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ABSTRACT

I briefly review the basic physical principles underlying the formation energy of various intrinsic defects in common photovoltaic materials (chalcopyrites, II-VI's). I then use the above principles to explain why doping of semiconductors is, in general, limited and which design principles can be used to circumvent such limits. This work can help design strategies of doping absorber materials as well as explain how TCOs work. Recent results on the surprising stability of *polar* $(112) + (\bar{1}\bar{1}\bar{2})$ surfaces of CIS will also be described in this context.

1. Introduction

In this paper, I review some of the recent results we found in our Solid State Theory group on dopability of chalcopyrites, II-VI's and TCO's. We were able to formulate the main conditions needed for good n-type and p-type doping, and outline the basic design principles needed to improve doping.

2. Conditions for n-type doping via intrinsic defects [1].

(i) Donors must have shallow levels so they are readily ionizable. For ZnO this means that V_O , or Zn_i , or Zn_O must have levels near the CBM. Our calculations show that Zn_i has indeed a shallow level (while V_O is deep). For SnO_2 , V_O is shallow, as is Sn_i . Surprisingly, we find that hydrogen impurity also forms a shallow donor in these materials, which can also lead to n-typheness.

(ii) Donors must have a low formation enthalpy so that the concentration of donors is high. For ZnO we find that this holds for Zn_i that is easily formed, whereas in SnO_2 this holds for Sn_i . For $ZnIn_2Se_4$ this is In-on-Zn antisite.

(iii) Electron-killer centers must have *high* formation enthalpy, so their concentration is low. This means that O_i , V_{Zn} (in ZnO) or V_{Sn} (in SnO_2) have high formation enthalpy. Our calculations show that this is the case for ZnO and SnO_2 . In $ZnIn_2Se_4$ this is V_{Zn} .

We see that ZnO and SnO_2 are predicted to be easily n-dopable via intrinsic defects, and H impurities.

The reason that n-type doping is limited in $CuGaSe_2$ is the failure to fulfill condition (iii). This situation is summarized via the "phenomenological doping-limit rule": a material cannot be doped successfully n-type if its CBM is too close to vacuum (i.e., its electron affinity is too small). This is the case for diamond, AlN, $CuGaSe_2$, etc. In these cases, electron-killer defects such as cation-vacancy will form and compensate the electron-producing agent. Conversely, a material can be doped successfully n-type if its CBM is as far away from vacuum as possible (large electron affinity). This is the case in ZnO, SnO_2 , InP.

Design Principles: One can enhance n-type dopability by lowering the CBM, e.g., via N-alloying of III-V's or oxygen alloying in II-VI's.

3. Conditions for good p-type dopability via intrinsic defects:

(i) Acceptors must have shallow levels so they are readily ionizable. For ZnO this means that O_i and V_{Sn} are shallow, while for SnO_2 it means that O_i and V_{Sn} are shallow. Our calculation shows that for ZnO the V_{Sn} defect is shallow.

(ii) Acceptors must have low formation enthalpy so that the concentration of acceptors is high. Our calculation shows that for ZnO this is true only for O-rich but not for Zn-rich conditions.

(iii) Hole-killers must have high formation enthalpy so that they do not form. For ZnO this includes V_O , Zn_i or Zn_O . Our calculation shows that his condition is *not* met for ZnO where the hole-killer V_O and Zn_i are easily formed. This is the reason why ZnO cannot be doped (at least in equilibrium) p-type.

The situation can be summarized again by the phenomenological doping-limit rule: "a material cannot be doped p-type if its VBM is too far from the vacuum level (intrinsic work-function is too big). This is the case for common oxides such as ZnO, MgO, CaO, etc. In this case, hole-killers such as cation interstitials form readily, thus compensating hole formation. Conversely, a material can be doped p-type if its VBM is high in energy (small intrinsic work function). *Design principles:* p-type dopability can be enhanced by adding a d-band metal (e.g., Cu), since the d-states repel upwards the anion p-states that form the VBM. Thus, $CuB^{III}X_2^{VI}$ compounds are

easier to make p-type than II-VI's. Also, Telluride's (in II-VI's) and antimonides (in III-V's) have a high VBM energy, and thus are easily made p-type.

4. Origins of coexistence of conductivity and transparency in SnO₂ [2].

Stannic oxide (SnO₂) is a prototype "transparent conductor," exhibiting the seemingly contradictory properties of high metallic conductivity with nearly complete transparency in the visible range. First-principles calculations are employed to determine the conditions required for this unusual effect by investigating the role of intrinsic defects and hydrogen impurity. It is found that the tin interstitial and oxygen vacancy predominate in the defect structure of SnO₂ due to their low formation energies and attractive interaction between them. These intrinsic defects donate conduction electrons in undoped SnO₂ with almost no reduction in optical transparency. Moreover, hydrogen is found to act as an electron source in SnO₂.

We also find that (i) Sn_i has a very low formation energy in SnO₂ and will thus exist in large concentration. Furthermore, this off-stoichiometry-promoting defect also produces a donor level *inside* the conduction band, leading to instant ionization and conductivity. (ii) The reason for the stability of interstitial Sn in SnO₂ is the existence of *two* oxidation states of tin, i.e., Sn⁴⁺ (in SnO₂) and Sn²⁺ (in SnO). Thus, Sn_i can form in SnO₂ easily since it creates a local bonding environment that resembles that in stable SnO. (iii) The presence of Sn_i lowers dramatically the formation energy of V_O. This explains large oxygen deficiency. We explain (iv) the absence of spontaneous formation of acceptor "killer defects" and (v) the absence of inter conduction band absorption. Furthermore, (vi) despite the fact that H is expected to behave as an acceptor in an n-type material, the oxygen-bonded hydrogen in SnO₂ is found to enhance n-type conduction.

5. Defect-induced nonpolar-to-polar transition at the surface of chalcopyrite semiconductors [3].

In zinc-blende semiconductors, the *nonpolar* (110) surface is stabler than all polar surfaces because the formation of the latter require the creation of charge-neutralizing but energetically costly surface reconstruction. Our first-principles calculations on CuInSe₂ reveal that in the double-zincblende (chalcopyrite) structure, (112)-cation plus $(\bar{1}\bar{1}\bar{2})$ -

anion *polar* facets are lower in energy than the unafaceted nonpolar (110) plane, despite the resulting increased surface area. We show that this effect results from the remarkable stability of surface defects (Cu-vacancy, Cu-on-In antisite) in chalcopyrites, and explains the hitherto puzzling formation of polar microfacets when one attempts to grow a nonpolar chalcopyrite surface.

We predict the polar surface to be stabilized by Cu-vacancies (V_{Cu}) in Cu poor conditions, and by Cu-on-In antisite defects Cu_{In} in In poor conditions. Our result might explain the dramatic reduction in free-carrier density observed when growing the nominally nonpolar chalcopyrite surface that reverts to (112) + $(\bar{1}\bar{1}\bar{2})$ polar micro facets: The conditions for electrostatic stability require the surface defects considered here to be fully ionized, since otherwise they would not accomplish the needed charge neutralization of the polar surfaces. In particular, the electrostatic potential pushes the valence band up until it overlaps the acceptor defects at the (112) surface, ionizing them and releasing holes. These holes, however, do not provide free carriers within the bulk of the sample, as they are confined electrostatically at or near the anion surface. If the latter also has an ordered-defect reconstruction involving donors such as anion vacancies, these will exactly compensate the holes from the cation surface. In either case, the polar-faceted nonpolar plane is *autocompensated* by the equal areas of anion and cation facets leading to the observed dramatic decrease in carrier density. This compensation does not occur when the chalcopyrite (112) plane is grown alone.

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