

Antisite Disorder in the Native Oxide Insulator β -Bi₂SeO₅: A First-Principles Study

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Abstract—The native oxide β -Bi₂SeO₅ of the high-mobility semiconductor Bi₂O₂Se has emerged as a promising high- κ dielectric for future scaled nanoelectronic devices. While oxygen-related defects have recently been identified as the dominant reliability-active traps in this oxide, its complex stoichiometry and non-equilibrium oxidation pathway may also permit the formation of previously unexplored antisite defects, namely bismuth on selenium sites (Bi_{Se}) and selenium on bismuth sites (Se_{Bi}). Here, we combine hybrid density functional theory with TCAD simulations to investigate the electronic activity and hysteresis response of these defects. Our calculations show that both antisites introduce localized states within the bandgap. However, device-level simulations reveal a smaller hysteresis response compared to oxygen-related defects, indicating that antisite disorder is electrically active but unlikely to dominate hysteresis-related reliability issues in Bi₂O₂Se/ β -Bi₂SeO₅-based devices.

Index Terms—High- κ Dielectric, Bi₂O₂Se, 2D Semiconductor, Native oxide β -Bi₂SeO₅

I. INTRODUCTION

Continued transistor scaling requires aggressive reduction of the channel thickness to maintain electrostatic control and suppress short-channel effects. In conventional silicon devices, however, scaling the channel to only a few nanometers is accompanied by severe mobility degradation [1]. Two-dimensional (2D) semiconductors provide a promising alternative because they can retain excellent electrostatic control even at monolayer thickness while also offering high carrier mobilities [2]. Their successful integration into highly scaled field-effect transistors nevertheless requires ultrathin high- κ dielectrics with low leakage currents and high-quality interfaces, which remains a central challenge.

Among the potential channel materials, the layered semiconductor Bi₂O₂Se is particularly promising because of its high room-temperature Hall electron mobility of up to 812 cm² V⁻¹ s⁻¹ [3]. In addition, Bi₂O₂Se combines a moderate bandgap, excellent air stability, and compatibility with multiple scalable thin-film growth techniques, making it a technologically relevant platform for future electronic devices [4]. Unlike conventional van der Waals semiconductors, Bi₂O₂Se has been referred to as a *zipper* 2D material because it lacks a van der Waals gap and exhibits larger interlayer binding energies than typical vdW materials [5,6]. This lack of a vdW gap is also highly beneficial for electrostatic control [7]. A key advantage of Bi₂O₂Se is its ability to form the native oxide Bi₂SeO₅ as illustrated in Figure 1a [8]. As in any other

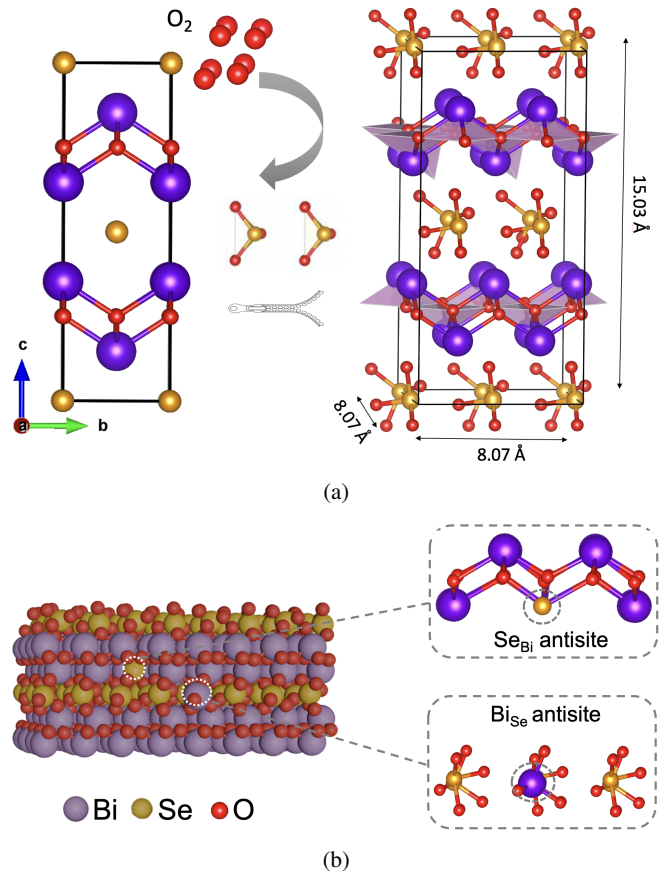


Figure 1: Schematic illustration of (a) UV-ozone-assisted intercalative oxidation of Bi₂O₂Se into β -Bi₂SeO₅, where oxygen intercalation oxidizes the Se layers while preserving the [Bi₂O₂] framework, and (b) possible antisite defects in β -Bi₂SeO₅: Se_{Bi} and Bi_{Se}. Purple, yellow, and red spheres denote Bi, Se, and O atoms, respectively.

material, intrinsic defects in the oxide can degrade device performance and stability by acting as charge-trapping centers and thereby contributing to hysteresis and bias-temperature instability [9]. Recent studies have identified oxygen-related intrinsic defects as the dominant trapping centers in β -Bi₂SeO₅ [10]. However, antisite disorder in this oxide has not yet been examined, even though its complex stoichiometry and non-equilibrium oxidation pathway may promote such defects

during oxide formation. The two antisites considered in this work, Bi_{Se} and Se_{Bi} , are schematically shown in Figure 1b. Here we combine hybrid density functional theory with TCAD simulations to assess both the electronic activity of Bi_{Se} and Se_{Bi} antisites and their impact on the hysteresis response. We find that both defects are electrically active, but their simulated hysteresis response of antisites is (considerably) smaller compared with oxygen-related defects, indicating that antisite disorder is unlikely to dominate hysteresis-related reliability issues in $\beta\text{-Bi}_2\text{SeO}_5$ -based devices.

II. METHODOLOGY

We follow the computational methodology described in detail in [6,10]. Antisite defects were modeled in a $2 \times 2 \times 1$ $\beta\text{-Bi}_2\text{SeO}_5$ supercell using hybrid DFT with the PBE0-TC-LRC functional, as implemented in CP2K [11]. The Bi_{Se} and Se_{Bi} configurations were relaxed in multiple charge states, from which formation energies and charge transition levels (CTLs) were extracted. For charged defects, finite-size effects were corrected using the FNV image-charge correction scheme, accounting for the anisotropic dielectric response of $\beta\text{-Bi}_2\text{SeO}_5$ [12,13]. The resulting antisite defect parameters, including charge-transition levels and relaxation energies, were included in TCAD simulations to evaluate their hysteresis response. Charge capture and emission were described using the nonradiative multiphonon (NMP) model, and the simulated hysteresis was extracted from the threshold-voltage difference between up- and down-sweeps under a triangular gate-voltage signal. The antisite response was then compared with previously identified oxygen-related defects in $\beta\text{-Bi}_2\text{SeO}_5$ [10,14,15].

III. RESULTS AND DISCUSSION

Previous DFT studies of $\beta\text{-Bi}_2\text{SeO}_5$ identified several intrinsic point defects associated with its distinct oxygen environments [10]. In particular, oxygen vacancies in both the interlayer SeO_3 units and the Bi_2O_2 framework were found to introduce localized in-gap states, hence forming deep traps [10]. These previously studied vacancy configurations and their representative localized wavefunctions are summarized in Figure 2. Building on this picture, we now consider antisite disorder in $\beta\text{-Bi}_2\text{SeO}_5$. Such defects are experimentally plausible because Bi/Se antisite disorder may form locally in the $\text{Bi}_2\text{O}_2\text{Se}$ precursor during non-equilibrium growth and could then be inherited by the oxide during intercalative oxidation, which largely preserves the parent lattice framework. Their resulting concentration is therefore not determined by formation energy alone, but also by the local chemical environment and kinetic constraints during growth and oxidation. Unlike conventional cation-anion antisites, Bi/Se site exchange in $\beta\text{-Bi}_2\text{SeO}_5$ occurs between oxygen-coordinated Bi- and Se-centered units, since oxidation converts Se from its -2 state in $\text{Bi}_2\text{O}_2\text{Se}$ to an effective $+4$ state in $\beta\text{-Bi}_2\text{SeO}_5$, giving Se a cation-like character with respect to the surrounding oxygen atoms. For Se_{Bi} , a selenium atom occupying a bismuth site perturbs the local oxide bonding

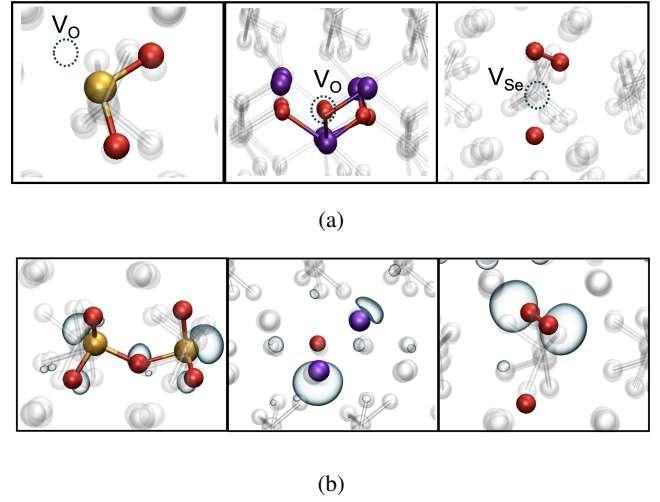


Figure 2: **(a)** Representative local configurations of vacancy defects in $\beta\text{-Bi}_2\text{SeO}_5$: left, an oxygen vacancy in the inter-layer SeO_3 layer; middle, an oxygen vacancy in the Bi_2O_2 framework; and right, a selenium vacancy. **(b)** Corresponding defect-state wavefunctions.

environment and introduces a defect-derived state within the bandgap. The comparison between the PDoS of the pristine BSO and the Se_{Bi} defect structure in Figure 3a shows that the Se_{Bi} defect introduces two defect states within the $\beta\text{-Bi}_2\text{SeO}_5$ bandgap, marked by dashed circles. The occupied defect state is located at approximately 0.65 eV above the valence-band maximum (VBM), while the corresponding unoccupied spin-

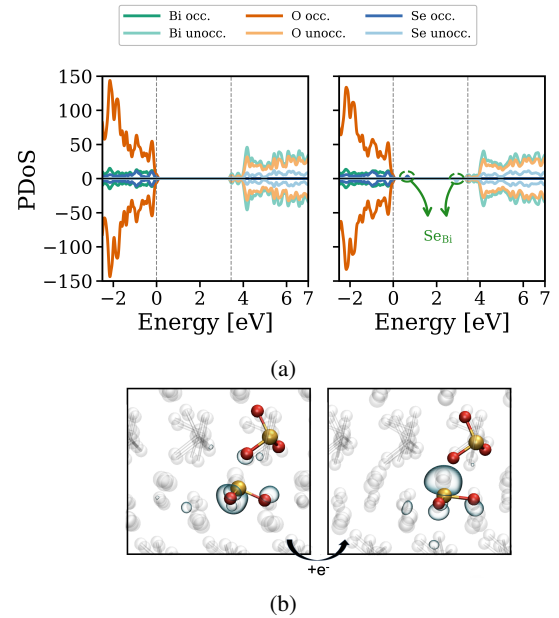


Figure 3: **(a)** PDoS of the pristine and Se_{Bi} -defective structures, where dashed circles indicate defect-related states. **(b)** Localized defect-state wavefunction associated with the Se_{Bi} transition.

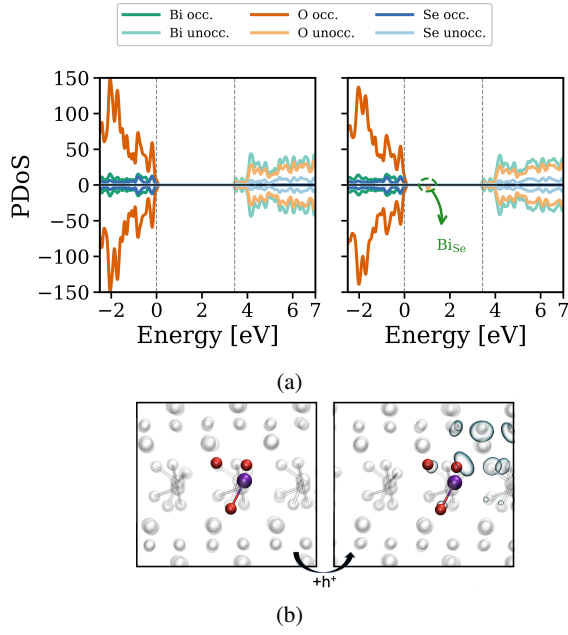


Figure 4: **(a)** PDoS of the pristine and Bi_{Se} -defective structures, where dashed circles indicate defect-related states. **(b)** Defect-related wavefunction associated with the Bi_{Se} transition.

down state appears around 0.44 eV below the CBM. In the defective structure, the corresponding wavefunction is strongly localized around the Se_{Bi} antisite and its neighboring oxygen atoms, consistent with a spatially confined trap state, as shown in Figure 3b. For Bi_{Se} , a bismuth atom substitutes a selenium site. The local oxide environment relaxes into an asymmetric, distorted configuration, with one neighboring oxygen atom remaining strongly bonded to the substituted Bi atom. The comparison between the pristine and defective PDoS in Figure 4a shows a defect-related in-gap state, circled for clarity. The corresponding wavefunction in Figure 4b is mainly distributed over the nearby Bi_2O_2 framework rather than being centered on the Bi_{Se} antisite itself. Bader analysis of the neutral antisites indicates local charge redistribution at the substituted sites. Relative to the corresponding pristine sites, the Bader electron population increases by $1.13e$ for Se_{Bi}^0 and decreases by $0.46e$ for Bi_{Se}^0 .

These local changes show that the neutral antisites substantially perturb the charge distribution around the substituted atoms, consistent with the defect-induced electronic states shown above. To assess the thermodynamic stability of the

Table I: Bader electron populations at the antisite position for neutral antisite defects. $\Delta N = N_{\text{defect}} - N_{\text{pure}}$ denotes the change in the Bader electron population relative to the corresponding site in pristine $\beta\text{-Bi}_2\text{SeO}_5$.

Defect	N_{pure}	N_{defect}	ΔN
Se_{Bi}^0	2.19	3.32	+1.13
Bi_{Se}^0	2.13	1.67	-0.45

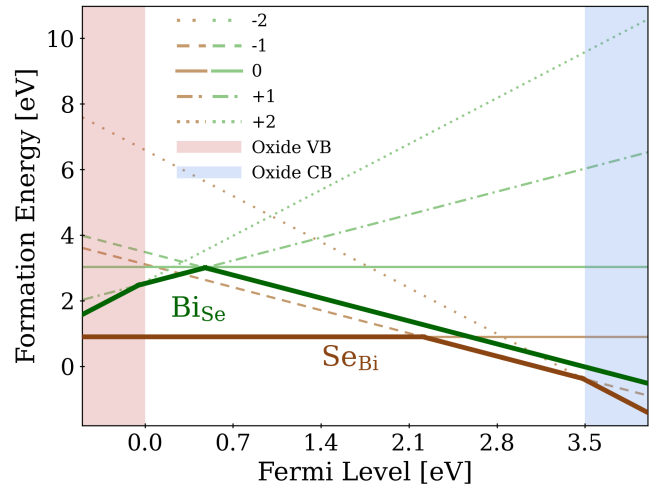


Figure 5: Formation energies of Bi_{Se} and Se_{Bi} antisite defects in different charge states as a function of the Fermi level in $\beta\text{-Bi}_2\text{SeO}_5$.

antisites, we calculate their formation energies in multiple charge states, as shown in Figure 5. Both Se_{Bi} and Bi_{Se} exhibit charge-transition levels within the $\beta\text{-Bi}_2\text{SeO}_5$ bandgap.

The band diagram in Figure 6 summarizes these transition levels together with those of other intrinsic defects, we previously calculated [10]. As can be seen, most CTLs are in the vicinity of the $\text{Bi}_2\text{O}_2\text{Se}$ CBM and the Fermi level of an Au gate contact, suggesting that the antisites can be electrically active. To further characterize charge-trapping behavior with, we extract the relaxation energies of the charge transitions. The evaluated parameters are given in Table II.

To evaluate the possible contribution of antisite defects to hysteresis in the transfer characteristics of field-effect transistors employing Bi_2SeO_5 as the gate insulator, we introduced a uniform distribution of oxide charge traps into a top-gated

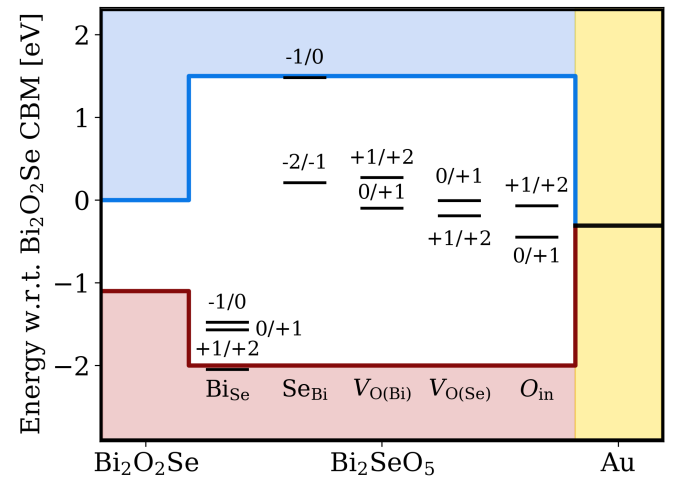


Figure 6: Charge-transition levels of Bi_{Se} and Se_{Bi} antisite defects given relative to the $\text{Bi}_2\text{O}_2\text{Se}$ conduction-band minimum, together with the band alignment to $\text{Bi}_2\text{O}_2\text{Se}$ and Au.

Table II: Theoretical antisite defect transitions and parameters predicted with DFT. E_T is given relative to the β -Bi₂SeO₅ valence-band maximum.

Defect	Transition	E_T [eV]	E_R [eV]
Se _{Bi}	0/−1	2.21	0.94
	−1/−2	3.48	0.055
Bi _{Se}	0/+1	0.43	0.62
	+1/+2	−0.05	0.35

planar device as shown in Figure 7a [6,16]. Charge transitions are modeled using NMP theory [17].

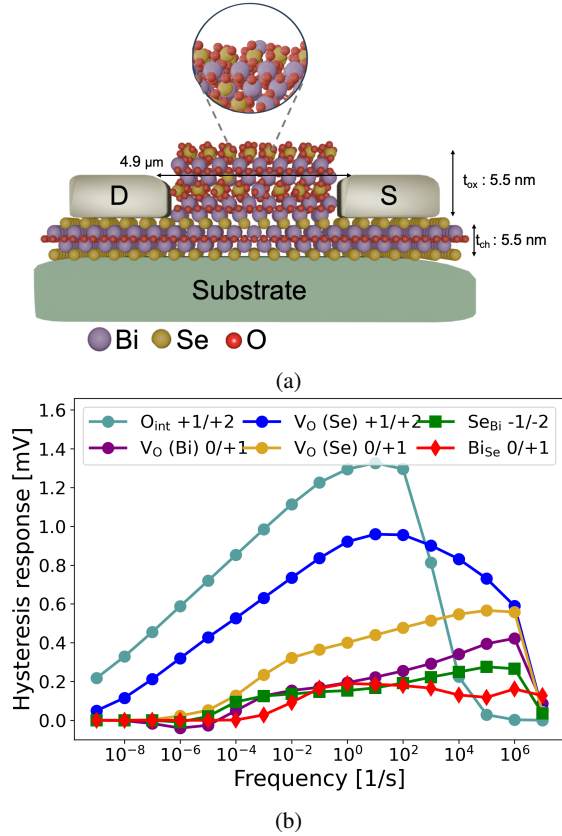


Figure 7: (a) Schematic of the simulated top-gated planar FET. (b) Simulated hysteresis response of different defects in a top-gated planar device [6] over a broad range of sweep frequencies. The antisite defects investigated in this work, shown by squares and diamonds, are compared with oxygen-related defects, shown by circles. The oxygen-related defects, previously identified as the dominant contributors to hysteresis [10], show a larger hysteresis response than the antisite defects.

The defect density was set to 10^{17} cm^{-3} and the hysteresis was simulated by evaluating the threshold-voltage shift between the up- and down-sweeps under a triangular gate signal over a wide range of sweep frequencies. The same procedure was applied to oxygen-related defects, which were previously identified as the dominant contributors to hysteresis [10]. As

shown in Figure 7b, the hysteresis response of the antisite defects is significantly smaller than that of the dominant oxygen-related defects.

IV. CONCLUSIONS

We investigated Se_{Bi} and Bi_{Se} antisite defects in β -Bi₂SeO₅ using hybrid DFT calculations combined with TCAD-based hysteresis simulations. Both antisites introduce localized defect states within the oxide bandgap and exhibit charge-transition levels inside the β -Bi₂SeO₅ bandgap, indicating that they are electrically active. The corresponding defect-state wavefunctions are spatially localized around the antisite and neighboring atoms, while the Bader analysis confirms a local charge redistribution at the substituted sites. Despite this electronic activity, the simulated hysteresis response of the antisites is smaller than that of the previously identified oxygen-related defects. This indicates that antisite disorder can occur in β -Bi₂SeO₅, particularly under non-equilibrium oxidation conditions, it is unlikely to dominate hysteresis-related reliability degradation. Instead, oxygen-related defects remain the primary reliability-relevant trap candidates in β -Bi₂SeO₅-based devices.

ACKNOWLEDGMENTS

This project was supported by the European Research Council (ERC) under grant agreement No. 101055379 (F2GO) and by the Austrian Science Fund (FWF) through project PAT1601525. The support of the Vienna Scientific Cluster through access to the Austrian high-performance computing resources VSC4 and VSC5 is gratefully acknowledged.

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