First-Principles Calculations of the Effective Mass Parameters of $Al_xGa_{1-x}N$ and $Zn_xCd_{1-x}Te$ Alloys

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First-principles calculations of electronic band structures of the ordered cubic alloys $Al_xGa_{1-x}N$ and $Cd_xZn_{1-x}Te$ are carried out. The band structures are used to provide effective masses and Luttinger parameters which are useful in the parametrization of theories based on effective hamiltonians.

I Introduction

The wide bandgaps of GaN and AlN make them ideal materials for the construction of blue/green light-emitting devices (*LED's* and lasers) and of transistors intended to operate at high power and temperatures [1, 2]. The alloying between GaN and AlN, producing $Al_xGa_{1-x}N$, allows the "engineering of the band gap" from 6.28 eV for AlN to 3.44 eV for GaN by controlling the composition x.

On the other hand the II-VI semiconductor compounds ZnTe and CdTe and their alloys $Zn_xCd_{1-x}Te$ have important applications such as infrared detectors, solar cells and other devices [3, 4].

Despite the recent intensive experimental and theoretical study of these materials some of the fundamental parameters which are essential to theoretical models used to account for the behavior of the alloys are either unknown or the subject of some debate. In particular, although the effective mass approximation is used extensively throughout in the literature, the actual electron and hole effective masses for the alloys in the whole range of x, are unknown. The transport and optical phenomena usually are governed by the band structures in the immediate vicinity of the Brillouin zone center. Thus the effective mass approximation turn to be an appropriate method to make the analysis of the electronic properties of materials amenable. The purpose of the present study is to obtain the electronic structure of those zinc-blende (cubic) materials and their alloys on the basis of first-principles band calculations and then link the electronic band calculations with the effective-mass theory. Therefore, we focus on electronic structures around the valence-band maximum (VBM) and the conduction-band minimum (CBM) and obtain the electron effective masses, hole effective masses, and, equivalently, the Luttinger-like parameters [5]. As a result, we present significant parameters of these materials, which can be used for the design of opto-electronic devices.

II Theoretical Framework

AlN and GaN usually have wurtzite structure and zinc-blende structure as well; ZnTe and CdTe have the zinc-blende structure. In the present study we consider the zinc-blende phase for all compounds and perform electronic structure calculations by means of the *ab initio* full-potential linearized augmented plane-wave (FLAPW) method [6, 7]. We use the Ceperley-Alder [8] of local-density approximation (LDA) for the exchange-correlation term. We do not consider relativistic effects.

Table I. Calculated effective electron masses (m_e^*), at CBM, light-hole (m_{lh}^*) and heavy-hole (m_{hh}^*) effective masses, at VBM, along [111], [100] and [110] directions for the $Zn_xCd_{1-x}Te$ and $Al_xGa_{1-x}N$ alloys (in the unit of free electron mass m_o).

	[111]			[100]			[110]		
Ligas	m_e^*	m_{lh}^*	m_{hh}^*	m_e^*	m_{lh}^*	m_{hh}^*	m_e^*	m_{lh}^*	m_{hh}^*
$CdZn_{(0.0)}Te$	0.135	0.106	1.099	0.135	0.137	0.490	0.122	0.101	0.424
$Cd_{(0.75)}Zn_{(0.25)}Te$	0.142	0.103	1.096	0.142	0.132	0.496	0.130	0.098	0.418
$Cd_{(0.50)}Zn_{(0.50)}Te$	0.140	0.101	1.058	0.147	0.130	0.464	0.127	0.096	0.414
$Cd_{(0.25)}Zn_{(0.75)}Te$	0.143	0.100	1.001	0.141	0.132	0.435	0.131	0.096	0.387
$Cd_{(0.0)}ZnTe$	0.129	0.102	0.960	0.129	0.139	0.419	0.148	0.098	0.365
$GaAl_{(0.0)}N$	0.186	0.153	1.895	0.185	0.190	0.848	0.169	0.144	0.738
$Ga_{(0.75)}Al_{(0.25)}N$	0.223	0.181	2.430	0.223	0.231	1.018	0.201	0.171	0.847
$Ga_{(0.50)}Al_{(0.50)}N$	0.267	0.285	2.711	0.321	0.284	1.098	0.235	0.294	0.920
$Ga_{(0.25)}Al_{(0.75)}N$	0.268	0.231	3.752	0.268	0.304	1.287	0.239	0.217	1.117
$Ga_{(0.0)}AlN$	0.305	0.252	4.289	0.306	0.330	1.395	0.271	0.236	1.206

The Ga(3d)-, Zn(3d)-, Cd(4d)-and Te(4d)-electrons are treated as part of the valence-band states, since they are relatively high in energy even though they constitute a well-localized narrow band. Inside the muffin-tin spheres, the angular momentum expansion is truncated at $\ell = 9$ for the wave functions. We use the parameter $R_{mt}K_{max} = 9$ which yields to a set of about 10^4 LAPW basis functions. The charge density was self-consistently determined using 63 k-points in the irreducible wedge of the first Brillouin zone. The total energy criterion for convergence was 10^{-7} Ry.

In order to simulate the ordered alloys with zinc-blende structure and compositions $x = 0.0$; 0.25; 0.50; 0.75; 1.00, we adopt a very approximate model based on an eight-atoms supercell with cubic symmetry. Large supercells that would be necessary to allow a more continuous variation of the composition x would be more computationally demanding. The alloy consists of a cation sublattice where the metals are interchanged (Ga and Al; Zn and Cd) and of an anion sublattice (N;Te), both originated from the zinc-blende structure. The cubic supercells were built by placing the anions at the positions (0,0,0), (0,1/2,1/2), (1/2,0,1/2) and (1/2,1/2,0); Zn(Al) atoms replacing successively the Cd(Ga) atoms initially placed at the positions (1/4,1/4,1/4), (1/4,3/4,3/4), (3/4,1/4,3/4) and (3/4,3/4,1/4) simulate the compositions $x = 0.25$; 0.50; 0.75; 1.00, respectively. The lattice parameters, a, were optimized for each composition x by means of total energy and force calculations. The results were found to obey a Vegard-type law [9]. The muffin-tin sphere radii for all atoms were taken with the same value 0.21 a, since the use of the full-potential ensures that the calculation is independent of the choice of the sphere radii.

III Results and Discussion

We calculate the bottom of the conduction band and the heavy hole and light hole bands at 21 $\vec{k}$-points with $\mid \vec{k} \mid$ ranging from $-0.05(2\pi/a)$ to $0.05(2\pi/a)$. The corresponding effective masses can be fitted using $E = \hbar^2 \mid \vec{k}^2/2m^* \mid$. The heavy hole and the light hole effective masses, m_{hh}^* and m_{lh}^*, and the electron effective masses, m_e^*, were then determined along the [111], [100] and [110] directions, and are shown in Table I. Using $\gamma_1 = 1/2(1/m_{lh}^{100}+1/m_{hh}^{100})$; $\gamma_2 = 1/4(1/m_{lh}^{100}-1/m_{hh}^{100})$ and $\gamma_3 = 1/4(1/m_{lh}^{100}+1/m_{hh}^{100}-2/m_{hh}^{111}$ we obtain the Luttinger parameters [5] which are shown in Table II.

IV Discussion

The literature is scarce in experimental and first-principles calculated values of the effective masses for the materials studied in this work. There is a broad general agreement between the results presented here and those of other calculations. For instance m_e^* for GaN is $0.17m_o$ in our calculation, $0.15m_o$ obtained by electron spin-resonance experiment [10], $0.21m_o$ by a first-principle pseudopotential calculation [11] and $0.13m_o$ by an empirical pseudopotential calculation. On the other hand our effective masses along the [100] direction for CdTe, $m_e^* = 0.13m_o$, $m_{lh}^* = 0.14m_o$ and $m_{hh}^* = 0.42m_o$ are to be compared to the values $m_e^* = 0.11m_o$, $m_{lh}^* = 0.18m_o$ and $m_{hh}^* = 0.60m_o$, obtained by empirical pseudopotential calculations [12], while, in particular, the heavy-hole effective mass along the growth (z) direction of a multiple-quantum-well has been assigned values ranging from $0.4m_o$ to $0.6m_o$ [13]. The effective masses we obtain for the alloys are almost all unknown in the literature.

Table II. Luttinger parameters for the $Zn_xCd_{1-x}Te$ and $Al_xGa_{1-x}N$ alloys.

-	γ_1	γ_2	γ_3
$CdZn_{0.0}Te$	4.67	1.314	1.880
$Cd_{0.75}Zn_{0.25}Te$	4.796	1.390	1.942
$Cd_{0.50}Zn_{0.50}Te$	4.923	1.384	1.989
$Cd_{0.25}Zn_{0.75}Te$	4.937	1.319	1.969
$Cd_{0.0}ZnTe$	4.789	1.201	1.873
$GaAl_{0.0}N$	3.221	1.021	1.346
$Ga_{0.75}Al_{0.25}N$	2.655	0.837	1.122
$Ga_{0.50}Al_{0.50}N$	2.216	0.653	0.923
$Ga_{0.25}Al_{0.75}N$	2.033	0.628	0.884
$Ga_{0.0}AlN$	1.873	0.778	0.820

According to our first-principles calculations, the energy dispersion of the lowest conduction band has some anisotropy for $\vec{k}$ directions. On the other hand the hole masses have non-negligible $\vec{k}$-directional dependence which is important when designing devices like laser diodes (LD's). So the Luttinger parameters γ_i, in the zinc-blende structure, may be very useful for technological applications. The effective masses of $Ga_{1-x}Al_xN$ alloys exhibit a stronger dependence on the compositon than the $Cd_{1-x}Zn_xTe$ alloys. This behavior may reflect the dehibridization of the *d*-electrons of Ga atom with the top of valence band as the composition x increases. In the case of the $Cd_{1-x}Zn_xTe$ alloys the hibridization of the Cd(4d)-electrons with the top of the valence band is continously substituted by the Zn(3d)-electrons. The effective masses of the $Cd_{1-x}Zn_xTe$ alloys have an almost linear dependence on x, showing small bowing factors. The calculated effective masses along the [110] direction are slightly smaller ($\sim$ 4%) than the calculated masses along the [100] and [111] directions, which are coincident. The calculated effective masses of the light holes along the [100] direction are bigger ($\sim$ 29%) than the calculated masses along the [111] and [110] directions which are almost coincident. On the other hand the calculated effective masses of the heavy holes along the [111] direction are bigger ($\sim$ 134%) than the masses along the [100] and [110] directions, which are also almost coincident.

The effective masses of the $Ga_{1-x}Al_xN$ alloy, except for x = 0.5, also have an almost linear behavior with the composition x, and exhibit the same features as described for the $Cd_{1-x}Zn_xTe$: m_e^{110} is about 5% smaller than $m_e^{110} \approx m_e^{111}$. $m_{lh}^{100} > m_{lh}^{111} \approx m_{lh}^{110}$; $m_{hh}^{111} >> m_{hh}^{100} \approx m_{hh}^{110}$. The lost of symmetry occuring for $x = 0.25$; 0.50 or 0.75 should be responsible for some of these fluctuations. On the other hand, as mentioned before, these results also depends on the small size of our supercells.

V Conclusions

We have performed first-principles FLAPW band calculations within the LDA for the zinc-blende $Ga_{1-x}Al_xN$ and $Cd_{1-x}Zn_xTe$ alloys (x = 0.0; 0.25; 0.50; 0.75; 1.00). The electron effective mass, hole effective masses, or equivalently, the Luttinger parameters, were derived from the calculated band structures near the CBM and VBM. These results provide the basis for the study of the electronic structure and physical properties of alloys of varying compositions. A more detailed analysis of the structural, electronic and thermodynamic properties of these alloys will appear soon elsewhere.

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