Supplementary information for “Effective chemical potential for non-equilibrium system and its application to molecular beam epitaxy of Bi$_2$Se$_3$”

Na Wang$^{1,2,3}$, Damien West$^3$, Wenhui Duan$^1$, and S. B. Zhang$^{3,4}$

$^1$Department of Physics, Tsinghua University, Beijing 100084, China

$^2$Department of Physical Chemistry, University of Science and Technology Beijing, Beijing 100083, China

$^3$Department of Physics, Applied Physics & Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180

$^4$Beijing Computational Science Research Center, Beijing 100193, China
General expression for the association rate $k_{\alpha}^{+i}$

When the association is not diffusion-limited, the following rate equation applies [1],

$$k_{\alpha}^{+i} = 2\pi(D_\alpha + D_i)\frac{k_{\alpha,0}^{+i}}{k_{\alpha,0}^{+i} + k_{\alpha@i}^{-i}}$$

(S1)

where

$$k_{\alpha,0}^{+i} = \nu \exp(-\varphi_{\alpha,0}^{+i}/kT)$$

(S2)

is the on-site association rate between cluster $\alpha$ and cluster $i$. Here, on-site means the two clusters are nearest-neighbor clusters (denoted as $\alpha@i$), and

$$k_{\alpha@i}^{-i} = \nu \exp(-\varphi_{\alpha@i}^{-i}/kT)$$

(S3)

is the dissociation rate of the above nearest-neighbor cluster pair $\alpha@i$. $k_{\alpha@i}^{-i}$ enters the denominator in Eq. (S1) because it competes with on-site association to form cluster $\alpha + i$. In Eqs. (S2) and (S3), $\varphi_{\alpha,0}^{+i}$ and $\varphi_{\alpha@i}^{-i}$ are the respective activation barriers.
FIG. S1: (a) Calculated association barriers ($\varphi_{\alpha}^{+i}$) for the clusters in Fig. 2. (b) Concentrations of
the clusters: (red open squares) both association and diffusion processes are considered; (black
filled squares) only diffusion-limited process is considered. In the calculation, we ignore the
weak interaction between clusters, whereby we approximate $\varphi_{\alpha,0}^{+i} \approx E_{0\alpha} + E_{0i} - E_{0\alpha+i} + \varphi_{\alpha+i}^{-i}$,
where $E_{0\alpha}$ is the total energy of cluster $\alpha$ on the surface relative to the isolated constituent atoms,
and $\varphi_{\alpha+i}^{-i} \approx \varphi_{diff}^{diff}$. The reason that the diffusion-limited-process assumption works for Bi$_2$Se$_3$ is
because the most probable clusters, i.e., atomic Se and BiSe$_2$, happen to have the largest
diffusion barriers in Fig. 3(a).
FIG. S2: Cluster concentration $c_\alpha$ as a function of the maximum cluster size $N_{max}$ used in the calculation, which is defined by the red dashed lines in the inset. In principle, two clusters can associate to form a larger one so the inclusion of larger clusters will affect the concentration of the smaller clusters. If we define $\delta N_\alpha = N_{max} - N_\alpha$, where $N_\alpha$ is the size of cluster $\alpha$, then the effect of $N_{max}$ on $c_\alpha$ appears to be the largest only when $\delta N_\alpha = 1$, as can be seen in Fig. S2. In the current study, we choose $N_{max} = 4$ but exclude Bi$_3$Se for its relatively high energy. We also include Bi$_2$Se$_3$ in the cluster set for it is the smallest molecular unit to build bulk Bi$_2$Se$_3$. Our use of $N_{max} = 4$ is reasonable, as our results show that the largest cluster relevant to the growth, BiSe$_2$, has $N_{max} = 3$. 

FIG. S3: Desorption barrier ($\varphi_{des}^d$) for molecular clusters ($\text{Bi}_2\text{Se}_3)_n$, as a function of molecule size $n$. The general trend is that as $n$ increases, it gets harder to desorb the molecules.
FIG. S4: Calculated (a) cluster concentration $c_\alpha$ and (b) chemical potential $\mu_\alpha$, as a function of the predetermined island density $c_{isl}$. These results show that the change in $\mu_\alpha$ due to $c_{isl}$ is relatively small, only 0.3 eV, which is on par with the numerical accuracy achievable in this kind of calculations.

Reference