

# Predictive models for co-doping effects between combinations of donors (P/As/Sb) and acceptors (B/Ga/In)

Chihak Ahn

Department of Physics  
University of Washington  
Seattle, Washington 98195  
Email: chahn@u.washington.edu

Scott T. Dunham

Department of Electrical Engineering  
University of Washington  
Seattle, Washington 98195  
Email: dunham@ee.washington.edu

**Abstract**— We studied co-doping effects in silicon using first principles calculations, with particular attention to charge compensation, Coulomb interactions and strain compensation. We find that for B-doped systems, As or Sb counter-doping reduces the hole concentration, but that due to strong binding of multiple P atoms, Ga or In counter-doping can increase electron density in P doped material. For acceptor-acceptor pairing, we find the B-B interaction to be repulsive as expected due to Coulombic effects, but calculations show a surprisingly strong attractive binding between B and In, which we attribute to hole localization. However, B-In binding is not promising for enhancing hole concentration since BIn pairs are deep acceptors. Both donor-acceptor and acceptor-acceptor pairing can be helpful in reducing dopant diffusion leading to more abrupt junctions.

## I. INTRODUCTION

At the cutting edge of silicon technology, understanding interactions between multiple dopants is required to continue MOSFET scaling. In modern ULSI technology, heavily co-doped regions frequently occur, and it is observed that counter-doping is beneficial to reduce the junction depth [1]. There are two primary factors we consider for counter-doping effects: global strain compensation and local binding energy. Strain compensation between a small atom and a large atom can enhance the dopant segregation [2] and reduce diffusivity [3]. For dopants, a major component of local binding is the Coulomb interaction.

Co-doping can increase chemical concentration of dopants and retard dopant diffusion as experimentally observed [4], [5], [6]. However, it is hard to separate out the effects of strain, electrostatics, or local chemical bonding from other dopant/defect interactions by experiment, since in many experimental setups there is no simple way to control individual effects. In our *ab-initio* study, we separate strain energy and binding energy within linear elasticity limit and investigate strain compensation and local binding individually.

## II. METHODS

We calculated total free energy of 64 atoms supercells, using density functional theory (DFT) code VASP [7] in generalized gradient approximation (GGA) with ultrasoft Vanderbilt type

pseudopotentials [8]. All B related calculations were done with 340 eV cut-off and P related calculations were done with 250 eV cut-off.  $2^3$  Monkhorst-Pack  $\vec{k}$ -points sampling [9] was used throughout.

When donors and acceptors coexist in silicon matrix, charge transfer occurs and bandgap crossing should be taken into account in calculating the formation energy of donor-acceptor pairs in reference to neutral donors and acceptors. However, it is known that DFT is inaccurate in calculating bandgaps. To avoid this bandgap crossing, we used charged donors and acceptors as reference states. For acceptor-acceptor pairs (e.g. BIn) neutral supercells were used as a reference, since there is no bandgap crossing. The formation energy of a donor-acceptor pair is given as,

$$E_{MN}^f = E_{Si_{62}MN} - E_{Si_{63}M^+} - E_{Si_{63}N^-} + E_{Si_{64}}. \quad (1)$$

Table II lists the calculated formation energies. Since DFT overestimates the free energy of charged supercells [10], the first order correction was applied ( $q^2\alpha/2\epsilon L \sim 0.16$  eV). For comparison, the two primary components of the formation energy, electrostatic energy and stress energy, are also listed in Table II.  $E^C$  is calculated by monopole approximation, assuming fully ionized donor and acceptor.

Within elastic limit of material, the free energy of supercell is represented as

$$E = E_0 + \frac{V_0}{2}(\vec{\epsilon} - \Delta\vec{\epsilon})\mathbf{C}(\vec{\epsilon} - \Delta\vec{\epsilon}), \quad (2)$$

where  $E_0$  is the minimum energy at relaxed lattice constant,  $V_0$  is the volume of super cell,  $\epsilon$  is applied strain,  $\Delta\epsilon$  is the induced strain, and  $\mathbf{C}$  is the elastic stiffness tensor of Si.  $E^S$  in Table II was calculated from Eq. 1, Eq. 2 and the induced strains listed in Table I.

The binding energy of a donor-acceptor pair can increase solubility and retard diffusion as reported previously [4], [5], [11], [12]. To estimate the impact of ion pairing on charge carrier density, we calculated the pairing ratio between primary dopant and counter dopant due to binding. In this calculation, the global strain compensation is ignored since

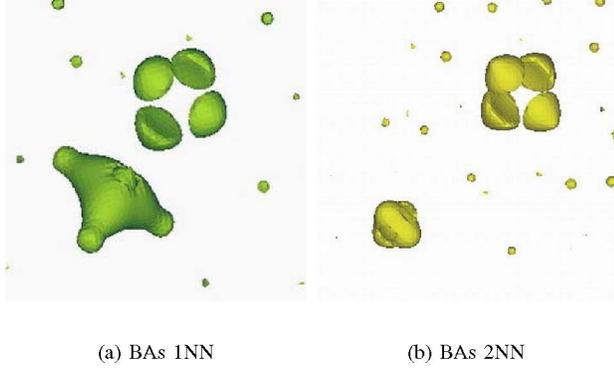


Fig. 1. Charge distribution of BAs at 1NN and 2NN. B is located lower left and As is at upper right. Electrons around As are distributed approximately symmetrically in both cases. Their distribution around B is skewed away from As ion at 1NN, but is nearly symmetric at 2NN.

TABLE I

INDUCED STRAIN DUE TO GROUP III/V ELEMENTS. THE VALUES ARE NORMALIZED TO SI ATOMIC VOLUME AND REPORTED IN REFERENCE TO THE GGA SI EQUILIBRIUM LATTICE PARAMETER OF 5.457 Å.

	B	As	Sb	P	Ga	In
$\Delta\epsilon$	-0.30	0.018	0.18	-0.078	0.066	0.21

it is minimal within the equilibrium solubility limit (ESL) of counter dopant. The ratio between total number of paired primary dopant atoms (e.g., B or P) and total number of secondary dopant atoms (co-dopants) is given by

$$\frac{N_{paired}}{N_c^{Total}} = \frac{\sum_i i C(f_i)}{\sum_i C(f_i)}, \quad (3)$$

where  $C(f_i)$  is the concentration of given configuration  $f_i$ , and using mass action law at the equilibrium it is given by

$$C(f_{i+1}) = \frac{A_{i+1}}{D_{i+1}} C(f_i) \frac{C^{free}}{C_s} \exp(-\Delta E^b(f_{i+1})/kT), \quad (4)$$

where  $A_{i+1}$  ( $D_{i+1}$ ) is possible number of distinct association (dissociation) reactions associated with reaction to form  $f_{i+1}$  ( $f_i$ ) from  $f_i$  ( $f_{i+1}$ ).  $C^{free}$  and  $C_s$  are free primary dopant concentration and silicon lattice concentration, and  $\Delta E^b(f_{i+1})$  is the change in energy between configuration  $f_{i+1}$  and  $f_i$ .

Eqs. 3 and 4 are generally applicable to binding beyond 1NN, but we have included only 1NN multiple binding in pairing calculations reported below. Under this restriction,  $C(f_i)$  can be simplified to  $C_i$  (the concentration of pairs with  $i$  primary dopant atoms at 1NN). Then Eq. 4 can be expressed as

$$C_i = \frac{4!}{(4-i)!(i)!} \left( \frac{C^{free}}{C_s} \right)^i C_0 \quad (i = 1, 2, 3, 4). \quad (5)$$

Using Eqs. 3 and 5, we plotted differential carrier density per co-doping atom (number of primary dopants in pairs divided by the total number of co-dopant atoms) as a function of the concentration of free primary dopant (Fig. 3).

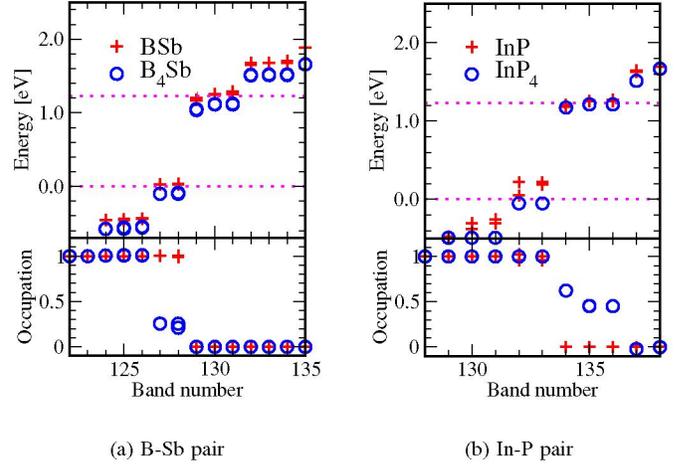


Fig. 2. Density of states of donor-acceptor pairs with multiple binding. In contrast to B-Sb pairs, the energy levels associated with In near top of the valence band are lowered significantly with P addition. The large binding energy of  $\text{InP}_n$  is attributed to this energy level lowering.

### III. RESULTS AND DISCUSSION

#### A. donor-acceptor pairs

As listed in Table II, all the donor-acceptor pairs except pairs at first nearest neighbor (1NN) show binding which is closely approximated by sum of stress energy plus and Coulombic interactions. At least a portion of the modest difference between  $E^f$  and sum of  $E^C$  and  $E^S$  (less than 0.15 eV) may arise from inaccuracy of point charge approximation for the charged ions. We attribute the large energy discrepancy for donor-acceptor pairs at 1NN to direct local binding and higher order multipole interactions. Fig. 1 shows highly asymmetric charge distribution for B-As at 1NN. Thus monopole approximation is not sufficient to accurately estimate Coulomb energy.

The formation energy of  $\text{B}_n\text{Sb}$  does not monotonically increase as B is added to Sb. This is because small B atom produces large strain energy. Once strain energy (the third column in Table III) is factored out, the binding energy monotonically increases for all multiple binding species. It is notable that the binding energy of  $\text{InP}_n$  is much greater than Coulomb interaction. We believe that strong binding between In and P is related with In energy level lowering of initially deep In acceptor level when P binds to In (Fig. 2). Based on multiple binding between donors and acceptors, the differential carrier density due to counter-doping was calculated. Fig. 3 shows change in carrier density as a function of free primary dopant (P or B). The negative value for  $\text{B}_n\text{Sb}$  up to well above equilibrium B solubility implies that binding is not strong enough to overcome charge compensation between donor and acceptor for this combination. Consistent with this prediction, Solmi *et al.* reported carrier density decreases due to B-Sb pairing [5]. For the case of  $\text{InP}_n$ ,  $dn/dC_{\text{In}}$  becomes positive well below P solubility. The effect of  $\text{InP}_n$  pairing on carrier

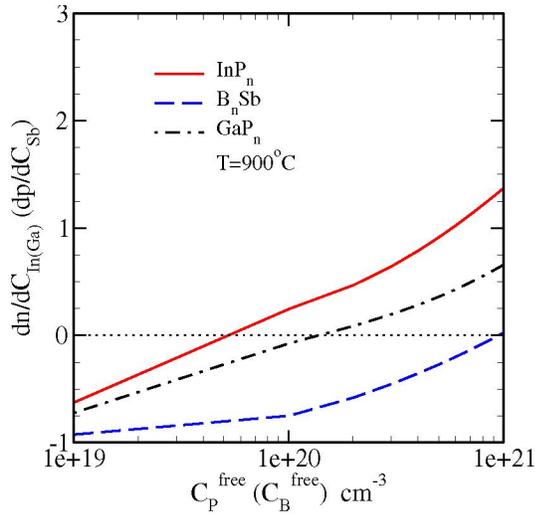


Fig. 3. Differential free charge concentration per co-dopant atom as a function of concentration of free primary dopants. The number of paired B atom per Sb is less than 1, which means BSb binding energy is not enough to overcome charge compensation. However, strong multiple binding between In and P may be beneficial to increase electron charge density.

concentration is limited by low In solubility ( $1.5 \times 10^{18} \text{cm}^{-3}$  at  $900^\circ\text{C}$  [13]) and already high P solubility. However, it should be noted that pairing with P substantially increases In solubility well above normal value. Counter-doping and associated pairing can also be beneficial in formation of abrupt junctions by suppressing dopant diffusion [4], [5], [6].

### B. acceptor-acceptor pairs

When two acceptors are closely spaced, Coulomb repulsion is expected. Although this is true for two B atoms, as listed in Table IV, B-Ga binding is weakly attractive, and B-In have a substantial binding energy. We believe that the holes associated with B are well delocalized and thus ionized B atoms repel each other. However, in conjunction with the larger ionization energy, holes associated with In atoms (and to a lesser extent Ga) are more localized, and the localization is enhanced by the presence of an additional acceptor. Localized holes then stabilize the formation of B-In (and B-Ga) pairs. This mechanism is supported by the fact that removing the holes by considering negatively charged cells leads to elimination of B-In binding (Table V).

Unlike donor-acceptor pairing, no charge compensation is involved, so acceptor-acceptor binding might be expected to lead to enhanced hole concentrations. Unfortunately, our calculations indicate that the BIn pair is a deep acceptor as shown in Fig. 4(d), with both acceptor levels located well within the gap. This prediction is supported by experimental results of Scalse *et al.* [6], who found that In co-doping deactivates B. As in the case of donor-acceptor pairing, In can be used to reduce B diffusion [3].

## IV. CONCLUSION

We investigated electronic structure of various donor-acceptor pairs and acceptor-acceptor pairs and their impact on

TABLE II  
NET FORMATION ENERGY OF VARIOUS ION PAIRS. EXCEPT FOR INN, THE SUMS OF APPROXIMATE COULOMB ENERGY ( $E^C$ ) AND STRAIN COMPENSATION ENERGY ( $E^S$ ) ARE WITHIN 0.15 eV OF  $E^f$ . BAS/INP 1NN SHOWS WEAKER/STRONGER BINDING THAN COULOMB INTERACTION.

eV	$E^f$	$E^S$	$E^C$
Si <sub>62</sub> BA <sub>s</sub> 1NN	-0.34	-0.02	-0.55
2NN	-0.36	-0.02	-0.32
3NN	-0.32	-0.02	-0.27
Si <sub>62</sub> BSb 1NN	-0.46	-0.08	-0.52
2NN	-0.32	-0.08	-0.32
3NN	-0.22	-0.08	-0.27
Si <sub>62</sub> GaP 1NN	-0.66	-0.008	-0.50
2NN	-0.29	-0.003	-0.32
3NN	-0.21	0.0	-0.27
Si <sub>62</sub> InP 1NN	-0.88	-0.02	-0.48
2NN	-0.38	-0.02	-0.31
3NN	-0.28	-0.02	-0.27

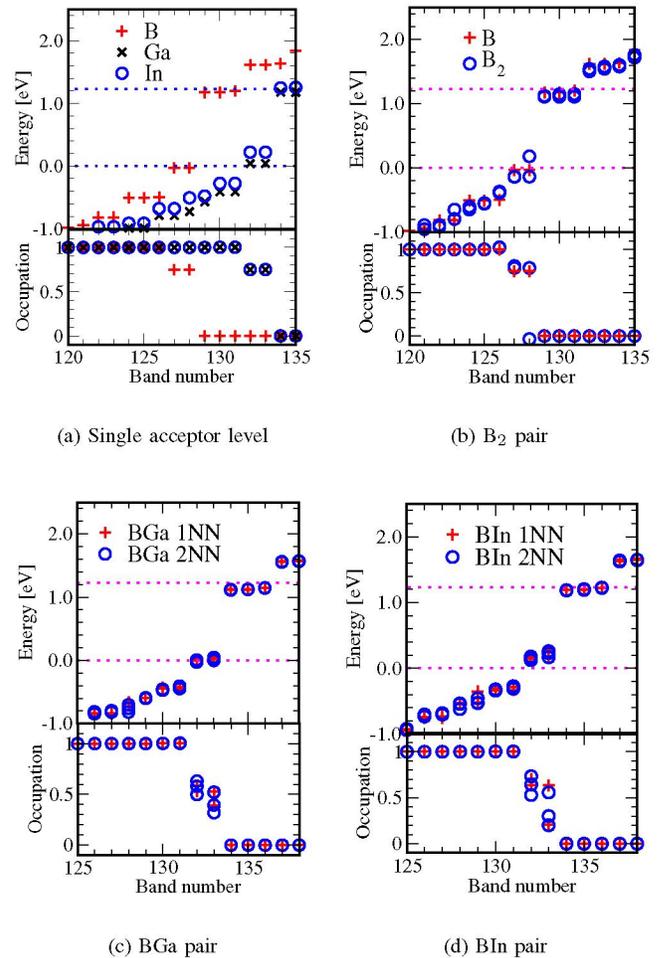


Fig. 4. Density of states of single acceptors and acceptor-acceptor pairs. In B<sub>2</sub>, acceptor states are located below the top of the valence band maximum, but in BIn pair two holes are in deep level.

TABLE III

FORMATION ENERGY AND BINDING ENERGY OF DONOR-ACCEPTOR PAIRS WITH MULTIPLE BINDING. IN CONTRAST TO B-Sb MULTIPLE BINDING, IN-P MULTIPLE BINDING PRODUCES LARGE NEGATIVE FORMATION ENERGY BEYOND COULOMB INTERACTION. FIG. 2 SHOWS IN-RELATED ACCEPTOR LEVELS LOWERING AS MULTIPLE P ATOMS ARE BOUND TO IN.

$eV$	$E^f$	$E^S$	$E^b$
BSb	-0.46	-0.09	-0.37
B <sub>2</sub> Sb	-0.62	-0.06	-0.56
B <sub>3</sub> Sb	-0.67	0.11	-0.78
B <sub>4</sub> Sb	-0.62	0.41	-1.03
GaP	-0.66	-0.01	-0.65
GaP <sub>2</sub>	-1.01	-0.01	-1.00
GaP <sub>3</sub>	-1.29	0.0	-1.29
GaP <sub>4</sub>	-1.48	0.02	-1.50
InP	-0.88	-0.02	-0.86
InP <sub>2</sub>	-1.36	-0.04	-1.32
InP <sub>3</sub>	-1.77	-0.05	-1.72
InP <sub>4</sub>	-2.19	-0.05	-2.14

TABLE IV

FORMATION ENERGY OF ACCEPTOR-ACCEPTOR PAIRS. B-B INTERACTION IS REPULSIVE, WHILE BIn SHOWS STRONG ATTRACTIVE BINDING.

$eV$	B <sub>2</sub>	BGa			BIn		
	1NN	1NN	2NN	3NN	1NN	2NN	3NN
$E^f$	0.93	-0.06	-0.10	-0.08	-0.41	-0.29	-0.20
$E^S$	0.28		-0.03			-0.10	
$E^b$	0.65	-0.03	-0.07	0.05	-0.31	-0.19	-0.10

charge carrier density. Counter-doping B with As or Sb can reduce the junction depth due to retarded B diffusivity, but calculated pairing effect is not large enough to overcome charge compensation between opposite dopant types. Counter-doping P with Ga or In, however, is predicted to enhance electron concentration via pairing of multiple P atoms with single In or Ga atom, thereby providing an increase in maximum concentration of electrically active P which exceeds compensation via the acceptors. We attribute the large binding energy of InP<sub>n</sub> to lowering of initially deep In acceptor levels as multiple P atoms are bound to a single In atom. BIn shows a surprisingly large attractive binding, which we attribute to localized holes overcoming expected ionized acceptor repulsion. However, B-In co-doping leads to reduced rather than enhanced hole density since it produces deep acceptor levels. For both donor-acceptor and acceptor-acceptor co-doping, attractive binding is also expected to lead to reduced diffusion and thus more abrupt junction formation.

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TABLE V

FORMATION ENERGY OF BIn FOR VARIOUS CHARGE STATES. WHEN HOLES ARE REMOVED, BIn INTERACTION GOES FROM ATTRACTIVE TO REPULSIVE.

$eV$	BIn	BIn <sup>-</sup>	BIn <sup>2-</sup>
$E^f$	-0.41	-0.21	0.12

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