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

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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 $\beta_{\text{std}}$ of the nucleant surface on the layering and nucleation was examined. We found that nucleants with larger $D_w$ and smaller $\beta_{\text{std}}$ induce more ordered pre-nucleation layers to enhance nucleation, and proposed that $D_w$ and $\beta_{\text{std}}$ shall be considered when searching for effective nucleants.

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Pre-nucleation liquid layering has been accepted as a ubiquitous phenomenon at the heterogeneous nucleation interface. It is triggered by the dangling bonds of the nucleation substrate (NS) surface and is featured by the formation of partially ordered liquid layers (termed pre-nucleation layers, PNLs) before nucleation takes place. PNLs can serve as a template to promote nucleation or manifest as an amorphous or quasicrystal structure to hinder nucleation. 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, lattice mismatch between NS and nucleus has been demonstrated to play a vital role in influencing the PNL structure, especially its in-plane order. It is worth noting that $f$ is not the only intrinsic factor influencing the structural feature of the PNLs. Chemical interaction and dynamics 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) TiB$_2$, Al-terminated (0001) AlB$_2$, Mg-terminated (111) MgO, (112) Al$_3$Ti, and (0001) sapphire ($\alpha$-Al$_2$O$_3$) 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 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 TiB$_2$, TiC, MgO and AlB$_2$ 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 and the in-plane bond-angle distributions in Figure 2(a), it can be illustrated by $\rho_t$ and the in-plane atomic density distributions ($\rho_{\parallel}$) (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 $\rho_t$ 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, which can also be illustrated by $\rho_t$ 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...
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 ($q_0$) are summarized. A similar trend between $\rho_{max}$ and $q_0$ is observed, indicating that $\rho_{max}$ is also effective in representing the degree of in-plane order which is quantitatively described by $q_0$. 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\cite{1} the free-energy change associated with the PNL formation is expressed as follows:

$$D_{PNL} = (\gamma_{NS-PNL} - \gamma_{NS-L} + \gamma_{PNL-L} + \gamma_0 e^{-l/b}) \cdot A + (\Delta g_v + e(f, M)) \cdot A \cdot l.$$  

where $\gamma_{NS-PNL}$, $\gamma_{NS-L}$ and $\gamma_{PNL-L}$ are the interfacial free energies of the NS-PNL, NS-liquid, and PNL-liquid interfaces (Figure 3(a)). $\gamma_0 e^{-l/b}$ is the gradient energy stored in the PNLs where $l$ and $l_0$ are the PNL length and the interaction length, respectively, and $\gamma_0 = \gamma_{NS-L} - \gamma_{NS-PNL} - \gamma_{PNL-L}$ (see ESM). $\Delta g_v$ denotes the volumetric Gibbs-free energy change, and $e(f, M)$ 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 $\gamma_{NS-PNL} - \gamma_{NS-L}$ and $e(f, M)$ are influenced by the NS, in which the role of $e(f, M)$ has been discussed above. Therefore, more attention should be paid to uncover the role of $\gamma_{NS-PNL} - \gamma_{NS-L}$ in dictating the degree of order of the PNLs.

Additionally, according to our previous study\cite{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, $\gamma_{NS-PNL} - \gamma_{NS-L}$ and NS surface vibration are modeled as the NS surface potential-well depth $D_w$ (Figures 4(a) and (b)) and vibration strength $\beta_{std}$ (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 $\gamma_{NS-PNL} - \gamma_{NS-L}$ 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 $d_{NS-Al}$ (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 $U(d_{NS-Al})$:

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

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

$U(d_{NS-Al})$ 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 $U(d_{NS-Al})$ of different NS, they are normalized to $U(d_{NS-Al})$ as displayed in Figure 4(b):

$$U(d_{NS-Al}) = \frac{1}{N}(U(d_{NS-Al}) - d_0) - U_{inf}),$$  

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 TiB$_2$ NS are obviously larger than those of the MgO and AlB$_2$ NS. This indicates that a greater chemical driving force is provided by the TiC and TiB$_2$ 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 $\beta_{std}$ is defined as follows:

$$\beta_{std} = \sqrt{\frac{\sum^n_{i=1} (z_i - \bar{z})^2}{n}},$$  

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 $z_i$. $\beta_{std}$ distributions $P(\beta_{std})$ of the four interfaces are depicted in Figure 4(c) where $\beta_{std}$ indicates the mean of $\beta_{std}$. Our previous study has demonstrated that a large $\beta_{std}$ is an impediment to the PNL formation,\cite{14} from which it can be deduced that a larger $\beta_{std}$ would lead to a smaller $\rho_{max}$. Such a deduction is
consistent with the $\rho_{\text{max}}-\bar{\beta}_{\text{std}}$ 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 $\rho_{\text{max}}$. Here, we use a concise formulation to describe the coupling of $D_w$ and $\bar{\beta}_{\text{std}}$/C0h $D_w$ = $h_{\beta_{\text{std}}} = \frac{\rho_{\text{max}}}{\rho_{\text{TiC}}}$. Dependency of $\rho_{\text{max}}$ on $\bar{\beta}_{\text{std}}$ is depicted in Figure 5, in which the B-terminated (0001) AlB$_2$ NS is added. It should be noted that at the (0001) AlB$_2$/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) AlB$_2$ NS (see Figure S-5 in ESM for more details). A two-regime feature of the $\rho_{\text{max}}$ relationship is observed. In regime I, $\rho_{\text{max}}$ grows in an exponential manner; in regime II, $\rho_{\text{max}}$ gradually approaches to a constant value of the solid phase when $\bar{\beta}_{\text{std}}$ 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 $\rho_{\text{max}} = \langle D_w \rangle$ 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 $\rho_{\text{max}}$ obtained at 950 K and 900 K, which clearly illustrate that the $\rho_{\text{max}}$ trend observed at 950 K maintains when the liquid Al is supercooled.

Finally, the effect of $\rho_{\text{max}}$ 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 $\rho_{\text{max}}$), since a poorly ordered PNL1 impedes the subsequent liquid layering which is believed to be the basis of epitaxial heterogenous nucleation. The case of (0001) AlB$_2$ NS (Figure 6(d)) well explains such an argument. It is clearly observed that liquid Al adjacent to the (0001) AlB$_2$ NS (Figure 6(d)) presents a much poorer layering ability compared with the (0001) TiB$_2$ NS (Figure 6(f)), even though $f$ of the (0001) AlB$_2$/Al interface is smaller than that of (0001) TiB$_2$/Al interface. This is caused by the poorly ordered PNL1 adjacent to the (0001) AlB$_2$ NS. It can be deduced that the epitaxial heterogeneous nucleation mode is more difficult to be triggered by the (0001) AlB$_2$ NS than the (0001) TiB$_2$ NS. Instead, the classical nucleation theory (CNT)-based nucleation mode is more likely to happen on the (0001) AlB$_2$ NS (Figure 6(f)), similar to the previously studied (0001) sapphire NS.[1]

The above discussion demonstrates that $\rho_{\text{max}}$ plays a critical role in determining the heterogeneous nucleation mode: a large $\rho_{\text{max}}$ tends to trigger the epitaxial heterogeneous nucleation mode (Figure 6(e)) while a small $\rho_{\text{max}}$ 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) TiB$_2$ NS (Figure 6(b)) than the (111) TiC NS (Figure 6(a)) at 900 K. This suggests a better nucleation potency of the (111) TiB$_2$/Al interface despite a very close $\langle D_w \rangle$.
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 ($F(v)$) computed within different sub-regions of the above four NS/liquid Al interfaces.
for these two NS (Figure 5), which is ascribed to the smaller $f$ of the (111) TiB$_2$/Al interface. Such a phenomenon implies that neither $h_{Dw}$ 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 $\langle D_{w} \rangle / \langle P_{std} \rangle$ 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.
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SUPPLEMENTARY INFORMATION

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