Band offsets and polarization effects in wurtzite ZnO/Mg$_{60.25}$Zn$_{0.75}$O superlattices from first principles

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Using first-principles calculations, we investigate the band offsets, built-in electric fields, and band gaps of (0001)-oriented wurtzite ZnO/Mg$_{60.25}$Zn$_{0.75}$O superlattices, including the dependence on superlattice geometry and strain. Significant built-in electric fields form inside the quantum-well region that are found to be tunable over the range 0.24 MV/cm ≤ $E_{\text{in}}$ ≤ 0.63 MV/cm, and potentially up to 1 MV/cm by varying the relative width of the well and barrier regions. The valence band offset at the ZnO/Mg$_{60.25}$Zn$_{0.75}$O interface is calculated to be 0.25–0.26 eV which, in contrast to the “common anion rule,” is a significant portion of the total band offset, and this is in support of recent experiment. Calculated values for the valence band offset were found to be insensitive to variations in superlattice geometry and strain. The band gap of the superlattice is determined by the competing effects of quantum confinement and the quantum-confined Stark effect, with the former being more dominant for the systems investigated. These findings will be useful in the design and optimization of ZnO/Mg$_x$Zn$_{1-x}$O superlattices for electronics and optoelectronics applications.

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I. INTRODUCTION

Wide-band-gap semiconductors, particularly those with a wurtzite structure, are of interest for a range of technological applications involving thin-film heterostructures. For example, III-V systems such as GaN/In(Al)N have been widely adopted for applications involving thin-film heterostructures. For example, wurtzite structure, are of interest for a range of technological applications. Moreover, Mg incorporation affects the ZnO crystal structure in-plane lattice constant, such that an in-plane strain is present due to a number of outstanding properties, some of which are far superior to the more conventional III-V compounds. These include a larger exciton binding energy of 60 meV (compared to 25 meV for GaN) as well as the availability of large native substrates for epitaxial growth of high-quality thin films.

Alloying of Mg into ZnO increases the magnitude of the fundamental band gap, allowing Mg$_x$Zn$_{1-x}$O to be exploited as a barrier material in QW structures for electronic devices. Moreover, Mg incorporation affects the ZnO crystal structure in two important ways: (i) an increase in the magnitude of the spontaneous polarization, such that an in-plane strain is present at a ZnO/Mg$_x$Zn$_{1-x}$O interface, resulting in piezoelectric polarization. Consequently, a discontinuity arises in the macroscopic polarization, both spontaneous and piezoelectric, at a lattice-matched Mg$_x$Zn$_{1-x}$O junction, creating bound sheet charges and the confinement of a two-dimensional electron layer. In recent years, development of growth processes such as molecular beam epitaxy (MBE) have seen a drastic improvement in the quality of ZnO epilayers such that atomic precision is now available, with 2DEG mobilities as high as 300 000 cm$^2$/V·s at cryogenic temperatures. In fact, remarkably, the quality of ZnO/Mg$_x$Zn$_{1-x}$O layers is now so high that the integer and fractional quantum Hall effects have been observed.

Progress in understanding and optimization of phenomena at the ZnO/Mg$_x$Zn$_{1-x}$O interface is developing at a rapid rate; however, current knowledge is not at the detailed level as that of III-nitride systems, which have benefited from several decades of investigation. To date, many important properties of the interface remain controversial. For example, the valence and conduction band offsets (VBO/CBO), which are both fundamental properties of the interface as well as input parameters for non-self-consistent simulations, are still not agreed upon. It has often been suggested that, based on the “common anion rule,” the VBO at the ZnO/Mg$_x$Zn$_{1-x}$O interface should be negligible. Using the indirect method of obtaining the band-offset ratio (CBO:VBO) as a fitting parameter to spectral data, reported this quantity to be 90:10. Somewhat larger, using first-principles calculations, reported the VBO to be 19% of the total band offset for a ZnO/MgO interface. Another experimental study, also based on fitting the CBO:VBO to spectra, but including the effects of the exciton-phonon interaction, found the VBO to be an even more significant portion of the total band offset with CBO:VBO determined in the range 60:40–70:30. This result is supported by the recent investigation of using a direct measurement of the band offsets at a ZnO/Mg$_{60.25}$Zn$_{0.75}$O junction by x-ray photoelectron spectroscopy (XPS); the CBO:VBO ratio was found to be close to 60:40.

At the ZnO/Mg$_x$Zn$_{1-x}$O interface, where charge monopoles are formed due to the polarization discontinuity, large built-in electric fields arise which affect significantly the optical properties of the QW, and...
Morhain et al.\textsuperscript{22} have evaluated the strength of this field to be 0.9 MV/cm in ZnO/Mg\textsubscript{0.25}Zn\textsubscript{0.75}O QWs based on the magnitude of the shift in the exciton transition energy caused by the quantum-confined Stark effect. In a similar system ($x = 0.22$), Makino et al.\textsuperscript{23} reported a somewhat smaller 0.65 MV/cm for the built-in electric field and attributed the discrepancy to a geometrical effect: the strength of the electric field in the QW may be reduced if the barrier region is sufficiently narrow.\textsuperscript{24} Moreover, for epitaxial layers, strain effects must be considered and piezoelectric contributions to the polarization may be significant.\textsuperscript{7} Indeed, both experimental\textsuperscript{25} and theoretical studies\textsuperscript{26–28} of wurtzite III-nitride systems have shown that the properties of the superlattice, including the strength of the built-in electric field and band offsets, strongly depend on the superlattice geometry and strain. The sensitivity of ZnO/Mg\textsubscript{x}Zn\textsubscript{1−x}O to variations in these conditions is still not known in detail.

In this paper, we report fundamental properties of the ZnO/Mg\textsubscript{x}Zn\textsubscript{1−x}O interface including the band offsets, built-in electric fields, and band gaps, and investigate the effects of superlattice geometry and strain using first-principles calculations. Excellent agreement is found with recent experiments\textsuperscript{8,12,22} for the magnitude of the built-in electric field. We show that the strength of the electric field, as well as the band gap, is a function of superlattice geometry and that variations are well explained by electrostatic arguments and by considering confinement effects in the QW. Importantly, we report that the VBO is comparable in magnitude to that of the CBO and that this quantity is highly insensitive to variations in these conditions.

II. METHODOLOGY

A. Computational details

Using periodic superlattices (SL), we simulate multiple-quantum-well (MQW) structures consisting of an infinite number of repeating ZnO (well) and Mg\textsubscript{x}Zn\textsubscript{1−x}O (barrier) regions. We perform all-electron density functional theory (DFT) calculations within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof\textsuperscript{69} as implemented in the DMOL\textsuperscript{3} code.\textsuperscript{30,31} The wave functions are expanded in terms of a double-numerical quality localized basis set with a real-space cutoff of 9 bohrs. Using periodic boundary conditions, we construct ZnO/Mg\textsubscript{0.25}Zn\textsubscript{0.75}O(0001) MQW structures with varying well and barrier thicknesses. Superlattice structures consist of consecutive layers along the [0001] direction with Zn-face polarity, each layer containing eight atoms (four O and four Zn/Mg) and with dimensions $2a \times 2a \times c/2$, where $a$ and $c$ are the lattice constants of the wurtzite supercell. Figure 1(a) displays the geometry of a single layer (undoped) viewed down the $c$ axis. We construct the QW region to consist of pure ZnO, while in the barrier region a single Zn atom is replaced by a Mg atom per layer to achieve the desired 25% doping concentration.

We denote the number of layers in the well (barrier) region as $m$ ($n$), such that any superlattice is described as $(m+n)$, with dimensions $2a \times 2a \times (m+n)c/2$. Figure 1(b) displays an example for the $(6 + 4)$ ZnO/Mg\textsubscript{x}Zn\textsubscript{1−x}O SL. We note the formation of two different interfaces which we label “type A” (Mg\textsubscript{x}Zn\textsubscript{1−x}O/ZnO) and “type B” (ZnO/Mg\textsubscript{x}Zn\textsubscript{1−x}O). The Brillouin zone integrations are performed using a $9 \times 9 \times 6$ k-point grid for the wurtzite supercell and an equivalent mesh for the SL calculations, i.e., we use a $5 \times 5 \times 2$ grid for the $(6 + 4)$, $2a \times 2a \times 5c$ 80-atom SL. For SLs of varying sizes, we use the same/similar sampling of reciprocal space.

B. Built-in electric field

The magnitude and direction of the built-in electric field inside the well and barrier regions can be determined from the energetic shift of a selected core-level eigenvalue.\textsuperscript{32} We use the binding energy of the O 1s core level in each layer (taking the mean of the four O atoms per layer gives an average for the microscopically inhomogeneous potential). For a constant electric field along the [0001] direction, the electrostatic potential (and the O 1s binding energy) varies linearly in space; the slope of the line of best fit in each region...
corresponds to the built-in electric field \( E \) (Ref. 32):

\[
E \approx \frac{\Delta E_{b}^{CL}}{\Delta z},
\]

where \( E_{b}^{CL} \) is the binding energy of the O 1s core level and \( z \) is the distance along the [0001] direction.

C. Valence band offset

To calculate the VBO at the ZnO/Mg\(_{0.25}\)Zn\(_{0.75}\)O interface, we adopt a method used widely in all-electron calculations by again utilizing the energy shift of a core-level eigenvalue.\(^{27,32}\)

The VBO is calculated as follows:

\[
\Delta E_{v} = \left( E_{O_{1s},VBM}^{MgZnO} - E_{O_{1s},VBM}^{ZnO} \right) + \Delta E_{O_{1s},O_{1s}}^{ZnO/MgZnO},
\]

where \( \Delta E_{v} \) represents the VBO. In the above, “MgZnO” denotes Mg\(_{0.25}\)Zn\(_{0.75}\)O. The term in the brackets is the so-called bulk term, where \( E_{O_{1s},VBM}^{MgZnO} \) (and similarly \( E_{O_{1s},VBM}^{ZnO} \)) is the energy difference between the O 1s core level and the valence band maximum (VBM) in the respective bulk materials, i.e., bulk ZnO and Mg\(_{0.25}\)Zn\(_{0.75}\)O (with in-plane lattice constant fixed to that of the corresponding SL) without the formation of an interface. The term \( \Delta E_{O_{1s},O_{1s}}^{ZnO/MgZnO} \) is known as the interface term and is the difference between the O 1s core-level binding energies of ZnO and Mg\(_{0.25}\)Zn\(_{0.75}\)O at the interface plane; more precisely, \( \Delta E_{O_{1s},O_{1s}}^{ZnO/MgZnO} = E_{O_{1s},O_{1s}}^{MgZnO} - E_{O_{1s},O_{1s}}^{ZnO} \) where \( E_{O_{1s},O_{1s}}^{MgZnO} \) and \( E_{O_{1s},O_{1s}}^{ZnO} \) are the O 1s core-level binding energies in the ZnO and Mg\(_{0.25}\)Zn\(_{0.75}\)O regions, respectively. Thus, we find the interface term from a linear extrapolation of the O 1s core levels in each region to the interface plane,\(^{27,32}\) which is taken to be the midpoint of the interface bond. As pointed out in Ref. 32, it is noted that there is some uncertainty related to the choice of the exact position of the interface plane. However, due to the relatively small electric fields in the present system, it is found that the choice of any arbitrary point along the interface bond does not significantly affect the result.

III. RESULTS AND DISCUSSION

A. Bulk properties

We investigate the fundamental properties of the parent compound, namely, bulk ZnO in the wurtzite phase. In Table I, we present the calculated equilibrium values for the lattice constants \((a, c, \text{ and } c/a)\), the internal parameter \((u)\), band gap \((E_{g})\) as well as the cohesive \((E_{c})\) and formation \((\Delta H)\) energies. For comparison, results from other calculations, including those performed within the GGA (Refs. 33 and 34) and the local density approximation (LDA),\(^{7,35}\) as well as the relevant experimental quantities are presented.\(^{5,36–38}\)

Our calculations show good agreement with previous GGA results; the small discrepancies with LDA calculations are related to the underbinding of the GGA compared to the LDA, i.e., for GGA larger lattice constants and smaller energetic quantities are typical.\(^{39}\) Compared to experiment, our calculations overestimate the lattice constants slightly (1%–2%). The calculated thermodynamic quantities agree reasonably well with experiment, particularly the cohesive energy which is determined to within 1.6% of experiment; the enthalpy of formation is underestimated somewhat, which is a consequence of the underbinding of the GGA.\(^{39}\) Additionally, as expected, our calculations underestimate the band gap significantly, which is characteristic of DFT GGA (and LDA).\(^{40}\) As has been found experimentally,\(^{5}\) deviation from the ideal wurtzite geometry is noted, i.e., we calculate the parameters \(c/a\) and \(u\) to be 1.615 and 0.379, respectively; this is compared to \(c/a = 1.633\) \((8/7)\) and \(u = 0.375\) \((3/8)\) for the ideal case.\(^{41}\) Consequently, spontaneous polarization along the \(c\) axis is expected, which is increased in the nonideal geometry.\(^{34,41}\)

In developing an understanding of phenomena at the ZnO/Mg\(_{x}\)Zn\(_{1−x}\)O interface, the properties of the bulk wurtzite Mg\(_{x}\)Zn\(_{1−x}\)O alloy are investigated. At this point, we note that for the experimental case, Mg\(_{x}\)Zn\(_{1−x}\)O alloys contain a certain degree disorder. Malashevich \textit{et al.}\(^{7}\) performed a first-principles investigation of Mg\(_{x}\)Zn\(_{1−x}\)O and found that the Mg distribution does not significantly impact the properties of the alloy. Most importantly, Malashevich \textit{et al.}\(^{1}\) found that the polarization, which is the key parameter affecting the properties of the heterointerface, is mostly dependent on the Mg concentration and not the distribution. To confirm this finding and to ascertain the magnitude of uncertainties relating to Mg distribution in our study, we perform calculations for a \(4a \times 4b \times c\) supercell in which the Mg concentration is kept constant at 6.25\% (two Mg atoms per supercell) while the relative positions of dopant atoms are changed. Four configurations are considered, as illustrated in Fig. 2. The \(4a \times 4b \times c\) supercell contains two layers along the \(c\) axis. The configurations in Figs. 2(a)–2(c) are such that there is one Mg atom per layer where the position of the dopant in the top layer is kept fixed, while that of the dopant in the bottom layer is varied. The structure in Fig. 2(d) is somewhat different in that both Mg atoms are placed in the top layer, while the bottom layer contains only Zn and O atoms. As summarized in Table II, the uncertainties related to Mg distribution are small. The lattice constants and internal parameter \(u\) are highly insensitive to the variations; since \(u\) and the ratio \(c/a\) are direct

### Table I. Lattice constants \((a, c, \text{ and } c/a)\), internal parameter \((u)\), band gap \((E_{g})\), cohesive energy \((E_{c})\), and enthalpy of formation \((\Delta H)\) of bulk wurtzite ZnO.

<table>
<thead>
<tr>
<th>Method</th>
<th>(a) (Å)</th>
<th>(c) (Å)</th>
<th>(c/a)</th>
<th>(u)</th>
<th>(E_{g}) (eV)</th>
<th>(E_{c}) (eV)</th>
<th>(\Delta H) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present</td>
<td>3.287</td>
<td>5.307</td>
<td>1.615</td>
<td>0.379</td>
<td>0.81</td>
<td>7.40</td>
<td>2.84</td>
</tr>
<tr>
<td>GGA (Ref. 33)</td>
<td>3.286</td>
<td>5.299</td>
<td>1.613</td>
<td>0.74</td>
<td>0.38</td>
<td>7.69</td>
<td>2.82</td>
</tr>
<tr>
<td>GGA (Ref. 34)</td>
<td>1.614</td>
<td>0.380</td>
<td>0.382</td>
<td>0.80</td>
<td>3.50</td>
<td>7.52</td>
<td>3.60</td>
</tr>
<tr>
<td>Exp. (Refs. 5, 36–38)</td>
<td>3.250</td>
<td>5.204</td>
<td>1.602</td>
<td>0.382</td>
<td>3.44</td>
<td>7.52</td>
<td>3.60</td>
</tr>
</tbody>
</table>
the effects of this strain on the electronic structure to be small.\textsuperscript{20} The results are given in Table III where the dependence of the atomic structure and fundamental gap on the Mg fraction is shown. With increasing Mg content, the length of the $c$ axis exhibits a decrease which is in agreement with experimental reports.\textsuperscript{6} Importantly, with increasing $x$, the ratio $c/a$ decreases while the internal parameter $a$ increases indicating an increase in the spontaneous polarization.\textsuperscript{3,4} Moreover, this indicates a polarization discontinuity at the ZnO/Mg$_x$Zn$_{1-x}$O interface of increasing magnitude with increasing Mg fraction. It is also clear that Mg incorporation increases the band gap of ZnO, which is in qualitative agreement with experiment.\textsuperscript{5,6}

### B. (5 + 5) ZnO/Mg$_{0.25}$Zn$_{0.75}$O superlattice

We first consider a (5 + 5) ZnO/Mg$_{0.25}$Zn$_{0.75}$O SL, with an in-plane lattice constant matched to pure ZnO (strain-free QW). We study this system in detail as an example, and to demonstrate the methodology. A barrier doping concentration of $x = 0.25$ is chosen since there have been a number of experimental studies near this doping concentration which have focused on determining the key properties of the interface.\textsuperscript{20–22}

#### 1. Built-in electric field

The (5 + 5) SL has a ZnO/Mg$_{0.75}$Zn$_{0.25}$O interface, at which there exists a discontinuity in the macroscopic polarization;\textsuperscript{7} consequently, bound sheet charges are formed, giving rise to built-in electric fields and affecting the local band structure at the interface. To demonstrate this, the total Mulliken charge for each layer, calculated by summing the individual Mulliken charges of each atom in the layer, is plotted in Fig. 3(a). In the bulk, since each layer contains equal anion/cation contributions, it should be expected that the net Mulliken charge for each layer is close to zero; at the interface, however, this is not the case. Interface charges can be decomposed into dipole and monopole contributions arising, respectively, due to the sudden shift in the electrostatic potential and the polarization discontinuity at the interface.\textsuperscript{44} From Fig. 3(a), local charge accumulation, in the form of interface monopoles, is clearly demonstrated, which is a direct consequence of the polarization discontinuity.\textsuperscript{44} It is noted that the monopole contribution to the interface Mulliken charge is large compared to that of the dipole, which is in contrast to GaN/AlN;\textsuperscript{45} this discrepancy may be related to the larger band offsets in GaN/AlN.\textsuperscript{46} Interface charges lead to built-in electric fields in each region $E_w$ and $E_b$ of opposing direction.

### Table III. Lattice constants ($a$, $c$, and $c/a$), internal parameter ($u$), and band gap ($E_g$) of Mg$_x$Zn$_{1-x}$O alloys for different Mg fractions ($x$).

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$c/a$</th>
<th>$u$</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0625</td>
<td>3.287</td>
<td>5.303</td>
<td>1.613</td>
<td>0.379</td>
<td>0.957</td>
</tr>
<tr>
<td>0.125</td>
<td>3.287</td>
<td>5.296</td>
<td>1.611</td>
<td>0.379</td>
<td>0.957</td>
</tr>
<tr>
<td>0.167</td>
<td>3.287</td>
<td>5.289</td>
<td>1.609</td>
<td>0.380</td>
<td>1.095</td>
</tr>
<tr>
<td>0.25</td>
<td>3.287</td>
<td>5.276</td>
<td>1.605</td>
<td>0.381</td>
<td>1.220</td>
</tr>
<tr>
<td>0.33</td>
<td>3.287</td>
<td>5.258</td>
<td>1.600</td>
<td>0.382</td>
<td>1.572</td>
</tr>
</tbody>
</table>
as indicated. In Fig. 3(b), the mean O 1s core-level binding energy for each layer is plotted as a function of distance along the [0001] direction. In the bulk portion of each region, the electrostatic potential varies linearly as a result of interface charges; least-squares fitting to the linear portion determines the magnitude of $E_w$ and $E_b$. Also demonstrated in Fig. 3(b) is the interface term $(\Delta E_{1s,01s})$ for the (5 5) SL, which is found by extrapolating the O 1s core levels to the interface plane.

By analysis of the O 1s core levels in the (5 5) SL, the magnitude of the built-in electric field in the well and barrier regions is evaluated to be 0.51 and 0.56 MV/cm, respectively. The slightly higher value of $E_b$ compared to $E_w$ is due to the reduced $c$-axis length in Mg$_{0.22}$Zn$_{0.78}$O compared to ZnO. Note that we are concerned only with the magnitude of the electric fields $(|E_w|$ and $|E_b|)$; however, from the Mulliken charge analysis in Fig. 3(a) and the V-shaped potential profile in Fig. 3(b), it is clear that the fields in the well and barrier regions point in opposite directions. The calculated value of $E_w$ is somewhat smaller than the experimental value of $0.9$ MV/cm obtained by both Bretagnon et al. and Morhain et al. in ZnO/Mg$_{0.22}$Zn$_{0.78}$O QWs. Moreover, experimentally, the magnitude of $E_w$ was found to be linearly dependent on the Mg concentration in the barrier.

Extrapolating the experimental $E_w$ for the ZnO/Mg$_{0.22}$Zn$_{0.78}$O system to $x = 0.25$ gives a built-in electric field in the QW of $1.02$ MV/cm, which is twice our calculated value. This discrepancy can be explained by electrostatic and geometric arguments and, as will be shown, the calculated result is in accordance with experiment.

The electromagnetic boundary condition requires that the displacement vector $(D = \varepsilon E + P)$ be conserved across the heterointerface. A second boundary condition, for a periodic superlattice, requires that $L_w E_w + L_b E_b = 0$ in order to prevent divergence of the electrostatic potential. Combining these two gives an expression for the built-in electric field in the QW which is a function of the relative widths of the well and barrier regions

$$E_w = \frac{L_b(P_b - P_w)/(\varepsilon_b L_w + \varepsilon_w L_b)}{-E_b/L_b};$$

Thus, the electric field inside the QW reaches a maximum $[E_w(\text{max})]$ in the limit $L_b \gg L_w$, which is defined only by the difference in the polarization between the two regions $E_w(\text{max}) = (P_b - P_w)/\varepsilon_b$. The difference in the dielectric constants of the two mediums can be assumed negligible, leaving a description of the built-in electric field as a function of the ZnO/Mg$_x$Zn$_{1-x}$O SL geometry in terms of the maximum electric field $E_w(L_w, L_b) = E_w(\text{max})L_b/(L_b + L_w)$.

The experimental measurement by Morhain et al. was carried out for quantum wells in the range $1.6 \text{ nm} \leq L_w \leq 9.5 \text{ nm}$ and with a barrier width of $200 \text{ nm}$. In this case, the geometric term is close to unity, i.e., $L_b/(L_b + L_w) \sim 1$, and the electric field should be near the maximum value $E_w(\text{max})$. The (5 5) SL in our calculation certainly does not satisfy the condition $L_b \gg L_w$; considering the geometric arguments outlined previously, for the (5 5) SL with $L_b = L_w$, $E_w = E_w(\text{max})/2$. Thus, extrapolating our result to the limit $L_b \gg L_w$, the maximum electric field for the (5 5) SL is twice the calculated value, i.e., $E_w(\text{max}) = 1.02$ MV/cm, which matches the experimental reports.

It is noted that in the experimental case, charge screening by free carriers can potentially reduce the magnitude of the built-in electric field which could account for some of the slightly lower $E_w$ values reported in the literature; as such, we consider this result to be an upper bound.

2. Band offsets

Considering now the band offsets, we find the bulk and interface terms of Eq. (2) for the (5 5) SL to be $-0.48$ and $0.22$ eV, respectively. With these values, the magnitude of the VBO is found to be $0.26$ eV. The CBO is then calculated from the difference between the total band offset $(\Delta E_\varphi)$ and the VBO. Since band gaps from the GGA are unreliable, experimental band gaps must be used to calculate the CBO.
From experiment, $\Delta E_g$ is 0.59 eV and, using this value, the CBO is calculated to be 0.33 eV and the CBO:VBO ratio for the ZnO/Mg$_{0.25}$Zn$_{0.75}$O system is 56:44; this is in excellent agreement with several experimental reports. It is important to emphasize, however, that there is disagreement in the literature regarding the magnitude of the VBO and the CBO:VBO ratio which has been reported as, or assumed to be, anywhere in the range 60:40–90:10. Recently, Su et al. have measured the band offsets at a ZnO/Mg$_{0.15}$Zn$_{0.85}$O heterojunction using the direct method of XPS, based on a similar analysis of core-level binding energies as is our method. The VBO and CBO were evaluated to be 0.13 and 0.18 eV, respectively, giving a CBO:VBO ratio of 58:42, in excellent agreement with our result. It is noted that this finding is in contrast to the “common anion rule,” which predicts the VBO to be a small fraction of the total band offset at interfaces between compounds with a common anion, since the VBM is comprised mostly of the anion p states. However, this rule should fail for ZnO/Mg$_{0.25}$Zn$_{0.75}$O since the increased p$-d$ coupling in ZnO pushes the VBM upward in energy compared to Mg$_{0.25}$Zn$_{0.75}$O.

The band gap of the (5 + 5) ZnO/Mg$_{0.25}$Zn$_{0.75}$O SL is calculated to be 1.00 eV; ZnO/Mg$_{0.25}$Zn$_{0.75}$O interfaces are type I, meaning that the VBM and CBM are both found in the QW region and hence the fundamental gap of the SL originates from states in the QW. The calculated band gap of the QW is 0.19 eV higher than that of pure ZnO (0.81 eV), which can be accounted for by quantum-confinement effects.

C. (m + n) ZnO/Mg$_{0.25}$Zn$_{0.75}$O superlattice

To investigate the role of SL geometry, a detailed study is performed in which the number of (m + n) layers is varied, and the key properties of the interface are calculated. We do this to (i) investigate the effects of SL geometry on the interface properties, i.e., $E_w$, $E_b$, VBO, and $E_g$, and (ii) determine if variations in $E_w$ with (m + n) configuration are well described by the geometric factor $L_b/L_w$. We investigate $m = n$ structures for the range 4 $\leq$ m $\leq$ 7; furthermore, (m + 4) and (4 + n) SL structures are studied for which the width of the barrier (well) is fixed at four layers while the number of layers in the well (barrier) is varied over the range 4 $\leq$ m(n) $\leq$ 8. For the (m + n) SLs, we consider the case of a ZnO substrate, i.e., the in-plane lattice constant is fixed to the calculated value of pure ZnO.

Figure 4 shows the mean O 1s core level for each layer as a function of distance along the [0001] direction for the $m = n$ (a), (m + 4) (b), and (4 + n) (c) SLs. Each set of core levels is shifted such that the interface plane coincides with $x = 0$. Properties of the (m + n) SLs are determined by the same procedure outlined for the (5 + 5) system. The results are presented in Table IV including the built-in electric fields ($E_w, E_b$), VBO, and band gap ($E_g$) of the SL. Note that while we include the value of the interface term ($\Delta E_{ZnO/MgZnO}^{\text{ZnO/O1}}$), we do not include that of the bulk term since, being a uniquely bulk parameter, this is a constant for each SL ($-0.48$ eV).

The magnitude of $E_w$ and $E_b$ remains almost unchanged for the $m = n$ SLs; this is as expected because the geometric term $L_b/L_w$ remains a constant (since $L_w = L_b$). For the (m + 4) and (4 + n) SLs, $L_w \neq L_b$; it is expected that variations in the relative number of layers in each region will have a strong effect on the magnitude of $E_w$ and $E_b$ due to the boundary condition $E_wL_w + E_bL_b = 0$ for a periodic SL. As expected, for the (m + 4) case, increasing m leads to a reduction and increase in the magnitude of $E_w$ and $E_b$, respectively.

![FIG. 4](image_url) (Color online) Calculated O 1s core-level binding energies for $m = n$ (a), (m + 4) (b), and (4 + n) (c) SLs plotted as a function of distance along the [0001] direction. Note: core levels are shifted along the x axis such that x = 0 coincides with the interface plane.

| Table IV. ZnO/Mg$_{0.25}$Zn$_{0.75}$O interface properties including built-in electric fields in the quantum well ($E_w$) and barrier ($E_b$), interface term ($\Delta E_{ZnO/MgZnO}^{\text{ZnO/O1}}$), valence band offset (VBO), and band gap ($E_g$) for a range of $m = n$, (m + 4), and (4 + n) superlattices (SL). |
|---|---|---|---|---|
| SL | $E_w$ (MV/cm) | $E_b$ (MV/cm) | $\Delta E_{ZnO/MgZnO}^{\text{ZnO/O1}}$ (eV) | VBO (eV) | $E_g$ (eV) |
| m = n | | | | | |
| 4 + 4 | 0.47 | 0.49 | 0.23 | 0.26 | 1.025 |
| 5 + 4 | 0.51 | 0.56 | 0.22 | 0.26 | 1.000 |
| 6 + 6 | 0.50 | 0.51 | 0.23 | 0.25 | 0.981 |
| 7 + 7 | 0.50 | 0.52 | 0.23 | 0.26 | 0.964 |
| m + 4 | | | | | |
| 6 + 4 | 0.35 | 0.48 | 0.23 | 0.26 | 0.961 |
| 8 + 4 | 0.32 | 0.66 | 0.23 | 0.25 | 0.922 |
| 10 + 4 | 0.24 | 0.69 | 0.23 | 0.26 | 0.897 |
| 4 + n | 4 + 4 | 0.57 | 0.40 | 0.23 | 0.25 | 1.054 |
| 4 + 8 | 0.61 | 0.30 | 0.23 | 0.25 | 1.071 |
| 4 + 10 | 0.63 | 0.24 | 0.24 | 0.25 | 1.083 |
with $E_w$ decreasing to 0.24 MV/cm for the $(10 + 4)$ SL. The $(4 + n)$ SLs are also in accordance with expectation: increasing $n$ brings about an increase (decrease) in $E_w$ ($E_b$). We note the high tunability of $E_w$, which is demonstrated in the range 0.24 MV/cm $\leq E_w \leq 0.63$ MV/cm. The results in Table IV indicate that $E_w$ in ZnO/Mg$_{25}$Zn$_{75}$O should be fully tunable over the range 0 MV/cm $< E_w < \sim 1$ MV/cm by varying the SL geometric term over the range 0 $< L_b/(L_w + L_b) < 1$. This extra degree of freedom could be exploited; for example, efficient excitonic QW devices without carrier separation (small $E_w$) or highly confined 2DEG systems (large $E_w$).  

The VBO at the ZnO/Mg$_{25}$Zn$_{75}$O interface has been calculated for all $n = m$, $(m + 4)$, and $(4 + n)$ SLs. The VBO is in the range 0.25–0.26 eV for all; the interface term, and hence the VBO, is insensitive to the SL geometry. Thus, we expect our calculated VBO to be valid for any $(m + n)$ ZnO/Mg$_{25}$Zn$_{75}$O SL (for epitaxial Mg$_{25}$Zn$_{75}$O on strain-free ZnO). This finding is not entirely unexpected since the variation in the interface term is typically small. 

Band gaps in QW heterostructures are subject to two key effects in varying SL geometry: (i) the ground-state confinement energy, and hence the band gap, decreases with increasing $L_w$, and (ii) the quantum-confined Stark effect (QCSE). The latter is the well-known shifting of the band edges as a consequence of the built-in electric field. For the $m = n$ SLs, the band gap decreases by 61 meV as $m$ increases over the range 4 $\leq m \leq 7$. This can be attributed to both a reduction in the confinement energy and the QCSE with increasing $E_w$. Similarly, for the $(m + 4)$ SLs, $E_b$ constantly decreases as $E_w$ increases. These findings are as expected and in qualitative agreement with first-principles studies of GaN/AlN SLs. For the $(4 + n)$ SLs, the behavior with increasing $n$ is unexpected; we find the band gap increases by over 80 meV as $n$ is increased over the range 4 $\leq n \leq 10$. This is unexpected since an increase in $E_w$ is observed over this range and, as such, we expect a red-shift in $E_b$ due to the QCSE. Indeed, for GaN/AlN SLs, the band gap was found to decrease with increasing $L_b$. Our result can be explained, however, in terms of finite barrier effects: the ground-state confinement energy decreases with $L_b$ due to interwell coupling of confined wave functions. The apparent absence of this effect for the GaN/AlN has two explanations. First, the band offsets are larger for GaN/AlN SLs; accordingly, carriers are more confined within the QW. Second, $E_b$ is around an order of magnitude higher for the GaN/AlN system, and with such strong electric fields the QCSE dominates the trend. 

D. Strained $(6 + 6)$ ZnO/Mg$_{25}$Zn$_{75}$O superlattice

Up to this point, we have considered relaxed, or strain-free, ZnO QWs representing the experimental case of a ZnO substrate. However, Mg$_x$Zn$_{1-x}$O or, potentially, another substrate with an in-plane lattice constant that differs from pure ZnO may be used. ZnO and Mg$_x$Zn$_{1-x}$O can exhibit strong piezoelectric polarizations along the [0001] direction in the presence of in-plane strain; accordingly, one might expect that the choice of substrate and subsequent strain conditions may have consequences for the properties of the ZnO/Mg$_x$Zn$_{1-x}$O interface. In particular, the band offsets and built-in electric fields could be sensitive to the choice of substrate; this has been demonstrated for GaN/In(Al)N SLs. We investigate the significance of QW strain by simulating $(6 + 6)$ ZnO/Mg$_{25}$Zn$_{75}$O SLs with in-plane lattice constant $a = a_{ZnO}(1 + \Delta a)$, where $a_{ZnO}$ is the (calculated) in-plane lattice constant of pure ZnO and $\Delta a$ is the in-plane strain. Two $(6 + 6)$ SLs are considered, with QW tensile strain $\Delta a$ chosen corresponding to Mg$_x$Zn$_{1-x}$O substrates with $x = 0.25$ and 0.5, respectively. The magnitude of the strain is small, i.e., for $x = 0.025$ $\Delta a = 0.0038$ and for $x = 0.50$, $\Delta a = 0.0109$; these small strains reflect the close match for the in-plane lattice constants of ZnO and Mg$_x$Zn$_{1-x}$O. 

The O 1s binding energies for the strained QW SLs are plotted in Fig. 5 and the corresponding properties are listed in Table V. Clearly, no major changes in the interface properties are observed. The calculated $E_w$ and $E_b$ do not deviate significantly when compared to the strain-free QW $(m = n)$ SLs in Table IV. The band alignment also appears

TABLE V. ZnO/Mg$_{25}$Zn$_{75}$O interface properties including built-in electric fields in the quantum well ($E_w$) and barrier ($E_b$), bulk term and interface term ($\Delta E_{O_{1s}}^{ZnO/\Gamma_{1s}}$) of Eq. (2), valence band offset (VBO), and band gap ($E_b$). Calculations are performed for strained quantum-well superlattices (str-SL) with in-plane strains, respectively, of 0.0038 and 0.0109 corresponding to a Mg$_x$Zn$_{1-x}$O substrates with $x = 0.25$ and 0.5.

| str-SL | $|E_w|$ (MV/cm) | $|E_b|$ (MV/cm) | Bulk term (eV) | $\Delta E_{O_{1s}}^{ZnO/\Gamma_{1s}}$ (eV) | |VBO| (eV) | $E_b$ (eV) |
|-------|----------------|----------------|---------------|----------------|----------------|----------------|
| $x = 0.25$ | 0.49 | 0.45 | $-0.49$ | 0.24 | 0.25 | 0.977 |
| $x = 0.50$ | 0.50 | 0.49 | $-0.48$ | 0.24 | 0.24 | 0.968 |
insensitive to the QW strain condition. To determine the VBO, the bulk term is recalculated for ZnO and Mg$_{0.25}$Zn$_{0.75}$O at the new in-plane lattice constants; however, the variation in the bulk term is not significant for such small variations in $a$. Consequently, the magnitude of the VBO is insensitive to the imposed QW strain and is calculated to be 0.25 and 0.24 eV for SLs (i) and (ii), respectively. This finding is somewhat different to GaN/In$_N$Al$N$ SLs, in which large variations in the VBO resulted from different in-plane strain conditions. The insensitivity of ZnO/Mg$_{0.25}$Zn$_{0.75}$O can be explained in terms of two factors: First, the very small in-plane lattice mismatch of ZnO and Mg$_x$Zn$_{1-x}$O leads to only small strains for Mg$_x$Zn$_{1-x}$O substrates in the whole range 0 $\leq x \leq$ 1; this is compared to, for example, a 10% mismatch in the in-plane lattice constant for GaN/InN. Second, the deformation potentials of ZnO and Mg$_x$Zn$_{1-x}$O are smaller than those of the III-nitrides and as such strain-induced variations in the band edges are less significant.

IV. CONCLUSIONS

In summary, we have performed an all-electron, DFT investigation of the band alignment and polarization effects in wurtzite ZnO/Mg$_{0.25}$Zn$_{0.75}$O(0001) SLs where the importance of SL geometry and strain have been considered. The polarization discontinuity at the ZnO/Mg$_x$Zn$_{1-x}$O junction leads to charge accumulation in the form of interface monopoles, giving rise to built-in electric fields in the SL. The magnitude of the electric field in the QW can be tuned by varying the geometry of the SL; we have demonstrated that this quantity varies in the range 0.24 MV/cm $\leq E_w \leq$ 0.63 MV/cm. Variations in $E_w$ can be well described by a geometric factor $E_w \propto L_b/(L_w + L_b)$, and the maximum $E_w$ is calculated in the range 0.9–1.0 MV/cm in the geometric limit $L_b \gg L_w$, which is in agreement with recent experiments. The band gaps of the $m = n$ and $(m + 4)$ superlattices, which are dependent on the competing effects of quantum confinement and the quantum-confined Stark effect, show a red-shift with increasing $n$. Unexpectedly, for the $(4 + n)$ SLs, the band gap increased with $n$ which was explained in terms of an increase in the ground-state confinement energy with increasing barrier width. In contrast to the “common anion rule,” the magnitude of the VBO at the ZnO/Mg$_x$Zn$_{1-x}$O interface is evaluated to be 0.25–0.26 eV, which is 40% of the total band offset. A band-offset ratio CBO/VBO of 60:40 is found, in excellent agreement with direct experimental measurements by XPS. Due to the excellent match for the in-plane lattice constant of ZnO and Mg$_x$Zn$_{1-x}$O, the properties of the ZnO/Mg$_x$Zn$_{1-x}$O interface are not affected by the concentration of Mg$_x$Zn$_{1-x}$O substrate, which has been investigated in the range 0 $\leq x \leq$ 0.50.

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37Taken from Ref. 34, deduced from experimental Zn heat of vaporization, ZnO enthalpy of formation, and O$_2$ binding energy.


47Taken from Ref. 48, the static dielectric constant of Mg$_{0.25}$Zn$_{0.75}$O is 8.7, calculated by $\varepsilon_{Mg_{0.25}Zn_{0.75}O} = x\varepsilon_{MgO} + (1 - x)\varepsilon_{ZnO}$ where $\varepsilon_{MgO}$ and $\varepsilon_{ZnO}$ and $x$ are 9.8, 8.3, and 0.25, respectively.


50Taken from Ref. 6, the Mg$_x$Zn$_{1-x}$O band gap was reported to increase linearly from 3.30 to 4.15 eV over the doping range $0 \leq x \leq 0.36$.


57Taken from Ref. 10, the in-plane strain is calculated for different Mg concentrations by $\Delta a = 0.0027x^2 + 0.0083x$. 

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