Establishing composition dependent $\mathbf{k \cdot p}$ parameters for (Al,Ga)N alloys

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***Abstract*—Deep UV (Al,Ga)N-based light emitters exhibit very low quantum efficiencies when compared to UV emitters at longer wavelengths. To improve the efficiencies of e.g. (Al,Ga)N-based light emitting diodes, theory and simulation can help to guide the device design. The theoretical framework underlying device simulations is often based on drift-diffusion models coupled with a self-consistent Schrodinger-Poisson equation solver. To achieve accurate and predictive models, understanding the composition dependence of material input parameters is of central importance. We target the composition dependence of $\mathbf{k \cdot p}$ parameters in $\mathbf{Al_xGa_{(1-x)}N}$ alloys by using density functional theory (DFT) to obtain effective band structures from alloy disordered supercells. Building on these effective band structures, a numerically efficient fitting scheme based on the Sobol-sequence method is employed to extract effective electron masses, $\mathbf{m_e(x)}$, Luttinger-like parameters $\mathbf{A_i(x)}$, with $\mathbf{i = 1 \ldots 6}$, and crystal field splitting energy, $\mathbf{\Delta_{CF}}$, as a function of Al content, x, in the system. Our calculations reveal that for $\mathbf{m_e(x)}$ a linear interpolation of the GaN and AlN values provides a good description of the DFT data. However, for $\mathbf{A_i(x)}$ and $\mathbf{\Delta_{CF}(x)}$ this simple approximation breaks down and we find that composition dependent bowing parameters are required to describe effective DFT band structures accurately.**

***Index Terms*—(Al,Ga)N, DFT, $\mathbf{k \cdot p}$, alloys, electronic structure**

I. Introduction

Aluminium gallium nitride, (Al,Ga)N, alloys offer tremendous potential for developing compact, reliable, environment friendly, low-power and wavelength-tunable solid-state ultraviolet (UV) light emitters since the wide band gap of the alloy covers in principle the wavelength windows from UVA to UVC [1]. However, (AlGa)N-based UV emitters suffer from low external quantum efficiencies (EQEs) especially in the (300-350 nm) and deep UV (220-280 nm) wavelength ranges [1]. These wavelengths windows are of particular importance for biomedical applications ranging from curing of skin diseases, dentistry, disease diagnosis, UV sterilization and disinfection [2]. As discussed in the literature, several factors contribute to the low efficiency of (Al,Ga)N emitters [3]. For instance in the 220-280 nm wavelength range, the light extraction efficiency (LEE) of (Al,Ga)N UV light emitting diodes (LED) is quite low, which to a large extent stems from fundamental differences in the electronic band structures of AlN and GaN, namely a difference in the valence band ordering in these materials, which can for instance be classified by the crystal field splitting energy [4]. Alloy disorder in an (Al,Ga)N system can significantly impact the band ordering as well as band mixing effects, which in turn can affect the LEE. To model electronic, optical and carrier transport properties of (Al,Ga)N-based LEDs, (modified) continuum-based electronic structure models, such as the $\mathbf{k \cdot p}$ method, self-consistently coupled with Poisson and drift-diffusion equations, are widely employed in the literature. However, the impact of alloy disorder on input parameters such as crystal field splitting energies or effective electron and hole masses is largely unexplored in the $\mathbf{k \cdot p}$ framework; often a linear interpolation of GaN and AlN $\mathbf{k \cdot p}$ input parameters is employed to obtain $Al_xGa_{(1-x)}N$ data, without further justification. To gain insight into the composition dependence of $\mathbf{k \cdot p}$ input parameters in $Al_xGa_{(1-x)}N$ from first-principles, we combine density functional theory and a Sobol fitting scheme. Our work shows that especially for the valence band structure, the linear interpolation assumption breaks down.

II. Simulation Framework

To accurately model the electronic structure of $Al_xGa_{(1-x)}N$ alloys we build on plane-wave density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP) [5]. We use the generalized gradient approximation (GGA) based on the Perdew-Burke-Ernzerhof (PBE) [6] functional for the geometry optimizations and bandstructure calculations. Even though the PBE functional underestimates the band gap of the materials, we find that it predicts effective mass and Luttinger-like parameters A_i, with $i = 1 \ldots 6$, in good agreement with literature values for AlN and GaN. To calculate the electronic band structure of $Al_xGa_{(1-x)}N$ alloys, a $3 \times 3 \times 2$ supercell with 72 atoms is constructed for Al contents of $x = 0.25$, $x = 0.5$ and $x = 0.75$; for each alloy content x, 10 unique atomic configurations were generated randomly by substituting Ga with Al atoms. Here a Γ centered $4 \times 4 \times 4$ k-point mesh and plane wave cut-off energy of 600 eV has been used. Lattice parameters and internal degrees of freedom have been optimised until the pressure on the supercell is minimal. Effective (Al,Ga)N DFT band structures are obtain

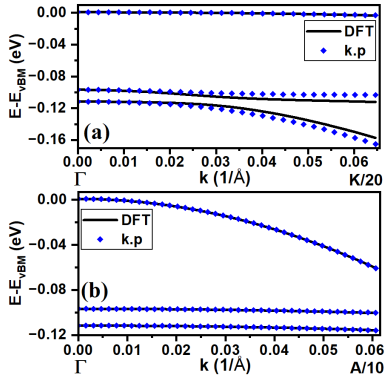

Fig. 1. Electronic band structure of an $Al_{0.75}Ga_{0.25}N$ random alloy obtained from a 72 atom supercell. The results are plotted along two different paths within the first Brillouin zone: a) $\Gamma \rightarrow \frac{K}{20}$ & b) $\Gamma \rightarrow \frac{A}{10}$. The solid black lines give the DFT data while blue diamonds denote the fitted $\mathbf{k} \cdot \mathbf{p}$ bandstructure.

along 4 high symmetry directions (K, L, M, A) with a very fine k-point mesh (200 points) along each direction.

Equipped with the DFT band structures, a Sobol-sequence based fitting procedure as implemented in the software packages SPHinX [7] is employed to obtain composition dependent $\mathbf{k} \cdot \mathbf{p}$ parameters. In this work we use a 6+2 band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian as it underlies most commercially available device simulation software packages. In doing so composition dependent effective electron masses, $m_e(x)$, Luttinger-like $A_i(x), i = 1, \ldots, 6$, parameters as well as the crystal field splitting energy, $\Delta_{\mathrm{CF}}(x)$, is obtained by fitting to the energetically highest three DFT valence bands from Γ to $(M/20, L/20, K/20, A/10)$.

III. Results

Figure 1 displays the $Al_{0.75}Ga_{0.25}N$ DFT and fitted $\mathbf{k} \cdot \mathbf{p}$ electronic band structures for one of the ten alloy configurations. The band structure is plotted along two of the four considered directions within the first Brillouin zone. The directions chosen are within (K-point) and perpendicular (A-point) to the c-plane. Overall, Fig. 1 reveals a very good fit of $\mathbf{k} \cdot \mathbf{p}$ to DFT band structure. Similarly good fits are obtained for the other directions and alloy configurations. Having established this fitting routine and by averaging of the different alloy configurations, we have obtained for instance composition dependent $A_i(x)$ parameters. Figure 2 displays $A_1(x)$ as a function of the Al alloy content x in an $Al_xGa_{(1-x)}N$ alloy. This figure clearly shows $A_1(x)$ deviating from the linearly interpolated values. We find a similar behavior for other parameters, including the crystal field splitting energy. Thus our analysis highlights that a linear interpolation, strongly deviates from our predicted values and may thus significantly impact electronic, optical and carrier transport properties of (Al,Ga)N systems and heterostructures.

IV. Summary and Outlook

We have developed a theoretical framework to extract composition dependent $\mathbf{k} \cdot \mathbf{p}$ parameters from effective DFT band structures obtained from alloy disordered supercells.

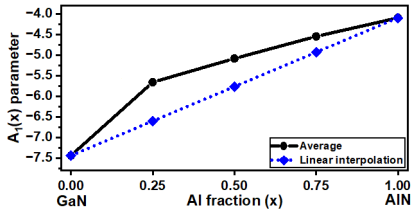

Fig. 2. Luttinger-like parameter $A_1(x)$ as a function of the alloy content x in an $Al_xGa_{(1-x)}N$ alloy. The black circles give the average value for all 10 configurations while blue diamonds denote the values obtained from a linear interpolation of the AlN and GaN values.

Our calculations show that for instance the Luttinger-like valence band parameters $A_i(x)$ can exhibit a strong composition dependence, which stands in contrast to the often assumed linear interpolation of GaN and AlN parameters with composition x in $Al_xGa_{(1-x)}N$ alloys. As such, our refined $\mathbf{k} \cdot \mathbf{p}$ parameters will provide an ideal starting point to study electronic, optical and carrier transport properties of (Al,Ga)N-based light emitters.

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