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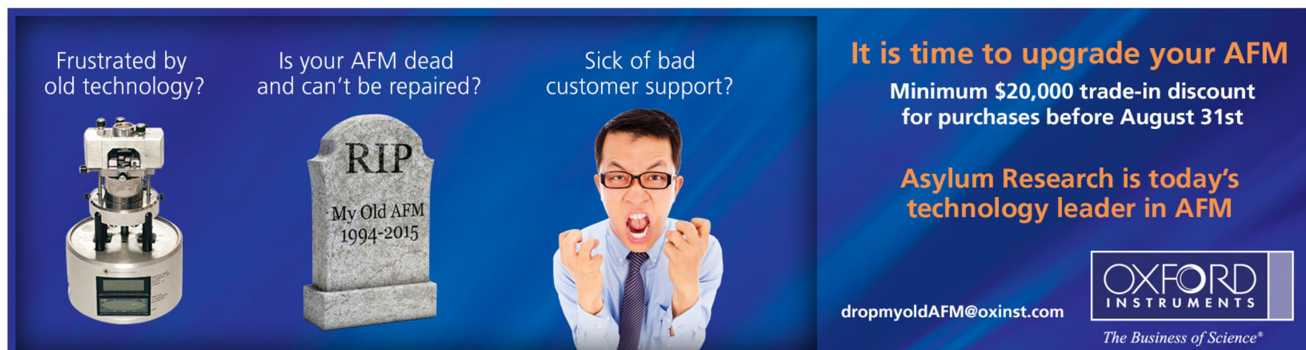

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A phenomenological model for systematization and prediction of doping limits in II–VI and I–III–VI_2 compounds

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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] We derive universal p-type pinning energy $E_{\rm pin}^{(p)}$ and n-type pinning energy $E_{\rm pin}^{(n)}$ for all II–VI and separately for all I–III–VI_2 semiconductors which not only systematize the known trends, but also predict dopability where it is unknown. The central insight of the model is that inability to dope and the p vs n asymmetry in dopability are not simply related to the existence of a wide gap, as assumed previously[30] but reflect the absolute position of the valence band maximum (VBM) and the conduction band minimum (CBM) with respect to some fixed energy (e.g., the vacuum).

In essence, doping limits exist because intentional doping by donors (acceptors) moves the Fermi energy E_F towards the CBM (VBM), thus lowering the formation energy of spontaneously formed acceptors (donors) which compensate the intentional donor (acceptor) dopants. This can be understood by noticing that the formation energy of a defect α of charge q is[31]

$$\Delta H(\alpha,q) = (\text{Constant}) + qE_F, \tag{1}$$

where the constant term is usually on the order of a few eV, and depends only on parameters such as the atomic chemical potentials during crystal growth but not on the Fermi energy.[32] The Fermi energy, measured from the valence band maximum, varies over the range of the band gap from the VBM to the CBM, typically also in eV range and its contribution to $\Delta H(\alpha,q)$ is magnified by a factor of q via Eq. (1). For acceptorlike defects, q is negative while for donorlike defects, q is positive. When we introduce donors, E_F moves towards the CBM, and consequently, by Eq. (1), the formation energies $\Delta H(\alpha,q)$ for α=acceptors ($q<0$) are lowered by amounts often comparable to the respective constant terms in Eq. (1). Lower formation energies result in higher (spontaneously formed) acceptor concentrations, thus compensating the intentionally introduced donors. This leads to the pinning of the Fermi energy near the CBM at an energy we term $E_{\rm pin}^{(n)}$. Likewise, doping by acceptors lowers E_F towards the VBM, so by Eq. (1), $\Delta H(\alpha,q)$ for α=donors ($q>0$) are lowered. This results in high concentrations of spontaneously formed donors that compensate the intentionally introduced acceptors, and pins the Fermi energy near the VBM at an energy we term $E_{\rm pin}^{(p)}$. These two processes thus set the upper and lower bounds for E_F,

$$E_{\rm pin}^{(p)} \leq E_F \leq E_{\rm pin}^{(n)}. \tag{2}$$

The maximal doping limit is hence decided by the value of E_F at which there are enough spontaneously generated defects to compensate the intentional dopants. The net concentration $N^{(n/p)}(T,E_F)$ of free carriers (electrons or holes) in a semiconductor is determined,[33] in the single, parabolic band approximation, by the position of the Fermi energy via Fermi–Dirac integral,

$$N^{(n/p)}(T,E_F^{(n/p)}) = \frac{1}{2\pi^2}(2m^{*,(n/p)})^{3/2} \times \int_0^\infty \frac{E^{1/2}dE}{\exp[\beta(E-E_F^{(n/p)})]+1}, \tag{3}$$

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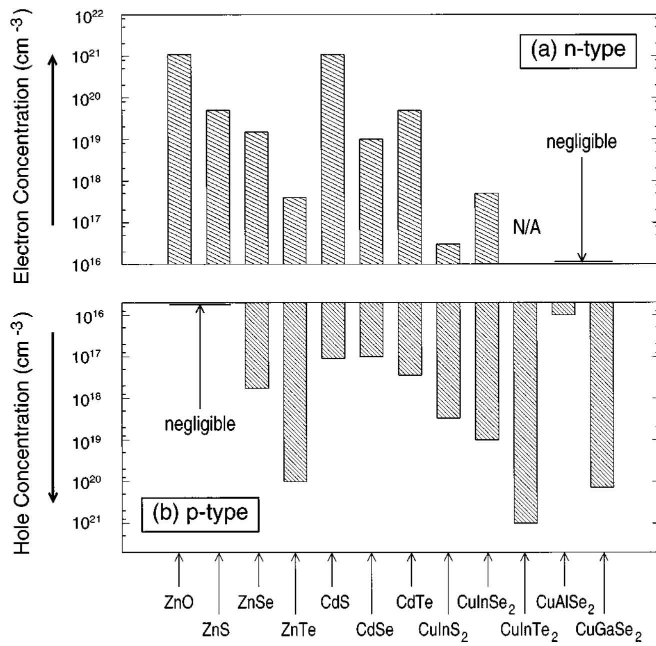

FIG. 1. Experimental maximum carrier concentrations in various II–VI and I–III–VI_2 compounds N/A means that, to our knowledge, no data are available. Note that data in this plot may correspond to different measurement temperatures. For details and references, see Table I.

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_F, i.e., $E_{\mathrm{pin,expt}}^{(n)}$ and $E_{\mathrm{pin,expt}}^{(p)}$ simply by inverting Eq. (3).

The pinning energies $E_{\mathrm{pin,expt}}^{(n)}$ and $E_{\mathrm{pin,expt}}^{(p)}$ from Eq. (3) have to be computed separately for each compound, and thus, by themselves, they contain no more information than $N_{\max}^{(n)}$ and $N_{\max}^{(p)}$. For example, knowing the values of the pinning energies for one compound does not tell us the values in another compound. This is evident when one refers, e.g., $E_{\mathrm{pin,expt}}^{(n)}$ of a given material to the CBM of that material, and inspects these band-edge-referred $E_{\mathrm{pin,expt}}$ values for a series of materials: no trends or regularities emerge.

Caldas *et al.*[34] have similarly noted that the band-edge-referred deep impurity levels (e.g., those of transition metals) in different semiconductors exhibit no chemical trends (e.g., Ref. 35, Fe is shallow in CdTe yet deep in ZnS and ZnSe). But, they noted that if the band edges of different host crystals are aligned according to their band offsets, the positions of a given deep impurity level in different materials become nearly a constant. Zunger[35,36] suggested that this ''vacuum pinning rule'' can be used in reverse to deduce band offsets by aligning the known levels of the transition metal impurities in different materials. Langer and Heinrich[37] have later applied this vacuum pinning rule[34–36] to a series of compounds. Walukiewicz[29,38] has then suggested that $E_{\mathrm{pin}}^{(n)}$ and $E_{\mathrm{pin}}^{(p)}$ can similarly be referred to the vacuum level, rather than to the band edge. He found for III–V compounds that if the band edges of different host materials are aligned according to their band offsets (or deep transition metal impurity levels), the position of $E_{\mathrm{pin}}^{(n)}$ and that of $E_{\mathrm{pin}}^{(p)}$ become nearly constants. This approach was applied[39] to a few II–VI compounds by Faschinger *et al.* We use here the same approach.

The argument given by Walukiewicz[29,38] for the alignment of $E_{\mathrm{pin}}^{(n)}$ and $E_{\mathrm{pin}}^{(p)}$ is that there is an intrinsic Fermi level stabilization energy, E_{FS}, due to the formation of some postulated amphoteric defect. E_F varies around E_{FS} up to a fixed amount ΔE_F: $E_{\mathrm{pin}}^{(n)} = E_{\mathrm{FS}} + \Delta E_F$ and $E_{\mathrm{pin}}^{(p)} = E_{\mathrm{FS}} - \Delta E_F$. E_{FS} has a fixed distance from absolute reference energy such as the vacuum level and will line up when two semiconductors are in close contact. Thus, $E_{\mathrm{pin}}^{(n)}$ and $E_{\mathrm{pin}}^{(p)}$ should also line up when referred to vacuum (i.e., when the band diagram is constructed according to the band offsets). The Walukiewicz model associating pinning with specific point defects is an Ansatz since so far it has not been rigorously proven by first-principles calculations. In fact, the pinning of $E_{\mathrm{pin}}^{(n)}$ and $E_{\mathrm{pin}}^{(p)}$ may have a much less specific origin. Nevertheless, the model provides useful insight consistent with available ex-

TABLE I. Measured carrier concentrations (at room temperature, or as shown in the parentheses), effective masses (in units of free electron mass), and energy band gaps (in units of eV) for various II–VI and I–III–VI_2 compounds.

	$p(\mathrm{cm}^{-3})$	$n(\mathrm{cm}^{-3})$	$m_{p,hh}^*$	m_n^*	E_g (Ref. 44)
ZnO	negligible	1.1×10^{21} (Ref. 1)		0.24 (Ref. 2)	3.20
ZnS	negligible	5×10^{19} (Ref. 3)		0.34 (Ref. 4)	3.74
ZnSe	5.7×10^{17} (300 °C) (Ref. 5)	1.5×10^{19} (Ref. 6)	0.58 (Ref. 7)	0.16 (Ref. 8)	2.67
ZnTe	10^{20} (Ref. 6)	4×10^{17} (Ref. 9)	0.60 (Ref. 10)	0.134 (Ref. 11)	2.26
CdS	1.1×10^{17} (Ref. 12)	1.1×10^{21} (Ref. 12)	0.51 (Ref. 13)	0.34[a]	2.42
CdSe	10^{17} (Ref. 14)	10^{19} (Ref. 15)	0.44 (Ref. 13)	0.11 (Ref. 16)	1.67
CdTe	2.8×10^{17} (Ref. 17)	5×10^{19} (Ref. 18)	0.40 (Ref. 19)	0.11 (Ref. 20)	1.53
$CuInS_2$	3×10^{18} (Ref. 21)	3×10^{16} (Ref. 22)	0.66[b]	0.09[b]	1.53
$CuInSe_2$	10^{19} (Ref. 23)	5×10^{17} (Ref. 24)	0.66 (Ref. 25)	0.09 (Ref. 26)	1.04
$CuInTe_2$	10^{20} (89 K) (Ref. 27)		0.66[b]		1.01
$CuAlSe_2$	$>10^{16}$ (Ref. 22)	negligible (Ref. 22)	0.73[c]		2.67
$CuGaSe_2$	1.4×10^{20} (Ref. 28)	negligible (Ref. 22)	0.73 (Ref. 28)		1.68
$CuIn_5Se_3$					1.28

[a]Value is taken from ZnS.
[b]Value is taken from $CuInSe_2$.
[c]Value is taken from $CuGaSe_2$.

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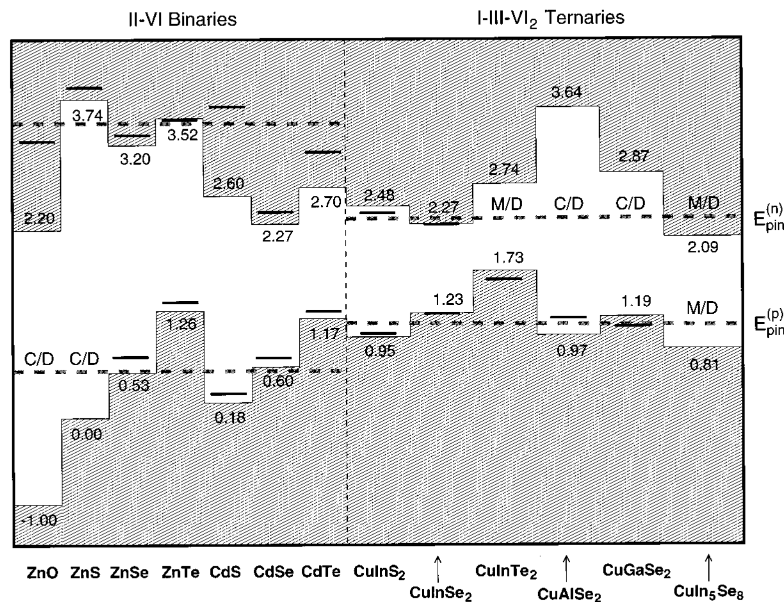

FIG. 2. Band diagram for II–VI and I–III–VI_2 compounds. Numerical values indicate the positions of the VBM and CBM in eV. Short solid lines indicate $E_{\text{pin,expt}}$ values, calculated using Eq. (3). Long dashed lines indicate E_{pin} values. C/D denotes ''consistent with data.'' In these cases, 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 $E_{\text{pin}}^{(n/p)}$, 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:

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

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 $\Delta E_{\text{VBM},c}$ 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_{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 $E_{\text{pin,expt}}$ values. Also, the measured doping limits $N_{\max}$ can be uncertain to within an order of magnitude. $E_{\text{pin,expt}}$ 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 $E_{\text{pin,expt}}^{(n)}$ and $E_{\text{pin,expt}}^{(p)}$ are also placed in Fig. 2. We see the following:

(i) The vacuum-referred $E_{\text{pin,expt}}^{(n/p)}$ values tend to line up. From this figure, we deduce, via arithmetic average the theoretical positions for $E_{\text{pin}}^{(n)}$ and $E_{\text{pin}}^{(p)}$ (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 $E_{\text{pin}}^{(n/p)}$ 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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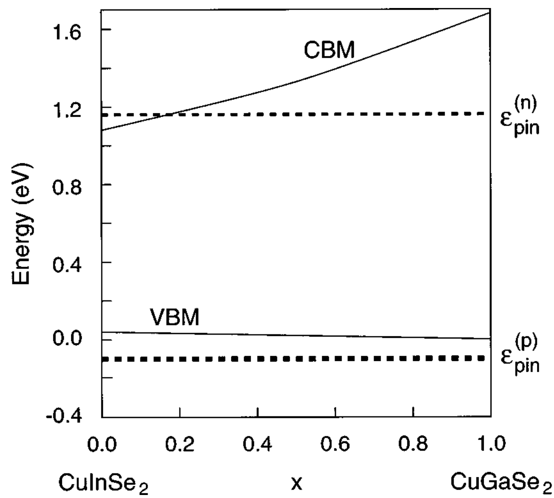

FIG. 3. Calculated E_{pin} values (dashed lines), with respect to the band edges (solid lines), for $(CuInSe_2)_x(CuGaSe_2)_{1-x}$.

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

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

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

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 $CuInTe_2$, $E_{pin,expt}^{(p)}$ is about 0.5 eV above $E_{pin}^{(p)}$. For p-type ZnTe and CdTe, $E_{pin,expt}^{(p)}$ is about 0.5 eV higher than $E_{pin}^{(p)}$. Also, for n-type ZnSe, $E_{pin,expt}^{(n)}$ is about 1 eV below $E_{pin}^{(n)}$. The four materials have been excluded from deriving the $E_{pin}^{(p)}$ 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 $E_{pin}^{(n)}$ value are difficult to dope n type. Materials in which the VBM is much lower than the lined up $E_{pin}^{(p)}$ 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 $E_{pin}^{(n)}$. This induces heavy n-type dopability. The large band gap of ZnO, due to the low energy of O $2p$ orbital, pushes its VBM much below $E_{pin}^{(p)}$, thus prohibiting p-type dopability.

(iv) Our $E_{pin}^{(n/p)}$ values show the following trends:

(1) Materials whose CBM are too high above $E_{pin}^{(n)}$ cannot be doped n type. These include $CuGaSe_2$, $CuAlSe_2$, and $CuInTe_2$.
(2) Materials whose VBM are too deep below $E_{pin}^{(p)}$ cannot be doped p type. These include ZnO and ZnS.
(3) Materials with CBM significantly lower than $E_{pin}^{(n)}$ can be doped heavily n type. These include ZnO, CdS, CdSe, and CdTe.
(4) Materials with VBM significantly higher than $E_{pin}^{(p)}$ can be doped heavily p type. These include $CuInTe_2$ and ZnTe.

(v) Figure 1 shows that II–VI compounds in general are better n-type conductors than the corresponding Cu–III–VI_2 compounds. This is mostly due to the much higher $E_{pin}^{(n)}$ for II–VIs than $E_{pin}^{(n)}$ for Cu–III–VI_2s (see Fig. 2).

(vi) Figure 1 shows that Cu–III–VI_2 compounds are in general better p-type conductors than the corresponding II–VI (Zn–VI or Cd–VI) compounds. This can be accounted for since the VBMs of the chalcopyrites are high due to p-d repulsion[46] with Cu d. Thus, strong p-d coupling seems to encourage p dopability.

(vii) For $Cu(Ga_xIn_{1-x})Se_2$ alloy, our calculation (see Fig. 3) shows that this material has good p-type conductivity for all x value while it is good n-type conductor only for $x < 0.2$ beyond which n-type conductivity is difficult.

V. SUMMARY

In summary, we have calculated the natural band offsets both within and between the II–VI and I–III–VI_2 compounds. We quantify the comparison of the doping pinning rule against available experimental data for II–VI compounds. Through this study, a more general trend in doping has been established that includes not only the conventional III–V and II–VI semiconductors but also the I–III–VI_2 ternaries and their alloys.

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