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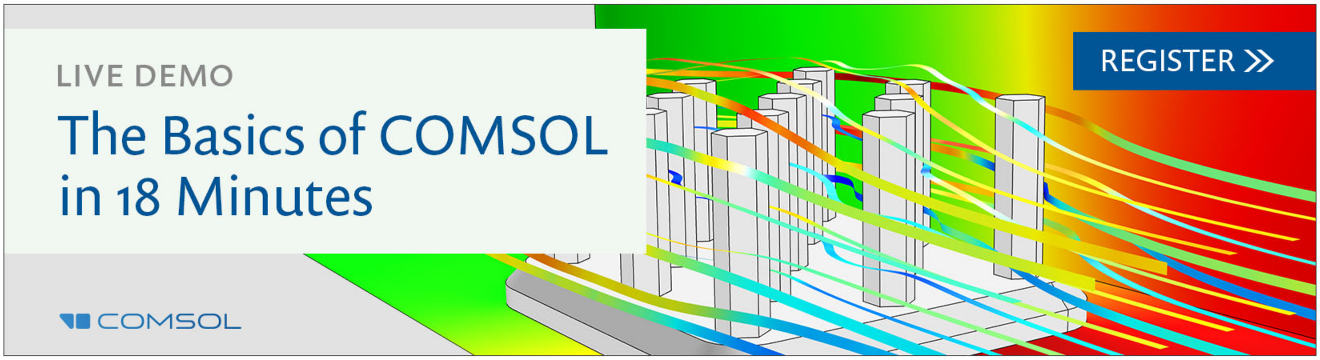

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Practical doping principles

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Theoretical investigations of doping of several wide-gap materials suggest a number of rather general, practical "doping principles" that may help guide experimental strategies for overcoming doping bottlenecks. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1584074]

Since the operation of carrier-transporting heterojunction devices is predicated on ambipolar (*p*- and *n*-type) doping, the failure to successfully dope certain classes of materials is an important bottleneck for the technological utilization of these materials in electronic devices. As the band gap of a material increases (e.g., Si→GaAs→ZnSe→ZnO) it generally becomes increasingly difficult to dope it in a symmetric (*n* and *p* type) fashion. For example, whereas diamond can be doped *p* type, its *n*-type doping is rather difficult;[1] conversely, while ZnO[2–5] and other main-group oxides[6] can be readily doped *n* type, their *p*-type doping is problematic. Striking doping regularities also appear in compounds belonging to the same chemical class, e.g., ZnTe and AlN are difficult to dope *n* type, whereas CdS and GaN can be readily doped *n* type;[7] $CuInSe_2$ can give *n*-type conduction whereas $CuGaSe_2$ can exhibit only *p*-type conduction.[8] Doping bottlenecks have attracted significant attention by both experimentalists (see reviews in Refs. 1 and 2) and theorists,[4–17] providing highly detailed studies on individual cases. Yet, this case-by-case focus has sometimes detracted from observing general regularities and formulating "doping rules." In this work, I attempt to distill from recent theoretical studies of individual hard-to-dope systems[4–17] some general, practical doping principles, loosely referred to as doping rules. Although such Pauling-esque rules do not cover all cases, or identify all exceptions, they might provide basic design guidelines for systematically navigating in the complex parameter space of experimental attempts to overcome doping bottlenecks.

I will divide the practical doping rules into those that emerge from (i) Fermi-level-induced compensation effects (spontaneous generation of "killer defects"), (ii) the effects of adjusting the chemical potentials of the different elements, and (iii) local bonding effects of the dopant to the lattice. These effects are encoded in the basic three-term formula that describes the formation enthalpy of dopant *D* of charge state *q* in host crystal *H*:

$$\Delta H^{(D,q)}(\mu,E_F)=qE_F+n_D(\mu_D-\mu_H)+\Delta E_b, \tag{1}$$

where μ_D and μ_H are the chemical potentials of the dopants and host, E_F is the electro (chemical) potential (Fermi energy), n_D is the number of dopants, $\Delta E_b = E(\text{host}+\text{defect}) - E(\text{host})$ is the excess energy of the local chemical bonds around the dopant, and E is the total energy.

(i) *Doping rules pertaining to Fermi-level-induced compensation effects.* When an electron-producing donor α (charge $q>0$) is incorporated into a solid, it donates electrons that join the free-carrier reservoir whose energy is E_F; thus, as Eq. (1) shows, the total donor formation energy increases linearly with E_F. Similarly, formation of electron-capturing acceptors (charge $q<0$) entails removing q electrons from the Fermi reservoir, thus, the acceptor formation energy decreases linearly with E_F. These trends are depicted schematically in Fig. 1(a). It follows from the linear dependencies on E_F that when we deliberately dope a materials *n*-type (via donors), thus shifting its E_F towards the conduction band, the formation energy of native acceptors, such as cation vacancies V_C^- or *DX* centers would decrease to a point that such "electron-killers" will form spontaneously. For example,[15] *n*-type doping of GaAs:Si is limited by the spontaneous formation of V_{Ga}, whereas *n*-type doping of Si:As is limited[16] by the formation of V_{Si}. An extreme example for the spontaneous formation of cation vacancies in response to *n*-type doping is the creation of the ordered-vacancy structure $\square CuGaGeSe_4$ when one dopes one of the Ga sites of chalcopyrite $2CuGaSe_2 = Cu_2Ga_2Se_4$ by germanium.[18] In general, once one reaches the Fermi energy E_F, called "*n*-

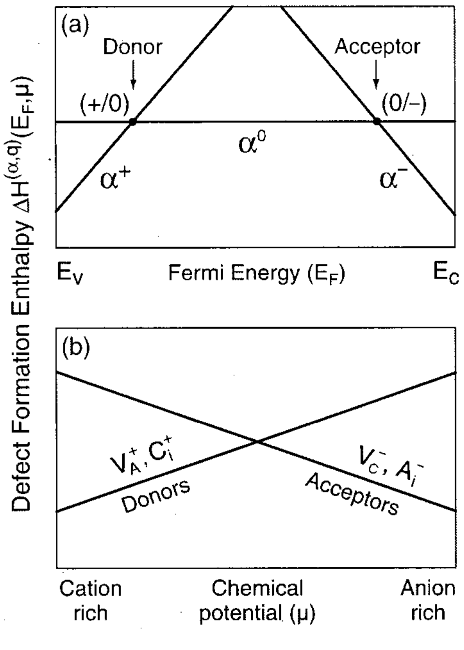

FIG. 1. (a) Schematic depiction of the dependence of the formation enthalpy of defect α in charge states $q=+$, 0 and $-$ on the Fermi energy. The solid dots denote the donor (0/+) and acceptor (0/−) transition energies. (b) Schematic depiction of the formation enthalpy of some intrinsic donors (anion vacancy V_A, cation interstitial C_i) and intrinsic acceptors (cation vacancy V_C and anion interstitial A_i) on the chemical potential.

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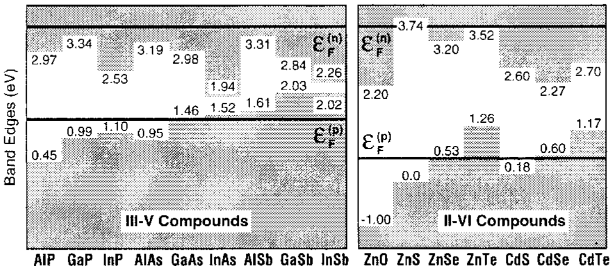

FIG. 2. The *n*-type pinning energy $\varepsilon_F^{(n)}$ and *p*-type pinning energy $\varepsilon_F^{(p)}$ are shown relative to the absolute band edge energies (from Ref. 19) of III–V and II–VI semiconductors.

type pinning energy" $E_F^{(n)}$, at which such killer defect (e.g., cation vacancy) forms, no further progress in *n* doping can be made, since the spontaneously generated electron killers will negate the deliberately introduced donors. Similarly, deliberate *p* doping by acceptors (shifting E_F towards the valence band) will instigate at some point $E_F^{(p)}$ called "*p*-type pinning energy" the spontaneous formation of native "hole killers" such as anion vacancy V_A^+ or cation interstitial C_i^+ at which point *p*-type doping is defeated. Figure 2 shows the approximate positions of $E_F^{(n)}$ and $E_F^{(p)}$ in a number of group III–V and II–VI semiconductors, as obtained from first-principles calculations[10] and independently from measured maximal carrier densities.[9,11] In this figure the valence band maxima were aligned according to the calculated (unstrained) band offsets, collected in Ref. 19 for most compound semiconductors, whereas the band gap values are taken from low-temperature experimental data. There is an approximate alignment[10] of the pinning levels (horizontal lines) within given chemical groups of compounds. The positions of the pining levels with respect to the host crystal band edges determine dopability. For example, in ZnO or ZnS the $E_F^{(p)}$ level is considerably above the valence band maximum (VBM). Thus, the downwards-moving E_F in deliberate *p*-type doping will encounter $E_F^{(p)}$ before encountering the VBM. At this point the system will generate spontaneous hole-killers (e.g., Zn_i or V_O) before any significant doping commences. Hence, the difficulty in equilibrium *p* doping of ZnO. In contrast, in tellurides or antimonides $E_F^{(p)}$ is at or below the VBM, so a considerable amount of holes can be generated before the pinning energy is encountered and killer defects form. The relevant doping rules summarized in Fig. 3 are as follows.

	n-Type Doping	**p-Type Doping**
Killer defects	V_C^-, A_i^+ [1]	V_A^+, C_i^+ [2]
To avoid killer, use	• Low CBM [1] • Cation rich [3]	• High VBM [2] • Anion rich [4]
To enhance solubility on **anion** site, use	Anion poor [5]	Anion poor [5]
To enhance solubility on **cation** site, use	Cation poor [6]	Cation poor [6]

FIG. 3. Summary of the doping rules. Their number is given in parenthesis.

Rule 1: "*n*-type doping is facilitated by materials whose conduction band minima (CBM) are far from the vacuum level, i.e., materials with large bulk-intrinsic electron affinities χ. Conversely, *n*-type doping tends to be compensated in materials with small bulk-intrinsic electron affinities." This rule reflects the difficulty in *n*-type doping of ZnTe and AlN (Ref. 7) or diamond[1] ($\chi \cong 0$), the ease of *n*-type doping InAs, ZnO, and CdS (large χ). This rule further suggests that lowering the CBM via selective alloying (e.g., adding nitrogen to III–V's which leads to huge downwards CBM bowing) will enhance *n*-type doping.[20] Any creative chemical modification that lowers the CBM could facilitate *n*-type doping.

Rule 2: "*p*-type doping is facilitated by materials whose VBM is close to the vacuum level, i.e., small bulk-intrinsic ionization potential Φ. Conversely, *p*-type doping tends to be compensated in materials with large bulk-intrinsic ionization energies." This rule reflects the ease of *p*-type doping of antimonides and tellurides (small Φ), and the difficulty in *p*-type doping of the more electronegative oxides and sulphides (large Φ). The rule suggests that enhanced *p*-type doping can be facilitated by alloying an element that leads to upward bowing of the VBM. One way to shift the VBM upwards is to add a tetrahedrally bonded 3*d* element with active *d* states, so that coupling with the anion *p* band will displace the latter to higher energies. An example is the *p* typeness[21] of $\mathrm{CuAlO_2}$ as compared with oxides such as MgO or ZnO that lack shallow *d* states and, consequently, have deeper VBM energies and are difficult to dope *p* type. Any creative chemical modification that raises the VBM could facilitate *p*-type doping.

Rules 1 and 2 explain why diamond is difficult to dope *n* type[1] (χ only <0.2 eV) but it is easier to dope diamond *p*-type (Φ as low as ~ 5 eV), whereas the other form of carbon[22] $\mathrm{C_{60}}$ is easy to dope *n* type (χ as big as 2.7 eV), but difficult to dope *p* type (Φ as big as 7.6 eV). Also, rules 1 and 2, taken together imply that ambipolar doping requires, in general, a small minimum (not necessarily optically allowed) gap, a well-known result. But these rules clarify that the origin of doping asymmetry in different materials depends on χ and Φ separately.

The next rules refer to ways of eliminating the particular pinning centers ("kill the killer").

Rule 3: "Since *n*-type doping is inhibited by electron-killers such as the cation vacancy V_C^-, this can be overcome by designing growth conditions which destabilize cation vacancies ("kill the killer"), e.g., the use of host cation-rich growth conditions." Naturally, the extent of attainable host cation richness is limited by the requirement of not precipitating competing cation phases such as elemental cation metals or cation-dopant compounds. Any other method that discourages formation of cation vacancies will facilitate *n*-type doping. This includes passivation of cation vacancies, e.g., by hydrogen.[13] In general, materials that form cation vacancies readily are difficult to dope *n* type.

Rule 4: "Since *p*-type doping is inhibited by hole killers such as anion vacancy V_A^+ and cation interstitials C_i^+, this can be overcome by designing growth conditions which destabilize these defects ("kill the killer"), e.g., the use of host anion-rich growth conditions, or agents that form complexes with killer defects, or prevent E_F from moving.'' An example is the use of H during Mg doping[12] of GaN: without H, excessive *p*-type Mg doping will lead to the spontaneous formation of V_N once the Fermi energy moves sufficiently towards the VBM. But since H acts as a donor, it prevents the movement of E_F towards the VBM, thus defeats the formation of the V_N killer defect. Subsequently, H is annealed out. This rule suggests, for example, that *p*-type doping of oxides can be facilitated by creating internal oxygen precipitates that eliminate oxygen vacancies, e.g., using NO or NO_2 sources[3,5] for nitrogen-doping of ZnO, or using Li_2O sources for Li doping of MgO (Ref. 23).

(ii) *Doping rules pertaining to chemical potential effects.* In general, the second term of Eq. (1) shows how ΔH for formation of anionic or cationic dopants can be regulated via control of the chemical potentials during growth [Fig. 1(b)]. This figure illustrates the fact that the enthalpy of forming anion vacancies decreases under host cation-rich conditions, whereas the enthalpy of forming cation vacancies decreases under host anion-rich conditions. Here, ''cation rich'' means the highest cation chemical potential affordable without precipitating the elemental cation metal or other competing phases. For a cation-site dopant (e.g., Mn in GaAs), a competing phase could be a compound between the dopant and the host anion (e.g., MnAs). The more stable this competing phase is, the lower the dopant chemical potential must be to avoid precipitation.

Rule 5: ''Anion-substituting dopants will be more soluble under host anion poor (=host cation rich) growth conditions.'' This rule reflects the fact that defects that donate host anions to the chemical reservoir (e.g., anion vacancy V_A^+ or cation antisite C_A^+) are easier to form if this reservoir has low anion chemical potential μ_A (i.e., anion-poor). Thus, *p*-type Zn$\underline{\mathrm{O}}$:N or *n*-type Zn$\underline{\mathrm{O}}$:F are best grown under Zn-rich conditions[24] and *p*-type GaAs:C is best grown under Ga-rich conditions. *n*-type doping via anion substitutions (using anion-poor conditions) satisfies simultaneously rules 3 and 5, e.g., *n*-type Zn$\underline{\mathrm{O}}$:F. (see Fig. 3)

Rule 6: ''Cation-substituting dopants will be more soluble under host-cation poor (=host anion rich) growth conditions.'' This rule reflects the fact that defects which donate host cations to the chemical reservoir (e.g., V_C^- or anion interstitial A_i^-) are easier to form if this reservoir has low cation chemical energy μ_C (cation poor). Indeed, *p*-type GaAs:Zn or GaAs:Mn are best grown under As-rich conditions (low-temperature growth). *p*-type doping via cation substitution (using cation-poor conditions) satisfies simultaneously rules 4 and 6, e.g., *p*-type GaAs:Zn (see Fig. 3).

As seen in Fig. 3, if one desires to attempt *n*-type doping via cation substitution, by rule 6 one needs cation-poor conditions. However, by rule 3 this could enhance the formation of electron killer V_C. One then needs to defeat the spontaneous formation of cation vacancy electron killers. Thus, the position of the pinning level (Fig. 2) alone does not guarantee doping in such cases because of the opposing trends of solubility rules 5 and 6, and pinning rules 3 and 4. Similarly, if one desires to attempt *p*-type doping via anion substitution, by rule 5 one needs anion-poor conditions. However, by rule 4 this could enhance the formation of hole killer V_A. Then, one needs to defeat the spontaneous formation of anion vacancy hole-killers. Thus, all other things being equal, it may prove easier to do *p*-type doping via cation-site substitution using anion-rich conditions, whereas *n*-type doping can be done via anion-site substitution using cation-rich conditions.

(iii) *Doping rules pertaining to local defect bonding effects.* Although large concentration of N can now be introduced into ZnO[3], the desired *p*-type doping is often unstable over time, since the nitrogen bond to Zn is not as stable as the original Zn–O bond [$\Delta E_b > 0$ in Eq. (1)]. This limitation might be overcome via ''cluster doping.''[14]

Rule 7: ''The local chemical bonding energy around the dopant could be enhanced via decorating the dopant by strongly bonding ligands which do not disrupt the host bonds.'' For example, whereas the four Zn–N bonds formed when N dopes the O site in ZnO are weak, replacing in otherwise pure ZnO one Zn by Al (a donor) and replacing the four oxygen neighbors by four nitrogen atoms (acceptors) creates in total four very strong Al–N bonds around $\mathrm{Al_{Zn}}$, followed by 12 weak Zn–N bonds around each of the four N sites. Since AlN is extremely stable, $\Delta E_b = 4E_{\mathrm{Al-N}} + 12E_{\mathrm{Zn-N}} < 0$. Such cluster doping ideas with ratio of 4:1 between acceptors and donors could facilitate stable local dopant bonding and enhanced solubility.[14] Interestingly, this cluster-doping is predicted to be more stable than ''codoping''[25] between acceptors and donor (ratio of 2:1).

The seven practical ''doping rules'' described here could provide guidelines for creative, yet educated experimentations with various doping strategies for difficult-to-dope wide-gap materials. They are summarized in Fig. 3.

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