and the introduction into the UHV chamber should be very short to avoid the contamination and partial re-oxidation of the c-Si in air during the sample transfer (as already observed for the standard Si cleaning procedure) [38].

We also investigated the effect of the vacuum on the dewetting. We showed that annealing in high vacuum ($\sim 10^{-6}$ torr) leads to irreproducible results despite the cleanliness of the furnace. All the experiments were then performed in UHV of the MBE growth chamber.

The best cleaning procedure selected was: firstly, a chemical step to remove the native oxide followed by an immediate transfer into the UHV–MBE chamber and, secondly, an in situ thermal cleaning step at temperatures below 780°C to avoid SiO$_2$ partial desorption.

The first step of hole nucleation was followed in situ by scanning tunnelling spectroscopy (STM) at annealing temperatures between 700 and 850°C. The size, shape and distribution of the dewetted areas and of the 3D islands were investigated ex situ by atomic force microscopy (AFM) in air in noncontact mode, scanning electron microscopy (SEM) and cross-section TEM. The dynamics of dewetting were determined by evaluating the average value over several measures of the fraction of uncovered area on large-scale SEM images. TEM investigations were performed using a Jeol 2010F equipped with an energy dispersive spectrometer (EDS) for x-ray analysis. Quantitative analyses were completed by selected area electron diffraction (SAED) with high spatial resolution. Cross-section TEM samples were prepared by mechanical polishing down to 10 $\mu$m and subsequent Ar$^+$ milling up to perforation.

The pa-Si samples were obtained by FIB direct writing. Patterning of the ultra-thin SOI film was carried out in a Tescan LYRA1 XMH dual-beam FIB workstation operating at 30 keV. This FIB is equipped with a mass-filtered ultra-high resolution FIB COBRA-FIB from Orsay Physics, which has an ultimate resolution of 5 nm (using Ga$^+$ ions). Special care was taken in
the removal of Ga ions at the end of the patterning process using a combination of thermal and chemical cleaning processes. The patterns consist of lines separated by 10 µm. The average evolution of the dewetted front was measured from the evolution of five lines.

The final validation of the cleaning process was obtained by electrical and optical characterizations of the structures before and after dewetting [40, 41]. Such characterizations are very sensitive to the presence of traces of impurities. The C(V) characteristics of MOS capacitors fabricated with the structures after dewetting exhibited standard MOS characteristics that were analysed in detail elsewhere [42]. Photoluminescence spectroscopy was also used to check the absence of impurities in the structures [43].

3. Results

We first investigated by STM the effect of annealing temperature on the dynamics of dewetting for temperatures between 700 and 900 °C. Due to the presence of the insulating SiO₂ layer underneath, it was very difficult to image the holes in the thin Si film. Nevertheless, crucial information about hole formation could be deduced. At annealing temperatures \( \geq 800 \, ^\circ \text{C} \), the surface forms holes that rapidly deepen and form cavities at their bottom that penetrate inside the SiO₂ substrate (STM images not shown here). Such cavities are attributed to the thermal desorption of the underlying SiO₂ substrate; this behaviour, which significantly modifies the mechanism of retraction and the dynamics of dewetting, should then be avoided [35]. All the subsequent annealing experiments were systematically performed at temperatures below the critical temperature of oxide desorption (i.e. \( \leq 800 \, ^\circ \text{C} \)).

We then investigated the kinetic evolution of dewetting for a c-Si layer 11 nm thick, at temperatures between 650 and 800 °C. We measured the evolution of the dewetted area \( A \) with time at temperatures between 730 and 770 °C. An illustration of large-scale SEM images of the surface after different annealing times at 750 °C is given in figure 1(a). On these large-scale images the small holes are not visible. It is then not possible to accurately determine the number of holes on these images. The range of temperatures 730–770 °C investigated is restricted due to experimental limitations: below 730 °C, dewetting does not occur, whereas above 770 °C, it evolves too rapidly to be accurately measured.

The evolution with time of the dewetted areas evidences three regimes of dewetting (figure 1(b)): (I) the nucleation of holes; (II) the film retraction and (III) the coalescence of holes. The three regimes are indicated on the plot at 750 °C (figure 1(b)). The dewetted area reported is the mean value of several measurements obtained on different areas at higher magnification (not shown here). During regimes I and III the dewetted area evolves slowly, whereas during regime II it increases linearly with time. The three different regimes are schematized in figure 1(c).

Regime I (nucleation of holes) was followed \textit{in situ} by STM for the c-Si film. After a specific time (hereafter called ‘breaking time’), we observed the formation of small holes randomly distributed on the surface. STM line profiles of the surface roughness show that the holes have a depth systematically equal to the thickness of the c-Si film. Moreover, the detection of SiO₂ at the bottom of the smallest holes (by XPS) demonstrates that the nucleation of holes takes place at the Si/SiO₂ interface. This heterogeneous nucleation of holes at the Si/SiO₂ interface could be favoured by the presence of O₂ interstitials injected during a previous step of Si thermal oxidation.
Figure 1. (a) Large-scale SEM images of the c-Si (11 nm thick) surface after (from left to right) 60, 120, 180 and 240 min of annealing at 750 °C; (b) evolution with time of the dewetted areas at 730 °C (dot symbols), 750 °C (triangle symbols) and 770 °C (square symbols); (c) schematization of the three different dewetting regimes: (I) nucleation of holes, (II) film retraction and (III) coalescence of the dewetted areas. During regime II, nucleation of new holes is also observed.

During this first regime, the hole nucleation rate can be described by: $v_H \approx v_0 e^{-E_H/k_B T}$, where $E_H$ is the barrier for hole nucleation. It requires a critical time ($t_H$) called breaking time which corresponds to the time needed to overcome the energy barrier of hole nucleation and to pierce the film. $t_H$ depends exponentially on the temperature (figure 2) with a nucleation barrier evaluated to $E_H \sim 3.2$ eV (figure 2, inset). This kinetics of hole nucleation is much slower than when voids are formed by grain boundary grooving [18], because it is limited by the self-diffusion of Si in our experimental conditions. The activation energy of self-diffusion is commonly larger ($E_d \sim 4.8$ eV) in clean silicon, but it can be reduced to $\sim 3$ eV due to the presence of O2 interstitials (in particular at the c-Si/SiO2 interface). The injection of O2 interstitials into Si is a well-known effect resulting from the thermal oxidation of Si [44].

During regime II (film retraction), the film starts to pinch off (figure 3(a)): the dewetted areas extend laterally by retraction of the c-Si film while keeping the same depth during the complete retraction process. This regime is driven by the reduction of the interfacial energy gained by the decrease of the SiO2 area covered by Si. Its dynamics is limited by the surface
Figure 2. Evolution of the breaking time ($t_H$) with temperature during homogeneous dewetting of c-Si (11 nm thick). The inset gives the Arrhenius plot of $v_H$.

diffusion of Si on Si. The dewetted areas always present irregular shapes, with a denuded central zone free of islands whose extension depends on the temperature and time of dewetting (figures 3(a)–(d)). Line profiles of the surface roughness across the interface between dewetted and non-dewetted areas show that the edges of the dewetted front are smooth and flat; they do not exhibit any visible thickening or formation of rim even for larger holes (figure 3(e)).

TEM cross-section observations of the film performed after partial dewetting (during regime II) evidence two different zones: (i) the non-dewetted areas, where the film is atomically flat and free of visible contaminants (figure 4(a)) and (ii) the dewetted areas (figure 4(b)) where large faceted islands could be observed (figure 4(b), upper part of the TEM sample) together with larger flat areas with rounded edges (figure 4(b), lower part of the TEM sample). Close to the dewetted areas, the film remains perfectly flat without the formation of rim at the edges of the holes. On some areas a thickening of the flat film on very large areas can be observed and the film thickness can reach $\sim 20$ nm (figure 4(c)). TEM image of the dewetted front evidences a contact angle ($\theta_c$) at the Si/SiO$_2$ interface at about $\theta_c = 75^\circ$ (figure 4(d)). This value is in good agreement with the equilibrium contact angle expected from energetic considerations for a clean Si/SiO$_2$ interface ($\theta_{eq} = 73^\circ$). The HRTEM images confirm that the film remains atomically flat, monocrystalline and free of extended defects during this retraction regime.

Both the TEM and AFM observations show that during the pinch-off process, the new edges of the holes (on both sides of the holes) rearrange instantly to form a flat layer with rounded edges and an equilibrium contact angle ($\theta_{eq}$) with the substrate. At this stage there is no formation of facets on the edge of the holes in agreement with the high dynamics of the system. The detached mass diffuses rapidly on the surface and forms a thicker uniform smooth layer. The lateral size of this thicker layer (length of matter redistribution) could extend over several micrometres. This lateral extension is at least one order of magnitude larger than the diameter of the nanocrystals that form subsequently. This regime of ultra-fast redistribution of matter on the surface is very different from the regime of instability with the formation of a thickened rim that was observed when the dewetting of the c-Si is initiated by the growth of epitaxial Ge islands on it [37]. Moreover, the difference to the observation in [33], which evidences the formation of...
Figure 3. AFM images of the evolution of dewetted areas during the annealing of SOI layer (11 nm thick) at 750 °C: (a) small holes as nucleated; (b) larger holes where islands start to form on the edges (scan size is 4 × 4 µm²); (c) larger holes with a few nanocrystals and a denuded central area (scan size is 8 × 8 µm²); (d) very large holes with several nanocrystals oriented perpendicular to the edges of the holes; (e) a typical example of the roughness line profile of the edge of the hole, showing the flatness of the Si layer even close to the hole (line scan along the arrow indicated in (a)).

a thickened rim, could be explained by the much slower matter redistribution due to the reduced surface diffusion in the presence of H₂ in the latter situation. Our results also differ from the KMC simulations of dewetting which evidenced that a multilayer rim always forms during homogeneous nucleation for \( h > 1 \) [39]. We attribute this different dynamics of redistribution to the much larger nominal thickness (\( h \sim 100 \text{ ML} \)) in our experimental conditions than the ultra-small \( h (1 < h < 3 \text{ ML}) \) considered in simulations.

During homogeneous dewetting of c-Si, the second regime results from a combination of film retraction and hole nucleation. In these conditions, for the three temperatures investigated, the dewetted area \( A \) evolves linearly with time (figure 1(b)) following a power law: \( x \sim t^{0.5} \) with \( x \) the position of the dewetted front. This regime is mainly dominated by the diffusion-based opening of existing rounded holes but the nucleation of new holes cannot be neglected. This explains the difference from previous studies where the opening of holes was found to follow \( x \approx t^{1/4} \) [28]. The larger dynamics found in our experimental conditions could be attributed to the nucleation of new holes that contribute to the increase of the dewetted area.
Figure 4. TEM cross-section images of c-Si (11 nm thick) after annealing at 750 °C for 120 min. (a) Large-scale view of a non-dewetted area where can be observed the atomically flat c-Si film; on this image, from top to bottom, one can observe the following: the 11 nm thick c-Si top layer (black contrast), the 135 nm thick SiO₂ thermal oxide and the Si(001) substrate; (b) large-scale view of two dewetted areas; on the first one, large nanocrystals with equilibrium facets are observed (upper part of the cross-section TEM sample); on the second one, large areas covered by a thicker film with rounded edges can be observed (lower part of the TEM sample); (c) partially denuded area where a flat monocrystalline film with a thickness almost twice the nominal thickness (∼20 nm) can be observed; (d) HRTEM image of the 11 nm flat film, which shows a contact angle about 75° at the c-Si/SiO₂ interface. The image confirms that the edge of the c-Si film is not faceted and has no trace of agglomerated silicon.
In order to dissociate the effect of these two processes, namely surface diffusion and hole nucleation, we measured the time evolution of the retraction distance of pa-Si when lines are patterned in the SOI layer up to the SiO$_2$ substrate. An image of the lines patterned by FIB before dewetting is given in figure 5(a). The time evolution of the dewetted front is presented in figures 5(b)–(d). One can clearly see the extension of the denuded area and the random nucleation of nanocrystals along the dewetted front. The best fit of the time evolution of the dewetted front (dotted line) is obtained for $x \approx t^{0.45}$ (figure 5(e)).

This value is in good agreement with the evolution of a straight front reported in the literature ($x \approx t^{2/5}$) [28]. It is also in good agreement with a surface-diffusion-limited process [37], where the evolution of the dewetted area ($A$) follows: $A \approx \int_0^t df(t)$, where $f(t) \approx D_{Ht_0}$ and $t_0$ is the time since the birth of the hole. It was found that $A \approx t$ ($x \approx t^{0.5}$) in the early stages, before holes come into contact, in agreement with our data. However, we find that the ($x \approx t^{0.45}$) time evolution follows the same trend all over the dewetting process (even for longer time), in contrast to the previous experimental results reported in [34]. This difference is explained by the different annealing temperature used: in the latter study, oxide desorption was reported to occur during dewetting, while in our experimental conditions Si/SiO$_2$ reaction is prevented by the low temperature of annealing used.

The evolution of the retraction speed with the thickness of the nominal c-Si during homogeneous dewetting was measured at 770°C for c-Si thickness varying between 6 and
30 nm (figure 6). The evolution of the retraction speed can be fitted by: $V \approx 1/h$ (dotted line fit in figure 6) as expected from matter conservation law and in agreement with a very fast surface diffusion limited dewetting. Such an evolution denies the formation of a thickened rim on the edges of the denuded areas, which would lead to an evolution $V \approx 1/h^2$ as reported for the mass shedding behaviour described in [28].

The surface energy anisotropy is an important parameter that considerably affects the dynamics of dewetting and its phenomenology (breaking time) [33]. To determine its influence in our experimental conditions, we have compared the evolution of dewetting for crystalline and amorphous silicon. In the latter situation, because the matter is amorphous, the surface energy is fully isotropic. One should note that due to the very different kinetics of dewetting for c-Si and am-Si, the annealing was not performed in the same range of temperatures: c-Si was annealed at $750 \pm 50^\circ$C, whereas am-Si was annealed at $550 \pm 50^\circ$C. At $T \geq 700^\circ$C, the am-Si dewets almost instantly and the evolution of the dewetted area cannot be measured. We find that for am-Si, in the absence of surface energy anisotropy, the breaking time is almost negligible whatever the annealing temperature, in agreement with the theory [33]. Moreover, we extracted the activation energies for these two systems on the small temperature range investigated. They were deduced from the evolution of the dewetting speed (nm$^2$/min$^{-1}$) with the inverse of temperature: $\Delta A/\ell \propto K \exp \left( -E/kT \right)$ (figure 7). Despite the experimental error bars, it can be seen that they differ considerably ($E_c \sim 4.6 \pm 2$ eV and $E_{am} \sim 2.6 \pm 2$ eV for c-Si and am-Si, respectively) as a function of the crystallinity of the matter. This is explained by the very different driving force of dewetting: for c-Si, it is mainly limited by surface diffusion, whereas for am-Si it is controlled by crystallization and redistribution of matter around the nuclei. In conclusion, the absence of crystallinity suppresses the breaking time and increases by two orders of magnitude the dewetting speed (in agreement with theory). It also shows that the activation energy is much smaller for am-Si than for c-Si due to the different phenomenology of the processes in the two situations.

This conclusion is consistent with the results on the effect of Ge on the thermal dewetting and agglomeration of the Si(001) template layer that were reported previously [45].
shown that the incorporation of Ge in the nominal ultra-thin Si film destroys the long-range ordering of the decomposed nanocrystals and reduces the dewetting initiation temperature. This effect was qualitatively explained by Ge-induced bond weakening and decreased surface energy anisotropy. The last regime, regime III, corresponds to the coalescence of the denuded areas. In these areas, islands form along the front of the dewetted areas (on the edges of the holes) when the mean diameter of the holes reaches about $\sim 1 \mu m$. On the dewetted areas, nanocrystals exhibit an equilibrium symmetric shape representative of a clean c-Si surface with the onset of the low-energy facets of silicon (113), (111) and (001) as commonly reported for the equilibrium shape (figure 8(a)) [46]. The symmetric faceted regular shapes of the islands can be well appreciated on SEM images (figure 8(b)).

During regime III, the nanocrystals’ shape and orientation evolve when the holes come close to each other (figure 9). The AFM images illustrate three different stages of hole
Figure 9. AFM images that illustrate regime III of hole coalescence: from left to right, (a) the two dewetted fronts propagate in the direction of each other; (b) the fronts and the islands on the edges merge; (c) a larger hole is formed by the coalescence of three holes that have merged along the dashed lines.

coalescence (from left to right): (i) the two dewetted fronts propagate in the direction of each other; (ii) they come into contact and the islands close to the edges merge and reorientate; (iii) a larger dewetted zone is formed by the coalescence of three smaller holes that have merged along the dashed lines.

During this stage, the energetic driving force of dewetting becomes smaller because of the reduced size of the non-dewetted areas between the holes. In addition, when the edges of the holes merge, the islands also merge and should reorientate. This rearrangement of the matter needs to overcome an additional nucleation barrier. The combination of these two effects slows down the dynamics of dewetting during this regime.

4. Conclusion

We have quantitatively measured the evolution of dewetting of ultra-thin silicon films with temperature, time and thickness. The dewetting could be divided into three different regimes: (i) hole nucleation, which takes place at the Si/SiO₂ interface. The activation energy of hole nucleation ($E_H \sim 3.2$ eV) is attributed to the self-diffusion of Si enhanced by the presence of O₂-injected interstitials at the interface (coming from the previous thermal oxidation step). (ii) Film retraction, which follows a time evolution $x \sim t^{0.45}$ for a pre-existing linear front. This regime does not produce a thickened rim on the edges of the denuded zones due to the ultra-fast redistribution of matter onto the film to form a thicker atomically flat layer. The edges of the holes rearrange instantly to form the equilibrium angle $\alpha_{eq} \sim 75^\circ$ at the trijunction vacuum/Si/SiO₂. They have a rounded shape and no visible facets until the stabilization of the faceted nanocrystals with equilibrium shape. The dewetted front evolves inversely with the initial thickness: $x \sim h^{-1}$ in agreement with mass conservation. This evolution also confirms the absence of a multilayer rim on the edges of the dewetted areas. For isotropic surface energy, there is no breaking time and the dewetting speed increases by two orders of magnitude as compared to anisotropic surface, in agreement with theory. The activation energy of dewetting is considerably smaller for amorphous silicon, due to its driving force based on crystallization and redistribution of matter around the crystalline nuclei. (iii) The coalescence of dewetted areas...
involves the merging of the dewetted fronts and of the islands close to the edges. This imposes a slower dynamics of dewetting since the energetic driving force is lower: the energy gain is reduced due to the small increase of the dewetted zones, while there is an additional nucleation barrier to overcome. The complex universal dewetting behaviour described in this study could be expanded to many other systems. The laws deduced enable us to predict the size and density of nanocrystals in many experimental conditions.

References

[1] De Salvo D, Ghibaudo G, Pananakakis G, Guillaumot B and Baron T 2000 Superlatt. Microstruct. 28 339
[2] Liu Y, Chen T P, Tse Y Q, Hsieh J H, Ho P F and Liu Y C 2003 J. Phys. D: Appl. Phys. 36 L97–L100
[3] Chang T C, Jian F Y, Chen S C and Tsai Y T 2011 Mater. Today 14 608
[4] Lu J, Zuo Z, Chen Y B, Shi Y, Pu L and Zheng Y D 2008 Appl. Phys. Lett. 92 013105
[5] El Hdiy A, Gacem K, Troyon M, Ronda A and Berbezier I 2008 J. Appl. Phys. 104 063716
[6] Gacem K, El Hdiy A, Troyon M, Berbezier I and Ronda A 2010 Nanotechnology 21 065706
[7] Gerardi C et al 2007 IEEE Trans. Electron Devices 54 1376
[8] Perniola L, Salvo B D, Ghibaudo G, Para A F, Pananakakis G, Baron T and Lombardo S 2003 Solid State Electron. 47 1637
[9] Nuryadi R, Ishikawa Y and Tabe M 2000 Appl. Surf. Sci. 159–160 121
[10] Yang B, Zhang P, Savage D E, Lagally M G, Lu G-H, Huang M and Liu F 2005 Phys. Rev. B 72 235413
[11] Karmous A, Berbezier I and Ronda A 2006 Phys. Rev. B 73 075323
[12] Karmous A, Berbezier I, Ronda A, Hull R and Graham J 2007 Surf. Sci. 601 2769
[13] Karmous A, Cuenat A, Ronda A, Berbezier I, Atha S and Hull R 2004 Appl. Phys. Lett. 85 6401
[14] Coll M, Gazquez J, Pomar A, Puig T, Sandiumenge F and Obradors X 2006 Phys. Rev. B 73 075420
[15] Wong H, Voorhees P W, Miksis M J and Davis S H 2000 Acta Mater. 48 1719
[16] Jiran E and Thompson C V 1990 J. Electron. Mater. 19 1153
[17] Rodel J and Glaeser A M 1990 J. Am. Ceram. Soc. 73 592
[18] Mullins W W 1963 Metal Surfaces: Structure, Energetics and Kinetics ed N A Gjostein and R W Roberts (Metals Park, OH: American Society for Metals) p 17
Mullins W W 1957 J. Appl. Phys. 28 333
Mullins W W 1959 J. Appl. Phys. 30 77
[19] Legrand B, Agache V, Nys J P, Senez V and Stevenard D 2000 Appl. Phys. Lett. 76 3271
[20] Kennefick C M and Raj R 1989 Acta Metall. 37 2947
[21] Nuryadi R, Ishikawa Y and Tabe M 2000 Appl. Surf. Sci. 159 121
Nuryadi R, Ishikawa Y, Ono Y and Tabe M 2002 J. Vac. Sci. Technol. B 20 167
[22] Agrawal D C and Raj R 1989 Acta Metall. 37 2035
[23] Jiran E and Thompson C V 1990 J. Electron. Mater. 19 1153
[24] Powers J D and Glaeser A M 1993 J. Am. Ceram. Soc. 76 2225
[25] Srolovitz D J and Safran S A 1986 J. Appl. Phys. 60 255
[26] Takahashi Y, Ueno F and Nishiguchi K 1988 Acta Metall. 36 3007
[27] Bullard J W 1997 J. Appl. Phys. 81 159
[28] Wong H, Miksis M J, Voorhees P W and Davis S H 1997 Acta Mater. 45 2477
[29] Saxena R, Frederick M J, Ramanath G, Gill W N and Plawsky J L 2005 Phys. Rev. B 72 115425
[30] Dufay M and Pierre-Louis O 2011 Phys. Rev. Lett. 106 105506
[31] Sutter P, Ernst W, Choi Y S and Sutter E 2006 Appl. Phys. Lett. 88 141924
[32] Danielson D T, Sparacino D K, Michel J and Kimerling L C 2006 J. Appl. Phys. 100 083507
[33] Dornel E, Barbé J-C, de Crécy F, Lacolle G and Eymery J 2006 Phys. Rev. B 73 115427

New Journal of Physics 14 (2012) 063038 (http://www.njp.org/)
[34] Bussmann E, Cheynis F, Leroy F, Müller P and Pierre-Louis O 2011 New J. Phys. 13 043017
[35] Bussmann E, Cheynis F, Leroy F and Müller P 2010 IOP Conf. Series: Mater. Sci. Eng. 12 012016
[36] Sudoh K and Naito M 2010 J. Appl. Phys. 108 083520
[37] Sutter E and Sutter P 2006 Nanotechnology 17 3724
[38] Berbezier I and Ronda A 2007 Phys. Rev. B 75 195407
[39] Pierre-Louis O, Chame A and Saito Y 2009 Phys. Rev. Lett. 103 195501
[40] Nassiopoulou A G, Olzierski A, Tsoi E, Berbezier I and Karmous A 2007 J. Nanosci. Nanotechnol. 7 316
[41] Scarselli M, Masala S, Castrucci P, De Crescenzi M, Gatto E, Venanzi M, Karmous A, Szkutnik P D, Ronda A and Berbezier I 2007 Appl. Phys. Lett. 91 141117
[42] Gacem K, El Hdiy A, Troyon M, Berbezier I, Szkutnik P D, Karmous A and Ronda A 2007 J. Appl. Phys. 102 093704
[43] Rowell N L, Lockwood D J, Berbezier I, Szkutnik P D and Ronda A 2009 J Electrochem. Soc. 156 H913
[44] Seeger A 2011 Phys. Status Solidi b 248 2772
[45] Zhang P P, Yang B, Rugheimer P P, Roberts M M, Savage D E, Liu F and Lagally M G 2009 J. Phys. D: Appl. Phys. 42 175309
[46] Bermond J M, Métois J J and Floret F 1995 Surf. Sci. 330 48