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A phenomenological model for systematization and prediction of doping limits in II–VI and I–III–VI_2 compounds

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Semiconductors differ widely in their ability to be doped. As their band gap increases, it is usually possible to dope them either n or p type, but not both. This asymmetry is documented here, and explained phenomenologically in terms of the ''doping pinning rule.'' © *1998 American Institute of Physics.* [S0021-8979(98)03506-3]

I. INTRODUCTION

Technological applications of semiconductors depend critically on the ability to dope them. Yet, surprisingly, documentation, systematization, and our understanding of semiconductor dopability are quite limited. For example, Fig. 1 shows the experimentally observed n- and p-type maximal doping limits of II–VI and I–III–VI_2 semiconductors, as tabulated in Table I.[1–28] For different materials, the maximal doping limits vary by over 5 orders of magnitude. There are noticeable, but unexplained systematic trends in Fig. 1 showing asymmetry of n vs p dopability: e.g., ZnO, ZnS, CdS, and CdTe are good n-type conductors while ZnTe and $CuInTe_2$ are good p-type conductors. On the other hand, ZnO and ZnS cannot be made p type while $CuAlSe_2$ and $CuGaSe_2$ cannot be made n type. Another striking puzzle is that while $CuInSe_2$ can be doped both p and n type,[22] as we add Ga to form the $Cu(In_{1-x}Ga_x)Se_2$ alloy, the system can no longer be doped n type for large x.[22] Also, despite ZnO having the band gaps typical of an insulator, ZnO can be doped strongly n type, but not p type.

II. THE MODEL

Here we analyze the systematics underlying these data, using the phenomenological ''doping pinning rule.''[29]

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where $\beta = 1/kT$ is the temperature factor, and m^* is the appropriate effective mass. If we know the measured maximum electron or hole concentration, $N_{\max}^{(n/p)}$, we may obtain the experimental values of the upper and lower bounds for E

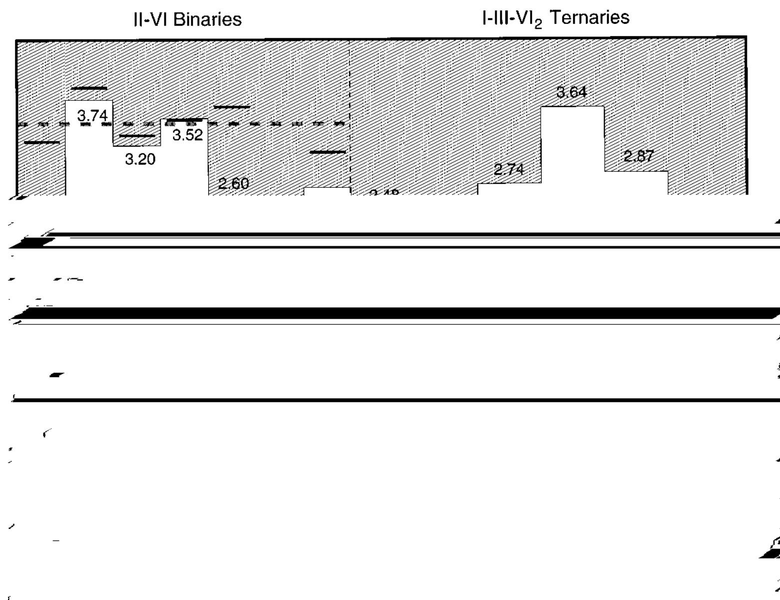

FIG. 2. Band diagram for II–VI and I–III–VI_2 compounds. Numerical values indicate the positions of the VBM and CBM in eV. Short solid lines indicate $E_{\rm pin,expt}$ values, calculated using Eq. (3). Long dashed lines indicate $E_{\rm pin}$ values. C/D denotes ''consistent with data.'' In these cases, the actual doping levels are too low to be measured. M/D denotes ''missing data.''

periments. It enables one to predict the pinning energies for a new material (and thus its maximal doping levels), if we know the pinning energies of the other materials and their band offsets with respect to the new material.

III. CALCULATION DETAILS

As discussed above, to line up $E_{\rm pin}^{(n/p)}$, we need the band offsets between semiconductors. While offsets can be measured, the measured values reflect not just the intrinsic (''natural'') band line up, but also the presence of a rough, impure interface or interfacial strains. Here, we adopt a consistent and uniform approach that is to calculate the ''natural band offset'' in which the effects of interfacial roughness, impurities, and strain are removed from the calculations. In particular, the calculations were performed using the local density approximation (LDA)[40,41] as implemented by the general potential, linearized augmented plan wave (LAPW) method.[42] The valence band offset $\Delta E_v(A/B)$ at the interface between two compounds A and B is calculated[43] using an analogous procedure employed in the photoemission core-level spectroscopy:

$$\Delta E_v(A/B)=\Delta E_{\rm VBM,c}^{B}-\Delta E_{\rm VBM',c'}^{A}+\Delta E_{c,c'}(A/B), \quad (4)$$

where the first two terms on the right hand side are the core level to valence band maximum energy separations for the individual solids A and B, respectively, and the last term is the difference in core level binding energy between A and B on each side of the A/B interface. The core-to-VBM energy difference $\Delta E_{\rm VBM,c}$ is calculated at their respective equilibrium structural parameters appropriate to the isolated compounds,[44] whereas the core energy level difference $\Delta E_{c,c'}$ between the two chalcopyrites is obtained from the calculation for the $(A)_n/(B)_n$ superlattice with (001) orientation. We have fully relaxed the strain at the interface. The conduction band offsets ΔE_c are obtained using the relation $\Delta E_g=\Delta E_c-\Delta E_v$, where $\Delta E_g=E_{g,B}-E_{g,A}$ is the measured (Table I) band gap difference between the compounds. The uncertainty in the calculated band offsets is less than 0.1 eV. Our calculated band offsets are shown in Fig. 2. For II–VI compounds, our values are different from what Faschinger *et al.*[39] have used.

IV. RESULTS AND DISCUSSION

Table I also shows the available experimental effective mass m^* for II–VI and I–III–VI_2 compounds. Effective mass enters $E_{\rm pin}$ via Eq. (3). Both the measured m^* and the use of the single band approximation for the valence band states in Eq. (3) lead to uncertainties. This can be improved, but has a moderate effect on the $E_{\rm pin,expt}$ values. Also, the measured doping limits $N_{\rm max}$ can be uncertain to within an order of magnitude. $E_{\rm pin,expt}$ deduced from the experimental data is thus only accurate to within a few tenths of an eV.

Figure 2 shows the aligned VBM and CBM using our calculated natural valence band offsets and the measured room temperature band gaps (Table I) for II–VI and I–III–VI_2 compounds. Experimentally deduced $E_{\rm pin,expt}^{(n)}$ and $E_{\rm pin,expt}^{(p)}$ are also placed in Fig. 2. We see the following:

(i) The vacuum-referred $E_{\rm pin,expt}^{(n/p)}$ values tend to line up. From this figure, we deduce, via arithmetic average the theoretical positions for $E_{\rm pin}^{(n)}$ and $E_{\rm pin}^{(p)}$ (shown by horizontal dashed lines in Fig. 2), for II–VI compounds, and separately for I–III–VI_2 compounds. The II–VI and I–III–VI_2 compounds have their own set of $E_{\rm pin}^{(n/p)}$ values (like the vacuum pinning rule for impurities).[34] The pinning energies that we deduced for the II–VI compounds are

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$$E_{\text{pin}}^{(n)} = E_{\text{CBM}}(\text{ZnSe}) + 0.25 \text{ eV}$$
$$E_{\text{pin}}^{(p)} = E_{\text{VBM}}(\text{ZnSe}) + 0.04 \text{ eV}, \qquad (5)$$

and for the I–III–VI_2 compounds, we have

$$E_{\text{pin}}^{(n)} = E_{\text{CBM}}(\text{CuInSe}_2) + 0.06 \text{ eV}$$
$$E_{\text{pin}}^{(p)} = E_{\text{VBM}}(\text{CuInSe}_2) - 0.12 \text{ eV}. \qquad (6)$$

Our calculated band offsets and the pinning energies for II–VI compounds agree reasonably well with those of Walukiewicz.[45]

There are a few exceptions to the line up, e.g., for p-type $CuInTe_2$, $E_{\text{pin,expt}}^{(p)}$ is about 0.5 eV above $E_{\text{pin}}^{(p)}$. For p-type ZnTe and CdTe, $E_{\text{pin,expt}}^{(p)}$ is about 0.5 eV higher than $E_{\text{pin}}^{(p)}$. Also, for n-type ZnSe, $E_{\text{pin,expt}}^{(\text{n})}$ is about 1 eV below $E_{\text{pin}}^{(n)}$. The four materials have been excluded from deriving the $E_{\text{pin}}^{(p)}$ values in Eqs. (5) and (6). Assuming that the line up rule is correct, we arrived at the conclusion that these materials could be doped more heavily p type than currently believed.

(ii) We can now phrase the doping limit rule: ''Materials in which the CBM is much higher than the lined up $E_{\text{pin}}^{(n)}$ value are difficult to dope n type. Materials in which the VBM is much lower than the lined up $E_{\text{pin}}^{(p)}$ value are difficult to dope p type.'' In other words, a good p-type conductor must have a sufficiently small work function, while a good n-type conductor must have a sufficiently large (positive) electron affinity.

(iii) The doping limit rule can explain some of the puzzles apparent in the doping data. In the past, dopability was thought (e.g., see Ref. 30) to be linked only to the size of the band gap: the larger the band gap is, the harder it is to dope the material. The argument was that larger band gap materials lower the formation energy of charge-compensating acceptor (donor) defects through charge transfer from the intentional donor (acceptor) more efficiently than smaller band gap materials. According to this view, ZnO having a large band gap should not be dopable. In fact, however, ZnO can be doped highly n type making it a transparent conductor. Thus, there is a pronounced asymmetry in the n vs p type dopability. The band gap value alone cannot explain such an asymmetry. Figure 2 provides the explanation for the asymmetry: what matters is not just the band gap, but the relative position of the band edges (the CBM and the VBM) with respect to the respective E_{pin} values. Despite the large band gap, the CBM of ZnO is significantly lower than $E_{\text{pin}}^{(n)}$. This induces heavy n-type dopability. The large band gap of ZnO, due to the low energy of O $2p$ orbital, pushes its

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