Buckling-driven self-formation of microchannels
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In this chapter 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 neighbouring 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 to experimental results. The good agreement provides insight to the physical mechanisms that govern the complex interplay during evolutionary etching and channel formation.

6.1 Introduction

Buckling and wrinkling of materials is ubiquitous in every day life from human skin to dried vegetables and fruits [Cerda and Mahadevan, 2003]. Despite the complexity of such patterns in natural systems, many technological applications of wrinkled surfaces in micro- and nanosystems have been realized in recent years. Such applications include smart adhesives [Crosby et al., 2005], cellular engineering [Wilkinson et al., 1998], optical gratings [Harrison et al., 2004], measurement of elastic moduli of thin films [Stafford et al., 2004], marine anti-fouling [Efimenko et al., 2009], fabrication of bendable electronics [Jiang et al., 2007a] and microfluidic large scale integration [Thorsen et al., 2002]. Owing to the numerous technological applications of patterned surfaces, the development of non-conventional methods of fabrication that circumvent the limitations of conventional lithography [Okazaki, 1991] has become an important field of research. Bowden et al. [1998] demonstrated a promising methodology based on the controlled buckling of pre-stressed thin films on compliant substrates. Since then, buckling has been often employed to induce regular patterns on pla-
nar surfaces, either by buckling of stiff films on compliant substrates or by buckle-driven delamination of films on stiff substrates. Recently, a new approach of controlled buckling has been reported, based on the partial release and bond-back of pre-stressed thin films on rigid substrates [Edmondson et al., 2006; Malachias et al., 2008; Mei et al., 2007]. 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 pre-stressed multi-layer architectures in NEMS and MEMS [Hendricks et al., 2010]. While theoretical studies of wrinkle/buckle formation of pre-stressed films on rigid and compliant substrates has been reported by many researchers [Audoly, 2000; Cerda and Mahadevan, 2003; Hutchinson et al., 1992; Jiang et al., 2007a,b; Moon et al., 2004; Ortiz and Gioia, 1994; Song et al., 2008; Yin et al., 2008], the understanding of buckle patterns based on the “release-and-bond-back” mechanism is only starting to emerge [Annabattula et al., 2010a; Annabattula and Onck, 2011; Annabattula et al., 2010b; Edmondson et al., 2006; Malachias et al., 2008; Mei et al., 2007].

Recently, a new class of nanochannel networks was reported [Malachias et al., 2008] in which InGaAs films were grown on a GaAs substrate separated by an AlAs sacrificial layer. Using lithographic techniques, periodically-spaced holes were introduced in 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 non-uniform 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 [Annabattula et al., 2010b; Mei et al., 2007, Ch. 4]. First, the two-dimensional patterning introduces spatially non-uniform 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 [Annabattula et al., 2010b; Mei et al., 2007]. 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 chapter 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 chapter is as follows. In Sec. 6.2, we describe the finite element model to study the nanochannel network formation based on the InGaAs film system. We re-
6.2. Model and simulation procedure

Figure 6.1: Schematic showing the process of evolutionary etching. (a) Initial configuration of a $3 \times 3$ array of etch pits. (b) Zoomed view of a unit-cell (highlighted by the white square in Fig. (a)) of the $3 \times 3$ 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 $L_e$.

fer 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 6.1(a) shows a schematic of the initial configuration of a $3 \times 3$ film array of etch pits with an etch-pit size $W$ and periodicity (spacing) $P$. Figure 6.1(b) shows a zoomed view of a unit-cell (shown as a dashed white square in Fig. 6.1(a)) of the system. Figure 6.1(c) shows the partial removal of the sacrificial layer over a distance $L_e$ allowing the film to release its eigenstrains by forming wrinkles. In this chapter, we explore how the periodicity ($P$), size of etch-pit ($W$) and the film thickness ($t$) influence the channel morphology for both the single (Fig. 6.1(b) and 6.1(c)) and multi-etch-pit (Fig. 6.1(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 $\varepsilon^*$ are induced in the film due to the lattice mis-match between the film and the sacrificial layer. Then, holes of size $W$ with a periodicity $P$ are introduced in 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 \( \varepsilon^* \) by buckling, forming wrinkles as shown in Fig. 6.1(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 non-linear plate theory, the total strain in the film can be written as the sum of three contributions: 

\[
\varepsilon = \varepsilon^{\text{str}} + \varepsilon^{\text{rot}} + \varepsilon^{\text{bend}} \tag{6.1}
\]

with \( u_i \) the in-plane displacements and \( w \) the out-of-plane displacements. For the constitutive behaviour of the film, we assume that the total strain consists of an elastic part \( \varepsilon^{\text{el}} \) and an eigenstrain part \( \varepsilon^{\text{eig}} \): 

\[
\varepsilon^{\text{eig}} = \varepsilon^* \delta_{ij}, \quad i = 1, 2, \quad j = 1, 2, \tag{6.2}
\]

with \( \delta_{ij} \) 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 \( \sigma \) in the film are given by

\[
\sigma_{ij} = \frac{E}{1 + \nu} \left( \varepsilon_{ij}^{\text{el}} + \frac{\nu}{1 - \nu} \varepsilon_{kk}^{\text{el}} \delta_{ij} \right), \tag{6.3}
\]

where \( i = 1, 2, \quad j = 1, 2, \quad E \) is Young’s modulus and \( \nu \) is Poisson’s ratio of the film. To mimic the complex interplay between the film and substrate during 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 non-linear traction-separation relation given by [Xu and Needleman, 1993]

\[
T_n = \sigma_{\text{max}} \frac{w_n}{\delta_n} \exp \left( 1 - \frac{w_n}{\delta_n} \right), \tag{6.4}
\]

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

We use the finite element method [Zienkiewicz and Taylor, 2000] to solve the boundary value problem described above and study the mechanism of wrinkle evolution during etching. The film is modelled using four-noded shell elements (S4) and the substrate is modelled as a rigid surface [ABAQUS, 2007]. To mimic stage (i) of the experimental process (see Fig. 6.1), we initially constrain the film during which the eigenstrains are applied. A compressive bi-
axial stress state develops in the film. Next, a set of nodes within a distance of $L_e$ from the etch-pit periphery are 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 modelled through the normal traction-separation relation law given by Eq. 6.4. The same traction-separation law is used to prescribe the non-uniform 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 together with rough-friction. 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 a mass-proportional damping *. A similar procedure as described above is also used in chapters 4 and 5 [see also Annabattula and Onck, 2011; Annabattula et al., 2010b].

6.3 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 section 6.3.1 and 6.3.2 we study the wrinkle evolution around a single etch-pit for different combinations of $W$, $P$ and $t$ (see Figs. 6.1(b) and 6.1(c)). In section 6.3.1 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 boundary value problem with two limiting cases studied before [Annabattula and Onck, 2011; Annabattula et al., 2010b]. In section 6.3.2 we study the wrinkle evolution around a single etch-pit for different combinations of $W$, $P$ and $t$ (see Fig. 6.1(b) and 6.1(c)). In section 6.3.3 we study the evolution of wrinkles in a $3 \times 3$ pit array 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 set-up.

6.3.1 Buckling analysis

In this section, a buckling analysis of a single etch-pit (see Fig. 6.1(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 plate [Annabattula and Onck, 2011] and a linear channel [Annabattula et al., 2010b]. When the size of the pit $W$ is very small compared to the size of the film $P$ the boundary value problem approaches that of the clamped square plate, while

*The damping matrix (relating forces to velocities) is taken to be proportional to the mass matrix and the eigen frequency of the system ABAQUS [2007].
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 6.2(a) shows (symbols) the buckling strain ($\varepsilon_{cr}$) 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 by Annabattula and Onck [2011]

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

Figure 6.2(a) clearly shows that the buckling strain converges to Eq. 6.5 (see dashed line) when the pit size $W$ reduces to zero. The solid line in Fig. 6.2(a) shows the buckling strain of a linear channel given by Annabattula et al. [2010b]

$$\varepsilon_{cr}^l = \frac{1.28\pi^2}{12(1 - \nu^2)} \left( \frac{t}{L_e} \right)^2$$  

with $L_e = (P - W)/2$. Indeed, for large values of $W$ relative to $P$, the results converge to Eq. 6.6.

The results of Fig. 6.2(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. 6.2(b)). Figure 6.2(b) shows the effect of fillet radius $R$ on the critical buckling strain $\varepsilon_{cr}^R$ of a film with $W = 2.5 \, \mu m$, $P = 4 \, \mu m$ and $t = 20 \, nm$. The results are normalized with the buckling strain of the film with zero fillet radius ($\varepsilon_{cr}^0$) 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. 6.2(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 Annabattula and Onck [2011]).

6.3.2 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. 6.1(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. Figure 6.3 shows the evolution of wrinkles in a square film with an etch-pit size $W = 3 \, \mu m$, a periodicity $P = 4 \, \mu m$ and thickness $t = 20 \, nm$ for three values of the etch width: $L_e = 0.3 \, \mu m$ (left column), $L_e = 0.45 \, \mu m$ (Figs. 6.3(b), (e)) or $0.4 \, \mu m$ (Fig. 6.3(h)) (middle column) and $L_e = 0.707 \, \mu m$ (right column). Figures 6.3(a)-(c) show the 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 $H^* = 120 \, nm$. The position $z = 0$ corresponds to the substrate and $z = 80 \, nm$ to the initial position of the fully constrained film. The maximum etch width in this case is $\sqrt{2}(P - W)/2 = 0.707 \, \mu m$ (distance from the etch-pit corner to film edge corner) which is considerably smaller than the size of the etch-pit (3 $\mu m$) and hence the evolution of wrinkle wavelength resembles the evolution in the case of linear channels studied in Ch. 4. 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, see Figs. 6.3(d)-(f). For this we use an interfacial energy of 0.01 J/m$^2$ (corresponding to $\delta_0 = 10 \, nm$ and $\sigma_{max} = 0.37$ MPa). In Fig. 6.4(a) we plot the $z$-profile along the etch-pit boundary at the end of complete relaxation (i.e. $L_e = 0.707 \, \mu m$) with (solid) and without (dotted) interface interaction, corresponding to Figs. 6.3(f) and (c), respectively. 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. 6.4(b) we analyze the effect of the film thickness in the presence of interface interaction. For the thinner film ($t = 10 \, nm$) it can be clearly seen that the entire film bonds to the substrate due to the lower bending stiffness. It can also be seen that the wavelength of the wrinkles of the thinner film is much smaller than for the thicker film, due to the quadratic dependence of wavelength on film thickness, see Ch. 4 [Annabattula et al., 2010b].

In Fig. 6.5(a)-(c) we show the evolution of the wrinkle profile for a unit-cell of a pit
Figure 6.3: 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 $t = 20 \, \text{nm}$ without interaction (first row) and with interaction (second row) between the film and the substrate. The third row corresponds to the case of rounded corners of the etch-pit with a fillet radius $R$ of 600 nm and no interface interaction. The contours show the normalized out-of-plane position ($\bar{z} = z/H^*$) of the film with $H^* = 120 \, \text{nm}$ and $z_{\text{min}} = 0.0$. The corresponding etch-widths ($L_e$) are 300 nm (a, d, g), 450 nm (b, e), 400 nm(h), and 707 nm (c, f, i), respectively.
Figure 6.4: (a) Out-of-plane position $z$ of the film ($P = 4 \mu m$) plotted along the periphery of the etch-pit ($W = 3 \mu m$) for a film thickness of 20 nm with and without interaction (conform Fig. 6.3). (b) Out-of-plane position $z$ of the film ($P = 4 \mu m$) plotted along the periphery of the etch-pit ($W = 3 \mu m$) with interaction for different film thicknesses. Both cases correspond to $R = 0$.
Figure 6.5: 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 \( t = 20 \) 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 \( H^* = 220 \) nm (See Fig. 6.3 for legend).

\( W = 1.5 \) \( \mu \text{m} \) 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 buckling [Cheo and Reiss, 1974] effect at the film boundary as also observed in linear channels (see the buckles in the encircled region in Fig. 6.5(f)). Note the drop in the wavelength for the film \( W, P = 1.5, 4 \) \( \mu \text{m} \) with sharp corners in Fig. 6.6(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. 6.5(b) and (c)). Next, we study the wavelength variation with increase in \( L_e \) for all the film geometries studied in this work in Fig. 6.6(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 to 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 in Ch. 4 (also see Fig. 4.7(a)). Figure 6.6(b) shows the normalized wavelength \( \lambda/L_e \) plotted as a function of the non-dimensional 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
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Figure 6.6: (a) Effect of fillet radius \( R \) on the wavelength (\( \lambda \)) of the wrinkles plotted as a function of the etch width during 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 \( \lambda/L_c \) with the master curve for linear channels (Fig. 4.7(a)) for different \( W \) and \( P \) combinations. The numbers in the legend correspond to \( W/P \) for each case (in \( \mu \text{m} \)) shown in symbols and the subscript of \( t \) corresponds to the thickness of the film in nm.

- Different \( L_c \) showing good agreement with the linear channel prediction in the small \( L_c \) range and deviating from the curve with increase in etch width \( L_c \). Another influencing parameter on the wrinkle morphology is the ratio of \( \lambda/W \). For a small \( \lambda/W \) value the system approaches a linear channel solution, but for higher ratios the system goes through a gradual transition from edge wrinkles (\( \lambda/W < 1 \), see Fig. 6.3) to corner wrinkles (\( \lambda/W = 1 \), see Fig. 6.5). Hence, the identification of that combination of parameters \( W, P \) and \( t \) for which the system goes through an edge-to-corner buckle transition would be of interest for the design of channel morphologies. Figure 6.7(a) shows the region of data points obtained from the master curve for linear channels (solid line in Fig. 6.6(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 \( L_c = (P - W)/2 \) and use \( t \) and \( \varepsilon^* \) to obtain \( \lambda \) from the master curve. The red region corresponds to \( \lambda > W \) (corner/diagonal buckles) while the grey region corresponds to \( \lambda < W \) (edge buckles). Also plotted on Fig. 6.7(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. 6.5 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, conform 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 (for large $W/t$ values) as confirmed by the simulations. Instead, the system shows a pronounced secondary buckling propagating from the edges to the centre of the film while the overall buckling pattern still remains in a corner buckle configuration. This regime is identified in Fig. 6.6(b) 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. 6.6(b)) 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 6.7(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.
6.3.3 Evolution of channels in multi-etch-pit systems

In this section, the process of channel formation in a $3 \times 3$ etch-pit array (see Fig. 6.1(a)) will be studied. In particular, we carry out simulations for different combinations of $W$, $P$ for a thickness $t$ of 10 nm 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 6.8 shows the effect of interface interaction on the evolution of buckles in a $3 \times 3$ pit array with an etch-pit size $W = 4 \, \mu m$, periodicity $P = 5 \, \mu m$, fillet radius $R = 800 \, nm$ and a thickness of $t = 20 \, nm$. As explained in section 6.2, 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 section 6.3.2. The figures in the right column of Fig. 6.8 show the current etch-front position at a junction encircled in Fig. 6.8(b). The central black region depicts the sacrificial layer indicating that in this region the film is still fully constrained, while in the region between the initial etch-pit and black region the film has been released. Figure 6.8(b) shows the contour plots of the out-of-plane position $z$ of the film normalized with $H^* = 150 \, nm$ in the presence of interaction before the etch fronts meet. Figure 6.8(a) shows a zoomed view of the encircled region of Fig. 6.8(b). It can be observed that the evolution of buckles around individual etch-pits are similar to the single hole simulations shown in the previous section as there is no interaction between the buckles of the neighbouring etch-pits due to the constrained region between them. Furthermore, as the amplitude of the wrinkles at this stage of etching is limited, the buckle profile for the same case without interface interaction looks rather similar (not shown), see also Fig. 6.3 and 6.4(a). Figures 6.8(c) (without interface interaction) and 6.8(d) (with interaction) show the buckle morphology after the merger of the etch-fronts of neighbouring 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 right column). During the moment the final strip of sacrificial layer is removed between neighbouring unit-cells, multiple buckles collapse into one buckle connecting the neighbouring 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. [2010b]). Figure. 6.8(e) (without interaction) and 6.8(f) (with interaction) show 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 film without interface interaction lifts off completely from the substrate like a dome (conform the mode-I buckling configuration, see e.g. Annabattula and Onck [2011]). In contrast, the system with interface interaction results in a well-defined channel formation (see Fig. 6.8(f)). This phenomenon is central to the formation of channels in these perforated film systems. The above results also exemplify 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 $\sigma_{\text{max}}$ is gradually increased leading to $\Gamma = 0.1 \, J/m^2$ at the end of the bond-back process (see Eq. 6.4). During this stage the width and height of the buckles decrease until the final channel morphology changes from that shown in Fig. 6.8(f) to that depicted in Fig. 6.10(a). This
Figure 6.8: Contour plots of the normalized out-of-plane position ($\bar{z} = z/H^*$) for a film without (c, e) and with (a, b, d, f) interface interaction for $W = 4 \mu m$, $P = 5 \mu m$, thickness $t = 20 \text{ nm}$ and a fillet radius $R$ of 800 nm. The value of $H^*$ is equal to (a, b) 150 nm, (c, e) 400 nm and (d, f) 300 nm. The figures in the third column indicate the current position of the etch front zoomed at a junction of the four etch-pits as shown in Fig. (b). Figure (a) shows a zoomed view of the profile at the circled region in Fig. (b).
6.3. Results and discussion

The process is fully identical to the drape back process studied in detail in chapters 3, 4 and 5. Also plotted in Fig. 6.10(d) is a SEM image of the final morphology for the experimental system for exactly the same parameters [Malachias et al., 2008], showing a very good agreement.

We proceed by analyzing a situation in which the etch-pit width is considerably reduced ($W = 2 \mu m$), but for the same periodicity ($P = 5 \mu m$) and fillet radius ($R = 800 nm$) as shown in Fig. 6.8 and 6.10(a). We analyze two values for the film thickness: $t = 20 nm$ (conform Fig. 6.8) and a smaller thickness $t = 10 nm$. Three instances during the etching process are depicted in Fig. 6.9 for $t = 10 nm$ (left column) and $t = 20 nm$ (middle column). The right column again shows the current (still intact) state of the sacrificial layer. In the first row it can be observed that the wavelength is smaller for the smaller thickness, conform the scaling of the linear channels as shown by the master curve in Fig. 6.6(b). The $t = 10 nm$ film has bonded to the substrate in the region the sacrificial layer has been etched away (see Fig. 6.9(a)). However, for the $t = 20 nm$ film, around three etch-pits the released regions have buckled up (Fig. 6.9(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. 6.4(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 (second row of Fig. 6.9), 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 also diagonal (‘corner’) interactions are present. These interactions are still present in 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. Finally, we increase the interface energy to $\Gamma = 0.1 J/m^2$ and allow the film to further bond back on to the substrate. We compare the final bond-back configurations with the experimentally-obtained configurations for the same system parameters in Fig. 6.10. Clearly, both the simulations (Figs. 6.10(b) and 6.10(c)) as well as experiments (Figs. 6.10(e) and 6.10(f)) indicate a trend towards diagonal channel formation for the thin films, while for the thick and more stable films straight vertically and horizontally connected channels form along the shortest pit-to-pit distance.

This tendency towards diagonal channels has been observed in Malachias et al. [2008] to culminate into a highly ordered diagonal network for almost circular etch-pits of size $W = 1 \mu m$ and periodicity $P = 4 \mu m$ for a thickness $t = 10 nm$. Such a high level of order has not been observed to develop using the $3 \times 3$ etch-pit array as used here. Malachias et al. [2008] 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 chapter only provide a preliminary step towards 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, non-linear film/substrate interaction, uniform etching rate, limited system size, fillet radius, and specific dimensions. The present model does give insight into the edge to diagonal channel transition and provides evidence that a non-zero interface interaction during the etching
Figure 6.9: Contour plots of the normalized out-of-plane position \((\bar{z} = z/H^*)\) with \(H^* = 340\) nm for a 3 × 3 array with etch-pit size \(W = 2 \mu m\), periodicity \(P = 5 \mu m\), fillet radius \(R = 800\) nm with a thickness \(t = 10\) nm (first column) and 20 nm (second column). The figures in the third column indicate the current position of the etch front zoomed at a junction of the four etch-pits as shown in Fig. (b) (see Fig. 6.8 for the legend).
Figure 6.10: Comparison of the simulation results of the nanochannel networks at the end of bond-back ($\Gamma = 0.1$ J/m$^2$) for (a) $W = 4$ $\mu$m, $P = 5$ $\mu$m, $t = 20$ nm, (b) $W = 2$ $\mu$m, $P = 5$ $\mu$m, $t = 20$ nm and (c) $W = 2$ $\mu$m, $P = 5$ $\mu$m, $t = 10$ nm with the SEM images (reproduced with permission from Malachias et al. [2008]) of the corresponding experimental results (d), (e) and (f), respectively. Figures (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 $W = 2$ $\mu$m and $P = 5$ $\mu$m (b and c).

process is essential for channel formation. The model can be straight-forwardly extended to study the self-organization of nanochannel networks in various other etch-pit geometries (hexagonal, pentagonal, circular) as well.

6.4 Summary and 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 to 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 on 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 dominate. 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 neighbouring etch pits merge. Due to the relaxation of the constraints imposed by the sacrificial layer, multiple wrinkles coalesce and form one dominant channel connecting neighbouring etch pits. Whether a regular square network forms or diagonal connections will be 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 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.