Effect of Chemical Potential and Atomic-Scale Vibration of Nucleant Surface on Liquid Layering and Heterogeneous Nucleation

SIDA MA, ZIHUI DONG, NANFU ZONG, TAO JING, and HONGBIAO DONG

This study reveals the key role of chemical potential and atomic-scale vibration of the nucleant surface in dictating pre-nucleation liquid-layering and heterogeneous nucleation. The effect of potential-well depth D_w and vibration strength $\bar{\beta}_{\text{std}}$ of the nucleant surface on the layering and nucleation was examined. We found that nucleants with larger D_w and smaller $\bar{\beta}_{\text{std}}$ induce more ordered pre-nucleation layers to enhance nucleation, and proposed that D_w and $\bar{\beta}_{\text{std}}$ shall be considered when searching for effective nucleants.

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PRE-NUCLEATION liquid layering^[1,2] has been accepted as a ubiquitous phenomenon at the heterogeneous nucleation interface.^[3–6] It is triggered by the dangling bonds of the nucleation substrate (NS) surface^[7] and is featured by the formation of partially ordered liquid layers (termed pre-nucleation layers, PNLs) before nucleation takes place.^[1] PNLs can serve as a template to promote nucleation^[8] or manifest as an amorphous or quasicrystal structure to hinder nucleation.^[9] Therefore, it is of necessity to theoretically predict the structural feature of the PNLs to better understand the ensuing nucleation behavior. As an effective descriptor of nucleation potency,^[10] lattice mismatch (f) between NS and nucleus^[11] has been demonstrated to play a vital role in influencing the PNL structure, especially its in-plane order.^[10] It is worth noting that f is not the only intrinsic factor influencing the structural feature of the PNLs. Chemical interaction^[12,13] and dynamics^[14] have also been found to prominently alter the structural feature of a solid/liquid interface. However, it still remains elusive how the effect of f can be coupled with the other factors, or in other words, whether there exists another intrinsic property that plays an as important role as f in determining the PNL structure as well as the subsequent nucleation feature.

To resolve the above issue, the interfaces of liquid Al with a series of commonly used NS including Ti-terminated (111) TiC, Ti-terminated (0001) TiB₂, Al-terminated (0001) AlB₂, Mg-terminated (111) MgO, (112) Al₃Ti, and (0001) sapphire (α -Al₂O₃)^[14] have been comprehensively studied with the aim of establishing a general method to effectively predict the structural feature of the PNLs. *Ab initio* molecular dynamics (AIMD) simulations were conducted using the Vienna Ab-initio Simulation Package, VASP^[15] to model these solid/liquid interfaces. Please refer to the Electronic Supplementary Material (ESM) for the simulation details.

Since the structural feature of the above six interfaces are similar to each other except the degree of order of the PNLs, only four of them (interfaces with TiB₂, TiC, MgO and AlB₂ NS) are presented in detail, with the other two shown in ESM. Figure 1 depicts the out-of-plane and in-plane structural features of the studied NS/liquid Al interfaces which are all equilibrated at 950 K, a temperature higher than the Al melting point T_m (933 K). From the atomic density profiles (ρ_z) and the in-plane atomic density distributions ($\rho_{||}$) (Figures 1(f) through (i)) as well as the typical interfacial atomic arrangements (Figure S-2 in ESM), PNLs with apparently different degree of order are observed whose formation processes are described by the ρ_z contours (insets in Figures 1(b) through (e)) as a function of simulation time. It is found that formation of these PNLs is roughly within 10.0 ps, and a much longer simulation time is set to ensure their equilibrium. It should be noted that all these four NS tend to form an orientation relationship of NS/(111) Al,^[16–22] which can also be illustrated by $\rho_{||}$ and the in-plane bond-angle distributions in Figure 2(a). This allows us to simplify the structural analysis to the comparison of the degree of order. Here, we propose to quantify the degree of

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In-plane atomic density of PNL1

◀Fig. 1—Atomic density profiles (ρ_z) of Al at the interfaces (schematically represented in (a) of liquid Al with (b) Ti-terminated (111) TiC, (c) Ti-terminated (0001) TiB₂, (d) Mg-terminated (111) MgO, and (e) Al-terminated (0001) AlB₂ NS. These results are calculated at 950 K using the AIMD method. Inset in (b) through (e) are the ρ_z contours as a function of time showing the evolution feature of the PNLs. PNL1, PNL2, PNL3 in (b) represent the first three pre-nucleation layers, and $\rho_{\max}$ in (c) denotes the peak atomic density of PNL1. (f) through (i) Depict the in-plane atomic density distributions of the PNL1 at the above four interfaces.

order using the peak atomic density of PNL1 ($\rho_{\max}$) as shown in Figures 1(b) and (c). In fact, $\rho_{\max}$ also plays a critical role in influencing the nucleation mode which will be explained later. In Figure 2(b), the relationship among $\rho_{\max}$, f (see ESM for more details), and the orientational order parameter (q_6)^[23] are summarized. A similar trend between $\rho_{\max}$ and q_6 is observed, indicating that $\rho_{\max}$ is also effective in representing the degree of in-plane order which is quantitatively described by q_6 .^[23] More importantly, a positive correlation between $\rho_{\max}$ and f is observed (except the interface with sapphire NS), which is supposed to be a negative relationship since a larger f brings a higher barrier for liquid layering.

The above finding illustrates that f alone is insufficient to predict the structural feature of the PNLs. Following our previous modeling,^[1] the free-energy change associated with the PNL formation is expressed as follows:

$$\Delta G_{\text{PNL}} = (\gamma_{\text{NS-PNL}} - \gamma_{\text{NS-L}} + \gamma_{\text{PNL-L}} + \gamma_0 e^{-l/l_0}) \cdot A + (\Delta g_v + \varepsilon(f, M)) \cdot A \cdot l. \quad [1]$$

$\gamma_{\text{NS-PNL}}$, $\gamma_{\text{NS-L}}$ and $\gamma_{\text{PNL-L}}$ are the interfacial free energies of the NS-PNL, NS-liquid, and PNL-liquid interfaces (Figure 3(a)). $\gamma_0 e^{-l/l_0}$ is the gradient energy stored in the PNLs where l and l_0 are the PNL width and the interaction length,^[24] respectively, and $\gamma_0 = \gamma_{\text{NS-L}} - (\gamma_{\text{NS-PNL}} + \gamma_{\text{PNL-L}})$.^[25] Δg_v denotes the volumetric Gibbs-free energy change, and $\varepsilon(f, M)$ represents the interfacial strain energy density that is affected by the lattice mismatch f and elastic modulus M . A is the section area. In Eq. [1], only $\gamma_{\text{NS-PNL}} - \gamma_{\text{NS-L}}$ and $\varepsilon(f, M)$ are influenced by the NS, in which the role of $\varepsilon(f, M)$ has been discussed above. Therefore, more attention should be paid to uncover the role of $\gamma_{\text{NS-PNL}} - \gamma_{\text{NS-L}}$ in dictating the degree of order of the PNLs.

Additionally, according to our previous study,^[1] interfacial dynamics can also influence the PNL structure. In this work, phonon density of states (DoS) is computed (see ESM for more details) within the four sub-regions of each interface (Figures 3(c) through (f)) to characterize the interfacial dynamics. It is interesting to find Phonon DoS of the NS termination-layer and the PNLs exhibit a transition feature to accommodate the dynamical difference between the bulk NS and bulk Al sub-regions. Moreover, it is observed that the NS termination-layer exhibit a more similar vibrational characteristic to the PNLs instead of to the bulk NS. This suggests the vibration of the NS termination-layer should significantly influences the dynamics of the PNLs. Figure 3(b) shows the typical vibration profiles

of the NS termination-layers at the four focused interfaces. It illustrates that vibration leads to an atomic-scale corrugation of the NS surface. And presumably the different vibration feature of the four NS surfaces should cause different effects on the degree of order of the PNLs. On this ground, the NS surface vibration should also be considered to better estimate the structural feature of the PNLs.

At the atomic scale, $\gamma_{\text{NS-PNL}} - \gamma_{\text{NS-L}}$ and NS surface vibration are modeled as the NS surface potential-well depth D_w (Figures 4(a) and (b)) and vibration strength β_{std} (Figure 4(c)), respectively. As shown in Figure 4(a), liquid layering can be described as a process in which atoms gradually aggregate to the bottom of the potential well induced by the NS surface. Energy reduction associated with this process is exactly $\gamma_{\text{NS-PNL}} - \gamma_{\text{NS-L}}$ which serves as the only driving for pre-nucleation liquid layering and can be effectively indicated by D_w . D_w reflects the interfacial chemical affinity, and is computed following the next two steps based on *ab initio* calculations. (1) Discrete total energy points with different $d_{\text{NS-Al}}$ (distance of an Al atomic layer to NS surface) are first computed, (2) which are fitted to the Morse potential (Eq. [2]), to obtain the surface potential $U(d_{\text{NS-Al}})$:

$$U(d_{\text{NS-Al}}) = D_w((1 - e^{-\beta(d_{\text{NS-Al}} - d_0)})^2 - 1) + U_{\text{inf}}, \quad [2]$$

where D_w , β , d_0 , U_{inf} are all fitting parameters. We note that the Morse potential has been tested to be an appropriate function to described the NS-Al interaction.

$U(d_{\text{NS-Al}})$ of the four focused NS are fitted using MATLAB whose R^2 are all larger than 0.99 indicating an excellent fitting accuracy (details are shown in the Figure S-4 in ESM). To better compare $U(d_{\text{NS-Al}})$ of different NS, they are normalized to $\bar{U}(d_{\text{NS-Al}})$ as displayed in Figure 4(b):

$$\bar{U}(d_{\text{NS-Al}}) = \frac{1}{N}(U(d_{\text{NS-Al}} - d_0) - U_{\text{inf}}), \quad [3]$$

where N denotes the number of atoms in the Al atomic layer adhering to the NS. It is clearly illustrated that D_w of the TiC and TiB₂ NS are obviously larger than those of the MgO and AlB₂ NS. This indicates that a greater chemical driving force is provided by the TiC and TiB₂ NS to promote the ordering of the PNLs, which is in keeping with the $\rho_{\max}$ trend as illustrated in Figure 4(d).

Vibration strength β_{std} is defined as follows:

$$\beta_{\text{std}} = \sqrt{\frac{\sum_{i=1}^n (z_i - \bar{z})^2}{n}}, \quad [4]$$

where n is the number of atoms in the NS termination-layer; z_i is the z -coordinate of atom i , and $\bar{z}$ is the average of z_i . β_{std} distributions $P(\beta_{\text{std}})$ of the four interfaces are depicted in Figure 4(c) where $\bar{\beta}_{\text{std}}$ indicates the mean of β_{std} . Our previous study has demonstrated that a large $\bar{\beta}_{\text{std}}$ is an impediment to the PNL formation,^[14] from which it can be deduced that a larger $\bar{\beta}_{\text{std}}$ would lead to a smaller $\rho_{\max}$. Such a deduction is

Fig. 2—(a) Bond-angle distributions within the PNL1 induced by different NS. (b) The correlation among $\rho_{\max}$, q_6 and f at the NS/liquid Al interfaces.

consistent with the $\rho_{\max}$ - $\bar{\beta}_{\text{std}}$ relationship shown in Figure 4(d).

In fact, D_w and $\bar{\beta}_{\text{std}}$ have opposite effects on the PNL formation with the former promoting while the latter hindering it. It should be the coupled effect of these two factors that determines $\rho_{\max}$. Here, we use a concise formulation to describe the coupling of D_w and $\bar{\beta}_{\text{std}}$ - $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$, where $\langle \cdot \rangle$ denotes the normalization of the parameter relative to the TiC NS, *i.e.*, $\langle D_w \rangle = D_w / D_w^{\text{TiC}}$ and $\langle \bar{\beta}_{\text{std}} \rangle = \bar{\beta}_{\text{std}} / \bar{\beta}_{\text{std}}^{\text{TiC}}$. Dependency of $\langle \rho_{\max} \rangle$ on $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ is depicted in Figure 5, in which the B-terminated (0001) AlB₂ NS is added. It should be noted that at the (0001) AlB₂/liquid Al interface, the PNL1 is in contact with the B-terminating layer of the NS, which presents different D_w and $\bar{\beta}_{\text{std}}$ with the Al-terminated (0001) AlB₂ NS (see Figure S-5 in ESM for more details). A two-regime feature of the $\langle \rho_{\max} \rangle$ - $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ relationship is observed. In regime I, $\langle \rho_{\max} \rangle$ grows in an exponential manner; in regime II, $\langle \rho_{\max} \rangle$ gradually approaches to a constant value of the solid phase when $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ is sufficiently large. This implies that only the NS with a large D_w and meanwhile a small $\bar{\beta}_{\text{std}}$ is capable to induce a highly order PNL structure. We note that the above $\langle \rho_{\max} \rangle$ - $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ correlation is obtained based on the PNL structures above T_m . To test its applicability under supercooled conditions, the NS/liquid Al interfaces are cooled to 900 K (below T_m). Figures 6(a) through (d) compare the ρ_z obtained at 950 K and 900 K, which clearly illustrate that the $\rho_{\max}$ trend observed at 950 K maintains when the liquid Al is supercooled.

Finally, the effect of $\rho_{\max}$ on heterogeneous nucleation will be analyzed. As schematically illustrated in Figures 6(e) and (f), a premise of the epitaxial-growth-based nucleation^[8] is proposed to be the formation of a PNL1 with a sufficiently high degree of order (or a large enough $\rho_{\max}$), since a poorly ordered PNL1 impedes the subsequent liquid layering which is believed to be the basis of epitaxial heterogeneous nucleation. The case of (0001) AlB₂ NS (Figure 6(d)) well explains such an argument. It is clearly observed that liquid Al adjacent to the (0001) AlB₂ NS (Figure 6(d)) presents a much poorer layering ability compared with the (0001) TiB₂ NS (Figure 6(b)), even though f of the (0001) AlB₂/Al interface is smaller than that of (0001) TiB₂/Al interface. This is caused by the poorly ordered PNL1 adjacent to the (0001) AlB₂ NS. It can be deduced that the epitaxial heterogeneous nucleation mode is more difficult to be triggered by the (0001) AlB₂ NS than the (0001) TiB₂ NS. Instead, the classical nucleation theory (CNT)-based nucleation mode is more likely to happen on the (0001) AlB₂ NS (Figure 6(f)), similar to the previously studied (0001) sapphire NS.^[11] The above discussion demonstrates that $\rho_{\max}$ plays a critical role in determining the heterogeneous nucleation mode: a large $\rho_{\max}$ tends to trigger the epitaxial heterogeneous nucleation mode (Figure 6(e)) while a small $\rho_{\max}$ is likely to induce the CNT-based nucleation mode (Figure 6(f)). It is also worth noting that more liquid layers are induced by the (0001) TiB₂ NS (Figure 6(b)) than the (111) TiC NS (Figure 6(a)) at 900 K. This suggests a better nucleation potency of the (111) TiB₂/Al interface despite a very close $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$

Fig. 3—(a) A schematic representation of the NS/liquid Al interfaces before and after the formation of the PNLs. (b) Typical vibration profiles of the NS termination-layers at four NS/liquid Al interfaces. (c) through (f) Phonon DoS ($F(\nu)$) computed within different sub-regions of the above four NS/liquid Al interfaces.

Fig. 4—(a) TiB₂-induced liquid Al layering and a schematic diagram of the NS surface potential $U(d_{\text{NS-Al}})$. D_w denotes the surface potential-well depth; d_w shows the bottom of the potential well, where the PNL1 forms. (b) Normalized surface potentials, $U(d_{\text{NS-Al}})$, above four different NS. (c) β_{std} distributions ($P(\beta_{\text{std}})$) at the NS/liquid Al interfaces with different NS, where the mean of $P(\beta_{\text{std}})$, $\bar{\beta}_{\text{std}}$, is indicated by the dashed lines. (d) The relationships of ρ_{max} with D_w and $\bar{\beta}_{\text{std}}$.

Fig. 5—Dependency of $\langle \rho_{\text{max}} \rangle$ on $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ illustrated by seven different NS/liquid Al interfacial systems. Trend lines (both the solid and dashed lines) are plotted, which suggest a two-regime feature of the $\langle \rho_{\text{max}} \rangle$ - $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ correlation.

for these two NS (Figure 5), which is ascribed to the smaller f of the (111) TiB₂/Al interface. Such a phenomenon implies that neither $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ nor f should be neglected when searching for effective NS to promote or hinder nucleation.

In summary, large-scale AIMD simulations were performed to compare the structural feature of the PNLs at seven different NS/liquid interfaces. It is observed that NS with larger $\langle D_w \rangle / \langle \bar{\beta}_{\text{std}} \rangle$ tends to induce a more ordered PNL-structure. This is demonstrated to promote the epitaxial-growth based heterogeneous nucleation and meanwhile enhance the nucleation potency if f keeps unchanged. We emphasize the non-negligible role of the chemical potential and atomic-scale vibration of the NS surface in affecting the pre-nucleation liquid layering and nucleation, which should be considered to search for or design new NS to tune nucleation in addition to the lattice mismatch.

Fig. 6—(a) through (d) Comparison of the NS-induced liquid layering at 950 K and 900 K. Al atomic density profiles (ρ_z) of the (a) (111) TiC/Al, (b) (0001) TiB₂/Al, (c) (111) MgO/Al, and (d) (0001) AlB₂/Al interfaces are studied, respectively. (e) and (f) Schematically illustrate how the degree of order of the PNLs affects nucleation mode.

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SUPPLEMENTARY INFORMATION

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