Supplementary formation of Structures with Micro- and Nano-Scoptic Periodic Ripple Patterns

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Supplementary Material

S1. More information on experimental details

Once an excellent contact between Ga and the metal track is established and Ga has flowed over a short distance, the sample is placed inside an environmental SEM to observe the subsequent flow of Ga over the narrower region of the metal track. Most of the in situ experiments are performed on samples with 12 µm wide narrow section. The SEM chamber pressure during all the experiments is maintained at 100 Pa, to minimize the evaporation of liquid Ga. The SEM micrographs are taken at different time intervals over a single ripple formation to capture the evolution of shape change from the nucleation to the matured growth of a ripple. The time taken to form a single ripple ranges from 90-150 min depending on the track width (higher width, higher time)*. Higher experimental temperature will result in a shorter time span for ripple formation. In addition, an experiment on one sample captures multiple ripple formations. For avoiding any imaging ambiguity, the stage coordinates are not altered till the end of the experiment. The tilt of the stage has no significant role in the observed

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* The ripple formation time can reduce if external heat is provided.
velocity and ripple formation process. Continuous exposure to the electron beam is avoided as it leads to the formation of skewed ripples for reasons not known.

S2. Role of width

We have observed ripple flow on metallic tracks of various widths ranging from 4 to 35 µm. As shown in Figure S1, the height of the ripple pattern increases with the width of the substrate track. This can be attributed to a decrease in one of the principal radii of the ripple as the width of the metallic track increases, which reduces the overall Laplace pressure, leading to an increase in the structure's size (see Section 4.4 for detailed discussion).

![Figure S1](attachment:figure_s1.png)

Figure S1 Effect of the width of the substrate metal track on the ripple formed (example of Ga on Au): Variation of the height of the ripple pattern (see the inset for the definition of the height) as a function of the width of the metal track. The error bars associated with each ripple height datum point correspond to 4 independent measurements.

S3. Wetting of Ti by Liquid Ga

To further gain insight into the wetting response, the contact angle is measured using the images shown in Figure S2. Here, $\theta_t$ and $\theta_b$ are the angles made by the liquid with the top and the bottom surface (see Figure S2 c) respectively, and their values are measured as $55 \pm 4^0$ and $109 \pm 4^0$, respectively.
respectively. This further confirms that the liquid metal wets the top Pt-rich surface, whereas the bottom surface is a non-wetting one due to the presence of Ti thin film. The non-wetting angle $\theta_b$ made due to the contact with the Ti layer is shown with a highlighted white line in Figure S2d. The EDS-STEM maps reveal that a Ga-Pt intermetallic compound and Ti are at the top and the bottom of the flow, respectively. It is reasonable to assume that liquid Ga (or some liquidus mixture of Pt and Ga) will wet Ga-Pt intermetallic compound, and hence observation of a smaller contact angle is reasonable.

On the other hand, it is not known if liquid Ga will wet Ti. Hence, dedicated experiments are performed to qualitatively understand the wetting behavior of Ga on Ti using a sample design shown in Figure S2e. The experiments are performed by placing a drop of liquid Ga on a pristine Ti surface in an oxygen-free environment (< 0.1 ppm O$_2$ level). After deposition of Ti, the sample is exposed to ambient for only a very short time to minimize the contamination of Ti. Interestingly, unlike liquid Ga on Pt or Au substrates, liquid Ga did not flow outwards on Ti (even at high temperatures), and the Ga bead contracted to form a droplet (see Figure S2f). Based on this observation, it can be inferred that Ga does not wet Ti.
Figure S2: Wetting response of liquid Ga on Ti: (a) SEM micrograph showing the side view of the meniscus in the case of Ga-Au flow (see Supplemental Video 6 revealing the details of the flow at high magnification), (b) a HAADF micrograph of the lamellae extracted from the flow front, (c) the corresponding color map used for measurement of the contact angles (with definitions of $\theta_t$ and $\theta_b$) and (d) a magnified view of the colored map shown in (b). (e) Schematic illustration of the sample design and the test performed for directly estimating the wetting response of liquid Ga and Ti, and (f) an SEM micrograph showing the top view of Ga droplet placed on pristine Ti substrate after a long time (during which Ga would have flown over tens of micrometers on Pt or Au).
S4. **Role of oxidation on the formation in Ripple formation**

The static nature of the stable ripples indicates the formation of a hard shell on the top surface. One of the possibilities for forming such a hard shell is via oxidation of the top surface. An oxide shell forms on the liquid metals, even if its surface is exposed to the minute traces of oxygen in the atmosphere \(^1\)–\(^3\). Experiments are conducted in controlled environments, such as high-vacuum (pressure = \(10^{-6}\) Torr) and oxygen-free glovebox (<0.1 ppm oxygen), to examine the role of oxygen in creating the ripple patterns. It is known that Ga and its alloys are less prone to oxidation if the oxygen concentration level is < 0.5 ppm \(^4\). Interestingly, as shown in Figure S3, liquid Ga flow on Au in both the ambient and the glovebox environments leads to the formation of ripple patterns. This clearly indicates that oxygen does not play a significant role in the formation of ripples. Hence, the top-shell must be of a material that can spontaneously form (i.e., with all elements present during the flow), such as an intermetallic compound. Material characterization carried out on experimental samples of glovebox showed no traces of oxygen.

![Figure S3](image)

*Figure S3: SEM micrographs of the ripple structures of Ga formed on 30 µm wide Au track substrate: The ripple flow took place in (a) ambient and (b) a glovebox with < 0.1 ppm of oxygen.*

S5. **Role of Gravity**

The role of gravity is ruled out by a simple calculation of capillary length (see Section 4.1). In addition, we conduct experiments to confirm further that the role of gravity is indeed
negligible in ripple formation. For this purpose, we observe Ga flow on Pt substrate in two dramatically different conditions (see Figure S4). It can be observed that ripples form even when the Ga bead is hanging upside down, with very minimal difference in their sizes. This observation proves that gravity has a negligible effect on ripple formation and is certainly not the reason behind ripple flow.

Figure S4: Experiments revealing the role of gravity in the formation of ripple pattern, with the example shown using Ga on Pt system: (a) Schematic illustration of the experimental setup with the angle of the sample to vertical as 0° and the corresponding SEM micrograph, and (b) schematic illustration of the experimental setup with the angle of the sample to vertical as 180° and the corresponding SEM micrograph. Irrespective of the tilt of the sample, liquid Ga flowed on the Pt, forming ripple patterns.

S6. Ripple pinching simulation

Although the phenomenon of ripple pinching is wide open for better modeling, we have reported our current understanding based on the measurements reported here. Based on the experimental evidence described above, we also model the pinching part using the features currently available in COMSOL Multiphysics. To understand the effect of evolving wetting between the liquid metal and the substrate, the model shown in Figure 7 of the manuscript is slightly modified in the way shown in Figure S5a. Herein, the wetting contact angle of the
partially-wetting boundary adjacent to the orifice is considered to evolve with time, as the following (arbitrarily selected):

\[ f_1 = 30^\circ \sin \omega t \]  

where \( \omega \) is a constant (= 1 rad/s in the model, arbitrary chosen). Hence, with time, the wetting of liquid to this boundary becomes worse (as the contact angle increases with time), which is similar to the experimental observation. The contact angle between the rightmost boundary \( f_2 \) in Figure S5a) and the liquid is kept constant and wetting in nature. Interestingly, as shown in Figure S5b, the pinching event and the formation of a new ripple next to the penultimate ripple due to the change in the wetting conditions are reproduced in these simulations (see Supplemental Video 5 for the simulation video). Furthermore, these simulations retain the asymmetric shape of the penultimate ripple (consistent with the results shown in Figure 7 of the main manuscript, wherein the asymmetric wetting conditions are kept stationary).

Figure S5: Numerical simulation capturing the pinching event and nucleation of a new ripple: (a) Schematic of the COMSOL model (see Supplemental Material S5 for details) and (b) the volume fraction map after the onset of the flow and occurrence of a pinching event (after time, \( t = 27.5 \) s). The red-brown and blue colors in (b) represent the liquid (1 in color code) and air phases (0 in the color code), respectively, whereas the region in between these two pure phases is the interface region (as the boundary between these two phases is selected to be diffused in the COMSOL phase-field module) (See Supplemental Video 5 for simulation results).
It should be noted that although the values of the wetting angles and their variations are arbitrary, the goal here is to qualitatively understand if the dynamically worsening of the wetting between liquid metal and the substrate path can explain the pinching or nucleation of new ripple: These are reasonably confirmed with the performed qualitative numerical study. As mentioned earlier, comprehensive numerical modeling should also include the dynamic growth of the intermetallic compound layer on the top and the worsening of the wetting behavior of the substrate path. Furthermore, the constraints due to edges of the track and the scenario in which the top solidified structure and the liquid delivery channel co-exist are part of the unsolved puzzle, which can help in effectively modeling the pinching phenomenon. However, the simplified model and simulations presented here clearly show the role of the dissolution of the metallic path, formation of the intermetallic compound layer, and exposure of the liquid to a non-wetting boundary in the formation of the continuous ripple pattern.

S7. COMSOL Simulation Details

![Geometry of the model used for COMSOL simulation. Tiny droplet (highlighted in blue) is designed using Boolean operation. Wetted wall 1 is the non-wetting side of the model. Its value is maintained at 153° in](image-url)
all of our simulations. Pressure point constraint is applied on arbitrary points in the model to avoid convergence issues.

Figure S7: (a) Model tree of the physics interface used for the simulation. Laminar flow without inertial term is creeping flow inlet and outlet used in creeping flow are shown in (b) and (c), respectively.

Note that the interface sharpness depends on the few parameters used in the phase-field model. The following guidelines are followed as per the COMSOL website for sharp interface tracking in the case of multiphase flow simulation.

1. In the Parameter controlling the interface thickness is a function of mesh calculated from the formula by the COMSOL website. The advised model is half the size of the maximum mesh size.

2. Mobility tuning parameter (MTP) is a function of mesh and velocity used in the simulation. It is calculated from the formula.

   \[
   \text{MTP} = \frac{2u}{4.24\gamma} \times \frac{h}{\epsilon} \quad (\text{SM}-1)
   \]

   where \(u\) is the maximum velocity, \(\gamma\) is surface tension, \(h\) is maximum mesh size, and \(\epsilon\) is the Parameter controlling the thickness.

   The wetted wall used in the simulation plays a pivotal role and is defined by the direct assignment option in the respective dialogue box. As a better modeling practice, contact angle values are either ramped up or down to avoid convergence issues. The ramping function can be defined separately in the parameters section.
In the Multiphysics module, which combines the creeping flow and phase-field model, two liquids need to be chosen so that the density mismatch is the minimum. It is worth noting that the idea of asymmetry and splitting has nothing to do with the exact values of density. Hence, any arbitrary two fluids with reasonably minimal density mismatch also give similar results.
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