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Stability and electronic properties of SnS/ZnS interfaces in thin film solar cells

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Abstract

Thin-film solar cells utilizing tin sulfide (SnS) and zinc sulfide (ZnS) represent a promising avenue for advancing photovoltaic technologies. This research investigates the stability and electronic properties of bulk, surface, and interface structures between SnS and ZnS, addressing the critical need to enhance semiconductor interface efficiency and stability. A comprehensive approach employs first-principles calculations and advanced high-throughput interface structure search techniques to explore the structural and electronic characteristics of SnS and ZnS heterostructures.

The analysis begins with an examination of the bulk and surface properties using density functional theory (DFT). Results indicate that bulk SnS has a bandgap of 0.92 eV, while ZnS demonstrates a wider bandgap of 2.08 eV. The evaluation of surface stability reveals that SnS (100) and ZnS (110) exhibit lower surface energies than other low-index surfaces, establishing them as the most stable surfaces. Additionally, the assessment shows slight decreases in bandgap for surface structures, with SnS (100) at 0.91 eV and ZnS (110) at 1.87 eV, attributed to surface reconstructions and atomic rearrangements.

The pristine SnS/ZnS interface structure, modeled from SnS (100) and ZnS (110) surfaces, exhibits a staggered type-II band alignment that facilitates spatial separation of electron and hole states, significantly reducing charge recombination. This energy offset is crucial for optimized photovoltaic performance, with the electronic structure featuring a conduction band offset of 0.18 eV, a valence band offset of 1.28 eV, and a bandgap of 0.857 eV. These findings highlight the potential of the SnS/ZnS interface to enhance thin-film solar cell efficiency.

To investigate the effects of defects on the SnS/ZnS heterostructure, various interface compositions were analyzed by incorporating ad-atoms such as Sn, S, and Zn. Six distinct configurations were generated to simulate realistic defect conditions. Results show that interfaces with balanced atomic distributions from both SnS and ZnS retained their semiconducting properties, with a bandgap of 0.43 eV. Conversely, configurations dominated by a single element whether Sn-rich, S-rich, or Zn-rich exhibited metallic behavior characterized by overlapping valence and conduction bands near the Fermi level. This metallic behavior adversely affects device performance by increasing recombination rates and hindering effective charge transport. Additionally, introducing ad-atoms significantly alters the electronic structure, leading to reduced bandgaps in certain configurations. For instance, (Sn,S)-rich and (Zn,S)-rich interfaces displayed bandgaps of 0.27 eV and 0.32 eV, respectively, due to additional electronic states introduced within the bandgap.

In summary, this research underscores the importance of interface engineering in the development of SnS/ZnS heterostructures for solar energy applications. By tailoring interface compositions and reducing defect-induced alterations in electronic properties, the structural and operational stability of SnS/ZnS-based solar cells can be improved. These results contribute to advancing the understanding of interface phenomena, providing insights that are essential for the development of reliable and sustainable photovoltaic technologies.

Keywords: Thin-film solar cells, SnS, ZnS, Interface stability, First-principles calculations, Electronic properties

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Chapter 1

Introduction

1.1 Background

A crucial driver in the transition to a clean, renewable energy economy is the energy harnessed from solar cells, which offer an affordable and environmentally friendly solution to growing energy demands [4]. Solar cells convert sunlight into electricity, and among the various types available, thin-film solar cells (TFSCs) stand out for their innovative design and versatility [5]. Unlike traditional crystalline silicon cells, TFSCs are composed of semiconductor layers just a few micrometers thick, making them lightweight and adaptable for integration on diverse substrates such as glass, metal, or plastic. This flexibility enables TFSCs to be used in a range of applications, including building-integrated photovoltaics and portable solar devices [5].

Thin-film solar cells, as illustrated in Figure 1.1, consist of multiple functional layers that facilitate sunlight conversion into electricity. The substrate provides foundational support, while the back contact, typically made from conductive materials like molybdenum, enables electron flow into an external circuit. The absorber layer, critical for light absorption and electron-hole pair generation, can be made of materials like cadmium telluride (CdTe), copper indium gallium selenide (CIGS), or tin sulfide (SnS) [2, 6, 7]. The buffer layer, often composed of zinc sulfide (ZnS) or cadmium sulfide (CdS), enhances the efficiency of the absorber layer by improving charge collection and reducing recombination losses [8, 9]. The transparent conductive oxide (TCO) layer, typically made from indium tin oxide (ITO) or zinc oxide (ZnO), allows sunlight to pass through while also conducting electricity [9]. Finally, the top contact, made from materials such as silver or aluminum, collects the generated current and facilitates its flow to an external load. Each of these layers plays a critical role in ensuring the efficient operation of TFSC technology [5].

As the demand for sustainable energy solutions intensifies, TFSCs have emerged as a promising alternative to conventional silicon solar cells, which typically achieve efficiencies between 10% and 28% [10]. TFSCs, with potential efficiencies up to 23% [10], offer several advantages, including their ability to maintain performance in challenging environmental conditions such as low light or high temperatures. Moreover, TFSCs present opportunities for reducing material costs and expanding applications due to their flexibility. However, the use of scarce and toxic elements in some TFSC technologies, like CdTe and CIGS, limits their scalability and environmental sustainability. This has driven efforts to explore alternative materials like copper zinc tin sulfide (CZTS) and tin sulfide (SnS), both of which are more abundant and environmentally friendly [2, 5].

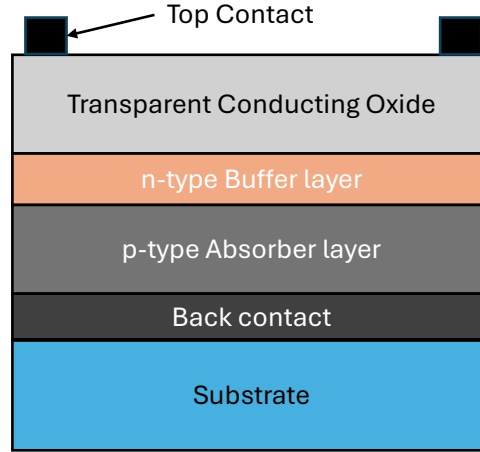


Figure 1.1: Schematic of thin film solar cell structure

In order to optimize the performance of TFSCs and address the challenges posed by material choices, a deep understanding of their electronic properties at the bulk, surface, and interface levels is essential [2, 11]. The electronic structure of semiconductor materials influences their efficiency in converting sunlight to electricity by determining key factors like band gaps and charge carrier dynamics.

Ab initio Density Functional Theory (DFT) is a powerful computational tool used to study the electronic structure of materials at the atomic level, providing insight into how electrons behave in bulk materials, at surfaces, and across interfaces [12, 13]. For TFSCs, DFT-based studies are especially valuable in understanding how surface states and interfacial phenomena impact charge transfer and recombination processes—key factors in determining device efficiency. By employing DFT, researchers can model and optimize the electronic properties of various material compositions, helping to design new materials and structures that minimize losses and enhance performance. This thesis aims to utilize DFT to investigate the electronic properties of bulk, surface and absorber/buffer interfaces in thin-film solar cells, with a focus on developing materials that can overcome the limitations of existing technologies while advancing the sustainability and efficiency of solar energy solutions.

1.2 Motivation

Despite significant advancements in thin film solar cell (TFSC) technology, optimizing material properties and enhancing overall efficiency remain key challenges [14]. These challenges are particularly pronounced when selecting appropriate materials and examining their surface and interface sections. As the demand for renewable energy sources intensifies, there is an urgent need to explore alternative materials that are not only efficient but also environmentally friendly. Conventional materials like cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) present significant challenges due to their reliance on scarce and toxic elements, raising concerns about their long-term sustainability [15]. The $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) offers some promise as an alternative, yet issues with phase purity persist due to the complexity of its multi-element composition [6].

In this context, tin sulfide (SnS) emerges as a promising candidate due to its low-cost, abundant composition and favorable optical properties. Investigating SnS offers the opportunity to

address the critical material selection challenges while also enhancing the overall performance of TFSCs. Unlike conventional TFSC like CdTe and CIGS, SnS is abundant and non-toxic, which enhances its sustainability [15]. Additionally, it possesses inherent p-type conductivity, high carrier concentrations ranging from 10^{15} to 10^{18} cm^{-3} , and a suitable bandgap of 1.25 eV, making it ideal for effective light absorption and charge transport in solar cells [16–18]. Current experimental efficiencies for SnS-based solar cells are approximately 4.63%, while theoretical assessments suggest that efficiencies could exceed 30% [19]. This notable disparity between experimental and theoretical performance highlights the significant opportunities for further research and enhancement of SnS-based TFSCs.

Efficiency losses in TFSCs stem from several key factors, including defect-assisted recombination in the bulk material, surface defects, and recombination at interfaces, particularly at the heterojunction between layers [20, 21]. Defect-assisted recombination occurs when charge carriers, such as electrons and holes, become trapped by material imperfections, leading to recombination and a consequent decrease in overall device efficiency [21]. Surface defects, especially on critical layers, exacerbate this problem by introducing more recombination sites, further impeding performance. For instance, studies on the SnS(111) surface have revealed that tin antisite defects notably disrupt the surface's electronic properties, causing a transition from semiconducting to metallic behavior, which severely hinders charge separation and transport [2].

Poor interface quality between the absorber and buffer layers in TFSCs can lead to the formation of undesired phases, such as SnS_2 or Sn_2S_3 , and the development of point defects at the interface [22]. These defects are particularly problematic as they serve as primary sites for recombination, which undermines the charge carrier dynamics essential for efficient solar cell operation. The buffer layer plays a key role in minimizing these losses by acting as a barrier, improving energy level alignment, and enhancing charge carrier separation at the interface [8, 23].

Several studies have explored various buffer materials, and it has been shown that the right choice of buffer layer can dramatically reduce recombination losses, thereby improving the solar cell's overall efficiency. For instance, changing the buffer layer has been found to increase open-circuit voltage (V_{oc}). A study by Xu et al. used numerical analysis to evaluate SnS heterojunctions with different buffer layers, including CdS, ZnS, ZnO, a-Si, and c-Si. Their results revealed that the SnS/ZnS heterojunction achieved the highest conversion efficiency, driven by its superior short-circuit current density [24]. Consequently, the SnS/ZnS heterojunction is considered one of the most effective structures for improving TFSC performance. ZnS is a particularly promising buffer layer due to its excellent optical properties, including 60-95% transmittance in the visible spectrum, low absorbance, and a wide band gap of 3.22 eV [25, 26]. This wide band gap enables ZnS to transmit a large portion of incident light to the absorber layer, maximizing energy capture. Given these advantages, our research focuses on investigating the interface properties of SnS and ZnS as p-type and n-type materials, respectively, with the goal of optimizing their interaction to improve TFSC efficiency.

The efficiency of thin-film solar cells (TFSCs) is often hindered by defects present in the bulk material, at the surfaces, and at the interfaces between different materials, particularly in SnS/ZnS heterojunctions. Poor interface quality can lead to the formation of undesirable phases and defects, negatively impacting solar cell performance. Moreover, the complexity and disorder characteristic of material interfaces present significant challenges for experimental characterization, making it difficult to fully understand defect formation and recombination pro-

cesses at the atomic level. To address these issues, advanced computational methods, especially ab initio simulations and materials informatics tools, are essential for exploring the electronic and structural properties of SnS/ZnS interfaces. This study aims to employ density functional theory (DFT) and high-throughput interface structure searches to investigate the interface properties of SnS/ZnS, providing crucial insights for optimizing material selection and enhancing the performance of TFSCs.

1.3 Outline

This work is divided into 5 chapters.

- **Chapter 1:** This chapter establishes the research's context, significance, and scope, detailing the motivation, primary objectives, and relevant literature.
- **Chapter 2:** This chapter outlines the existing literature related to the methodologies employed in this research, with a focus on DFT, interface structure search and supercell modeling.
- **Chapter 3:** Results and discussion for bulk and surfaces of SnS and ZnS.
- **Chapter 4:** Results and discussion for SnS/ZnS interfaces.
- **Chapter 5:** This chapter summarizes the key points, results, and conclusions from Chapters 2, 3, and 4.

Chapter 2

Methodology

Ab initio simulations, particularly those based on Density Functional Theory (DFT), provide a powerful first-principles approach to solving the fundamental "many-body Schrödinger equation" of quantum mechanics [9]. As a predictive method, DFT enables the calculation of material properties using only information about the constituent atoms, without relying on empirical or experimental data. By modeling electron density rather than wave functions, DFT simplifies the complex many-body problem, allowing for the accurate prediction of a wide range of material properties, including physical, electronic, optical, and magnetic characteristics. These simulations are applicable to materials modeled as crystals, atomic clusters, and other structures, and are also widely used to study chemical reactions and surface phenomena. Although newer methods, such as stochastic Quantum Monte Carlo and wave function-based techniques like coupled-cluster (CCSD), offer higher accuracy, DFT remains a popular choice due to its computational efficiency, making it suitable for systems with hundreds of atoms [27]. Moreover, continuous advancements in DFT have improved its accuracy and extended its applicability to previously challenging materials, such as those with strong electron correlation. This makes ab initio simulations using DFT indispensable in material science, driving innovations in energy storage, photovoltaic, and semiconductor technologies [27].

2.1 Quantum mechanics and schrödinger equation

Quantum mechanics provides the foundational framework for understanding the behavior of particles at atomic and subatomic scales [28, 29]. It reveals the intricate and often counterintuitive aspects of the quantum realm, where the rules governing particles differ significantly from our everyday experiences. A central concept in this framework is wave-particle duality, which states that particles like electrons and photons can exhibit both wave-like and particle-like properties, depending on how they are observed.

In classical physics, objects are typically seen as either particles, with definite positions and paths, or waves, characterized by their amplitude and frequency [29]. However, in the quantum world, particles can behave like waves, demonstrating phenomena such as interference and diffraction. For instance, light can produce patterns of bright and dark spots when passed through a double slit, indicating its wave nature. When measured, these particles appear as distinct entities with quantized properties. This duality alters our understanding of motion and interaction, suggesting that at microscopic scales, particles do not have fixed paths. Instead,

their behavior is described by probabilistic laws, captured in a mathematical function known as the wave function, denoted as Ψ , which outlines the likelihood of finding a particle in various positions.

The schrödinger equation is a fundamental equation in quantum mechanics that describes how the quantum state of a physical system changes over time. It plays a key role in understanding the behavior of particles at the quantum level. For a single particle in a potential field time-dependent schrödinger equation is expressed as [28]:

$$i\hbar \frac{d}{dt} \psi(r, t) = \hat{H} \psi(r, t) \quad (2.1)$$

Here, $\hbar$ is the Hamiltonian operator, E representing the total energy of the system, including both kinetic and potential energy. The wave function $\psi(r, t)$ represents the probability of finding the particle at a specific position r at time t , while the reduced Planck constant $\hbar$ links quantum mechanics to classical physics. The wave function is a complex function, and its square modulus $|\psi|^2$ gives the probability density of finding the particle in a particular region of space.

However, often we are not interested in how the quantum wave function will evolve over time. For example, in a steady-state system, we might be more concerned with the steady-state quantum wave function given an arbitrary potential field. Moreover, transitions in the quantum world occur on timescales of picoseconds to femtoseconds, making it more important to obtain the steady-state quantum wave function. This is where the time-independent schrödinger equation becomes crucial [28].

The time-independent schrödinger equation can be rewritten as:

$$E\psi(r) = \hat{H}\psi(r) \quad (2.2)$$

Here, $\psi(r)$ represents the corresponding eigenvectors, r is the position in 3-dimensional space. $\hat{H}$ is the Hamiltonian operator, which represents the total energy of the system E , encompassing both kinetic energy (the energy of motion) and potential energy (the energy due to position in a force field). In many cases, the hamiltonian can be expressed as:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad (2.3)$$

where $\hat{T}$ represents the kinetic energy operator and $\hat{V}$ represents the potential energy operator. The lowest energy eigenvalue is essentially the ground state energy of the system, and the corresponding eigenvector is the ground state quantum wave function

In practical atomic, molecular, and solid systems, the interactions among numerous particles lead to the emergence of complex many-body systems [29]. To effectively manage this complexity, the schrödinger equation has been expanded to incorporate the many-body schrödinger equation (MBSE). While the single-particle schrödinger equation concentrates on the behavior of an individual electron within a potential field, the MBSE is essential for accurately modeling the intricate interactions that occur in systems with multiple particles. The general form of the time-independent many-body schrödinger equation can be expressed as [29]:

$$E\psi(r_1, r_2, \dots, r_N) = \hat{H}\psi(r_1, r_2, \dots, r_N) \quad (2.4)$$

where $\psi(r_1, r_2, \dots, r_N)$ is the wave function of N interacting particles, and $\hat{H}$ is the Hamiltonian operator that accounts for the kinetic and potential energies of all particles in the system:

$$\hat{H} = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{e^2 Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{e^2}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{e^2 Z_A Z_B}{R_{AB}} \quad (2.5)$$

where, A and B run over nuclei, M_A is the mass of nucleus A , i and j run over electrons, ∇ is the Laplacian operator, m is the mass of an electron, e is the charge on an electron, Z_A is the atomic number of nucleus A , and r_{iA} is the distance between particles i and A , $\hbar$ is Planck's constant divided by 2π . The first two terms represent the kinetic energy of the electrons and the nuclei, and the other three terms are the potential energy between nuclei and electrons, electron-electrons and nuclei-nuclei.

To effectively solve the MBSE, various approximation methods have been developed due to the complexity of many-body systems. The Born-Oppenheimer (BO) approximation is one of the most widely used techniques, particularly in quantum chemistry [9, 29]. It simplifies the problem by decoupling the motions of nuclei and electrons, if nuclei move much more slowly than electrons. Consequently, the nuclear kinetic energy can be neglected, allowing the Hamiltonian to be separated into electronic and nuclear components:

$$\hat{H}_{\text{elec}} = -\sum_{i=1}^N \frac{\hbar^2}{2m} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{e^2 Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{e^2}{r_{ij}} \quad (2.6)$$

This leads to the effective electronic schrödinger equation:

$$E_{\text{elec}}\psi = \hat{H}_{\text{elec}}\psi \quad (2.7)$$

These frameworks deepen our comprehension of quantum phenomena and play a crucial role in advancing quantum chemistry, materials science, and condensed matter physics, fostering ongoing innovation in these areas, especially through the implementation of ab initio simulations and electronic structure methods [9].

2.2 Density functional theory

Density Functional Theory (DFT) emerges as a powerful and efficient framework for investigating the electronic structure of complex many-body systems, building upon the foundational principles established by the many-body schrödinger equation [9, 12, 13]. Instead of focusing on the intricate many-body wave function, $\psi(r_1, r_2, \dots, r_N)$. DFT emphasizes the more manageable electron density, $n(r)$, which can be experimentally measured and theoretically calculated.

$$n(r) = 2 \sum_i \psi_i^*(r) \psi_i(r) \quad (2.8)$$

where, $\psi_i^*(r)$ and $\psi_i(r)$ represent the wave functions of individual electron and its complex conjugate at position r . Multiplication factor 2 is due to the fact that electrons are spinning and therefore, as per the exclusion theory of Pauli, each independent wave function can now have two opposite spin electrons.

2.2.1 The Hohenberg-Kohn theorems

DFT is anchored in the Hohenberg-Kohn theorems [12], which assert that the ground state properties of a system are uniquely determined by its electron density [9]. The first theorem states [12] that “*The ground-state energy from the Schrödinger equation is a unique functional of the electron density*”. This statement interprets that the energy of the ground state can be expressed as a function of the electron density $E[n]$. This relationship can be expressed mathematically as:

$$E[n] = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.9)$$

where $\hat{H}$ is the Hamiltonian operator, and $\langle \Psi | \hat{H} | \Psi \rangle$ represents the expectation value of the energy in terms of the wave function Ψ . Since calculating the electron density is significantly simpler than solving the full multiparticle wave function, this theorem facilitates the effective application of DFT to many-body systems.

The second Hohenberg-Kohn theorem [12] states that “*The electron density that minimizes the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.*” This theorem applies the variational principle within the context of functionals, which can be expressed mathematically as:

$$E_0 = E_0[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{H} | \Psi \rangle \quad (2.10)$$

In this expression, E_0 denotes the ground-state energy corresponding to the electron density n , while Ψ represents the many-electron wave function that produces n . The notation $\min_{\Psi \rightarrow n}$ indicates that the minimum ground state energy is achieved by identifying the wave function Ψ that corresponds to the specified electron density n .

Furthermore, if the precise form of the functional is known, one can compute the true electron density relatively easily. However, the challenge arises from the fact that the exact form of the actual functionals is often unknown. This theorem thus establishes a framework for approximating these functionals, enabling accurate determination of the electron density.

2.2.2 Kohn-Sham equations

The Kohn-Sham equation [13] represent a pivotal advancement in DFT, providing a practical approach to calculate the electron density of many-body systems. By introducing a system

of non-interacting particles that reproduce the same electron density as the interacting system, Kohn and Sham transformed the complex problem of many-body interactions into a more tractable form. This transformation allows for the use of single-particle equations, facilitating the efficient computation of properties in quantum systems. The Kohn-Sham framework effectively separates the total energy of a system into contributions from kinetic, external, and electron-electron interactions, making it easier to analyze and compute electronic structures.

The Kohn-Sham equations can be mathematically expressed as follows:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \quad (2.11)$$

Here, $\psi_i(r)$ is a wavefunction of eigenvectors, ε_i are eigenvalues in the Kohn Sham equation, $-\frac{\hbar^2}{2m} \nabla^2$ is the kinetic energy of an electron and $V_{\text{eff}}(r)$ is the effective potential, defined as:

$$V_{\text{eff}}(r) = V_{\text{ext}}(r) + V_{\text{H}}(r) + V_{\text{XC}}(r) \quad (2.12)$$

1. **External Potential ($V_{\text{ext}}(r)$):** This term represents the sum of the contributions from the nuclei and the electron-electron interactions. Mathematically, it can be expressed as:

$$V_{\text{ext}}(r) = \sum_{i=1}^N \sum_{A=1}^M \frac{e^2 Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>1}^N \frac{e^2}{r_{ij}} \quad (2.13)$$

where Z_A is the charge of nucleus A , r_i is the position of electron and R_A is the position of the nucleus, This term directly influences the electrons' motion and their distribution in space.

2. **Hartree Potential ($V_{\text{H}}(r)$):** This term accounts for the classical Coulomb repulsion between electrons by representing the average potential due to the electron density $n(r)$. It is mathematically expressed as:

$$V_{\text{H}}(r) = e^2 \int \frac{n(r')}{|r - r'|} d^3 r' \quad (2.14)$$

This integral sums the contributions from the electron density $n(r')$ at all points r' in space, providing a mean-field description of electron-electron interactions.

3. **Exchange-Correlation Potential ($V_{\text{XC}}(r)$):** The exchange-correlation potential [12] incorporates the quantum mechanical effects of electron correlation and exchange, which are not captured by the Hartree term.

$$V_{\text{XC}}(r) = \frac{\delta E_{\text{XC}}[n]}{\delta n} \quad (2.15)$$

where, $E_{\text{XC}}[n]$ is the exchange-correlation energy functional, and $\frac{\delta E_{\text{XC}}[n]}{\delta n}$ represents the functional derivative, indicating how the exchange-correlation energy changes with respect to changes in the electron density.

2.2.3 Exchange-Correlation functional

The exchange-correlation functional [12] $E_{XC}[n]$ is a fundamental component of DFT, encapsulating the complex quantum mechanical effects of electron-electron interactions that are not accounted for by the Hartree term. It embodies both exchange effects, which arise from the anti-symmetry of the many-body wave function, and correlation effects, which describe the tendency of electrons to avoid each other due to their mutual repulsion. As previously described in the Kohn-Sham equations, the exchange-correlation potential V_{XC} is derived from this functional. The $E_{XC}[n]$ is crucial for accurately predicting the ground-state properties of a many-electron system, such as binding energies, molecular geometries, and electronic excitations.

Accurately describing the $E_{XC}[n]$ is a complex challenge in DFT, leading to the development of several approximations. The most widely utilized approximations are:

1. **Local Density Approximation (LDA):** The LDA [12] assumes that the exchange-correlation energy density at a point in space depends only on the electron density at that point. This can be expressed as:

$$E_{XC}^{LDA}(n) = \int n \varepsilon_{XC}^{unif}(n) dr \quad (2.16)$$

where, ε_{XC}^{unif} is the energy exchange-correlation per atom of uniform electron gas interacting with the density n .

2. **Generalized Gradient Approximation (GGA):** The GGA [30] improves upon LDA by incorporating the gradient of the electron density. The exchange-correlation energy is expressed as a function of both the electron density and its gradient:

$$E_{XC}^{GGA}(n) = \int n \varepsilon_{XC}(n, \nabla n) dr \quad (2.17)$$

GGA yields significantly better atomic energy and binding energy than LDA at a modest additional computational expense. In specific, they lead to better outcomes for the bandgap in semiconductors and insulators. There are several types of GGA functionals, such as the Perdew-Burke-Ernzerhof functional [30] (PBE) and the Perdew-Wang functional [31] (PW91) based on how the electron density gradient is integrated with the functional.

3. **Meta-GGA:** Meta-GGA [32] incorporates additional information, such as the kinetic energy density, into the exchange-correlation functional. It can be expressed as:

$$E_{XC}^{mGGA}(n) = \int n \varepsilon_{XC}(n, \nabla n, \nabla^2 n, \tau) dr \quad (2.18)$$

4. **Hybrid Functionals:** Hybrid functionals [33, 34] mix traditional DFT methods with Hartree-Fock (HF) exchange to improve the accuracy of the calculated properties. This functional can be represented as:

$$E_{XC}^{hybrid}(n) = \alpha E_X^{HF}(n) + E_C(n) \quad (2.19)$$

where α is mixing parameter, E_X^{HF} is Hartree Fock exchange and E_C is correlation energy. There are several types of Hybrid functional used like PBE0, B3YLP, HSE [33–35].

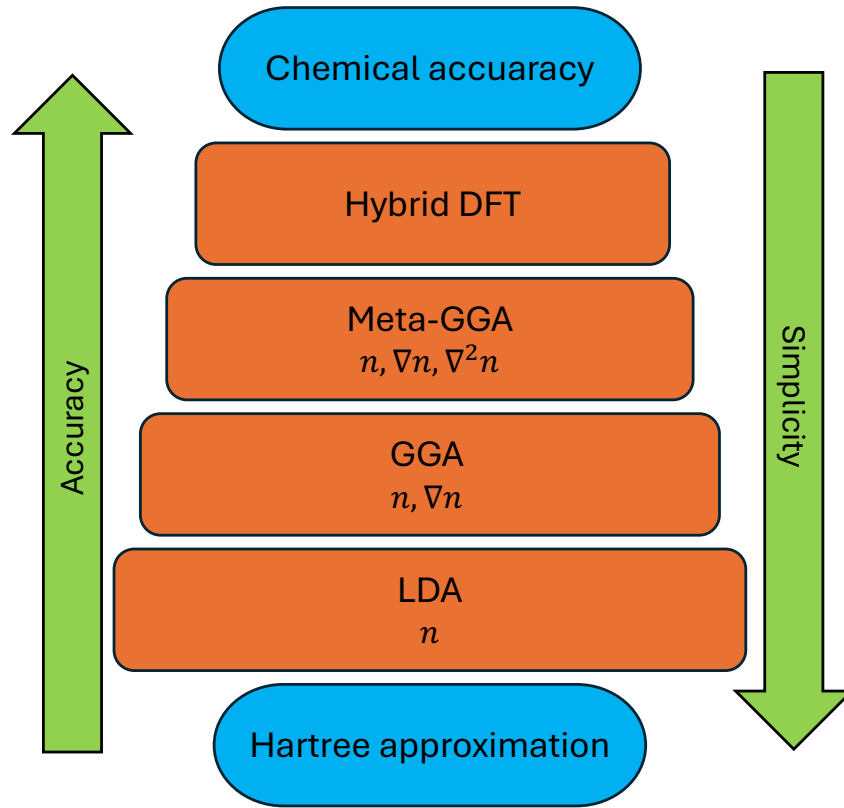


Figure 2.1: Jacob’s ladder of density functional approximations

The hierarchy of approximations for electronic structure calculations, commonly known as Jacob’s ladder [36] (as illustrated in Figure 2.1), categorizes various exchange- correlation functionals, $E_{\text{XC}}[n]$, according to their complexity. This framework positions functionals along a ladder, progressing from the Hartree approximation at the base to more precise functionals at the top. The LDA improves upon this by partially addressing exchange-correlation effects, although it is still rooted in the theoretical framework of electron gas. Moving up the ladder, the GGA incorporates gradients of electron density, resulting in enhanced accuracy for both molecular and solid-state systems. Further levels in this hierarchy provide additional refinements, employing various schemes to recover correlation energy and yielding increasingly precise calculations with fewer approximations. It is important to note that while Meta-GGA and other advanced theories achieve greater accuracy, they often require significantly more computational resources. In contrast, the GGA functional utilized in this study strikes a favorable balance between computational efficiency and accuracy, making it well-suited for a wide range of materials science applications, including the analysis of ground-state properties and structural optimization.

2.3 Ab initio DFT simulation

Ab initio DFT simulations provide a robust computational framework for exploring the electronic properties of materials, utilizing the principles of DFT to deliver precise predictions of

ground-state characteristics without reliance on empirical parameters [9]. These simulations employ a Self-Consistent Field (SCF) approach to determine the ground-state properties of electronic systems [9, 13]. In the SCF method, the electron density is iteratively refined until it converges to a stable solution, ensuring consistency between the calculated electron density and the potentials derived from it. Figure 2.2 illustrates the typical workflow for DFT simulations. The process begins with an initial guess of the electron density, followed by the resolution of the Kohn-Sham equations to obtain the effective potential. This potential is subsequently used to update the electron density, and the iterative procedure continues until convergence is reached, typically defined by a predetermined threshold for energy variation.

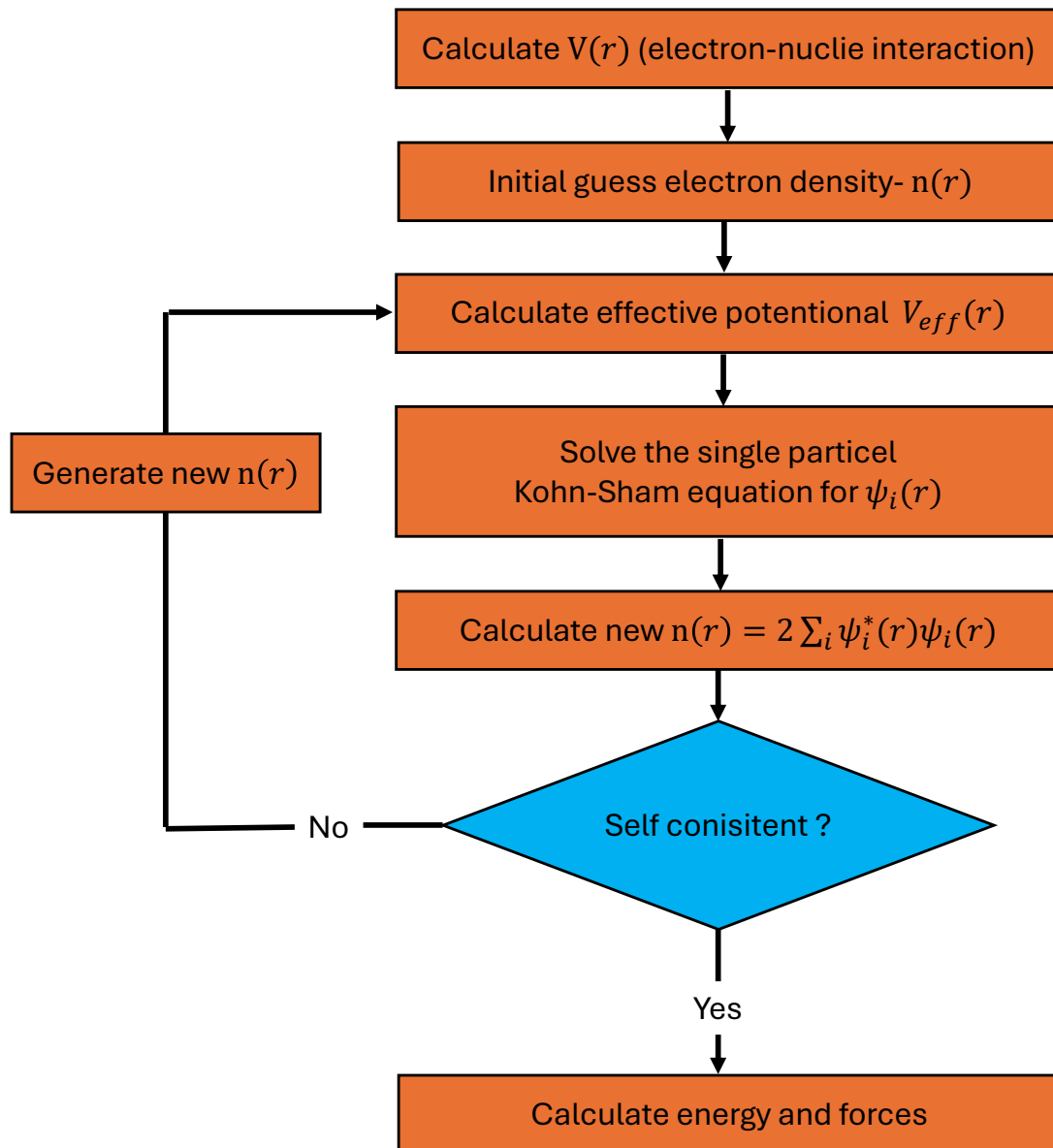


Figure 2.2: DFT calculation workflow for a self-consistent calculation using the Kohn-Sham equation

2.3.1 Basis set expansion

Plane waves form the complete basis for periodic wave functions [37]. The solution to the schrödinger equation in a periodic system adheres to a fundamental principle known as Bloch's theorem, which can be expressed as:

$$\phi_k(r) = e^{ik \cdot r} u_k(r) \quad (2.20)$$

In this equation, the exponential term represents plane waves characterized by the wave vector k , while $u_k(r)$ is a periodic function with the periodicity of the unit cell or supercell. The plane waves are represented by a set of wave vectors G , which correspond to the reciprocal lattice vectors of the periodic structure:

$$\phi_k(r) = \sum_G C_{k+G} e^{i(k+G) \cdot r} \quad (2.21)$$

Combining the equations (2.20) and (2.21) yields:

$$u_k(r) = \sum_G C_G e^{iG \cdot r} \quad (2.22)$$

Theoretically, a complete basis set for $\phi_k(r)$ would require an infinite number of plane waves. However, due to the higher curvature of the higher frequency components, these terms become less significant in the plane wave expansion of the bloch function. Therefore, a cutoff can be applied, allowing for a reasonable approximation. The cutoff energy is determined by the relationship:

$$\frac{\hbar^2}{2m} |k + G|^2 \leq E_{\text{cut}} \quad (2.23)$$

The cut-off effect is to generate some less accurate wavefunction and thereby higher energy of the system. It is essential to assess convergence to ensure that the results are not adversely affected by the truncation.

2.3.2 Brillouin-Zone Integration

To compute various physical properties of solids, including total energy and electron (spin) density, matrix element integrals over the Brillouin zone (BZ) are analyzed. k -points are the sampling points within the Brillouin zone [9]. In a periodic supercell, k denotes the wave vectors of the wave functions. Various methods exist for selecting the k -point grid, with the Monkhorst-Pack scheme being the most used [38]. This method specifies the number of k points in each direction of reciprocal space, which are then uniformly distributed by the DFT code to create a k -point grid.

2.3.3 Pseudopotential

The Coulomb potential surrounding an atomic nucleus is exceptionally strong. To counterbalance this effect, the kinetic energy of the wave function must also be substantial, leading to rapid oscillations that require a significant number of Fourier components for accurate representation. The use of pseudopotentials addresses this issue effectively. Pseudopotentials simplify the description of electron-ion interactions by allowing researchers to concentrate on valence electrons while effectively averaging out the contributions from core electrons. This method enhances computational efficiency by substituting the complex Coulomb potential of atomic nuclei with a smoother, effective potential, facilitating the calculation of electronic structures across a variety of materials. Pseudopotentials can be categorized into two primary types: norm-conserving and ultrasoft. Norm-conserving pseudopotentials maintain the total electron count, making them ideal for lighter elements. In contrast, ultrasoft pseudopotentials provide greater flexibility and significantly reduce the number of plane waves required for calculations, proving advantageous for heavier elements and more complex systems. Another approach, the Projector Augmented Wave (PAW) method [37], combines the benefits of pseudopotentials with full-wave calculations, offering a more accurate representation of core and valence electron interactions. In this study, PAW pseudopotential was used for computation.

The pseudopotential formalism serves two main purposes. First, it employs a much weaker pseudopotential to eliminate the effects of core electrons, which would otherwise necessitate representation by plane wave-based functions due to their deep potential. Second, it helps to mitigate the rapid oscillations of the valence electron wave functions in the vicinity of the core [9].

2.3.4 Smearing

In DFT simulations, particularly when dealing with metallic systems or materials with partially filled electronic states, the concept of smearing becomes essential. Smearing techniques are employed to distribute the occupancy of electronic states around the Fermi level, thereby enhancing numerical stability and convergence in calculations. This is achieved by broadening the sharp distribution of electron states using methods such as Gaussian smearing, Methfessel-Paxton smearing, or Marzari-Vanderbilt smearing [39,40]. For instance, in Gaussian smearing, the occupancy $f(E)$ of electronic states is expressed as:

$$f[E] = e^{-\frac{(E-E_f)^2}{2\sigma^2}} \quad (2.24)$$

where E is the energy of the state, E_f is the Fermi energy, and σ represents the smearing parameter, which controls the width of the Gaussian distribution. A careful selection of this parameter is crucial: while larger σ values provide increased numerical efficiency, they can also lead to inaccuracies in the results. Conversely, smaller σ values offer higher accuracy but may result in longer computational times. In the present work, we have utilized Gaussian smearing with a small σ value of 0.01 to balance efficiency and accuracy in this calculations.

2.3.5 Force calculation and geometry optimization

DFT calculations are instrumental in predicting the lattice parameters and atomic positions of a system due to their ability to compute forces using the Hellmann- Feynman theorem [41]. Through self-consistent cycles of DFT, the eigenvalue E and the eigenfunctions $\phi(r)$ can be obtained, allowing for the calculation of other observables, such as atomic forces. The forces acting on atoms are derived from the gradient of the energy with respect to atomic positions, enabling the determination of equilibrium geometries where the net forces on all atoms are zero. Geometry optimization involves iteratively adjusting atomic positions to minimize the total energy of the system, leading to a local minimum on the potential energy surface. This optimization process is essential for identifying the most stable configuration of a system. During each self-consistent field (SCF) loop, forces and stresses are calculated, and based on these results, the atomic parameters are perturbed for the subsequent SCF loop using a specific algorithm. In this work, the conjugate-gradient algorithm was employed to update the ionic positions throughout the geometry optimization process. The choice of convergence criteria, including energy and force tolerances, significantly influences the optimization outcome. In this study, a force tolerance of approximately 0.01 eV/Å and an energy tolerance of 1×10^{-6} eV were considered, ensuring that the optimization process achieves the desired accuracy and stability for the atomic configurations.

2.3.6 Dipole correction

Dipole correction is an essential technique employed in DFT simulations to account for the long-range interactions associated with dipole moments in periodic systems [42]. When studying surfaces, interfaces, or finite-sized systems, the use of periodic boundary conditions can lead to artificial interactions between the periodic images of the system, especially when a net dipole moment is present. This can distort key results, particularly those sensitive to electric fields, such as adsorption energies and charge distributions. To mitigate this issue, dipole correction involves adding a term to the total energy of the system that compensates for the energy associated with the interaction of the dipole moment with the electric field generated by the periodic images. The dipole moment $\mathbf{d}$ is defined as $\mathbf{d} = \sum_{i=1} q_i \mathbf{r}_i$, where q_i is the charge of atom i and $\mathbf{r}_i$ is its position vector. The correction to the energy can be expressed as $E_{\text{dipole}} = -\frac{1}{2} \mathbf{d} \cdot \mathbf{E}_{\text{field}} = \sum_{i=1} q_i \mathbf{r}_i \cdot \mathbf{E}_{\text{field}}$, where $\mathbf{E}_{\text{field}}$ is the electric field due to the periodic images. By incorporating this dipole correction, researchers can significantly improve the accuracy of their simulations, leading to more reliable predictions of electronic structure, adsorption energies, and structural optimizations in systems where dipole interactions play a critical role.

2.4 Supercell modelling and optimization

Supercell modeling is a crucial technique in computational materials science, particularly in the context of DFT, as it allows for the study of periodic systems with defects, interfaces, or other structural modifications. A supercell is constructed by repeating a unit cell in one or more dimensions, thereby enabling the simulation of larger, more complex systems while maintaining periodic boundary conditions.

2.4.1 Bulk structure

In this study, the bulk structure was optimized with specific convergence criteria for energy and forces, set to 1×10^{-6} eV and 0.01 eV/Å, respectively. These criteria ensure that the optimization process achieves the desired accuracy and stability for the atomic configurations. The optimization involves iterative adjustments to the atomic positions within the supercell, guided by the computed forces derived from the Hellmann-Feynman theorem [41]. The schematic of bulk supercell is shown in Figure 2.3 (a).

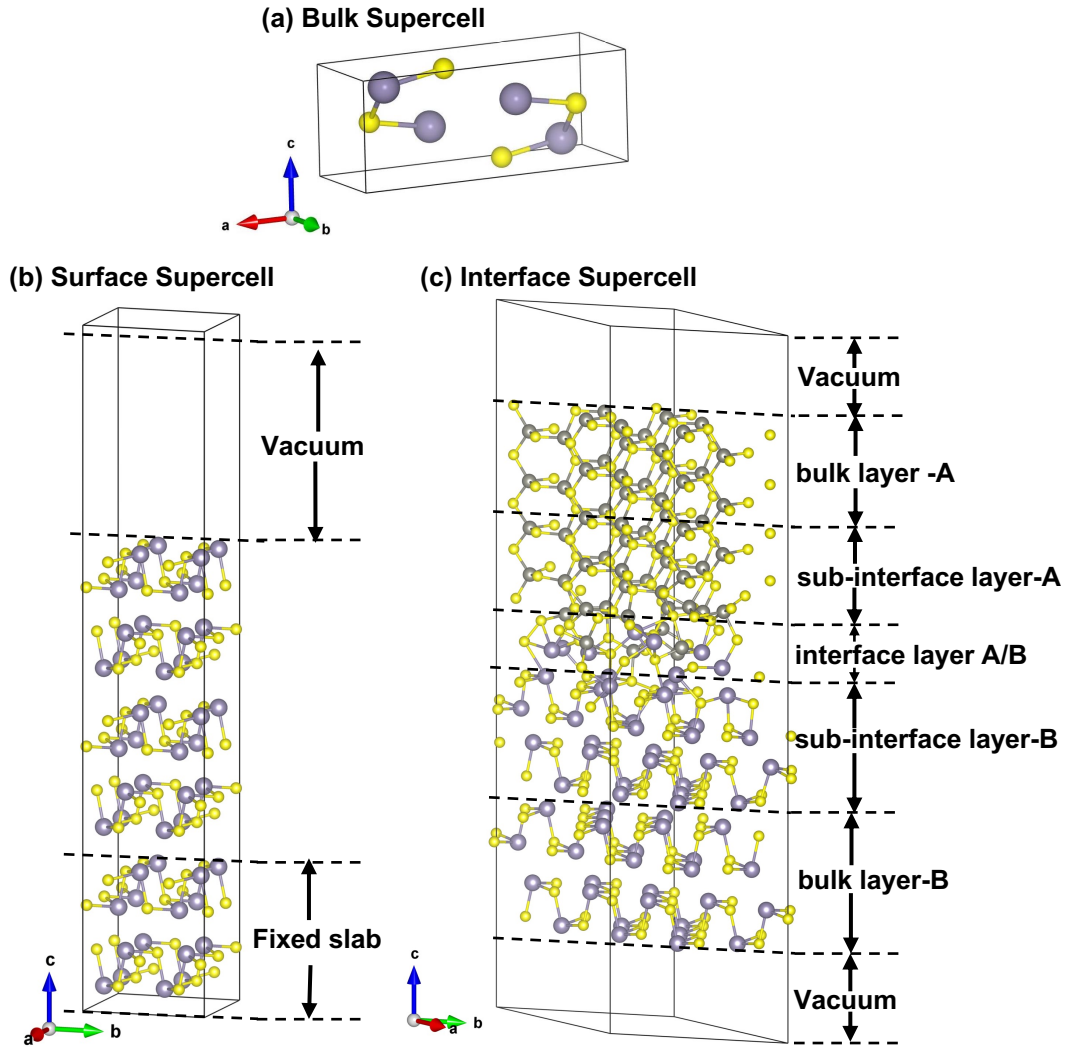


Figure 2.3: Schematic of (a) bulk, (b) surface and (c) interface supercells (created using VESTA software [1])

2.4.2 Surface structure

To create the surface structure, a surface supercell was modeled with a bulk slab and a vacuum layer on top of the surface as illustrated in Figure 2.3(b). In this study, seven different low-index surfaces were considered, corresponding to various surface orientations, namely (100), (010), (001), (011), (101), (110), and (111) planes. The surface supercells were constructed using

VASPKIT [43], ensuring accurate modeling of the desired surfaces.

Each surface supercell consisted of three slabs with a vacuum of 15 Å to minimize interactions between the top and bottom slabs. To simulate realistic surface conditions, the atoms in the bottom slab were fixed to behave like a substrate, while the atoms in the top two slabs were allowed to move freely in any direction (as shown in Figure 2.3). This setup enabled a comprehensive examination of surface relaxation and structural adjustments that occur during optimization.

Furthermore, a dipole correction was applied in the z -direction for the surface supercells to account for any potential dipole moments that could arise due to the asymmetry introduced by the vacuum layer. This correction is vital for accurately calculating the electronic properties and energies of the surface structure.

Similar to the bulk structure optimization, the surface structure was subjected to the same energy and force convergence criteria of 1×10^{-6} eV and 0.01 eV/Å, respectively. These stringent criteria ensure that the optimization process captures the stability and electronic characteristics of the surface configuration accurately.

2.4.3 Interface structure and lattice mismatch

The interface structure is critical in influencing the performance of nanoscale devices like solar cells [44]. The interface supercells were modeled by aligning the supercells of two distinct materials while maintaining periodic boundary conditions. Accurate modeling of the atomic-scale geometry at the interface is essential for predictive simulations.

The two materials involved have different lattice constants, requiring one or both surfaces to be strained to form a compatible supercell. In some cases, rotating the surfaces can alleviate the strain but often increases the supercell size, especially when preserving symmetry. Achieving a low-strain interface without overly expanding the supercell presents a significant challenge.

The strain induced by lattice mismatch can lead to defects or distortions at the interface, affecting the material's stability and electronic properties [45, 46]. The optimization process must carefully adjust atomic positions to minimize strain and create a stable interface configuration. A well-optimized interface model provides valuable insights into interfacial interactions, which are critical for the performance of heterostructures in photovoltaics, where the interface characteristics are key to their functionality.

A comprehensive screening procedure was developed to identify the lattice-matched interface structure [45, 46]. This process begins with the crystallographic unit cells of two materials, designated as A and B as depicted in Figure 2.4. Next, two surface supercells with respective lattice vectors of $(\vec{u}_a, \vec{v}_a)$ and $(\vec{u}_b, \vec{v}_b)$ are constructed from the surface unit cells of materials A and B. Moreover, in order to prevent the high computational cost, a threshold area of 200 Å² was maintained as a constraint for creating a superlattice. Further, these two supercells are rotationally aligned (step 3 of Figure 2.4) by rotation and then matched using the strain tensor ε . The individual strain components are defined as follows:

$$\varepsilon_{xx} = \frac{u_{b,x} - u_{a,x}}{u_{a,x}}, \quad (2.25)$$

$$\varepsilon_{yy} = \frac{v_{b,y} - v_{a,y}}{v_{a,y}}, \quad (2.26)$$

and

$$\varepsilon_{xy} = \varepsilon_{yx} = \frac{1}{2} \left(\frac{v_{b,x}}{v_{a,y}} - \frac{u_{b,x}v_{a,x}}{u_{a,x}v_{a,y}} \right) \quad (2.27)$$

To identify and optimize the misfit between different surfaces following equation for lattice mismatch was used [46]:

$$\bar{\varepsilon} = \frac{|\varepsilon_{xx}| + |\varepsilon_{yy}| + 2|\varepsilon_{xy}|}{4} \quad (2.28)$$

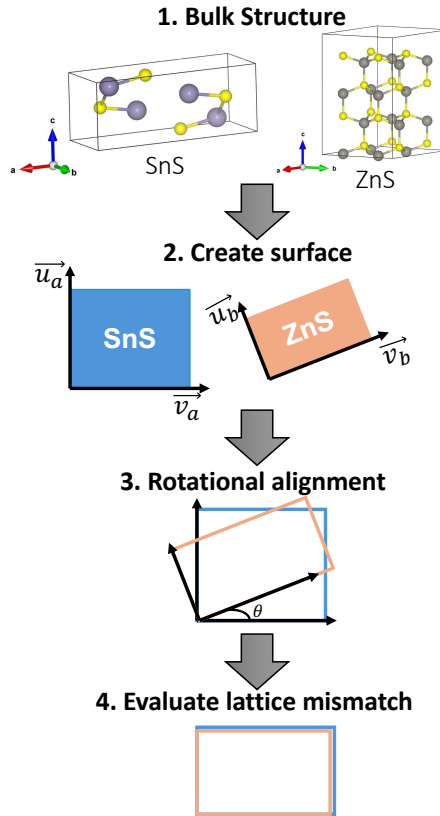


Figure 2.4: Flowchart diagram for matching two surfaces forming an interface with minimal strain

The interface structure with small values of $\bar{\varepsilon}$ was considered a well-matched superlattice.

The schematic of the interface supercell is depicted in Figure 2.3 (c). Vacuum layers are introduced at the top and bottom of the supercell to eliminate interactions between materials A and B across periodic boundaries, ensuring accurate simulation of the interface. The outermost layers of both materials, referred to as bulk layers, have atoms fixed in place before relaxation, maintaining the characteristics of bulk materials. This constraint stabilizes the structure and isolates the interface behavior. Meanwhile, atoms in the sub-interface layers and at the A/B interface were unconstrained and allowed to relax freely in all directions, simulating natural atomic rearrangements at the interface. This configuration enables an accurate study of the

atomic and electronic properties at the interface while preserving the bulk characteristics of the surrounding layers.

2.5 Formation energy

Formation energy is a critical parameter in materials science, particularly for assessing the stability and thermodynamic favorability of various structures, such as surface, interfaces, and compounds [47]. It is defined as the energy difference between the total energy of a system containing a specific configuration (such as a surface or an interface) and the energies of the individual components in their equilibrium states.

In the context of surface and interface structures, formation energy provides insight into the stability of the surface or interface. A lower formation energy indicates a more stable configuration, while a higher formation energy suggests that the system is less favorable and may be prone to defect formation or phase separation.

The surface formation energy (γ_{surface}) can be expressed mathematically as [44, 47]:

$$\gamma_{\text{surface}} = \frac{1}{2 \cdot A} \{E_s - N \times E_b\} \quad (2.29)$$

where, E_s represents the energy of the slab supercell, E_b is the bulk energy of the single bulk slab, A is the area of the surface unit cell, and N denotes the number of bulk slabs in the surface slab. The 1/2 pre-factor accounts for the two surfaces of a slab.

The interface formation energy [44] was calculated using the following relation:

$$\gamma_{\text{interface}} = \frac{1}{2 \cdot A} \left[E_{\text{total}} - E_{\text{bulk,A}} - E_{\text{bulk,B}} - \sum_i N_i E_i \right] \quad (2.30)$$

where, A is the cross-section area of the interface, $E_{\text{interface}}$, $E_{\text{bulk,A}}$, $E_{\text{bulk,B}}$ are the free energies (approximated as the total energies in DFT calculations) of the interface system, bulk A, and bulk B, respectively. N_i and E_i denote the total number and energy of atoms in the interface system, where i corresponds to distinct atoms.

2.6 Interface structure prediction

Interface structure prediction is a crucial aspect of materials science, particularly for understanding the atomic arrangements and properties at the junction between two materials [44]. This prediction plays a significant role in various applications, including electronics, photovoltaics, and catalysis, where the interface can dramatically influence device performance. Consequently, accurately predicting interface structures can drive advancements across multiple fields.

A powerful method for identifying the most stable structure from a given chemical composition is global optimization, which seeks the global minimum within a predefined multidimensional space [48]. The theoretical prediction of interface structures typically involves two key steps [44, 46]: (i) Lattice matching and (ii) characterizing the atomic structure at the interface.

Various optimization techniques, including genetic algorithms [49], particle swarm optimization (PSO) [46,48], and the stochastic surface walking (SSW) method [50], can be employed in this search. In this study, PSO was chosen due to its adaptability in identifying the most stable interface structure, which may not necessarily correspond to the global minimum but rather to a metastable configuration. This method effectively incorporates additional constraints, such as lattice matching and the inherent restrictions imposed by the neighboring bulk materials on either side of the interface [46]. Moreover, implementing physics-informed modifications in the global optimization process is essential for accurately determining the interface structure, ensuring that the unique characteristics of the materials involved are appropriately considered [48].

2.6.1 CALYPSO

The PSO algorithm was applied to crystal structure prediction using the CALYPSO code for crystal structure analysis through particle swarm optimization [46,48,51].

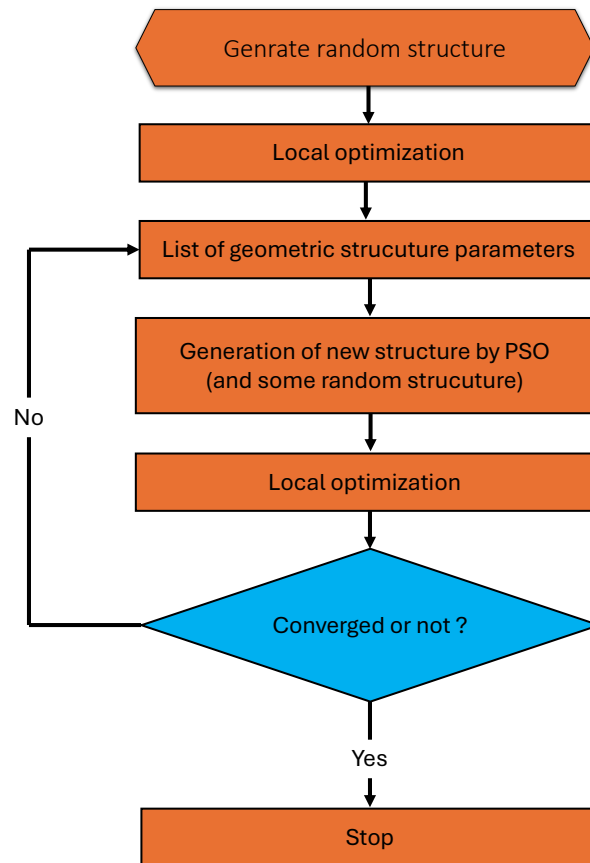


Figure 2.5: Flowchart diagram for CALYPSO simulations

The global minimization method through CALYPSO code [51] for predicting interface structures comprises mainly four steps as depicted in the flow chart of Figure 2.5:

1. Generate random interface structures with the bonding constraint:
The surface configuration is derived from the lattice mismatch value, and these surfaces are then used to form the interface supercell. The initial position of an atom in the interface region is randomly assigned, and its validity is then evaluated by checking the interatomic bond lengths and nearest-neighbor coordination numbers. If the bond lengths

are too short or the coordination numbers fall outside acceptable ranges, the atom's position is rejected and regenerated. This procedure is repeated iteratively until a physically valid interface structure is achieved.

2. Local optimization:

The potential-energy surface can be viewed as a multidimensional landscape of peaks and valleys, with saddle points linking different regions. The valleys correspond to local basins of attraction on the potential energy surface. Geometry relaxation is applied to move the system toward local minima within this landscape. In this process, the free energies determined using DFT simulation.

3. Identification of Local minima:

The energies of the structures, determined through DFT simulations, are used as fitness values to evaluate their stability. After optimization, several similar or identical structures may appear. To accelerate the search process, these duplicate structures are removed.

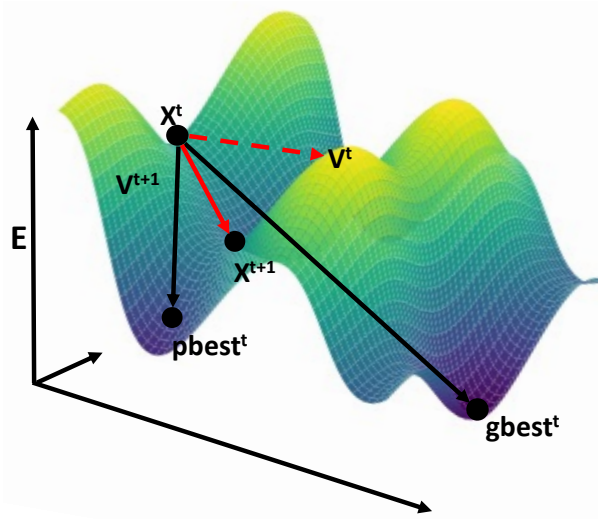


Figure 2.6: Illustration of update for position and velocity on potential energy surface in PSO. An initial velocity V^t evolves into V^{t+1} after one step of PSO, as described by Eq. 2.31. A high-energy structure (X^t) transitions to a significantly lower-energy structure (X^{t+1}) after one PSO operation.

4. New structures generation by PSO:

To thoroughly explore the potential energy landscape, the structures evolve using the interfacially confined PSO algorithm, which possesses global search capabilities. Assuming the interface region contains n atoms, a total of $3n+2$ search dimensions are needed to update the interface structure, with $3n$ dimensions corresponding to the atomic coordinates and 2 dimensions for rigid-body displacement. Specifically, the position of the structure (x) in each search dimension k is updated according to the following.

$$x_i^{t+1}(k) = x_i^t(k) + v_i^{t+1}(k) \quad (2.31)$$

where, i and t represent the indices of the structure in the population and the generation, respectively. The initial velocities (v) of the structures in the first generation were generated randomly. The new velocity of each individual i in the k^{th} dimension was calculated

based on its previous position (x) before optimization, its previous velocity (v), its current best position ($pbest_i^t$), determined by the lowest enthalpy, and the global best position ($gbest$) with the highest fitness value from the entire population. Each particle's position is updated using its velocity vector, as shown in Fig

$$v_i^{t+1}(k) = \omega v_i^t(k) + c_1 r_1 [pbest_i^t(k) - x_i^t(k)] + c_2 r_2 [gbest(k) - x_i^t(k)] \quad (2.32)$$

The inertia weight (ω) was dynamically and linearly reduced from 0.9 to 0.4 throughout the iterations. The factor c_1 represents self-confidence and indicates how much a particle relies on its own past experiences, while c_2 represents swarm confidence, reflecting how much it trusts the collective experience of the swarm. Both c_1 and c_2 , which are the learning factors, were fixed at 2. Additionally, r_1 and r_2 were two random numbers uniformly distributed in the range (0, 1) to ensure comprehensive coverage of the search space and to prevent entrapment in local optima. To mitigate premature convergence of the algorithm, the velocities were constrained within the range of $-1.2/l$ to $1.2/l$, where l (in Å) denotes the length of the corresponding lattice vector. To enhance the efficiency of the procedure and improve structural diversity, a selection of low-energy structures from the previous generation was chosen to generate the next generation using PSO (60%), while the remaining structures were generated randomly(40%).

Chapter 3

Bulk and surface of SnS and ZnS

This chapter explores the structural and electronic properties of the bulk and surface of tin sulfide (SnS) and zinc sulfide (ZnS). Understanding these properties is crucial for optimizing thin-film solar cell performance, as both bulk characteristics and surface phenomena significantly influence charge carrier dynamics and material interactions. We will first examine the bulk structures of SnS and ZnS, highlighting their crystal structures and inherent properties. Subsequently, the chapter will delve into the surface characteristics of both materials, discussing factors such as surface energy, defects, and their impact on interface stability and performance.

3.1 Computational methods

All density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [52–54]. The exchange-correlation interaction was treated using the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional [30]. The interactions between ions and electrons were described by the projector augmented wave (PAW) method [37]. For the electronic structure calculations, a plane-wave basis set with a kinetic energy cutoff of 450 eV was employed, which ensures sufficient convergence for total energy and forces. The Brillouin zone was sampled using a Monkhorst-Pack grid with k-spacing of $0.01 \text{ \AA}^{-1}$. The self-consistent field (SCF) convergence criterion was set to 1×10^{-6} eV for the total energy. For geometry optimizations, the atomic positions were relaxed until the forces on all atoms were less than $0.01 \text{ eV/\AA}$. In addition, pseudopotentials were used to simplify the computational treatment of core electrons, with valence configuration, where 4d, 5s, and 5p electrons of Sn; 3d, 4s electrons of Zn and 3s, 3p electrons of S were treated as valence electron configuration.

Seven different low-index surfaces were considered by cleaving the optimized bulk SnS and ZnS structures along the (100), (010), (001), (011), (101), (110), and (111) crystallographic planes. Surface supercells were generated using VASPkit [43], each consisting of three atomic slabs separated by a $15 \text{ \AA}$ vacuum layer, ensuring negligible interaction between the periodic images. The bottom slab atoms were fixed to simulate the behavior of a substrate, while the atoms in the top two slabs were allowed to relax in all directions. Notably, during the surface structure optimizations, the surface structure itself was kept constant to maintain the vacuum, and only the atomic positions of the top two slabs were relaxed as shown in Figure 3.4. To account for potential surface dipole effects, a dipole correction was applied along the z-direction

for all surface supercells [42].

3.2 Bulk structure of SnS and ZnS

Here, the lattice parameters and electronic structures of bulk SnS and ZnS as shown in Figures 3.1 (a) and (b) were investigated to ensure the reliability of the computational method applied. The lattice parameters for SnS and ZnS were consistent with previously reported values obtained through DFT calculations and experimentation as shown in Table 3.1 [2, 55–60]. This agreement provides confidence in the accuracy of the structural optimizations performed using the chosen computational setup. Moreover, the band gaps of bulk SnS and ZnS were found to be 0.92 eV and 2.08 eV, respectively, which were comparable to other computational work [2, 55, 56, 58, 60]. Whereas, the difference in the band gap with the experimentation value was due to the discontinuity in the gradient derivatives and self-interaction error in the DFT simulation [61, 62].

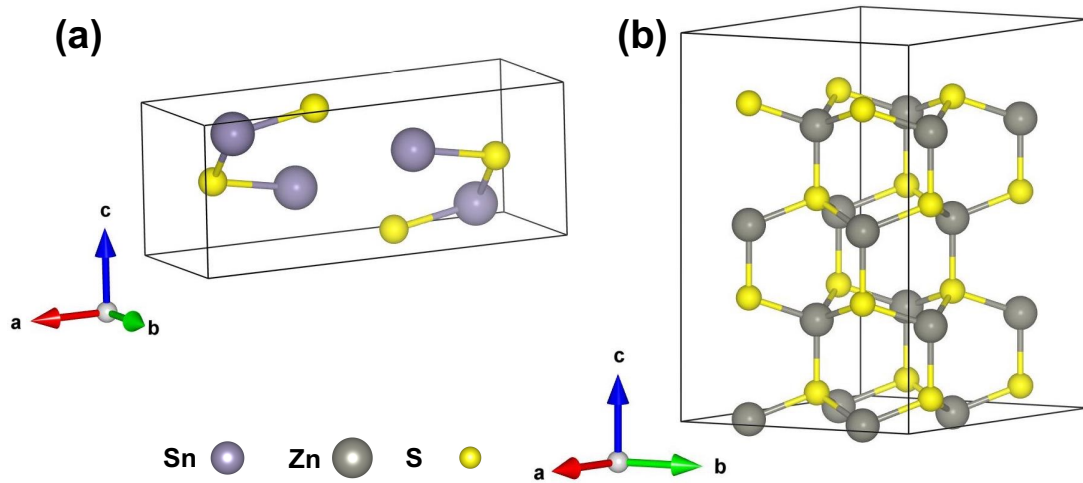


Figure 3.1: Schematic of bulk (a) SnS and (b) ZnS structure (created using VESTA software [1]).

Table 3.1: Lattice parameter (in Å) and bandgap (in eV) of bulk SnS and ZnS

		Lattice Parameter ($\alpha = \beta = 90^\circ$)				Bandgap
		<i>a</i>	<i>b</i>	<i>c</i>	γ	
SnS	Current computational work	11.410	4.026	4.427	90°	0.92
	Other computational work [2, 55]	11.202	4.023	4.459	90°	0.92
	Experimental Value [56, 57]	11.192	3.984	4.329	90°	1.25
ZnS	Current computational work	3.845	3.845	6.309	120°	2.08
	Other computational work [58–60]	3.843	3.843	6.299	120°	2.11
	Experimental Value [58]	3.850	3.850	6.290	120°	3.77

The electronic band structure and density of states (DOS) for bulk SnS and ZnS provide valuable insights into the electronic properties of both materials. Bulk SnS was found to be an indirect band gap semiconductor with a band gap of 0.9235 eV, as depicted in Figure 3.2(a) [2]. The analysis of the DOS reveals that the valence band edge (VBE) is primarily composed of S 3p orbitals, with a minor contribution from Sn 5s states. The conduction band edge (CBE), on the other hand, is dominated by Sn 5p orbitals, with smaller contributions from S 3p orbitals, as shown in Figure 3.2(b). Further analysis of the DOS reveals that the lower valence band (ranging from -2 to -4 eV) is primarily attributed to the occupied S 3p orbitals, along with a minor contribution from the occupied Sn 5p states. This suggests strong bonding interactions between the sulfur atoms and the neighboring tin atoms in this energy range. In contrast, the higher conduction band (from 2 to 4 eV) is largely dominated by unoccupied Sn 5p states, with small contributions from unoccupied S 3p states. This distribution of electronic states highlights the significant role of Sn 5p orbitals in defining the conduction properties of bulk SnS, making it a key factor in its electronic behavior.

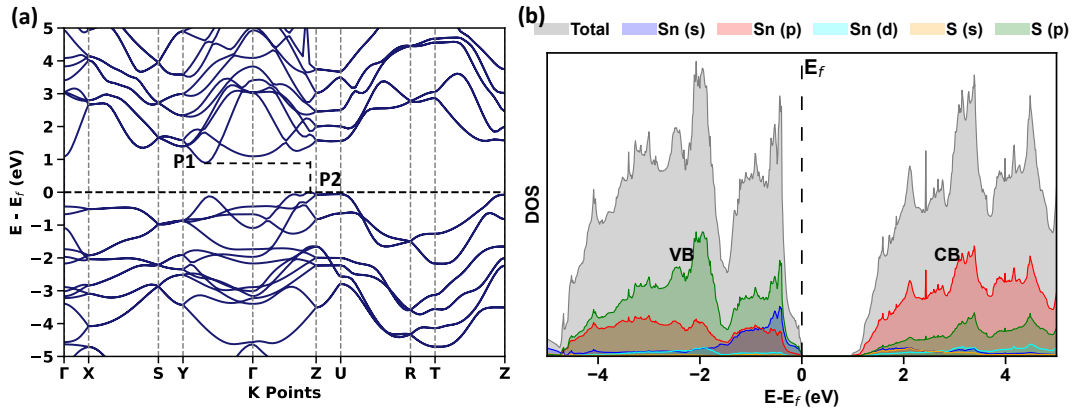


Figure 3.2: (a) Electronic band structures (P1 and P2 are the conduction band minima and valence band maxima, respectively) and (b) total and partial density of states (PDOS) of the bulk SnS (the dotted lines here represent the Fermi level (E_f), and these have been set to zero in the energy scale). (Adapted from Dahule et. al. [2])

The electronic band structure and density of states (DOS) for bulk ZnS reveal important insights into its electronic properties. Bulk ZnS was found to be a direct band gap semiconductor with a band gap of 2.08 eV, as depicted in Figure 3.3(a). The direct nature of the band gap indicates that the valence band maximum and conduction band minimum occur at the same k-point i.e., γ , making ZnS suitable for optoelectronic applications that require efficient photon absorption and emission. The DOS analysis shows that the VBE is primarily composed of S 3p orbitals, with a minor contribution from Zn 3d states. The CBE is dominated by Zn 4s orbitals, with smaller contributions from S 3p states, as shown in Figure 3.3(b). Further examination of the DOS reveals that the lower valence band (ranging from -2 to -4 eV) is primarily composed of occupied S 3p states, with additional contributions from occupied Zn 3d states. Beyond -4 eV, the valence band shows a significant contribution from both S 3p and Zn 4s states, indicating a complex interplay between the sulfur and zinc orbitals in defining the electronic structure of ZnS. In contrast, the higher conduction band (beyond 3 eV) is dominated by unoccupied Zn 4s orbitals, with minor contributions from unoccupied S 3p states. This highlights the critical role of Zn 4s orbitals in the conduction band, which is pivotal for the electronic and optical properties of ZnS. The predominance of Zn 4s states in the conduction band underscores the effectiveness of ZnS in applications requiring efficient charge carrier mobility and photonic

interactions, making it a suitable candidate for optoelectronic devices.

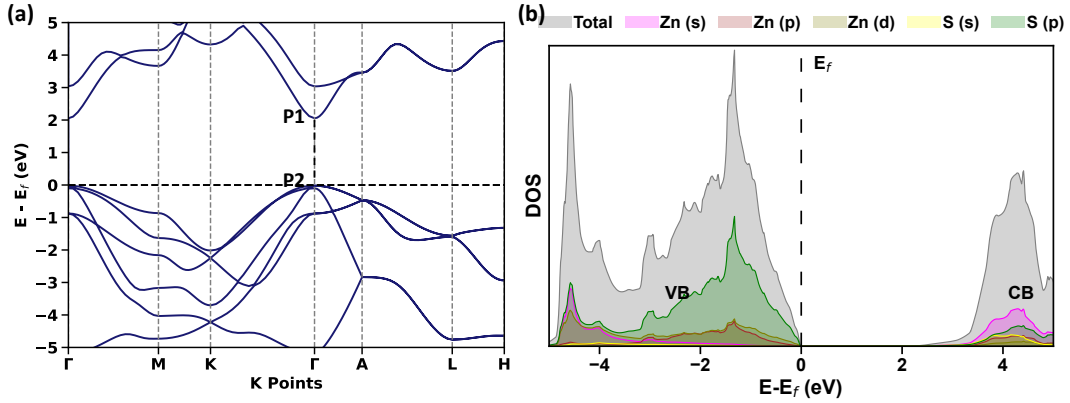


Figure 3.3: (a) Electronic band structures (P1 and P2 are the conduction band minima and valence band maxima, respectively) and (b) total and partial density of states (PDOS) of the bulk ZnS (the dotted lines here represent the Fermi level (E_f), and these have been set to zero in the energy scale) (Adapted from Dahule et. al. [3]).

3.3 Surface stability and electronic structure

The stability of a material's surface is a critical determinant of its overall performance and longevity of solar cells. The surfaces of these materials often exhibit distinct properties that diverge from their bulk counterparts, primarily due to factors such as reduced atomic coordination and the presence of defects. These surface characteristics significantly influence key aspects of solar cell performance, including charge carrier dynamics, light absorption, and surface reactivity with environmental factors. Understanding the electronic structure at the surface is essential for optimizing the functionality of thin-film solar cells, as it directly impacts the behavior of charge carriers and the stability of the material interfaces. In this context, the surface study of SnS and ZnS was conducted to understand their stability and electronic behavior. Moreover, the surface supercells were constructed using periodically repeated slab models cleaved from the bulk structure and 15 Å vacuum space to decouple the surfaces. The surface structure for SnS and ZnS are illustrated in Figure 3.4. Here the bottom slab of SnS(100) and ZnS(110) is a fixed slab as denoted in Figure 3.4 and other slab *i.e.* between fixed slab and vacuum consist of atoms free to move in any directions. The low index surfaces ((100), (010), (001), (011), (101), (110), and (111)) of SnS and ZnS were selected to find their stability using surface energies.

3.3.1 SnS surfaces

To evaluate the surface stability of SnS surfaces, the surface energies were calculated using equation (2.29) and presented in table 3.2. As shown in table 3.2, the surface energy of SnS(100) is lower than that of other low index surfaces considered. This suggests that the SnS(100) surface is the most stable among them. Our results for surface stability was in good agreement with the surface energy reported by Tritsrir et al., who also investigated the relative stability of the SnS surface using stoichiometric and oxygen-containing structural models and found the

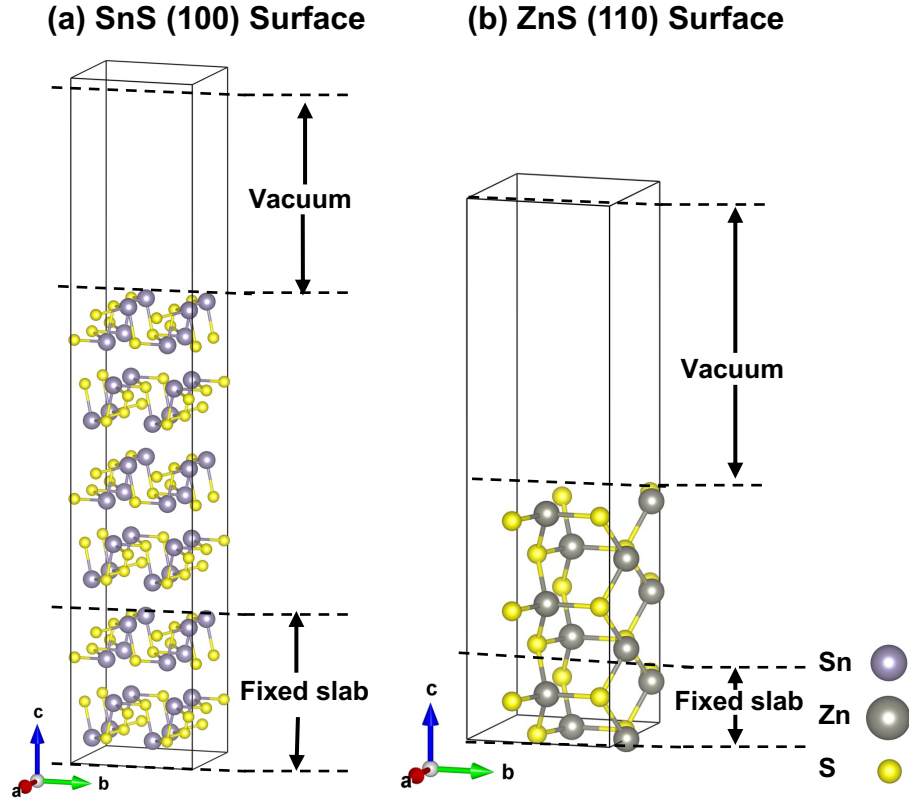


Figure 3.4: Schematic of (a) SnS (100) and (b) ZnS (110) surface structures. (created using VESTA software [1])

SnS (100) stable surface [63]. The surface structure for SnS(100) supercell was depicted in Figure 3.4 (a).

The electronic structure of SnS surfaces was analyzed to assess the influence of surface configurations. Figure 3.5 presents the total and partial density of states (DOS) for all surfaces considered. The SnS (100), (010), (011), (101), and (111) surfaces display similar orbital contributions to their valence band (VB) and conduction band (CB) compared to bulk SnS, indicating that the electronic structure remains largely preserved across these surface orientations. Among them, the SnS (100) surface most closely resembles the bulk structure. The band gap for the SnS (100) surface was calculated to be 0.91 eV, slightly lower than the bulk band gap of 0.92 eV. In contrast, for the SnS (010), (011), (101), and (111) surfaces, a sharp peak in the Sn 5p states was observed near the conduction band edge (CBE), which is attributed to surface reconstruction following relaxation and changes in the coordination of surface atoms. The band gaps for these surfaces were found to be 1.01 eV, 0.62 eV, 0.1 eV, and 0.77 eV, respectively. This variation in band gap suggests that surface reconstruction significantly impacts electronic properties and could influence their performance in photovoltaic applications. Additionally, the surface reconstruction of SnS (001) resulted in the formation of states above the Fermi level, a characteristic also observed in previous studies involving SnS surface defects, such as Sn vacancies (V_{Sn}) [2]. These surface states can introduce traps or recombination centers, which may affect charge transport efficiency.

SnS (101) and (110) surfaces exhibited an overlap of the valence and conduction bands, leading to metallic behavior. In these metallic surfaces, the DOS at the Fermi level primarily consists of S 3p states, with a minor contribution from Sn 5p states, highlighting the significant

role of sulfur atoms in influencing the electronic properties of these surfaces. The metallic behavior of these surfaces may have implications for the efficiency of thin-film solar cells, as it could result in increased surface conductivity, potentially impacting device performance by enhancing or inhibiting charge separation and transport.

Table 3.2: Surface energies (γ_{surface}) for SnS and ZnS surfaces.

Surface	Total Energy (eV)		Surface Area ($\text{\AA}^2$)	Surface Energy (eV/ $\text{\AA}^2$)
	E_b	E_s		
SnS	100	-35.464 -106.184	17.936	0.0058
	010	-35.464 -103.450	51.638	0.0280
	001	-35.464 -102.681	45.077	0.0412
	011	-70.949 -209.728	68.545	0.0228
	101	-70.929 -210.495	48.514	0.0236
	110	-70.930 -207.352	54.664	0.0497
	111	-106.39 -316.196	72.562	0.0206
ZnS	100	-13.688 -39.340	24.311	0.0355
	010	-13.688 -39.340	24.311	0.0355
	001	-13.688 -38.956	14.809	0.0712
	011	-27.381 -76.179	28.467	0.1048
	101	-27.381 -77.012	28.467	0.0902
	110	-27.379 -79.206	42.108	0.0346
	111	-41.080 -117.875	49.306	0.0544

3.3.2 ZnS surfaces

The stability of ZnS surfaces were evaluated through their surface energies. The surface energies for all low index surface of ZnS along with their total energies of slab and surface supercell were shown in Table 3.2. Among the surfaces analyzed, the most stable surface, ZnS (110), exhibits DOS orbital contributions that closely resemble those of bulk ZnS. Moreover, the surface structure of ZnS (110) are illustrated in Figure 3.4 (b). This similarity suggests that the ZnS (110) surface retains the essential electronic characteristics of the bulk material. The calculated electronic structure, represented by the total and partial density of states (DOS) for ZnS surfaces, is illustrated in Figure 3.6. Furthermore, the band gap of the ZnS (110) surface was determined to be 1.87 eV, which is consistent with the bulk ZnS value, confirming the stability of this surface from an electronic perspective. However, one key difference between the surface and bulk DOS is the presence of a sharp peak around 1.87 eV near to CBE in the ZnS (110) surface, as shown in Figure 3.6. These sharp DOS peaks are attributed to localized electronic states caused by changes in the coordination of surface atoms following surface relaxation [64].

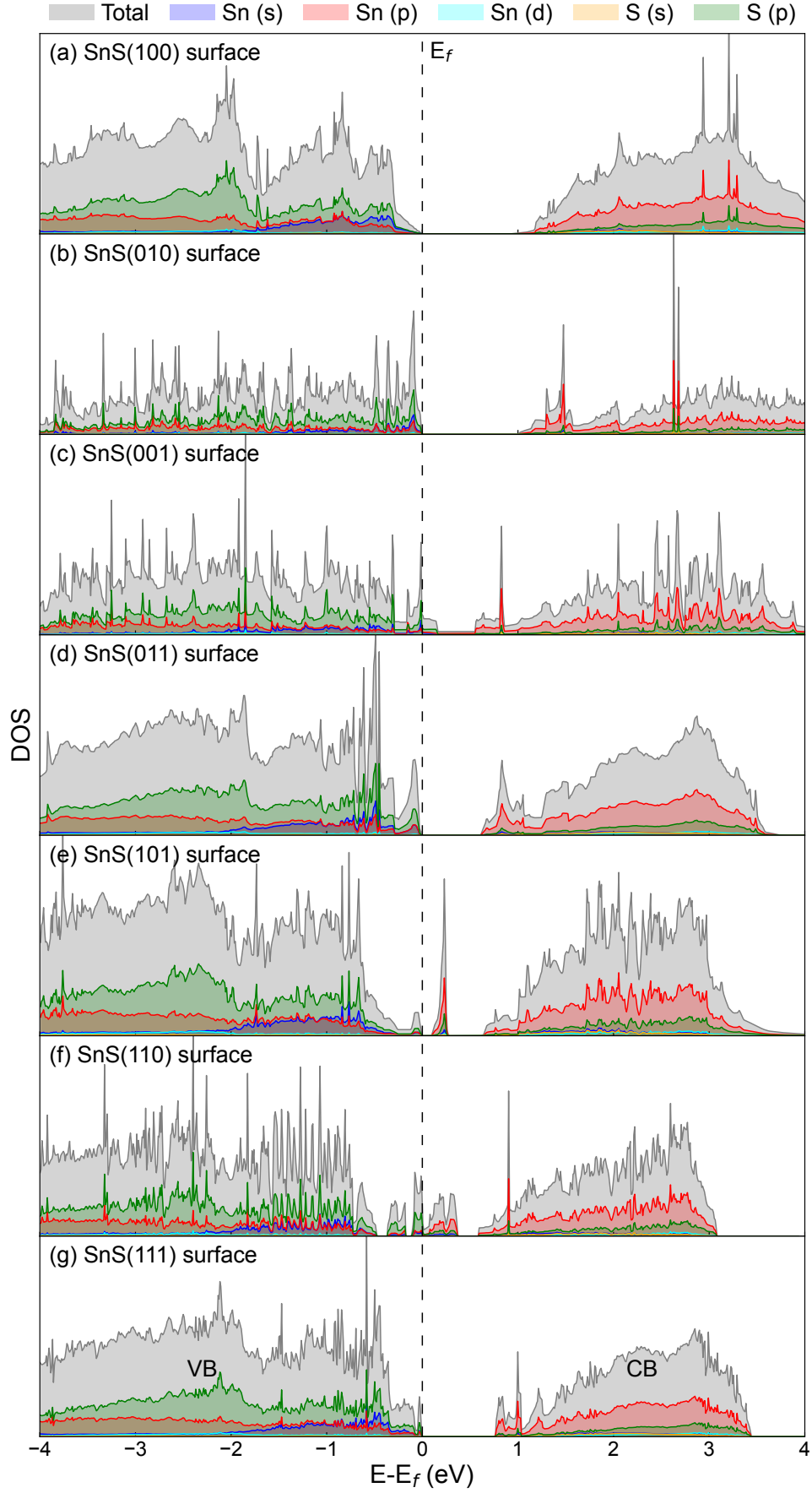


Figure 3.5: (a) Total and partial density of states of SnS surfaces (the dotted lines here represent the Fermi level (E_f), and these have been set to zero in the energy scale) (Adapted from Dahule et. al. [3]).

These states indicate the mixed ionic-covalent bonding character of ZnS, which is influenced by surface structure and atomic arrangement [65].

Variations in band gap values across the different ZnS surfaces are primarily influenced by broken bonds and atomic surface relaxation, particularly within the surface supercells. For instance, both the ZnS (100) and ZnS (110) surfaces exhibit similar orbital contributions in the valence band (VB) and conduction band (CB) when compared to bulk ZnS. However, subtle differences in their DOS peaks indicate that the surface morphology plays a significant role in modifying the electronic properties of these surfaces. Notably, the ZnS (100) and ZnS (010) surfaces share an identical surface structure, leading to equivalent surface energies, as detailed in Table 3.2. The band gap for these surfaces was calculated to be 1.53 eV, slightly lower than that of the ZnS (110) surface. Despite this, these surfaces also exhibit a sharp DOS peak near the conduction band edge (CBE), similar to the ZnS (110) surface, further distinguishing them from the bulk ZnS, which lacks such pronounced peaks.

Moreover, distinct DOS profiles were observed across different configurations of metallic ZnS surfaces, highlighting the diversity in their electronic structures. The overlap of the VB and CB for ZnS (001), (011), (101), and (111) surfaces not only signifies metallic characteristics but also suggests potential differences in surface reactivity, which could impact their performance in various device applications. For these metallic surfaces, the DOS at the Fermi level is predominantly composed of S 3p states, with a smaller contribution from Zn 4s and 3d states. This substantial presence of sulfur-derived states near the Fermi level emphasizes the critical role that sulfur atoms play in dictating the electronic properties of the ZnS surfaces. The strong contribution from sulfur orbitals in the metallic surfaces points to the complex interplay between atomic coordination, surface relaxation, and electronic structure.

The transition from semiconducting to metallic behavior on certain ZnS surfaces highlights the importance of understanding surface stability and electronic structure when designing materials for specific applications. In the context of thin-film solar cells, the stability of the ZnS (110) surface, coupled with its retained band gap and preserved electronic structure, makes it a promising candidate for use as a buffer or window layer. On the other hand, the metallic nature of the ZnS (001), (011), (101), and (111) surfaces could either be detrimental or advantageous, depending on the application. For instance, while metallic surfaces may offer enhanced surface conductivity, they may also introduce undesirable recombination centers in solar cells, negatively impacting device efficiency. Thus, a careful balance between surface stability and electronic properties must be achieved to optimize ZnS surfaces for photovoltaic and other optoelectronic applications.

Overall, the analysis of SnS and ZnS surfaces underscores the importance of understanding surface stability and electronic structure for optimizing these materials in photovoltaic and electronic applications. While stable surfaces like SnS (100) and ZnS (110) offer promising semiconducting properties for thin-film solar cells, the metallic characteristics observed in other surface orientations could influence their conductivity and performance. Careful surface engineering will be essential to harness the full potential of these materials in future device technologies.

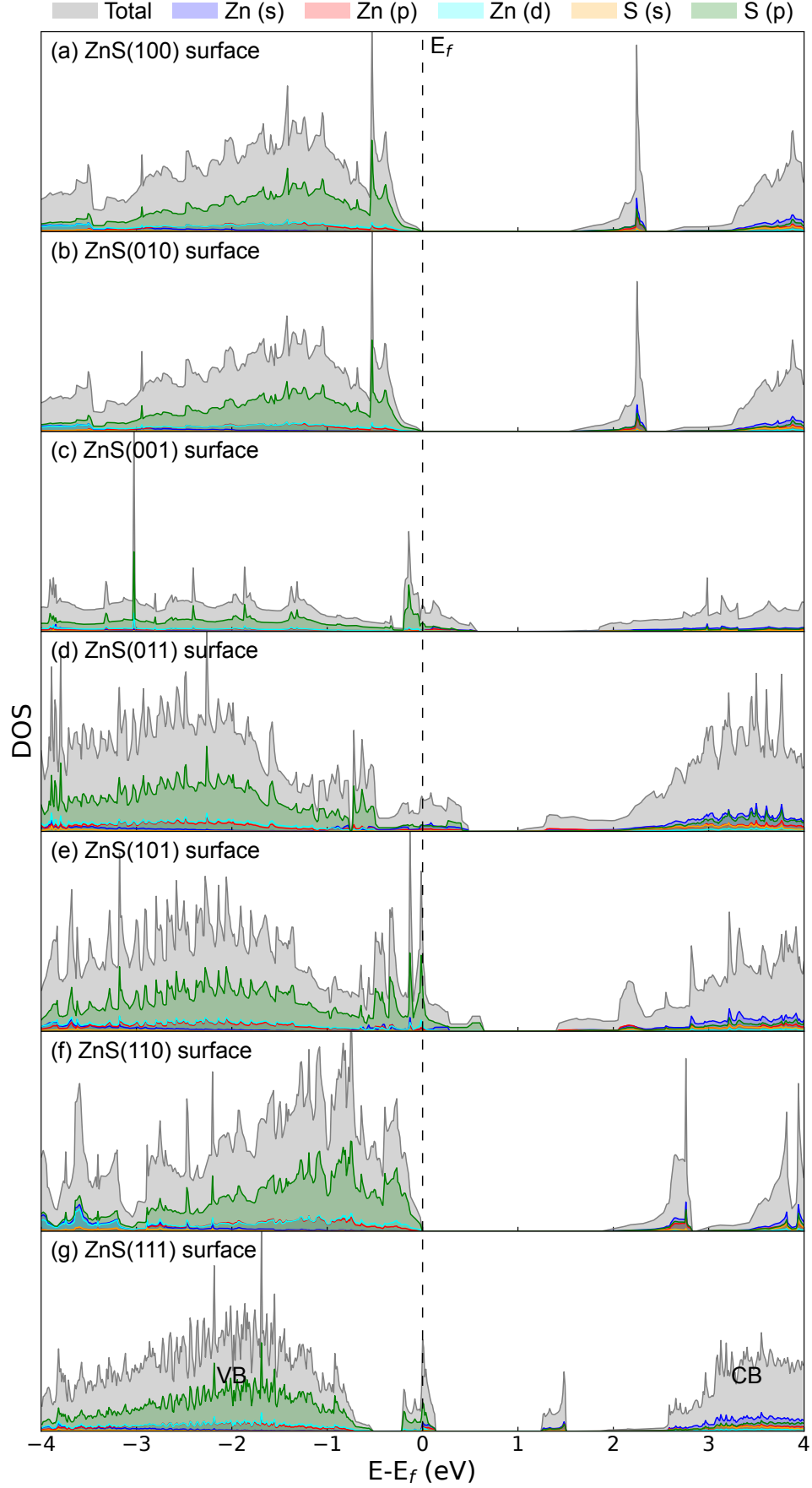


Figure 3.6: (a) Total and partial density of states of SnS surfaces (the dotted lines here represent the Fermi level (E_f), and these have been set to zero in the energy scale)(Adapted from Dahule et. al. [3]).

Chapter 4

SnS/ZnS Interfaces

Interfaces play a crucial role in determining the overall performance of thin-film solar cells (TFSC) and other optoelectronic devices, as they directly impact charge transfer, recombination processes, and overall device efficiency. The interaction between different materials at interfaces, particularly between the absorber layer and buffer or window layers, introduces complex phenomena such as lattice mismatch, interface reconstruction, and localized states. These factors influence both the structural and electronic properties of the interface, making it essential to understand their behavior at an atomic level.

In this chapter, we focus on the interface between SnS and ZnS, two promising materials for use in TFSCs due to their favorable optical and electronic properties. By analyzing the structural stability and electronic structure at these interfaces, we aim to elucidate the key mechanisms that govern interface behavior. Special attention is given to the impact of lattice mismatch, interface bonding characteristics, and the formation of interface states, all of which play a critical role in determining the efficiency and stability of TFSC devices. Additionally, we explore how defects and surface reconstructions influence the overall interface properties, providing insights for optimizing material combinations in photovoltaic applications.

4.1 Computational method

In this study, the structural and electronic properties of the SnS(100)/ZnS(110) interface, both in pristine and defect-rich configurations, were investigated using first-principles density functional theory (DFT) calculations [12, 13]. All simulations were performed within the framework of the projector augmented wave (PAW) method [37], as implemented in the Vienna Ab initio Simulation Package (VASP) [52–54]. The exchange-correlation interactions were treated using the Perdew-Burke-Ernzerhof Generalized Gradient Approximation (PBE-GGA) [30].

Supercell models were constructed for pristine and defective interface structures. The pristine SnS(100)/ZnS(110) interface structure consisted of an equal number of Sn, S, and Zn atoms. Defective interface structures were created by introducing additional Sn, S, or Zn ad-atoms, forming Sn-rich, S-rich, Zn-rich, (Sn,S)-rich, and (Zn,S)-rich configurations. A vacuum layer of 15 Å was added to avoid interactions between periodic images.

Geometry optimizations were performed by relaxing the atomic positions until the forces on all atoms were smaller than 0.01 eV/Å. The plane-wave cutoff energy was set to 450 eV, and the Brillouin zone was sampled using a Monkhorst-Pack grid of 4×5×1 k-points for the interface

supercells [38]. All calculations were performed with a convergence criterion of 1×10^{-6} eV for the total energy.

The electronic structure of the interface, including the partial density of states (PDOS) for individual atomic layers, was calculated for both pristine and defect-rich configurations. To obtain accurate band alignment and offsets, electrostatic potential profiles were generated using the planar and macroscopic average methods, as discussed in previous sections. The interface energies were calculated using Equation (2.30), and the resulting energies for different interface configurations were compared to determine the most energetically stable structure.

For the defect-rich models, additional CALYPSO interface structure prediction software was used to explore the potential configurations and optimize interface structures [46]. This approach combined particle swarm optimization (PSO) with DFT energies to identify the most stable atomic arrangements for the various defect compositions at the interface. Additional details regarding the CALYPSO method and its application to materials prediction, including specific parameter choices and validation techniques, are provided in Chapter 2.

4.2 Pristine interface structure

The pristine interface structure between materials in TFSCs plays a critical role in influencing the efficiency of charge separation and transport across the various layers. A pristine interface is characterized by an idealized, defect-free boundary where the structural and electronic properties of both materials remain intact, devoid of impurities or surface reconstructions. As outlined in Chapter 3, several surfaces were evaluated, including SnS(100) and ZnS(110), which demonstrated the lowest surface energies among the surfaces considered. Understanding the relationship between surface energy and electronic properties is essential for optimizing materials intended for solar cell applications, as stable semiconductor surfaces are crucial for maximizing device performance. Therefore, the choice of the most stable surfaces, as identified in Chapter 3, is fundamental in the design of interfaces, as the stability of these materials significantly affects the efficiency of solar cells. In particular, SnS(100) and ZnS(110) are noteworthy because they exhibit minimal surface energy and demonstrate advantageous semiconductor characteristics, positioning them as prime candidates for effective interface modeling.

The interface structure of the solar cell was carefully designed to minimize strain. The lattice mismatch between the SnS(100) and ZnS(110) heterostructure was assessed using Equation (2.28), resulting in a calculated mismatch of 1.291% ($\bar{\epsilon} = 0.0129$), which falls within an acceptable range. Generally, a lattice mismatch of less than 5% is necessary for effective epitaxial growth. Such a low mismatch is vital for minimizing defect formation at the interface and facilitating the relaxation process.

Initially, the interface models were developed by omitting the interface atoms, resulting in a pristine interface structure, as illustrated in Figure 4.1. This process involved merging the surfaces of SnS(100) and ZnS(110) to create the supercell for the SnS(100)/ZnS(110) interface. The SnS(100) surface consisted of 7 Sn atoms and 7 S atoms, while the ZnS(110) surface comprised 6 Zn atoms and 6 S atoms. These surface structures were meticulously cleaved to achieve minimal lattice mismatch, as described in Section 2.4.3 of the methodology. This careful approach ensured that the interface was constructed with a strong emphasis on optimal atomic arrangement, thereby improving compatibility and minimizing strain between the two materials.

In the interface model, the atoms located in the outermost layer, nearest to the vacuum, were fixed in place to replicate the bulk structure, thereby categorizing them as part of the bulk layer. In contrast, the atoms in the neighboring sub-interface regions were permitted to move freely in any direction, which is referred to as the sub-interface layer, as depicted in Figure 1. Additionally, the interface structure underwent further optimization, and the interface energy was calculated using equation (2.30) excluding any interface ad-atoms. The optimized pristine interface structure exhibited an interface energy of $-0.066 \text{ eV}/\text{\AA}^2$ and a thickness of $2.02 \text{ \AA}$. Measurements of atomic displacements near the interface revealed that atoms were displaced by up to $0.2 \text{ \AA}$, while sub-interface atoms experienced displacements of up to $0.1 \text{ \AA}$. These displacements diminished progressively with increasing distance from the interface, as shown in Figure 4.1 of the atomic structure.

The partial density of states (PDOS) for the pristine SnS(100)/ZnS(110) interface structure was thoroughly examined, with PDOS profiles plotted for various layers of atomic slabs, as shown in Figure 4.1. The pristine interface exhibited a bandgap of 0.8573 eV . Notably, the PDOS for the bulk layers closely resembled those of bulk SnS and ZnS. In the SnS bulk layer, the valence band edge (VBE) is primarily composed of S 3p orbitals, with a minor contribution from Sn 5s states, while the conduction band edge (CBE) is dominated by Sn 5p orbitals and includes a smaller contribution from S 3p orbitals. For the ZnS bulk layer, the density of states analysis shows that the VBE is mainly made up of S 3p orbitals, with a slight contribution from Zn 3d states, and the CBE is dominated by Zn 4s orbitals, along with minor input from S 3p states. Within the PDOS of the SnS bulk layer, a prominent peak corresponding to Sn 5p states was detected near the Fermi level, indicative of p-type semiconductor behavior, which suggests that the SnS bulk layer serves as a source of hole carriers typical of p-type materials. In contrast, the Fermi level for the ZnS bulk layer was situated near the CBE, reflecting n-type semiconductor behavior and signifying electron carrier contributions from the ZnS bulk layer. Additionally, Zn 4s states were identified at the CBE, as illustrated in Figure 4.1.

The displacement of ZnS sub-interface atoms adjacent to the interface led to the emergence of S 3p DOS states near the valence band edge (VBE) within the energy range of -2 to -0.1 eV , as depicted in the PDOS of the ZnS sub-interface layer. This finding indicates that atomic displacements influence the electronic states within the sub-interface region. Similarly, Zn 4s states were observed at 0.2 eV near the CBE in the ZnS sub-interface layer, suggesting a substantial contribution to the overall electronic structure. In the SnS sub-interface layer, the CBE, associated with Sn 5p states, shifted closer to the Fermi level, resulting in a reduced bandgap compared to the SnS(100) surface structure, as detailed in Figure 4.1. This shift implies enhanced electronic interactions at the interface, likely playing a significant role in the overall reduction of the bandgap compared to its SnS and/or ZnS bulk and surfaces.

The band alignment of the SnS(100)/ZnS(110) interface structure was assessed using the electrostatic potential alignment technique as detailed by Weston et al. [66]. The valence band offset (VBO) is determined as

$$VBO = \Delta E_v + \Delta V \quad (4.1)$$

where ΔE_v denotes the difference in the valence band maximum (VBM) between the two materials, relative to their average electrostatic potential, while ΔV represents the variation in the macroscopic electrostatic potential energy derived from the calculations of the interface structure. The change in electrostatic potential ($V(\bar{r})$) concerning the interface structure was

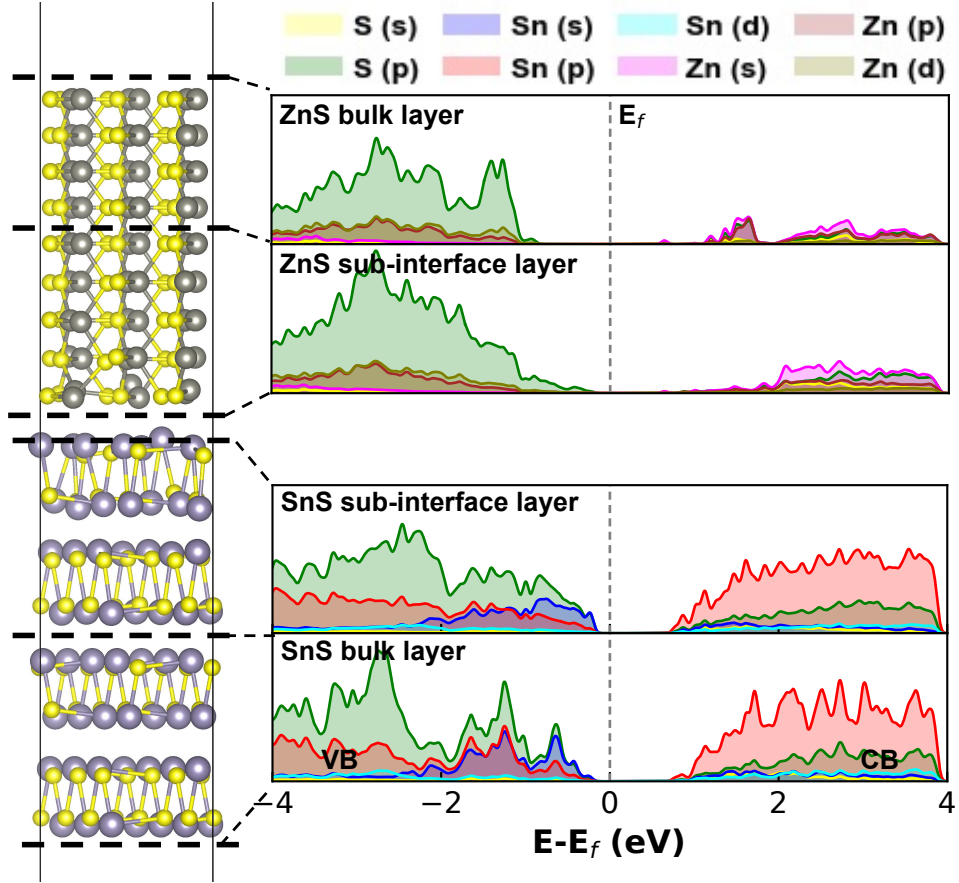


Figure 4.1: PDOS of corresponding layers in the pristine interface models (the dotted line in the right panel represented the Fermi level (E_f)) (The color schemes for the atom are Sn: Silver, Zn: Grey, S: Yellow)(Adapted from Dahule et. al. [3]).

assessed through the planar averaged electrostatic potential, defined as:

$$\bar{V}(z) = \frac{1}{S} \int V(\vec{r}) dx dy \quad (4.2)$$

where S refers to the surface area of the interface. Additionally, the reference value for potential alignment can be determined through macroscopic averaging, represented as $\bar{\bar{V}}(z)$, commonly referred to as the macroscopic averaged electrostatic potential:

$$\bar{\bar{V}}(z) = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} \bar{V}(z) dz \quad (4.3)$$

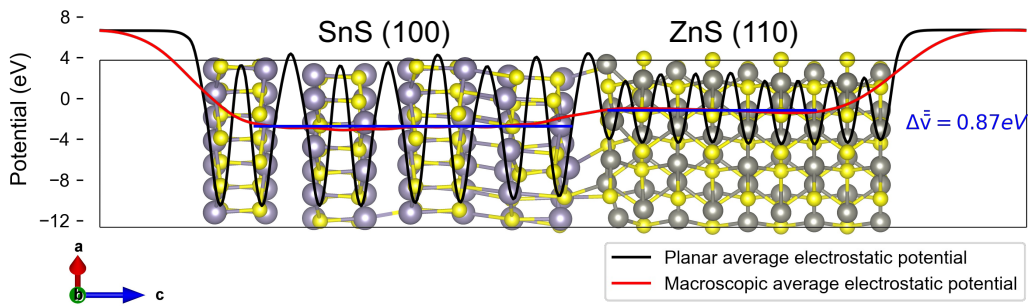


Figure 4.2: Geometry-optimized model of the SnS(100)/ZnS(110) pristine interface structure and the corresponding planar and macroscopic average electrostatic potential. The blue solid line represents the macroscopic average of the electrostatic potential across the interface and $\Delta\bar{V}$ stands for the potential alignment (Adapted from Dahule et. al. [3]).

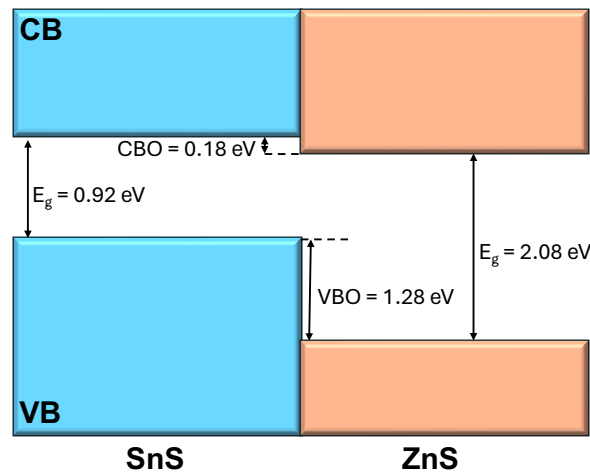


Figure 4.3: Energy band alignment diagram of SnS(100)/ZnS(110) interface structure (Adapted from Dahule et. al. [3]).

The planar and macroscopic average electrostatic potentials ($\bar{V}(z)$ and $\bar{\bar{V}}(z)$) related to the SnS(100)/ZnS(110) interface structure are illustrated in Figure 4.2. The conduction-band offset (CBO) for the SnS/ZnS heterostructure was calculated using the bandgap values derived from the bulk calculations of SnS and ZnS. As illustrated in Figure 4.3, the energy band alignment for the SnS/ZnS interface displays a staggered type II configuration, which is consistent with previous experimental findings related to SnS/ZnS heterostructures [26]. This staggered alignment is beneficial for charge separation, as it allows for efficient transfer of electrons and holes between the two materials, enhancing the overall performance of the solar cell. The calculated CBO and valence-band offset (VBO) for this heterostructure were determined to be 0.18 eV and 1.28 eV, respectively. These values indicate that the energy levels at the interface are well-aligned to facilitate optimal charge carrier dynamics, which is crucial for improving the efficiency of thin-film solar cells. Such favorable band alignments are essential for developing high-performance photovoltaic devices [4, 5].

4.3 Defects at SnS/ZnS interface

In real-world experimental conditions, interfaces often exhibit a range of defect structures resulting from the inherent complexities of their environments. These defects can significantly impact the electronic properties, stability, and overall performance of the SnS/ZnS heterostructure in TFSC. To explore these variations, we expanded our analysis beyond pristine models to investigate six distinct interface compositions between the SnS(100) and ZnS(110) surfaces. By introducing ad-atoms such as Sn, S, and Zn into the interface regions, we created interface supercells with various defect configurations. This method allowed us to capture the intricate behavior of these interfaces and assess how different ad-atom arrangements influence interface stability.

The initial interface configuration comprised an equal distribution of atoms from both surfaces, featuring 7 Sn atoms, 13 S atoms, and 6 Zn atoms, as illustrated in Figure 4.4. This balanced composition served as a reference point for subsequent modifications. We then varied the interface composition to enrich the configurations with additional Sn, S, and Zn atoms, resulting in Sn-rich, S-rich, and Zn-rich interface structures, respectively. Furthermore, we enhanced the interface composition to create (Sn,S)-rich and (Zn,S)-rich environments by increasing the quantities of Sn and S atoms, and Zn and S atoms, respectively.

All six configurations were employed to model the interface structure using CALYPSO, a widely utilized computational tool in materials science and chemistry for predicting and optimizing structures. CALYPSO integrates particle swarm optimization (PSO) with density functional theory (DFT) energies to effectively search for and identify stable atomic arrangements at the interface. This method is particularly advantageous in dealing with the complexity of materials, as it allows for efficient exploration of a vast configurational space, thereby increasing the likelihood of discovering energetically favorable structures. Through the use of CALYPSO, we successfully predicted and identified the energetically favorable interface structures for the SnS(100)/ZnS(110) system across all six distinct interface compositions.

The stability of the interface structure was evaluated using Equation (2.30), with the resulting interface energies summarized in Table 4.1. Notably, the SnS(100)/ZnS(110) interface configuration, characterized by an equal distribution of atoms, demonstrated the lowest interface energy among all the configurations examined. Consequently, this specific configuration

Table 4.1: Interface configurations with No. of atoms and interface formation energy ($\gamma_{\text{interface}}$) (Adapted from Dahule et. al. [3])

	No. of atoms			$\gamma_{\text{interface}}$ (eV/Å ²)
	Sn	S	Zn	
Equal atom	7	13	6	−0.114
Sn-rich	8	13	6	−0.082
S-rich	7	14	6	−0.101
Zn-rich	7	13	7	−0.095
(Sn,S)-rich	8	14	6	−0.094
(Zn,S)-rich	7	14	7	−0.093

was determined to be the most stable among the interface structures analyzed.

4.3.1 Equal atom interfaces

The electronic structure of the defect-containing interface supercell was meticulously analyzed through the partial density of states (PDOS) for the corresponding atomic layers, which included the bulk layers and sub-interface layers of SnS and ZnS, as well as the SnS/ZnS interface layer with ad-atoms. The layered PDOS for both SnS and ZnS is depicted in Figure 4.4, providing a comprehensive view of the electronic states within the materials. Notably, the SnS(100)/ZnS(110) interface structure with defects demonstrated significant atomic displacements of ≥ 0.2 Å for atoms adjacent to the interface and ≤ 0.1 Å for sub-interface atoms, resulting in notable surface reconstruction. This finding highlights the dynamic nature of the interface and its susceptibility to structural changes under realistic conditions.

Importantly, the bulk layers of SnS and ZnS remained unchanged, as their atoms were fixed in position, ensuring the integrity of their electronic properties. The VBE of the SnS bulk layer was primarily composed of S 3p and Sn 5s states, while the CBE featured Sn 5p states, as illustrated in Figure . Similarly, the ZnS bulk layer exhibited S 3p states at the VBE and Zn 4s states at the CBE. Additionally, the DOS of the bulk layers aligned closely with the bulk and surface states of SnS and ZnS affirming the expected electronic characteristics of these materials.

In the equal atom interface configuration, two distinct peaks of Sn 5p states, along with minor contributions from Sn 5s states, were identified near the VBE of the SnS bulk layer. Moreover, the presence of S 3p states at the ZnS sub-interface played a crucial role in facilitating a reduction in the bandgap. Specifically, the bandgap of the equal atom interface structure was reduced to 0.43 eV, compared to 0.83 eV for the pristine interface structure. This significant reduction in bandgap can be directly linked to the incorporation of ad-atoms at the interface, which altered the electronic structure and introduced new electronic states within the bandgap.

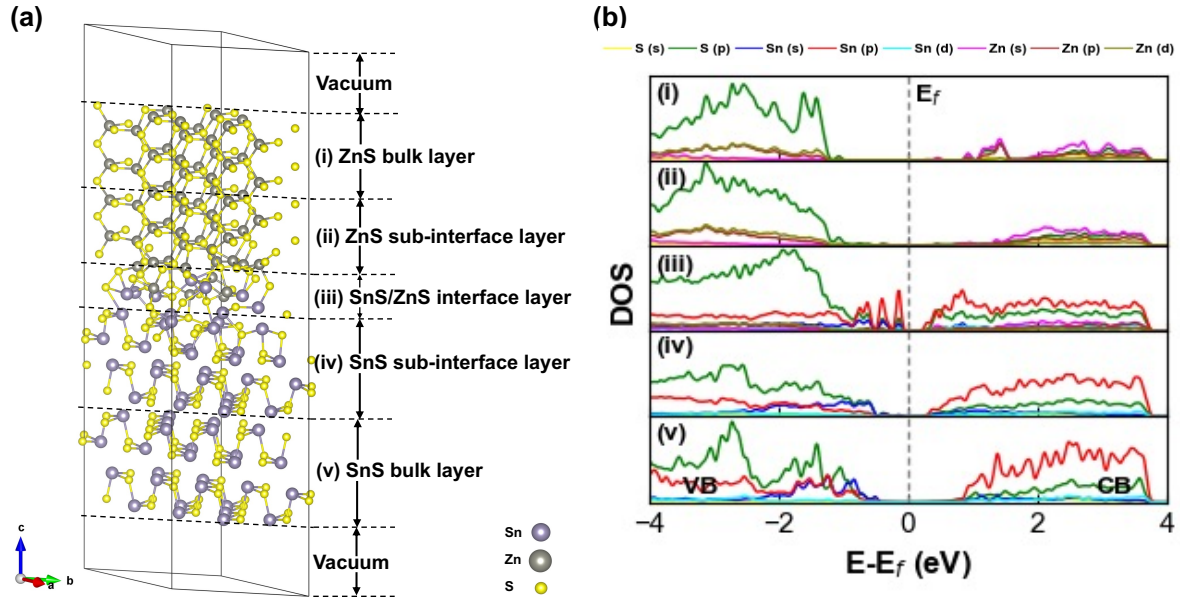


Figure 4.4: (a) SnS/ZnS interface structures with equal atom at interface. (b) The corresponding DOS layers in equal atom at interface structure. Here, SnS/ZnS interface layer have Sn:7, S:13 and Zn:6 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3])

4.3.2 Sn-/Zn-/S-rich interfaces

In cation-rich interfaces, particularly those with Sn-rich and Zn-rich compositions, the interface structure exhibited metallic characteristics due to the significant overlap between the valence band (VB) and conduction band (CB), as illustrated in Figures 4.5 and 4.6. This band overlap was not limited to the interface layer; it also extended into the sub-interface layers as seen in the SnS sub-interface layer (as illustrated in Figures 4.5 and 4.6), indicating a profound influence on the electronic properties of the entire heterostructure. The DOS analysis around the Fermi level revealed a dominant presence of Sn 5p states at the SnS/ZnS interface layer, contributing substantially to the observed metallic behavior. This is clearly depicted in Figures 4.5 and 4.6. Furthermore, the incorporation of excess Sn atoms led to the formation of Sn antisites on the surface, significantly enhancing the metallic nature of these interface structures, aligning with findings from previous studies [2]. In addition, the SnS and ZnS bulk layers for Sn-/Zn-rich interface structure configuration is same as that of the pristine interface structure as well as the equal-atom defect interface structure.

The presence of metallic characteristics in cation-rich interfaces is critical as it may facilitate charge carrier transport, potentially improving device efficiency. However, this enhancement also raises concerns about increased recombination losses, which could negatively impact the overall performance of the SnS/ZnS heterostructure in thin-film solar cells (TFSC).

In contrast, for the S-rich interface structure, the DOS analysis showed that S 3p states, along with minor contributions from Sn 5p states, crossed the Fermi level, as illustrated in Figure 4.7. In this case, the SnS sub-interface layer exhibited a shift in the VB states, with Sn 5p states moving closer to the VBE or even aligning with the Fermi level. The DOS for both bulk SnS and ZnS layers remained consistent with their respective pristine bulk layers. This

crossing at the Fermi level suggests a change in the electronic structure, potentially influencing the conductivity and charge transport properties of the interface.

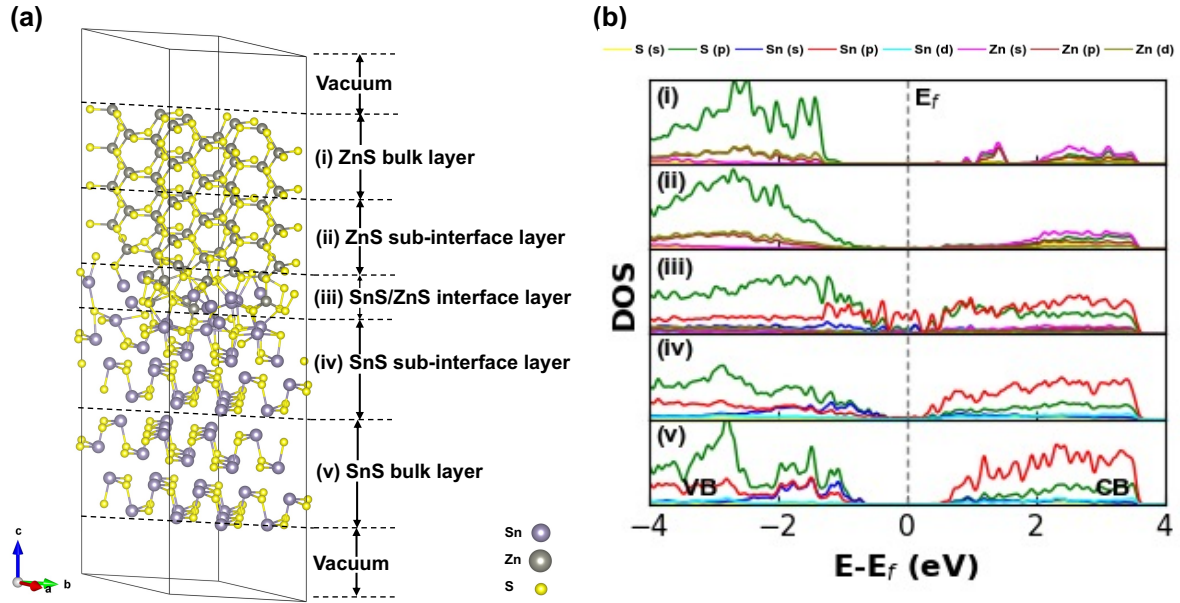


Figure 4.5: (a) SnS/ZnS interface structures with Sn-rich interface. (b) The corresponding DOS layers in Sn-rich SnS/ZnS interface structure. Here, SnS/ZnS interface layer have Sn:8, S:13 and Zn:6 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3]).

4.3.3 (Sn,S)-/(Zn,S)-rich interfaces

In the (Sn,S)-rich and (Zn,S)-rich interface configurations, distinct semiconductor behavior was observed, contrasting with the metallic characteristics present in the Sn-rich, S-rich, and Zn-rich interfaces (as illustrated in Figures 4.8 and 4.9). Despite exhibiting semiconductor properties, the bandgaps of the (Sn,S)-rich and (Zn,S)-rich interfaces were measured at 0.27 eV and 0.32 eV, respectively. These values signify a reduction compared to both the pristine and equal atom interface structures.

This phenomenon of reduced bandgaps is thought to arise from the presence of excess ad-atoms in these configurations compared to the equal atom interface structure. Notably, the (Sn,S)-rich interface exhibited a prominent DOS peak associated with Sn 5p states, similar to that observed in the PDOS of the equal atom interface, as depicted in Figure 4.8. Additionally, the DOS analysis of the (Zn,S)-rich interface revealed S 3p states near the CBE, which further emphasizes the unique electronic characteristics of these interfaces.

Incorporating both cationic (Sn and Zn) and anionic (S) elements into the interface structure, rather than relying solely on individual Sn, Zn, or S atoms, presents a promising approach for enhancing the electronic properties of the interface. This strategy could lead to optimized performance in TFSC, as the interplay of multiple elements may improve charge carrier dynamics and reduce recombination losses.

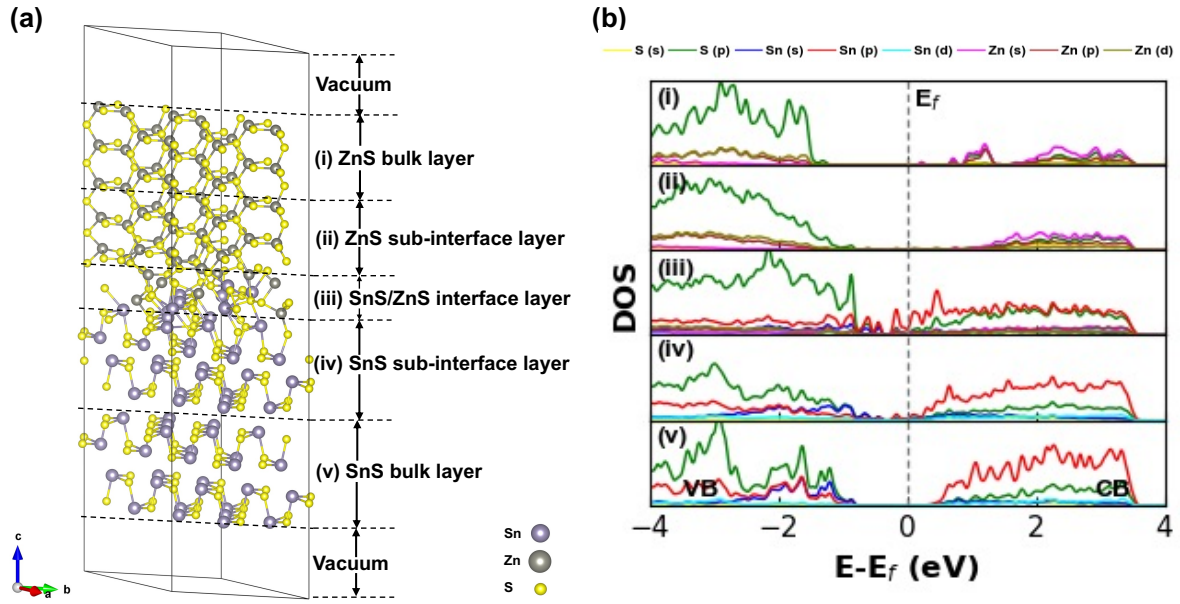


Figure 4.6: (a) SnS/ZnS interface structures with Zn-rich interface. (b) The corresponding DOS layers in Zn-rich SnS/ZnS interface structure. Here, SnS/ZnS interface layer have Sn:7, S:13 and Zn:7 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3]).

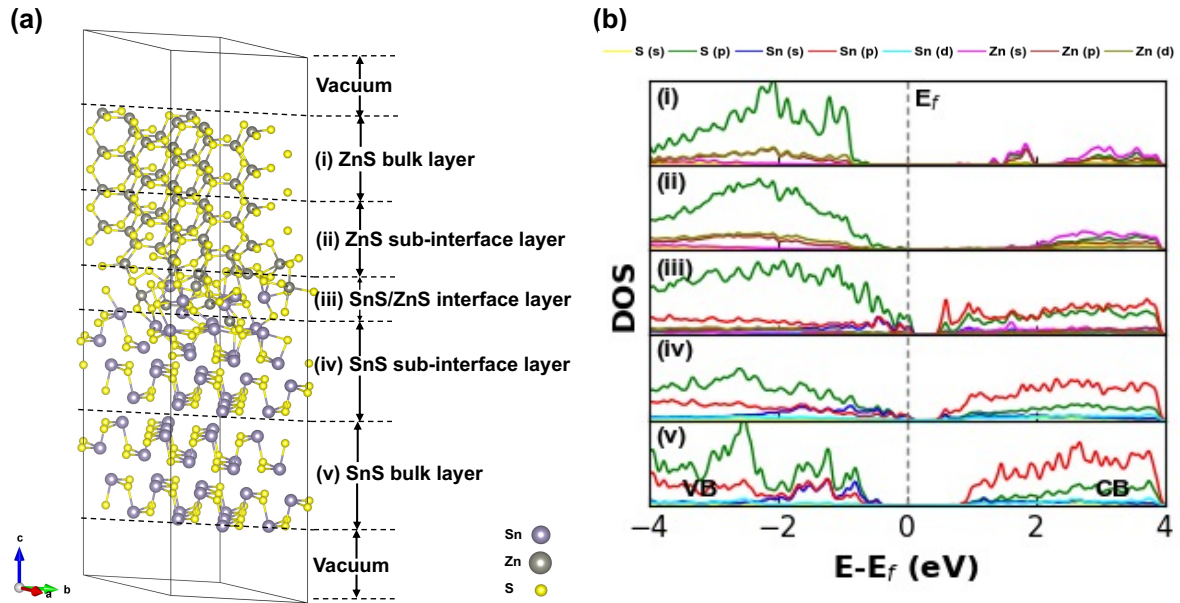


Figure 4.7: (a) SnS/ZnS interface structures with S-rich interface. (b) The corresponding DOS layers in S-rich SnS/ZnS interface structure. Here, SnS/ZnS interface layer have Sn:7, S:14 and Zn:6 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3]).

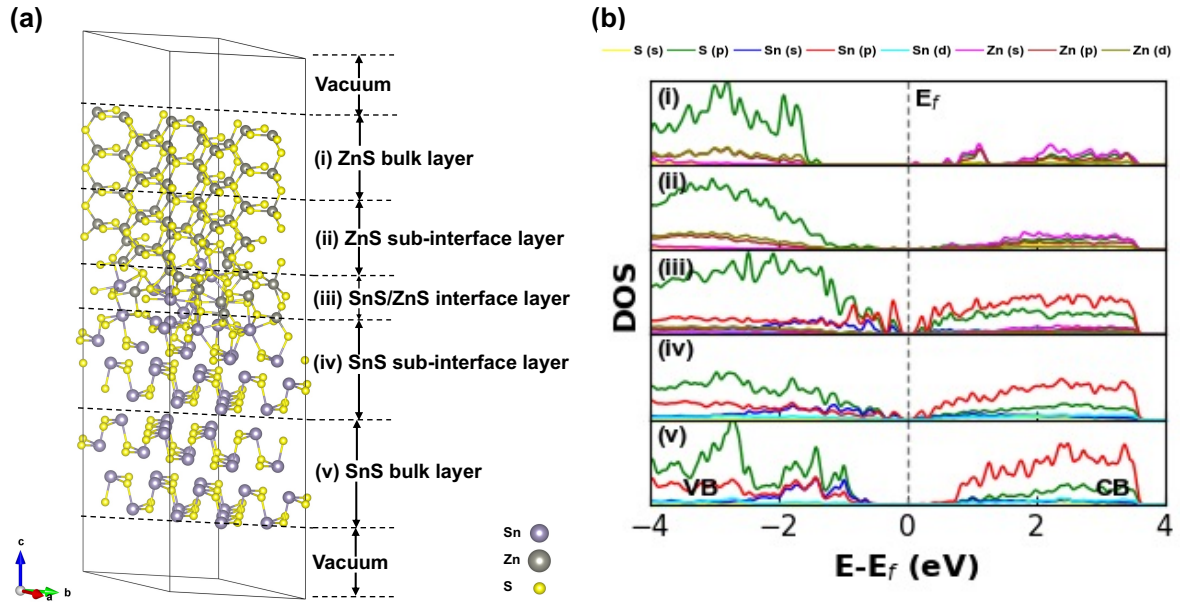


Figure 4.8: (a) SnS/ZnS interface structures with (Sn,S)-rich interface. (b) The corresponding DOS layers in (Sn,S)-rich SnS/ZnS interface structure. Here, SnS/ZnS interface layer have Sn:8, S:14 and Zn:6 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3]).

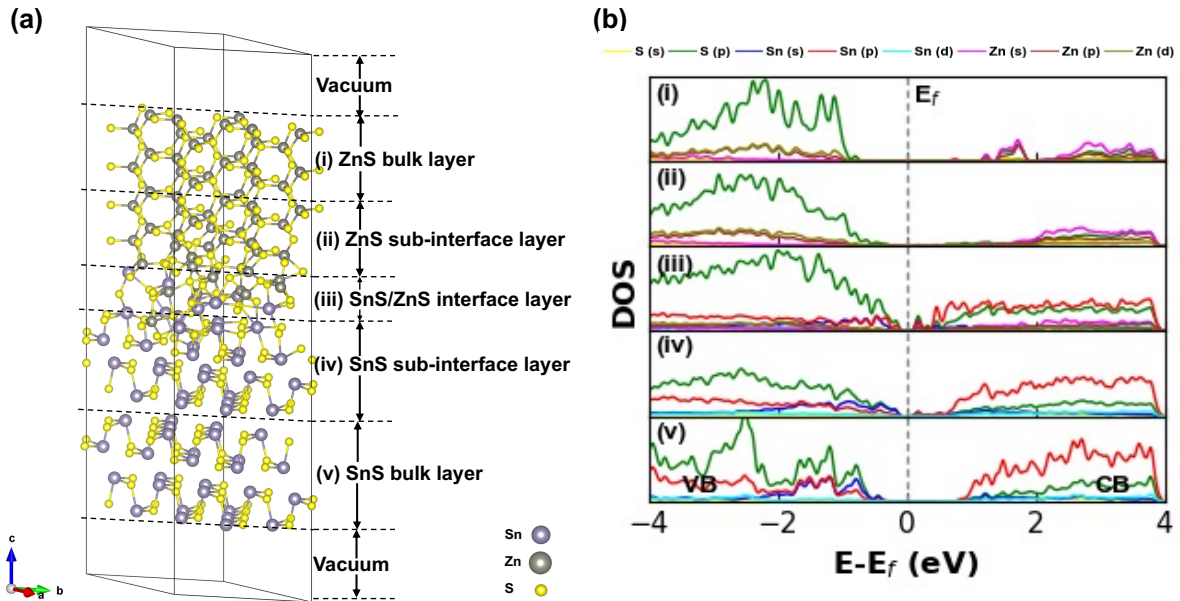


Figure 4.9: (a) SnS/ZnS interface structures with (Zn,S)-rich interface. (b) The corresponding DOS layers in (Zn,S)-rich SnS/ZnS interface structure. Here, SnS/ZnS interface layer have Sn:7, S:14 and Zn:7 atoms. (the vertical dotted line in DOS represented the Fermi level (E_f)) (Adapted from Dahule et. al. [3]).

In summary, the investigation into defect structures at the SnS/ZnS interface reveals a complex interplay between composition and electronic properties that significantly influences the performance of thin-film solar cells. The analysis of various interface configurations, including Sn-rich, S-rich, Zn-rich, and (Sn,S) and (Zn,S)-rich compositions, demonstrates how the presence of ad-atoms alters the electronic structure and bandgap characteristics. The transition from metallic behavior in cation-rich interfaces to distinct semiconductor properties in the (Sn,S)-rich and (Zn,S)-rich configurations underscores the importance of tailoring interface compositions for enhanced functionality. The observed reduction in bandgaps and the emergence of unique electronic states provide critical insights into optimizing the SnS/ZnS heterostructure for improved charge carrier dynamics and overall device efficiency.

Chapter 5

Conclusion

In this thesis, the stability and electronic properties of bulk, surface, and interface structures between tin sulfide (SnS) and zinc sulfide (ZnS) are investigated, focusing on their potential applications in thin-film solar cells. The motivation for this research arose from the need to enhance the efficiency and stability of semiconductor interfaces, which are critical to photovoltaic technologies. By leveraging first-principles calculations and advanced high-throughput interface structure search techniques, this study provides a comprehensive exploration of the structural and electronic properties of SnS and ZnS heterostructure. The Density Functional Theory (DFT) and CALYPSO were employed to analyze the behavior of these materials in various configurations, emphasizing bulk, surface, and interface structures.

The investigation into the electronic properties of SnS and ZnS in both bulk and surface forms revealed significant differences. Bulk SnS exhibited a bandgap of 0.92 eV, while ZnS had a wider bandgap of 2.08 eV. Additionally, the assessment of surface stability showed that SnS (100) and ZnS (110) possess lower surface energies than other low-index surfaces, confirming their status as the most stable configurations. The evaluation of surface structures indicated minor reductions in bandgap, with values of 0.91 eV for SnS (100) and 1.87 eV for ZnS (110), which were attributed to surface reconstructions and atomic rearrangements. These results contribute to a deeper understanding of the electronic behavior of these materials and establish a basis for a more detailed analysis of SnS/ZnS interfaces, where the interaction between atomic structure and electronic properties is further investigated.

The pristine SnS/ZnS interface structure was modeled based on the SnS (100) and ZnS (110) surfaces identified in the surface stability study. The analysis of its electronic properties demonstrated semiconductor characteristics, with a bandgap of 0.857 eV. Additionally, the interface exhibited a conduction band offset of 0.18 eV and a valence band offset of 1.28 eV. Notably, the pristine SnS/ZnS interface displays a staggered type-II band alignment, which is particularly advantageous for solar cell applications. This alignment facilitates charge separation by promoting the spatial separation of electron and hole states, thereby minimizing charge recombination and enhancing overall charge transfer efficiency.

To assess the impact of imperfections on the functionality of these heterostructures, the influence of interface defects was investigated. Six distinct interface compositions were created by introducing ad-atoms such as Sn, S, and Zn, simulating realistic conditions where defects are unavoidable. The findings indicated that interfaces with balanced atomic distributions from both SnS and ZnS surfaces preserved their semiconducting properties, akin to those of the pristine interface, thus maintaining the essential electronic structure required for solar cell applications,

with a bandgap of 0.43 eV. This balanced atomic configuration was identified as the most stable, exhibiting the lowest interface energy.

In contrast, interfaces that are predominantly composed of a single element—specifically, Sn-rich, S-rich, or Zn-rich configurations—exhibited a shift toward metallic behavior. This shift was characterized by the overlapping of the valence and conduction bands near the Fermi level, resulting in unwanted metallic properties. Such behavior can adversely affect device performance by increasing recombination rates, which in turn degrades the efficiency of solar cells by impeding effective charge separation and transport. Additionally, the introduction of ad-atoms at the interface significantly influenced the band structure, leading to reduced bandgaps in certain configurations. For instance, (Sn,S)-rich and (Zn,S)-rich interfaces exhibited semiconducting characteristics, but with notably decreased bandgaps of 0.27 eV and 0.32 eV, respectively. This reduction is attributed to the introduction of extra electronic states within the bandgap due to the presence of excess ad-atoms. While interfaces with defects can maintain some beneficial properties, careful control of atomic composition is essential to prevent compromising the electronic performance of the material.

Overall, the findings highlight the importance of controlling atomic composition and defect configurations at the SnS/ZnS interface to ensure both structural stability and advantageous electronic properties. If not effectively managed, interfaces rich in defects can lead to metallic behavior or a reduction in the bandgap, which may adversely affect the performance of SnS/ZnS-based solar cells. In contrast, balanced atomic arrangements help maintain semiconducting characteristics and facilitate efficient charge transport, which are crucial for achieving high-performance thin-film solar cells.

In conclusion, this study highlights the critical role of interface engineering in the development of next-generation SnS/ZnS heterostructures for solar energy applications. By optimizing interface compositions and reducing defect-induced alterations in electronic properties, the stability and efficiency of SnS/ZnS-based solar cells can be significantly improved. These findings establish a foundation for advancing sustainable, high-efficiency photovoltaic technologies.

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