Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information for "Effective Fermi level tuning of Bi_2Se_3 by introducing Cd_{Bi}/Ca_{Bi} dopant"

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(I) Firstly, the chemical potentials of Bi and Se in bulk Bi_2Se_3 satisfy the relationship:

$$\mu_{Bi_2Se_3}^{bulk} = 2\mu_{Bi} + 3\mu_{Se} \qquad (1a)$$

where $\mu_{Bi_2Se_3}^{bulk}$ is the chemical potential of one formula unit of Bi_2Se_3. The chemical potential of Bi(Se) is defined as: $\mu_{Se} = \mu_{Se}^0 + \Delta\mu_{Se}$, $\mu_{Bi} = \mu_{Bi}^0 + \Delta\mu_{Bi}$. The Gibbs free energy in the process of formation of one formula unit of Bi_2Se_3 is given as:[37]

$$\Delta G(Bi_2Se_3) = \mu_{Bi_2Se_3}^{bulk} - 2\mu_{Bi}^0 - 3\mu_{Se}^0$$
$$= 2\Delta\mu_{Bi} - 3\Delta\mu_{Se} \qquad (2a)$$

to avoid the formation of the pure metal and secondary phases A_nSe_m, the following relation must be satisfied:[34]

$$\Delta\mu_A < 0 \qquad (3a)$$

$$n\Delta\mu_A + m\Delta\mu_{Se} < \Delta G(A_nSe_m) \qquad (4a)$$

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).

$$n\Delta\mu_A + m\Delta\mu_{Se} = \Delta G(A_nSe_m) \qquad (5a)$$

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_2Se_3, $\Delta\mu_{Se}$ should meet the following condition:

$$\frac{1}{3}\Delta G(Bi_2Se_3) \le \Delta\mu_{Se} \le 0 \qquad (6a)$$

(II) We use Makov-Payne (M-P) corrections which formulated as $p^2\alpha / 2\epsilon L$, where L is

the linear dimension of the supercell, ϵ is the static dielectric constant, and α is the Madelung constant.[38]

(III) The E_{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_{av}^{defect}) and the average potential of the corresponding plane in the perfect system ($V_{av}^{perfect}$) 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:

$$E_{VBM}^{defect} = E_{VBM}^{perfect} + V_{av}^{defect} - V_{av}^{perfect} \qquad (7a)$$

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 $E_{VBM}^{perfect} = E_T\left(perfect:0\right) - E_T\left(perfect:+1\right)$ where $E_T(perfect:q)$ 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 $\Delta\mu_{Se}$=-0.491eV, equal to the concentration of V_{Se}^{+}) is equal to the total amount of negative charge (example: at $\Delta\mu_{Se}$ =-0.491eV, equal to the concentration of V_{Cd}^{-}), namely, $N_{V_{Se1}} \exp(-H_f^{V_{Se1}} / kT) = N_{Cd_{Bi}} \exp(-H_f^{Cd_{Bi}} / kT)$, where N_a is the concentration of atomic sites on which the defect can be incorporated and $N_{V_{Se1}} = N_{Cd_{Bi}}$. From the formula, we can conclude that the Fermi level moves linearly with the change of the growth condition. Take the area of $\Delta\mu_{Se}$ Є (-0.209, -0.491) eV for example, according to the calculation of the formation energies, we can get that $H_f^{V_{Se1}} = 0.422 + E_f + (\Delta\mu_{Se} - (-0.491))$ and $H_f^{Cd_{Bi}} = 0.883 - E_f - \frac{1}{2}(\Delta\mu_{Se} - (-0.491))$, and then $4E_f + 3\Delta\mu_{Se} = -0.551$. 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 $\Delta\mu_{Se} \in$ (-0.105, -0.462) eV, because of that the Se vacancy takes two positive charges, the equation is $2N_{V_{Se1}} \exp(-H_f^{V_{Se1}} / kT) = N_{Cd_{Bi}} \exp(-H_f^{Cd_{Bi}} / kT)$, in which $H_f^{V_{Se1}}$ changes to be $H_f^{V_{Se1}} = 0.213 + 2E_f + (\Delta\mu_{Se} - (-0.491))$. 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 Cd_{Bi} 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 Cd_{Bi} dopant in Bi_2Se_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.

$\Delta\mu_{Se}$	intersection	**350K**	**500K**	**750K**	**900K**
-0.491	**0.231**	**0.231**	**0.231**	**0.231**	**0.231**
-0.462	**0.209**	**0.216**	**0.219**	**0.224**	**0.227**
-0.105	**0.03**	**0.037**	**0.040**	**0.045**	**0.048**

(V) From the band structures shown in Fig.1a, we can also find that the Fermi level of the perfect Bi_2Se_3 locates above the VBM of the system. And the Fermi level of the Cd_{Bi} defective structure locates within the valence band. The result agrees well with the results of formation energies and the DOS in our manuscript.

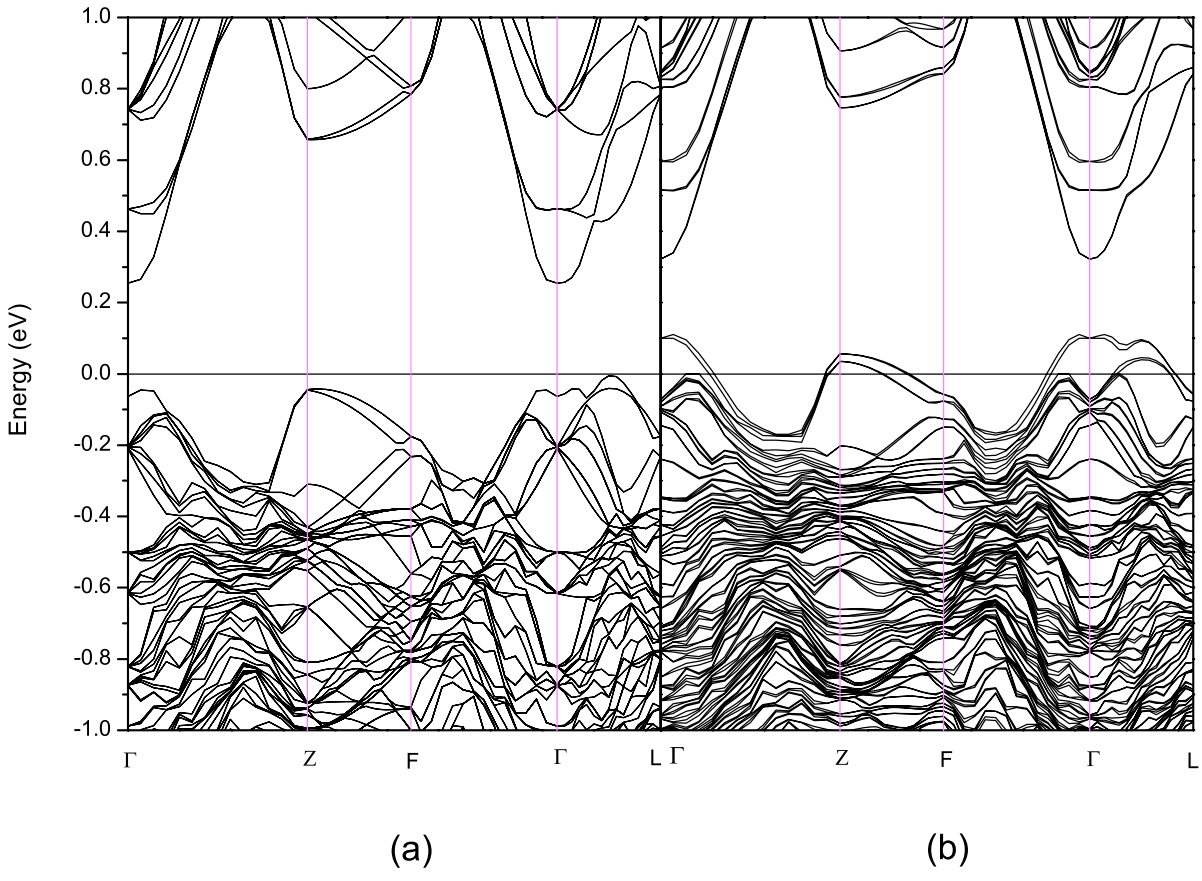

Fig. 1a. Band structures of pure structure (a) and Cd_{Bi} defective structure (b).