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Li AND NATIVE DEFECTS IN ZnSe INVESTIGATED BY FIRST-PRINCIPLES TOTAL ENERGY CALCULATIONS

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ABSTRACT

Native defect compensation is often suggested as the source of difficulty in doping p-type ZnSe. Using first-principles theoretical techniques, we show that native defect compensation in ZnSe is insignificant. For Li_{Zn} , a promising acceptor dopant, we show that the reaction $\text{Li}_{Zn} \rightarrow \text{V}_{Zn} + \text{Li}_{i}$ is a likely compensation mechanism.

Introduction

Wide band-gap II-VI semiconductors can usually be doped either p-type or n-type, but not both. ZnSe, for example, can easily be made n-type but not p-type. One of the simplest explanations for this phenomenon is that compensation occurs through the formation of native donor defects.^{1,2} Because of the wide band gap of ZnSe, the energy cost to create the defect in p-type material might be recouped by transferring electrons from an intrinsic donor level near the conduction band to the Fermi level. Though this mechanism is plausible and is often quoted in the literature as a cause of the trouble in H-VI doping, to our knowledge, there is no direct evidence to indicate whether it is significant or not. Here, we report first-principles calculations which show that the concentrations of native defects are too low in stoichiometric material to be responsible for compensation. Deviations from stoichiometry can enhance native defect compensation; however, they are as likely to compensate n-type material as p-type, and cannot explain why ZnSe prefers to be n-type. In the absence of a general mechanism, we examine a specific acceptor in ZnSe. We show that p-type doping of ZnSe by Li, a promising acceptor, is inhibited by motion of Li from the substitutional to the tetrahedral interstitial site. We have performed state-of-the-art first-principles total-energy calculations for native defects in ZnSe, based on density-functional theory, pseudopotentials and supercells.^{3.} An all-new mixed-basis total-energy program was written to represent the electronic wave functions by a basis set of plane waves and tightbinding functions. This allows us to include the Zn 3d electrons as valence, rather than core states. (Treating the d electrons as core states produces large errors in the properties of ZnSe.⁴) Test calculations successfully predict bulk properties: lattice constant to within 1% and bulk modulus to within 10%. These are the first defect calculations for a II-VI compound to reach the level of accuracy attained for Si and GaAs. For ZnSe we have calculated the formation energies for all of the basic intrinsic point defects: V_{Zn} , V_{Se} , Zn_i , Se_i , Zn_{Se} , and Se_{Zn} in all relevant charge states.

Native Defects in ZnSe

Defect concentrations are determined by the defect formation energies and entropies. Formation energies include the relaxation of each defect, which can be different for different charge Relaxations states. are calculated explicitly for the most important defects in p-type ZnSe. They are of the order of 0.5 eV. For other cases we assume a very liberal value of 1 eV for each defect. (Even a relaxation of 2 eV



does not change our results.) Entropies of formation do not affect our conclusions either, because the defect concentrations show little sensitivity to formation entropies over a wide range (0 to 10 k_B).

Defect concentrations are a function of the stoichiometry of the crystal. Our results for stoichiometric ZnSe are given in Fig. 1, which shows the number of electrons produced by native defects in p-type ZnSe doped with 10^{18} cm⁻³ acceptors. (The range of values shown is bounded by assuming relaxations of 1 eV and entropy of 10 k_B per defect for an upper bound and 0 k_B for a lower bound.) At MBE growth temperatures (T = 600 K), our results show that the number of defects is far too small to be a source of compensation. Even in material grown at higher temperatures, excess native defects will recombine during cooling, unless the sample is rapidly quenched. (The dominant native defects in ZnSe are still mobile at temperatures as low as 400 K.⁵) We conclude that in stoichiometric ZnSe, native defects will not compensate dopants.

We have also determined the concentration of native defects in nonstoichiometric ZnSe. Slight deviations from stoichiometry necessarily produce large concentrations of native defects, even at T = 0 K. For example, a deviation from stoichiometry of 10⁻⁵, which is too small to measure experimentally, requires a defect concentration of 10¹⁷ cm⁻³. (In this discussion we refer only to deviations from stoichiometry that are accommodated by native point defects. Deviations from stoichiometry due to precipitates, higher dimensional defects or dopant impurities are not included.) Our key finding is that the defects produced by a deviation from stoichiometry will always compensate the majority carriers. For p-type ZnSe, the dominant defect is Zn_i in Zn rich material, and Se_{Zn} in Se rich material. Both are double donors. For n-type ZnSe the dominant (acceptor) defects are Zn_{Se} and V_{Zn} for Zn and Se rich materials, respectively. Similar results were found by Jansen and Sankey.² Deviations from stoichiometry compensate acceptor and donor doping equally well. Consequently, they cannot explain why ZnSe prefers to be n-type.

Lithium in ZnSe

Having eliminated native defects as a generic source of compensation in ZnSe, we examine difficulties associated with individual dopants for p-type material. Li_{Zn} is known to be a shallow acceptor ($\text{E}_{A} = 114 \text{ meV}$), but attempts to achieve high hole concentrations with Li doping have generally been unsuccessful. One explanation is the possibility of Li moving to an interstitial site, where it becomes a donor. For the reaction $\text{Li}_{Zn} \rightarrow \text{V}_{2n}^2 + \text{Li}_{1}^+$ we find that the energy cost is 1 eV. But as the Fermi level approaches the valence-band edge, the reaction energy is reduced by a change in the charge state of the V_{Zn} and the Li will tend to become interstitial, compensating the material. This scenario

explains several experimental results,⁶ including electromigration studies of Lidoped ZnSe,⁷ which find substantial Li migration only in samples with a large Li concentration (where the Fermi level is near the valence band). For the reaction $\text{Li}_{Zn} + \text{Zn}_{,} \rightarrow \text{Li}_{,}$ we find that the Zn_{i} (when present in the crystal) will kick out the Li from the substitutional to the interstitial site, for any value of the Fermi level. We have also examined the behavior of interstitial Li, and find that the two tetrahedral sites (the one (T_{Zn}) surrounded by four Zn atoms, the other (T_{Se}) by four Se atoms) are close in energy. Interstitial Li is a fast diffuser, with a migration barrier of less than 0.5 eV for the path $T_{Zn} \rightarrow H \rightarrow T_{Se}$ where H is the hexagonal interstitial site.

In conclusion, we have shown that native defect compensation is not a problem in stoichiometric ZnSe; in non-stoichiometric material, both n- and p-type doping are equally well compensated. To minimize compensation one must strive for perfect stoichiometry. Difficulties with Li doping in ZnSe are due not to native defect compensation, but to the tendency of Li to move from the substitutional site, where it is an acceptor, to the interstitial site, where it is a donor.

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