

Strain-Enhanced Doping in Semiconductors: Effects of Dopant Size and Charge State

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When a semiconductor host is doped by a foreign element, it is inevitable that a volume change will occur in the doped system. This volume change depends on both the size and charge state difference between the dopant and the host element. Unlike the “common expectation” that if the host is deformed to the same size as the dopant, then the formation energy of the dopant would reach a minimum, our first-principles calculations discovered that when an external hydrostatic strain is applied, the change of the impurity formation energy is monotonic: it decreases if the external hydrostatic strain is applied in the same direction as the volume change. This effect also exists when a biaxial strain is applied. A simple strain model is proposed to explain this unusual behavior, and we suggest that strain could be used to significantly improve the doping solubility in semiconductor systems.

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Doping is an effective way to introduce free charge carriers in a semiconductor. It is one of the most important issues in semiconductor physics because most of the semiconductors will not be very useful if they cannot be doped [1]. However, for a large number of semiconductors, the efficiency of doping is rather limited. One of the reasons is that when a dopant atom replaces a host atom in a semiconductor lattice, it induces a strain and volume change when the dopant and the host elements have different sizes. This leads to a strain energy that can limit the dopant solubility in the host semiconductor, if the size difference between the dopant and the host element is large [1–3].

The atomic size of an element is not a constant as one might expect; it is determined both by its intrinsic size (e.g., the covalent radius) [4] and by its electronic environment. For example, in an ideal covalent environment, a Zn atom in ZnX ($X = \text{S, Se, Te}$) shows a +2 oxidation state and an almost identical covalent atomic size as the Ga atom in GaY ($Y = \text{P, As, Sb}$), where Ga has a +3 oxidation state (Table I). However, when Zn substitutes on the Ga site Zn_{Ga} in the GaP lattice, it is surrounded by anions with a −3 nominal ionization state. Thus its atomic size will not be the same as it is in a II–VI ZnX compound where it is surrounded by −2 valence anions. The change of the atomic size as its environment changes suggests that Zn_{Ga} in GaY will introduce a local strain and an electronic-environment-induced global volume change in GaY even if Zn and Ga may have identical covalent sizes. In principle, when a p -type dopant atom replaces a host element, the total number of electrons in the system and the pressure of the electron gas decrease. Therefore, the electronic environment induces a negative global volume change; that is, the system shrinks. The opposite will be true if the system is doped by an n -type dopant with extra valence electrons.

One might expect that to reduce the formation energy of the dopant inside the host, one can try to reduce the strain

energy by deforming the host so that the size of the host is closer to the dopant. Several theoretical studies [5–8] have shown that this may be the case. In 2002, Sadigh *et al.* suggested that the solubility of B in Si can be enhanced by a compressive biaxial strain due to the small size of B [5]. Recently, Ahn *et al.* proposed a general theory of strain effects on the solid solubility of impurities in Si, suggesting that the strain compensation energy is the primary contribution to the solubility enhancement [6].

The most direct and convincing evidence is the report by Bennett *et al.* that the solubility of the donor Sb in Si is enhanced to as high as 10^{21} cm^{-3} under tensile strain [7]. Ikuta *et al.* showed that the donor As doping concentration in Si was enhanced when Ge was alloyed with Si. The interpretation of this data is complex, but may indicate that the internal tensile strain provided by Ge in Si plays a role in reducing the As doping energy [8]. There are also experimental studies on the strain-induced effects on

TABLE I. Calculated dopant-induced volume change ΔV in GaP with one dopant per 64-atom cell. The volume change is divided into ΔV_i due to the intrinsic size difference and ΔV_e due to the electronic environment. The Phillips covalent radii are adopted from Ref. [4].

Dopant	ΔV (\AA^3)	ΔV_i	ΔV_e	p/n	R (\AA)
Ga	0	0	0	Neutral	1.225
Zn	−1.46	0	−1.46	p	1.225
Al	0.21	0.26	−0.05	Neutral	1.230
Cd	8.66	10.17	−1.51	p	1.405
In	9.54	10.17	−0.63	Neutral	1.405
Ge	4.54	0	4.54	n	1.225
Be	−12.88	−11.78	−1.1	p	0.975
Sn	13.25	10.17	3.08	n	1.405
Zn + Ge	−0.2	0	−0.2	Neutral	1.225

doping in III–V semiconductors but systematic studies are limited.

In this Letter, we investigate the strain-enhanced doping in III–V semiconductors. More importantly, we will test the validity of the long-standing speculation [9] that when a hydrostatic strain is applied to the host, the impurity formation energy might first decrease when the hydrostatic strain is applied in the same direction as the size-difference-induced volume change. Then after it reaches a minimum, it will increase when the size of the deformed host deviates from the size of the dopant again in the opposite direction. To test this speculation, we perform **first-principles total energy calculations for doping of zincblende GaP**. The dopants we considered **include Zn, Al, Cd, In, Ge, Sn, and Be**. To our surprise, we have found that the calculated impurity **formation energy is a monotonic (almost a linear) function of the applied strain**. It decreases if the external hydrostatic strain is applied in the same direction as the volume change. This effect also exists when a biaxial strain is applied. We have developed a simple strain model to explain this unusual behavior by showing that the dopant size also changes with the host elements when a global strain is applied. **Our findings indicate that hydrostatic or epitaxial strain can be used to significantly enhance the solubility of dopants in semiconductor systems by reducing its impurity formation energy**. This concept can also be used to select the doping site of an impurity, e.g., applying a compressive strain will favor a substitutional site over an interstitial site. Also, strain can have an effect on dopant diffusion [10,11] to further influence the doping concentration, which will be an interesting subject for future study.

Our total energy calculations were performed within the density functional theory as implemented in the **VASP** code [12]. We used the generalized gradient approximation and Perdew-Burke-Ernzerhof exchange-correlation potential. The core-valence interaction was treated using the frozen-core projected augmented wave method [13]. We used a plane wave cutoff energy of 400 eV and a $4 \times 4 \times 4$ k -point mesh for Brillouin zone sampling. For the defect calculation, we used the standard supercell approach with 64 atoms in the supercell. Total energy minimization was performed by relaxing atomic positions until the forces converged to less than 0.01 eV/Å. A calculated GaP lattice constant of 5.501 Å is in good agreement with the experimental value of 5.45 Å.

The calculated volume changes ΔV for various types of single dopants and the Zn + Ge dopant pair in a 64-atom GaP supercell are listed in Table I. To facilitate the analysis, we divide the volume change into two parts, i.e.,

$$\Delta V = \Delta V_i + \Delta V_e. \quad (1)$$

Here, **ΔV_i is due to the intrinsic size difference and ΔV_e is due to the change in the electronic environment**. The volume change due to the intrinsic size difference can be calculated as

$$\Delta V_i = \frac{16}{3\sqrt{3}}[(R_{\text{dopant}} + R_P)^3 - (R_{\text{Ga}} + R_P)^3], \quad (2)$$

where R_{Ga} , R_P , and R_{dopant} are the covalent radii of Ga, P, and the dopant, respectively. We took the covalent radius of $R_P = 1.157$ Å so that together with the values in Table I for the cations, the sum agrees with our calculated lattice constants. After we obtain ΔV_i , ΔV_e can be obtained from Eq. (1) and the calculated ΔV in Table I. All the results are listed in Table I.

We found the following trend from the calculated results:

(1) For all p -type dopants considered, Zn, Cd, and Be, the values of ΔV_e are about -1.1 to -1.5 Å³, which means that p -type dopants induce an electronic-environment-induced volume shrinkage, or an electronically originated tensile stress in the unrelaxed lattice [14]. For the two n -type dopants considered, Ge and Sn, ΔV_e is about 3 – 4 Å³, which means that n -type dopants induce an electronic-environment-induced volume expansion, or a compressive stress in the unrelaxed lattice. The larger absolute values for the n -type dopants, which provide one extra electron to the conduction band, compared to those for the p -type dopants, which remove one electron from the valence band, occur because the electron-conduction band state is more delocalized than the hole valence state at the band edge. For neutral elements, Al and In, the calculated values of ΔV_e are negligible.

(2) The Phillips' covalent radii of Zn (1.225 Å) and Ge (1.225 Å) are the same as that of Ga (1.225 Å) [4]. Thus, when Zn and Ge are separately doped into GaP, replacing Ga, ΔV_i will be zero by definition. However, the total volume change ΔV is not small, as one may naively think, because of the electronic-environment-induced effect. In this case, $\Delta V = \Delta V_e$ is equal to -1.46 Å³ and 4.54 Å³ for Zn and Ge, respectively. It would be interesting to see what happens when Zn and Ge are codoped into the system. Because Zn is a p -type dopant and Ge is an n -type dopant, they will passivate each other. We find that the total volume change that comes mostly from ΔV_e is very small, -0.2 Å³. However, we notice that this value is not a simple sum of the volume change caused by the individual substitution of Zn and Ge, reflecting the asymmetry of the valence and conduction band states.

(3) For isovalent Al and In, one would expect ΔV_e to be zero. Indeed, we find that $\Delta V_e = -0.05$ Å³, close to zero, in the Al_{Ga} case, but $\Delta V_e = -0.63$ Å³, which is rather small but not nearly zero in the In_{Ga} case. This discrepancy could be caused by the slight difference of the effective valence of In and Ga, despite the fact that they are nominally isovalent. It could also be due to the uncertainty in the determination of the intrinsic covalent radii of these two elements. For Al, ΔV is small and positive at 0.21 Å³, which is consistent with the experimental fact that the lattice constant of AlP (5.46 Å) [15] is slightly larger than that of GaP (5.45 Å) [16].

(4) Similar results are obtained when Ga is replaced by Cd and Sn in GaP. Cd and Sn with $R = 1.405 \text{ \AA}$ are much larger than Ga ($R = 1.225 \text{ \AA}$), so the volume change is dominated by the contribution of the intrinsic size difference ΔV_i . However, although the covalent radii of Cd and Sn are the same, the Cd-induced volume expansion at 8.66 \AA^3 is much smaller than that of Sn at 13.25 \AA^3 . The difference is due to two parts: the negative ΔV_e induced by Cd as a p -type dopant, which compensates part of the volume expansion due to the large size and lowers the overall volume expansion; and the positive ΔV_e induced by Sn, as an n -type dopant, which enhances the volume expansion due to the large size and increases the overall volume expansion.

(5) When the ΔV_e and ΔV_i have the same sign, the dopant-induced volume change will be the largest. Specifically, that requires either an n -type dopant with a larger atomic size than the host atom, thus both contributing a volume expansion, or a p -type dopant with a smaller atomic size than the host atom, thus both contributing a volume contraction. For all the dopants studied here, we found that Sn, as an n -type dopant, and Be, as a p -type dopant, induce the largest volume expansion of 13.25 \AA^3 and the largest volume contraction of -12.88 \AA^3 , respectively.

Next, we calculated the impurity formation energy as a function of strain for all the dopants listed in Table I. The impurity formation energy is defined as

$$E_f = E(\text{doped}) - E(\text{host}) + \mu(\text{Ga}) - \mu(\text{dopant}), \quad (3)$$

where $E(\text{doped})$ is the total energy of the doped system, $E(\text{host})$ is the total energy of the undoped system, and both are calculated under the same strain or pressure condition. $\mu(\text{Ga})$ and $\mu(\text{dopant})$ are the chemical potentials of Ga and the dopant. For simplicity, we assumed that the chemical potential difference between the two elements is not sensitive to the volume change (strain). We then considered hydrostatic and biaxial strains. In applying hydrostatic strain we change all three cell dimensions of the supercell equally; in applying biaxial strain we change the two supercell dimensions along x and y equally and allow the cell dimension along z axis to relax until the energy is minimized.

Figure 1 shows the calculated change of impurity formation energy ΔE_f as a function of hydrostatic strain (ϵ) for Be, Al, Zn, Ge, Cd, and Sn. As expected, the impurity formation energy decreases when the host is strained along the direction of volume change induced by the dopant, which means that the slope is positive when the effective size of the dopant is smaller than Ga (e.g., Be, and Zn) and negative when it is larger than Ga (e.g., Ge, Cd, and Sn). A larger effective size difference gives a larger slope of the doping energy difference. The doping energy of Be is reduced by about 0.2 eV for -1% compressive hydrostatic strain. This indicates that the solubility of Be in GaP could be increased by 3 orders of magnitude at room temperature or 10 times at about 900 K. A similar effect is found for Sn. For Al, $\Delta E_f \sim 0$. However, to our surprise, the change of

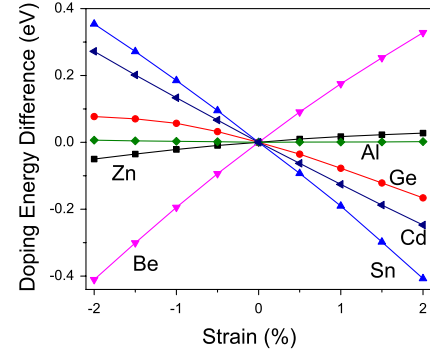


FIG. 1 (color online). Change of impurity formation energy vs hydrostatic strain for the dopants studied.

doping energy with increasing strain is monotonic, without showing a minimum at a specific strain where one would expect the deformed host lattice has the same size as the dopant (e.g., about -0.037% strain for Zn doping).

Below we provide a simple explanation of why there exists no minimum doping energy at a specific volume (or strain), as “commonly perceived.” Figure 2 shows a schematic illustration of total energy of the host lattice versus the doped lattice as a function of volume. Let us assume that near equilibrium, the total energy of the host lattice follows: $E(\text{host}) = \alpha(V - V_{\text{host}})^2$, where α is the elastic constant and V_{host} is the equilibrium volume of the host lattice. The energy of the doped lattice follows: $E(\text{host} + \text{dopant}) = \alpha'(V - V_{\text{host}+\text{dopant}})^2$, where α' is the elastic constant and $V_{\text{host}+\text{dopant}}$ is the equilibrium volume of the doped lattice. Then, the change of the impurity formation as a function of strain or volume will be $E(\text{doping}) = E(\text{host} + \text{dopant}) - E(\text{host}) = (\alpha' - \alpha)V^2 - 2(\alpha'V_{\text{host}+\text{dopant}} - \alpha V_{\text{host}})V + \alpha'V_{\text{host}+\text{dopant}}^2 - \alpha V_{\text{host}}^2$. If the two elastic constants are assumed to be the same, i.e., $\alpha' = \alpha$, as a first order approximation, the change of the impurity formation energy is proportional to

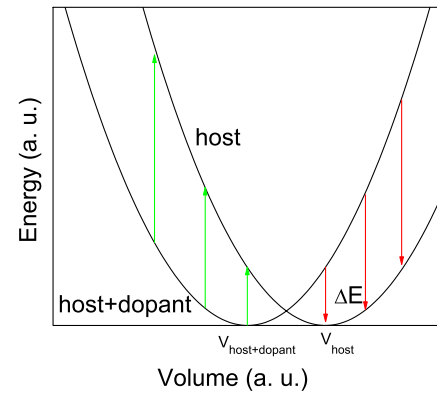


FIG. 2 (color online). Schematic plot of the quadratic function of total energy vs volume for host and doped lattice. Assuming the two curves are simply laterally shifted (i.e., having the same quadratic coefficients), ΔE (as indicated by arrows) will be a linear function of volume V .

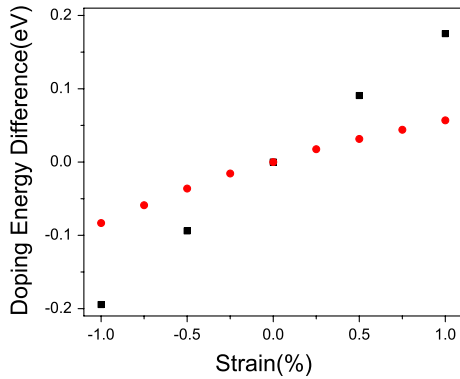


FIG. 3 (color online). **Change of impurity formation energy vs biaxial strain and hydrostatic strain** for Be in GaP. Red circles: biaxial strain; black squares: hydrostatic strain.

$V(V_{\text{host}} - V_{\text{host+dopant}})$. It is **a linear function of V (or strain)** and the slope is proportional to the volume change or the effective size difference between the host and the dopant atom. The above analysis explains the calculated results shown in Fig. 2. This behavior can also be understood as follows: under strain, the size of the host elements and the dopants are changed in the same way so that their difference is kept nearly constant. Consequently, the doping energy in the strained lattice, which is proportional to the product of stress and strain, is nearly a linear function of strain.

The above calculations used hydrostatic strain. However, in practice, biaxial strain may be easier to apply, e.g., during epitaxial growth. Therefore, we also performed calculations of impurity formation energy versus biaxial epitaxial strain. We chose Be as the dopant because it shows the largest volume reduction, thus the largest change in the impurity formation energy. For GaP, the calculated Poisson ratio is $\epsilon(z)/\epsilon(x) = -0.86$, which is in good agreement with the experimental value $-2C(12)/C(11) = -0.89$ [17]. The change of impurity formation energy as a function of the biaxial strain (red circles) is shown in Fig. 3, for comparison with the hydrostatic strain calculations (black squares). We found that the impurity formation energy is reduced by about 80 meV under a 1% biaxial compressive strain. This indicates that the Be concentration can be enhanced by about 3 times for a typical OMVPE growth temperature of 900 K for GaP. The trends of the strain-enhanced doping for the bi-axial and the hydrostatic strain are about the same, except that the effect of the bi-axial strain is smaller.

In summary, we have demonstrated that the dopant-induced volume change arises as a result of two factors: **the intrinsic size difference ΔV_i and the electronic-environment-induced volume change ΔV_e . n -type dopants induce a positive ΔV_e due to the extra valence electron that expands the lattice, whereas p -type dopants induce a negative ΔV_e due to the missing valence electron that shrinks**

the lattice. The sign of dopant-induced volume change determines how the strain affects doping, and contrary to “common perception,” we show that the doping energy does not exhibit a minimum at a particular volume (or strain) but changes monotonically in a linear fashion with the applied external strain. We propose that the intriguing unbounded strain-induced change in impurity formation energy can be used effectively to enhance dopant solubility in a wide range of semiconductors.

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