Auger recombination rates in ZnMgO from first principles

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We investigate direct electron-electron-hole interband Auger recombination for wurtzite $Zn_{1-x}Mg_xO$ alloys in the range $0 \leq x \leq 1$. Recombination rates are computed by interpolating the band structure and transition matrix elements from *ab initio* calculations of bulk ZnO, $Zn_{0.5}Mg_{n0.5}O$, and MgO primitive cells. We find that interband Auger recombination is most probable for Mg concentrations around 50%, where ZnMgO does not exist in a stable wurtzite phase. Since, for low Mg concentrations, the calculated Auger coefficients are far below 10^{-32} cm^6/s, we do not expect significant nonradiative loss through direct interband recombination in wurtzite ZnMgO. © *2011 American Institute of Physics*. [doi:10.1063/1.3651391]

I. INTRODUCTION

Due to its direct bandgap of 3.4 eV and the large exciton binding energy of 60 meV at room temperature, zinc oxide has caught attention as a promising material for various applications, ranging from transparent electronics to solid-state lightsources in the blue to UV spectrum. Essential for the realization of optoelectronic devices is the ability to modify the bandgap over a certain range of energies. For ZnO structures, an increasing energy gap up to about 4.4 eV can be achieved by the substitution of zinc with magnesium atoms and thus makes ZnMgO interesting for applications in the ultraviolet range.

It is known from theoretical investigations[1,2] of wurtzite (wz) GaInN alloys that the change in the fundamental gap with varying In content may open a channel for direct interband Auger recombination when the size of the energy gap E_g approximately reaches the energy distance Δ between the first and the second conduction band at Γ. From sophisticated *ab initio* band structure calculations[3] of bulk wz-ZnO and wz-MgO, it can be estimated that, with increasing Mg content in wurtzite $Zn_{1-x}Mg_xO$, the energy gap can become as large as the distance Δ and, hence, interband Auger recombination is in principle possible in this ternary compound as well. At the moment, the realization of ZnO-based light emitters is still under experimental research. The investigation of possible nonradiative loss due to Auger recombination in this system, therefore, can be of interest for future applications.

Stable wurtzite $Zn_{1-x}Mg_xO$ thin films have been grown successfully by various techniques for Mg concentrations up to about 40%.[4–6] The production of wurtzite ZnMgO structures with higher Mg content is problematic, as a phase shift from the wurtzite structure of ZnO to the rock salt (rs) phase of MgO needs to be considered. Experimental[4–6] and theoretical[7,8] works suggest that a change in coordination from four-fold (wurtzite) to six-fold rock salt (rs) occurs for Mg molar fractions $x > 0.4$.

We find that direct interband Auger recombination in wurtzite ZnMgO alloys is most probable for Mg molar fractions around $x \approx 0.5$. Since experimentally stable wurtzite ZnMgO is not producible with such a high Mg content and our calculated interband recombination coefficients for lower Mg concentrations range below 10^{-32} cm^6/s, direct interband Auger recombination should not be a dominant loss mechanism in this system.

II. METHOD

In this report, we use first principles methods to study Auger recombination in bulk ZnMgO alloys by first-order perturbation theory. For *n*-type semiconductors with direct energy gap, electron-electron-hole recombination is expected to be the dominant direct Auger transition. It is, however, possible that Auger transitions with hole excitation (so called CHHH processes) might have some contribution to the total rate. In this report, we focus on *e-e-h* recombination. In this process, the recombination energy of an electron in the conduction band with a hole in the valence band is used to excite a second electron to a higher state, which can be in the same (intraband) or a higher conduction band (interband transition). Our investigations focus on interband recombination, because intraband transitions are highly unlikely, due to the large bandgap of the system. Since, in an Auger process, the *e-h* recombination does not lead to the emission of a photon, the probability of Auger recombination can considerably influence the quantum efficiency of a system.

In the framework of perturbation theory, the Auger recombination rate can be expressed as[9,10]

$$R = 2\frac{2\pi}{\hbar}\frac{V^3}{(2\pi)^9}\int\int\int\int \left|M_{1,2,1',2'}\right|^2 P_{1,2,1',2'} \times \delta\left(E_{1,2,1',2'}\right)\delta\left(\boldsymbol{k}_{1,2,1',2'}\right)\mathrm{d}\boldsymbol{k}_1\mathrm{d}\boldsymbol{k}_2\mathrm{d}\boldsymbol{k}_{1'}\mathrm{d}\boldsymbol{k}_{2'}, \quad (1)$$

where the integrals run over the first Brillouin zone. The indices 1, 2, and 1′ denote the states of the electrons in the conduction band and the hole in the valence band before recombination, and 2′ is the state of the excited electron after the transition. The δ-functions ensure the conservation of

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energy and momentum during the transition and $E_{1,2,1',2'}$ and $\boldsymbol{k}_{1,2,1',2'}$ are abbreviations for $E_1+E_2-E_{1'}-E_{2'}$ and $\boldsymbol{k}_1+\boldsymbol{k}_2-\boldsymbol{k}_{1'}-\boldsymbol{k}_{2'}$. The matrix elements are defined by the screened Coulomb interaction between the involved particles and can be evaluated to[9–11]

$$M=\frac{4\pi e^2}{V}\frac{I(\boldsymbol{k}_1,\boldsymbol{k}_{1'})I(\boldsymbol{k}_2,\boldsymbol{k}_{2'})}{|\boldsymbol{k}_1-\boldsymbol{k}_{1'}|^2\varepsilon(\boldsymbol{k}_1-\boldsymbol{k}_{1'})}+\text{exchange term}, \quad (2)$$

where I are overlap integrals of the lattice periodic part of the respective Bloch states and ϵ is the wave vector dependent dielectric function. The statistical factor $P=f(E_1)f(E_2)[1-f(E_{1'})][1-f(E_{2'})]$ in the rate takes into account the occupation probabilities of the involved states. In the Boltzmann approximation for $f(E)$ and under consideration that $E_{2'}\gg E_c$, it can be written as[10]

$$P(\boldsymbol{k}_1,\boldsymbol{k}_2,\boldsymbol{k}_{1'},\boldsymbol{k}_{2'})\cong\frac{n^2p}{N_c^2N_v}\mathrm{e}^{-E_{\text{sum}}/kT}, \quad (3)$$

where $E_{\text{sum}}=(E_1-E_c)+(E_2-E_c)-(E_{1'}-E_v)$ is determined by the energetic distance of the initial states from the conduction and valence band edges E_c and E_v.

In our approach to compute the recombination rate, we use density functional theory and a plane wave expansion within a pseudopotential method[12] implemented in the ABINIT software package[13,14] to calculate the band structure and wavefunctions *ab initio*. For all calculations, we use the LDA as exchange correlation functional and a plane wave cut-off of 40 Ha. In a first step, the energy dispersion is determined on a dense mesh of k points in the Brillouin zone, where we use 125 000 k points to converge the Auger rate within 10% with respect to the rate at a three times denser k point mesh. Momentum and energy conservation can then be exploited to search for possible Auger transitions on the mesh. The numerical effort of that search scales at least with the third power of the number of k points. Thus, it is sensible to use a cut-off energy $E_{\text{sum}}<E_{\text{sum}}^{\text{cut}}$ in the statistical factor in Eq. (3) to restrict the integration to those regions in k space, where transitions notably contribute to the Auger rate, i.e., the vicinity of the Γ point. In our calculations, we use a cut-off energy of $E_{\text{sum}}^{\text{cut}}=400$ meV, since we checked that higher values do not affect the result. Because of the exponential factor in Eq. (3), states with higher E_{sum} practically do not contribute to the rate. To tackle the problem of finding energy conserving transition k points on the discrete k mesh, we leave one coordinate of $\boldsymbol{k}_{1'}$ as a (discrete) variable κ during the integration and then look for sign changes in $\eta(\kappa)=E_1+E_2-E_{1'}(\kappa)-E_{2'}(\kappa)$. If such a sign change occurs, the set of k points for which η is closest to zero is attributed to a possible transition.

To calculate the Auger recombination rate for a wide range of Mg molar fractions in $Zn_{1-x}Mg_xO$, one needs to know the dependence of the band structure on the alloy composition. LDA valence and conduction band structures for ZnO, $Zn_{0.5}Mg_{0.5}O$, and MgO in the wurtzite structure are illustrated in Fig. 1 and can be computed by subsequently substituting the two Zn atoms in the ZnO primitive cell with Mg atoms. In the case of $x=0.5$, this approach does not take into account any disorder and, therefore, has to be seen as an approximation. It is clearly visible that particularly the dispersion of the valence bands in the $\Gamma\rightarrow$ A direction remarkably changes with increasing Mg content. Also, the conduction bands show some slight alterations in bending. Since these band effects occur in the vicinity of the Γ point, they influence the possibility of Auger transitions and therefore have to be considered in the rate calculation. This is different from the situation in $Ga_{1-x}In_xN$, as reported in Ref. 1, where the band dispersion shows no significant changes, and different alloy compositions can be simulated by adjusting the bandgap within the $x=0$ band structure. In the case of ZnMgO, we use a quadratic interpolation scheme to approximate the band structure for arbitrary Mg concentrations x. Within this scheme, we first compute the LDA energy dispersion for the three structures ZnO, $Zn_{0.5}Mg_{0.5}O$, and MgO. The fundamental gap is then adjusted to the Mg content by a scissor shift. Eventually for every k point, the energy dispersion is interpolated according to

$$E_{nx}(\boldsymbol{k})=(1-x)E_n^{\text{ZnO}}(\boldsymbol{k})+xE_n^{\text{MgO}}(\boldsymbol{k})-b_n(\boldsymbol{k})x(1-x), \quad (4)$$

$$b_n(\boldsymbol{k})=2\left(E_n^{\text{ZnO}}(\boldsymbol{k})+E_n^{\text{MgO}}(\boldsymbol{k})\right)-4E_n^{\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}}(\boldsymbol{k}). \quad (5)$$

Since the bandgap is systematically underestimated in the LDA, we use the experimental value[15] 3.36 eV for the ZnO

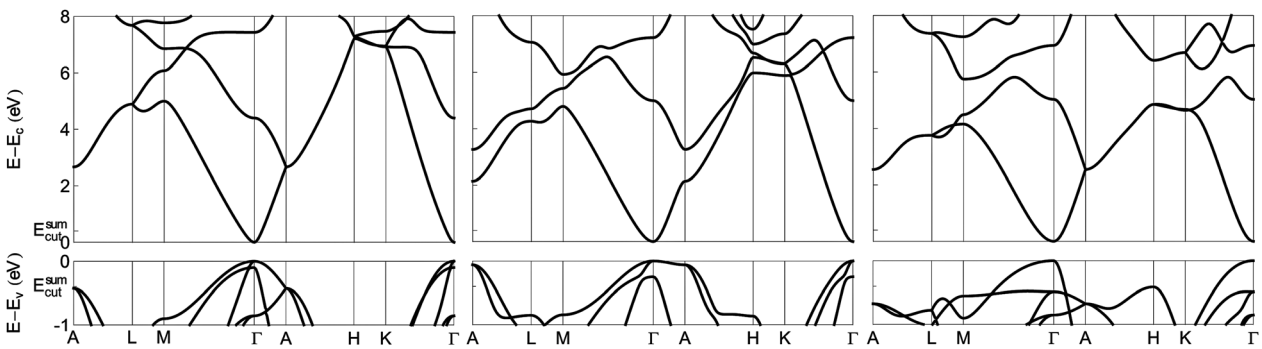

FIG. 1. Valence and conduction band structures for ZnO, $Zn_{0.5}Mg_{0.5}O$, and MgO in the wurtzite phase obtained by LDA calculations. Especially the structure of the valence bands around the Γ point significantly changes with the Mg content. To consider these changes, an interpolation scheme for intermediary Mg concentrations is applied for the rate computation. The assumed band gaps of the three structures are 3.36 eV (ZnO), 4.64 eV ($Zn_{0.5}Mg_{0.5}O$), and 6.45 eV (MgO), as indicated in the text.

gap. For wz-MgO, we estimate the bandgap from the LDA error in rs-MgO to 6.45 eV, as no experimental data is available for this hypothetical wurzite structure. To approximate the bandgap of ZnMgO for arbitrary Mg concentrations, we use a formula analog to Eq. (4), where the bowing parameter $b = 1.06$ eV can be obtained directly from LDA calculations, since for chemically identical systems, the systematical errors in LDA cancel here.[16] The bandgap then matches the distance Δ obtained by the interpolated LDA band structure at a Mg concentration of 60% as can be seen in the inset of Fig. 2.

For every possible transition, the matrix element [Eq. (2)] is computed using the plane wave expansion of the wavefunction for the overlap integrals. A simple isotropic model dielectric function[17] is fitted to previously calculated values of $\epsilon(\boldsymbol{q})$ for ZnO, $Zn_{0.5}Mg_{0.5}O$, and MgO to approximately take into account the screening. The quadratic interpolation scheme is then applied to the matrix elements as well in order to take into account the alloy composition x.

III. RESULTS

In Fig. 2, we present the calculated Auger coefficient $C_n = R/(Vn^2p)$ for various Mg concentrations. The highest probability for interband transitions occurs for Mg molar fractions around 50%. Interestingly, this peak in the spectrum is located below the concentration where E_g and Δ match in size, and transitions can occur closely to the statistically favored Γ point. However, due to the flat dispersion of the valence bands in $Zn_{0.5}Mg_{0.5}O$, transitions can have relatively large occupation probabilities even for this region.

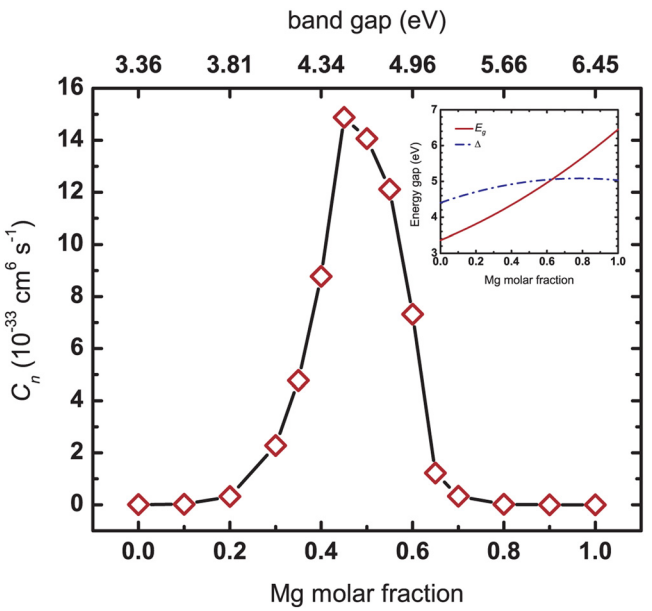

FIG. 2. (Color online) Interband Auger coefficient in wurtzite ZnMgO at $T = 300$ K. Interband recombination is most probable for Mg concentrations x around 50%, where transitions into all three valence bands are possible and the flatband dispersion allows high occupation probabilities. The relatively small size of the Auger coefficient, especially for lower x, indicates, however, that interband recombination may not be a dominant loss mechanism in wurtzite ZnMgO. The inset shows the assumed relation between the energy gaps E_g (straight line) and Δ (dashed line) and the Mg molar fraction.

Further, at $x \approx 50\%$, the band structure allows transitions into all three considered valence bands, whereas for higher concentrations, only transitions into the highest valence bands are possible. In the peak region, we find about 7×10^6 possible transitions on the k mesh. To estimate the size of the Auger coefficients, we use an effective mass model to calculate the effective electron and hole densities N_c and N_v in Eq. (3). Using the effective masses $m_c^* = 0.24$ and $m_{lh}^* = m_{hh}^* = 0.59$ for ZnO, as reported in Ref. 15, we find $N_c = 3 \times 10^{18}$ cm^{-3} and $N_v = 2 \times 10^{19}$ cm^{-3}. The coefficients we gain this way, with Eq. (1), are valid for densities $n \ll N_c$, $p \ll N_v$ and have a maximum value of 1.5×10^{-32} cm^6/s at $x = 0.45$. As can be seen in Fig. 2, they drop very fast with decreasing Mg concentrations. Up to $x = 0.3$, the interband coefficient is at least one order of magnitude below the peak value and three orders of magnitude below the value which is considered significant for nonradiative loss in nitride-based optoelectronical devices.[1] We thus do not expect substantial loss from radiationless direct interband Auger recombination in ZnMgO-based devices.

Recent first principles investigations of Auger recombination in GaInN[18] identified indirect processes that are assisted by phonons and alloy disorder as a possible dominant loss mechanism. In the present investigation for ZnMgO, we do not take into account these processes. From Ref. 18, it can be seen that the Auger coefficient of the indirect recombination processes in GaInN decreases steadily with an increasing energy gap. For the wide bandgap system ZnMgO, we hence also expect the Auger coefficients of indirect recombination to be lower than in the GaInN system, especially for alloys with high Mg molar fractions, i.e., large band gaps. However, the role of indirect Auger recombination as a possible loss mechanism in ZnO-based systems remains to be further investigated.

IV. CONCLUSIONS

In conclusion, we numerically investigate the possibility of interband Auger recombination in bulk wurtzite ZnMgO alloys of varying Mg content. The framework of density functional theory is used to obtain the band structures and wavefunctions needed for the computation of Auger rates. Different alloy compositions are approximated by an interpolation scheme for the band structure and matrix elements. We find that interband Auger recombination is most probable for Mg concentrations around 50%, where ZnMgO ceases to exist in a stable wurtzite phase. For experimentally amenable $Zn_{1-x}Mg_xO$ structures with $x < 0.4$, the Auger coefficients are smaller than 10^{-32} cm^6/s. We therefore do not see direct interband recombination as a critical loss mechanism in ZnMgO.

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