

Supplementary Information for “Effective Fermi level tuning of Bi$_2$Se$_3$ by introducing Cd$_{Bi}$/Ca$_{Bi}$ dopant”


(I) Firstly, the chemical potentials of Bi and Se in bulk Bi$_2$Se$_3$ satisfy the relationship:

\[ \mu_{\text{bulk}}^{\text{Bi}_2\text{Se}_3} = 2\mu_{\text{Bi}} + 3\mu_{\text{Se}} \quad (1a) \]

where \( \mu_{\text{bulk}}^{\text{Bi}_2\text{Se}_3} \) is the chemical potential of one formula unit of Bi$_2$Se$_3$. The chemical potential of Bi(Se) is defined as: \( \mu_{\text{Bi}} = \mu_{\text{Bi}}^0 + \Delta\mu_{\text{Bi}} \), \( \mu_{\text{Se}} = \mu_{\text{Se}}^0 + \Delta\mu_{\text{Se}} \). The Gibbs free energy in the process of formation of one formula unit of Bi$_2$Se$_3$ is given as:

\[ \Delta G(Bi_2Se_3) = \mu_{\text{bulk}}^{\text{Bi}_2\text{Se}_3} - 2\mu_{\text{Bi}}^0 - 3\mu_{\text{Se}}^0 \]
\[ = 2\Delta\mu_{\text{Bi}} - 3\Delta\mu_{\text{Se}} \quad (2a) \]

to avoid the formation of the pure metal and secondary phases \( A_nSe_m \), the following relation must be satisfied:

\[ \Delta\mu_j < 0 \quad (3a) \]
\[ n\Delta\mu_j + m\Delta\mu_{\text{Se}} < \Delta G(A_nSe_m) \quad (4a) \]

In which \( \Delta G(A_nSe_m) \) is Gibbs free energy of formation of one formula unit of \( A_nSe_m \). In our calculation, we take the maximum of Eq. (4a).

\[ n\Delta\mu_j + m\Delta\mu_{\text{Se}} = \Delta G(A_nSe_m) \quad (5a) \]

From Eq. (1) in manuscript, (1a), (2a) and (5a), the Eq. (2) in manuscript can be obtained. In addition, Eq. (2a) tells us that to form Bi$_2$Se$_3$, \( \Delta\mu_{\text{Se}} \) should meet the following condition:

\[ \frac{1}{3} \Delta G(Bi_2Se_3) \leq \Delta\mu_{\text{Se}} \leq 0 \quad (6a) \]

(II) We use Makov-Payne (M-P) corrections which formulated as \( p^2\alpha / 2eL \), where L is
the linear dimension of the supercell, \( \varepsilon \) is the static dielectric constant, and \( \alpha \) is the Madelung constant.\(^{38}\)

(III) The \( E_{\text{VBM}} \) of the system with defect needs to be corrected. Firstly, we assume that the potentials in the perfect supercell are similar to those far from a defect in a defective supercell. Then, the average potential of the plane farthest from the defect in the defective system \( (V_{\text{av}}^{\text{defect}}) \) and the average potential of the corresponding plane in the perfect system \( (V_{\text{av}}^{\text{perfect}}) \) are determined. The difference of the average potentials between the perfect and defective supercells is used to determine the EVBM of the defective supercell as follows:

\[
E_{\text{VBM}}^{\text{defect}} = E_{\text{VBM}}^{\text{perfect}} + V_{\text{av}}^{\text{defect}} - V_{\text{av}}^{\text{perfect}} \quad (7a)
\]

The first term on the right-hand side of Eq. 7a is the valence band maximum (VBM) of the perfect supercell and can be obtained by

\[
E_{\text{VBM}}^{\text{perfect}} = E_T(\text{perfect}:0) - E_T(\text{perfect}:+1)
\]

where \( E_T(\text{perfect}:q) \) indicates the total energy of a perfect supercell with the charge state \( q \).\(^{39-41}\)

(IV) The Fermi-level position \( (E_F) \) is determined by the charge neutrality condition\(^{43}\) which imposes that the total amount of positive charge (example: at \( \Delta \mu_{\text{Se}} = -0.491 \text{eV}, \) equal to the concentration of \( \text{V}_{\text{Se}}^{+} \)) is equal to the total amount of negative charge (example: at \( \Delta \mu_{\text{Se}} = -0.491 \text{eV}, \) equal to the concentration of \( \text{V}_{\text{Cd}}^{-} \)), namely,

\[
N_{\text{V}_{\text{Se}}} \exp(-H_{\text{V}_{\text{Se}}}^{\text{f}} / kT) = N_{\text{Cd}} \exp(-H_{\text{Cd}}^{\text{f}} / kT), \quad \text{where} \quad N_a = \text{the concentration of atomic sites on which the defect can be incorporated} \quad \text{and} \quad N_{\text{V}_{\text{Se}}} = N_{\text{Cd}}. \quad \text{From the formula, we can conclude that the Fermi level moves linearly with the change of the growth condition. Take the area of \( \Delta \mu_{\text{Se}} \in (-0.209, -0.491) \text{ eV for example, according to the calculation of the formation energies, we can get that} \quad H_{\text{V}_{\text{Se}}}^{\text{f}} = 0.422 + E_f + (\Delta \mu_{\text{Se}} - (-0.491)) \quad \text{and} \quad H_{\text{Cd}}^{\text{f}} = 0.883 - E_f - \frac{1}{2}(\Delta \mu_{\text{Se}} - (-0.491)), \quad \text{and then} \quad 4E_f + 3\Delta \mu_{\text{Se}} = -0.551. \quad \text{So the Fermi level}
\]
moves linearly with the change of the growth condition and the line is the intersection line as shown in Fig2. (c). For the area of $\Delta \mu_{Se}$C $(-0.105, -0.462)$ eV, because of that the Se vacancy takes two positive charges, the equation is \[ 2N_{Vc} \exp(-\frac{H^{Vc}_{f}}{kT}) = N_{CdBi} \exp(-\frac{H^{CdBi}_{f}}{kT}) \], in which $H^{Vc}_{f}$ changes to be $H^{Vc}_{f} = 0.213 + 2E_{f} + (\Delta \mu_{Se} - (-0.491))$. And then we get \[ 6E_{f} + 3\Delta \mu_{Se} = -0.133 + 2kT \ln 2 \]. So, the Fermi level moves also linearly with the change of the growth condition but the line moves slightly from the intersection line shown in Fig2. (c).

Based on the inflexion values (as shown in Fig 2 (c)), we estimate the Fermi-level positions under different temperatures for CdBi dopant. And the results indicate that all the Fermi level positions are hardly affected by the temperature and locate within 0.02eV around the point where the formation energies intersect as shown in Table. 1a. As discussed in our manuscript, the Fermi level positions are approximated to be pinned at the intersection.

Table.1a. Our estimated Fermi-level positions ($\mu_{e}(eV)$) under different temperature for CdBi dopant in Bi$_{2}$Se$_{3}$ at $\Delta \mu_{Se}$ = $-0.491eV, -0.462eV, -0.105eV$, respectively. The intersections indicate the points ($\mu_{e}(eV)$) where the formation energies intersect.

<table>
<thead>
<tr>
<th>$\Delta \mu_{Se}$</th>
<th>intersection</th>
<th>350K</th>
<th>500K</th>
<th>750K</th>
<th>900K</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.491</td>
<td>0.231</td>
<td>0.231</td>
<td>0.231</td>
<td>0.231</td>
<td>0.231</td>
</tr>
<tr>
<td>-0.462</td>
<td>0.209</td>
<td>0.216</td>
<td>0.219</td>
<td>0.224</td>
<td>0.227</td>
</tr>
<tr>
<td>-0.105</td>
<td>0.03</td>
<td>0.037</td>
<td>0.040</td>
<td>0.045</td>
<td>0.048</td>
</tr>
</tbody>
</table>

(V) From the band structures shown in Fig.1a, we can also find that the Fermi level of the perfect Bi$_{2}$Se$_{3}$ locates above the VBM of the system. And the Fermi level of the CdBi defective structure locates within the valence band. The result agrees well with the results of formation energies and the DOS in our manuscript.
Fig. 1a. Band structures of pure structure (a) and Cd$_{Br}$ defective structure (b).