
Supplementary information

**Oscillatory bifurcation patterns initiated
by seeded surface solidification of liquid
metals**

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Supplementary Information

Oscillatory bifurcation patterns initiated by seeded surface solidification of liquid metals

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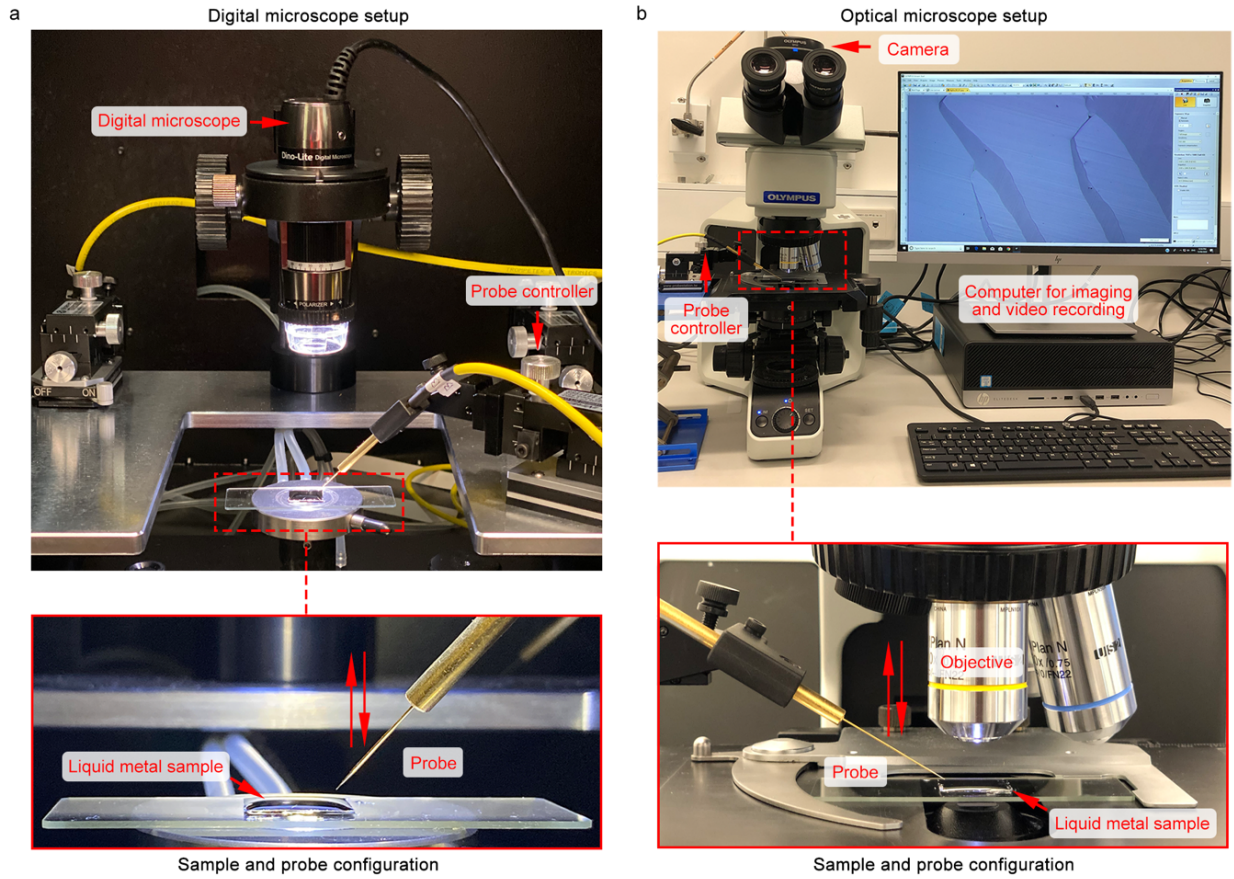
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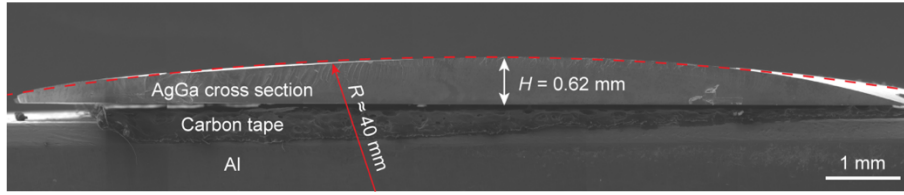
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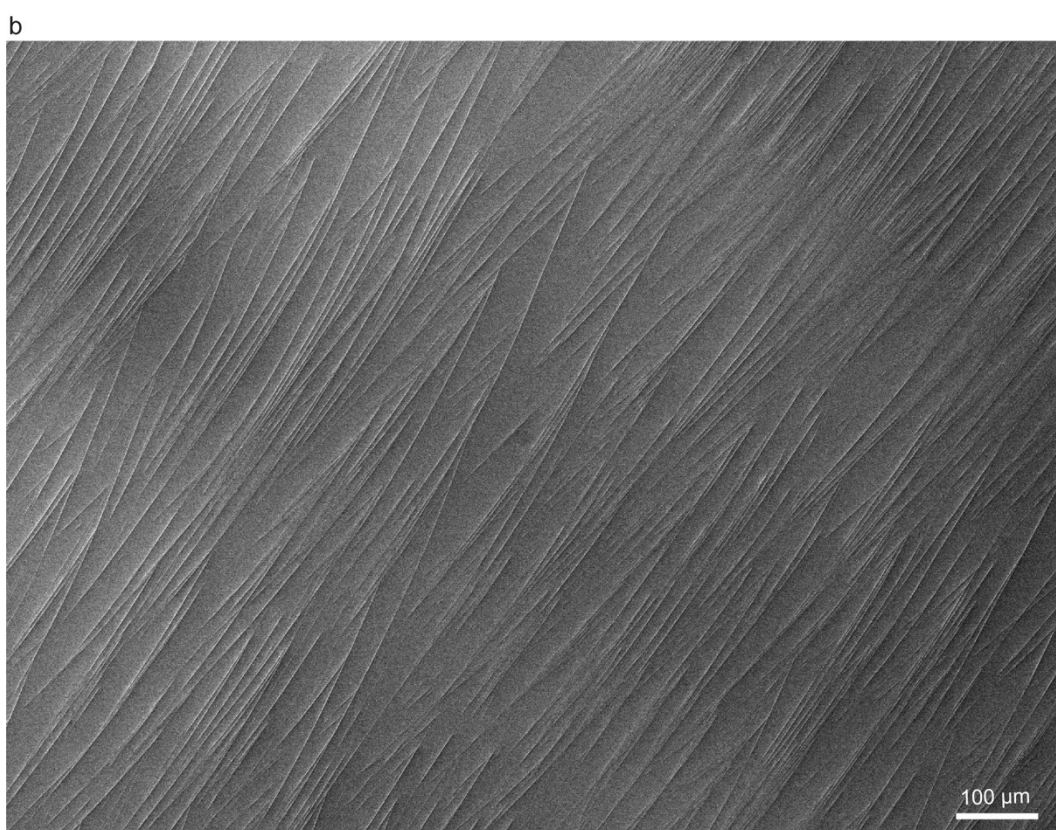
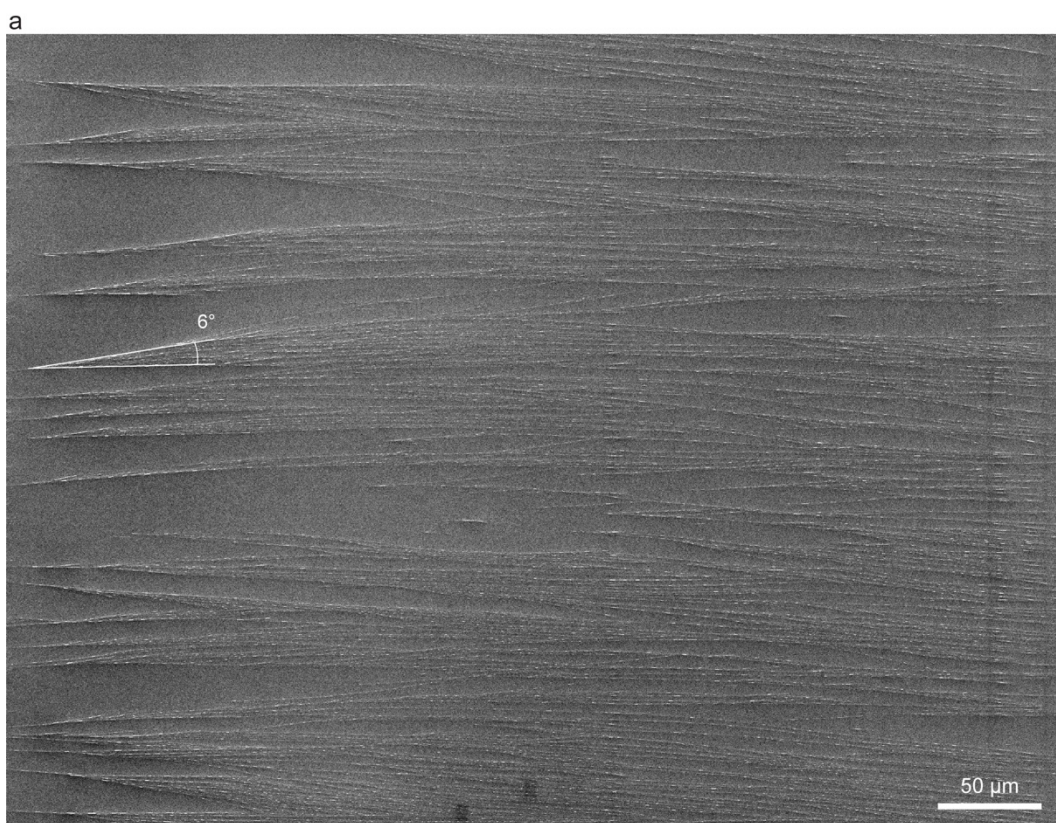
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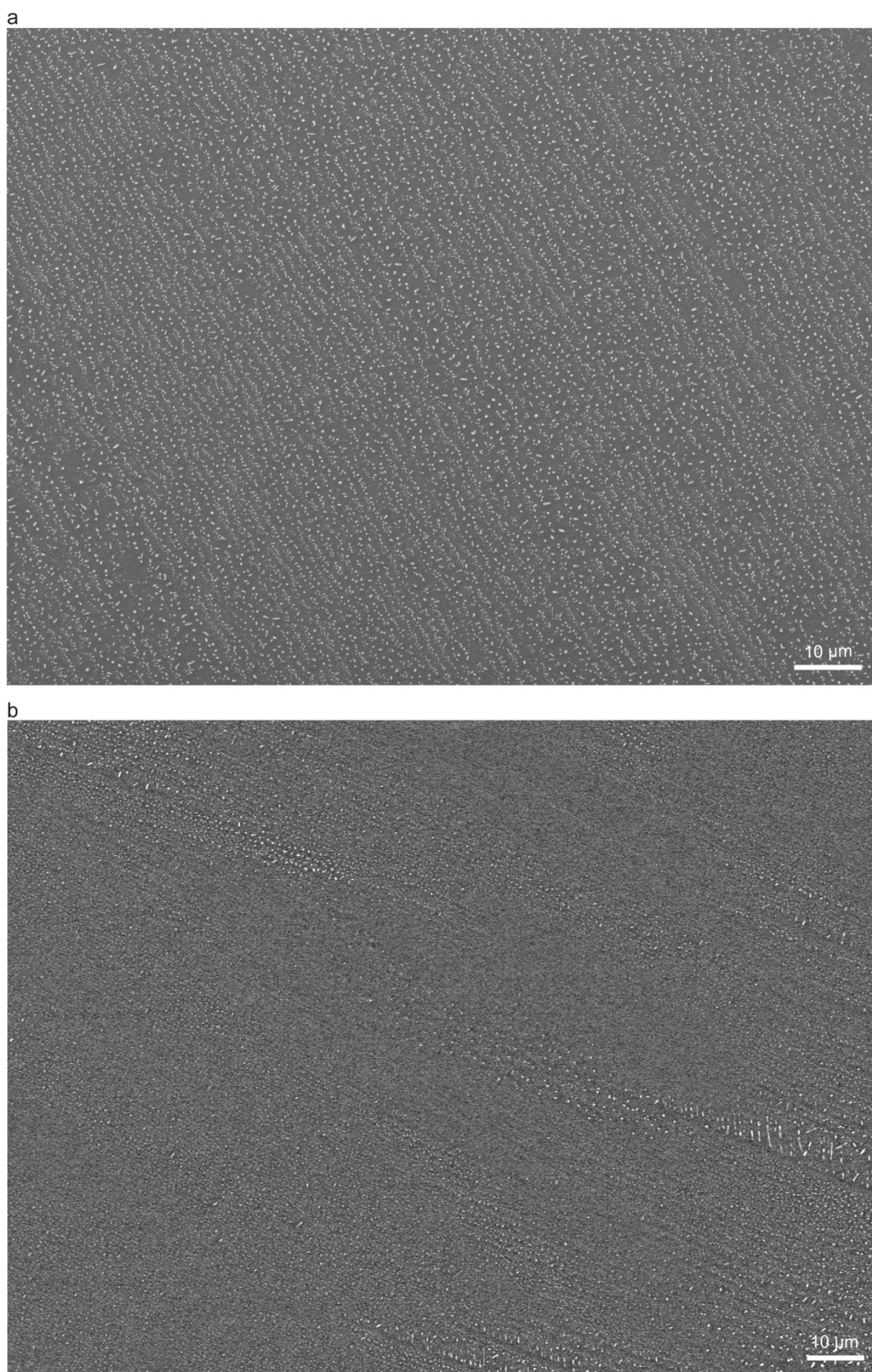
Supplementary Figure 1 | Setups for imaging the seeded surface solidification process. **a**, The digital microscope setup for recording the seeded surface solidification process shown in Fig. 1d of the main text. The digital microscope is connected to an imaging/video recording software. **b**, The optical microscope setup for recording the surface solidification front and pattern formation shown in Figs. 2a and 2c of the main text. The latter has a higher magnification than the former.



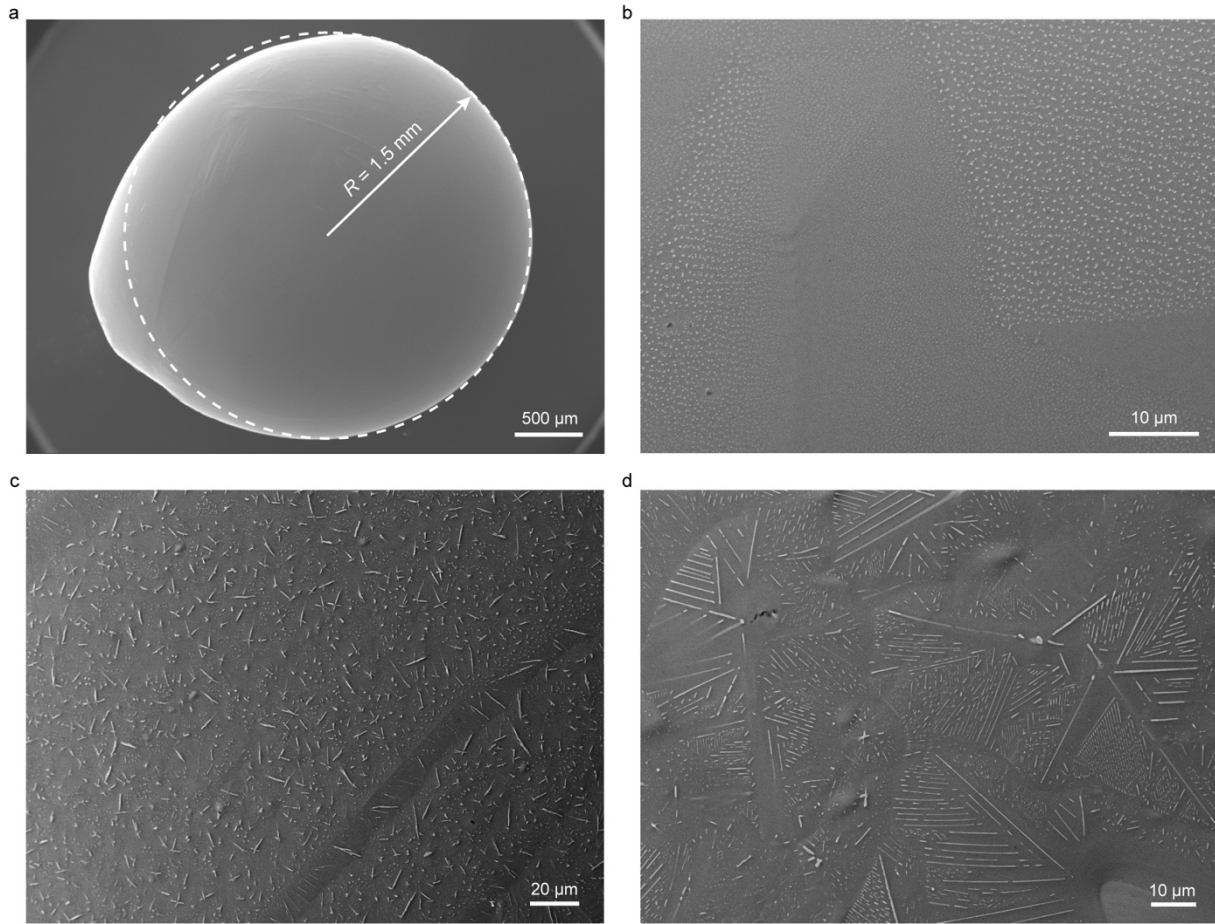
Supplementary Figure 2 | The cross section of a solidified $\text{Ag}_{0.001}\text{Ga}_{0.999}$ film sample. A cross-sectional SEM image showing the (maximum) thickness and curvature ($1/R \approx 0.025 \text{ mm}^{-1}$).



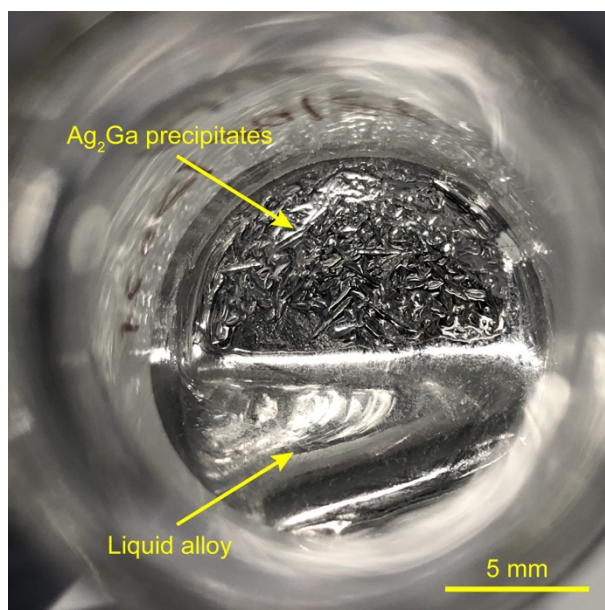
Supplementary Figure 3 | Additional examples of large-area Ag₂Ga bundle surface patterns formed in the BSP.



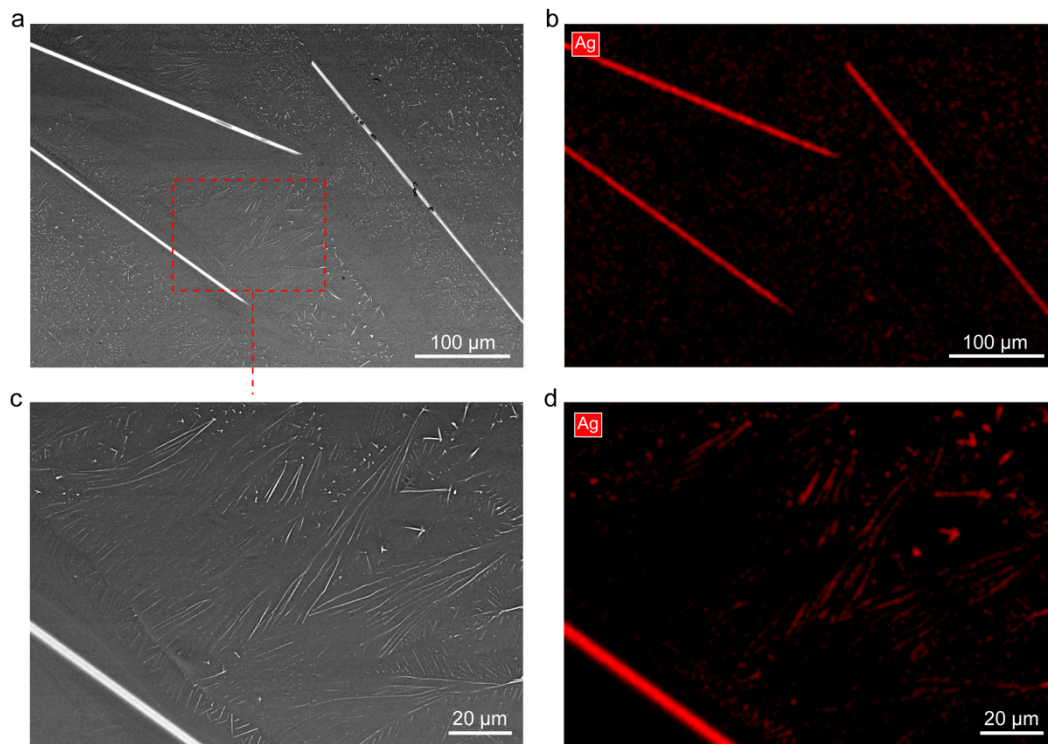
Supplementary Figure 4 | Additional examples of large-area Ag₂Ga particulate surface patterns formed in the PSP.



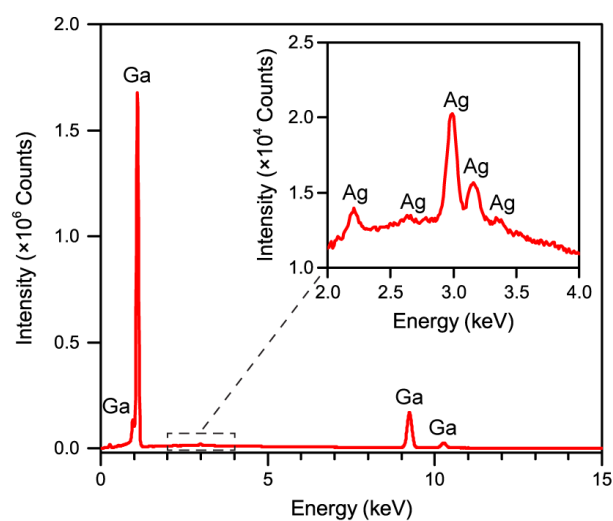
Supplementary Figure 5 | Surface solidification patterns on millimetric $\text{Ag}_{0.001}\text{Ga}_{0.999}$ droplet samples. **a**, An SEM image of a solidified $\text{Ag}_{0.001}\text{Ga}_{0.999}$ droplet sample with a curvature $1/R \approx 0.667 \text{ mm}^{-1}$, which is about 27 times larger than the film sample in Supplementary Fig. S2. **b-d**, Typical surface patterns formed on droplet samples. The solidification of the droplet was also triggered by touching its surface with a crystal seed. However, unlike the $\text{Ag}_{0.001}\text{Ga}_{0.999}$ film samples presented in the main text, no branched and aligned patterns were observed to form on the droplets. The large curvature of the surface of the droplets is thought to be the reason for preventing the formation of such large-area well-defined patterns.



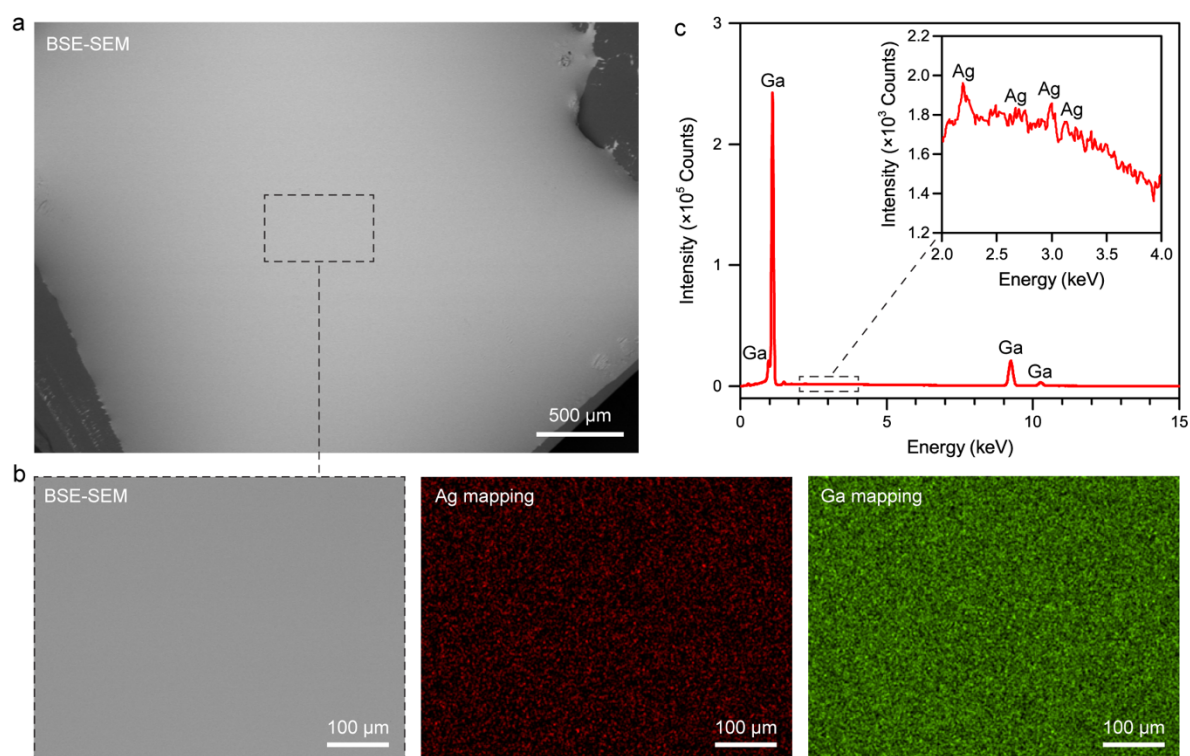
Supplementary Figure 6 | A photo of the $\text{Ag}_{0.005}\text{Ga}_{0.995}$ sample stored in a glass container which is tilted to show Ag_2Ga precipitates at the bottom, co-existing with the liquid alloy. The Ag_2Ga precipitates did not trigger the sample to solidify automatically at room temperature, indicating the seeded solidification was actually triggered by Ga crystals.



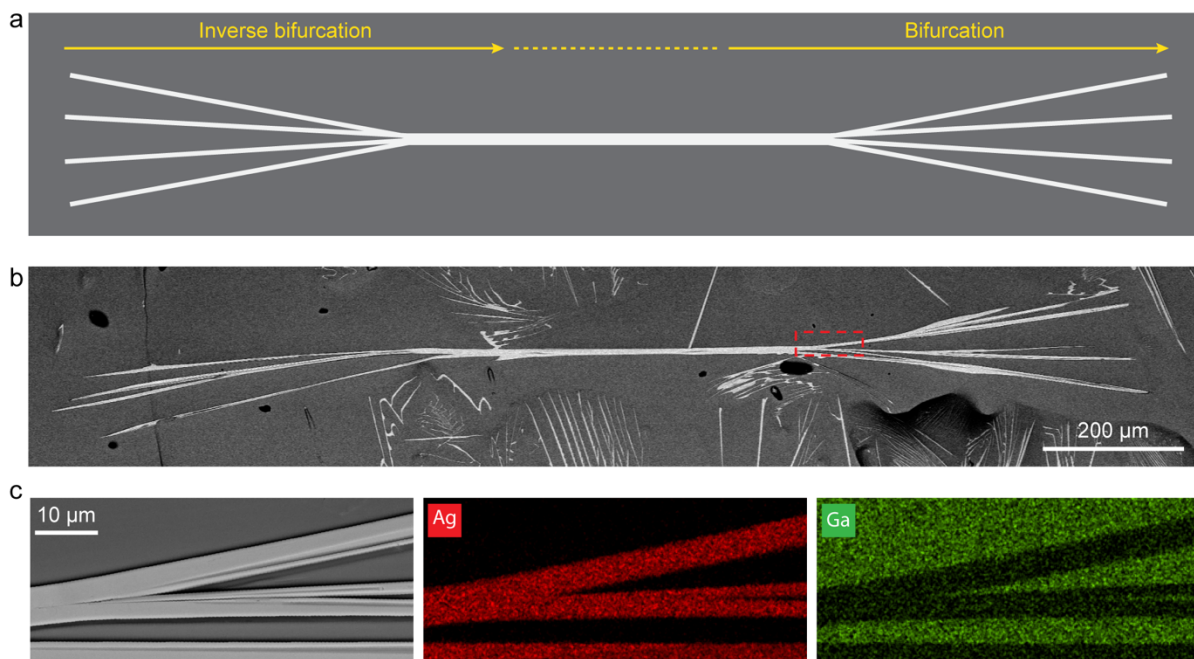
Supplementary Figure 7 | Influence of Ag concentration on surface pattern formation. **a,b,** Surface solidification patterns formed on a $\text{Ag}_{0.005}\text{Ga}_{0.995}$ sample (**a**) and the corresponding EDX mapping of Ag (**b**). **c,d,** A zoom-in region of **a** showing the termination of the branching Ag_2Ga patterns approaching a long Ag_2Ga rod (**c**) and the corresponding Ag mapping (**d**).



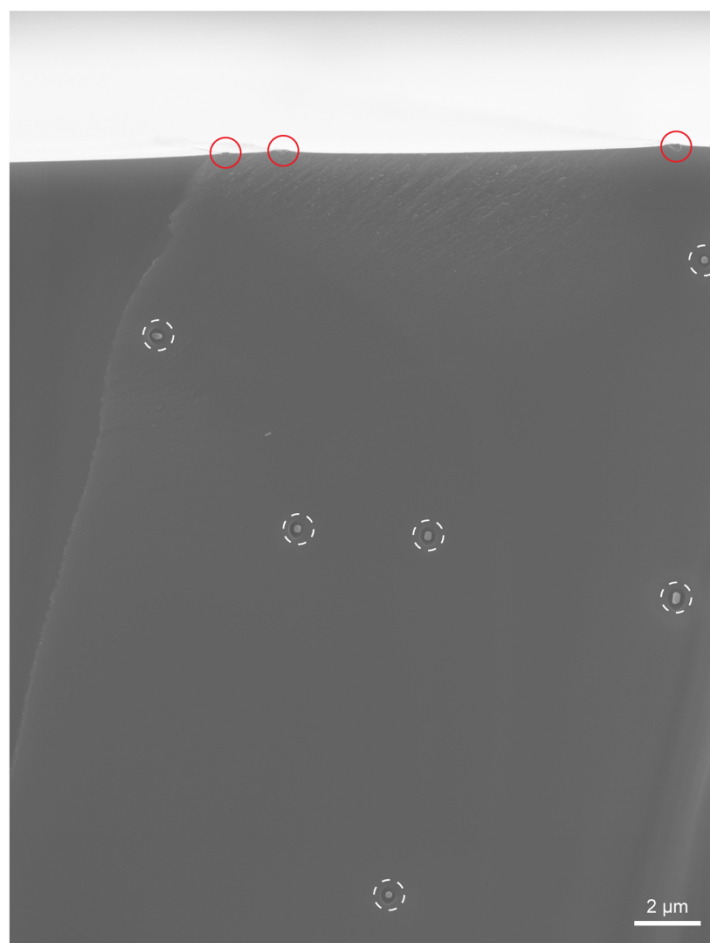
Supplementary Figure 8 | EDX analysis of the surface the solidified $\text{Ag}_{0.001}\text{Ga}_{0.999}$ alloy. A typical EDX spectrum collected from the surface of a solidified $\text{Ag}_{0.001}\text{Ga}_{0.999}$ sample. The inset magnifies the spectrum between 2.0 keV and 4.0 keV to show the Ag peaks.



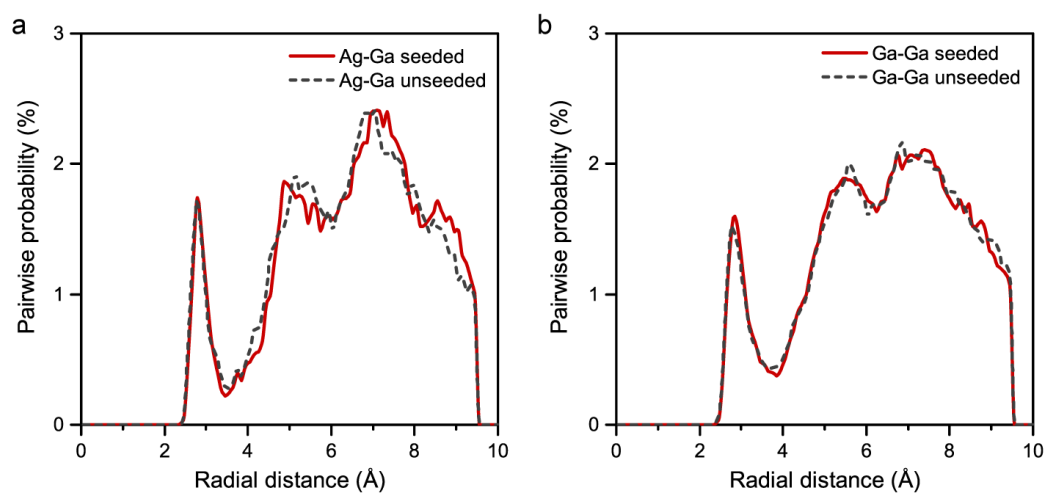
Supplementary Figure 9 | BSE-SEM and EDX analyses of the liquid $\text{Ag}_{0.001}\text{Ga}_{0.999}$ alloy surface. **a**, BSE-SEM phase-contrast image of a $\text{Ag}_{0.001}\text{Ga}_{0.999}$ liquid alloy film (light grey region) spread on a Si substrate (dark grey corner regions). The liquid alloy shows a uniform phase contrast, indicating that the liquid alloy is a homogeneous mixture. **b**, BSE-SEM and EDX mappings at a higher magnification, both showing uniform distribution of Ag in liquid Ga. **c**, The EDX spectrum of the liquid $\text{Ag}_{0.001}\text{Ga}_{0.999}$ surface. The inset magnifies the spectrum between 2.0 keV and 4.0 keV to show the Ag peaks. The spectrum was collected from the region in **b** and the same magnification was kept for the quantitative EDX analysis.



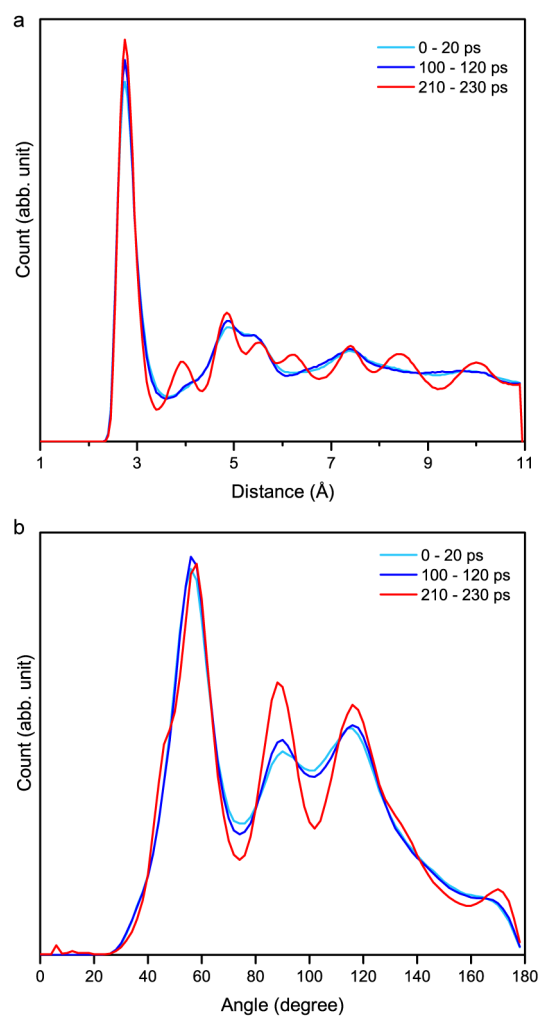
Supplementary Figure 10 | Oscillatory bifurcation surface solidification patterns formed on an oxide-free $\text{Ag}_{0.001}\text{Ga}_{0.999}$ alloy. **a**, Schematic drawing of a surface Ag_2Ga pattern (white) on Ga (grey) which undergoes bifurcation and inverse bifurcation during solidification. **b**, BSE-SEM images of surface patterns formed in a nitrogen-filled glovebox ($\text{O}_2 < 0.5$ ppm). **c**, Magnified view of the dashed box in **c** to show the characteristic thickness of the surface pattern and the EDX elemental mapping of Ag and Ga.



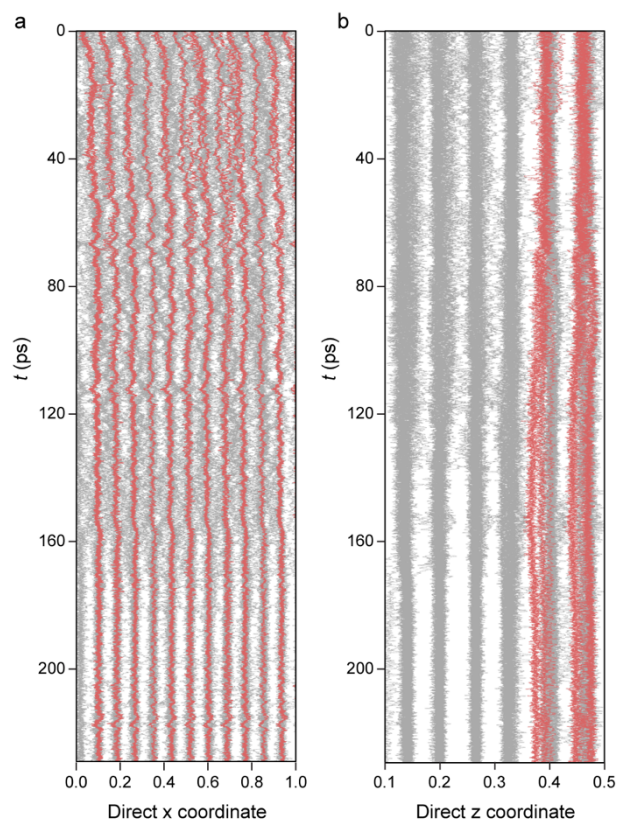
Supplementary Figure 11 | Cross-sectional characterisation. A magnified SEM image featuring the cross section of a $\text{Ag}_{0.001}\text{Ga}_{0.999}$ sample at its near surface region. The surface and interior Ag_2Ga structures are marked by solid red circles and the dashed white circles, respectively.



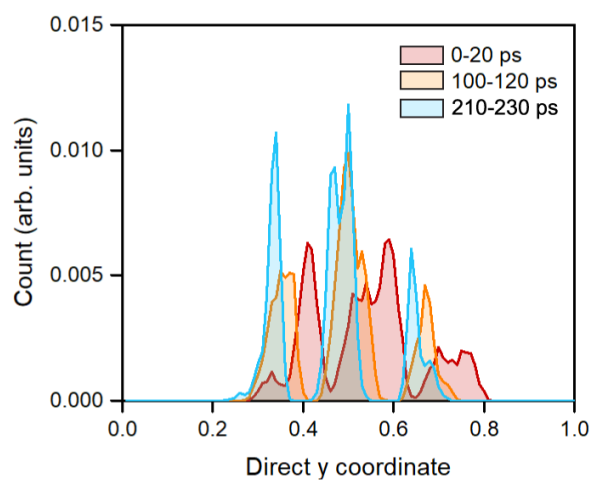
Supplementary Figure 12 | Probability distribution functions for the atom pair distances for the seeded and unseeded cases. a, Ag-Ga. b, Ga-Ga.



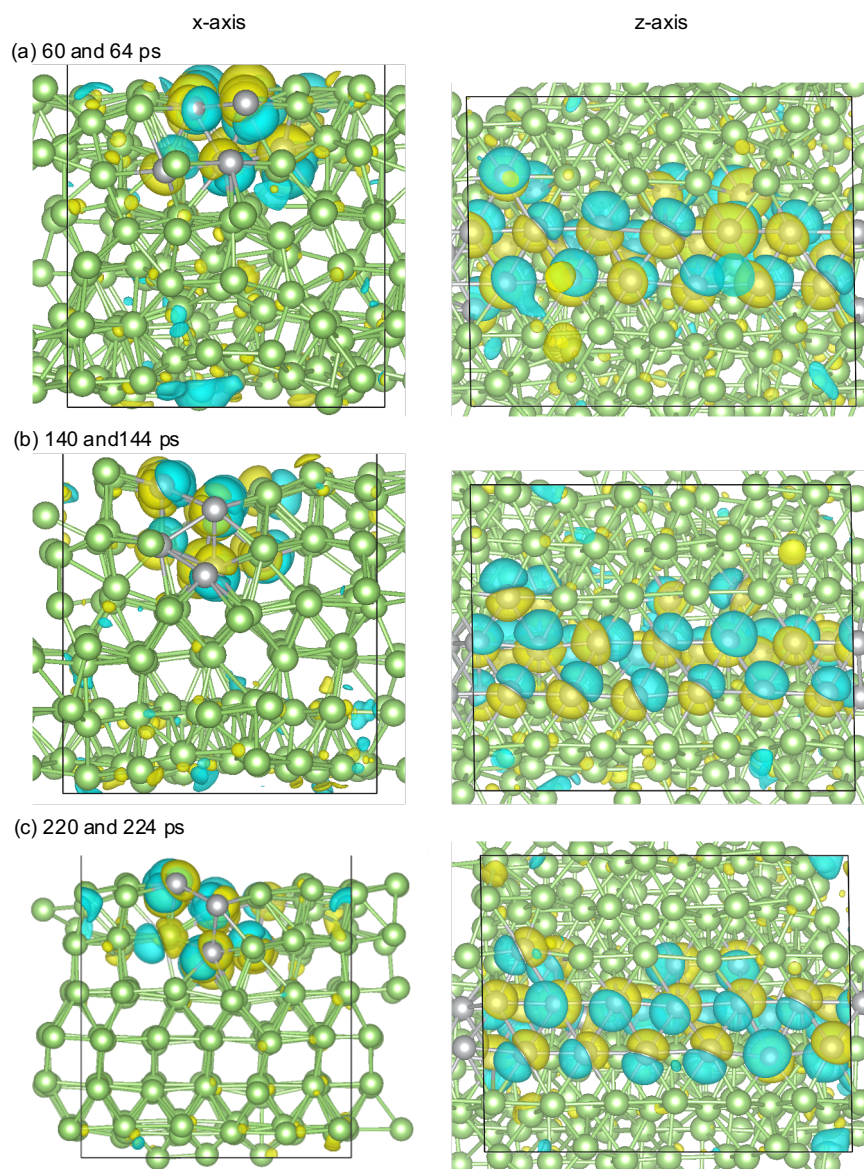
Supplementary Figure 13 | Radial distribution function (RDF) and angular distribution function (ADF) characterisations. a,b, RDF (a) and ADF (b) of the Ag-Ga system over 20 ps time intervals throughout the AIMD simulations.



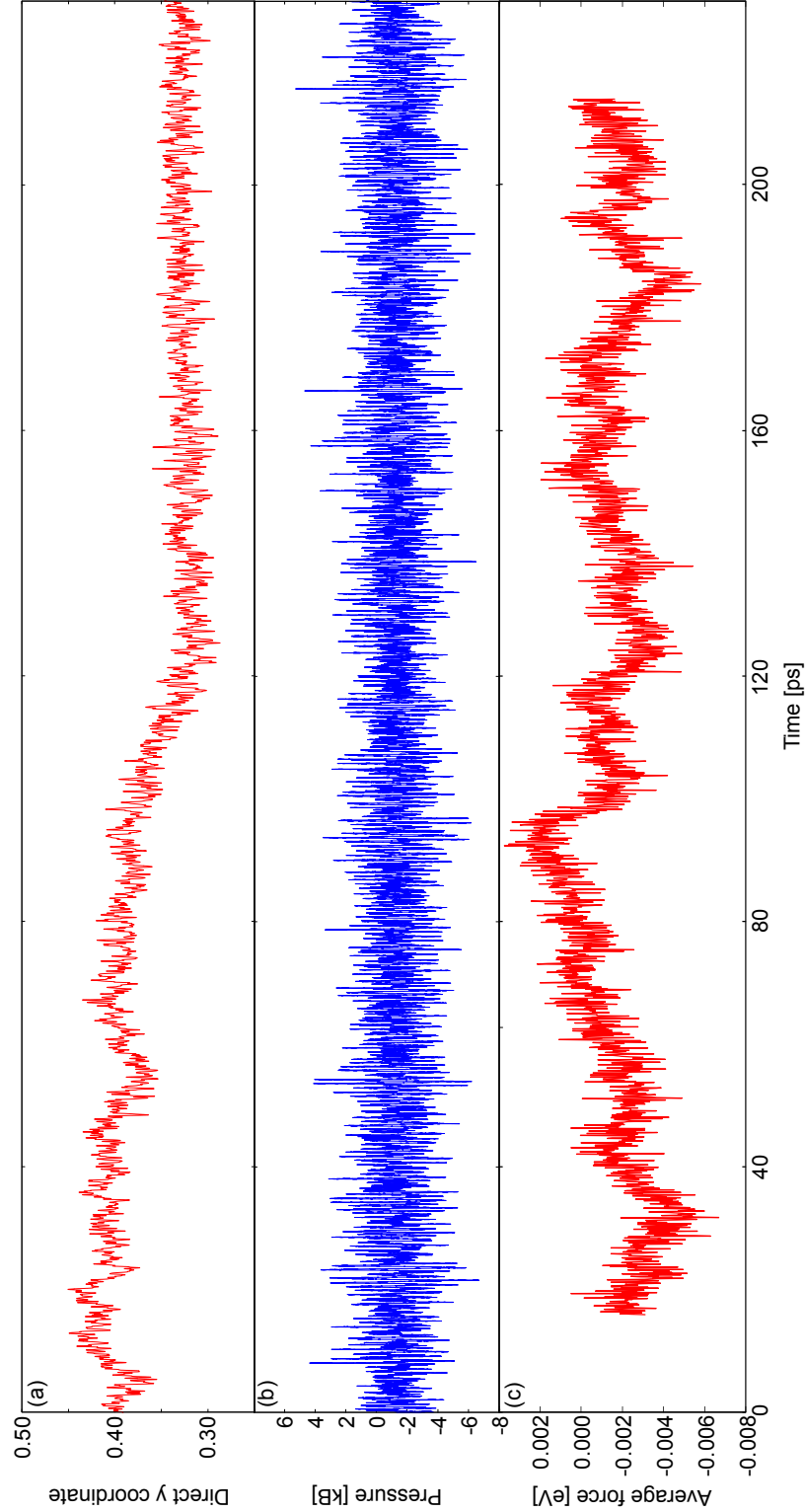
Supplementary Figure 14 | Single coordinate atomic trajectories. **a**, Single coordinate atomic trajectories in the x -direction and **b**, that in the z -direction with respect to time. Ga atoms are shown in grey and Ag atoms in pink.



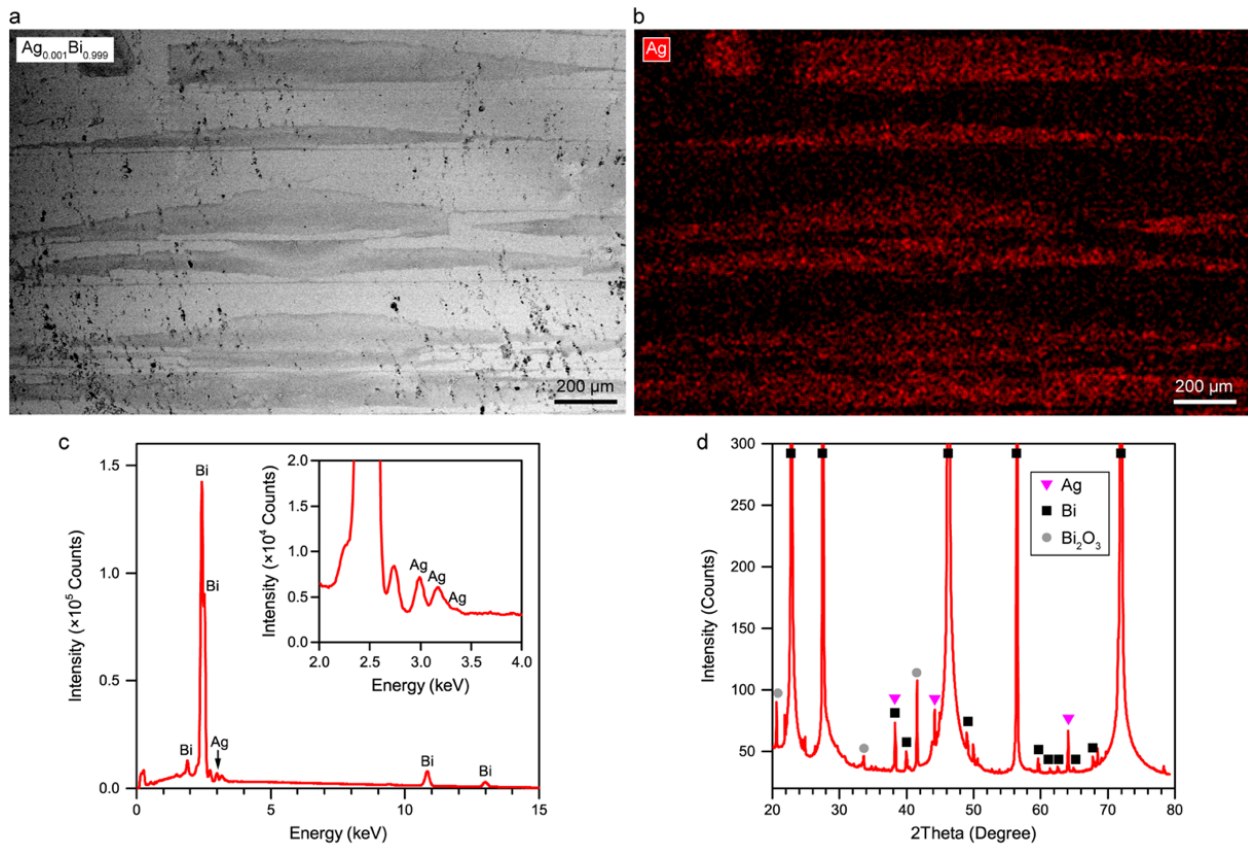
Supplementary Figure 15 | Comparison of Ag atom y-distribution. The y-distribution plots for all Ag atoms over the course of the AIMD simulations (over 20 ps time periods) show a collective drift of the Ag atoms to the left side of the y coordinate (i.e., smaller y values).



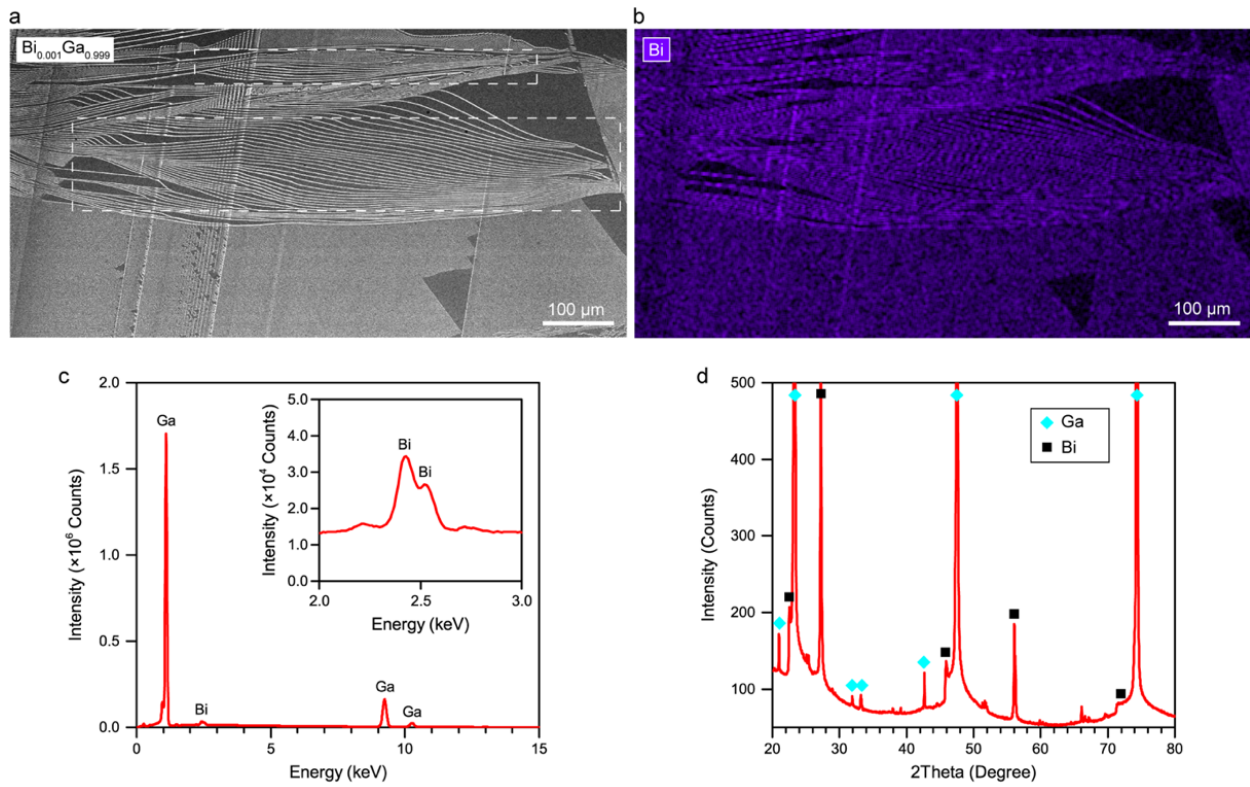
Supplementary Figure 16 | Charge density differences at different simulation stages. (a) The initial stage of the simulation between 60 and 64 ps, (b) the transition stage of the simulation between 140 ps and 144 ps, and (c) the final stage of the simulation between 220 and 224 ps. The isosurface value was set in each to 0.023. Ga atoms in green and silver atoms in grey. Positive change in charge density in yellow and negative in blue. The observed charge density differences are a reflection of atomic movement over the 4 ps window, rather than being the driving force for this motion.



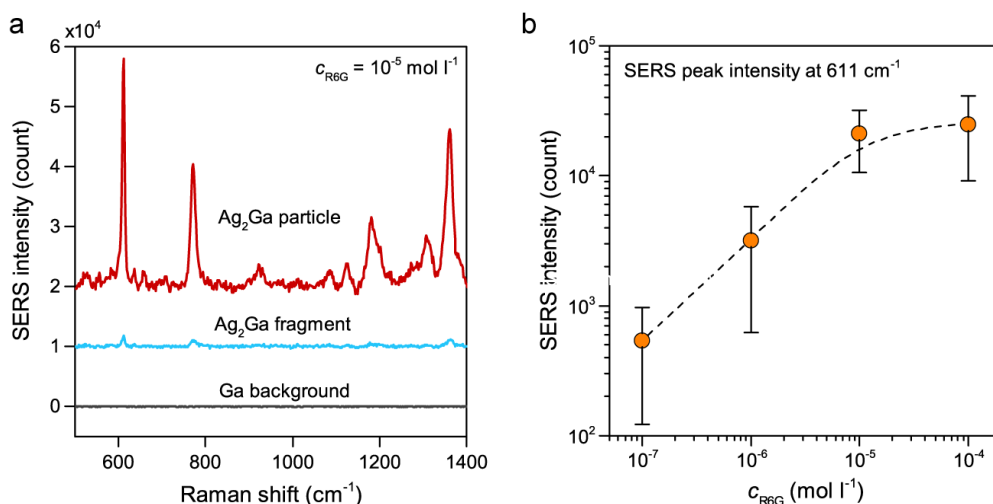
Supplementary Figure 17 | Driving forces for atomic movement. **a**, The direct atom position of a Ag atom in the y-direction from 0.4 to less than 0.35, indicating movement in the negative y-direction. **b**, The total force exerted on the cell in the y-direction is constant throughout the simulation around 0 kBar, displaying that the lateral movement of the atoms in the simulation does not create pressure on the cell. **c**, The running average of the y-force exerted on a surface Ag atom directly coupled to the movement; that is, the movement of the Ag atom in the negative y-direction is reflected in the, on average, negative y-force being exerted on the atom. The same analysis could be carried out for all the atoms but would yield the same results.



Supplementary Figure 18 | Characterisation of oscillatory bifurcation surface patterns of the $\text{Ag}_{0.001}\text{Bi}_{0.999}$ alloy. **a**, SEM of large-area Ag surface patterns on a Bi background. **b,c**, The corresponding EDX mapping of Ag (**b**) and EDX spectrum (**c**). The inset of **c** is a magnified region which shows the peaks of the minor Ag phase. The EDX analysis shows a surface Ag enrichment of $\phi_{\text{Ag},s}/\phi_{\text{Ag},0} = 66.9$. **d**, XRD of the $\text{Ag}_{0.001}\text{Bi}_{0.999}$ alloy showing phase-separated Bi, Ag, together with Bi_2O_3 in the sample.

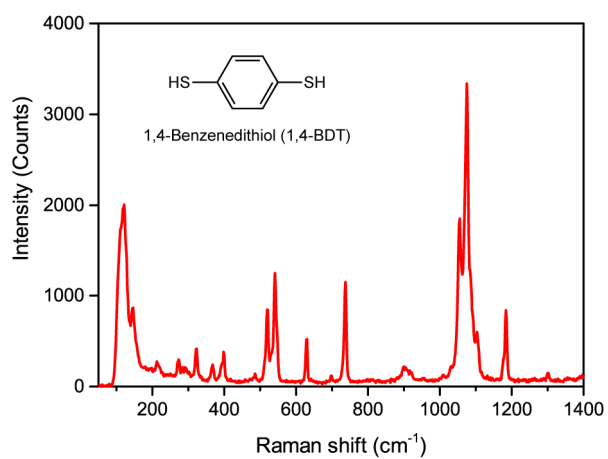


Supplementary Figure 19 | Characterisation of oscillatory bifurcation surface patterns of the $\text{Bi}_{0.001}\text{Ga}_{0.999}$ alloy. **a**, SEM of large-area Ag surface patterns on a Bi background. Two examples of bifurcation/inverse-bifurcation patterns can be found in the two regions outlined by the dashed boxes. **b,c**, The corresponding EDX mapping of Bi (**b**) and the EDX spectrum (**c**). The inset of **c** is a magnified region which shows the peaks of the minor Bi phase. The EDX analysis shows a surface Bi enrichment of $\phi_{\text{Bi,s}}/\phi_{\text{Bi,0}} = 16.6$. **d**, XRD of the $\text{Bi}_{0.001}\text{Ga}_{0.999}$ alloy showing phase-separated Ga and Bi in the sample.



Supplementary Figure 20 | Surface-enhanced Raman spectroscopy enabled by the Ag₂Ga surface patterns. **a**, The SERS spectra of Rhodamine 6G (R6G) collected from surface Ag₂Ga and Ga structures as indicated. **b**, The SERS intensity (at 611 cm^{-1}) collected from Ag₂Ga particle sites as a function of c_{R6G} . The scatters and error bars represent the average values and the standard deviations calculated based on multiple data points (>10) while the dashed line is a fitting curve.

As an intermetallic phase, Ag₂Ga nanostructures show plasmon resonance which was utilised here to enable surface enhanced Raman spectroscopy (SERS). R6G was deposited onto the Ag₂Ga surface patterns (surface oxide removed using 0.1 mol l^{-1} HCl) as the Raman tracer¹. Typically, $20 \mu\text{l}$ R6G ethanol solution was drop-cast onto the sample surface and then dried naturally in air. The laser power was set to 1% of the maximum power of the 532 nm laser (36 mW) for all the SERS measurements. The Raman spectra were processed by standard background subtraction for later analysis. The SERS signal was detected from the Ag₂Ga region, while the Ga background showed no R6G signature (Figs. 5a). Furthermore, the Ag₂Ga particles generated much higher enhancement than the fragments, which was attributed to both the smaller dimensions of the former (Figs. 3f, 3g) and the amplified plasmon excitation induced by the ‘hotspot’ gaps between the closely packed Ag₂Ga nanoparticles (Fig. 2f). When the R6G concentration (c_{R6G}) was investigated, the SERS intensity showed a near exponential increase in the range from $10^{-7} \text{ mol l}^{-1}$ to $10^{-5} \text{ mol l}^{-1}$ (Fig. 5c, Supplementary Fig.13). Further increasing c_{R6G} from $10^{-5} \text{ mol l}^{-1}$ to $10^{-4} \text{ mol l}^{-1}$ did not lead to an increase in SERS intensity, suggesting that the R6G tracer became saturated at concentrations above $10^{-5} \text{ mol l}^{-1}$.



Supplementary Figure 21 | Raman spectrum of the as-received 1,4-BDT powders. The inset shows the molecular structure of 1,4-BDT.

Supplementary Table 1. Bond dissociation energies of the GaAg, GaBi, and BiAg systems².

GaAg		
Ga-Ga <106.4 kJ mol ⁻¹	Ag-Ag 162.9 ± 2.9 kJ mol ⁻¹	Ga-Ag 159 ± 17 kJ mol ⁻¹
GaBi		
Ga-Ga <106.4 kJ mol ⁻¹	Bi-Bi 204.4 kJ mol ⁻¹	Ga-Bi 158.6 ± 16.7 kJ mol ⁻¹
BiAg		
Bi-Bi 204.4 kJ mol ⁻¹	Ag-Ag 162.9 ± 2.9 kJ mol ⁻¹	Bi-Ag 192 ± 42 kJ mol ⁻¹

Regarding the bond-strength discussion, we note that it is not a complete answer to the question of why we see the bifurcation and inverse bifurcation effect, as there are many other factors at play in bimetallic alloys including composition, size and temperature^{3, 4}. Transitions from mixing to segregation of the nanoalloys with respect to size, composition and temperature has been observed. In the GaBi and BiAg systems, we note the size-dependence of the patterns at the point of bifurcation (and inverse bifurcation) – this transition occurs at considerably smaller nanowire widths for BiAg than for GaBi systems. The size, composition, temperature and bond energy dependence of these processes may provide additional insight into the mechanism of bifurcation and inverse bifurcation in these systems.

Reference

1. Hildebrandt, P., Stockburger, M. Surface-enhanced resonance raman spectroscopy of rhodamine 6G adsorbed on colloidal silver. *J. Phys. Chem.* **88**, 5935-5944 (1984).
2. Luo, Y.-R. *Comprehensive Handbook of Chemical Bond Energies* (CRC Press, 2007).
3. Calvo, F. Thermodynamics of nanoalloys. *Phys. Chem. Chem. Phys.* **17**, 27922-27939 (2015).
4. Jellinek, J. Nanoalloys: Tuning properties and characteristics through size and composition. *Faraday Discuss.* **138**, 11-35 (2008).