First Principles Study of Band Offsets and Band Bending of InGaN/GaN and ZnO/\textit{Zn}$_{1-x}$\textit{B}$_{x}$O/\textit{Zn}O Heterostructures and Quantum Wells

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First Principles Study of Band Offsets and Band Bending
of In$_x$Ga$_{1-x}$N/GaN and Zn$_{1-x}$Be$_x$O/ZnO Heterostructures and Quantum Wells

Liang Dong, Ph.D.
University of Connecticut, 2013

In$_x$Ga$_{1-x}$N (InGaN) and Zn$_{1-x}$Be$_x$O (ZnBeO) are compound semiconductor solid solutions that display a wide band gap tuning range and strong spontaneous and piezoelectric polarizations due to the wurtzite crystal structure. They have gained significant importance in electronic and optoelectronic devices where the active layers are often fabricated as InGaN/GaN and ZnBeO/ZnO multiple quantum well (MQW) structures to take the advantage of an enhanced quantum confinement. The performances of devices based on such polarizable MQWs are significantly affected by band offsets and band bending, two critical interlayer interfacial parameters closely related to the electronic structure of the barriers and the wells.

In this thesis, first principles calculations based on density functional theory are carried out to study how the properties of each layer in InGaN/GaN and ZnBeO/ZnO MQWs and their band offsets and band bending can be altered by different heteroepitaxial growth conditions. The
results show that for bulk InGaN and ZnBeO, the band gap energy, spontaneous polarization, and elastic properties are nonlinearly dependent on the In and Be concentrations, respectively. For heteroepitaxial InGaN and ZnBeO thin films on suitable (0001) substrates, their band gap energy is significantly reduced for a tensile in-plane misfit strain and for a compressive misfit strain larger than −6%.

For InGaN/GaN and ZnBeO/ZnO MQWs, it is found that a combination of mechanical boundary conditions, epitaxial orientation, and the In (or Be) concentration can be used as design parameters in optoelectronic devices. Taken InGaN/GaN MQWs as an example, the valence band offset ($\Delta E_V$) increases with In concentration in InGaN/GaN superlattices regardless of the mechanical boundary conditions and growth epitaxy. For low In compositions ($x<0.5$), our calculations show that nonpolar and polar MQWs yield similar $\Delta E_V$ values. The valence band offset is more enhanced in polar c-plane conditions for In concentrations larger than 0.5. For non-polar m-plane InGaN/InN MQWs, the role of epitaxial strains that increase with increasing In concentration according to Vegard’s law have very little effect on $\Delta E_V$ for $x<0.8$. On the other hand, the difference between valence band offset of epitaxial and stress-free c-plane MQWs is substantial, especially for larger In concentrations ($x>0.5$).
First Principles Study of Band Offsets and Band Bending of \( \text{In}_x\text{Ga}_{1-x}\text{N} / \text{GaN} \) and \( \text{Zn}_{1-x}\text{Be}_x\text{O} / \text{ZnO} \) Heterostructures and Quantum Wells

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First Principles Study of Band Offsets and Band Bending of In$_x$Ga$_{1-x}$N/GaN and Zn$_{1-x}$Be$_x$O/ZnO Heterostructures and Quantum Wells

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Chapter 1: INTRODUCTION

1.1 Compound Semiconductors

Since the 1940s semiconductor materials have found numerous applications in microelectronics, optoelectronics, solar panels, and sensing and actuation devices. This interest stems from their electric and electronic properties that can be easily tuned via operation temperature, doping/alloying, and growth morphologies, etc. Most of the commonly used semiconductors are crystalline inorganic solids, including elementary materials (such as Si and Ge) and compound materials that are usually composed of groups III-V or II-VI atoms in the Periodic Table of Chemical Elements.

Commercial semiconductor devices are primarily based on Si because it is robust, inexpensive, and relatively easy to fabricate for high volume productions. However, compound semiconductors have also gained a significant importance in the recent three decades because of their great potential for electronic and optoelectronic devices. Firstly, compared to Si, most of the III-V or II-VI compound semiconductors have smaller effective electron and/or hole masses and thus a higher carrier mobility. As such, these compound semiconductors are suitable for high frequency and high power applications. For example, high-electron-mobility transistors (HEMTs) based on GaAs have been widely used in mobile phones, satellite communications, radars, and fast electronic switches. Secondly, a lot of the compound semiconductors (e.g., GaN, GaAs, and ZnO) display a direct band gap in their electronic structure [Fig. 1.1(a)] wherein an electron at the bottom of the conduction band carries the same momentum as a hole at the top of the valence band. Within such an electronic structure, the conservation of momentum is satisfied.
in the electron excitation and electron-hole recombination processes that absorb and generate a photon, respectively, with a wavelength corresponding to the band gap energy of the semiconductor. On the contrary, for indirect-band-gap semiconductors (such as Si) [Fig. 1.1(b)], the absorption and generation of a photon must be accompanied by a phonon (lattice vibration) which transfers the electronic energy into heat. Therefore, compound semiconductors with a direct band gap are more energy efficient for optoelectronic and photovoltaic applications. In recent years, III-V and II-VI semiconductors have become key enabling materials in light emitting diodes (LEDs) and thin-film solar cells. ²,³

Figure 1.1 Schematic show of the electronic structure and photon generation mechanism for semiconductors with (a) a direct and (b) an indirect band gap.
1.2 Ternary Alloys of III-V and II-VI Semiconductors

A binary compound semiconductor can only be used to absorb or generate photons within a narrow spectrum range because its band gap energy ($E_g$) is fixed at a given temperature. A tunable $E_g$ will greatly expand the applications of these materials under specific conditions and/or restrictions. This can be accomplished using solid solutions of two binary compound semiconductors with different values of $E_g$. Preferably, the two ending components of such an alloy should have the same crystal structure and should share a common cation or anion because they are most likely to be miscible over a broad or even the entire composition range. In this dissertation, two examples of such ternary solid solutions of compound semiconductors are considered: the InN-GaN ($\text{In}_x\text{Ga}_{1-x}\text{N}$, or InGaN) system and the ZnO-BeO ($\text{Zn}_{1-x}\text{Be}_x\text{O}$ or ZnBeO) system.

1.2.1 $\text{In}_x\text{Ga}_{1-x}\text{N}$ (InGaN) Solid Solutions

The InGaN solid solutions have been intensively studied during the last two decades.\(^4,5\) They are often synthesized as epitaxial films on suitable substrates via molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD).\(^6-8\) In the past, the MBE and MOCVD growth temperature of InGaN were usually at 700–800 °C. However, a strong phase separation was observed in epitaxial InGaN films for In concentration $x>0.3$.\(^7\) This is due to the large atomic size mismatch between Ga and In.\(^9\) Recently, it was found that the miscibility limit of InGaN in the solid state can be overcome using MBE and MOCVD at lower substrate
temperatures (550–700 °C), resulting in uniform single-phase InGaN films and one-dimensional nano structures over the entire In concentration range.\textsuperscript{8,10}

The band gap energy of InGaN varies from 0.7 eV (InN) to 3.4 eV (GaN) and covers the entire visible light spectrum and beyond. As such, these materials have been widely used in solid state lighting industry. The history of light emitting diodes (LEDs) based on InGaN dates back to the early 1990s when high quality $n$- and $p$-doped of InGaN films became available.\textsuperscript{11} In 1994, the first commercial high-brightness blue LED was fabricated using an InGaN/AlGaN double heterostructure.\textsuperscript{11,12} Since then long-lifetime (>50,000 hours) LEDs and lasers based on InGaN have been considered as the most reliable sources for blue light emissions.\textsuperscript{12} The market of such devices grows rapidly due to the huge demand in flat panel displays, optical fiber communications, and high-volume storage media such as blue-ray discs. Currently, With the In concentration $x$ continuously changed from 0 to 1, violet, green, yellow, and red light emissions have also been achieved in InGaN-based thin film and one-dimensional nanowire heterostructures.\textsuperscript{5,10,11} These advancements have enabled full-spectrum (white) photoluminescence from a single InGaN-based device.\textsuperscript{13,14}

InGaN solid solutions have also gained a considerable interest in photovoltaics since the band gap energy is tunable from 0.7 eV to 3.4 eV with increasing Ga concentration. As a comparison, other semiconductor systems commonly used in solar cells (e.g., Si, Ge, InGaAs, InGaP, CdTe, and CuInGaSe) can only cover a much narrower spectrum range, from 0.7 eV to 1.9 eV. Currently, InGaN solid solutions are primarily considered in multiple-junction solar cells that use an InGaN junction ($x \leq 0.5$) together with other semiconductor junctions.\textsuperscript{5} The introduction of the InGaN layer has been shown to greatly enhance overall energy conversion efficiency of such solar cells. For example, the theoretical efficiency of an In\textsubscript{0.5}Ga\textsubscript{0.5}N/Si double
junction can reach up to 31%, much higher than that of a single-junction solar cell that is based on polycrystalline Si (17%).

In addition to optoelectronic and photovoltaic applications, InGaN heteroepitaxial thin films or nanowires have been recently used to fabricate chemical and bio-sensors for hydrogen molecules (H₂), PH value, and DNA. The electric resistivity and optical properties (intensity and peak wavelength of the photoluminescence spectra) of such constructs change significantly if their surfaces are exposed to various gases and chemical solutions.

1.2.2 Zn₁₋ₓBeₓO (ZnBeO) Solid Solutions

ZnO thin films and one-dimensional nanostructures have gained significant importance in recent years in electronic, electromechanical, optoelectronic and magnetic devices. This interest stems from the electronic properties including a large direct band gap ($E_g = 3.37$ eV at 300 K), a large exciton binding energy ($\sim 60$ meV), strong spontaneous ($P_S = -0.57$ C/m²) and piezoelectric ($e_{33} = 1.20$ C/m², $e_{31} = -0.56$ C/m²) polarizations, as well as the relative ease of synthesis of ZnO powders, single-crystals, thin films, and nanostructures. As such, ZnO is a key enabling material in sensors and actuators, transparent thin-film electronics, and optoelectronic and piezoelectric devices.

Since the electronic properties of ZnO can be readily tuned by doping/alloying, it is possible to expand its applications by designing materials systems for specific conditions and/or restrictions. For example, doping ZnO with Al (1-2 %) or Ga (2-7 %) results in a solid solution with a high carrier concentration ($\sim 10^{21}$ cm⁻³) and a commensurate low electric resistivity ($\sim 10^{-5}$
Such materials have already been incorporated in flat panel displays and solar cells as transparent electrodes to replace the relatively expensive In-Sn oxide (ITO). As another example, wider band gap materials are desired in highly sensitive UV detectors whose cut-off energy falls into a solar-blind energy region from 4.40 to 5.65 eV (220-280 nm), in which the sunlight is absent on earth because of strong atmospheric absorption. There are other materials suitable for this range of wavelength spectrum (e.g., diamond and AlGaN). However, if ZnO-based solid solutions could be developed that would work in this range, this would significantly reduce cost since ZnO is compatible with IC and can be synthesized with good stoichiometric control via a number of deposition methods.

Band gap engineering of ZnO can be achieved by alloying with MgO \( (E_g=7.70 \text{ eV}) \) for UV applications and such alloys can also be used as barrier layers in \( \text{ZnO}/(\text{Zn},\text{Mg})\text{O} \) superlattices for quantum well devices. However, phase separation occurs in \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) solid solutions when the Mg composition exceeds 33%. This is due to the differences in the crystal structures of ZnO [wurtzite, P6\(_3\)mc] and MgO (rocksalt, Fm\(_3\)m). As such, the UV absorption range is limited to 3.37-3.90 eV in the \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) system for \( x<0.33 \). \( \text{BeO} \ (E_g=10.60 \text{ eV}) \) that also crystallizes in the wurtzite structure has been considered as an alloying system for ZnO for UV optoelectronic devices and sensors, despite the high degree of toxicity of elemental Be. It was shown that \( \text{Zn}_{1-x}\text{Be}_x\text{O} \ (\text{ZnBeO}) \) thin films can be deposited using hybrid beam deposition with no phase separation over the entire composition range. Furthermore, since in ZnBeO the band gap can theoretically be tuned from 3.37 to 10.60 eV, this materials system may replace \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) solid solutions that are being considered in applications such as field effect transistors, polymer-oxide hybrid solar cells, quantum Hall effect devices, high-\( k \) films on Si, and acoustic resonators.
While there have been some efforts to understand, describe, and measure the lattice parameters, the band gap, and optical properties of ZnBeO in thin films, the potential of this materials system for applications described above has not been fully explored. For the ZnBeO system to be viable alternatives to materials systems in current and potential electronic and optoelectronic devices, it is imperative to obtain a deep and complete understanding of their physical properties. For example, considering that these materials are piezoelectric and possess a spontaneous polarization, how does the polarization change with varying Be composition? The answers to such problems will be addressed in this dissertation.
1.3 Wurtzite Crystal Structure and Polarizations

GaN, InN, ZnO, and BeO crystalize into the wurtzite structure (Fig. 1.2). The term “wurtzite” is originally the name of zinc-iron sulfide [(Zn, Fe)S] mineral, but now it is more commonly used to represent the general hexagonal close packed (HCP) crystal structures with space group P6₃mc [Fig. 1.2(a)].

![Figure 1.2](image)  (a) Schematic show of the wurtzite crystal structure with polar c- and nonpolar m-planes, and (b) the unit cell of GaN.
The unit cell of the wurtzite structure is shown in Fig. 1.2(b) using GaN as an example. Within such a lattice, each Ga (N) atom is nearly equidistant to the four nearest N (Ga) atoms which form a tetrahedron. Due to the non-centrosymmetric arrangement of Ga and N atoms in the wurtzite structure, there exists a displacement between the positive and the negative charge centers along the [0001] (c-) direction, giving rise to a macroscopic dipole moment. This phenomenon can also be observed in InN, ZnO, and BeO, and hence their alloys (InGaN and ZnBeO). Therefore, these materials possess a large spontaneous polarization ($P_S$) under equilibrium stress-free conditions. For a given material composition, the magnitude of $P_S$ is found to be linearly related to the interatomic distance along the $c$-axis [$u_0$ in Fig. 1.2(b)] if the lattice parameters $a_0$ and $c_0$ are fixed. $^{45}$ The ratio of $d(P_S)/d(u_0)$ per unit area is defined as the Born effective charge (BEC), which describes the coupling between lattice displacements and the electric field. $^{45}$ For GaN, InN, ZnO, and BeO, BEC is $2.72e$, $3.02e$, $2.05e$, and $1.72e$, respectively, where $e=1.6\times10^{-19}$ C is the elementary charge. $^{46}$ BEC of these compound materials is close to their respective nominal charge ($3e$ for GaN and InN and $2e$ for ZnO and BeO), showing a strong degree of ionicity of the Ga-N, In-N, Zn-O, and Be-O bonds. $^{46}$

InGaN and ZnBeO thin films are usually deposited on hetero-epitaxial substrates with a lattice mismatch between the film and the substrate. For such mechanical boundary conditions, the misfit strain may substantially change the bond length of a polarizable material, and hence produce an additional polarization which is called piezoelectric polarization ($P_{PZ}$). The total polarization of the hetero-epitaxial films is the sum of $P_S$ and $P_{PZ}$.

To obtain spontaneous and piezoelectric polarizations, the InGaN and ZnBeO films must be deposited with certain preferred crystal cuts of the wurtzite structure, i.e., with the easy ($c$-) axis of polarization not in the plane of films growth. For example, the $c$-plane in Fig. 1.2(a) is
completely polarizable with the two surfaces that terminate with a pure cation layer (e.g. Ga) and a pure anion (e.g. N) layer. Conversely the \( m \)-planes in the same figure are nonpolar since they are stoichiometric and hence the centers of positive and charges coincide along the direction of the surface normal. There are also planes with surface normal between the above two cases (not shown), which are usually called semi-polar orientations. The physical and chemical properties of InGaN and ZnBeO materials are significantly anisotropic in polar, semi-polar, and nonpolar orientations because of the differences in electrostatic interactions.
1.4 Multiple Quantum Wells: Benefits and Challenges

To further achieve a high power, a high frequency, a high brightness, and a high energy efficiency in electronic and optoelectronic devices, the electronic active layers in such devices are frequently fabricated as multiple quantum well (MQW) structures. Within a quantum well, the layers with a wider band gap are defined as the barriers, and those with a narrower band gap are called the wells. MQW structures are of great importance both academically and technologically. The source of advantages to use MQWs resides in the following extraordinary properties that are not available in bulk materials or in thin films:

1. Due to the differences in $E_g$ between barriers and wells, the electronic structure of a MQW displays abrupt discontinuities in the conduction and valence band edges at the interlayer interfaces, resulting in localization of electrons and/or holes within the well layers. Such localizations are desired for optoelectronic devices since carriers are more difficult to reach the surfaces and hence the energy is less likely to be dissipated through nonradiative electron-hole recombination at the surface defects. Furthermore, under a given bias along the growth direction of a MQW (perpendicular to the layers), the motion of charge carriers is primarily achieved by tunneling between the well layers, rather than drifting continuously across the two electrodes. This transport mechanism can be utilized in resonant tunneling devices to achieve a high oscillation strength and operation frequency.47

2. Since the well layers in a MQW are usually ultrathin with a dimension of several unit cells (nanometer scale), the electrons and holes experience strong quantum confinement that would greatly reduce the widths of the electronic energy bands of the well material.
If the well depths, i.e., the conduction and valence band offsets at the interlayer interfaces are sufficiently large, the continuous band structures in the well layers may even be replaced by discrete energy levels. The narrowing of energy bands significantly decreases the energy dispersion of electrons at the bottom of the conduction band and the energy dispersion of holes at the top of the valence band. Consequently, the photons generated by the electron-hole recombination are more likely to carry a peak wavelength that corresponds to $E_g$ of the well layer, reducing the spectra width of light emissions significantly for LEDs and lasers.

3. The quantum confinement perpendicular to the layers of a MQW results in an astonishingly high in-plane mobility for the electrons and/or holes within the well layers. Such 2-dimensional electron and hole gases (2DEG and 2DHG) provide great potentials for both device applications such as high-electron-mobility transistors and academic researches on the topic of quantum hall effects. 2DEG and 2DHG in MQWs are often obtained from doping in the barrier and well layers. However, this method would simultaneously increase the probability of impurity scatterings for the carriers and substantially decreases the mobility. A better approach to obtain 2DEG and 2DHG can be achieved using the MQWs based on polarized semiconductors, such as InGaN/GaN and AlGaAs/GaAs. Within these MQWs, the polarization mismatch at the interlayer interfaces gives rise to a bound sheet charge that can be screened by the formation of 2-dimensional free carriers with an opposite sign of charges. Due to the electrostatic interactions, the generated 2DEG or 2DHG are more strongly confined at the interfaces, and are hence of a higher mobility than those obtained from impurity doping.
The active layers of LEDs and laser diodes based on InGaN and ZnBeO solid solutions are frequently fabricated as MQWs sandwiched by alternating InGaN/GaN or ZnBeO/ZnO thin layers. Great successes have been accomplished with these devices for violet, blue and green light emissions. However, the output power and radiative efficiency of such MQWs drops dramatically when the operation wavelength goes in the regime that is longer than 500 nm, mainly due to their relatively low crystal qualities. For example, as the In concentration $x$ varies in InGaN/GaN MQWs, per Vegard’s law the lattice mismatch and hence the in-plane misfit strain increase from 0 for $x=0$ to $10\%$ for $x=1$. Such extremely high internal strains would certainly be relaxed via the formation of defect structures (misfit dislocations, delamination, and cracking) for film thicknesses larger than a few unit cell dimensions. The defects can serve as non-radiative recombination centers for electrons and holes that greatly degrade the performance of MQWs. Although advances in thin film growth technology [molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD)] now allow the deposition of InGaN/GaN superlattices one atomic layer at a time, defects still form in these structures for $x>0.2$.

In addition to the lattice imperfections, the uniquely strong polarizations also have a strong bearing on the efficiencies of InGaN/GaN and ZnBeO/ZnO MQWs that is grown along polar or semi-polar orientations. As the polarization state changes abruptly from a barrier layer to an adjacent well layer, a net bound charge density is expected at the interfaces, giving rise to volumetric internal electric fields, i.e., band bending throughout each layer. The built-in electric fields would cause a spatial separation of electron and hole wave functions in the well layers and therefore decreases the probability of their recombination. In addition, they may narrow the effective band gap of the well layer and reduce the oscillation strengths for the carriers.
Chapter 2: OBJECTIVE AND METHODOLOGY

2.1 Objective

As introduced in Chapter 1, InGaN/GaN and ZnBeO/ZnO MQWs have a great potential in electronic, optoelectronic, and photovoltaic applications. With a rapidly growing demand for the devices based on such constructs, it is becoming more and more imperative to obtain better performances and higher efficiencies from them in order to reduce their energy cost. The optimization of these devices should be built upon a thorough understanding of the electronic and optical properties of the barrier and well materials, which are most often measured in their respective bulk or thin films. However, semiconductors within the ultra-thin layers are often significantly different from their bulk form. The electronic properties of materials in thin films are more sensitive to the ambient background such as growth orientation, interface termination, thermal stresses, misfit strains, and defect microstructures (misfit and threading dislocations, impurities, phase/grain boundaries, etc.), which are intimately tied to the growth methodology, conditions, parameters, and film growth mechanisms.

In addition to the bulk properties of each single layer, the interfacial properties and interlayer coupling such as band offsets and band bending play more important roles in the performance of a MQW. These properties are related to the bulk properties of barrier and well materials. For example, band offsets is the difference in conduction or valence band edge energies between the barrier regions and the well regions. However, due to the electrostatic interactions at the interfaces, these properties are also sensitive to growth conditions of the MQWs. Therefore, a conclusion made from one experiment may not be applied to another. For
example, the results from different groups show a large disparity (0.5−1.1 eV) in the valence band offsets of InN/GaN heterostructures. 52-57

To address these problems, the physical properties of semiconductor materials in multiple quantum well structures (and superlattice) are theoretically studied in this thesis for InGaN/GaN and ZnBeO /ZnO MQWs. Our motivation is to figure out how electronic and optoelectronic properties of such MQWs can be optimized using a combination of growth conditions as design parameters. To guide the research that follows, we will focus on the general questions shown below:

1. What are the properties of semiconductors that are important for electronic and optoelectronic devices? How do they vary as a function of In or Be concentrations in ternary InGaN or ZnBeO alloys, respectively?
2. Is it possible to engineer the properties of InGaN and ZnBeO solid solutions in their thin films using heteroepitaxial growth technologies?
3. What are the properties related to the surface and interfaces of InGaN/GaN and ZnBeO /ZnO MQWs and superlattices? How do they change with composition variations?

To answer the above questions, our study is carried out at three levels of length scales for these materials. In the first step (Chapter 3), the structural, electronic, polarization, and elastic properties of bulk InGaN and ZnBeO solid solutions will be studied with emphasis on their compositional variations. Next, these materials will be constrained with bi-axial in-plane misfit strains to simulate their epitaxial thin films on suitable substrates. We will look into the changes in both crystal structures and electronic structures from the bulk format. Finally, InGaN/GaN and
ZnBeO/ZnO MQWs (with layer thickness <10 nm) will be constructed to find out the band offsets and band bending. The effects of misfit strains and defects microstructures will be discussed in detail at this level.
2.2 Methodology: Density Functional Theory

Our theoretical studies are based on density functional theory (DFT). DFT is an *ab initio* method, meaning that it relies on the well-established laws of nature without any additional assumptions or speculations. DFT provides an atomistic description of various kinds of materials systems (atoms, molecules, and condensed matter such as solids) in terms of their structural, elastic, electronic, magnetic, surface, and chemical properties with excellent agreements with the experimental findings. 58 Recent advantages have enabled the incorporation of molecular dynamics into DFT, making it more powerful in predicting these properties over a wide range of temperature (0 K–several hundred K or higher). The computational cost of DFT is much more inexpensive compared to other theoretical method at the same precision level, such as the Hartree-Fock method. Therefore, it has been widely applied in the fields of physics, chemistry, and materials engineering as a successful microscopic tool to understand and control the materials at length scales of interatomic distances (0.5–1 nm) or larger. 58,59

DFT is originated from the quantum mechanical (QM) theory that describes the stationary states of materials using the Schrödinger equation. For a system with $N$ electrons, the time-independent Schrödinger equation is given as

$$
\left[ -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V(r_i) + \sum_{i=1}^{N} \sum_{j<i} U(r_i, r_j) \right] \psi(r_1, r_2, \cdots, r_N) = E \psi(r_1, r_2, \cdots, r_N),
$$

where $m$ is the electron mass, $\hbar$ is the reduced Plank constant, $i$ and $j$ are the electron index, $\nabla_i^2$ is the Laplacian operator (for kinetic energy) of the $i^{th}$ electron, $r_i$ is the position of the $i^{th}$ electron, $V(r_i)$ is the Coulomb interaction between the $i^{th}$ electron and the nuclei, $U(r_i, r_j)$ represents the exchange-correlation (XC) interaction between the $i^{th}$ and $j^{th}$ electrons,
\( \psi(r_1, r_2, \cdots, r_N) \) is the electron wave function, and \( E \) is the eigenenergy that corresponds to a given \( \psi(r_1, r_2, \cdots, r_N) \).

An exact solution to Eq. (2.1) is only available to materials with a single electron, such as the hydrogen atom. For materials with two or more electrons (large atoms, molecules, and condensed matter), the Schrödinger equation is getting too complex to be solved analytically because an exact mathematical expression for the XC interactions is unknown. As such, certain approximations have to be made to simplify the form of XC terms. In DFT, this is done using a single electron picture that describes the electron wave function in a many-body system as a multiplication of the wave functions of all single electrons in this system \( [\psi(r_1, r_2, \cdots, r_N) = \psi_1(r_1)\psi_2(r_2)\cdots\psi_N(r_N)] \). Subsequently, the electron density of this system can be determined by

\[
n(r_1, r_2, \cdots, r_N) = \sum_{i=1}^{N} \psi_i^*(r_i)\psi_i(r_i), \tag{2.2}
\]

where \( \psi_i^*(r_i) \) is the complex conjugate of wave function of \( i^{th} \) the electron. The essential of DFT is to use a fictitious system with \( N \) non-interacting electrons to replace the interacting electrons, under the restriction that the two system generates the same \( n(r_1, r_2, \cdots, r_N) \). In this way the Schrödinger equation is simplified as the so called one electron Kohn-Sham Equation given as

\[
\begin{bmatrix}
-\frac{\hbar^2}{2m} \nabla_i^2 + V_{\text{eff}}(r_i)
\end{bmatrix} \psi_i^{KS}(r_i) = E\psi_i^{KS}(r_i), \tag{2.3}
\]
where $V_{\text{eff}} (r_i)$ is the sum of the second and third terms on the left side of Eq. (2.1), and $\psi_{i}^{KS} (r_i)$ is the wavefunction of the $i^{th}$ electron in the non-interacting system. The XC energy is calculated by the local densities of electrons and/or their volumetric gradients. This approach would introduce an error (underestimation or overestimation) in the XC energies, and is thus infeasible for strongly-correlated materials. However, for InGaN and ZnBeO materials systems that are considered in this thesis, this problem is may be negligible since they have relatively low XC energies.

All the simulations in this thesis are carried out using the Vienna ab initio Simulation Package (VASP), 60 which has been well recommended as one of most reliable DFT computation softwares. The XC interactions are treated within the PW91 generalized gradient approximations (GGA). 61 The electron wave functions are descripted utilizing projector-augmented wave 62 pseudopotentials with the plane-wave expansions. The term “pseudopotential” means that the states of the valence electrons in an atom are explicitly considered while inner shell electrons are frozen and combined with the nuclei as rigid non-polarizable ion cores. Pseudopotentials enables substantial reduction in the number of electrons compared to the all-electron potentials while at the same time keeps a high accuracy since the physical and chemical properties of materials are mainly determined by the electrostatic interactions between valence electrons. The computational details that enter the calculations can be found elsewhere for each specific materials system. 63-68
Chapter 3: BULK InGaN AND ZnBeO SOLID SOLUTIONS

In this chapter, bulk InGaN and ZnBeO solutions are studied under equilibrium stress-free conditions. Their crystal structures, electronic band structures, spontaneous polarization, piezoelectric coefficients, and elastic coefficients will be investigated using DFT. The purpose of this chapter is to understand how these physical properties vary as a function of In or Be compositions in InGaN or ZnBeO solid solutions, respectively.

Since both InGaN and ZnBeO crystalize in the wurtzite structure, the compositional variations in their properties are similar. Considering that InGaN alloys has been intensively studied previously while ZnBeO solid solutions are much less reported in the literature (see Sec. 1.2), the analysis and discussion in this chapter are primarily focused on the ZnBeO system. The results on InGaN alloys can be found elsewhere. 65

3.1 End Components of ZnBeO : ZnO and BeO

Both ZnO and BeO have the wurtzite (W in this section) structure which consists of alternating hexagonal closed-packed metal (Zn or Be) and oxygen layers [Fig. 3.1(a)]. Each metal (oxygen) is nearly equi-distant to its four nearest oxygen (metal) atoms which form a tetrahedron. The structure is characterized by an in-plane lattice parameter \(a_0\), an out-of-plane lattice parameter \(c_0\), and an internal lattice parameter \(u_0\) measuring the interatomic distance, i.e., the bond length along the \(c\)-axis. The atomic size of Zn and the size of the ZnO unit cell are larger than that of Be and BeO (Table 3.1). The W structure and the primitive periodicity of the
(0001) layers in the P6\textsubscript{3}mc base (hexagonal 1×1 hereafter) are shown in Figs. 3.1(a) and (b), respectively.

Figure 3.1 (a) The wurtzite (W) unit cell of ZnO; the planar view along the c-axis of (b) W ZnO, (c) W Zn\textsubscript{0.5}Be\textsubscript{0.5}O, and (d) O-16 Zn\textsubscript{0.5}Be\textsubscript{0.5}O. The base of each structure in (b), (c), and (d) is shown by dashed lines.
The fundamental properties of ZnO and BeO in the W phase have been studied extensively via DFT. We provide in Table 3.1 previously obtained experimental and theoretical values for the lattice parameters, band gap energy, and spontaneous polarization of ZnO and BeO. Table 3.1 shows that our calculated lattice parameters \( a_0 \) and \( c_0 \) for both ZnO and BeO are in good agreement with the data in the literature. The electronic structures of ZnO and BeO display a direct bang gap in the \( \Gamma \) point of the first Brillouin zone. Similar to other DFT results, theoretical band gap energies are lower than the experimental values (0.758 eV c.f. 3.37 eV for ZnO and 7.509 eV c.f. 10.6 eV for BeO). Although experimental \( E_g \) can be reproduced by more recent time-intensive beyond DFT calculations, the relatively simpler GGA is employed in our analysis. This is primarily done to focus on the relative variations in \( E_g \) of the alloys with respect to pure ZnO and BeO, noting that such changes in \( E_g \) can be predicted accurately via DFT.

The positive direction of the spontaneous polarization \( P_S \) is conventionally defined as pointing from the O atom to its nearest-neighboring Zn or Be atom along the [0001] direction. There are two distinct contributions from the W unit cells of ZnO and BeO to \( P_S \): the lack of centro-symmetry, and the deviation from the ideal W unit cell for which \( c_0/a_0 \approx 1.633 \) and \( u_0 = 0.375 \). Obviously, there is a strong correlation between \( u \) which is the bonding length between the Zn (Be) and O atoms along [0001] and \( P_S \) (Table 3.1). For ZnO our calculations yield \( u_0 = 0.379 \) which is closer to the ideal value of \( u \) (for which \( P_S=0 \)), resulting in \( P_S=−0.031 \text{ C/m}^2 \). This is in agreement with one theoretical finding (−0.029 C/m\(^2\)) and significantly smaller than another calculation (−0.057 C/m\(^2\)).
Table 3.1: Calculated and experimental values of the structural parameters $a_0$, $c_0/a_0$ and $u_0$, the band gap energy $E_g$, and the spontaneous polarization $P_S$ of ZnO and BeO in the W structure.

<table>
<thead>
<tr>
<th></th>
<th>$a_0$ [Å]</th>
<th>$c_0/a_0$</th>
<th>$u_0$</th>
<th>$E_g$ [eV]</th>
<th>$P_S$ [C/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>This work</td>
<td>3.277</td>
<td>1.616</td>
<td>0.3787</td>
<td>0.758</td>
</tr>
<tr>
<td></td>
<td>Other DFT</td>
<td>3.183</td>
<td>1.620</td>
<td>0.379 $^a$, 0.383 $^b$</td>
<td>0.804 $^c$</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>3.250</td>
<td>1.603</td>
<td>0.382</td>
<td>3.37</td>
</tr>
<tr>
<td>BeO</td>
<td>This work</td>
<td>2.710</td>
<td>1.626</td>
<td>0.3773</td>
<td>7.509</td>
</tr>
<tr>
<td></td>
<td>Other DFT</td>
<td>2.688</td>
<td>1.619</td>
<td>0.379 $^b$</td>
<td>7.36 $^d$</td>
</tr>
<tr>
<td></td>
<td>Experimental</td>
<td>2.698</td>
<td>1.622</td>
<td>0.378</td>
<td>10.6</td>
</tr>
</tbody>
</table>

$^a$ Ref. [71]  $^b$ Ref. [72]  $^c$ Ref. [69]  $^d$ Ref. [70]
3.2 Supercell of ZnBeO

The lattice parameters of ZnBeO has been studied by θ-2θ X-ray Diffraction (XRD) experiments on epitaxial or highly oriented ZnBeO films grown on the (0001) α-Al₂O₃ substrates. However, information regarding other structural or crystallographic properties, such as the relative atomic positions and symmetry in the basal plane, that are needed to completely characterize the crystal structure of these alloys is lacking. Such factors play a significant role on the growth morphology, band structure, spontaneous polarization, and piezoelectric properties of a material. Provided that the same interlayer distance along the c-axis is maintained, other crystal structures than the W lattice may indeed become possible, especially in one-dimensional nanostructures. As an example, we point to recent calculations in the (In,Ga)N system showing that certain orthorhombic lattices which are obtained by breaking the in-plane hexagonal symmetry of the (0001) layers of the W unit cell may become energetically favorable under 0 K. We present in Figs. 3.1(c) and (d) the basal planes of two different unit cells for the Zn₀.₅Be₀.₅O composition, both of which can be constructed from Fig. 3.1(b). Fig. 3.1(c) corresponds to a hexagonal 2x2 or a rectangular 1x√3 base that generates a W lattice but with Pmc2₁ symmetry whereas Fig. 3.1(d) is a rectangular 2x√3 base that may produce a Pna2₁ unit cell. This way one can envision composition-dependent supercells that have orthorhombic symmetry, in addition to the prototypical W structure.
Figure 3.2  The supercells of Zn$_{1-x}$Be$_x$O solid solutions in the W, O-16, and O-32 structures for Be compositions $x=0.25$, 0.50, and 0.75. Also shown are the space groups of each structure.
In Fig. 3.2 we provide the possible crystal structures and space groups of the compositions that were considered in this study. These are: (i) the W structure (P6$_3$mc or Pmc2$_1$), (ii) orthorhombic O-16 structures (Pmn2$_1$ or Pna2$_1$), and (iii) orthorhombic O-32 structures (P2$_1$). The basal plane of the W, O-16, and O-32 are hexagonal 2×2, rectangular 2×$\sqrt{3}$, rectangular 4×$\sqrt{3}$, respectively. All unit cells retain the same periodicity as ZnO or BeO along the c-axis. Since there are 8 atoms in the basal plane in O-32, this allows us to model several other compositions with $x=0.125$, 0.375, 0.625, and 0.875 (Fig. 3.3).

![Figure 3.3](image-url)  

**Figure 3.3** The P2$_1$ crystal structures of O-32 Zn$_{1-x}$Be$_x$O alloys for (a) $x=0.125$, (b) $x=0.375$, (c) $x=0.625$, and (d) $x=0.875.
The lattice parameters of $\text{Zn}_{1-x}\text{Be}_x\text{O}$ as a function of $x$ in the W, O-16, and O-32 structures are plotted in Fig. 3.4(a). For a more meaningful comparison of these crystal structures, we use the equivalent in-plane lattice parameter $a_0$ in the hexagonal $1\times1$ format [(Fig. 3.1(b)]. Despite different in-plane symmetries and atomic arrangements, the lattice parameters $a_0$ and $c$ of the three structures have nearly identical values at a given Be composition $x$ and obey Vegard's law,

\begin{align}
    a_0(\text{Zn}_{1-x}\text{Be}_x\text{O}) &= xa_0(\text{BeO}) + (1-x)a_0(\text{ZnO}), \quad (3.1) \\
    c(\text{Zn}_{1-x}\text{Be}_x\text{O}) &= xc(\text{BeO}) + (1-x)c(\text{ZnO}), \quad (3.2)
\end{align}

where Eq. (3.2) is in agreement with the experimental measurements of Ryu et al.\textsuperscript{32}
Figure 3.4  (a) Equilibrium lattice parameters $a_0$ and $c$ of $\text{Zn}_{1-x}\text{Be}_x\text{O}$ solid solutions in the W $1\times 1$ base and (b) the formation energy of the W, O-16, and O-32 structures as a function of Be concentration.
The relative stability of the structure of a particular ZnBeO composition is determined by its formation energy per cation-anion pair at 0 K given by:

\[ E_{\text{form}}(\text{Zn}_{1-x}\text{Be}_x\text{O}) = E(\text{Zn}_{1-x}\text{Be}_x\text{O}) - xE(\text{BeO}) - (1-x)E(\text{ZnO}), \]  

(3.3)

which is essentially the difference between the total internal energies of formation of ZnBeO and the weighed internal energies of formations of ZnO and BeO. \( E_{\text{form}} \) can be related to the lattice distortions arising from interatomic interactions in the W, O-16 and O-32 structures. Due to the different atomic sizes of Zn and Be, the position of each atom deviates slightly from that of a pure ZnO or BeO in the W, O-16, or O-32 lattice. As a consequence, the O tetrahedron surrounding each Zn (Be) atom is deformed, so that the four Zn-O (Be-O) bonding lengths within the tetrahedron are no longer equi-distance and their average value changes from that of pure ZnO (BeO). As such, ZnBeO alloy requires an additional bonding energy contribution, which is qualitatively proportional to the square of the percent variation in the average Zn-O and Be-O bonding lengths compared to bulk ZnO and BeO (Table 3.2).
Table 3.2: Percent variation in the average Zn-O and Be-O bonding lengths in the W, O-16 and O-32 alloys compared to bulk ZnO and BeO.

<table>
<thead>
<tr>
<th></th>
<th>W</th>
<th>O-16</th>
<th>O-32</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn-O</td>
<td>Be-O</td>
<td>Zn-O</td>
</tr>
<tr>
<td>Zn$<em>{0.875}$Be$</em>{0.125}$O</td>
<td></td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>Zn$<em>{0.75}$Be$</em>{0.25}$O</td>
<td>0.19</td>
<td>1.86</td>
<td>0.11</td>
</tr>
<tr>
<td>Zn$<em>{0.625}$Be$</em>{0.375}$O</td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Zn$<em>{0.5}$Be$</em>{0.5}$O</td>
<td>-0.71</td>
<td>2.08</td>
<td>0.00</td>
</tr>
<tr>
<td>Zn$<em>{0.375}$Be$</em>{0.625}$O</td>
<td></td>
<td></td>
<td>-0.28</td>
</tr>
<tr>
<td>Zn$<em>{0.25}$Be$</em>{0.75}$O</td>
<td>-2.73</td>
<td>1.86</td>
<td>-1.55</td>
</tr>
<tr>
<td>Zn$<em>{0.125}$Be$</em>{0.875}$O</td>
<td></td>
<td></td>
<td>-2.16</td>
</tr>
</tbody>
</table>
Furthermore, Be-O bonds are stronger than the Zn-O bonds, simply considering the fact that the bulk modulus of BeO is almost double that of ZnO.\textsuperscript{22,78} The reason for this is the larger number of electrons in Zn\textsuperscript{2+}. For a given percent variation, the formation of Be-O bonds would require higher energy than the formation of Zn-O bonds. Thus, $E_{\text{form}}$ in the alloys is mainly determined by the length variation of the Be-O bonds. The magnitude of percent variation of average Be-O bonding length in the W structure is almost twice as large as that in the O-16 and O-32 structures for $x=0.25$, 0.5 and 0.75 (Table 3.2). As seen in Fig. 3. 4(b), this agrees well with the much larger $E_{\text{form}}$ in W structures.

As $x$ varies from 0 to 1, Zn-O bonds are gradually replaced by Be-O bonds in Zn\textsubscript{1-x}Be\textsubscript{x}O. Hence for a given alloy structure, if the length variation in Be-O and Zn-O bonds remains constant as a function of $x$, $E_{\text{form}}$ would still increase from $x=0.25$ to $x=0.75$. This is the case in the W and O-16 structures. The slope of the increase in $E_{\text{form}}$ in the O-16 structure is smaller compared to that in the W structure, due to a smaller value of bond length variation. However, $E_{\text{form}}$ in the O-32 structure shows a slight decrease in the range $0.5<x<0.875$, because the increase in the number of Be-O bonds is partially compensated by the reduction in the magnitude of variation in Be-O bonding lengths in this composition range.
3.3 Electronic Structure of ZnBeO

The electronic band structures (not shown) and density of states of ZnO and BeO in our study agree well with previous experimental and theoretical studies (taking into account the underestimation in DFT).\(^{69,79}\) The band gap originates from the bonding-antibonding interaction between Zn 3s (Be 2s) electrons, which dominate the bottom of the conduction bands (CBs), and O 2p electrons, which dominate the top of the valence bands (VBs). Compared to that of BeO, VBs of ZnO have an additional (and relatively large) contribution from the Zn 3d electrons [Fig. 3.5(a)]. The strong O 2p and Zn 3d hybridization in ZnO results in two major effects: (i) the top of VBs are shifted closer to the Zn 4s states, reducing the band gap energy; (ii) the original narrow Zn 3d bands are significantly dispersed (-3.9 eV − -6.2 eV) and separated into two groups of peaks around -4.3 eV and -5.4 eV. For the solid solutions, as \(x\) increases from 0 to 1, the Zn 3d contribution and hence the \(p-d\) repulsion is continuously weakened [Figs 3.5(b)-(d)]. The lower Zn 3d peak (-5.4 eV) gradually decreases and disappears completely for BeO. The density of states for the compositions analyzed in this study does not display a discernible change for the three different crystal structures considered here.
Figure 3.5  The electronic density of states of Zn$_{1-x}$Be$_x$O at (a) $x=0$, (b) $x=0.25$, (c) $x=0.5$, and (d) $x=0.75$. The maximum of the valence bands is set to be 0 eV for each concentration.
The band gap energies of the alloys for the three structures as a function of $x$ are plotted in Fig. 3.6(a). Similar to the lattice parameters, $E_g$ is nearly the same for the W, O-16, and O-32 configurations at a given $x$. Over the entire composition range, $E_g$ displays a nonlinear dependence on $x$ which can be described using a parabolic approximation:

$$E_g (\text{Zn}_{1-x}\text{Be}_x\text{O}) = xE_g (\text{BeO}) + (1-x)E_g (\text{ZnO}) - bx(1-x),$$  

(3.4)

where $b$ is the bowing parameter. Average values of $b$ ($<b>$) for the W, O-16, and O-32 structures are 6.17 eV, 5.54 eV, and 5.33 eV, respectively, which are consistent with the result of a previous DFT study. 41 Compared to the linear interpolation of $E_g$ in Zn$_{1-x}$Mg$_x$O alloys with 0 $< x < 0.33$, 80 $<b>$ of Zn$_{1-x}$Be$_x$O is significantly larger due to the large size difference between Zn$^{2+}$ (0.74 Å) and Be$^{2+}$ (0.45 Å). 81 However, further analysis of the data shown in Fig. 3.6(a) indicates that a single average bowing parameter over the whole composition range is not sufficient to describe the dependence of $E_g$ as a function of $x$. In Fig. 3.6(b), we plot $b(x)$ in the O-32 structure as a function of the Be concentration. $b(x)$ is smaller than $<b>$ and is relatively composition independent until $x = 0.5$ [$b(x) \sim 4.5$ eV]. It increases sharply with $x$ from $\sim 5.0$ eV at $x=0.5$ to $\sim 13.0$ eV for $x=0.875$. The larger value of $b(x)$ in Be-rich alloys is due to the additional interaction resulting from the 3$d$ Zn$^{2+}$ and 2$p$ O$^{2-}$ repulsions that shift the valence band up. 44 Although $E_g$ is typically underestimated in DFT calculations, the trend in the variation in $b(x)$ is in good agreement with experimental results [Fig. 3.6(b)] derived from the measured $E_g$ of alloys. 32
Figure 3.6  (a) The band gap energy ($E_g$) of Zn$_{1-x}$Be$_x$O solutions from DFT calculations and (b) the theoretical band gap bowing parameter $b(x)$ of the O-32 structure as a function of the Be concentration derived from the theoretical $E_g$ together with the experimental bowing parameter obtained from the measured $E_g$. 32
3.4. Spontaneous Polarization and Piezoelectric Properties of ZnBeO

The particular shape of nanostructures of polarizable piezoelectric materials depends closely on the crystal structure and the magnitude and orientation of the spontaneous polarization. Several different nanostructures of ZnO (such as nano-helices, nano-spirals and nano-rings) have been synthesized using these principles. In this section, we calculate the spontaneous polarization of Zn$_{1-x}$Be$_x$O alloys in the W, O-16, and O-32 lattices by comparing these with the reference zinc-blende structure [Fig. 3.7(a)]. Our results show that for all three structures, $P_S$ deviates from the Vegard’s linear approximation. $P_S$ of Zn$_{1-x}$Be$_x$O in the W structure as a function of Be composition $x$ can be described via a parabolic function given by:

$$P_S(Zn_{1-x}Be_xO) = xP_S(BeO) + (1-x)P_S(ZnO) - b_Sx(1-x),$$

where the polarization bowing parameter $b_S$ is $-0.0916$ C/m$^2$. Fig. 3.7(a) shows that $P_S(x)$ in the W structure is significantly less in magnitude than the weighted averages of $P_S$ of ZnO and BeO; for $x=0.5$, $P_S = -0.011$ C/m$^2$ compared to the Vegard’s Law approximation of $-0.033$ C/m$^2$. On the other hand, O-32 structures have higher polarization throughout the composition range that was investigated in this study. The largest difference occurs at $x=0.5$ for which $P_S$ are $-0.011$ C/m$^2$ and $-0.083$ C/m$^2$ in the W and O-32 structures, respectively.
Figure 3.7  (a) Spontaneous polarization and (b) the average internal lattice parameter of the W, O-16, and O-32 structures as a function of the Be concentration.
Since $P_S$ (along the $c$-axis) arises from relative displacements of the anions and cations, it is closely related to the bonding length along this direction. In Fig. 3.7 (b), we plot the average value of bonding lengths along the $c$-axis ($\bar{u}$) in the W, O-16, and O-32 structures as a function of $x$. The correlation between $\bar{u}$ and $P_S$ is obvious and can be attributed to an internal strain effect resulting from the variation of Zn-O and Be-O bond lengths in the alloys. 83 The fluctuation of $P_S$ agrees with that of $\bar{u}$ in the O-16 structure. In W and O-16 structures, this internal strain is compressive so that the average bonds are shortened along the $c$-axis. As a comparison, the internal tensile strain in the O-32 structure results in a relatively large elongation of bonds in the same direction. The strength of this internal strain is proportional to the deviation of $\bar{u}(x)$ from the Vegard’s law prediction: it is strongest in the O-32 structure and weakest in the O-16.

Besides internal strains, there might be two other distinct effects resulting in non-linear interpolation of $P_S$ in the alloys: the volume deformation of the parent binaries which are compressed or stretched from their individual equilibrium lattices to the alloy values; and the chemical disorder effects due to the random distribution of metal on the cation sites. The relative contribution of these can be estimated in O-16 Zn$_{0.5}$Be$_{0.5}$O for which the internal strain effect is negligible since $\bar{u}$ is close to the linear approximation. Since the bowing of $P_S$ of it is small, one can conclude that in the Zn$_{1-x}$Be$_x$O alloy system, the contributions of the volume deformation and chemical disorder on $P_S$ are not as significant as the internal strain effect. Furthermore, these two effects would not result in any discrepancy in $P_S$ of the W, O-16 or O-32 alloys at a given Be concentration. This is a straightforward conclusion considering: (i) these structures have almost identical lattice parameters [Fig. 3.4(a)]; (ii) they have the same periodicity along the polarization direction ($c$-axis) despite different in-plane symmetries; and (iii) each O atom in the
W and O-16 structures has to be surrounded by Zn \textit{and} Be atoms commensurate with its stoichiometry (Fig. 3.2).

Piezoelectric polarization ($P_{PZ}$) results from external strain $\varepsilon_j$ which can be expressed as

$$P_{PZ} = \sum_j e_{ij} \varepsilon_j,$$

where $e_{ij}$ are the components of the piezoelectric tensor in Voigt notation. In the W structure, $P_{PZ}$ along the $c$-axis is reduced to:

$$P_{PZ}^{W} = e_{31}^{W} (\varepsilon_1 + \varepsilon_3) + e_{33}^{W} \varepsilon_3 = 2e_{//}^{W} \varepsilon_{//} + e_{33}^{W} \varepsilon_3,$$

where $\varepsilon_{//}=\varepsilon_1=\varepsilon_2$ is the equi-biaxial in-plane strain, $\varepsilon_3$ is the strain along the $c$-axis, and $e_{//}^{W} = e_{31}^{W}$.

The calculated piezoelectric coefficients of ZnO ($e_{31}=-0.58$ C/m$^2$, $e_{33}=1.20$ C/m$^2$) and BeO ($e_{31}=-0.14$ C/m$^2$, $e_{33}=0.22$ C/m$^2$) agree well with experimental and other DFT results. On the other hand, in the O-16 structures

$$P_{PZ}^{O-16} = e_{31}^{O-16} \varepsilon_1 + e_{32}^{O-16} \varepsilon_2 + e_{33}^{O-16} \varepsilon_3 = (e_{31}^{O-16} + e_{32}^{O-16}) \varepsilon_{//} + e_{33}^{O-16} \varepsilon_3,$$

To compare the piezoelectric response of the W and O-16 structures, we use an effective coefficient $e_{//}^{O-16} = (e_{31}^{O-16} + e_{32}^{O-16})/2$ in the O-16 structure such that:

$$P_{PZ}^{O-16} = 2e_{//}^{O-16} \varepsilon_{//} + e_{33}^{O-16} \varepsilon_3.$$

The calculated piezoelectric coefficients $e_{//}$ and $e_{33}$ for both the W and O-16 structures show a roughly linear interpolation with the Be concentration $x$ (Fig. 3.8).
Figure 3.8  Piezoelectric polarization (a) $e_{//}$ and (b) $e_{33}$ of the W and O-16 structures as a function of the Be concentration.
3.5. Elastic Properties of ZnBeO

In the Voigt notation, the elastic stress ($\sigma$) and commensurate strain ($\varepsilon$) in the W structures are related by the elastic stiffness tensor $C_{ij}$ through Hooke’s law \(^{85}\)

$$
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\sigma_4 \\
\sigma_5 \\
\sigma_6 
\end{pmatrix} = \begin{pmatrix}
C_{11} & C_{12} & C_{13} & \cdot & \cdot & \cdot \\
C_{12} & C_{11} & C_{13} & \cdot & \cdot & \cdot \\
C_{13} & C_{13} & C_{33} & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & C_{44} & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & C_{44} & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & 0.5(C_{11} - C_{12}) 
\end{pmatrix} \begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6 
\end{pmatrix}. \quad (3.10)
$$

And the bulk modulus ($B$) of the three structures can be obtained by

$$
B = \frac{(C_{11} + C_{12})C_{33} - C_{13}^2}{C_{11} + C_{12} + C_{33} - 4C_{13}} . \quad (3.11)
$$

The calculated values of $C_{ij}$ and $B$ of the W ZnO and BeO are listed in Table 3.3, in agreement with previous results. \(^{22,71}\) From Table 3.3, $C_{11}$, $C_{33}$, and $C_{44}$ of BeO are much larger than those of ZnO, indicating a much stronger strength in Be-O bonds than that of Zn-O bonds. This result is expected due to the large differences in sizes of Zn\(^{2+}\) (0.74 Å) and Be\(^{2+}\) (0.45 Å).

Table 3.3: Elastic stiffness coefficients ($C_{ij}$) and bulk modulus ($B$) of ZnO and BeO (unit: GPa).

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>196</td>
<td>117</td>
<td>105</td>
<td>211</td>
<td>36</td>
<td>140</td>
</tr>
<tr>
<td>BeO</td>
<td>432</td>
<td>118</td>
<td>84</td>
<td>470</td>
<td>138</td>
<td>216</td>
</tr>
</tbody>
</table>
On the other hand, for an alloy supercell in the orthorhombic structure, the elastic stiffness tensor $C_{ij}^O$ is different from that of the W lattice such that

$$
\begin{array}{c}
\sigma_1 = \begin{pmatrix}
C_{11}^O & C_{12}^O & C_{13}^O \\
C_{12}^O & C_{22}^O & C_{23}^O \\
C_{13}^O & C_{23}^O & C_{33}^O
\end{pmatrix} = \begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3
\end{pmatrix}, \\
\sigma_2 = \begin{pmatrix}
. & . & C_{44}^O \\
. & . & . \\
. & . & C_{55}^O
\end{pmatrix} = \begin{pmatrix}
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6
\end{pmatrix}
\end{array}
$$

(3.12)

where the superscript O denotes the original formats of the stiffness tensors. For each of the O-16 and O-32 lattices considered in this study, our results show that $C_{11}^O \approx C_{22}^O$, $C_{13}^O \approx C_{23}^O$, and $C_{44}^O \approx C_{55}^O$ with very small differences (typically <5%). Therefore, to make a comparison between the three structures, we construct an equivalent elastic stiffness tensor $C_{ij}^E$ in the hexagonal format for the O-16 and O-32 supercells in such a way that

$$
\begin{array}{c}
\sigma_1 = \begin{pmatrix}
C_{11}^E & C_{12}^E & C_{13}^E \\
C_{12}^E & C_{11}^E & C_{13}^E \\
C_{13}^E & C_{13}^E & C_{33}^E
\end{pmatrix} = \begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3
\end{pmatrix}, \\
\sigma_2 = \begin{pmatrix}
. & . & C_{44}^E \\
. & . & . \\
. & . & C_{55}^E
\end{pmatrix} = \begin{pmatrix}
\varepsilon_4 \\
\varepsilon_5 \\
\varepsilon_6
\end{pmatrix}
\end{array}
$$

(3.13)

where $C_{11}^E = 0.5(C_{11}^O + C_{22}^O)$, $C_{12}^E = C_{12}^O$, $C_{13}^E = 0.5(C_{13}^O + C_{23}^O)$, $C_{33}^E = C_{33}^O$, $C_{44}^E = 0.5(C_{44}^O + C_{55}^O)$, and $C_{66}^E = C_{66}^O$. We note that the special relation in a W lattice

$$
C_{66}^E = 0.5(C_{11}^E - C_{12}^E)
$$

(3.14)

is always satisfied in the orthorhombic structures used in this study with high precision.

As such, we simply use $C_{ij}$ to present our results of the elastic stiffness coefficients of the W, O-16, and O-32 structures. $C_{ij}$ and $B$ of the alloys are plotted in Figs. 3.9-3.14 as a function of
the Be composition $x$. The results show that the elastic properties of ZNBEO do not show any discernible variation with crystal structure except for $C_{33}$ at $x=0.5$ where its value in the O-32 supercell is approximately 26% smaller than those in the W and O-16 structures. As seen in Figs. 10 and 11, $C_{12}$ and $C_{13}$ of ZnBeO are fluctuating around Vegard’s law predictions. The discrepancy (or the standard deviation) from the linear interpolation as a function of the supercell is relatively small. This leads us to believe that in truly disordered alloys, Vegard’s law can be applied to $C_{12}$ and $C_{13}$ and this can be thought of as an averaging over all possible ordered states. The variation pattern is entirely different in W, O-16, and O-32 supercells for $C_{11}, C_{33}, C_{44}$, and $B$. Figures plotting $C_{11}, C_{33}, C_{44}$, and $B$ (Figs. 9, 12, 13, and 14) show a distinct downward bowing, regardless of the supercell constructions. Therefore, this provides a strong indication that Vegard’s law will not hold for these coefficients even if a completely random alloy were considered. The bowing parameter ($b_{EL}$) of the parabolic fitting equation of $C_{11}$ is obtained as

$$C_{11}(\text{Zn}_{1-x}\text{Be}_x\text{O}) = x \cdot C_{11}(\text{BeO}) + (1-x) \cdot C_{11}(\text{ZnO}) - b_{EL} \cdot x \cdot (1-x),$$

(3.15)

where $b_{EL} = 130.6$ GPa in the O-32 structures. Using data from the same structure, $b_{EL}$ of $C_{33}, C_{44}$, and $B$ are determined to be 217.5 GPa, 42.3 GPa, and 41.9 GPa, respectively. $b_{EL}$ here are relatively large and cannot be ignored. For example, at $x=0.5$, the true values of $C_{11}, C_{33}, C_{44}$, and $B$ are smaller by 10.4%, 16.0%, 13.8%, and 6.0% than the results from a simple Vegard’s linear approximation, respectively.
Figure 3.9  \( C_{11} \) of the W, O-16, and O-32 alloys as a function of the Be concentration.

Figure 3.10  \( C_{12} \) of the W, O-16, and O-32 alloys as a function of the Be concentration.
Figure 3.11  $C_{13}$ of the W, O-16, and O-32 alloys as a function of the Be concentration.

Figure 3.12  $C_{33}$ of the W, O-16, and O-32 alloys as a function of the Be concentration.
Figure 3.13 $C_{44}$ of the W, O-16, and O-32 alloys as a function of the Be concentration.

Figure 3.14 $B$ of the W, O-16, and O-32 alloys as a function of the Be concentration.
Based on the elastic stiffness coefficients, one can precisely determine the strains of ZnBeO for a given mechanical boundary condition. Firstly, most of devices based on ZnBeO epitaxial heterostructures or quantum wells are grown on the (0001) ZnO substrate, where equibiaxial in-plane strains ($\varepsilon_{//} = \varepsilon_1 = \varepsilon_2$) are given by the lattice misfit between layers or the substrate. The commensurate out-of-plane strain ($\varepsilon_3$) can be obtained by $\sigma_3 = 0$, which yields

$$\frac{\varepsilon_3}{\varepsilon_{//}} = \frac{-2C_{13}}{C_{33}}.$$  \hspace{1cm} (3.16)

In the second case, a uniaxial strain $\varepsilon_3$ is applied on a free-standing film or a one-dimensional nanostructure along the c-axis, the stress free condition in the basal plane ($\sigma_1 = \sigma_2 = 0$) leads to

$$\frac{\varepsilon_{//}}{\varepsilon_3} = -\frac{C_{13}}{(C_{11} + C_{12})}.$$  \hspace{1cm} (3.17)
Chapter 4: InGaN AND ZnBeO HETEROEPITAXIAL FILMS

Heteroepitaxial thin films deposited on suitable substrates may display changes in their crystal structures due to the in-plane misfit strains corresponding to the lattice mismatches between film and the substrate. It is well-known that the structure and electronic properties of semiconductors can be altered by applying external stresses (such as hydrostatic pressure) or inducing internal strains (through lattice and/or thermal mismatch strains in thin films). In fact, “strain engineering” in semiconductors as well as functional materials has been widely employed to obtain desired physical and electrical properties. Interatomic distances and the relative positions of atoms have a strong bearing on the band structure and $E_g$ in compound semiconductors. This makes it possible to control and tune $E_g$ through in-plane misfit strains in epitaxial thin films.

In this chapter, we take GaN as an example to show the changes structural and electronic properties of GaN under equibiaxial in-plane strains in the (0001) plane to simulate GaN films for $c$-plane [Fig. 1.1 (a)] epitaxy. As one will see in the following sections, for relatively small compressive misfits (-6%-0%), the band gap is estimated to be around its strain-free value, while for small tensile strains (0%-6%), it decreases by approximately 45%. In addition, at large tensile strains (>14.5%), our calculations indicate that GaN may undergo a structural phase transition from wurtzite to a graphite-like metallic phase.
4.1 Changes in Crystal Structures

The wurtzite unit cell of GaN is shown in Fig. 4.1(a). The strain-free equilibrium lattice parameters $a_0$, $c_0$, and $u_0$ obtained from our calculations are 3.223 Å, 5.239 Å and 0.377$c_0$, respectively, in excellent agreement with findings (3.189 Å, 5.186 Å and 0.377$c$) and previous calculations.  

![Figure 4.1](image)

Figure 4.1  (a) Strain-free wurtzite unit cell and (b) graphite-like metallic phase unit cell under large compressive in-plane strains. The $c$-axis is along [0001] direction in each case.
In the presence of equibiaxial in-plane stresses, a certain value of the in-plane strain is specified which corresponds to a new lattice parameter \( a \). This strain is given by \( \varepsilon = \varepsilon_{11} = \varepsilon_{22} = (a - a_0)/a_0 \) and the commensurate out-of-plane stress-free strain is \( \varepsilon_{33} = (c - c_0)/c_0 \). Therefore, the in-plane lattice parameter \( a \) (and, as such, \( \varepsilon \)) is taken as the parameter of the calculations and varied in our simulations from 2.65 Å to 3.80 Å, corresponding to \(-17.8 \% < \varepsilon < 17.9 \%\). As shown in Fig. 4.2, for the wurtzite structures \((-17.8 \% < \varepsilon < 14\%)\), the calculated values of \( \varepsilon_{33} \) display approximately a linear response as a function of \( \varepsilon \) while \( u \) varies slightly non-linearly from 0.325 to 0.400 in the same \( \varepsilon \)-range.

![Figure 4.2](image)

**Figure 4.2** Out-of-plane strain \( \varepsilon_{33} \) and the internal lattice parameter \( u \) as a function of \( \varepsilon \). The open circle and triangle represent the strain-free values. The wurtzite to graphite-like metallic phase occurs at \( \varepsilon \approx 14\% \) (dashed line).
The linear dependence of $\varepsilon_{33}$ on $\varepsilon$ can be easily understood through the Hooke’s law:

$$\sigma_{ij} = C_{ijkl} \cdot \varepsilon_{kl}, \quad (4.1)$$

which is reduced to:

$$\begin{pmatrix}
\sigma_{11} & 0 & 0 \\
0 & \sigma_{22} & 0 \\
0 & 0 & 0
\end{pmatrix}
= C_{ijkl} \cdot \begin{pmatrix}
\varepsilon & 0 & 0 \\
0 & \varepsilon & 0 \\
0 & 0 & \varepsilon_{33}
\end{pmatrix}, \quad (4.2)$$

In Eqs. (4.1) and (4.2), $\sigma_{ij}, \varepsilon_{kl}$, and $C_{ijkl}$ are stress, strain, and elastic coefficients, respectively. We note that the mechanical boundary conditions require that all $\sigma_{ij}$ except $\sigma_{11}$ and $\sigma_{22}$ are zero. Similarly, all $\varepsilon_{kl}$ except $\varepsilon_{kk}$ are zero and $\varepsilon_{33}$ is a stress-free strain. Therefore, taking into account the anisotropy in the elastic coefficients, it can be easily shown that

$$\frac{\varepsilon_{33}}{\varepsilon} = -\frac{2C_{1133}}{C_{3333}}, \quad (4.3)$$

Previous experimental and theoretical results of the stiffness ratio of $C_{1133}/C_{3333}$ fall into a range from 0.184 to 0.261, corresponding to $\varepsilon_{33}/\varepsilon$ from -0.364 to -0.522.\(^4,90,91\) This range is shown as the shaded area in Fig. 4.2. Our calculations yield $\varepsilon_{33}/\varepsilon$ as -0.468 which is consistent with prior experimental findings.

More interestingly, there is a discontinuity in $\varepsilon_{33}$ and $u$ at $\varepsilon=14.5\%$, corresponding to a phase transition from wurtzite [Fig. 4.1 (a)] to a graphite-like phase [Fig. 4.1(b)]. The cation (anion) becomes coplanar with the three anions (cations) in the basal plane, thus resulting in $u=0.5$. We note that this structure is slightly different from graphite because each cation (anion) has bonds with the two adjacent anions (cations) along the c-axis, in addition to bonds with three anions (cations) in the same plane. Our results indicate that when GaN is subjected to equibiaxial in-plane strains, the unit cell volume increases by 20% from $\varepsilon=0\%$ to 14.5% followed by an abrupt 14% drop at the phase transition to the graphite-like phase (not shown).
4.2 Changes in Electronic Structures

The electronic properties of GaN are also modified by the misfit strains. Four band structures under different strains are plotted in Fig. 4.3. The band structures of Figs. 4.3(a), (b), and (c) correspond to wurtzite structures which display direct band gaps, with both valence band minimum (VBM) and conduction band maximum (CBM) at Γ point. However, the graphite-like phase shows an “indirect” zero band gap semi-metallic band structure [Fig. 4.3(d)]; the CBM is still at Γ point but the VBM now has shifted to H point. At both large compressive and tensile in-planes strains [Fig. 4.3(c) and (d)], the Fermi level becomes equal to the CBM and VBM, introducing another important transition from semiconductor to semi-metallic phases. The mechanism by which \( E_g \) becomes smaller is very similar to that of ZnX materials. The VBM states of GaN are mainly occupied by the N \( p_x, p_y, \) and \( p_z \) orbitals, which overlap in a “degenerate” manner when GaN is strain-free. But under strain, the \( p_z \) orbital would split away from the \( p_x \) and \( p_y \) orbitals. However, we note that these are purely bulk calculation results. For ultra-thin films with a thickness of 10-100 Å, the surface electron accumulation by defect states would raise the Fermi level to the upper part of the band gap, and the CBM would reach the Fermi level at a smaller in-plane strain. Hence, it should be easier to obtain the metallic phase in thin film GaN.
Figure 4.3  Band structure of GaN for (a) $\varepsilon = -3.8\%$; (b) $\varepsilon = 3.9\%$; (c) $\varepsilon = -17.8\%$; (d) $\varepsilon = 14.8\%$. The crystal structures are wurtzite in (a), (b) and (c), and the graphite-like phase in (d). Fermi level is set to be zero in each figure.
Our results show that $E_g$ of strain-free GaN is 1.709 eV. The relative variation in the band gap $\Delta E_g$ with respect to the $E_g(\varepsilon=0)$ as a function of $\varepsilon$ is shown in Fig. 4.4. The band gap tuning is asymmetric with respect to the sign of the in-plane strain. For $-6\%< \varepsilon <0$, $E_g$ increases only by 6%. Beyond this range, $E_g$ drops dramatically to 0 eV ($\Delta E_g = -100\%$) at $\varepsilon = -17\%$. On the other hand, for tensile in-plane strains, $\Delta E_g$ is negative, and varies linearly with strain. Relatively small tensile strains result in a significant narrowing of the gap such that $\Delta E_g = -42.4\%$ for $\varepsilon = 5.5\%$. $E_g$ (under tensile strains) reaches a zero value when the transformation to the graphite-like phase is complete. We note that although DFT underestimates the absolute value of the band gap, trends in band gap value changes are well predicted by DFT. For instance, pressure coefficients of the band gap computed using DFT are in excellent agreement with experiments, and trends in relative variations of band gaps computed using different levels of theory are in mutual agreement with each other.\textsuperscript{89}
Figure 4.4  Relative variation of band gap $\Delta E_g$ with $\varepsilon$. The in-plane strain between some commercially available substrate materials and GaN are marked on the figure. The inset shows $\Delta E_g$ as a function of $\varepsilon$ for $-6\% < \varepsilon < 6\%$. 
4.3 Discussion

Based on the results in Secs. 4.1 and 4.2, we expect that appropriate equibiaxial strains in ultra-thin pseudomorphic GaN films on suitable substrates may be used to “tune” the GaN band gap to span the solar spectrum, thereby enabling a number of important technological applications. For instance, to result in a band gap value in the blue to green light region (-42.5\% < ΔE_g < -19.0\%), substrates with 2.5-5.5% lattice mismatch would be needed. This would require substrate materials with lattice parameters in the range of 3.273-3.369 Å and with similar thermal expansion parameters as GaN. A number of materials were investigated as potential substrates for epitaxial GaN such that appropriate levels of in-plane stresses may be imposed. The lattice mismatch between commercially available substrates and epitaxial pseudomorphic GaN films are marked on Fig. 4.4, and more are listed in the literature. 93

We note that epitaxial stresses may be relaxed by the formation of misfit dislocations at the film substrate interface. The equilibrium critical thickness for the formation of misfit dislocations (h_ρ) in epitaxial GaN films can be determined using the Matthews-Blakeslee (MB) criterion. 94 For wurtzite films, taking the Burgers vector and the dislocation line as \( \frac{1}{3}[\overline{1}2\overline{1}0] \) and \([2\overline{1}00]\), respectively, 95 and a deposition temperature of \( T_G=650^\circ C \), we can determine the \( h_\rho \) as a function of the pseudomorphic misfit at \( T_G \). The results show that as the magnitude of the strain increases from 2% to 6%, \( h_\rho \) decreases from 30 Å to 5 Å. For larger strains, \( h_\rho \) from MB criteria should be expected to be less than one unit cell although the film may grow via island coalescence rather than the MB assumption of layer-by-layer growth. Although the range of strains considered here is enormous, appreciable changes (i.e., reductions) of the band gap may be accomplished for modest and realistic strains. Finally, we note that the theory developed in
this Letter can be validated through deposition of epitaxial (0001) GaN on (0001) ZnO or (111) ZrN which would generate in-plane strains of about 1.8% in pseudomorphic films of GaN, resulting in a band gap reduction of about 15%.
Chapter 5: InGaN/GaN and ZnBeO/ZnO SOLID SOLUTIONS

In Chapter 4, we see variations in structural and electronic properties of InGaN and ZnBeO thin films under in-plane misfit strains on lattice-mismatched substrates. Our findings indicate that the band gap decreases for both tensile and sufficiently strong compressive in-plane strains. This conclusion can also be applied to multilayer heterostructures such as InGaN/GaN and ZnBeO/ZnO MQWs because of the in-plane lattice mismatch between adjacent interlayers. As the layer thickness in MQWs is typically decreased to the order of a few nanometers, i.e., several unit cell distances, even atoms at the center of an interlayer may be electrostatic interacted with atoms from another material from adjacent layers. As such, the electronic structure of the interlayers in a MQW may experience further modifications compared to that in a single heteroepitaxial thin film.

Changes in electronic properties of the material within the interlayers have a significant impact on the interfacial conduction and valence band offsets which determine the degree of quantum confinement and carrier localization. In this chapter, the band offsets will be studied in InGaN/GaN and ZnBeO/ZnO MQWs. We show that a combination of mechanical boundary conditions, epitaxial orientation, and the In concentration can be used as design parameters to engineer the band offsets in optoelectronic devices.

Another topic covered in this chapter is the band bending, i.e., built-in electric fields that are raised by the polarization mismatch between two adjacent layers, even when the device is unbiased (no external voltages or electric fields). This is a unique phenomenon for MQWs based on compound semiconductors in the wurtzite crystal structure. These materials, e.g., InGaN and ZnBeO, have a spontaneous polarization under equilibrium strain-free conditions and a strong
piezoelectric polarization due to the in-plane misfit strain when they are epitaxially grown on suitable substrates with c-axis ([0001]) epitaxy. The internal electric fields are simulated by both atomistic DFT calculations and continuum level electrostatic analysis, with excellent agreements between the results of the two methods.

5.1 Band Offsets—Literature Review

Experimentally, the band offsets in InGaN/GaN heterostructures have been investigated extensively via a wide variety of techniques including X-Ray photoemission spectroscopy (XPS), photocurrent spectroscopy, internal photoemission measurements, and capacitance-voltage measurements. These studies focus mainly on [0001] InN/GaN heteroepitaxial films consisting of an InN capping layer on thick GaN substrates/templates. The c-plane cut corresponding to [0001] epitaxy is more commonly used than the non-polar and semi-polar orientations because of the ease of availability of single crystal substrates such as sapphire onto which these multilayers can be grown. The measured values of InN/GaN valence band offset (ΔEv) from such structures show a relatively large disparity. ΔEv is relatively large (0.8–1.1 eV) for capping layers with high defect densities or for relatively thick capping layers (>200 nm) compared to cases where ultrathin capping layers (~5 nm) with a high crystal quality are used (0.5–0.6 eV). This is understandable since the electronic structures of InN and GaN change significantly as functions of crystal orientations, interface terminations, in-plane misfit strains, and defect microstructures (misfit and threading dislocations, impurities, phase/grain boundaries, etc.). We also note that for InGaN/GaN MQWs with polar and semi-polar interfaces,
the strong band bending due to large built-in electric fields, on the order of a few MV/cm, \(^9\)_resulting from the polarization mismatch between adjacent layers must be taken into account.

DFT has been employed to investigate the band offsets between InGaN and GaN in the wurtzite structure. \(^9\)_D-F-T These studies mainly focus on InN/GaN band offsets, \(^9\)_D-F-T although InGaN/GaN MQWs are more commonly used in device applications. The purpose of such simplifications is to reduce computational costs since InN can be simulated using a relatively small unit cell containing 4 atoms, whereas disordered InGaN solid solutions require a much bigger unit cell (with at least 16 atoms) to reproduce their bulk properties. \(^6\)_D-F-T Recent results by Moses et al. show that \(\Delta E_V\) of InGaN/GaN at the (10\(\bar{1}0\)) \(m\)-plane interface is a linear function of the In concentration \(x\) in InGaN from 0 eV (GaN) to 0.62 eV (InN). \(^9\)_D-F-T These calculations are based on DFT supplemented by modern hybrid Heyd-Scuseria-Ernzerhof (HSE06) functionals and utilize InGaN unit cells with 16 or 32 atoms for In concentrations \(x=0.25, 0.5, \) and 0.75. Moreover, the selection of the non-polar \(m\)-plane epitaxy allows carrying out relatively easier computations in which it avoids consideration of the polarization mismatch at the interlayer interfaces. To further simplify the calculations, the analysis is limited to natural band alignments corresponding to strain-free (and unconstrained) InGaN and GaN in the InGaN/GaN MQW constructs. Because GaN-based materials are often deposited on appropriate substrates with a \(c\)-alignment direction, \(^1\)_D-F-T it is necessary to expand such a theoretical method to InGaN/GaN MQWs with polar interfaces. Obviously, \(m\)- and \(c\)-plane orientations have different atomic arrangements (and hence different surface terminations), producing different magnitudes of in-plane misfit strains. As such, these factors need to be incorporated into a theoretical analysis to determine band offsets more accurately.
Band offsets in ZnBeO/ZnO heterostructures and MQWs have not been experimentally or theoretically studied in the previous. However, considering the large difference in band gap energy of ZnO and BeO (3.37 eV and 10.6 eV, respectively), the band offsets in ZnBeO/ZnO system are expected to be large as well. The large band offsets will benefit the optical and electronic performances of devices based on ZnBeO/ZnO heterostructures. The commensurate strong quantum confinement may be the reason of an astonishingly high exciton binding energy (263 meV) that was found in a ultraviolet LED based on a (0001) Zn$_{0.8}$Be$_{0.2}$O/ZnO MQW, noting that the exciton binding energy in ZnO film is only 60 meV.

5.2 Band Offsets in InGaN/GaN MQWs

In this section, DFT calculations are carried out to systematically analyze $\Delta E_V$ and band bending as a function of composition in heteroepitaxial InGaN/GaN MQWs on $m$-plane and $c$-plane GaN substrates. Results in ZnBeO/ZnO MQWs can be found elsewhere. InGaN ternary alloys are simulated by O-32 supercells as shown in Figs. 3.2 an 3.3. These supercells are employed to determine $\Delta E_V$ between InGaN and GaN under four different mechanical boundary conditions [see Fig. 1.2(a) for crystal orientations]:

1. $m$-plane strain-free InGaN/GaN bilayers;
2. Epitaxial InGaN/GaN MQWs on $m$-plane GaN substrates with $[1\overline{2}10]_{\text{InGaN}}//[1\overline{2}10]_{\text{GaN}}$ and $[0001]_{\text{InGaN}}//[0001]_{\text{GaN}}$ epitaxial alignments;
3. $c$-plane strain-free InGaN/GaN bilayers;
4. Epitaxial InGaN/GaN MQWs on c-plane GaN substrates with $[\overline{1}0\overline{1}0]_{\text{InGaN}} / [\overline{1}0\overline{1}0]_{\text{InGaN}}$

and $[\overline{1}2\overline{1}0]_{\text{InGaN}} / [\overline{1}2\overline{1}0]_{\text{GaN}}$. 

For mechanical boundary conditions 1 and 3, we employ a stack consisting of an InGaN slab with $m$- (nonpolar) or $c$-plane (polar) surfaces exposed to vacuum [Figs. 5.1(a) and (b)]. For a given In composition, the non-polar (polar) InGaN slab contains 14 (16) atomic layers that are constrained to their bulk lattice parameters in the $m$- ($c$-) planes but completely relaxed along the out-of-plane $[10\overline{1}0]$ ([0001]) direction. The vacuum region in such stacks is 20 Å ($m$-plane) or 25 Å ($c$-plane) thick to prevent interactions between periodic images.
Figure 5.1  Heterostructures consisting of GaN (or InGaN) and vacuum region along (a) the nonpolar $[10ar{1}0]$ direction, (b) the polar $[0001]$ direction. Also shown schematically are (c) $m$- and (d) $c$-plane InGaN/GaN MQWs, respectively.
To simulate the polar and non-polar epitaxial InGaN/GaN MQWs on GaN substrates, a \((\text{InGaN})_6/(\text{GaN})_6\) superlattice is constructed along the [0001] and [10\overline{1}0] directions as shown in Figs. 5.1(c) and (d), respectively. For both epitaxial conditions, GaN is assumed to be strain-free (thick substrate) while in InGaN there exist in-plane compressive strains \(u_1\) and \(u_3\) along the [1\overline{2}10] and [0001] directions, respectively, and a commensurate tensile stress-free strain \(u_2\) along the [10\overline{1}0] direction. The strain conditions in the epitaxial \(m\)-plane InGaN layers are

\[
\mathbf{u}_m(m\text{-plane}) = \begin{pmatrix} u_1 & 0 & 0 \\ 0 & u_2 & 0 \\ 0 & 0 & u_3 \end{pmatrix}.
\tag{5.1}
\]

In Eq. 5.1, \(u_1\) and \(u_3\) are determined by the differences in lattice parameters \(a_0\) and \(c_0\) [Fig. 1(a)] between bulk (relaxed) InGaN and bulk (relaxed) GaN, respectively. On the other hand, the principal axial strains for InGaN layers for \(c\)-plane epitaxy are:

\[
\mathbf{u}_c(c\text{-plane}) = \begin{pmatrix} u_1 & 0 & 0 \\ 0 & u_2 & 0 \\ 0 & 0 & u_3 \end{pmatrix},
\tag{5.2}
\]

where \(u_1\) is the equi-biaxial in-plane misfit strain that is determined by the mismatch in \(a_0\) between InGaN and GaN, and \(u_3\) is the out-of-plane stress-free strain. The specific values of the strains in Eqs. (5.1) and (5.2) are provided in Table 5.1 as a function of the In concentration.

In the following subsections, we show that \(\Delta E_V\) in the \(m\)-plane InGaN/GaN MQWs increases linearly as \(x\) varies from 0 to 1 and is relatively insensitive to the in-plane misfit strains, while \(\Delta E_V\) in the \(c\)-plane MQWs increases non-linearly in the entire composition range and is significantly lower than the corresponding strain-free value for \(x \geq 0.5\).
Table 5.1: Strain conditions as a function of In composition $x$ in InGaN/GaN MQWs on $m$- and $c$-plane GaN substrates.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$m$-plane</th>
<th>$c$-plane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$u_1$</td>
<td>$u_2$</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.1003</td>
<td>0.0920</td>
</tr>
</tbody>
</table>
5.2.1 InGaN/GaN Band Offsets For m-Plane Interfaces

We begin the analysis of $\Delta E_V$ with the non-polar undoped $m$-plane InGaN/GaN interfaces, which are relatively simple to compute due to the absence of polarization-induced charge at the interfaces. We first assume both InGaN and GaN are fully relaxed (strain-free) as in thick layers, corresponding to the mechanical boundary condition 1 in Sec. 5.2. The strain-free $\Delta E_V$ is determined by comparing their respective valence band positions ($E^{\text{GaN}}_V$ and $E^{\text{InGaN}}_V$) with the energy of vacuum ($U^{\text{Vac}}$) at the $m$-plane surfaces, so that

$$\Delta E_V = (U^{\text{Vac}} - E^{\text{GaN}}_V) - (U^{\text{Vac}} - E^{\text{InGaN}}_V),$$

$$\equiv I^{\text{GaN}} - I^{\text{InGaN}},$$

(5.3)

where $I^{\text{GaN}}$ and $I^{\text{InGaN}}$ are the ionization energies. To derive an expression for $I^{\text{GaN}}$, we employ a three-step process for the $m$-plane GaN stack shown schematically in Fig. 5.1(a). First, we calculate its electrostatic potential with 3-dimensional periodic boundary conditions. Next, the potential is averaged within each $m$-plane cross-section, which, we find, demonstrates an oscillatory “bulk-like” pattern in the GaN region and a flat band, i.e., $U^{\text{Vac}}$ in the vacuum region [see the dashed curve in Fig. 5.2(a)]. The potential is further averaged over the length of one GaN unit cell along the [10 10] direction [shown as the solid line in Fig. 5.2(a)], leading to a volumetric average of the GaN potential energy ($U^{\text{GaN}}$) at the center of the GaN slab. Finally, $I^{\text{GaN}}$ is found by identifying the position of $E^{\text{GaN}}_V$ in the same figure. This is easily done since the difference between $E^{\text{GaN}}_V$ and $U^{\text{GaN}}$ can be determined by a separate calculation that only involves bulk GaN.
Figure 5.2  Electrostatic potentials in (a) an $m$-plane GaN/vacuum heterostructure as shown in Fig. 5.1(a) and in (b) a In$_{0.5}$Ga$_{0.5}$N/GaN MQW on an $m$-plane GaN substrate as shown in Fig. 5.1(c).
The above process similarly applied to InGaN for $x$=0.25, 0.5, 0.75, and 1. Based on these values, the strain-free InGaN/GaN $\Delta E_V$ is calculated using Eq. (5.3) and is found to vary almost linearly from 0 eV to 0.57 eV as the In composition $x$ increases from 0 to 1 (see Fig. 5.3). Our results from the relatively simple GGA agree well with those of a previous DFT study using the HSE06 functional. 

Figure 5.3 $\Delta E_V$ of $m$-plane InGaN/GaN for two mechanical boundary conditions: strain-free $m$-plane InGaN and GaN slabs (by HSE $^{97}$ and GGA), and epitaxial InGaN/GaN MQW on $m$-plane GaN substrate (by GGA).
In the above analysis, both GaN and InGaN are considered to be strain-free and unconstrained. However, the electronic structure of a heterostructure or MQW are very sensitive to the misfit strain, which arises from the lattice mismatch between the film and the substrate and between adjacent layers. To assess the effect of strain in non-polar InGaN/GaN MQW devices, we construct pseudomorphic \((\text{InGaN})_6/(\text{GaN})_6\) superlattices on \(m\)-plane GaN substrates [Fig. 5.1(c)]. The electrostatic potential of such a superlattice is first averaged over the unit cell length of the strain-free GaN along the \([10\bar{1}0]\) direction and then along the strained InGaN, respectively, to find out the relative positions of \(U^\text{GaN}\) and \(U^\text{InGaN}\) [Fig. 5.2(b)]. \(E^\text{GaN}_v\) and the valence band position in strained InGaN layers \(E^\text{InGaN}_v\) were determined per Fig. 5.2(b) without reference to the vacuum energy level. Such a procedure has been widely applied to other non-polar lattice mismatched heterostructure materials systems, e.g., Si/Ge and GaAs/InAs. The calculated \(\Delta E_v\) in the epitaxial \(m\)-plane superlattices does not display a large deviation from the corresponding strain-free values for \(x=0.25, 0.5, \text{ and } 0.75\) (Fig. 5.3). For InN/GaN MQWs (\(x=1\)) \(\Delta E_v\) is 31% higher than that in the strain-free bilayers.
5.2.2 InGaN/GaN Band Offsets For c-Plane Interfaces

Polar c-plane InGaN/GaN heterostructures and MQWs are important as they lend themselves to practical applications in devices such as LEDs and lasers because to large extent the substrates for c-plane epitaxy (e.g., sapphire) are relatively inexpensive and the growth techniques are better developed than those in nonpolar or semi-polar orientations. To compute $\Delta E_V$ between (0001) InGaN and GaN layers, the constructs in Figs. 5.1(b) and (d) are utilized under mechanical boundary conditions 3 and 4 in Sec. 5.2, respectively.

The profiles of the volumetrically averaged electrostatic potential for strain-free InGaN ($0 \leq x \leq 1$) slabs [Fig. 5.1(b)] and pseudomorphic (InGaN)$_6/(GaN)_6$ superlattices [Fig. 5.1(d)] are obtained following the procedure outlined above in Sec. 5.2.1, and are plotted in Fig. 5.4(a) and (b), respectively. For both cases, the inclined potential with respect to the distance from the basal plane ($z$) indicates the existence of built-in electric field, the result of the compositional variation along the direction of polarization. The bulk-like potential energies ($U^{GaN}$, $U^{Vac}$, and $U^{InGaN}$) have to be extended to the interfaces (see arrows in Fig. 5.4) to calculate $\Delta E_V$ under such circumstances.
Figure 5.4  Electrostatic potentials (solid curve) and bound charge distribution (dashed curve) in (a) a $c$-plane GaN/vacuum slab as shown in Fig. 5.1(b) and in (b) a In$_{0.5}$Ga$_{0.5}$N/GaN MQW on a $c$-plane GaN substrate as shown in Fig. 5.1(d).
We note that the magnitudes of $\Delta E_V$ determined by this procedure are dependent on the selection of GaN/Vacuum or InGaN/GaN interface positions in Fig. 5.4. In fact the interfaces span a narrow region (usually within 2 Å in Fig.5.4) wherein the electrostatic potential changes continuously. Nevertheless, abrupt interface conditions and the corresponding band offsets are favored for device designs at larger length scales (μm or higher) in order to simplify the simulations. Thus, to determine the optimal positions of the left and right interface planes, we first identify a folding plane between the two interfaces ($z_0$ in Fig. 5.4). For this purpose, we follow the methodology developed by Bernardini and Fiorentini for polar (0001) AlN/GaN superlattices and utilize the bound charge density ($\rho_D$) that results from the polarization mismatch between GaN and vacuum or between InGaN and GaN. From Fig. 5.4, one can see that $\rho_D$ is primarily distributed across the interfaces, permitting us to decompose $\rho_D$ an odd and an even terms, i.e., a monopole and dipole distribution ($\rho_D^{mono}$ and $\rho_D^{dip}$) with respect to $z_0$ such that

\[
\rho_D^{mono}(z-z_0) = \frac{1}{2}[\rho_D(z-z_0) - \rho_D(z_0-z)], \quad \text{(5.4a)}
\]

\[
\rho_D^{dip}(z-z_0) = \frac{1}{2}[\rho_D(z-z_0) + \rho_D(z_0-z)]. \quad \text{(5.4b)}
\]

The optimal position for $z_0$ is chosen so that the dispersions of the monopole and dipole moments ($\int |\rho_D^{mono}(z-z_0)|^2 dz$ and $\int |\rho_D^{dip}(z-z_0)|^2 dz$, respectively) are minimized around the interfaces. Subsequently, the optimal positions of the interface planes in Fig. 5.4 are given as $z_0 \pm 0.5L^{GaN}$, where $L^{GaN}$ is the thickness of GaN region.

It is interesting to note that in Fig. 5.4(a), the calculated potential offsets at the left and right interfaces are unequal, due to the asymmetric surface terminations of the GaN slab, i.e., the left and right $c$-plane surfaces are terminated with a pure Ga and N atomic layer, respectively.
Similar phenomena occur in InGaN/GaN superlattices [Fig. 5.4(b)] because the left and right interfaces are composed of N-Ga bonds and N-(In, Ga) bonds, respectively. The average of the two potential offsets is used throughout the calculations to determine $\Delta E_V$. In both strain-free InGaN/GaN bilayers and epitaxial MQWs on GaN substrates, $\Delta E_V$ increases nonlinearly (Fig. 5.5) as $x$ varies from 0 (GaN) to 1 (InN). $\Delta E_V$ in pseudomorphic (0001) InGaN/GaN superlattices is reduced compared to the corresponding strain-free value. The decrease in $\Delta E_V$ for InGaN/GaN superlattices can be attributed to the dependence of the band structure of InGaN on the lattice deformation. A compressive equi-biaxial misfit strain $u_1$ in the $c$-plane and acommensurate tensile strain $u_3$ along the [0001] direction shift down the valence band edge of InGaN from its strain-free energy level. As the In concentration increases, per Vegard’s law $u_1$ in InGaN grows as well from 0 ($x$=0, GaN) to -10% ($x$=1, InN) (Table 5.1). Therefore, the decrease in $\Delta E_V$ becomes more significant for higher In compositions ($x \geq 0.5$).

The calculated strain-free $\Delta E_V$ of InN/GaN for $c$-plane epitaxy (0.90 eV) agrees well with experimental results (0.94–0.95 eV) reported by Wang et al. using a 200 nm-thick InN capping layer with a dislocation density around $4 \times 10^{-11}$ cm$^{-2}$ on a (0001) GaN template. Our calculations indicate that $\Delta E_V$ in pseudomorphic (0001) InN/GaN superlattice is 0.64 eV, in good agreement with 0.58±0.08 eV measured by King et al. for 5 nm thick (0001) InN on GaN samples.
Figure 5.5 $\Delta E_V$ for strain-free $c$-plane InGaN/GaN slabs and epitaxial InGaN/GaN MQWs on $c$-plane GaN substrate.
5.3 Band Bending in Polar InGaN/GaN MQWs

From the DFT calculated electrostatic potential shown in Fig. 5.4(b), one can easily see the existence of external electric field that is induced by the bound sheet charge at the polar InGaN/ GaN interfaces. Band bending in polar MQWs can also be calculated using continuum level modeling taking into account the electrostatic interactions at the interlayer interfaces. In this section, we carry out an electrostatic analysis (ESA) using Maxwell and Poisson’s relations to analyze band bending in epitaxial (0001) InGaN/GaN MQWs on GaN substrates to supplement the ab-initio calculations.

Assuming that GaN barrier layers are strain-free in such a MQW, only spontaneous polarization exists (\( P_{3}^{GaN} = -0.0329 \text{ C/m}^2 \)). In the InGaN layer, in addition to spontaneous polarization \( P_{3}^{InGaN} \), equi-biaxial in-plane strain \( u_1 \) and the stress-free strain \( u_3 \) are present which result in a strong piezoelectric polarization \( P_{piz}^{InGaN} \) (Table 5.2). While most device simulations assume a linear (first-order) coupling between the polarization and the strains, recent theoretical and experimental findings indicate that second-order coupling may be significant in III-nitrides semiconductors AlN, GaN, and InN and their alloys. In the present work, the polarization state for bulk InGaN under the strain condition given by Eq. (5.2) are obtained through our DFT calculations based on the Berry-phase approach. Our results show that \( P_{piz}^{InGaN} \) can be precisely described via

\[
P_{piz}^{InGaN} = Au_1 + Bu_1^2 + Cu_3 + Du_3^2,
\]

\( (5.5) \)
where $A$ and $C$ are first-order and $B$ and $D$ are second-order piezoelectric coefficients, respectively. These coefficients for all seven In compositions considered in this study are given in Table 5.2 along with $P_{S}^{\text{InGaN}}$ and $P_{PZ}^{\text{InGaN}}$ in the polar InGaN/GaN MQWs.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D$</th>
<th>$P_{S}^{\text{InGaN}}$</th>
<th>$P_{PZ}^{\text{InGaN}}$</th>
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<tr>
<td>0.125</td>
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<tr>
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<td>1.1558</td>
<td>-8.1965</td>
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<td>0.1471</td>
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</table>
Built-in electric fields arise from the polarization mismatch between the barrier and well layers in the polar MQWs. At finite temperatures, the electric fields produce two-dimensional electron and/or hole accumulation at the interlayer interfaces. Because DFT calculations are typically performed for 0 K, the inherent assumption in the calculations that follow is that all carriers are frozen and there are no free charges at the interfaces. Under these conditions, the relevant Maxwell’s equation describing dielectric displacement is

\[
D = \varepsilon_0 \kappa_{\text{GaN}} E_{\text{GaN}} + P_{\text{GaN}}^	ext{S} \\
= \varepsilon_0 \kappa_{\text{InGaN}} E_{\text{InGaN}} + P_{\text{InGaN}}^	ext{S} + P_{\text{PZ}}
\]

(5.6)

where \( D \) is the total electric displacement, \( \varepsilon_0 \) is the permittivity of vacuum, \( \kappa_{\text{GaN}} \) (\( \kappa_{\text{InGaN}} \)) is the static dielectric constant of GaN (InGaN), and \( E_{\text{GaN}} \) (\( E_{\text{InGaN}} \)) is the built-in electric field in the GaN (InGaN) layer. Our DFT calculations show that \( \kappa_{\text{InGaN}} \) varies almost linearly from 11.71 to 15.28 as \( x \) increases from 0 (GaN) to 1 (InN).

The DFT potential profile of the (0001) InGaN/GaN superlattice shown in Fig. 5.4(b) is obtained using standard 3-dimensional periodic boundary conditions. To directly compare the results of DFT and ESA, we apply the same restrictions which reduced to the [0001] direction are given by:

\[
E_{\text{GaN}} L_{\text{GaN}} + \Delta U_1 + E_{\text{InGaN}} L_{\text{InGaN}} - \Delta U_2 = 0.
\]

(5.7)

In Eq. (5.7), \( L_{\text{GaN}} \) and \( L_{\text{InGaN}} \) are the thicknesses of GaN and InGaN layers, respectively, and are given by \( L_{\text{GaN}} = 3c_0^{\text{GaN}} \) and \( L_{\text{InGaN}} = 3(1 + u_3)c_0^{\text{InGaN}} \) where \( c_0^{\text{GaN}} \) and \( c_0^{\text{InGaN}} \) are the lattice parameters of bulk GaN and InN along the [0001] direction, respectively. Also entering Eq. (5.7) are \( \Delta U_1 \) and \( \Delta U_2 \) which correspond to the potential offsets at the left and the right interfaces, respectively. Combining Eqs. (5.6) and (5.7), \( E_{\text{GaN}} \) is obtained as:
In Eq. (5.8), the second term of the numerator is much smaller compared to the first term for all seven In compositions. Therefore, Eq. (5.8) can be simplified as

$$E_{\text{GaN}} = \frac{L_{\text{InGaN}} \left( P_{S}^{\text{InGaN}} + P_{PZ}^{\text{InGaN}} - P_{S}^{\text{GaN}} \right) - \kappa_{\text{InGaN}} \left( \Delta U_{1} - \Delta U_{2} \right)}{\varepsilon_{0} \left( \kappa_{\text{GaN}} \frac{L_{\text{InGaN}}}{L_{\text{GaN}}} + \kappa_{\text{InGaN}} \frac{L_{\text{GaN}}}{L_{\text{GaN}}} \right)}. \quad (5.9)$$

Similarly,

$$E_{\text{InGaN}} = \frac{-L_{\text{GaN}} \left( P_{S}^{\text{InGaN}} + P_{PZ}^{\text{InGaN}} - P_{S}^{\text{GaN}} \right) - \kappa_{\text{InGaN}} \left( \Delta U_{1} - \Delta U_{2} \right)}{\varepsilon_{0} \left( \kappa_{\text{GaN}} \frac{L_{\text{GaN}}}{L_{\text{GaN}}} + \kappa_{\text{InGaN}} \frac{L_{\text{GaN}}}{L_{\text{GaN}}} \right)}. \quad (5.10)$$

Based on the built-in electric fields, the total polarization in either GaN or InGaN layer is given by

$$P_{T}^{\text{GaN}} = \varepsilon_{0} \left( \kappa_{\text{GaN}} - 1 \right) E_{\text{GaN}} + P_{S}^{\text{GaN}}, \quad (5.11a)$$

$$P_{T}^{\text{InGaN}} = \varepsilon_{0} \left( \kappa_{\text{InGaN}} - 1 \right) E_{\text{InGaN}} + P_{S}^{\text{InGaN}} + P_{PZ}^{\text{InGaN}}. \quad (5.11b)$$

Combining Eqs. (5.6) and (5.11), the polarization mismatch at the interlayer interfaces, i.e., the bound sheet charge density ($\sigma_{D}$) is

$$\sigma_{D} = P_{T}^{\text{InGaN}} - P_{T}^{\text{GaN}} = \varepsilon_{0} \left( E_{\text{GaN}} - E_{\text{InGaN}} \right). \quad (5.12)$$

The ESA and DFT calculated built-in electric fields and the bound sheet charge densities are given in Table 5.3. There is an excellent agreement between ESA and atomic-level DFT computations. We note that the accuracy of ESA in this study is significantly improved by taking into account second-order piezoelectric coupling compared to a previous theoretical study on (0001) InN/GaN MQWs that only considers first-order piezoelectric coefficients. 98
Table 5.3: The magnitudes of built-in electric fields $E_{\text{GaN}}$ and $E_{\text{InGaN}}$ (unit: MV/cm) and bound sheet charge densities $\sigma_D$ (unit: $\mu$C/cm$^2$) obtained by DFT and ESA.

<table>
<thead>
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<th>$x$</th>
<th>DFT</th>
<th>ESA</th>
</tr>
</thead>
<tbody>
<tr>
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<td>$E_{\text{InGaN}}$</td>
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<tr>
<td>0.125</td>
<td>0.54</td>
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<tr>
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<td>-6.81</td>
</tr>
</tbody>
</table>
5.4 Discussion

The results on the role of mechanical boundary conditions and the compositional variations on the band bending and band offsets InGaN/GaN MQWs have several implications related to how optoelectronic properties of such constructs can be optimized by tuning $\Delta E_V$. The valence band offset increases with In concentration in InGaN/GaN superlattices regardless of the mechanical boundary conditions and growth epitaxy. For low In compositions ($x<0.5$), our calculations show that nonpolar and polar MQWs yield similar $\Delta E_V$ values. The valence band offset is more enhanced in polar $c$-plane conditions for In concentrations larger than 0.5. For non-polar $m$-plane InGaN/InN MQWs, the role of epitaxial strains that increase with increasing In concentration according to Vegard’s law have very little effect on $\Delta E_V$ for $x<0.8$. On the other hand, the difference between valence band offset of epitaxial and stress-free $c$-plane MQWs is substantial, especially for larger In concentrations ($x>0.5$). An important conclusion of these results is that a combination of mechanical boundary conditions (constrained vs. unconstrained), epitaxy (choice of growth plane), and the In concentration can be used as design parameters in optoelectronic devices.

We note that the in-plane misfit strain in pseudomorphic heteroepitaxial InGaN/GaN MQWs considered in this study from both atomistic and continuum level simulations can reach as high as 10% (InN/GaN). For $c$-plane epitaxial conditions, our results suggest that for InGaN/GaN with high In concentrations, the in-plane misfit strains reduce $\Delta E_V$ and thus increase the conduction band offset, resulting in an enhancement in quantum confinement for conduction electrons and hence the optoelectronic properties of MQWs. However, such extremely high internal strains would (if not controlled through materials tailoring) certainly be relaxed via the
formation of detrimental defects (misfit dislocations, delamination, and cracking) for film thicknesses larger than a few unit cell dimensions. A straightforward application of the Matthews–Blakeslee (MB) criterion \(^9^4\) shows that for \(0.05 \leq x \leq 0.3\) the critical thickness for misfit dislocation formation varies from 20 nm to 2 nm and from 100 nm to 15 nm for an epitaxial InGaN layer on \(c\)- and \(m\)-plane GaN substrates, respectively. \(^{10^5,10^6}\) For higher In concentrations, the MB critical film thickness is even smaller, of the order of one unit cell length. The formation of interfacial dislocations may partially or fully relax in-plane misfit strains, reducing the magnitudes of built-in electric fields within the multilayer structure. Their actual values may vary depending on the strain state and the defect microstructure of the specific MQW.

The internal electric fields due to the polarization mismatch and the strain due to the lattice mismatch are volumetric quantities. While the introduction of dislocation network results in global relaxation of mechanical strains, it also produces localized strain fields of the order of the characteristic length of the dislocation (magnitude of the Burgers vector). In a polarizable, piezoelectric medium, variations in stress/strain conditions immediately generate localized electrostatic fields around the defect. \(^{10^7,10^8}\) Previous theoretical study by Shi et al. has shown that defect induced charge densities at the surfaces of GaN may reach up to \(10^{11}\) e/cm\(^2\) within a distance of 100 nm from the dislocation core. \(^{10^9}\) As such, optoelectronic properties of InGaN/GaN-based devices will actually be degraded because of the inelastic scattering of free carriers from the charged defects.

Recent advances in thin film growth technology [molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD)] now allow the deposition of thin films one atomic layer at a time. Such techniques have been used to synthesize pseudomorphic (0001) InGaN/GaN MOWs at the nanometer scale (i.e., InGaN/GaN superlattices) with low In
concentrations ($x \leq 0.15$). For such superlattices, our results show that DFT and ESA can be used to determine the band offset $\Delta E_V$, the internal electric fields, and the bound sheet charge density $\sigma_D$ quite accurately. However, relatively low $\Delta E_V$ observed in such supercells results in a smaller degree of quantum confinement and hence reduces the enhancement in the optoelectronic properties. Again, for maximum enhancement, one would ideally require strain-free InN/GaN superlattices for red/infrared light emissions due to the small band gap energy of InN (0.7 eV). It is important to note that high-quality (0001) InGaN/GaN superlattices that are vertically aligned in one-dimensional nanorod constructs can be synthesized via MOCVD and metal organic-hydride vapor phase epitaxy with higher In concentrations ($x > 0.15$). But such a configuration corresponds to a different set of mechanical boundary conditions compared to the thin film structures investigated in this report. Smaller internal strains and lower defect densities can be achieved in such nanostructures because of the elimination of the 2-dimensional constraint imposed by the substrate in a thin film structure and the increased surface area provided by the nanorod geometry which acts as a sink for point and line defects.

At elevated temperatures, internal electric fields due to the bound sheet charges may partially be screened by the formation of 2-dimensional electron/hole gases at the interfaces. The density of such free carries or the density of the 2-dimensional electron gases in epitaxial $c$-plane InGaN/GaN MQWs have been determined using empirical relations taking into account the bound charge density, relative position of Fermi Energy, and the conduction band offset.

In conclusion, we have carried out atomistic DFT computations and macroscopic (continuum) level ESA using first and second-order piezoelectric coefficients obtained from DFT. Both DFT and electrostatic computations are in excellent agreement. This should provide experimentalists with predictive and self-consistent tools across multiple length scales. Our
results show that the valence band offset may be engineered through a combination of variables including mechanical boundary conditions, epitaxy, and In (Be) concentration.
**Chapter 6: SUMMARY AND CONCLUSIONS**

In$_{x}$Ga$_{1-x}$N (InGaN) and Zn$_{1-x}$Be$_x$O (ZnBeO) are compound semiconductor solid solutions that display a wide band gap tuning range and strong spontaneous and piezoelectric polarizations due to the wurtzite crystal structure. They have gained significant importance in electronic and optoelectronic devices where the active layers are often fabricated as InGaN/GaN and ZnBeO/ZnO multiple quantum well (MQW) structures to take the advantage of an enhanced quantum confinement. The performances of devices based on such polarizable MQWs are significantly affected by band offsets and band bending, two critical interlayer interfacial parameters that determine the electronic structure of the barriers and the wells.

In this Thesis, first principles calculations based on density functional theory are carried out to study how the properties of each layer in InGaN/GaN and ZnBeO/ZnO MQWs and their band offsets and band bending can be altered by different heteroepitaxial growth conditions. The results show that for bulk InGaN and ZnBeO, the band gap energy, spontaneous polarization, and elastic properties are nonlinearly dependent on the In and Be concentrations, respectively. Taking ZnBeO as an example, we construct three distinct super cells for ZBO solid solutions, including the prototypical wurtzite (P6$_3$mc) structure and orthorhombic supercells with Pmn2$_1$/Pna2$_1$, or P2$_1$ symmetry. For a given Be composition, the band gap energy and the elastic tensor coefficients of ZnBeO in the three constructs are almost identical. The bowing of the band gap energy increases with increasing Be concentration. The spontaneous polarization of Zn$_{1-x}$Be$_x$O varies nonlinear as a function of Be concentration, and its magnitude depends on the internal lattice parameter that measures the average of Zn(Be)-O bond lengths along the c-axis of
the supercell structures. The piezoelectric polarization in the wurtzite and orthorhombic structures varies linearly with the Be concentration.

For heteroepitaxial InGaN and ZnBeO thin films on suitable (0001) substrates, the band gap energy is significantly affected by in-plane misfit strains: it is reduced for tensile in-plane misfit strains and for compressive misfit strains larger than $-6\%$. For example, in GaN the band gap is estimated to be around its strain-free value for relatively small compressive misfits ($-6\%$-$0\%$); while for small tensile strains ($0\%$-$6\%$), it decreases by approximately $45\%$. In addition, at large tensile strains ($>14.5\%$), our calculations indicate that GaN may undergo a structural phase transition from wurtzite to a graphite-like semi-metallic phase.

For InGaN/GaN and ZnBeO/ZnO MQWs, it is found that a combination of mechanical boundary conditions, epitaxial orientation, and the In (or Be) concentration can be used as design parameters in optoelectronic devices. Taking InGaN/GaN MQWs as an example, the valence band offset ($\Delta E_V$) increases with In concentration in InGaN/GaN superlattices regardless of the mechanical boundary conditions and growth epitaxy. For low In compositions ($x<0.5$), our calculations show that nonpolar and polar MQWs yield similar $\Delta E_V$ values. The valence band offset is more enhanced in polar c-plane conditions for In concentrations larger than 0.5. For non-polar m-plane InGaN/InN MQWs, the role of epitaxial strains that increase with increasing In concentration according to Vegard’s law have very little effect on $\Delta E_V$ for $x<0.8$. On the other hand, the difference between valence band offset of epitaxial and stress-free c-plane MQWs is substantial, especially for larger In concentrations ($x>0.5$).

In conclusion, the band offsets and band bending may be engineered through a combination of variables including mechanical boundary conditions (strain and defect microstructure), epitaxy (growth orientation), and In or Be concentration for InGaN/GaN or
ZnBeO/ZnO MQWs, respectively. Since the electronic band structure of heterostructures and quantum wells can be completely characterized by band offsets and internal electric fields, the results of this research can be directly applied in the design of current and potential electronic and optoelectronic devices based on InGaN/GaN and ZnBeO/ZnO material systems to enhance their relevant properties and performance.
References:


