THEORETICAL STUDIES OF ZnO AND RELATED $Mg_xZn_{1-x}O$ ALLOY BAND STRUCTURES

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ABSTRACT

First principles calculations are carried out for ZnO, MgO and $ZnMgO_2$ in various crystal structures. The nature of the valence band ordering in ZnO is shown to depend strongly on the Zn3d band position. MgO in the wurtzitic form is found to gave an unusual 5-fold coordiated structure. The band gap dependence in the alloy system is found to be in fair agreement with experimental data and the band-offset is predicted to be type I.

INTRODUCTION

Recently, ZnO has attracted attention not only as a suitable closely lattice-matched substrate for GaN but also as a potentially useful active optoelectronic material in its own right [1, 2, 3, 4, 5] This raises new questions not only about the basic properties of ZnO but also about those of related materials which can be combined with ZnO in heteroepitaxial device structures. In fact, one would need a material with a higher band gap to use as barrier in order to make ZnO quantum wells. Ohtomo et al. [6] showed that it is possible to grow $Mg_xZn_{1-x}O$ alloy films with the wurtzite structure over a certain range of concentrations. This possibility was far from obvious because MgO has the rocksalt rather than the wurtzite structure.

In this paper, we first re-examine the band structure of ZnO. Although this material has been studied extensively in the past, [7, 8, 9, 10] there are some remaining open questions about its band structure. Most notably, there has been a long-standing controversy over the nature of the valence band ordering. The question is: is it the usual Γ_9 above Γ_7 as proposed by Park et al. [13] or the inverse ordering as suggested by Thomas [12]. Recently, new results supporting Park et al.'s point of view has been obtained by Reynolds et al. [14]. We show that this ordering depends crucially on the position of the Zn3d bands, which is not correctly obtained in the local density approximation (LDA). We also present results of our total energy results for ZnO in both wurtzite and zincblende structure.

Next, we present results of first-principles calculations of the relative stability of the wurtzite, zincblende and rocksalt forms of MgO and obtain an estimate for the expected gap in wurtzitic MgO. We also present preliminary results for an ordered $ZnMgO_2$ structure, which allows us to obtain a first idea of the expected band gap dependence in this system. Using the dielectric midgap energy charge neutrality point model, [11] we obtain an estimate of the band-offset between ZnO and MgO.

METHOD OF CALCULATION

The computational method used in this work is the density functional theory in the local density approximation (LDA). The Kohn-Sham equations are solved using the full-potential linear muffin-tin orbital (LMTO) method developed by Methfessel [15]. Details of the computational procedure (sphere radii choice, angular momentum cut-off paramters, size of basis sets) are similar to those in recent work on GaN and related materials and were carefully checked for convergence [17].

For the study of the alloys, we used zincblende derived structures as a model system. The gaps in wurtzite are usually slightly larger than those in zincblende forms. The differences between the gaps in the two structures typically vary linearly across the alloy system as we found in previous

Table I: Properties of ZnO

	wurtzite		zincblende
	expt	theory	theory
a (Å)	3.25	3.21	
c/a (Å)	1.602	1.608	
u	0.382	0.380	
a_{cubic}			4.49
volume per molecule (Å^3)	23.8	23.4	22.6
E_{coh} (eV/molecule)		8.9	8.9
bulk modulus B (GPa)		157	159

Table II: Selected eigenvalues (in eV) from the top of the valence band.

	present FP-LMTO	pseudopotential[a]	GW[b]	expt[c]
Γ^d_{5v}	-0.7	-0.85	-0.8	-0.85
Γ_{3v}	-3.8	-4.0	-5.0	-4.3
$A_{1,3}$	-2.1	-2.37	-2.48	-2.0
$A_{5,6}$	-0.4	-0.43	-0.43	-0.45
Zn 3d average	-5.1	-5.21	-6.4	-6.95

[a] Schröer et al. [9]

[b] Massida et al. [10]

[c] Girard et al. [8]

[d] Note that we use Rashba's [19] notation for the symmetrylabeling and thus our Γ_5 and Γ_6 are interchanged from those in Girard et al. [8]

work on In$_x$Ga$_{1-x}$N alloys [18]. As a model 50 % compound, we used the chalcopyrite structure. While this is usually a low energy modification and does not quite display the properties of a random alloy, it does nevertheless give some idea of the band-gap bowing. More extensive studies of the disorder effects on band gap bowing are required and are in progress.

The valence band ordering depends crucially on the nature of the spin-orbit coupling. We have studied these within the atomic sphere approximation [16] to the LMTO method. Prior checks show that the band-structure without spin-orbit coupling in this approximation is close to that obtained in the full-potential method.

RESULTS

ZnO total energy and band structure

Our calculated total energy and related parameters are summarized in Table I and are seen to be in good agreement with experimental data.

In Table II, we compare some of the band structure energies with photoemission data by Girard et al. [8]. One may see that the deeper eigenvalues are slightly too high in LDA (except for $A_{1,3}$) which is a result of the increasing self-energy corrections. In particular, one may notice the underestimate of the Zn 3d bands. The latter is of special importance because its hybridization with the O2p band strongly affects the details of the valence band maximum near the gap.

Table III gives our results for the eigenvalues near the band gap. These were obtained in the ASA because we only have spin-orbit coupling included in that version of our LMTO codes. However, the ASA band structure without spin-orbit coupling is in good agreement with that obtained from the FP-LMTO method, except for having a slightly larger band gap. Since the gap needs to be corrected anyway, this is not a serious problem.

We now discuss the effects of the Zn3d band position on the valence band maximum. Accord-

Table III: Band gaps and valence band splittings in ZnO.

	theory without Zn 3d shift	 with	Expt.[a]
minimum gap at Γ	1.4	1.8	3.437
$E_A - E_B$ (meV)	37	9.5	9.5
$E_B - E_c$ (meV)	80	34.0	39.7
Zn 3d band position (at Γ) (eV)	-5.05	-6.25	-6.95[b]

[a] Ref. [14]

[b] Ref. [8]

ing to the Hopfield model,[20] the $\Gamma_9 - \Gamma_7$ splittings are given by

$$E_{\Gamma_9} - E_{\Gamma_7} = \frac{\Delta_c + \Delta_s}{2} \pm \sqrt{(\Delta_c + \Delta_s)^2 - \frac{8}{3}\Delta_c\Delta_s} \tag{1}$$

The Δ_s denotes the spin-orbit splitting that would be obtained in the cubic zincblende structure and is 3 times the value of the $\Delta_2 = \Delta_3$ parameters of the Rashba-Shika-Pikus model Hamiltonian.[17]

The experimental values for the A-B, and B-C splittings, where the A, B, and C valence band states are given in order of decreasing energy, are given in the last column of Table III. Now, one can interpret these with A having Γ_9 and B and C having Γ_7 symmetry, in which case one obtains as crystal field and spin-orbit coupling parameters $\Delta_c = 42.0$ meV and $\Delta_s = 16.7$ meV, or with B having Γ_9 and A and C having Γ_7 character, in which case one obtains Δ_c=43.3 meV and $\Delta_s = -13.1$ meV. The possibility of a negative spin-orbit coupling arises from the hybridization with the Zn3d band. Indeed, a lower lying d band contributes a negative component to the spin-orbit splitting.[21, 22]

Without spin-orbit coupling and in a pure LDA calculation, we obtain a band gap of 1.3 eV and a crystal field splitting of the valence band maximum $\Gamma_6 - \Gamma_1$ of 95 meV. The results with spin-orbit included also indicate too large a spin-orbit and crystal field splitting. When we empirically shift the Zn3d band position in our Hamiltonian, we find that the gap, the crystal field splitting and the spin-orbit splitting depend sensitively on the Zn3d band position. However, if we shift the Zn 3d band all the way down to its experimental position [8] of -6.95 eV, we find that the crystal field splitting becomes as low as 16 meV. The best fit is obtained for a shift of about 1.2 eV and is included in Table III. In order to see whether this case corresponds to a negative or positive spin-orbit splitting, we perform an analogous calculation for zincblende ZnO. In that case, the spin-orbit coupling splits the Γ_{15} into a quadruplet Γ_8 and a doublet Γ_7 and we can unambigously determine the sign of the spin-orbit splitting without the need for a tedious inspection of the eigenvectors. When we shift the Zn3d band in zincblende to the same position as in wurtzite, we find a spin-orbit splitting of -12 meV. This is consistent with the value extracted from the wurtzite case using Hopfield's model. Hence, our present results seem to support a negative spin-orbit splitting. Our calculated values extracted from column 2 of Table III are $\Delta_s = -12.9$ meV and $\Delta_c = 37.4$ meV. However, we caution that the results are quite sensitive to the d-band position. A slightly larger d-band shift results in a positive spin-orbit splitting. However, we then would face the problem of how to explain the serious underestimate of Δ_c. We note that our LDA calculaton should tend to overestimate the Δ_c because the underestimate of the gap increases the repulsive coupling between the Γ_1 valence and Γ_1 conduction band states. Further work is required to fully interpret the data of Ref. [14].

The question now arises as to why the required shift of the Zn3d band appears to be less than that indicated by the photoemission data. This is a rather subtle question. The origins of the discrepancies between theory and experiment are the difference between Kohn-Sham eigenvalues

Table IV: Total energy results for MgO.

	theory				expt.[a]
	relaxed wurtzite	ideal wurzite	zinc-blende	rock-salt	rock-salt
a (Å)	3.413	3.199			
c/a	1.204	1.633			
u	0.5	0.375			
bond length (Å)	$1.971 \perp c$ $2.055 \parallel c$	1.959	1.959	2.071	2.1075
a_{cubic}		4.524		4.141	4.215
volume per molecule (Å^3)	20.7	17.8	17.8	17.8	18.7
Bulk modulus B (GPa)	148		129	178	153-162
E_{coh} (eV/molecule)	11.56	11.39	11.36	11.67	10.41

[a] From Ref. [25] and refs. therein.

of density functional theory and quasiparticle energies. Because of the energy dependence of the self-energy operator, it may be impossible to obtain both valence band maximum and Zn3d bands consistently from one energy independent Hamiltonian. Clearly, part of the shift must arise from a better treatment of exchange, one of the main errors of LDA being the incomplete cancellation of the self-interaction by the averaged exchange [23, 24]. This can be handled by an improved energy independent Hamiltonian, (here obtained empirically but in possibly justifiable by means of improved density functionals). However, there still remains an energy dependent part in the true quasiparticle shift, in particular for deep localized narrow bands such as Zn 3d bands.

MgO wurtzite/rocksalt stability

As a starting point for investigating the rocksalt versus wurtzite relative stability in the alloy system, we here examind the end compound MgO. In Table IV we give our total energy results for four structures of MgO, the equilibrium structure (rocksalt), the relaxed (and ideal) wurtzite structure, and the zincblende structure. The ideal wurtzite has bond lengths and cohesive energy very close to that of zincblende. When the structural parameters for MgO in a wurtzitic lattice (c/a and u) are relaxed, however, we find that $u = 1/2$. This implies that the Mg and O atoms lie in the same plane. In other words the buckled hexagonal rings of the wurtzitic basal plane become flat. It also means that the Mg is at equal distance from the O below and above it along the c-axis. The coordination is thus either 3-fold if one only counts the atoms in the plane or rather 5-fold when one includes the atoms above and below, for which the bond lengths are slightly larger than the in-plane ones. (See Table IV). The five-fold coordination is consistent with the tendency for ionic compounds to prefer a high coordination. The energy of this hypothetical structure is 0.10 eV/molecule above that of the rocksalt structure and lower than zincblende (or ideal wurtzite) by 0.2 eV/molecule. We found that a further continuous distortion can turn this "degenerate" wurtzitic structure into the rocksalt structure. Calculations with the structure confined to such a transformation path indicate that there is a barrier which would mean that the wurtzitic structure is indeed metastable. Details of this will be presented elsewhere. The c/a and u parameters of MgO are thus very different from those in ZnO, which are closer to ideal wurtzite and are given in the previous section.

Alloys

In view of the above noted complication of MgO and ZnO having very different types of c/a and u parameters, it is far from obvious what will happen to the structure at intermediate compositions. In order to bypass this problem, we decided to first investigate the alloy band gap bowing behavior in zinblende alloys first.

Table V: LDA band gaps.

	ZnO	MgO	$ZnMgO_2$
zincblende	0.75	3.76	2.115
wurtzite	1.27	3.69	
rocksalt		5.24	

Our LDA band gaps for zincblende ZnO, MgO and chalcopyrite $ZnMgO_2$ are given in Table V along with those of some of the other structural modifications. From the zincblende results we obtain a slight bowing toward lower gaps with bowing coefficient b of 0.56 eV, defined in the usual manner by

$$E_g(x) = (1-x)E_g(A) + xE_g(B) - bx(1-x), \tag{2}$$

where A=ZnO, B=MgO and x is the relative amount of MgO in the alloy.

The experimental gap of MgO in rocksalt is 7.8 eV, which requires a gap correction of 2.56 eV. With this correction applied to wurtzitic MgO, we obtain an estimated gap of 6.25 eV. This is consistent with the experimental results of Ohtomo et al. [6] who obtained $Mg_xZn_{1-x}O$ alloys up to $x = 0.4$. Beyond 0.3, MgO phase-separation started to occur. These results were obtained by a laser ablation growth technique. The band gaps obtained from the shift of the optical transmission measurements varied from 3.3 eV in ZnO to 4.1 eV at about $x = 0.36$. These are all room temperature gaps which differ from our theory estimates by about 0.1 eV. Using our estimated value of 6.25 for MgO and a gap of 3.4 eV for ZnO, and our bowing coefficient of 0.56 eV predict a gap of 4.2 eV at 33 % MgO, consistent with their results.

Band-offsets

Within the dielectric midgap energy model, the band-offsets are obtained by aligning a suitably defined midgap point which plays the role of a charge neutrality point. In other words, when this level is aligned, negligible charge transfer from one material to the other is assumed to occur. This defines the self-consistent line-up of the two band structures. So, one only needs to calculate where the valence band maximum lies with respect to this midgap point. Our midgap energy points for relaxed wurtzitic MgO and ZnO are 3.03 eV and 1.55 eV above their valence band maxima respectively. This would result in a valence band offset between pure MgO and ZnO of 1.48 eV. With the above estimated gap difference of 2.85 eV, this gives a conduction band offset of 1.37 eV. Taking into account the various uncertainties, the conduction band to valence band ratio is predicted to be about 1. The alignment is of type-I.

CONCLUSIONS

In summary, we have obtained total energy and band structure results for ZnO and MgO in various relevant crystal structures. Our results of LDA calculations for ZnO total energy properties and band structure are in good agreement with experimental data, except for the details of the valence band splitting at the meV scale and the usual LDA shortcomings regarding gaps and deep semicore like band positions. We showed that the latter play a crucial role in determining the sign of the spin-orbit coupling and while we could not definitively solve the controversy about the valence band ordering, our present results seem to support a negative spin-orbit splitting. We found that MgO confined to the wurtzite structure has an unusual behavior with a structure which is really 5-fold rather than 4-fold coordinated. We found a small gap bowing and an overall gap dependence consistent with the data by Ohtomo et al. [6]. We find that the gap of wurtzitic MgO is significantly lower than that of rocksalt MgO. We predict type-I band offsets between ZnO and $Mg_xZn_{1-x}O$ alloys with an approximately 1/1 valence band to conduction offset ratio.

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