

to a certain extent the particle-particle attraction. Normally, the solution is deposited on to a plain silicon substrate that is covered by the native oxide layer only [34]. However, one may locally change the wetting behaviour of the solvent by further oxidising the substrate [38]. By adding excess thiol one can also vary the properties of the solvent [40].

Two different procedures are employed for the deposition of the solution on to the substrate: spin-coating or a meniscus technique [61, 62]. The choice is important as it strongly influences the evaporation rate and, as a result, the pattern formation process. When using spin-coating, one finds that directly after deposition, evaporation competes with dewetting until all the solvent has evaporated. The resulting deposits of nanoparticles are imaged by atomic force microscopy (AFM). For spin-coated films, the evaporation rate is high and structuring is normally finished before the spin-coater is stopped. Conversely, the solvent evaporation rate is strongly decreased when employing the meniscus technique [61], i.e., by depositing a drop of solution on a Teflon ring that is wetted by the solvent. This allows for a better control of the process and enables the use of contrast-enhanced microscopy to observe the dewetting process in situ [40]. All pattern formation is confined to the region of the receding contact line of toluene, silicon and air. With both techniques one may find mono-modal or bi-modal polygonal networks [34], labyrinthine spinodal structures, or branched patterns (see Fig. 1). The meniscus technique allows for the study of branched structures in a more controlled manner. The work in Ref. [40] indicates that fingering strongly depends on the interaction strength of the particles, i.e., on the chain length of the thiol molecules coating the gold cores. For short chains (C_5 and C_8) no formation of branched structures is observed. At similar concentrations, well-developed branched structures are formed for longer chains (C_{10} and C_{12}). For even longer chains (C_{14}), however, one again finds less branching. It also depends on the amount of excess thiol in the solvent (for details see Ref. [40]).

When following the evolution of the branched patterns in situ (see the complementary video material of Ref. [40]), one clearly observes that different processes occur on different length scales. First, a macroscopic dewetting front recedes, leaving behind a seemingly dry substrate. The macroscopic front can be transversely unstable resulting in large-scale ($> 100\mu\text{m}$) strongly anisotropic fingered structures. For fronts that move relatively quickly these macroscopic structures cover all the available substrate. However, when at a later stage the macroscopic front becomes slower, those fingers become scarce and ‘macroscopic fingering’ finally ceases. At this stage it is possible to appreciate that the seemingly dry region left behind by the front is not at all dry, but covered by an ultrathin ‘postcursor’ film that is itself unstable. The thickness of this film