Strain effects and band parameters in MgO, ZnO, and CdO
Qimin Yan, Patrick Rinke, Momme Winkelnkemper, Abdallah Qteish, Dieter Bimberg, Matthias Scheffler, and Chris G. Van de Walle

Citation: Applied Physics Letters 101, 152105 (2012); doi: 10.1063/1.4759107
View online: http://dx.doi.org/10.1063/1.4759107
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/101/15?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Impact of strain on electronic defects in (Mg,Zn)O thin films

Computational identification of single-layer CdO for electronic and optical applications

Interband emission energy in a strained CdxZn1-xO quantum dot

Wurtzite-to-tetragonal structure phase transformation and size effect in ZnO nanorods
J. Appl. Phys. 107, 023512 (2010); 10.1063/1.3277053

Band discontinuities in ZnMgSe/ZnCdSe(001) lattice-matched heterostructures
Appl. Phys. Lett. 78, 1574 (2001); 10.1063/1.1350968
Strain effects and band parameters in MgO, ZnO, and CdO

Qimin Yan,1 Patrick Rinke,1,2 Momme Winkelkemper,3 Abdallah Qteish,4 Dieter Bimberg,3 Matthias Scheffler,1,2 and Chris G. Van de Walle1

1Materials Department, University of California, Santa Barbara, California 93106-5050, USA
2Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195 Berlin, Germany
3Institut für Festkörperphysik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin, Germany
4Department of Physics, Yarmouk University, 21163-Irbid, Jordan

We have derived consistent sets of band parameters (bandgaps, crystal-field splittings, effective masses, Luttinger, and E_p parameters) and strain deformation potentials for MgO, ZnO, and CdO in the wurtzite phase. To overcome the limitations of density-functional theory in the local-density and generalized gradient approximations, we employ a hybrid functional as well as exact-exchange-based quasiparticle energy calculations in the G_0W_0 approach. We demonstrate that the band and strain parameters derived in this fashion are in very good agreement with the available experimental data and provide predictions for all parameters that have not been determined experimentally so far.

© 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4759107]
Equilibrium lattice parameters obtained with HSE06 (Table I) agree very well with experiment for ZnO (<1% overestimation). Bandgaps and crystal-field splitting ($\Delta_{cr}$) obtained from both $G_0W_0$@OEPx(cLDA) and HSE06 calculations at HSE06 equilibrium lattice parameters are listed in Table I. Note that while the HSE06 functional greatly improves the bandgap of ZnO (2.48 eV) compared to PBE calculations (1.18 eV), it still underestimates the fundamental bandgap. The bandgap for ZnO with $G_0W_0$@OEPx(cLDA) calculations agrees very well with experiment (to within 0.2 eV). The crystal-field splitting is positive for CdO and ZnO, while for MgO it is negative.

Four types of strain components may be present in the wurtzite system: isotropic biaxial strain in the c plane ($\epsilon_{\perp} = \epsilon_{xx} + \epsilon_{yy}$), anisotropic biaxial strain in the c plane ($\epsilon_{\perp} = \epsilon_{yy}$), uniaxial strain along the c axis ($\epsilon_{xx}$), and shear strain ($\epsilon_{xx}$ and $\epsilon_{yy}$). Using the k · p method, strain components are treated as perturbations in the Hamiltonian and the modifications of the band structure by strain are quantified by conduction-band deformation potentials ($a_{cz}$ and $a_{ct}$) and valence-band deformation potentials ($D_1$ to $D_6$). By applying strain and fitting the eigenenergies of the $6 \times 6$ k · p Hamiltonian\(^{28}\) to first-principles band structures at the $\Gamma$-point, we can obtain all deformation potentials.\(^{19,29}\) In this work, we determined all deformation potentials from HSE06 calculations. Explicitly performing $G_0W_0$@OEPx(cLDA) calculations for all strain configurations would be prohibitive; for nitrides, we verified that deformation potentials obtained from $G_0W_0$@OEPx(cLDA) calculations and from HSE06 agree to be within 0.40 eV.\(^{19}\)

As shown in Figure 1, the change of the crystal-field splitting ($\Delta_{cr}$) in wurtzite MgO, ZnO, and CdO under biaxial strain in the c plane and uniaxial strain along the c axis ($\epsilon_{xx}$) is nonlinear. This implies that the deformation potentials vary with lattice parameters, as previously observed for group-III nitrides,\(^{19}\) the behavior can be well described with a parabolic fit. We focus on the linear regime in the vicinity of the experimental lattice parameters for ZnO, and around the HSE06 equilibrium lattice parameters for MgO and CdO (where no experimental data are available).

A complete set of deformation potentials from HSE06 calculations is listed in Table II. With the exception of $a_{cz} - D_1$, the deformation potentials increase as the bandgap increases from CdO to ZnO and MgO, showing the same trend as in the group-III nitrides (deformation potentials increase from InN to GaN and AlN).\(^{19}\) Differing from ZnO and MgO, the deformation potential $D_3$ of CdO is negative, which is consistent with the change of $\Delta_{cr}$ under uniaxial strain as shown in Figure 1(b). Compared with GaN, the deformation potentials of ZnO are much smaller in magnitude. The experimental data\(^{10,11}\) for ZnO are included for comparison. Generally, HSE06 results show good agreement with experimental data.

Our first-principles calculations also indicate that the quasicubic approximation\(^{10}\) breaks down for the group-II wurtzite oxide system. In the quasicubic approximation, the deformation potentials are related as follows: $D_3 + 2D_4 = 0$, $D_1 + D_2 = D_3$, and $D_3 + 4D_5 = \sqrt{2}D_4$. However, we find that $D_3 + 2D_4$ is equal to 1.93 eV for MgO, −1.21 eV for ZnO, and −2.46 eV for CdO, i.e., significantly different from zero. Due to the lack of experimental data for wurtzite MgO and CdO, the deformation potentials of ZnO have been used over the entire alloy range in device modeling of group-II oxide alloys.\(^{30}\) Our calculations show that this is a poor approximation: the variation of deformation potentials among the three oxides is large, and independent sets of deformation potentials for MgO and CdO are necessary for accurate device simulations.

TABLE I. Equilibrium lattice parameters (a, c, and $u$) obtained with HSE06 and $G_0W_0$@OEPx(cLDA) calculations at HSE06 equilibrium lattice parameters. For ZnO, experimental lattice parameters at $T = 300$ K, bandgap at $T = 300$ K and crystal-field splitting values are included for comparison (from Refs. 26 and 27).

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>$u$</th>
<th>$E_g$ (eV)</th>
<th>$\Delta_{cr}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO HSE06</td>
<td>3.278</td>
<td>5.062</td>
<td>0.3919</td>
<td>5.21</td>
<td>−346</td>
</tr>
<tr>
<td>$G_0W_0$</td>
<td></td>
<td></td>
<td></td>
<td>7.16</td>
<td>−402</td>
</tr>
<tr>
<td>ZnO HSE06</td>
<td>3.264</td>
<td>5.238</td>
<td>0.3807</td>
<td>2.48</td>
<td>66</td>
</tr>
<tr>
<td>$G_0W_0$</td>
<td></td>
<td></td>
<td></td>
<td>3.26</td>
<td>74</td>
</tr>
<tr>
<td>Exp.</td>
<td>3.249</td>
<td>5.205</td>
<td></td>
<td>3.43</td>
<td>43</td>
</tr>
<tr>
<td>CdO HSE06</td>
<td>3.652</td>
<td>5.739</td>
<td>0.3878</td>
<td>1.13</td>
<td>117</td>
</tr>
<tr>
<td>$G_0W_0$</td>
<td></td>
<td></td>
<td></td>
<td>1.23</td>
<td>145</td>
</tr>
</tbody>
</table>

TABLE II. Deformation potentials (in eV) of wurtzite MgO, ZnO, and CdO obtained by HSE06 calculations. Experimental data for ZnO are also shown.

<table>
<thead>
<tr>
<th>Method</th>
<th>$a_{cz} - D_1$</th>
<th>$a_{ct} - D_2$</th>
<th>$D_3$</th>
<th>$D_4$</th>
<th>$D_5$</th>
<th>$D_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO HSE06</td>
<td>−1.95</td>
<td>−7.96</td>
<td>5.87</td>
<td>−1.97</td>
<td>−1.93</td>
<td>−3.03</td>
</tr>
<tr>
<td>ZnO HSE06</td>
<td>−3.06</td>
<td>−2.46</td>
<td>0.47</td>
<td>−0.84</td>
<td>−1.21</td>
<td>−1.77</td>
</tr>
<tr>
<td>Exp.a</td>
<td>−3.80</td>
<td>−3.80</td>
<td>0.80</td>
<td>−1.40</td>
<td>−1.20</td>
<td>−2.0b</td>
</tr>
<tr>
<td>Exp.e</td>
<td>−3.90</td>
<td>−4.13</td>
<td>1.15</td>
<td>−1.22</td>
<td>−1.53</td>
<td>−2.88</td>
</tr>
<tr>
<td>CdO HSE06</td>
<td>−2.81</td>
<td>−0.29</td>
<td>−1.86</td>
<td>−0.30</td>
<td>−0.91</td>
<td>−1.21</td>
</tr>
</tbody>
</table>

\(^{a}\)Reference 10.

\(^{b}\)Only the magnitude of $D_6$ was obtained in this experiment.

\(^{c}\)Reference 11.
The calculated effective masses, Luttinger parameters, and transition matrix element $E_F$ of wurtzite MgO, ZnO, and CdO with both the HSE06 and the $G_0W_0@OEPx(cLDA)$ approach are shown in Table III. Generally, the effective masses and Luttinger parameters obtained by HSE06 agree very well with the $G_0W_0@OEPx(cLDA)$ ones. This implies that HSE06 produces conduction- and valence-band dispersions that are very similar to those of $G_0W_0$. Our effective masses are in overall good agreement with recent quasiparticle calculations.\textsuperscript{15,25}

It is remarkable that, in contrast to the group-III nitrides,\textsuperscript{9} the Luttinger parameters in the group-II oxides are fairly similar across the oxides series. For example, the $A_1$ parameter in the nitrides varies from $-3.991$ in AlN to $-15.803$ in InN (a difference of a factor of 3.96) and $A_6$ from $-1.952$ to $-10.078$ (a difference of a factor of 5.16), whereas in the oxides the corresponding variations are only by factors of 1.16 and 2.15. For $A_4$ and $A_5$, the variations across the respective series are more similar, although the absolute magnitudes of the parameters are larger in the nitrides ($A_4 = -1.147$ (AlN) to $-7.151$ (InN) and $A_5 = -1.329$ (AlN) to $-7.060$ (InN)). Another noteworthy observation is the fact that, unlike in the nitrides, the $E_F$ parameters in the oxides are highly anisotropic.

Since the bandgap calculated from HSE06 for the oxides is in worse agreement with $G_0W_0$ and experiment than it is for the nitrides, we check whether the band parameters and deformation potentials can be improved by modifying the mixing parameter. For ZnO, as a test case, we modify the mixing parameter ($\alpha = 0.36$) to reproduce the experimental bandgap (3.41 eV) and calculate the band parameters and deformation potentials of ZnO.\textsuperscript{25} Note that the changes in deformation potentials are less than 0.3 eV, and the changes in band parameters are also very small. This check indicates that the choice of the mixing parameter for ZnO only slightly affects the calculated parameters, which is reassuring. We hence believe that the deformation potentials and band parameters listed in the tables with default HSE06 parameters are reliable.

Note that the linear interpolation between binary compounds when describing alloy properties is only an approximation and there may be some nonlinearities in different physical quantities of ZnXO ($X = \text{Cd, Mg}$) alloys. For example, the nonlinearity in the bandgap has been quantified as a bowing parameter and this parameter has been measured experimentally. Special attention regarding such nonlinearities should be paid when using these band parameters and deformation potentials to describe electronic properties of ZnXO alloys.

In conclusion, we have presented a systematic study of the band dispersion and strain effects on electronic band structures of the group-II oxides MgO, ZnO and CdO. Using hybrid functional calculations, we report a consistent and complete set of deformation potentials that describes bandstructure modifications in the presence of strain. We also obtain a consistent set of band parameters that agrees well with values obtained with $G_0W_0@OEPx(cLDA)$. These first-principles deformation potentials and band parameters provide a solid foundation for an accurate modeling of oxide-based device structures.

This work was supported by the Solid State Lighting and Energy Center at the University of California, Santa Barbara. P.R. acknowledges the support of the Deutsche Forschungsgemeinschaft, the UCSB-MPG Program for International Exchange in Materials Science, and the NSF-IMI Program (DMR08-43934). We acknowledge the use of the CSC/CNSI/MRL Computing resources (NSF-CNS-09-60316 and DMR11-21053) as well as TeraGrid (NSF DMR07-0072N).

\begin{table}[h]
\centering
\caption{Luttinger parameters ($A_i$ is in eV Å, all others are dimensionless) and transition matrix elements $E_F$ (in eV) of wurtzite MgO, ZnO, and CdO obtained with both HSE06 and the $G_0W_0@OEPx(cLDA)$ approaches.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Param. & MgO & ZnO & CdO \\
\hline
Method & HSE06 & $G_0W_0$ & HSE06 & $G_0W_0$ & HSE06 & $G_0W_0$ \\
\hline
$A_2$ & $-0.199$ & $-0.211$ & $-0.386$ & $-0.393$ & $-0.380$ & $-0.393$ \\
$A_3$ & $2.732$ & $2.546$ & $2.386$ & $2.377$ & $2.936$ & $2.770$ \\
$A_4$ & $-0.495$ & $-0.484$ & $-2.089$ & $-2.069$ & $-3.783$ & $-3.810$ \\
$A_5$ & $-0.687$ & $-0.692$ & $-2.059$ & $-2.051$ & $-3.685$ & $-3.711$ \\
$A_7$ & $-0.133$ & $-0.119$ & $0.028$ & $0.001$ & $-0.046$ & $-0.010$ \\
$m^*_i$ & $0.369$ & $0.379$ & $0.239$ & $0.246$ & $0.168$ & $0.173$ \\
$m^*_i^{\text{HSE}}$ & $0.371$ & $0.383$ & $0.244$ & $0.250$ & $0.154$ & $0.150$ \\
$m^*_C$ & $6.416$ & $6.105$ & $2.769$ & $2.732$ & $2.755$ & $2.603$ \\
$m^*_C^{\text{HSE}}$ & $1.441$ & $1.441$ & $0.404$ & $0.406$ & $0.240$ & $0.238$ \\
$m^*_W$ & $0.347$ & $0.370$ & $2.563$ & $2.567$ & $2.442$ & $2.416$ \\
$m^*_W^{\text{HSE}}$ & $4.982$ & $4.727$ & $0.408$ & $0.410$ & $0.244$ & $0.240$ \\
$m^*_1$ & $6.132$ & $5.923$ & $0.368$ & $0.368$ & $0.306$ & $0.320$ \\
$m^*_1^{\text{HSE}}$ & $1.444$ & $1.443$ & $2.434$ & $2.417$ & $2.271$ & $2.304$ \\
\hline
\end{tabular}
\end{table}
25. See supplementary material at http://dx.doi.org/10.1063/1.4759107 for details of convergence studies; details of effective mass calculations and comparison; and the dependence of band parameters and deformation potentials of ZnO on the mixing parameter.