

First-Principles Evaluation of p -Type Conductivity in Zn-Doped Bismuth Oxyselenide ($\text{Bi}_2\text{O}_2\text{Se}$)

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Abstract—Bismuth oxyselenide ($\text{Bi}_2\text{O}_2\text{Se}$) is a promising 2D-layered semiconductor to replace silicon as the channel material of ultra-scaled electronics. However, to meet the downscaling requirements of the International Roadmap for Devices and Systems (IRDS), reliable p -doping strategies for the fabrication of complementary field-effect transistors (CFETs) must be developed. In this work, we use hybrid density functional theory (DFT) to analyze the stability and doping behavior of Zn in $\text{Bi}_2\text{O}_2\text{Se}$ at different lattice sites based on the defect formation energy formalism. Our investigations reveal that Zn acts as a shallow acceptor when substituting for Bi in the $\text{Bi}_2\text{O}_2\text{Se}$ lattice, providing a viable pathway for controlled hole densities in next-generation devices. Additionally, we assess the chemical potential range for thermodynamically stable growth of Zn-doped $\text{Bi}_2\text{O}_2\text{Se}$.

Index Terms— $\text{Bi}_2\text{O}_2\text{Se}$, bismuth oxyselenide, 2D-layered semiconductor, doping, density functional theory, charged defects, thermodynamic stability

I. INTRODUCTION

As the downscaling of Si/SiO₂-based field effect transistors (FETs) approaches its physical limits, alternative material systems are being explored for their viability to enable next-generation nanoelectronic devices. Recently, the 2D-layered semiconductor $\text{Bi}_2\text{O}_2\text{Se}$ (BOS) and its native oxide Bi_2SeO_5 have gained significant attention in electronic device applications as potential successors of established technologies. Despite the relative novelty of BOS as a channel material, planar FinFETs and gate-all-around FETs (GAAFETs) have already been demonstrated [1]. These devices show highly promising performance, which is attributed to the exceptionally high electron mobility of BOS, induced by a self- n -doping mechanism from selenium vacancies [2], and the naturally lattice-matched interface with the native oxide [3].

Still, to meet the downscaling requirements of the International Roadmap for Devices and Systems (IRDS) for the year 2037 and beyond, complementary FET (CFET) architectures must be developed, motivating the search for reliable p -doping strategies for BOS. While prototype p -type BOS transistors have already been fabricated by Zn-doping using pulsed laser deposition [4], the microscopic mechanisms responsible for p -conductivity still remain unknown.

In this work, we investigate the impact of Zn impurities on the conductivity of BOS using hybrid density functional theory (DFT). First, we calculate the electronic structure of the Zn impurity at various sites in the BOS lattice. We then determine the chemical potential region for thermodynamically stable growth of Zn-doped BOS and evaluate the resulting doping levels within the defect formation energy formalism. Our analysis demonstrates that Zn introduces shallow acceptor

levels when substituting Bi in the BOS lattice, thereby identifying the Zn_{Bi} complex as an efficient p -type dopant.

II. COMPUTATIONAL SETUP

All DFT calculations were carried out with the Gaussian plane wave (GPW) method as implemented in the CP2K code [5]. We employ the hybrid functional PBE0 [6] with a 15 % portion of exact Hartree-Fock exchange, obtaining an electronic band gap of 0.82 eV in agreement with spectroscopy measurements of bulk BOS [4, 7]. Van der Waals forces are described with the DFT+D3 correction as implemented in CP2K. We use double-zeta GTH-PBE0 basis sets and GTH-PBE0 pseudo potentials for the expansion of the electron density with an energy cutoff of 1000 Ry and include auxiliary basis sets of type FIT9 to reduce the computational costs of the Hartree-Fock calculations. The cell parameters of all investigated compounds were relaxed to release the internal stress below 0.01 GPa. Subsequent geometry optimizations were performed on the Zn-doped BOS supercells in different charge states to reduce the atomic forces below 0.025 eV/Å. Chemical bonds were analyzed using the Hirshfeld partial charge method.

III. ELECTRONIC STRUCTURE OF ZINC DOPANTS

The defect calculations were carried out using a $5 \times 5 \times 2$ conventional cell of BOS containing 500 atoms. We evaluated zinc impurities incorporated via substitution at the Bi (Zn_{Bi}), Se (Zn_{Se}) and O (Zn_{O}) lattice sites. Additionally, a stable interstitial position of Zn (Zn_{i}) was identified within the Bi_2O_2 -layer. The geometry of each defect configuration was relaxed in the relevant charge states from $q = -1$ to $q = +4$.

In the following, the optimized atomic structures and associated projected density of states (PDOS) for the various Zn defect configurations are analyzed across different charge states. All PDOS energies are referenced to the valence band maximum (VBM) of pristine $\text{Bi}_2\text{O}_2\text{Se}$, with positive and negative values denoting the spin-up and spin-down channels, respectively. In particular, we will discuss the electronic states around the band gap introduced by the Zn-dopants for different charge states.

A. Zinc substitution at a bismuth site

The Zn atom at the Zn_{Bi} site is bonded to its four adjacent O atoms, exhibiting Zn–O bond lengths of 2.04 Å. In its neutral charge state, the Zn_{Bi} defect introduces an unoccupied state closely above the valence band maximum (VBM) (Fig. 1c). The corresponding wave function is weakly localized around

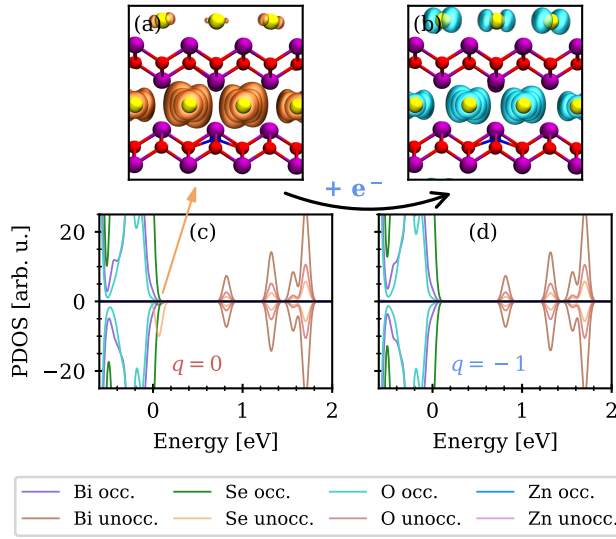


Fig. 1. Relaxed defect structures of ZnBi in its (a) neutral and (b) negative charge states. The PDOS of the neutral charge state exhibits a shallow unoccupied state (c), which hybridizes with the valence band when an electron is trapped (d). All illustrations in this work employ the following color code for the different atoms: Bi – purple, O – red, Se – yellow, Zn – blue. The defect wave functions are always drawn as colored bubbles (blue – occupied, orange – unoccupied) at an isovalue of $\pm 0.01 a_0^{-3/2}$.

the neighboring Se atoms surrounding the dopant site, as illustrated in Fig. 1a. By trapping an electron ($q = -1$), the newly occupied defect state hybridizes strongly with the host valence band states, becoming delocalized upon structural relaxations (Figs. 1b and 1d).

B. Zinc substitution at a selenium site

The ZnSe defect in its neutral charge state introduces two electrons into the delocalized states at the conduction band minimum (CBM) as shown in Fig. 2c. As demonstrated in Fig. 2a and Fig. 2b, the Zn atom remains at its initial lattice position even when the electrons are removed from the conduction band states. This defect can thus be easily ionized and stabilizes in the positive charge states $q = +1$ and $q = +2$.

C. Zinc substitution at an oxygen site

In the neutral state of ZnO , the electronic structure features two localized occupied states within the band gap alongside two delocalized occupied states at the CBM as shown in Fig. 3d. The corresponding wave functions are illustrated above in Figs. 3a and 3b. Removing electrons to reach the $q = +1$ and $q = +2$ charge states depopulates these shallow CBM states while leaving the system structurally unperturbed.

However, the introduction of a third hole ($q = +3$) triggers a strong, charge-induced structural reconstruction. As illustrated in Fig. 3c, this causes the Zn atom to migrate out of the Bi_2O_2 plane and into the interlayer space toward the Se layer. The remaining Zn–O bonds shorten significantly to $1.97 - 1.99 \text{ \AA}$, and the Hirshfeld charge of the adjacent Se shifts from an initial $-0.02e$ to a positive value of $+0.12e$, indicating

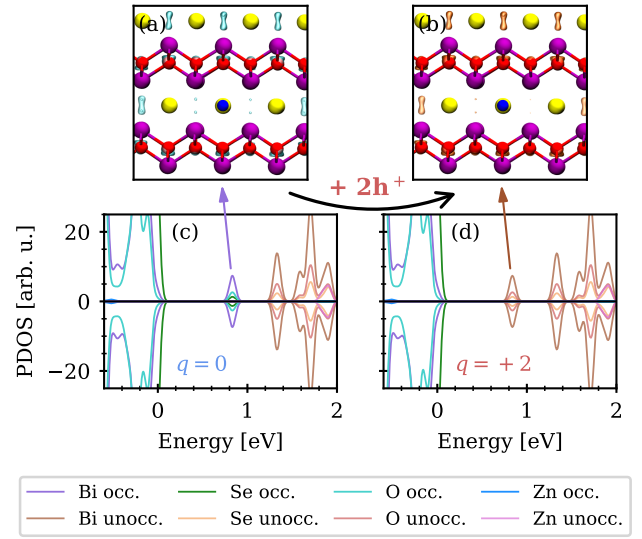


Fig. 2. Relaxed defect structures of ZnSe in its (a) neutral and (b) +2 charge states, demonstrating that the Zn stays at the initial Se position in the lattice even when charged. This defect introduces two electrons into conduction band states (c), which are removed when two holes are added to the system (d).

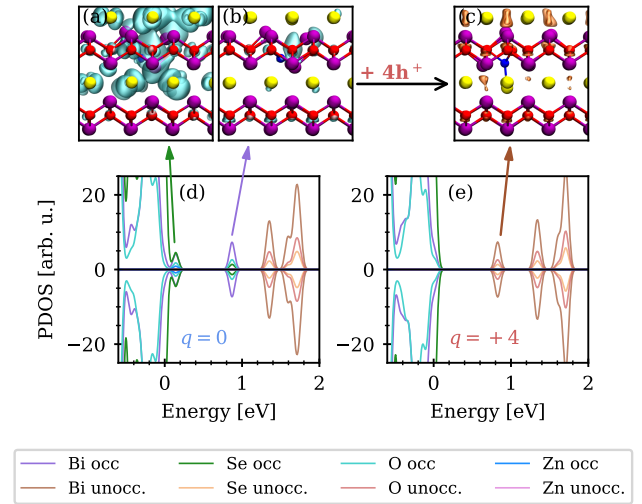


Fig. 3. Relaxed neutral structure of ZnO with the wave function of the occupied states above the VBM (a) and at the conduction band (b). In charge state $q = +4$, the Zn is bonded to the adjacent Se and the corresponding holes are delocalized (c). The PDOS in charge states $q = 0$ and $q = +4$ are shown in (d) and (e).

a strengthening of the covalent Zn–Se bond ($2.31 \text{ \AA}$). The structural relaxations stabilize this configuration, leaving one occupied delocalized state at the CBM. Finally, this remaining shallow state is depopulated when a fourth hole is added to the system ($q = +4$), with the resulting PDOS shown in Fig. 3e.

D. Zinc interstitial

In addition to the substitutional sites, an interstitial configuration Zn_i is identified embedded within the Bi_2O_2 layer. In its optimized neutral state, the interstitial Zn atom coordinates

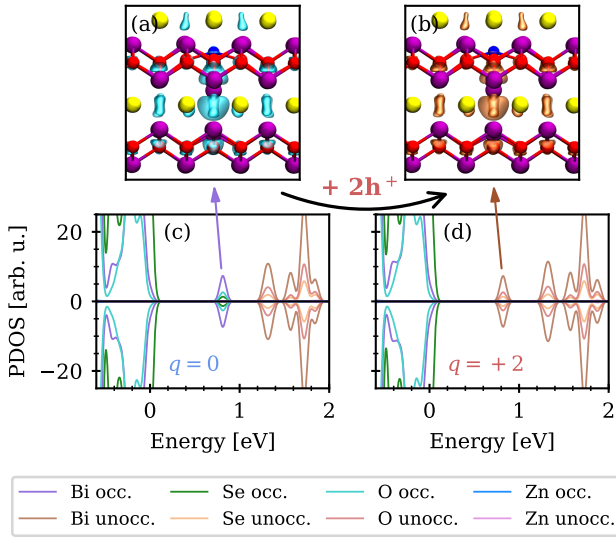


Fig. 4. Atomic structure of Zn_i for the $q = 0$ (a) and $q = +2$ (b) charge states. The Zn occupies an interstitial position within the Bi_2O_2 layer, introducing two electrons in the conduction band with weakly localized wave functions around the Zn. The corresponding PDOS are plotted below (c, d).

with the surrounding lattice, forming Zn–O bond lengths of 2.06 Å as illustrated in Fig. 4a. The nearest-neighbor Se atom is at a distance of 2.44 Å from Zn. Upon defect formation, the Hirshfeld charge of the Se changes from $-0.3e$ to $0.01e$, indicating strong charge redistribution. Furthermore, the defect induces a structural distortion where an adjacent Bi atom is displaced along the c -axis toward the Se layer, while the four in-plane Bi atoms experience an increase in their Hirshfeld charges from $0.43e$ to $0.52e$ due to local polarization.

This defect introduces two occupied delocalized states at the CBM (Fig. 4c), which are depopulated upon hole injection ($q = +1$ and $q = +2$) (Fig. 4d). The Zn atom remains virtually fixed at its initial position throughout these charge transitions (Fig. 4b), demonstrating that the local chemistry remains relatively unperturbed.

IV. CHEMICAL POTENTIALS

The formation energy E_{form}^q of a doped structure in charge state q as a function of the Fermi level E_F is given by

$$E_{\text{form}}^q = E_{\text{tot}}^q - E_{\text{tot}}^{\text{bulk}} - \sum_i n_i \mu_i + qE_F + E^{\text{corr}}, \quad (1)$$

where E_{tot}^q and $E_{\text{tot}}^{\text{bulk}}$ are the energies of the doped and pristine supercells, respectively. E_F is referenced to the VBM of the pristine $\text{Bi}_2\text{O}_2\text{Se}$. The chemical potential of element i is defined as $\mu_i = \mu_i^0 + \Delta\mu_i$, where n_i represents the number of atoms added ($n_i > 0$) or removed ($n_i < 0$) to create the doped structure, with $\Delta\mu_i \leq 0$. E^{corr} was evaluated with the FNV-scheme [8] using the experimentally determined permittivity of $\epsilon_r = 155$ [9]. The potential alignment corrections were thereby omitted, as strong oscillations in the defect Hartree potentials prohibited the extraction of a reliable alignment value. The upper boundary μ_i^0 in eq. (1) is given by the total energy of atom i in its most stable form, associated with the lowest

energy crystal structure for metals and semiconductors and the triplet state of the O_2 molecule for oxygen.

DFT is known to overbind the O_2 molecule, which introduces a systematic underestimation in the calculated formation enthalpies of oxides when compared to experimental data [10]. To account for this overbinding, we add a correction term C_O to $\Delta\mu_O$ [11], calibrated to match the experimentally determined formation enthalpy of ZnO ($\Delta h^{\text{exp}}(\text{ZnO}) = \Delta h(\text{ZnO}) - C_O$), giving $C_O = 0.51 \text{ eV}$ for $\Delta h^{\text{exp}}(\text{ZnO}) = -3.61 \text{ eV}$ [12]. Calculated formation enthalpies Δh for all considered compounds are in good agreement with experimental values obtained from thermochemical measurements [12, 13] as summarized in Table I, with the space group numbers of the investigated crystal structures given next to the respective chemical compositions.

TABLE I
CALCULATED FORMATION ENTHALPIES PER FORMULA UNIT COMPARED WITH EXPERIMENTAL VALUES.

Compound	Space Group Nr.	Δh [eV]	Δh^{exp} [eV]
$\text{Bi}_2\text{O}_2\text{Se}$	139	-5.20	-4.54 [13]
Bi_2O_3	14	-6.61	-5.95 [12]
Bi_2Se_3	166	-1.94	-1.48 [12]
Bi_2SeO_5	39	-10.17	-
ZnO	186	-3.61	-3.61 [12]
ZnSe	216	-1.71	-1.69 [12]
ZnSeO_3	61	-6.75	-6.87 [12]

We find that applying C_O improves the agreement of Δh with experimental data for all compounds involving O atoms. The remaining deviations are attributed to the inherent shortcomings of DFT in describing systems with heavy elements such as Bi. We note that including spin-orbit coupling effects could improve the agreement with experiment [14]. However, such calculations are highly expensive, in particular when structural optimizations are required, and were thus not feasible for the large supercells investigated in this work.

The changes of μ_i are further constrained by the stability condition of the host

$$2\Delta\mu_{\text{Bi}} + 2\Delta\mu_{\text{O}} + \Delta\mu_{\text{Se}} = \Delta h(\text{Bi}_2\text{O}_2\text{Se}). \quad (2)$$

To avoid the formation of competing phases $\text{A}_\alpha\text{B}_\beta\text{C}_\gamma$, the additional constraints

$$\alpha\Delta\mu_{\text{A}} + \beta\Delta\mu_{\text{B}} + \gamma\Delta\mu_{\text{C}} \leq \Delta h(\text{A}_\alpha\text{B}_\beta\text{C}_\gamma) \quad (3)$$

are enforced for ZnO, ZnSe, ZnSeO_3 , Bi_2O_3 , Bi_2Se_3 and Bi_2SeO_5 . The feasible regions of $\Delta\mu_i$ within these constraints were evaluated with the `spinney` code [15] and are shown for Bi-poor and Zn-rich conditions in Fig. 5. These considerations resulted in $\Delta\mu_{\text{Bi}}^{\text{min}} = -0.93 \text{ eV}$, $\Delta\mu_{\text{Zn}}^{\text{max}} = -1.97 \text{ eV}$, $\Delta\mu_{\text{O}} = -1.66 \text{ eV}$ and $\Delta\mu_{\text{Se}} = -0.03 \text{ eV}$, which will be used in the analysis of E_{form}^q .

V. FORMATION ENERGY ANALYSIS

The formation energies of the different defect types as a function of E_F are shown in Fig. 6. Zn_{Bi} has a shallow acceptor level 0.02 eV above the VBM and can thus be easily ionized at room temperature to its negative charge state, effectively introducing free holes in the $\text{Bi}_2\text{O}_2\text{Se}$ bulk.

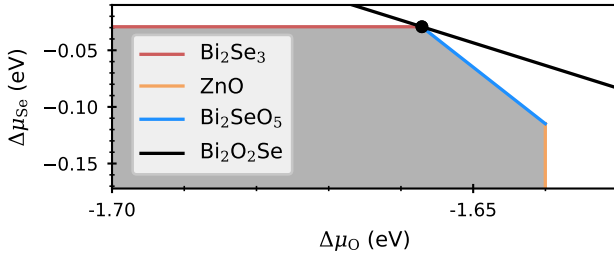


Fig. 5. Intersection of the feasible chemical potential region for $\text{Bi}_2\text{O}_2\text{Se}:\text{Zn}$ with the $\Delta\mu_{\text{Bi}}^{\text{min}} = -0.93$ eV and $\Delta\mu_{\text{Zn}}^{\text{max}} = -1.97$ eV plane.

Conversely, Zn_i , Zn_{Se} and Zn_O act as shallow donors. However, compared to Zn_{Bi} and Zn_O , the concentrations of Zn_{Se} and Zn_i are expected to be negligible due to their considerably higher E_{form}^q for most E_F . This aligns with scanning transmission electron microscope observations, confirming that Zn preferably substitutes the Bi site [4].

The intersection of the dominant donor Zn_O^{4+} with Zn_{Bi}^- at 0.35 eV suggests a Fermi level pinning below midgap, effectively shifting the conductivity of $\text{Bi}_2\text{O}_2\text{Se}$ to p -type. X-ray photo-electron spectroscopy measurements of Zn-doped BOS films indicate that the experimental Fermi level is even lower, sitting at ≈ 0.1 eV above the VBM [4]. This deviation might be attributable to the enforced stability conditions when evaluating the chemical potentials for the presented E_{form} analysis, as real-world synthesis often operates under non-equilibrium kinetics, which directly affects the dopant incorporation. For example, maximizing μ_O and μ_Zn to their elemental ground-state values μ_i^0 would increase E_{form}^q of Zn_O and decrease that of Zn_{Bi} . In this extreme scenario, Zn_i^{+2} becomes the dominating donor, yielding a crossing point with $\text{Zn}_{\text{Bi}}^{-1}$ at 0.1 eV which aligns with experimental observations. Finally, we note that for a complete analysis of Fermi level pinning in BOS also native defects should be included. In particular, Se and O vacancies are shallow donors and can therefore further compensate the desired p -doping mechanism [16].

VI. CONCLUSIONS

We investigated the microscopic p -doping mechanisms of Zn in bulk $\text{Bi}_2\text{O}_2\text{Se}$ using hybrid density functional theory. The electronic structure and local lattice relaxations of both substitutional and interstitial Zn defect configurations in the $\text{Bi}_2\text{O}_2\text{Se}$ lattice were analyzed for different charge states. Additionally, we evaluated the chemical potential region required for the thermodynamically stable growth of Zn-doped $\text{Bi}_2\text{O}_2\text{Se}$. Our calculations reveal that Zn acts as a shallow acceptor when substituting for Bi (Zn_{Bi}) in the $\text{Bi}_2\text{O}_2\text{Se}$ lattice, providing a low ionization energy of only 0.02 eV that explains the p -type conductivity observed in experiment.

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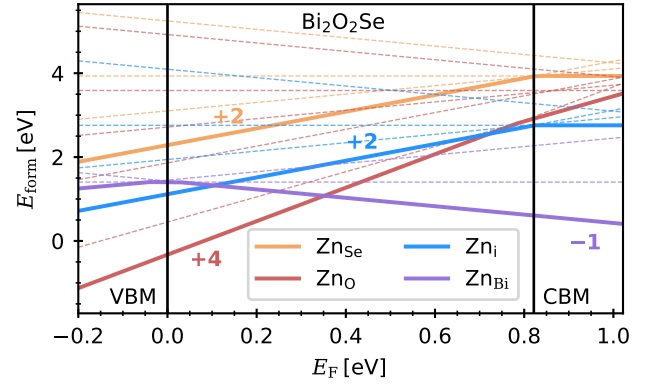


Fig. 6. Formation energies (E_{form}^q) of Zn-defects in $\text{Bi}_2\text{O}_2\text{Se}$ as a function of the Fermi level (E_F), calculated with the chemical potentials associated with Zn-rich and Bi-poor conditions as evaluated in Section IV. The thermodynamically stable charge states of each defect are drawn as bold lines, the vertical lines illustrate the electronic band edges of the bulk.

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