Electronic supplementary information

Solute-adsorption enhanced heterogeneous nucleation: effect of Cu adsorption on α -Al nucleation at sapphire substrate

Sida Ma,^a Zihui Dong, ^b Nanfu Zong, ^a Tao Jing, *^a and Hongbiao Dong *^b

1. Construction of the (0001) sapphire/Al solid-solid interfacial structure

Terminations of the (0001) sapphire surface can be classified into two types: non-hydroxylated and hydroxylated ones.¹ Given that adsorption of Al atoms destroys² or eliminates³ the surface hydroxyls, the second type of surface termination was not considered here. For the non-hydroxylated type, four different kinds of surface terminations exist^{4, 5}: (1) 1Al-termination that indicates the surface is terminated by 1 layer of Al atoms, similarly hereafter, (2) O-termination, (3) 2Al-termination, and (4) reconstructed surface. According to Jarvis *et al.*,⁵ the reconstructed surface can be described by the $(\sqrt{31} \times \sqrt{31})R \pm 9^{\circ}$ surface model which was usually approximated by removing the outmost two oxygen layers of the 1Al-terminated sapphire surface in the *ab initio* simulations.^{5, 6} In this work, in order to obtain the neated at 1700 K using the canonical (NVT) ensemble prior to the final relaxation. These four sapphire surfaces were then combined coherently with two 7-layer solid Al slabs to form the sandwich interfacial models using the following orientation relationship (OR)⁷ to form the sapphire/Al interface:

Sapphire
$$(0001) [10\overline{1}0] || AI (111) [1\overline{1}0].$$
 (S1)

Three different interfacial stacking modes of Al (AtopO, AtopAl, and AtopHollow that was designated AtopH)⁸ that ensure the highest symmetry of the interface were considered. For each interface model, a separation curve was calculated firstly (Fig. S1) with both the sapphire substrate and Al kept unrelaxed to

^{a.} School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China.

^{b.} School of Engineering, University of Leicester, Leicester, LE1 7RH, UK.

^{*}Corresponding authors: Tao Jing (<u>jingtao@mail.tsinghua.edu.cn</u>) and Hongbiao Dong (<u>h.dong@le.ac.uk</u>)

obtain a good guess of the initial separation⁷, which was then relaxed to find the equilibrated interfacial geometries. Work of separation W_{sep}^{7} was calculated for each interface using the following formula:

$$W_{\rm sep} = \left[(E_{\rm sapphire} + E_{\rm AI}) - E_{\rm int} \right] / A , \qquad (S2)$$

where E_{int} , $E_{sapphire}$, and E_{Al} are the total energies of the sapphire/Al interface, sapphire substrate, and Al slabs, respectively; A denotes the total interfacial area. W_{sep} quantifies the energy required to separate the interface and was used to determine the most stable interfacial structure in this work.



Fig. S1. Separation curves obtained for the twelve (0001) sapphire/solid Al interfacial models with different sapphire surface terminations ((a) 1Al-termination, (b) 2Al-termination, (c) reconstructed surface, and (d) O-termination) and Al stacking modes (AtopAl, AtopO, and AtopH).



Fig. S2. Initial models (a1) to (d1) and the corresponding optimized interfacial geometries (a2) to (d2) of the (0001) sapphire/Al interface with different sapphire surface terminations. Column 1 to 4 exhibit results obtained using 1Al-terminated, 2Al-terminated, O-terminated, and $(\sqrt{31} \times \sqrt{31})R \pm 9^\circ$ reconstructed sapphire models, respectively. The blue dashed lines indicate the positions of interfaces in these atomic configurations, and the arrows show the position of the 2Al-layer, which is a typical feature of the (0001) sapphire/Al interface.

For each termination, only the relaxed interfacial structure with the lowest total energy (or largest W_{sep}) was retained, which is displayed in Figs. S2. It is interesting to find that an extra Al layer adsorb onto

the 1Al-terminated sapphire surface when it is in contact with the Al slab (Fig. S2 (a2)). This forms a 2Alterminated sapphire surface, which was also observed in Siegel's calculations.⁹ In addition, after relaxation, interfaces with initial 2Al-terminated (Fig. S2 (a2)) and reconstructed (Fig. S2 (a3)) sapphire surfaces exhibit an identical atomic configuration that features an 2Al-layer (indicated by an arrows in Figs. S2 (b2) and (d2)), which are also similar to the structure observed at the relaxed 1Al-terminated sapphire/solid Al interface. However, such a 2Al-layer is not observed at the relaxed interface with initial O-terminated sapphire surface. Instead a 3Al-layer becomes the sapphire surface termination which results from the adsorption of a total (111) Al layer from Al slab onto the O-terminated sapphire surface. In fact, such a situation is unlikely to exist for a solidified sapphire/Al interface, since according to Kang's research¹⁰ and our previous studies,^{11, 12} an O-terminated (0001) sapphire surface will evolve into a 2Alterminated one within several picoseconds when it is brought into contact with Al melt. Therefore, the solidified sapphire/Al interface is expected to evolve into the 2Al-terminated structure, as shown in Fig. S2 (b2).

2. Two-phase thermodynamic (2PT) model

The 2PT approach was initially proposed by Lin *et al.*¹³ and then modified by Desjarlais¹⁴ to solve the "excess entropy" problem caused by the long Lorentzian tail of the hard sphere system. It proves to be a feasible method to estimate the vibrational entropy of melts by using trajectories obtained from the molecular dynamics. The main idea of this method is to decompose the phonon density of state (DoS) function F(v) (v is phonon frequency) of a liquid phase, into a solid-like part $F_{\rm s}(v)$ and a gas-like part $F_{\rm g}(v)$ (schematically presented in Fig. S3) through the following formula:

$$F(\nu) = (1 - f_G)F_S(\nu) + f_GF_G(\nu) .$$
(S3)

 f_{G} is the gas-like fraction of the system. Then vibrational entropy of the liquid phase ΔS_{liq} can be calculated using Eq. (S4):

$$\Delta S_{\text{liq}} = Nk \int_0^\infty d\nu [(1 - f_G) S_{\text{S}}(\nu) W_{\text{S}}(\nu) + f_G S_{\text{G}}(\nu) W_{\text{G}}], \qquad (S4)$$

where $W_{\rm s}(v)$ and $W_{\rm g}$ are weighting functions for solid-like and gas-like components, respectively; N is the number of atoms in the studied liquid system; k is Boltzmann's constant. To obtain $\Delta S_{\rm liq}$, we need to determine F(v), $W_{\rm s}(v)$, $W_{\rm g}$, $f_{\rm g}$ and $S_{\rm g}(v)$.



Fig. S3. Schematic presentation of the 2PT approach.

F(v) was determined through Fourier transformation of velocity autocorrelation function (VAF) $\phi(t)$. Here we followed the definition of the normalized VAF in Ref. ¹⁴:

$$\phi(t) = \left\langle \frac{\sum_{i=1}^{N} m_i \mathbf{v}_i(t) \cdot \mathbf{v}_i(0)}{\sum_{i=1}^{N} m_i \mathbf{v}_i(0) \cdot \mathbf{v}_i(0)} \right\rangle,$$
(S5)

where *i* denotes the atoms in the studied liquid system; m_i is the mass of atom *i*; $\mathbf{v}_i(t)$ and $\mathbf{v}_i(0)$ represent velocities of atom *i* at the starting moment and timestep *t*, respectively. $\langle \cdot \rangle$ indicates average over different time windows. In this work, (0001) sapphire/liquid Al-Cu interfaces were studied using the AIMD method with a timestep of 1.0 fs. The studied interfaces were simulated for 10000 timesteps during which 16 uncorrelated time windows with each length of 0.5 ps were averaged to obtain $\phi(t)$ and the corresponding errors. The obtained $\phi(t)$ was then converted to F(v) through Fourier transformation:

$$F(\nu) = \int_0^{tw} 12\phi(t)\cos(2\pi\nu t)dt , \qquad (S6)$$

where the integration was done over the time window [0, tw].

 $W_{\rm s}(v)$ was derived under the quantum harmonic approximation¹³:

$$W_{\rm s}(\nu) = \frac{h\nu / kT}{\exp(h\nu / kT) - 1} - \ln[1 - \exp(-h\nu / kT)].$$
(S7)

h is the Planck's constant, and *T* is the absolute temperature of the liquid system. To obtain $W_{\rm G}$, $f_{\rm G}$ and $S_{\rm G}(\nu)$, the gas-like phase was modeled by the hard sphere model. A new parameter was defined: $f_{\rm G}^{\rm HS}$ is the hard sphere fluidity factor, which replaces $f_{\rm G}$ hereafter. $f_{\rm G}^{\rm HS}F_{\rm G}(\nu)$ was then given by $F(0)/[1+(2\pi\nu F(0)/f_{\rm G}^{\rm HS})^2]$ according to the hard sphere model. It was modified in Desjarlais' work by using the memory function.¹⁴ $W_{\rm G}$ was expressed as follows,

$$W_{G} = \frac{1}{3} \left\{ \frac{S_{IG}}{k} + \ln[\frac{1+\gamma+\gamma^{2}-\gamma^{3}}{(1-\gamma)^{3}}] + \frac{\gamma(3\gamma-4)}{(1-\gamma)^{2}} \right\}.$$
 (S8)

Different from the weighting function of the solid-like phase $W_{s}(v)$, W_{g} is independent on phonon frequency v. S_{IG} is the ideal gas component with the following formula:

$$S_{IG} = \frac{5}{2}k + k \ln[(\frac{2\pi m kT}{h^2})^{3/2} \frac{\Omega}{f_G^{HS} N}].$$
 (S9)

 Ω is the volume for *N* atoms. γ is the hard sphere packing fraction of the gas-like component, which was obtained by solving the following equation:

$$\frac{2(1-\gamma)^3}{2-\gamma} - \gamma^{2/5} \Delta^{3/5} = 0.$$
 (S10)

 Δ is a constant determined by the system parameters:

$$\Delta = \frac{8}{3}F(0)\sqrt{\frac{\pi kT}{m}} \left(\frac{N}{\Omega}\right)^{1/3} \left(\frac{6}{\pi}\right)^{2/3}.$$
 (S11)

Finally, $f_{\rm G}^{\rm HS}$ was determined as:

$$f_{\rm G}^{\rm HS} = \gamma^{2/5} \Delta^{3/5}$$
. (S12)

By combination of Eq. (S3) to Eq. (S12), vibrational entropy of a liquid phase can be finally obtained.

3. Details of fitting the adhesion-energy and surface-force curves to the Morse potential (Eq. (5)) and force (Eq. (6)) functions

Table S1

Fitting results of the adhesion-energy curves. D_{e} , r_{0} , β and u_{ref} are the fitting parameters as explained in Eq. (5). R-square and RMSE indicate the fitting accuracy. The 95% confidence bounds of D_{e} are also listed in the table.

parameters	D _e	<i>r</i> ₀	β	$u_{\rm ref}$	R-square	RMSE
0 ML	0.59[0.59,0.56]	2.343	1.334	-258.7	0.999	0.0091
1/27 ML	0.65[0.63,0.66]	2.281	1.423	-258.7	0.995	0.4501
1/12 ML	0.68[0.66,0.69]	2.277	1.407	-258.5	0.997	0.1662
1/6 ML	0.72[0.71,0.73]	2.229	1.435	-260.75	0.997	0.1375
1/3 ML	0.76[0.75,0.78]	2.257	1.391	-258.5	0.997	0.0415
2/3 ML	0.86[0.84,0.87]	2.107	1.471	-258.4	0.998	0.0420

Table S2

Fitting results of the surface force curves. D_e , r_0 and β are the fitting parameters in the Morse force function (Equ. (6)). R-square and RMSE measure the fitting accuracy. The 95% confidence bounds of D_e are also shown in the table.

Parameters	D _e	r _o	β	R-square	RMSE
0 ML	0.59[0.56,0.62]	2.350	1.323	0.999	0.0268
1/27 ML	0.70[0.60,0.79]	2.329	1.210	0.984	0.0845
1/12 ML	0.73[0.63,0.82]	2.321	1.208	0.985	0.0806
1/6 ML	0.76[0.68,0.84]	2.260	1.253	0.987	0.0708
1/3 ML	0.80[0.74,0.87]	2.286	1.235	0.993	0.0593
2/3 ML	0.89[0.82,0.95]	2.115	1.277	0.982	0.0566



Fig. S4. Fitting of the adhesion-energy curves ($E^{ad}(z)$) to the Morse potential function (Eq. (5)). $E^{ad}(z)$ was obtained by adhering an Al atomic layer to the <Al-Cu>-terminated (0001) sapphire substrate, where <Al-Cu> denotes the Al-Cu adsorption layer that has been explained in the main text. It should be noted that these adhesion-energy curves have been normalized to the basic (1×1) sapphire substrate. 1/27 ML, 1/12 ML, and 2/3 ML indicate the Cu coverage in the <Al-Cu> layer.



Fig. S5. Fitting of the surface-force curves ($F_z(z)$) to the Morse force function (Eq. (6)). $F_z(z)$ denotes the *z*-component of the force imposed on an Al atom above the sapphire substrate. 0 ML, 1/27 ML, 1/12 ML, 1/3 ML and 2/3 ML indicate the Cu coverage in the <Al-Cu> layer.

4. Calculation of d_{AI-Cu} using molecular dynamics simulations

To calculate d_{AI-Cu} of different Cu concentrations (0.5, 1.0, 1.5, 2.0, 4.0 at. %), a 4.05 nm × 4.05 nm × 4.05 nm pure Al supercell was constructed, which was heat to the desired temperatures (821K and 933 K) with a heating rate of $2 \times 10^{11} \text{ K} \cdot \text{s}^{-1}$ and then was relaxed for 5.0 ns to reach the equilibrated state. For all the simulations, a timestep of 1.0 fs was employed. Then Cu atoms were incorporated by randomly substituting Al atoms in the matrix. For each concentration, 20 randomly generated initial configurations with different Cu distributions were run at the desired temperatures for 5.0 ns to obtain a series of lattice parameters which were averaged to get the final lattice parameter.

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