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Commentary by U. Thiele: "Tentative interpretation of the dewetting morphologies presented by Tsui et al. in the preceding paper"

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References [1] and [2] report on dewetting experiments for polystyrene (PS) films on silicon substrates covered with a 106 nm thick oxide layer [3]. They describe *three* different types of rupture process:
(i) For very thin films below about 5 nm the film ruptures through spinodal dewetting characterized by a bicontinuous pattern known from spinodal decomposition.
(ii) For slightly larger thicknesses between 5 nm and about 13 nm individual dimples in the film surface are found in the course of the rupture process The dimples subsequently evolve into a pattern of holes. There is a smooth transition between the typical length scales of the pattern found in (i) and (ii) ([1] Fig. 4b).
(iii) For thicknesses larger than 13 nm patterns of holes form that have, however, typical distances about one order of magnitude larger than the length scale of the pattern found in (ii).

If defects are caused in the initially flat film by rubbing it with a rayon cloth the patterns become visibly anisotropic in all the above cases. However, the typical length scale does not change for (i) and (ii), whereas it becomes smaller for case (iii) until it reaches for a large number of rubbings the scale known from (ii) [1].

We will try to give a tentative interpretation in terms of the theory presented in [4–6] and sketched in the present Focus Point in [7].

The main difference of the systems studied in references [1] and [8] consists in the thickness of the oxide layer covering the silicon substrate (but see [3]). Using the expression for the effective interface potential and the Hamaker constants given in reference [8] one finds that for the oxide layer used in references [1,2] PS films are linearly unstable up to thicknesses of about 140 ± 30 nm. This im-

plies that *all* the morphologies (i) to (iii) are observed in the linearly unstable thickness range.

The transition from (i) and (ii) on the one hand to (iii) on the other hand fits very well with the transition between instability-dominated and nucleation-dominated sub-ranges within the linearly unstable film thickness range (see [4,7]). Regime (iii) agrees with the signature of the nucleation-dominated regime [4] in that it is very sensitive to the number of initial defects, whereas the initial defects have rather no influence on the outcome in the instability-dominated (i) and (ii). The lower bound of the distance of active (i.e. leading to a hole) defects that is approached by a large number of rubbings [1] can be understood as an effect of the increasing importance of interactions between different defects. This is also reflected in the underlying solution structure of the film thickness equation as shown for one-dimensional solutions in ([4] Fig. 2). The solution branches shown there in the middle row (corresponding to the nucleation-dominated regime in the linearly unstable range) have a saddle-node (or fold) that corresponds, roughly speaking, to the minimal possible distance of active defects. Because this distance is smaller than the smallest linearly unstable wavelength we would expect that very intense (isotropic) rubbing (but without taking away material) could shift the curve for (iii) in ([1] Fig. 4b) to be even slightly above the continuation of the curve for (i) and (ii). However, time simulations and the determination of stationary solutions for two-dimensional film thickness profiles using the disjoining pressure given in [8] are necessary to further validate our interpretation.

The transition from (i) to (ii) only affects the morphology of the evolving structure. Its length scale changes smoothly with the film thickness also over the 'morphology border'. A similar change of morphology was found in simulations for dewetting due to effective molecular interactions [9,10] and also for the mathematically similar

system of a thin liquid layer heated from below [11]. There deep inside the spinodal regime, i.e. close to the minimum of the second derivative of the effective interface potential, the surface instability leads to a maze-like (or labyrinthine, or bicontinuous) pattern, whereas for slightly larger thicknesses a hole pattern emerges. This difference can be seen even in the weakly nonlinear stage of the evolution. For even smaller film thicknesses the maze-like pattern should be replaced by an emerging drop pattern [9–11]. In reference [2] the emergence of the hole pattern is thought to be caused by thermal nucleation. However, the only difference between thermal and heterogeneous nucleation is the way how the threshold for film rupture (the critical surface depression) is overcome: by thermal fluctuations or by a mechanical disturbance (like rubbing, dust, substrate heterogeneities). So in our opinion thermal nucleation can be accompanied by nucleation at defects and therefore should be sensitive to rubbing. This is not the case for regime (ii). Our interpretation is also supported by Figure 6a of reference [2]. There it is shown that the initial stage of the growth of the individual holes (before nonlinearities take over) follows closely the (exponential) curve of the increase of the intensity of the most dominant fourier mode of the whole pattern. This implies that both processes are governed by the *same* linear process.

We think that large scale simulations with a variety of initial conditions like different defect densities and also with the inclusion of thermal noise should be performed to further advance our knowledge.

To conclude, a tentative interpretation of the different morphologies found in references [1, 2] can be given building on existing theories. However, our interpretation rests on the basic assumption that the qualitative features of the dewetting process and their dependence on film thickness *do not* depend on the details of the involved effective interface potential as long as the studied systems coincide in the general properties. This allows to draw on a variety of results for different systems with destabilizing short-range part (representing here the silicon oxide layer) and stabilizing long-range part (representing here the silicon substrate) of the potential.

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Reply by O.K.C. Tsui to the Commentary by U. Thiele

Thiele [1] proposed an interpretation to our experimental data [2,3] on the polystyrene (PS) thin films dewetting from Si covered with a 106 nm thick SiO_x. In Thiele's interpretation, dewetting of all our films was due to spinodal rupturing. From the different dewetting behaviors noted, he divided the films into three thickness (h) regions: (i) $h < 5$ nm, (ii) 5 nm $\leq h < 13$ nm, and (iii) 13 nm $< h \leq 30$ nm. In region (i) spinodal rupture takes place through the formation of a bicontinuous morphology as was first found by Cahn by linear simulation of phase separating mixtures [4]; in region (ii) spinodal rupture occurs by the formation of isolated holes as was noted in non-linear 3D simulations [5–7]; in region (iii) "nucleation in spinodal regime" takes place [8,9]. This short note aims to communicate several noteworthy considerations concerning Thiele's proposal to interpret the 5.1 nm PS film studied in reference [3] as a prototype of region (ii).

The major result found from the 5.1 nm PS film [3] was its dewetting process obtained by in situ topographic imaging with atomic force microscopy (AFM). Nucleation of holes was found to occur at random positions and times, with simultaneous appearance of surface fluctuations that demonstrated full characteristics of spinodal rupturing (Fig. 4 of Ref. [3]). By estimating the energy change that can possibly take place in forming those holes through some specific pathways, we found that some pathways may have energy barriers of the order of $k_B T$ [3], thereby are susceptible to the thermal nucleation process. With regard to the alternative suggestion by Thiele to consider the holes to arise from non-linear spinodal rupturing [5–7], we should point out some discrepancies we have noticed between the holes morphology observed in experiment [3] and those reported from simulation results [5–7]. References [5–7] reported that holes originating from non-linear spinodal rupturing, when just have all reached the maximum depth, typically have separations approximately equal to the characteristic spinodal wavelength, λ_m, unless if the sample thickness is near the upper critical thickness, hc_2 (whereas $d^2G/dh^2|_{h=hc2} = 0$) upon which the average holes separation may become much larger than λ_m [9]. Prediction with the former condition for h far removed from hc_2 has found excellent corroboration with experiment [10]. Since the value of hc_2 estimated for the PS thin film system studied in reference [3] is >100 nm [1], one should expect the 5.1 nm PS film to have holes separation $\cong \lambda_m$. But from what was found in reference [3], even upon coarsening in the rupturing morphology (starting at ~3129 s from Fig. 4 of Ref. [3]), the typical distances between full thickness holes were noticeably far greater than λ_m (Fig. 3 of Ref. [3]).

By the time the holes separation attained its mininum (at about 11020 s), sufficient coarsening had already taken place so that its average value was ~0.5 μm, i.e., 25% larger than λ_m. To judge whether such discrepancy between the results of experiment [3] and non-linear simulations [5–7] is acceptable in qualifying the 5.1 nm film as an example of region (ii), one needs to know the tolerance of the simulation studies. Another noteworthy point is that the time typically reported [5] for a dewetting film to achieve the minimum holes separation via non-linear spinodal rupture is between 25 and 130 non-dimensional spinodal times. But the corresponding time found in the experiment [3] was much shorter, only ~5.5 spinodal times (the spinodal time was $\cong$ 2000 s), which seems to us an indication that additional mechanism(s) was (were) at work in causing the holes. Along this line, thermal nucleation is a natural cause that comes to mind. The vastly different evolution paths demonstrated by various holes in Figure 6a of reference [3] – with the depths whereat the holes exhibited onset of the rapid collapse differed by up to a factor of 2.5 – also favors the holes formation process to be random more than ones governed by some deterministic equations of motion. The fact that the holes demonstrated spinodal growth prior to the rapid collapse (Fig. 6a of Ref. [3]) revealed that the holes nucleation was largely assisted by the spinodal process rather than by inhomogeneity or defects in the film or on the substrate interface. This finding helps explain why with the thermal nucleation picture the onset times for the collapse of various holes were quite similar despite of the up to 10 times variations in the estimated energy barriers for different holes (Fig. 7 of Ref. [3]), which should have caused large variations of order $\sim e^{10} = 22\,000$ times in the nucleation time. Along this line, one also expects thermal induced surface fluctuations to have important effects on the non-linear spinodal process by providing the initial condition at some presumed starting time. Simulations that include thermal noise should allow more realistic comparison with experiment.

Finally, we clarify whether the suggestion of thermal nucleation as a possible cause of holes formation is consistent with our earlier finding [2] that the dewetting length scale is insensitive to the density of rubbing induced defects for PS films with thickness $h < 13$ nm. As noted in reference [2], this result merely confirmed dominance of spinodal dewetting over nucleation dewetting. By no means can it preclude the possibility of nucleation dewetting in the $h < 13$ nm films. In fact, previous experimental studies had found coexistence of nucleation and spinodal dewetting [11,12].

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