

Band-edge density-of-states and carrier concentrations in intrinsic and p -type $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$

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The electronic structures of chalcopyrite $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ have recently been reported to have strongly anisotropic and non-parabolic valence bands (VBs) even close to the Γ -point VB maximum. Also, the lowest conduction band (CB) is non-parabolic for energies 50–100 meV above the CB minimum. The details in the band-edge dispersion govern the material's electrical properties. In this study, we, therefore, analyze the electronic structure of the three uppermost VBs and the lowest CB in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x = 0, 0.5$, and 1). The parameterized band dispersions are explored, and the density-of-states (DOS) as well as the constant energy surfaces are calculated and analyzed. The carrier concentration and the Fermi energy E_F in the intrinsic alloys as functions of the temperature is determined from the DOS. The carrier concentration in p -type materials is modeled by assuming the presence of Cu vacancies as the acceptor type defect. We demonstrate that the non-parabolicity of the energy bands strongly affects the total DOS. Therefore, it is important to take into account full band dispersion of the VBs and CB when analyzing the free carrier concentration, like for instance, in studies of electronic transport and/or measurements that involve strong excitation conditions. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4767120>]

I. INTRODUCTION

The chalcopyrite $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ alloy is one of the most important absorber material in the thin-film photovoltaic technology.¹ The performance of the solar cell is directly related to fundamental transport physics of the device.² The electrical properties of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ are dominated by the native defects, and whereas the defect concentration can vary in the order of percentage, the carrier concentration is typically well below 10^{20} cm^{-3} and the concentration can be controlled by the stoichiometry.^{3–5} Whereas CuInSe_2 can become n -type like, the Ga-rich compounds are compensated by charged Cu vacancies that will counteract the n -type character.^{3,6} $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ is, therefore, preferable p -type. At very low temperatures, the acceptors are not fully thermally activated, and the electronic properties are governed by hopping conductivity.^{7–9}

Analyses of the measurements and modeling of for instance excitonic effects,¹⁰ carrier mobilities,¹¹ and current-voltage characteristics¹² require knowledge of basic the material electronic properties. Although most macroscopic properties of the compound are fairly well understood, there are only a handful studies on the details in the electronic energy dispersion near the valence-band (VB) and conduction-band (CB) edged.^{13,14} These studies consider primarily the characterization of the Γ -point states, involving measurements or calculations of the VB crystal-field and spin-orbit split-off energies. More detailed understanding of the energy dispersion at the VB maximum and the CB minimum is required to better understand the electrical properties of the material.

We have in Ref. 15 presented a parameterization of the energy bands $E_j(\mathbf{k})$ for the three energetically uppermost

VBs ($j = v1, v2$, and $v3$) and the lowest CB ($j = c1$) in $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ with $x = 0, 0.5$, and 1. The parameterization was based on an expansion of the traditional $\mathbf{k} \cdot \mathbf{p}$ expression¹⁶ to higher order in order to describe the electronic band curvatures near the Γ -point. It was demonstrated that the VBs and CB are very non-parabolic away from the Γ -point. This indicates that one cannot use the Γ -point effective masses to describe material properties that depend on band filling and/or strong excitation effects. Instead, a full description of the band curvatures is required in combination with proper physical model of band filling.

In this work, we utilize these parameterized band dispersion $E_j(\mathbf{k})$ of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ from Ref. 15 for the group-III cation composition $x = 0, 0.5$, and 1, and we analyze the impact on the carrier concentrations n and Fermi energy $E_F(n)$ due to the non-parabolicity and anisotropy of the energy bands. The density-of-states (DOS) and the constant energy surface $S_j(E)$ are calculated for the three topmost VBs as well as for the lowest CB. From these calculations, we describe the intrinsic carrier concentration and the Fermi energy as functions of temperature T . Since as-grown $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ typically has p -type character, we model also the carrier concentration in p -type materials by assuming the presences of the native Cu vacancies V_{Cu} as acceptors.¹⁷ Our main conclusion is that it is crucial to consider the non-parabolicity of the VBs and CB dispersions when analyzing properties that are related to band filling. For instance, the intrinsic carrier concentration in CuInSe_2 increases by a factor of 2.4 at $T = 300 \text{ K}$ when the non-parabolicity is included.

We believe the results are important for accurately describing electron and hole dynamics in the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ alloys. For example, the DOS and the Fermi energy are fundamental quantities in Monte Carlo simulations of electronic transport