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Self-organizing nanochannel networks in periodically perforated semiconductor films

R. K. Annabattula and P. R. Onck*

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands

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In this paper we theoretically analyze the mechanism of nanochannel formation by an evolutionary etching process in periodically perforated semiconductor films. The compressive stresses due to lattice mismatch of the epitaxially grown nanoscale films are gradually relaxed; leading to an evolutionary buckling process. We quantitatively analyze the mechanics of wrinkle evolution around an isolated etch-pit, and a predictive tool to determine the edge-to-corner channel transition is developed. The buckling wavelength increases with increasing etch depth until the etch fronts of neighboring etch-pits merge and multiple channels coalesce. The effect of various system parameters such as etch-pit size, periodicity, and film thickness on the channel morphology has been studied and compared with experimental results. The good agreement provides insight into the physical mechanisms that govern the complex interplay during evolutionary etching and channel formation.

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I. INTRODUCTION

The buckling and wrinkling of materials are ubiquitous in everyday life, from human skin to dried vegetables and fruits.¹ Despite the complexity of such patterns in natural systems, many technological applications of wrinkled surfaces in microsystems and nanosystems have been realized in recent years. Such applications include smart adhesives,² cellular engineering,³ optical gratings,⁴ measurement of elastic moduli of thin films,⁵ marine antifouling,⁶ fabrication of bendable electronics,⁷ and microfluidic large-scale integration.⁸ Owing to the numerous technological applications of patterned surfaces, the development of nonconventional methods of fabrication that circumvent the limitations of conventional lithography⁹ has become an important field of research. Bowden *et al.*¹⁰ demonstrated a promising methodology based on the controlled buckling of prestressed thin films on compliant substrates. Since then, buckling has been often employed to induce regular patterns on planar surfaces, either by buckling of stiff films on compliant substrates or by buckle-driven delamination of films on stiff substrates. A new approach of controlled buckling was reported some years ago, based on the partial release and bond-back of prestressed thin films on rigid substrates.^{11–13} From a theoretical point of view, a thorough understanding of the mechanisms of wrinkle formation is not only useful for a better design of the buckling-induced morphologies, but also to prevent buckling at the nanoscale in the case of prestressed multilayer architectures in nano-electromechanical and micro-electromechanical systems.¹⁴ While theoretical studies of wrinkle/buckle formation of prestressed films on rigid and compliant substrates has been reported by many researchers,^{1,7,15–21} the understanding of buckle patterns based on the “release-and-bond-back” mechanism is only starting to emerge.^{11–13,22–24}

Recently, a new class of nanochannel networks was reported¹³ in which InGaAs films were grown on a GaAs substrate separated by an AlAs sacrificial layer. Using lithographic techniques, periodically spaced holes were introduced into the film that were used as etch-pits, allowing the etching solution to gradually etch away the sacrificial layer starting at the pit locations. The spatially nonuniform etching process resulted in ordered networks of nanochannels whose morphology can

be controlled by the size, shape, and spacing of the etch-pits. Two important aspects set these results apart from the previously studied linear networks.^{12,23} First, the two-dimensional patterning introduced spatially nonuniform stress distribution in the plane of the film, which is absent in the one-dimensional formation of linear channels. Second, a strong interaction between the film and the substrate was observed to be present in the InGaAs film system, unlike the previously studied SiGe system.^{12,23} As a result, the continuous film-substrate interaction needs to be accounted for during the evolutionary etching process of the AlAs system. The aim of this paper is to numerically simulate the above-mentioned evolutionary etching process and to study the influence of the system parameters (e.g., etch-pit size, spacing, and film thickness) on the channel morphology.

The outline of the paper is as follows. In Sec. II, we describe the finite-element model to study the evolutionary etching process and the simulation procedure. In Sec. III A we investigate the buckling strain of an isolated single etch-pit and study the influence of various system parameters on the critical buckling strain. In Sec. III B we study the evolutionary etching process for an isolated single etch-pit. Next, in Sec. III C, we study the evolution of channels in a film with periodically placed etch-pits and their interaction. Finally, in Sec. IV, we summarize the results and draw conclusions.

II. MODEL AND SIMULATION PROCEDURE

In this section, we describe the model to study the nanochannel network formation based on the concept of evolutionary etching in the InGaAs film system.¹³ We refer to the process as “evolutionary etching” as the sacrificial layer is gradually removed from the periphery of the etch-pit during the channel evolution. Figure 1(a) shows a schematic of the initial configuration of a 3×3 film array of etch-pits with an etch-pit size W and periodicity (spacing) P . Figure 1(b) shows a zoomed-in view of a unit cell [shown as a dashed white square in Fig. 1(a)] of the system. Figure 1(c) shows the partial removal of the sacrificial layer over a distance L_e , allowing the film to release its eigenstrains by forming

FIG. 1. (Color online) Schematic showing the process of evolutionary etching: (a) Initial configuration of a 3×3 array of etch pits, (b) zoomed-in view of a unit cell [highlighted by the white square in (a)] of the 3×3 array, (c) profile of the film after the release of eigenstrain in a single-etch-pit (outer boundary constrained) due to the etching of the sacrificial layer up to an etch width of L_e .

wrinkles. In this paper, we explore how the periodicity (P), size of etch-pit (W), and the film thickness (t) influence the channel morphology for both the single- [Figs. 1(b) and 1(c)] and multi-etch-pit [Fig. 1(a)] systems. The thickness of the sacrificial layer is t_{sl} .

The process of channel formation can be described in three steps: (i) InGaAs film is grown epitaxially on a sacrificial layer (AlAs) covering a GaAs substrate during which eigenstrains ϵ^* are induced in the film due to the lattice mismatch between the film and the sacrificial layer. Then, holes of size W with a periodicity P are introduced into the InGaAs film by photolithography to be used as etch pits during later stages. (ii) The system is placed in an etchant solution (hydrofluoric acid) such that the solution entering through the etch-pits gradually removes the sacrificial layer. The removal of the sacrificial layer allows the otherwise constrained film to release its eigenstrain ϵ^* by buckling, forming wrinkles as shown in Fig. 1(c). The etch width L_e gradually increases until the sacrificial layer is completely removed. This is called the release stage. (iii) After the release phase, the system is left for drying during which the film bonds back to the substrate, freezing in a final channel morphology.

Using von Karman nonlinear plate theory, the total strain in the film can be written as the sum of three contributions: $\epsilon = \epsilon^{\text{str}} + \epsilon^{\text{rot}} + \epsilon^{\text{bend}}$.²⁵ The first term, ϵ^{str} , is the strain caused by the in-plane stretching of the material, the second term, ϵ^{rot} , is the contribution caused by the out-of-plane displacement w , and the third term, ϵ^{bend} , is the contribution due to bending. The coefficients of the strains with respect to a Cartesian frame

in the X - Y plane [see Fig. 1(a)] are

$$\epsilon_{ij}^{\text{str}} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right), \quad \epsilon_{ij}^{\text{rot}} = \frac{1}{2} \frac{\partial w}{\partial x_i} \frac{\partial w}{\partial x_j}, \quad (1)$$

$$\epsilon_{ij}^{\text{bend}} = -z \frac{\partial^2 w}{\partial x_i \partial x_j} = -z \chi_{ij},$$

where u_i are the in-plane displacements and w is the out-of-plane displacement. For the constitutive behavior of the film, we assume that the total strain consists of an elastic part ϵ^{el} and an eigenstrain part ϵ^{eig} : $\epsilon = \epsilon^{\text{el}} + \epsilon^{\text{eig}}$, with the eigenstrain given by

$$\epsilon_{ij}^{\text{eig}} = \epsilon^* \delta_{ij}, \quad i = 1, 2, \quad j = 1, 2, \quad (2)$$

δ_{ij} is the Kronecker delta. The film is in a state of plane stress ($\sigma_{13} = \sigma_{23} = \sigma_{33} = 0$) so that the coefficients of the stress σ in the film are given by

$$\sigma_{ij} = \frac{E}{1 + \nu} \left(\epsilon_{ij}^{\text{el}} + \frac{\nu}{1 - \nu} \epsilon_{kk}^{\text{el}} \delta_{ij} \right), \quad (3)$$

where $i = 1, 2, j = 1, 2$, E is Young's modulus, and ν is Poisson's ratio of the film. To mimic the complex interplay between the film and substrate during the evolutionary etching and drying, we assume a phenomenological interaction relation that consists of a short-range repulsive part and a long-range attractive part, also often employed for van der Waals-type interactions. For this we use a nonlinear traction-separation relation given by²⁶

$$T_n = \sigma_{\text{max}} \frac{w_n}{\delta_n} \exp \left(1 - \frac{w_n}{\delta_n} \right), \quad (4)$$

where T_n is the normal traction, w_n is the normal separation, and $\sigma_{\max}$ is the maximum normal traction attained at the critical normal opening δ_n . The cohesive energy per unit area is equal to $\Gamma = \int_{w_n} T_n dw_n = \sigma_{\max} \delta_n \exp(1)$.

We use the finite-element method²⁷ to solve the boundary-value problem described above and study the mechanism of wrinkle evolution during etching. The film is modeled using four-noded shell elements (S4) and the substrate is modeled as a rigid surface. To mimic stage (i) of the experimental process (see Fig. 1), we initially constrain the film, during which the eigenstrains are applied. A compressive biaxial stress state develops in the film. Next, a set of nodes within a distance of L_e from the etch-pit periphery is released (i.e., their boundary conditions are redefined to be free while all other nodes are still constrained), thus allowing the film to release its eigenstrains. As a result, the film buckles into a wrinkled configuration to accommodate the “extra skin” due to the released eigenstrains. This process is continued with small increments of L_e until the sacrificial layer is completely removed or, in other words, until all the nodes of the film are released. The interaction between the film and the substrate is modeled through the normal traction-separation relation law given by Eq. (4). The same traction-separation law is used to prescribe the nonuniform traction during the bond-back process. During evolutionary etching we use a normal contact between the film and substrate with rough friction, while during bond-back a “no-separation” contact condition is employed. The simulations are carried out using an explicit dynamic solution procedure to overcome the local instabilities. Each incremental release step results in a sudden jump in kinetic energy of the system. The system is given sufficient time for relaxation in each step to reduce the kinetic energy to zero. To speed up this process we use mass-proportional damping.²⁸ A similar procedure as described above is used in Annabattula *et al.*²³ and Annabattula and Onck,²⁴ to which the reader is referred for details.

III. RESULTS AND DISCUSSION

In this section, we present the results of the simulations carried out and compare the results with the experimental channel morphologies. In Secs. III A and III B we study the wrinkle evolution around a single etch-pit for different combinations of W , P , and t [see Figs. 1(b) and 1(c)]. In Sec. III A we carry out a buckling analysis to obtain the initial buckling strain and analyze the effect of a finite fillet radius. We also compare the buckling strain of the current boundary-value problem with two limiting cases studied before.^{23,24} In Sec. III C we study the evolution of wrinkles in a 3×3 pit array [see Fig. 1(a)] and compare the simulated channel morphologies with experimental results. All simulations are carried out using $E = 80$ GPa, $\nu = 0.32$, a sacrificial layer thickness $t_{sl} = 80$ nm, and an eigenstrain $\varepsilon^* = 1.4\%$ conform the experimental setup.

A. Buckling analysis

In this section, a buckling analysis of a single-etch-pit [see Fig. 1(b)] will be carried out to investigate the effect of the system parameters on the critical buckling strain. The boundary-value problem described above can be identified as

an intermediate problem between two limiting cases, i.e., a clamped square plate²⁴ and a linear channel.²³ When the size of the pit W is very small compared with the size of the film P the boundary-value problem approaches that of the clamped square plate, while for large values of W , the etch depth $(P - W)/2$ is much smaller than W and the solution approaches that of the linear channel. In the following, we study how the critical buckling strain evolves for different combinations of the system parameters and compare the results to the two mentioned limiting cases. Figure 2(a) shows (symbols) the buckling strain (ε_s^{cr}) of a film with dimensions W , P , and thickness t , normalized with the buckling strain of a film without an etch-pit, i.e., $W = 0$, corresponding to a clamped square film of size P which has a buckling strain, given by²⁴

$$\varepsilon_s^{cr} = \frac{5.3\pi^2}{12(1+\nu)} \left(\frac{t}{P} \right)^2. \quad (5)$$

Figure 2(a) clearly shows that the buckling strain converges to Eq. (5) (see dashed line) when the pit size W reduces to zero. The solid line in Fig. 2(a) shows the buckling strain of a linear channel given by²³

$$\varepsilon_l^{cr} = \frac{1.28\pi^2}{12(1-\nu^2)} \left(\frac{t}{L_e} \right)^2, \quad (6)$$

with $L_e = (P - W)/2$. Indeed, for large values of W relative to P , the results converge to Eq. (6).

The results of Fig. 2(a) correspond to square etch-pits with sharp corners. However, as a consequence of the lithographic production process, the corners are somewhat rounded, with a finite radius R [see inset of Fig. 2(b)]. Figure 2(b) shows the effect of fillet radius R on the critical buckling strain ε_R^{cr} of a film with $W = 2.5 \mu\text{m}$, $P = 4 \mu\text{m}$, and $t = 20$ nm. The results are normalized with the buckling strain of the film with zero fillet radius (ε_0^{cr}) and are plotted against the normalized fillet radius R/W . It can be clearly seen that the buckling strain reduces with an increase in fillet radius. This can be attributed to the reduction in the stress concentration at the corners, which smoothes out the stress state, making it easier for the system to buckle in a low-energy mode. This observation is also consistent with the results of Fig. 2(a), where a decrease in buckling strain is observed with a decrease in etch-pit size when the system makes a transition from the high-energy buckling mode of multiple wavelengths to the low-energy mode of a smooth single-wavelength dome (see Ref. 24).

B. Evolution of channels around a single-etch-pit

In this section, we present the results for the evolution of wrinkles during the evolutionary etching process [i.e., the release stage (ii)] for a unit cell [Fig. 1(b)] of a large film with periodically perforated etch-pits. The four edges on the outer boundary of the film are constrained while the four edges of the etch-pit are stress free, similar to the previous section. Figure 3 shows the evolution of wrinkles in a square film with an etch-pit size $W = 3 \mu\text{m}$, a periodicity $P = 4 \mu\text{m}$, and thickness $t = 20$ nm for two values of the etch width: $L_e = 0.3 \mu\text{m}$ [Figs. 3(a) and 3(c)] and $L_e = 0.707 \mu\text{m}$ (Figs. 3(b) and 3(d)). Figures 3(a) and 3(b) show the

FIG. 2. (a) Normalized buckling strain ($\epsilon^{\text{cr}}/\epsilon_s^{\text{cr}}$) as a function of normalized film size $[(P - W)/P]$, (b) normalized buckling strain ($\epsilon_R^{\text{cr}}/\epsilon_0^{\text{cr}}$) as a function of normalized fillet radius (R/W).

evolution of buckles in the film without interface interaction between the film and the substrate. The contours in the figures show the out-of-plane position z of the film normalized with $H^* = 120 \text{ nm}$. The position $z = 0$ corresponds to the substrate and $z = 80 \text{ nm}$ to the initial position of the fully

constrained film. The maximum etch width in this case is $\sqrt{2}(P - W)/2 = 0.707 \mu\text{m}$ (distance from the etch-pit corner to film edge corner) which is considerably smaller than the size of the etch-pit ($3 \mu\text{m}$), and hence the evolution of wrinkle wavelength resembles the evolution in the case of linear channels.²³ Indeed, the wavelength and the buckling amplitude increases as the etch width increases. Next, we study the same case but now in the presence of interface interaction during the evolution process (results not shown). For this we use an interfacial energy of 0.01 J/m^2 (corresponding to $\delta_n = 10 \text{ nm}$ and $\sigma_{\text{max}} = 0.37 \text{ MPa}$). In Fig. 4(a) we plot the z profile along the etch-pit boundary at the end of complete relaxation (i.e., $L_e = 0.707 \mu\text{m}$) with (solid) and without (dotted) interface interaction. It can be observed that the height and depth of wrinkles in the corners is larger than along the edges, for both cases. The number of wiggles is slightly lower for the case with interface interaction, but the profiles do not show a significant difference. In Fig. 4(b) we analyze the effect of the

FIG. 3. (Color online) Evolution of wrinkle wavelength during the process of evolutionary etching for a film with $W = 3 \mu\text{m}$, $P = 4 \mu\text{m}$, and $t = 20 \text{ nm}$ (a), (b) without and (c), (d) with rounded corners. The contours show the normalized out-of-plane position ($\bar{z} = z/H^*$) of the film with $H^* = 120 \text{ nm}$. The corresponding etch widths (L_e) are (a), (c) 300 nm and (b), (d) 707 nm , respectively.

FIG. 4. (a) Out-of-plane position z of the film ($P = 4 \mu\text{m}$) plotted along the periphery of the etch-pit ($W = 3 \mu\text{m}$) for a film thickness of 20 nm with and without interaction. (b) Out-of-plane position z of the film ($P = 4 \mu\text{m}$) plotted along the periphery of the etch-pit ($W = 3 \mu\text{m}$) with interaction for different film thicknesses. Both cases correspond to $R = 0$.

FIG. 5. (Color online) Evolution of wrinkle wavelength during the process of evolutionary etching without interface interaction for a film of $W = 1.5 \mu\text{m}$, $P = 4 \mu\text{m}$, and $t = 20 \text{ nm}$ without (top row) and with (bottom row) rounded etch-pits of fillet radius 300 nm. The contours show the normalized out-of-plane position ($\bar{z} = z/H^*$) of the film with $H^* = 220 \text{ nm}$ (see Fig. 3 for legend).

film thickness in the presence of interface interaction. For the thinner film ($t = 10 \text{ nm}$) it can be clearly seen that the entire film bonds to the substrate due to the lower bending stiffness. It can also be observed that the wavelength of the wrinkles is much smaller than for the thicker film, due to the quadratic dependence of wavelength on film thickness.²³

In Figs. 5(a)–5(c) we show the evolution of the wrinkle profile for a unit cell of a pit array with the same spacing (periodicity $P = 4 \mu\text{m}$), but with a smaller pit size, $W = 1.5 \mu\text{m}$. Initially, for smaller etch widths L_e , multiple waves develop as in Fig. 3, but as the etch width increases, the number of waves decreases until the wavelength equals the width of the etch-pit and the evolution process saturates. Clearly, at the maximum etch width L_e a completely different wave pattern has developed, consisting of corner buckles compared with the edge buckles in the case of large etch-pit sizes (Fig. 3). To investigate the effect of a nonzero fillet radius, we have repeated the calculations of Figs. 3 and 5 for rounded etch-pits with a fillet radius R of one fifth of the etch-pit size, $R = W/5$, shown in Figs. 3(c) and 3(d) and 5(d)–5(f). The introduction of a fillet reduces the stress concentration at the pit corner, smoothing out the stress distribution along the pit periphery. As a result, we can observe a slight decrease in the total number of waves along the periphery and a more prominent presence of the waves located in the corners, having a somewhat larger wavelength. In Fig. 6(a) we quantitatively compare the wavelength as a function of etch width for the small and large etch-pit sizes shown in Figs. 3 and 5, with and without rounded corners. In the initial stages of wrinkling (i.e., at small L_e), the number of wrinkles can vary, somewhat depending on fillet radius for the small pit size, but is approximately the same for the larger size. We also observe a plateau in the wavelength for large L_e for both the etch-pit sizes, with wavelengths slightly smaller for the rounded etch-pits due to

FIG. 6. (a) Effect of fillet radius R on the wavelength (λ) of the wrinkles plotted as a function of the etch width during the evolution for films of $W = 1.5 \mu\text{m}$ and $3 \mu\text{m}$ for a spacing of $P = 4 \mu\text{m}$ and thickness $t = 20 \text{ nm}$. (b) Comparison of normalized wavelength λ/L_e with the master curve for linear channels²³ for different W and P combinations. The numbers in the legend correspond to W/P for each case (in μm) shown in symbols, and the subscript of t corresponds to the thickness of the film in nm.

the smaller circumference of these pits. In the case of $W = 3 \mu\text{m}$, the plateau is reached as the etch width is approaching the boundary of the film, while in the case of $W = 1.5 \mu\text{m}$ the plateau symbolizes the transition from edge wrinkling to corner wrinkling. Once the corner wrinkles set in there is no further increase in wavelength around the etch-pit boundary, but we can observe a secondary buckling²⁹ effect at the film boundary, as also observed in linear channels [see the buckles in the encircled region in Fig. 5(f)]. Note the drop in the wavelength for the film $W = 1.5 \mu\text{m}$ and $P = 4 \mu\text{m}$ with sharp corners in Fig. 6(a). This is due to the presence of edge buckles in the system which were not prominent in their amplitude until $L_e = 1.25 \mu\text{m}$ [see Figs. 5(b) and 5(c)]. Next, we study the wavelength variation with increase in L_e for all the film geometries studied in this paper in Fig. 6(b). As mentioned already, the wrinkles start as edge wrinkles, similar to the linear channel case, when the etch width L_e is still small compared with the etch-pit size W . Hence, we can compare the results of the present simulations with the master curve obtained for the wavelength evolution in linear channels, studied earlier.²³ Figure 6(b) shows the normalized wavelength λ/L_e plotted as a function of the nondimensional parameter $\varepsilon^* L_e^2/t^2$. The solid line shows the linear channel case corresponding to the situation in which the etch-pit size W is much larger than the etch width L_e and thickness t . The symbols in the figure correspond to different geometries (with different L_e), showing good agreement with the linear channel prediction in the small L_e range and deviating from the curve with an increase in etch width L_e . Another influencing parameter on the wrinkle morphology is the ratio of λ/W . For a small λ/W value the system approaches a linear channel solution, but for higher ratios the system much closer resembles the configuration of a clamped plate with a small hole (see Sec. III A). As a result, the system goes through a transition from edge wrinkles ($\lambda/W < 1$; see Fig. 3) to corner wrinkles ($\lambda/W = 1$; see Fig. 5). Hence, the identification of that combination of parameters W , P , and t for which the system goes through an edge-to-corner buckle transition

FIG. 7. (Color online) (a) Influence of film geometry on edge-to-corner buckle transition for an eigenstrain of 1.4%. The region in light gray corresponds to the "edge-buckle" regime, while the region in red and blue corresponds to the "corner-buckle" regime. The data points correspond to the hole sizes $W = \{1, 1.5, 2, 3\} \mu\text{m}$ and periodicities $P = \{4, 5\} \mu\text{m}$. (b) Effect of eigenstrain ϵ^* on the edge-to-corner transition.

would be of interest for the design of channel morphologies. Figure 7(a) shows the region of data points obtained from the master curve for linear channels [solid line in Fig. 6(b)] for different combinations of W/P and W/t values for an eigenstrain of 1.4%. For each combination of W , P , and t we calculate $L_e = (P - W)/2$ and use t and ϵ^* to obtain λ from the master curve. The red region corresponds to $\lambda > W$ (corner/diagonal buckles) while the gray region corresponds to $\lambda < W$ (edge buckles). Also plotted on Fig. 7(a) are the data points of various W, P, t values used in the simulations. When the simulations show edge buckles, an open symbol is used, and when corner buckles are observed, closed symbols are used. Clearly, the theoretical prediction based on the master curve nicely agrees with the simulations. It is interesting to observe that for $W = 1.5 \mu\text{m}$, $P = 4 \mu\text{m}$, and $t = 20 \text{ nm}$ the data point (open circle at $W/P = 0.375$ and $W/t = 75$) lies just on the boundary of the transition region. This data point corresponds to the simulation results shown in Fig. 5 in which the film with sharp etch-pit shows edge buckles as well as corner buckles. For rounded etch-pits the edge buckles are absent, pushing this case fully in the corner-buckle regime and conforming the theoretical prediction. It should be noted that the edge-to-corner transition is based on the results for linear channels. As a result, for small values of W/P ($W/P < 0.3$) the transition to edge buckles does not occur, as confirmed by the simulations. Instead, the system shows a pronounced secondary buckling propagating from the edges to the center of the film while the overall buckle pattern still remains in a corner-buckle configuration. This regime is identified in Fig. 7(a) as a separate region in blue. We have also added two data points for large thickness (triangles). The filled triangle corresponds to $W/P = 0.5$, $W/t = 40$ with a film thickness of 50 nm [i.e., t_{50} in Fig. 7(a)], and the open triangle corresponds to $W/P = 0.6$, $W/t = 40$ with a film thickness of 75 nm (t_{75}), clearly demonstrating the corner-to-edge transition at large values of W/P and small values of W/t , as well. Figure 7(b) shows the lines of edge-to-corner buckle transition for different values of eigenstrain. For a given W/P and W/t combination, an increase in eigenstrain increases the edge-buckle region

relative to the corner-buckle region, which is due to the fact that the wavelength decreases with increasing eigenstrain.

C. Evolution of channels in multi-etch-pit systems

In this section, the process of channel formation in a 3×3 etch-pit array [see Fig. 1(a)] will be studied. In particular, we carry out simulations for different combinations of W , P for thicknesses t of 10 and 20 nm. In the previous section, we analyzed only one unit cell with fully constrained boundary conditions all around. In this section, we will relax these conditions and analyze the linking of individual unit cells when the etch fronts of individual unit cells meet. Here, the interaction between the film and the substrate is essential, as we will show in the following. Figure 8 shows the evolution of wrinkles in a 3×3 pit array with $P = 5 \mu\text{m}$ and different etch-pit sizes and film thicknesses $W = 4 \mu\text{m}$, $t = 20 \text{ nm}$ (left column), $W = 2 \mu\text{m}$, $t = 20 \text{ nm}$ (middle column), and $W = 2 \mu\text{m}$, $t = 10 \text{ nm}$ (right column). The fillet radius in all cases is $R = 800 \text{ nm}$. As explained in Sec. II, initially the film is fully constrained and an eigenstrain of 1.4% is applied, introducing a compressive equibiaxial stress state in the film plane. Then, the evolutionary process is started from the etch-pits as in Sec. III B. At a junction of four etch-pits in the upper-right corner of each figure, the current etch-front position is depicted by means of a black region, indicating that in this region the sacrificial layer is still intact and thus the film is still fully constrained. The figures in the last row correspond to complete removal of the sacrificial layer. Figure 8(a) shows the contour plots of the out-of-plane position z of the film normalized with $H^* = 150 \text{ nm}$ in the presence of interaction before the etch fronts meet. It can be observed that the evolution of buckles around individual etch-pits is similar to the single-hole simulations shown in the previous section as there is no interaction between the buckles of the neighboring etch-pits due to the constrained region in between. Figure 8(d) shows the buckle morphology after the merger of the etch fronts of neighboring unit cells. Note that the film is not completely released as some portion of the sacrificial layer is still intact (see the etch-front position in the inset). During the moment the final strip of sacrificial layer is removed between neighboring unit cells, multiple buckles collapse into one buckle connecting the neighboring etch-pits. This is due to the sudden removal of the boundary constraint that is responsible for the typical linear channel morphology (see also Annabattula *et al.*²³). Figure 8(g) shows the configuration at the end of the release process when all the film nodes are free, except the outer film boundary. It can be clearly seen that the system shows a well-defined channel formation. We proceed by analyzing a situation in which the etch-pit width is considerably reduced ($W = 2 \mu\text{m}$), but for the same periodicity ($P = 5 \mu\text{m}$) and fillet radius ($R = 800 \text{ nm}$), as shown in Fig. 8(a). We analyze two values for the film thickness: $t = 20 \text{ nm}$ and a smaller thickness $t = 10 \text{ nm}$. Three instances during the etching process are depicted in Fig. 8 for $t = 20 \text{ nm}$ (middle column) and $t = 10 \text{ nm}$ (right column). The inset at the upper-right junction again shows the current (still intact) state of the sacrificial layer. In Figs. 8(b) and 8(c) it can be observed that the wavelength is smaller for the smaller thickness, conforming the scaling of the linear

FIG. 8. (Color online) Contour plots of the normalized out-of-plane position ($\bar{z} = z/H^*$) for films of dimensions (a), (d), (g) $W = 4 \mu\text{m}$, $P = 5 \mu\text{m}$, and $t = 20 \text{ nm}$; (b), (e), (h) $W = 2 \mu\text{m}$, $P = 5 \mu\text{m}$, and $t = 20 \text{ nm}$; (c), (f), (i) $W = 2 \mu\text{m}$, $P = 5 \mu\text{m}$, and $t = 10 \text{ nm}$. The fillet radius of the etch-pit $R = 800 \text{ nm}$ for all the cases. The value of H^* is equal to (a) 150 nm , (d), (g) 300 nm , and (b), (c), (e), (f), (h), (i) 340 nm . The dark region in the inset at the junction of four etch-pits at the upper-right corner shows the sacrificial layer still being intact.

channels, as shown by the master curve in Fig. 6(b). The $t = 10 \text{ nm}$ film has bonded to the substrate in the region where the sacrificial layer has been etched away [see Fig. 8(c)]. However, for the $t = 20 \text{ nm}$ film, around three etch-pits the released regions have buckled up [Fig. 8(b)], while in other regions the film has collapsed to the substrate, similar to the

smaller-thickness film. These observations are in accordance with the results shown in Fig. 4(b), where the thinner films are much more susceptible for bonding to the substrate due to the lower bending stiffness of the film. When the etching fronts meet [see Figs. 8(e) and 8(f)], the number of waves drastically reduces when the released wrinkles collapse. It can

be observed that there is a strong direct interaction between the etch-pits in the vertical and horizontal directions for $t = 20$ nm, but that for the $t = 10$ nm film diagonal (“corner”) interactions are also present. These interactions are still present in the final channel morphology (bottom row), showing that straight channels are formed, connecting the etch-pits along the shortest distance for thicker films, while for thinner films, a strong tendency can be observed for diagonal channels to form.

We have also carried out the above simulations in the absence of interface interaction. In that case, the film lifts off completely and buckles conform the mode-I buckling configuration, forming a dome; see, e.g., Annabattula and Onck.²⁴ This phenomenon is central to the formation of channels in these perforated film systems, exemplifying the necessity of having a rather pronounced film-substrate attraction for channel formation to develop.

Next, we proceed with stage (iii) of the channel formation process, the bond-back stage. During bond-back we use $\delta_n = 20$ nm and $\sigma_{\max}$ is gradually increased, leading to $\Gamma = 0.1$ J/m² at the end of the bond-back process [see Eq. (4)]. During this stage the width and height of the buckles decrease until the final channel morphology changes from that shown in Figs. 8(g), 8(h), and 8(i) to that depicted in Figs. 9(a), 9(b), and 9(c), respectively. This process is fully identical to the drape-back process studied in detail in Annabattula *et al.*^{22,23} and Annabattula and Onck.²⁴ Also plotted in the bottom row of Fig. 9 are scanning electron microscope images of the final morphologies for the experimental systems for exactly the same parameters,¹³ showing a very good agreement. For the case of $W = 4$ μ m well-defined edge channels form, confirming the experimental findings [Figs. 9(a) and 9(d)]. Clearly, for $W = 2$ μ m and

$t = 20$ nm, the shortest pit-to-pit connections are established, although also diagonal interactions are observed to be present [see Fig. 9(e)]. For $W = 2$ μ m and $t = 10$ nm both the simulations [Fig. 9(c)] as well as experiments [Fig. 9(f)] indicate a trend toward diagonal channel formation in contrast to the thick and more stable films, in which straight vertically and horizontally connected channels form along the shortest pit-to-pit distance. This tendency toward diagonal channels has been observed in Malachias *et al.*¹³ to culminate in a highly ordered diagonal network for almost circular etch-pits of size $W = 1$ μ m and periodicity $P = 4$ μ m for a thickness $t = 10$ nm. Such a high level of order has not been observed to develop using the 3×3 etch-pit array as used here. Malachias *et al.*¹³ have shown that such a regular order can be obtained numerically by enforcing symmetry restrictions as observed in the final pattern morphologies. Possibly, the small size of the system studied here does not properly account for the experimental conditions so that boundary effects due to the constrained outer boundary are still prominent.

The simulations presented in this paper provide only a preliminary step toward a thorough understanding of the mechanism of channel formation in these complex systems. The present model is based on a number of assumptions, including isotropic film elasticity, nonlinear film-substrate interaction, uniform etching rate, limited system size, and specific fillet radius dimensions. The present model does give insight into the edge-to-diagonal-channel transition and provides evidence that a nonzero interface interaction during the etching process is essential for channel formation. The model can be straightforwardly extended to study the self-organization of nanochannel networks in various other etch-pit geometries (hexagonal, pentagonal, circular) as well.

FIG. 9. (Color online) Comparison of the simulation results of the nanochannel networks at the end of bond-back ($\Gamma = 0.1$ J/m²) for (a) $W = 4$ μ m, $P = 5$ μ m, $t = 20$ nm; (b) $W = 2$ μ m, $P = 5$ μ m, $t = 20$ nm; and (c) $W = 2$ μ m, $P = 5$ μ m, $t = 10$ nm with the scanning electron microscope images of corresponding experimental results (d), (e), and (f), respectively. (a), (b) and (c) correspond to the systems with a fillet radius of 800 nm resembling almost circular holes as in the experiments for the case of $W = 2$ μ m and $P = 5$ μ m [(b) and (c)].

IV. CONCLUSIONS

A finite-element model describing the mechanism of nanochannel formation in semiconductor films by an evolutionary etching process has been presented. The critical buckling strain of an isolated single etch-pit is found to be an intermediate solution of two limiting cases, i.e., a linear channel and a clamped square film. The evolution of wrinkles around a single etch-pit has been studied for different etch-pit sizes W , periodicities P , and thicknesses t . The results show that, for small etch widths L_e compared with the etch-pit size W , the wavelength is much smaller than the etch-pit size, so that the channel formation process fully resembles the formation of linear nanochannels. When the wavelength becomes of the order of the etch-pit size, a transition occurs from linear edge channels to diagonal corner channels. By using a dimensionless master curve for linear channels, regions of P/W and W/t values have been identified in which either one of these mechanisms dominates. This mechanism map can provide guidelines for the design of specific nanochannel network morphologies.

In multi-etch-pit simulations, the wrinkle evolution around each etch-pit is similar to isolated etch-pit simulations until

the wrinkles from neighboring etch-pits merge. Due to the relaxation of the constraints imposed by the sacrificial layer, multiple wrinkles coalesce and form one dominant channel connecting neighboring etch-pits. Whether a regular square network forms or diagonal connections are established depends on the thickness of the film and the film-substrate interaction, in addition to the initial tendency to form edge or corner channels as governed by the relative spacing P/W and etch-pit size W/t . A minimal amount of film-substrate bonding is required for channel formation, since in the absence of interaction the film buckles up like a dome (first buckling mode) without any channel network formation. For the cases analyzed we found good agreement with the experiments, giving insight into the physical mechanisms that govern the complex interplay during evolutionary etching.

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*P.R.Onck@rug.nl

¹E. Cerda and L. Mahadevan, *Phys. Rev. Lett.* **90**, 074302 (2003).

²A. J. Crosby, M. Hageman, and A. Duncan, *Langmuir* **21**, 11738 (2005).

³C. D. W. Wilkinson, A. S. G. Curtis, and J. Crossan, *J. Vac. Sci. Technol. B* **16**, 3132 (1998).

⁴C. Harrison, C. M. Stafford, W. Zhang, and A. Karim, *Appl. Phys. Lett.* **85**, 4016 (2004).

⁵C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. VanLandingham, H. C. Kim, W. Volksen, R. D. Miller, and E. E. Simonyi, *Nat. Mater.* **3**, 545 (2004).

⁶K. Efimenko, J. Finlay, M. E. Callow, J. A. Callow, and J. Genzer, *ACS Appl. Mater. Interfaces* **1**, 1031 (2009).

⁷H. Jiang, D. Y. Khang, J. Song, Y. Sun, Y. Huang, and J. A. Rogers, *Proc. Natl. Acad. Sci.* **104**, 15607 (2007).

⁸T. Thorsen, S. J. Maerkl, and S. R. Quake, *Science* **298**, 580 (2002).

⁹S. Okazaki, *J. Vac. Sci. Technol. B* **9**, 2829 (1991).

¹⁰N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, and G. M. Whitesides, *Nature* **393**, 146 (1998).

¹¹S. Edmondson, K. Frieda, J. E. Comrie, P. R. Onck, and W. T. S. Huck, *Adv. Mater.* **18**, 724 (2006).

¹²Y. Mei, D. J. Thurmer, F. Cavallo, S. Kiravittaya, and O. G. Schmidt, *Adv. Mater.* **19**, 2124 (2007).

¹³A. Malachias, Y. Mei, R. K. Annabattula, C. Deneke, P. R. Onck, and O. G. Schmidt, *ACS Nano* **2**, 1715 (2008).

¹⁴T. R. Hendricks, W. Wang, and I. Lee, *Soft Matter* **6**, 3701 (2010).

¹⁵M.-W. Moon, K.-R. Lee, K. H. Oh, and J. W. Hutchinson, *Acta Mater.* **52**, 3151 (2004).

¹⁶J. Song, H. Jiang, W. M. Choi, D. Y. Khang, Y. Huang, and J. A. Rogers, *J. Appl. Phys.* **103**, 014303 (2008).

¹⁷H. Jiang, Y. Sun, J. A. Rogers, and Y. Huang, *Appl. Phys. Lett.* **90**, 133119 (2007).

¹⁸J. Yin, Z. Cao, C. Li, I. Sheinman, and Xi. Chen, *Proc. Natl. Acad. Sci.* **105**, 19132 (2008).

¹⁹J. W. Hutchinson, M. D. Thouless, and E. G. Linger, *Acta Metal. Mater.* **40**, 295 (1992).

²⁰M. Ortiz and G. Gioia, *J. Mech. Phys. Solids* **42**, 531 (1994).

²¹B. Audoly, *J. Mech. Phys. Solids* **48**, 2315 (2000).

²²R. K. Annabattula, W. T. S. Huck, and P. R. Onck, *J. Mech. Phys. Solids* **58**, 447 (2010).

²³R. K. Annabattula, J. M. Veenstra, Y. Mei, O. G. Schmidt, and P. R. Onck, *Phys. Rev. B* **81**, 224114 (2010).

²⁴R. K. Annabattula and P. R. Onck, *J. Appl. Phys.* **109**, 033517 (2011).

²⁵F. Bloom and D. Coffin, *Handbook of Thin Plate Buckling and Postbuckling* (Chapman & Hall/CRC, Boca Raton, FL, 2001).

²⁶X. P. Xu and A. Needleman, *Model. Simul. Mater. Sci. Eng.* **1**, 111 (1993).

²⁷ABAQUS, *Analysis User's Manual*, Version 6.7, Dassault systems (Simulia, Providence, RI, 2007).

²⁸The damping matrix (relating forces to velocities) is taken to be proportional to the mass matrix and the eigenfrequency of the system.²⁷

²⁹L. S. Cheo and E. L. Reiss, *SIAM J. Appl. Math.* **26**, 490 (1974).