# Limits to Doping of Wide Band Gap Semiconductors

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Ⓢ *Supporting Information*

The role of defects in materials is one of the long-standing issues in solid-state chemistry and physics. On one hand, intrinsic ionic disorder involving stoichiometric amounts of lattice vacancies and interstitials is known to form in highly ionic crystals, e.g., Frenkel disorder in $CaF_2$ and Schottky disorder in NaCl.[1] On the other hand, intrinsic electronic disorder occurs in traditional semiconductor materials involving electron and hole carriers, e.g., thermal band gap excitations in Si or Ge.[2] The difficulty arises intermediate of these two regimes, for materials that fall between the large band gap ionic solids and small band gap covalent semiconductors: the case of wide band gap semiconductors. These materials can exhibit a combination of ionic and electronic conduction and have applications ranging from optoelectronic devices[3,4] (e.g., exploiting the coexistence of optical transparency and electrical conduction in transparent oxide electronics) to photocatalysis[5,6] (e.g., combining the catalytic activity of redox active metal ions with the conduction of electrons and holes in the photoelectrochemical water-splitting process).

Due to the large electronegativity difference between the constituent elements, the chemical bonds in wide band gap binary materials such as ZnO, GaN, and SiC are heteropolar; the definition of a quantitative degree of ionicity remains an ill-defined concept, especially for electronic Bloch waves.[7,8] As a result of their intermediate character, these compounds exhibit a complex combination of intrinsic ionic and electronic defect disorder, transport, and conduction. For example, depending on the preparation conditions, samples of ZnO may contain a combination of site vacancies, interstitials, hydrogen, and conduction electrons.[9,10]

Regardless of the complexity of the underlying defect reactions, the overarching law of electroneutrality must be satisfied for a crystal in equilibrium, $[D^\bullet] + [h^\bullet] = [A'] + [e']$. The terms $[e']$ and $[h^\bullet]$ represent the concentrations of electron and hole carriers (electronic disorder), while $[D^\bullet]$ and $[A']$ represent the concentrations of charged donor or acceptor defects. The superscript dots and dashes refer to the positive and negative charge of the species, the cross is reserved for neutral defects, following the standard notation of Kröger and Vink.[9] The overall balance of positive and negative charges must be conserved, but the electroneutrality principle allows for the interchange of charged species. Conventionally, the ionization of a neutral point defect to produce electron or hole carriers is the primary focus; however, the exchange of hole carriers for charged donor defects or electron carriers for negatively charged acceptor defects can also occur. For the case of ZnO, this could represent the exchange of a hole in the valence band for an oxygen vacancy, $h^\bullet + {}^1/_2O_O^\times \rightarrow {}^1/_2V_O^{\bullet\bullet} + {}^1/_4O_2(g)$.

There is a substantial literature on defect formation[11] and the phenomenological limits of doping[12] in this class of materials; in particular, involving the application of predictive quantum mechanical electronic structure computations.[13] Most wide band gap materials conduct only electrons and few conduct holes, but rarely are both modes of conduction accessible in a single chemical system. Building upon almost a century of developments in the theory of point defects, the equilibrium between electronic and ionic defects has been addressed recently, with the development of a thermodynamic model based on quantum chemical calculations.[14]

In this Communication, we demonstrate that electro−ionic defect equilibrium determines the stability of hole and electron carriers in wide band gap semiconductors and that the equilibrium constant is related to the absolute valence and conduction band energies. To illustrate the underlying chemical trends, we have performed calculations on ZnO, GaN, and SiC, which are all wide band gap (>3 eV) materials, with tetrahedral ion coordination, and complex defect chemistry. They also form the logical series of first row binary semiconductors: II−VI, III−V, and IV−IV compounds, in the language of solid-state physics.

The reaction energies involving the formation and compensation of native defects in each of the three materials have been calculated within the framework of Kohn−Sham Density Functional Theory (DFT),[15] using a hybrid exchange-correlation functional, which represents the state-of-the-art in

**Table 1. Computed Reaction Energies ($\Delta E_f$ in kJ/mol) for Processes in which Electron and Hole Carriers are Charge Compensated by Ionic Defects in ZnO, GaN, and SiC$^a$**

| ZnO | $\Delta E_f$ | $K_C$ | GaN | $\Delta E_f$ | $K_C$ | SiC | $\Delta E_f$ | $K_C$ |
|---|---|---|---|---|---|---|---|---|
| **(a) Hole Carriers** | | | | | | | | |
| *anion rich* | | | | | | | | |
| $h^{\bullet} \to \frac{1}{2}V_O^{\bullet\bullet}$ | $-71$ | $3\times10^{12}$ | $h^{\bullet} \to \frac{1}{3}V_N^{\bullet\bullet\bullet}$ | $-74$ | $1\times10^{13}$ | $h^{\bullet} \to \frac{1}{2}V_C^{\bullet\bullet}$ | $76$ | $4\times10^{-14}$ |
| $h^{\bullet} \to \frac{1}{2}Zn_i^{\bullet\bullet}$ | $-48$ | $3\times10^{8}$ | $h^{\bullet} \to \frac{1}{3}Ga_i^{\bullet\bullet\bullet}$ | $-11$ | $7\times10^{1}$ | $h^{\bullet} \to \frac{1}{2}C_i^{\bullet\bullet}$ | $235$ | $6\times10^{-42}$ |
| $h^{\bullet} \to V_{Zn}^{\bullet}$ | $158$ | $2\times10^{-28}$ | | | | $h^{\bullet} \to \frac{1}{2}V_{Si}^{\bullet\bullet}$ | $407$ | $5\times10^{-72}$ |
| *cation rich* | | | | | | | | |
| $h^{\bullet} \to \frac{1}{2}V_O^{\bullet\bullet}$ | $-250$ | $6\times10^{43}$ | $h^{\bullet} \to \frac{1}{3}Ga_i^{\bullet\bullet\bullet}$ | $-114$ | $9\times10^{19}$ | $h^{\bullet} \to \frac{1}{2}V_C^{\bullet\bullet}$ | $51$ | $1\times10^{-09}$ |
| $h^{\bullet} \to \frac{1}{2}Zn_i^{\bullet\bullet}$ | $-227$ | $5\times10^{39}$ | $h^{\bullet} \to \frac{1}{3}Ga_i^{\bullet\bullet\bullet}$ | $-50$ | $6\times10^{8}$ | $h^{\bullet} \to \frac{1}{2}C_i^{\bullet\bullet}$ | $261$ | $2\times10^{-46}$ |
| $h^{\bullet} \to V_{Zn}^{\bullet}$ | $515$ | $5\times10^{-91}$ | | | | $h^{\bullet} \to \frac{1}{2}V_{Si}^{\bullet\bullet}$ | $432$ | $2\times10^{-76}$ |
| **(b) Electron Carriers** | | | | | | | | |
| *anion rich* | | | | | | | | |
| $e' \to \frac{1}{2}O_i''$ | $167$ | $6\times10^{-30}$ | $e' \to N_i'$ | $450$ | $2\times10^{-79}$ | $e' \to \frac{1}{2}C_i''$ | $270$ | $5\times10^{-48}$ |
| $e' \to \frac{1}{2}V_{Zn}''$ | $72$ | $2\times10^{-13}$ | $e' \to \frac{1}{3}V_{Ga}'''$ | $134$ | $3\times10^{-24}$ | $e' \to \frac{1}{4}V_{Si}''''$ | $57$ | $1\times10^{-10}$ |
| | | | $e' \to V_N'$ | $449$ | $3\times10^{-79}$ | $e' \to \frac{1}{3}V_C'''$ | $426$ | $2\times10^{-75}$ |
| *cation rich* | | | | | | | | |
| $e' \to \frac{1}{2}O_i''$ | $251$ | $1\times10^{-44}$ | $e' \to N_i'$ | $567$ | $4\times10^{-100}$ | $e' \to \frac{1}{2}C_i''$ | $295$ | $2\times10^{-52}$ |
| $e' \to \frac{1}{2}V_{Zn}''$ | $345$ | $3\times10^{-61}$ | $e' \to \frac{1}{3}V_{Ga}'''$ | $173$ | $6\times10^{-31}$ | $e' \to \frac{1}{4}V_{Si}''''$ | $69$ | $7\times10^{-13}$ |
| | | | $e' \to V_N'''$ | $330$ | $2\times10^{-58}$ | $e' \to \frac{1}{3}V_C'''$ | $432$ | $2\times10^{-76}$ |

$^a$Negative values refer to exothermic reactions. Some values were previously reported for ZnO and GaN;[18] however, more rigorous convergence has been achieved for the computational parameters that are included in this work. The reactions are written using a concise notation, where mass balance is implicitly included, and only the most stable charge states are shown. Anion and cation rich conditions refer to a material in equilibrium with the anion or cation standard states, e.g. elemental exchange with oxygen gas or zinc metal for ZnO. The associated equilibrium constants ($K_C$) are calculated at 298.15 K from the relation $\Delta E_f = -k_B T \ln K_C$.

terms of first-principles solid-state defect techniques. All calculations were converged with respect to the pertinent parameters, such as region size and basis sets, and the full details are included as Supporting Information. The reaction energies are listed in Table 1 using a shorthand notation compared to eq 2; in all cases the equations are fully balanced in terms of charge and mass and are with reference to the elemental standard states. The energies of electrons and holes are taken from the vertical ionization potentials and electron affinities; polaronic trapping of carriers is excluded. While the focus here is defect energetics, the atomic and electronic structures have been carefully examined in all cases to ensure physical results were obtained.

The most striking result from Table 1 is that electron carriers are stable species in all three materials. Reactions involving the exchange of electrons for negatively charged ionic defects are endothermic by at least 57 kJ/mol. The stability of holes is more limited, with large exothermic reactions for their exchange by point defects of up to 250 kJ/mol for ZnO, smaller exothermic reactions up to 114 kJ/mol for GaN, and endothermic reactions of at least 50 kJ/mol for SiC. The associated equilibrium constants (Table 1) reflect almost complete conversion for the exothermic reactions, and this behavior has been confirmed to be independent of the assumed temperature or partial pressures (see Supporting Information).

*Are these results consistent with experimental evidence?* All three materials are known to conduct electrons, and n-type conductivity can be found even in undoped samples.[16] SiC is known to conduct holes (p-type) when doped with trivalent acceptor impurities such as B and Al,[17] but the behavior of holes in ZnO and GaN is a more controversial matter. Very high dopant concentrations and/or extreme preparatory conditions such as strain are required to produce significant concentrations of hole carriers, and meta-stability of p-type materials is a likely phenomenon.[18−20] A thermodynamic analysis of the reaction energies in Table 1 as a function of the temperature and pressure of the standard states demonstrates that the balance of the reaction will not be altered under normal equilibrium conditions. We emphasize that this analysis is independent of the choice of donor or acceptor species that were ionized to produce the electrons or holes.

*What is the origin of carrier stability?* Intuitively, the stability of electrons and holes will be related to the electron affinity and ionization potential of a material, respectively. The calculated energetic alignment of bands for the three materials, with respect to a common vacuum level, is shown in Figure 1. The decrease in ionization potential from ZnO to SiC is related to the decreasing binding energy of the anionic 2p valence states from O to N to C. The energetic cost associated with removing an electron (forming a hole) in the valence band of ZnO is therefore substantially larger than the cost to remove an
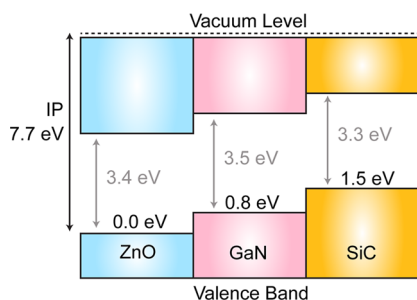
**Figure 1.** Calculated valence band energy of wurtzite ZnO, GaN, and SiC with respect to ZnO, which has an ionization potential (IP) of 7.7 eV. The known band gap values (from the literature[16]) can be used to determine the associated energies of the conduction band (i.e., the electron affinity).

electron from the valence band of SiC. Similar effects are seen in stannic oxide $(SnO_2)$,[21] and we expect related transparent conducting oxide materials (e.g., $TiO_2$ and $In_2O_3$), where the electron carrier stability dominates over electron rich defects, while holes are thermodynamically unstable.

There is not a 1:1 correspondence, however, between the band energies and the defect equilibrium. For example, the difference in ionization potential between ZnO and GaN is 77 kJ/mol (0.8 eV), and between ZnO and SiC it is 145 kJ/mol (1.5 eV), while the energy difference associated with exchanging a hole for a charged anionic lattice vacancy is −3 kJ/mol and +151 kJ/mol, respectively. Here, the ionization potential of GaN is lower in energy, but the defect level associated with the anion vacancy of ZnO is deeper in the band gap, so that the net change in energy is equivalent. The local chemistry of the lattice defect and the stability of charge states, as well as the long-range dielectric response of the material, contribute to the reaction energies. This analysis is consistent with recent results on the defect chemistry of another wide-gap semiconductor, CdO,[22] which possesses a relatively low ionization potential and is exclusively of n-type behavior. It is therefore incorrect to judge the stability of electrons and holes in a material by the band energies alone: a complete thermodynamic analysis is necessary.

*Where can we go from here?* For overcoming the fundamental preference for electron or hole carriers within a given material, in addition to kinetic control,[23] it should also be possible to vary the system boundary. For example, encapsulation with a robust low-permittivity oxide (e.g., $Al_2O_3$) would produce a prohibitively large barrier for chemical exchange, e.g., by atomic layer deposition.[24] Materials modeling approaches are also becoming more accurate, and the use of advanced density functionals, combined with the ability to treat system sizes beyond thousands of ions, will allow for the quantitative prediction of reactions for a wide range of materials. The thermodynamic approach discussed here will facilitate the study of electron and hole stability in functional systems, where experiments have not yet been performed, and can form a valuable component of computational materials design.[25−27]

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information
Computational methods and thermodynamic approach. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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