Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary information for "Effective chemical potential for non-equilibrium system and its application to molecular beam epitaxy of Bi_2Se_3"

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General expression for the association rate k_{α}^{+i}

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

$$k_{\alpha}^{+i} = 2\pi\left(D_{\alpha} + D_{i}\right)\frac{k_{\alpha,0}^{+i}}{k_{\alpha,0}^{+i} + k_{\alpha\oplus i}^{-i}}, \tag{S1}$$

where

$$k_{\alpha,0}^{+i} = \nu\, Exp(-\varphi_{\alpha,0}^{+i}/kT) \tag{S2}$$

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

$$k_{\alpha\oplus i}^{-i} = \nu\, Exp(-\varphi_{\alpha\oplus i}^{-i}/kT) \tag{S3}$$

is the dissociation rate of the above nearest-neighbor cluster pair $\alpha\oplus i$. $k_{\alpha\oplus i}^{-i}$ 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 $\varphi_{\alpha\oplus i}^{-i}$ are the respective activation barriers.

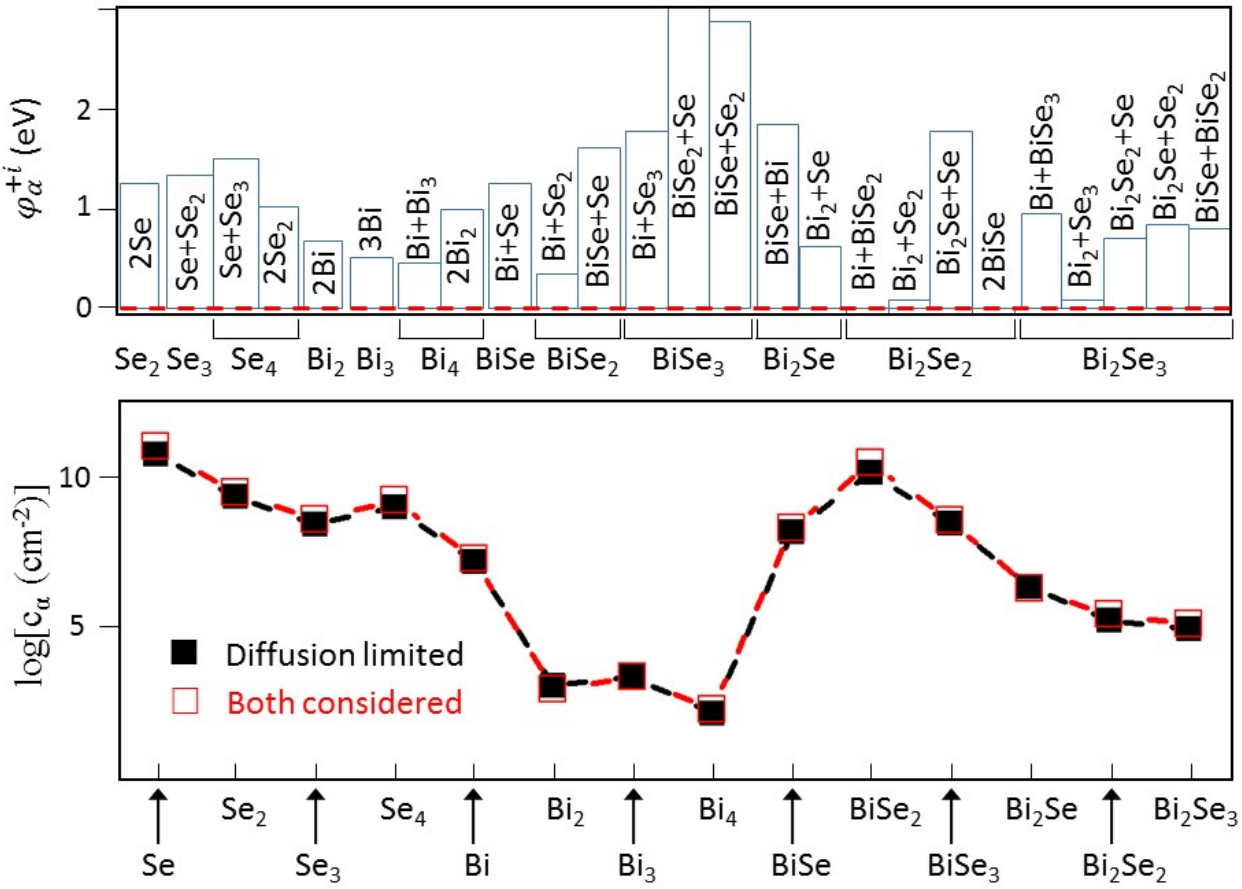

FIG. S1: (a) Calculated association barriers (φ_α^{+i}) for the clusters in Fig. 2. (b) Concentrations of the clusters: (red open squares) both association and diffusion processes are considered; (black filled squares) only diffusion-limited process is considered. In the calculation, we ignore the weak interaction between clusters, whereby we approximate $\varphi_{\alpha,0}^{+i} \simeq E_{0\alpha} + E_{0i} - E_{0\alpha+i} + \varphi_{\alpha+i}^{-i}$, where $E_{0\alpha}$ is the total energy of cluster α on the surface relative to the isolated constituent atoms, and $\varphi_{\alpha\oplus i}^{-i} \simeq \varphi_i^{diff}$. The reason that the diffusion-limited-process assumption works for Bi_2Se_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).

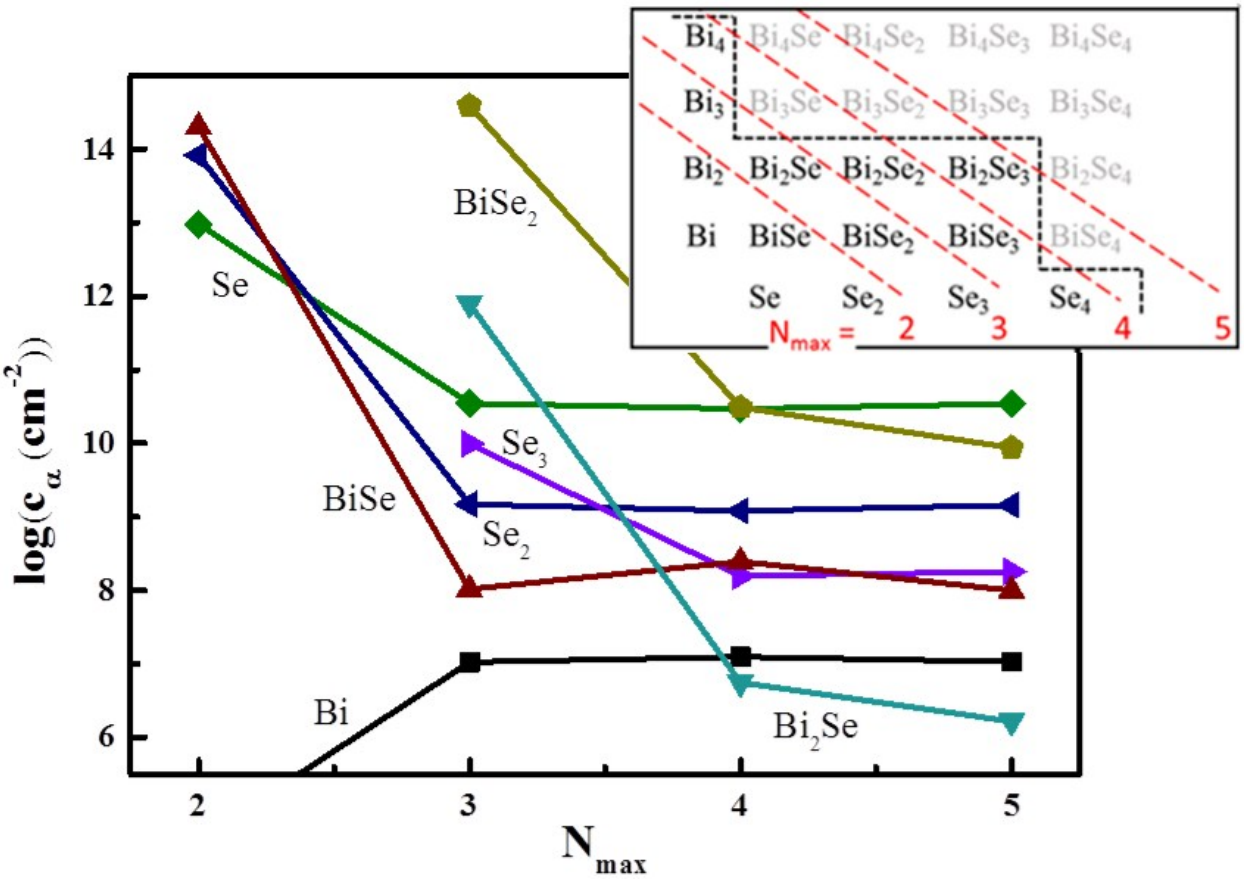

FIG. S2: Cluster concentration c_α as a function of the maximum cluster size N_{max} used in the calculation, which is defined by the red dashed lines in the inset. In principle, two clusters can associate to form a larger one so the inclusion of larger clusters will affect the concentration of the smaller clusters. If we define $\delta N_\alpha = N_{max} - N_\alpha$, where N_α is the size of cluster α, then the effect of N_{max} on c_α 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_3Se for its relatively high energy. We also include Bi_2Se_3 in the cluster set for it is the smallest molecular unit to build bulk Bi_2Se_3. Our use of $N_{max} = 4$ is reasonable, as our results show that the largest cluster relevant to the growth, $BiSe_2$, has $N_{max} = 3$.

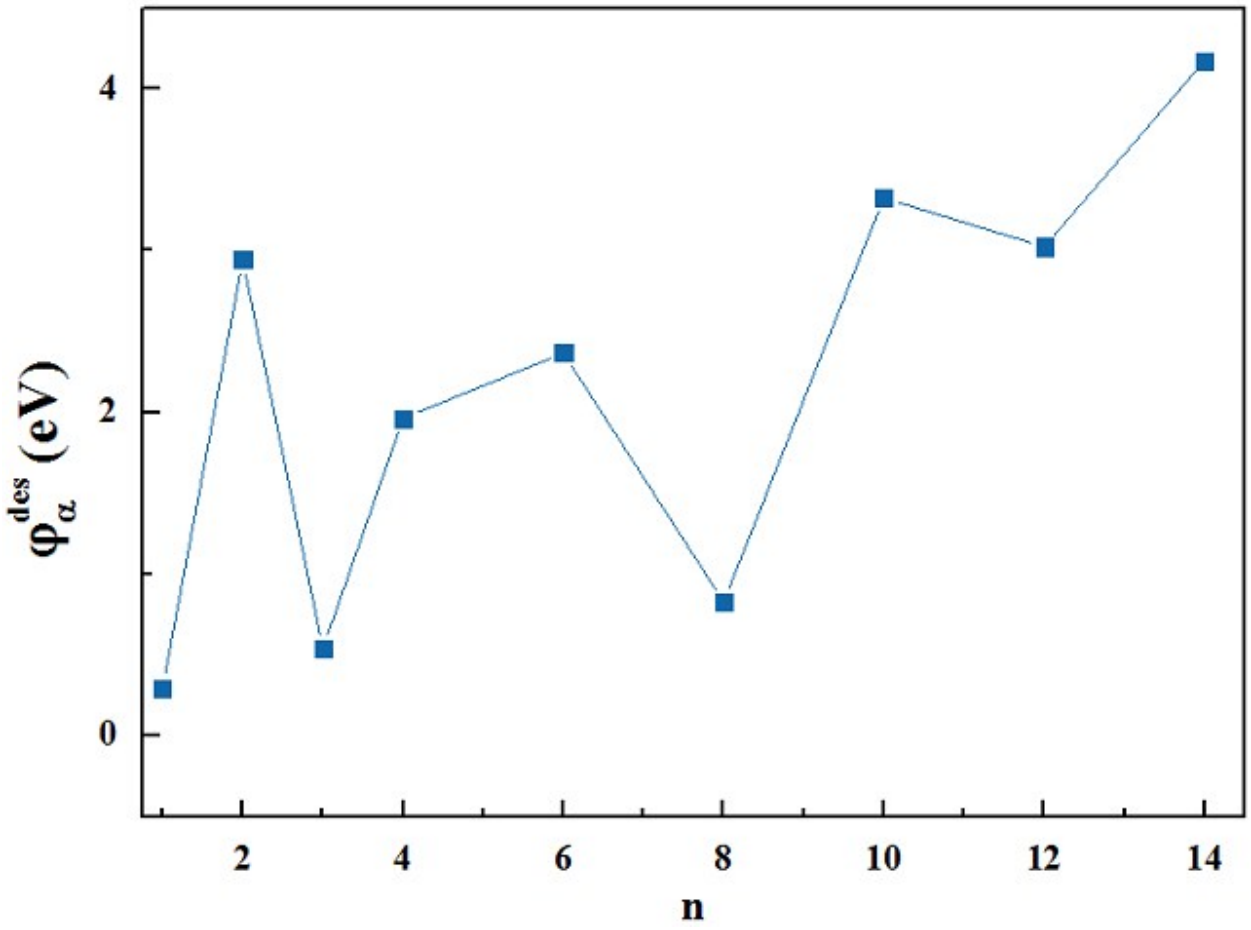

FIG. S3: Desorption barrier (φ_α^{des}) for molecular clusters $(Bi_2Se_3)_n$, as a function of molecule size *n*. The general trend is that as *n* increases, it gets harder to desorb the molecules.

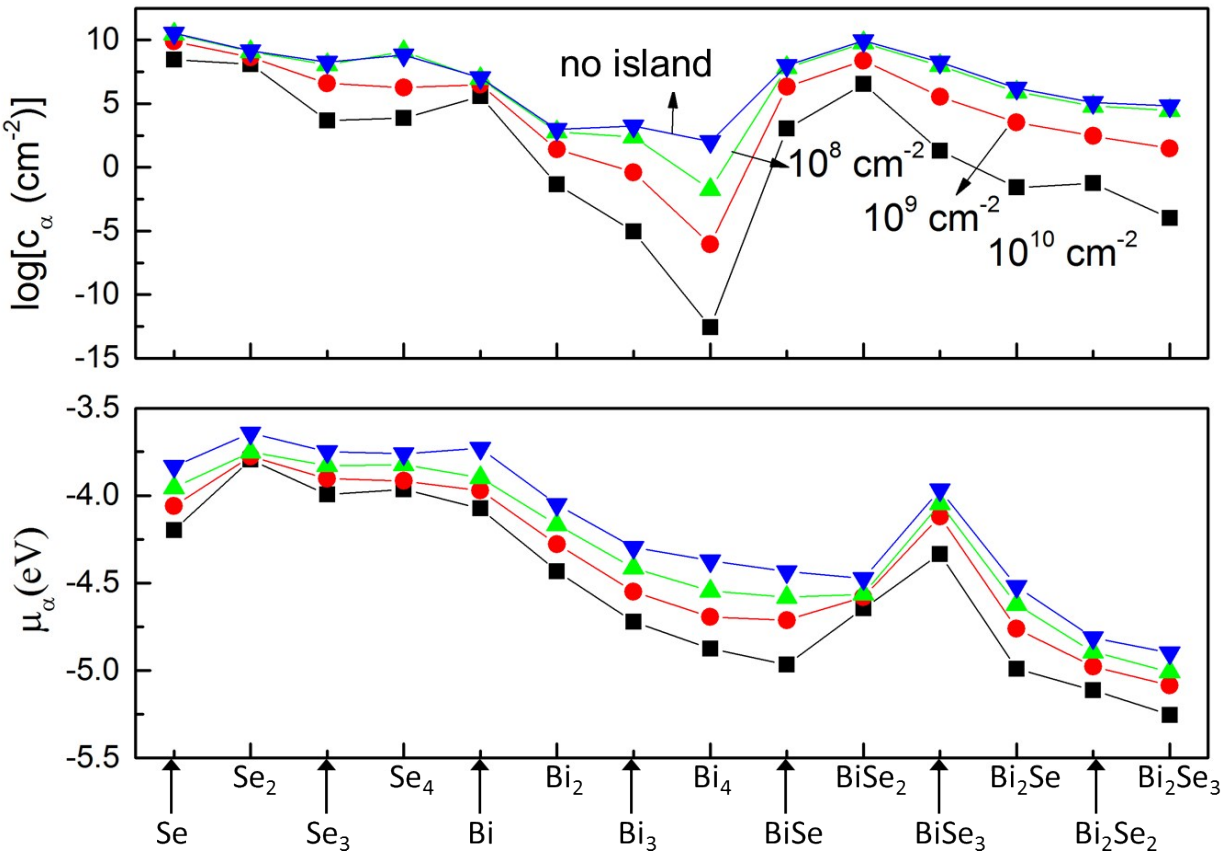

FIG. S4: Calculated (a) cluster concentration c_α and (b) chemical potential μ_α, as a function of the predetermined island density c_{isl}. These results show that the change in μ_α due to c_{isl} is relatively small, only 0.3 eV, which is on par with the numerical accuracy achievable in this kind of calculations.

Reference

[1] P. Atkins and J. D. Paula, *Physical Chemistry* (Oxford University Press, Great Britain, 2006), 8th edn.