Electronic Supplementary Information

High-throughput drawing and testing of metallic glass nanostructures

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1. Thermoplastic embossing and elongation

For single filament stretching experiments, Al templates made by mechanical milling were used. Cylindrical holes of 200 μm diameters and 800 μm length were machined using carbide micro drill bits. All embossing and pulling experiments were conducted in air using custom-built heating platens installed on Instron 5966 mechanical tester. The templates and the metallic glass discs were mechanically secured with the lower and the upper heating plates, respectively. The metallic glass discs were first slowly (< 0.5 mm/min) pressed on the templates followed by pulling at different speeds (0.5-80 mm/min) till rupture. As explained in the manuscript, failing to demold is the key requirement to controllably elongate and rupture the metallic glass structures. We observed that the filling aspect-ratio of 2-3 was necessary during pressing to prevent subsequent demolding during pulling. Pressure in the range of 20-30 MPa was sufficient for the all four metallic glass formers to achieve an aspect-ratio of 3 during thermoplastic pressing.

2. Effect of temperature and pulling speed on single filament

Supplementary Figure S1 shows the effects of processing temperature and pulling speed on the final diameter of metallic glass filament during elongation. Pt-based metallic glass disc (5-6 mm diameter) was pressed against a cylindrical cavity (diameter = 200 μm, length = 800 μm) at 533 K under an applied load of 400 N. Subsequently, the metallic glass was pulled at different temperatures and speeds until rupture. For a constant pulling speed (0.5 mm/min), the filament diameter decreased with increasing temperature. The sample necks increasingly to smaller diameter with increasing temperature before elongation and fracture. This is due to decrease in viscosity and diminishing non-Newtonian effects at higher temperature. The smallest diameter obtained after fracture at 543 K was about 100 nm. In contrast, the increase in pulling speed showed an opposite effect to that of temperature. The filament diameter increased with increasing pulling speed when the processing temperature was kept constant at 533 K. The smallest diameter of about 300 nm was obtained after elongation and fracture at 10 mm/min.

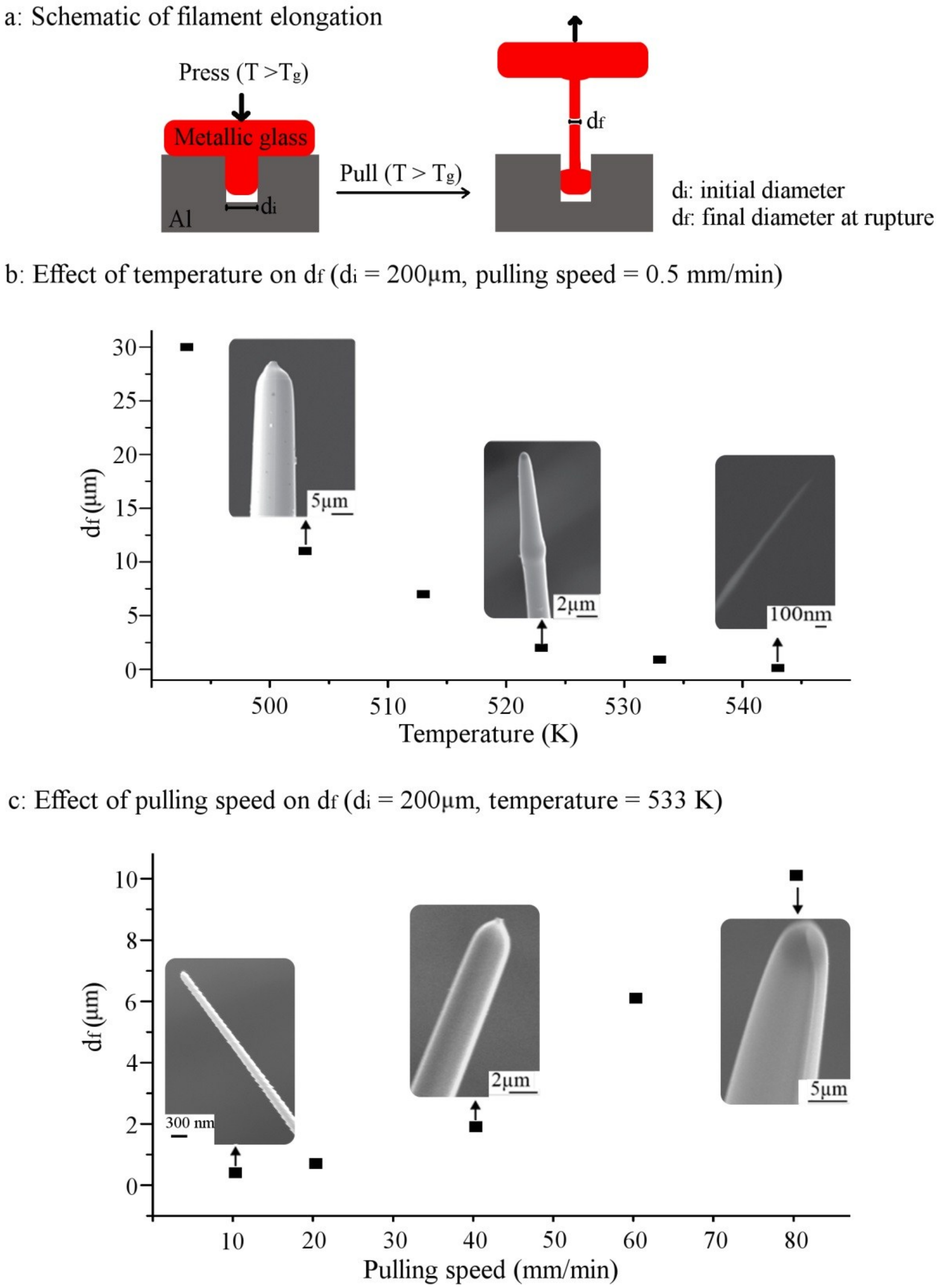

Figure S1: Schematic illustration of thermoplastic molding and drawing of metallic glass using an Al template with a cylindrical cavity (a). Effect of processing temperature on the final diameter of Pt-based metallic glass filament after fracture (b). Effect of pulling speed on the final diameter of Pt-based metallic glass filament after fracture (c)

3. Array drawing of metallic glass nanostructures

Figure S2 shows arrays of metallic glass nanostructures with controllable aspect-ratios ranging from 5 to more than 1000 fabricated by thermoplastic drawing. For all these samples, Si templates with cylindrical holes of 20 μm diameters were used. The metallic glass nanostructures are attached to the metallic glass substrate as well as the Si template. The varying aspect-ratios were obtained by optimizing the processing conditions (temperature and pulling speed). We observed that increase in processing temperature and pulling speed both resulted in higher aspect-ratio nanostructures during thermoplastic drawing. However, change in aspect-ratio also affected the diameter of metallic glass nanostructures. This constraint could be removed by using a multi-speed pulling protocol.

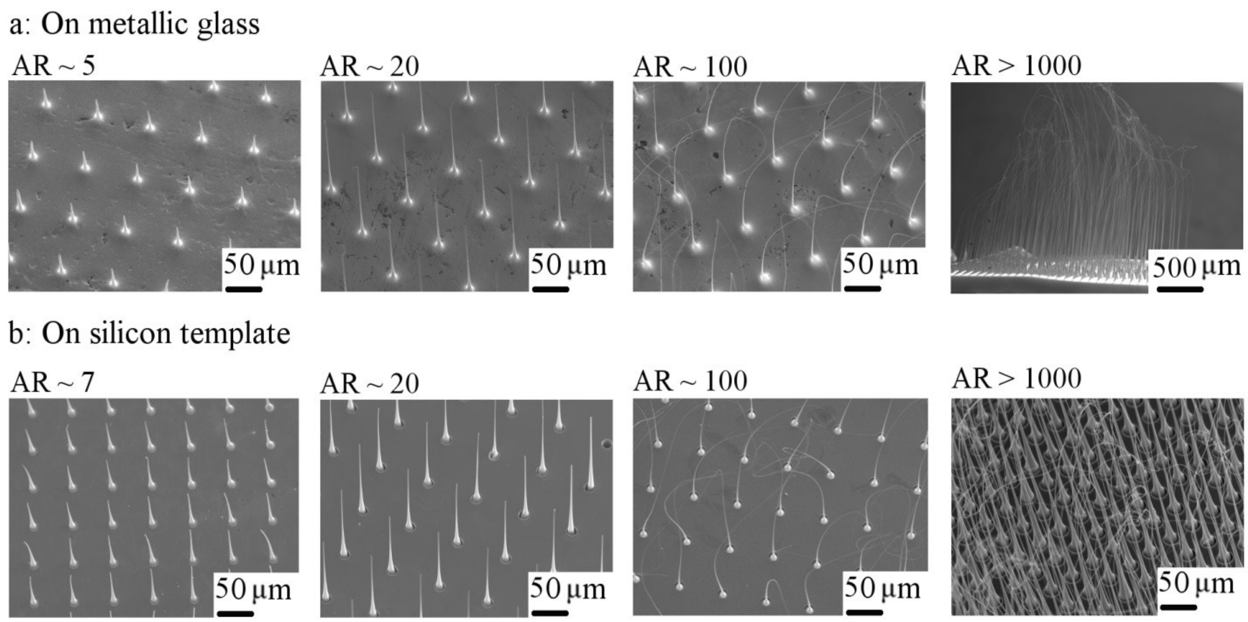

Figure S2: Arrays of Pt-based metallic glass nanostructures with varying AR attached to the metallic glass substrate itself (a) and silicon template (b). AR higher than 1000 can be achieved by thermoplastic drawing method.

4. Structural characterization

The Figure S3 shows TEM image and DSC curves of Pt-based metallic glass nano-wires fabricated by thermoplastic drawing. It has been reported that thermoplastic forming at high shear strain-rates can accelerate crystallization process[1]. Our TEM and DSC experiments confirm that the samples remain amorphous after thermoplastic drawing used here. This is because the shear strain-rate during tensile deformation does not exceed the critical value reported for crystallization.

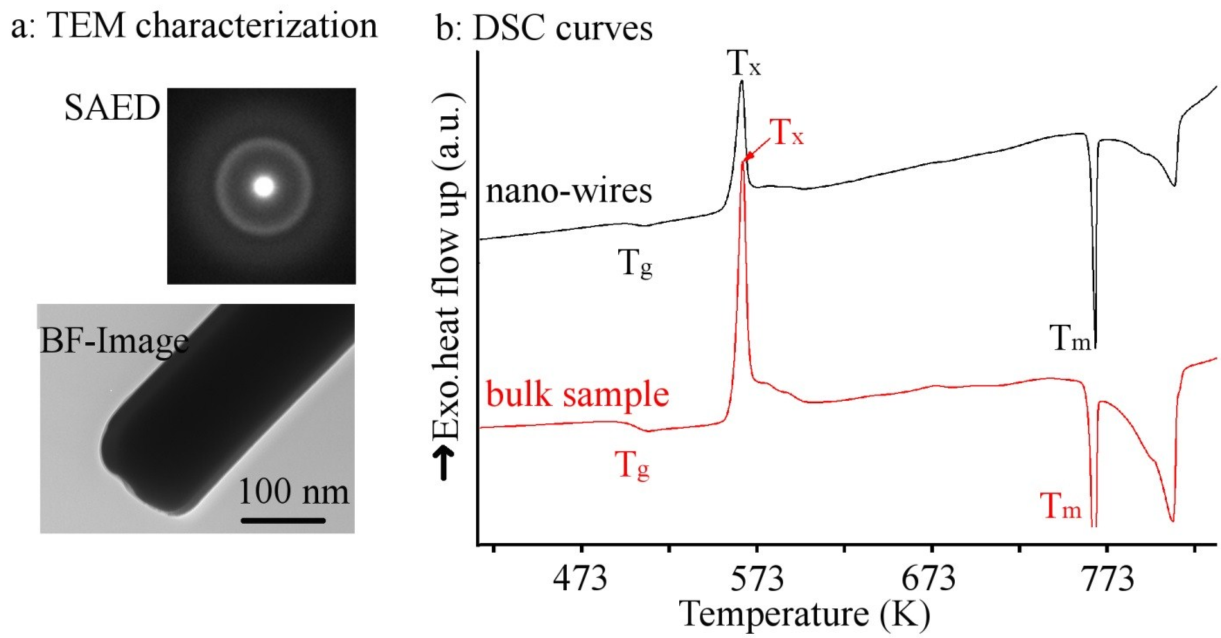

Figure S3: The bright field (BF) TEM image and the corresponding selected area electron diffraction (SAED) of a nano-wire (a). Differential scanning calorimeter (DSC) curves of nano-wires and a virgin bulk sample show comparable glass transition (T_g), crystallization (T_x), and melting (T_m) temperature peaks.

5. High-throughput tensile testing

To fabricate tensile specimens with different sizes, Si templates with cylindrical features of varying diameters (20-100 μm) were used. The first step of thermoplastic embossing was same as for the fabrication of nanostructures described above. Subsequently, the metallic glass was pulled away from the template and stopped before rupture. At this stage, the cylindrical features had reshaped into dog-bone geometries vertically aligned between the metallic glass substrate and the Si template (Figure S4). The metallic glass substrate and the template serve as grips for subsequent tensile testing. In the images shown in supplementary Figure S4, the Si template was etched away to reveal the overall shapes of tensile specimens. For testing purpose, the entire assembly was cooled to a desirable temperature below T_g. After temperature stabilization, the pulling was resumed to fracture the array of tensile specimens. The final pulling speed was adjusted to achieve a tensile strain-rate of 10^{-4}-10^{-5} s^{-1}. The fractured surfaces were analyzed using SEM to reveal the size dependent change from shear-localized to homogeneous flow. By performing these experiments at different testing temperatures, the deformation map was constructed.

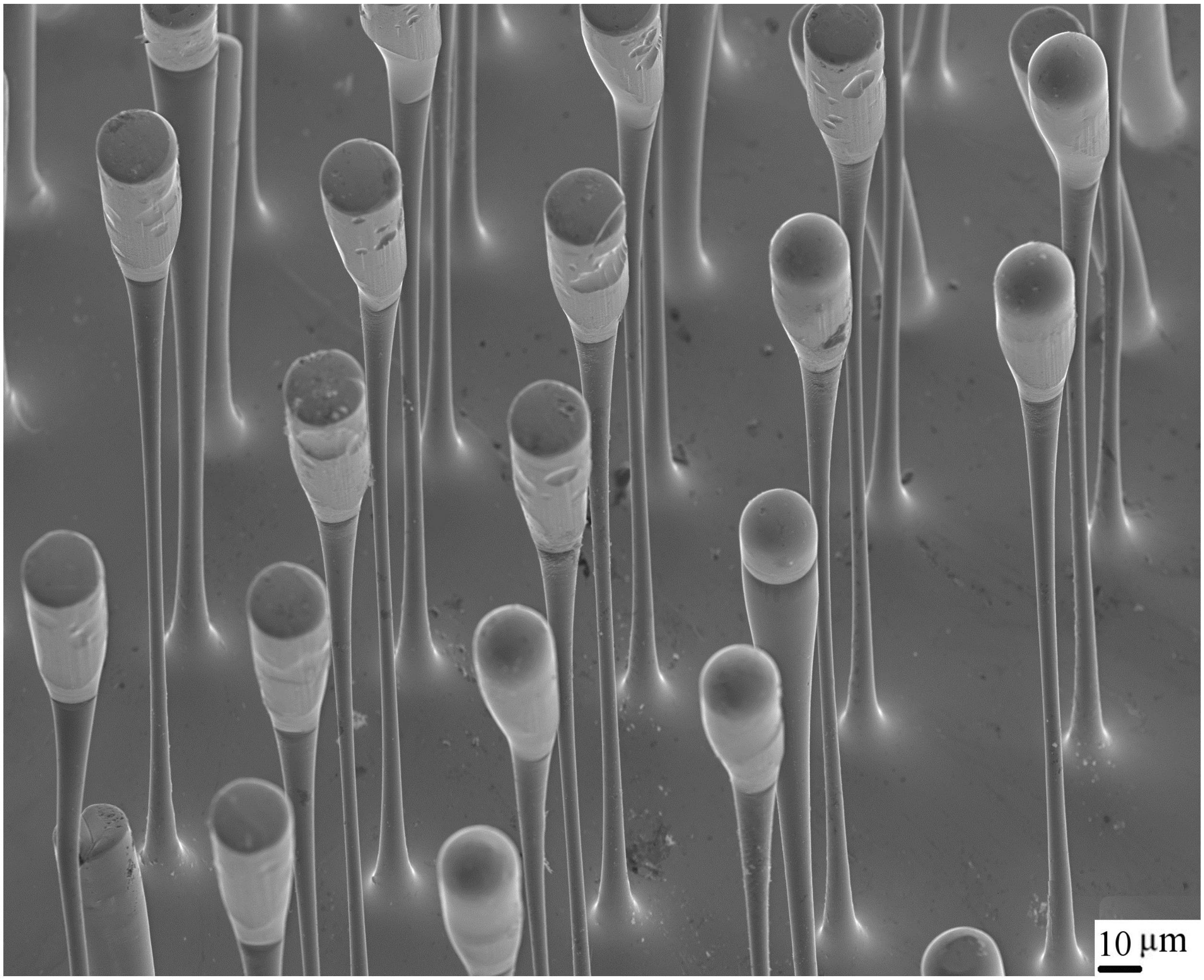

Figure S4: An array of Pt-based metallic glass tensile specimens fabricated by thermoplastic drawing. The Si template was etched away and the specimens are attached to the metallic glass substrate.

References

1. Shao, Z. *et al.* Shear-accelerated crystallization in a supercooled atomic liquid. *Phys. Rev. E* **91**, 020301 (2013).