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Supplemental Material for Crystallization of Highly Supercooled Glass-forming Alloys Induced by Anomalous Surface Wetting†

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1 Computational Methods

1.1 The mean first-passage time method

The mean first-passage time (MFPT) $\tau(x)$ is defined as the average elapsed time that a system reaches the state x from its initial state x_0 for the first time. For a activated process, $\tau(x)$ shows a sigmoidal shape. The dynamics of many activated processes can be described in terms of the Fokker-Planck[1]

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x}[D(x)e^{-\beta\Delta G(x)}\frac{\partial}{\partial x}(P(x,t)e^{\beta\Delta G(x)})] = -\frac{\partial J(x,t)}{\partial t}, \tag{1}$$

where $P(x,t)$ is the probability density for the state x at time t. $D(x)$ is the generalized diffusion coefficient, $J(x,t)$ is the state current, $\Delta G(x)$ is the free energy difference and $\beta = 1/k_BT$. The MFPT for an activated process described in Eq. 1 is then given by

$$\tau(x) = \int_{x_0}^{x} \frac{1}{D(y)} dyexp[\beta\Delta G(y)] \int_{a}^{y} dzexp[-\beta\Delta G(z)], \tag{2}$$

We use the embryo size, n, to identify the thermodynamic state during nucleation. Eq. 2 can be fitted by the following expression[2],

$$\tau(n) = \frac{1}{2JV}[1 + erf((n-n^*)c)], \tag{3}$$

where n^* is the critical size of the nucleus, J is the nucleation rate, $erf(x)$ is the error function, and $c = \sqrt{|\Delta G''(n^*)|/2k_BT}$. From the fit of $\tau(n)$, J and n^* are obtained accordingly.

If the system reaches the steady state, ie $\partial Pst(x)/\partial t = 0$, Eq.1 can be rewritten as,

$$\frac{\partial(\beta\Delta G(x))}{\partial x} = -\frac{\partial \ln P_{st}(x)}{\partial x} - \frac{J}{D(x)P_{st}(x)}, \tag{4}$$

upon integration yields

$$\beta\Delta G(x) = -\ln P_{st}(x) - J\int \frac{dx'}{D(x')P_{st}(x\prime)} + C, \tag{5}$$

The free energy barrier is then given by[3,4]

$$\beta\Delta G(x) = \ln[B(x)] - \int_{a'}^{x} \frac{dx'}{B(x')} + C, \tag{6}$$

where

$$B(x) = \frac{1}{P_{st}(x)}[\int_0^x P_{st}(x')dx' - JV\tau(x)]. \tag{7}$$

Using the knowledge of $P(n,t)$, J and $\tau(n)$, the nucleation barrier is calculated.

2 Supplemental Figures

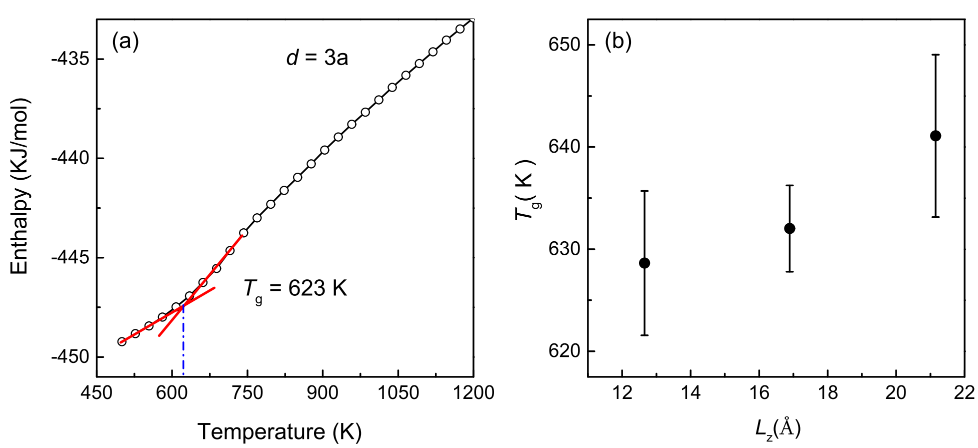

Fig. 1 The glass transition temperature T_g of $Cu_{50}Zr_{50}$ film. (a) The film with the thickness of $d = 3a$. (b) Tg as a function of thickness

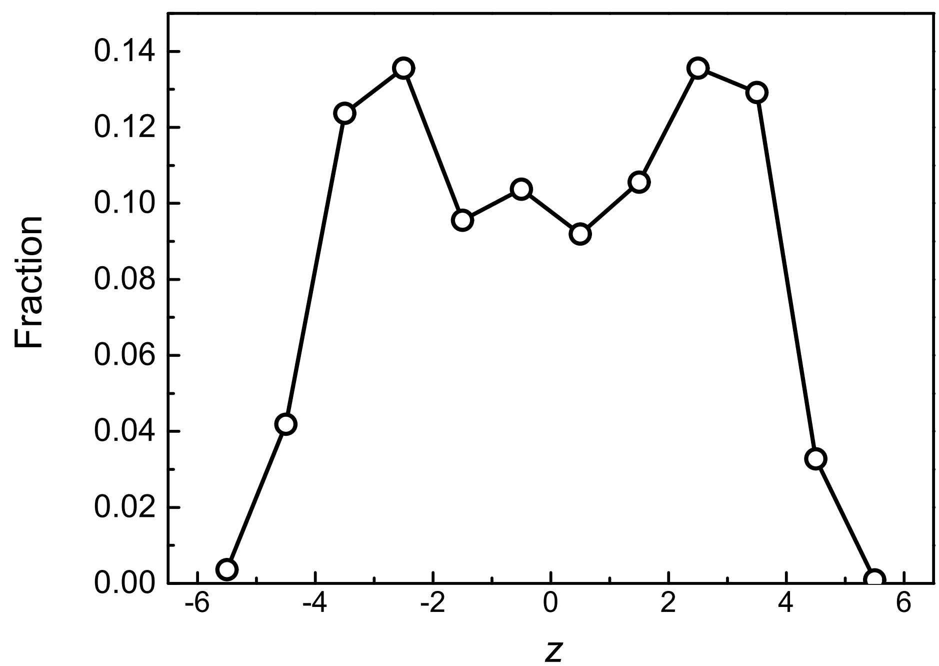

Fig. 2 The location distributions of crystal nucleus for $Cu_{50}Zr_{50}$ film with the thickness of $d = 3a$ along the z direction.

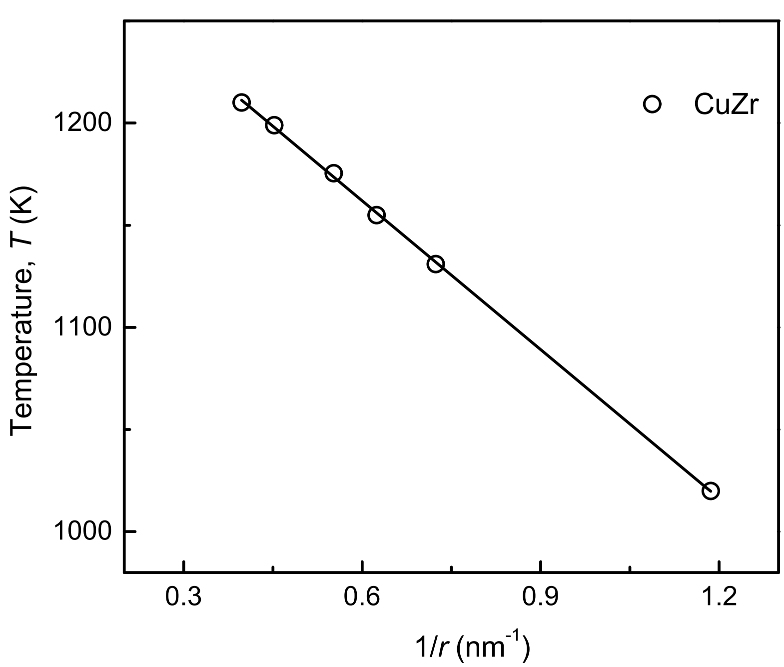

Fig. 3 The liquidsolid equilibrium temperature of sphere-like nucleus versus the inverse of nucleus radius for CuZr. The solid lines are linear fits.

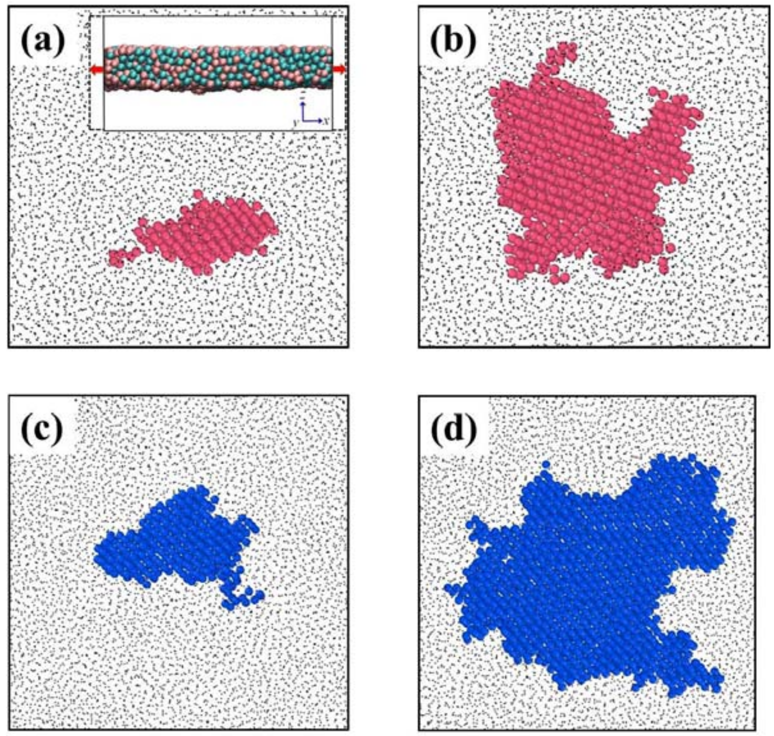

Fig. 4 Morphological evolution of crystal clusters in $Cu_{50}Zr_{50}$ liquid films. The red balls in (a) and (b) represent the cluster shapes for $d = 4a$ at 800 K and the blue balls in (c) and (d) refer to the cluster for $d = 5a$ at 800 K, respectively. The gray dots denote the liquid-like atoms.

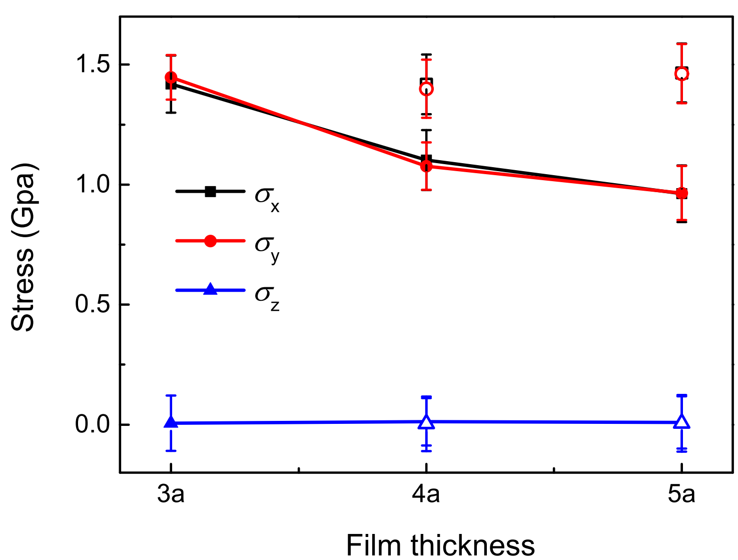

Fig. 5 Stress along the x, y, and z directions for $Cu_{50}Zr_{50}$ film with different thickness ($a = 4.22$ Å, the lattice constant of CuZr compound), the open symbols denote the value of samples when the tensile stresses are applied.

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