## 3. Computational design of semiconductor systems

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## **3.5 Bandgap engineering of semiconductors**

Why using semiconductor alloys? From the viewpoint of technological interest, we can tune materials properties with strain such as strained-layer epitaxy proposed by Prof. Fitzgerald. [see Modification of bandstructures]

## **3.6 Doping control of wide bandgap semiconductors**

The key quantities that characterize a defect in a semiconductor are its concentration and the position of the energy levels with respect to the band edges of the host material. Defects that occur in low concentrations will have a negligible impact on the properties of the material. The position of the defect levels with respect to the host band edges determines the effects on the electrical and optical properties of the host. Both of the defect formation energies and transition levels can be determined entirely from first-principles calculation.

There are three main modes of failure to dope a material: (a) The desired impurity atom has limited solubility in a host crystal and cannot be introduced into the lattice. Examples include large impurity atoms in small host crystals. (b) Inside a host crystal, the desired dopant produces a deep level, so the impurity remains un-ionized at normal temperatures. (c) The impurity atom inside a host crystal can ionize. But as the free carriers are spontaneously generated, oppositely charged native defect forms and compensates the effect of the intentional dopant. This type of "failure to dope" is from the free-carriers themselves, thus represents the true doping limit of a material.

The energy of a charge-neutral impurity  $A_0$  in a crystal depends on the atomic chemical

potential of the impurity *A*. As shown in the figure on the left side, to introduce a charge-neutral impurity into the crystal, the impurity element is first taken from a given

reservoir having a finite energy  $\mu_A$ . After it is inserted into the host crystal, the host atom must

be removed and moved to a reservoir as depicted in the right figure.



From the relationship of total energy conservation law  $E_{tot}(0) + \mu_A = E_{tot}(A^0) - E(A^0) + \mu_{host}$ , the formation energy of the impurity can be determined:

 $E(A^{0}) = E_{tot}(A^{0}) - E_{tot}(0) - \mu_{A} + \mu_{host} , \qquad (1)$ 

where  $E_{tot}(A^0)$  is the total energy of the host crystal having one impurity;  $E_{tot}(0)$  is the total energy of the host without any impurity;  $\mu_A$  is the energy of the impurity in the reservoir from which it is taken, *e.g.*, atomic or molecular gas of the impurity atoms; and, in the case of a substitutional impurity,  $\mu_{host}$  is the energy of the host atom in its respective reservoir. In thermal equilibrium, the reservoir energy for impurity in host cannot be higher than the energy of pure solid of impurity element; otherwise, impurity will leave the host and

precipitate as a solid. Furthermore, thermal equilibrium requires that  $\mu_{host}$  equals the energy

of the host solid to make the host crystal stable under the doping condition. For convenience, we will set the energies of all elemental solids (or molecules) to zero; so, in addition to Eq. (1), we have the following restrictions on the atomic chemical potentials

$$\mu_A \le 0, \quad \mu_{host} = \Delta H_{host}, \quad (2)$$

where  $\Box \Delta H_{host}$  is the formation enthalpy of the host.

For binary crystals  $C^+ - X^-$ , the host is made of cation ( $C^+$ ) and anion (X), the formation energy of the impurity becomes

$$E(A^0) = E_{tot}(A^0) - E_{tot}(0) - \Delta N_C(E_C + \Delta \mu_C) - \Delta N_X(E_X + \Delta \mu_X),$$

where  $\Delta N_C$  and  $\Delta N_X$  are the differences in the number of cation *C* and anion *X* between these supercells. For instance,  $\Delta N_C = 0$  and  $\Delta N_X = -1$  for the *X* vacancy and  $\Delta N_C = 1$  and  $\Delta N_X = 0$  for the *C* interstitial.  $E_C$  and  $E_X$  are the total energies of the *C* solid and X<sub>2</sub> molecule per atom, respectively.

The chemical potentials  $\mu_C$  and  $\mu_X$  must satisfy

$$\mu_C \le 0, \, \mu_X \le 0, \, \mu_A \le 0; \quad \mu_C + \mu_X = \Delta H_{host} \quad .$$
 (3)

In the binary compounds, it is a common practice to consider only  $\mu_C$  from which  $\mu_X$  is determined by Eq. (3), one then found that  $\mu_C$  is bounded by  $\Delta H_{host} \leq \mu_C \leq 0$ . Native defects are a special case, where the defect formation enthalpy  $E(D^0)$  is only a function of  $\mu_C$ . As an example of calculated formation enthalpies of a few native defects in p-type GaAs. The Ga-on-As antisite  $Ga_{As}$  and the As vacancy  $V_{As}$  are easy to form in Ga-rich conditions, whereas in As-rich conditions, the  $Ga_{As}$  and  $V_{As}$  are easy to form instead.

The energy of introducing a neutral impurity  $A^0$  into a crystal does not depend on  $E_F$ .

However, the energy of introducing a positively charged impurity  $A^+$  equals the energy of introducing a neutral impurity  $A^0$ , minus the energy E(0/+) needed to ionize  $A^0$  to form  $A^+$ ,

plus the energy of the ionized electron. Because this electron resides in the Fermi reservoir, its energy is  $E_F$ , thus  $E(A^+) = E(A^0) - E(0 / +) + E_F$ . So, donors that produce electrons in the

reaction  $A^0 \to A^+ + e^-$  are more difficult to form in electron-rich (n-type) materials. Similarly, for acceptors, the formation enthalpy decreases as  $E_F$  increases:

$$E(A^{-}) - E(- \ / \ 0) + E_{F} = E(A^{0}) \quad \Rightarrow E(A^{-}) = E(A^{0}) + E(- \ / \ 0) - E_{F}.$$

So, acceptors (that produce holes in the reaction  $A^0 \rightarrow A^- + h$ ) are more difficult to form in hole-rich (*p*-type) materials.

Simple considerations show the following: (a) If we dope a material intentionally *n*-type via some donor impurity, as  $E_F$  moves up in the gap, the formation enthalpy of native acceptors  $E(A^-)$  decreases. At some point, the formation energy is so low that such native acceptors could form spontaneously, thus negating the effect of the intentionally introduced donors. (b) If we dope a material intentionally *p*-type via some acceptor impurity, as  $E_F$  moves down in the gap, the formation enthalpy of native donors  $E(A^+)$  decreases. At some point, the formation enthalpy is so low that such native donors could form spontaneously, thus negating the effect of the intentionally, thus negating the effect of the intentionally, thus negating the effect of the intentionally thus negating the effect of the intentionally introduced acceptors.

## **3.7 Diluted magnetic semiconductors (DMS)**

See Lecture 12.