Dilute nonisovalent (II-VI)-(III-V) semiconductor alloys: Monodoping, codoping, and cluster doping in ZnSe-GaAs

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A dilute nonisovalent semiconductor alloy, made of a III-V semiconductor component (GaAs) mixed with a II-VI semiconductor (ZnSe), can be viewed as the doping of a host semiconductor with a lower (higher) valent cation and a higher (lower) valent anion. We have investigated different doping types, i.e., monodoping, triatomic codoping, and cluster doping, in the ZnSe-GaAs system using *ab initio* pseudopotential plane-wave calculations. We find the following: (i)

Se-Zn_4 and Zn-Se_4 tetrahedra in GaAs) is stable and produces free carriers. We further explain the surprising phenomenology in this nonisovalent alloy: (ii) it exhibits *either* *n*-type *or* *p*-type behavior, rather than charge compensation; (iii) the dependence of band gap on the alloy composition is asymmetric; and (iv) free carriers have a high mobility.

II. METHOD OF CALCULATION

A. Formation enthalpy and defect transition energy

The formation enthalpy $H^{(\ ,q)}(\ ,E_F)$ of defect in charge state q depends on the chemical potentials of all species involved and on the Fermi energy E_F, and is given by

$$H^{(\ ,q)}(\ ,E_F) = H^{(\ ,0)}(\ ) - q\ (0/q) + qE_F . \quad (1)$$

Here, $H^{(\ ,0)}(\ )$ is the formation enthalpy of the neutral $(q=0)$ defect, and $(0/q)$ is the defect transition energy from charge state 0 to q, *i.e.* the value of the Fermi energy where $H^{(\ ,q)} = H^{(\ ,0)}$. The formation energy of a neutral defect,

$$H^{(\ ,0)} = E_{tot}^{(\ ,0)}$$

GaAs -1.078 $_{As}-$ $_{Se}$ 0.002 eV for $K=0$ and -1.078 $_{As}-$ $_{Se}$ 1.002 for $K=-1$ eV. For Ga+As doping of ZnSe, we can perform a similar analysis. The allowed chemical potential ranges are shown in Fig. 2. We obtain -1.078 $_{As}-$ $_{Se}$ 0.002 eV for $K=0$, and -2.078 $_{As}-$ $_{Se}$ 0.002 for $K=-1$ eV. We will thus compare different forms of doping in these allowed ranges of chemical potentials.

III. DOPING GaAs BY Zn+

bulk, that the Zn-Se bond length increases in the GaAs environment, and this increase is greater the more As exists in the Zn-$Se_{4-n}As_n$ clusters. The same is true for the Zn-Se bond in the Se-centered clusters Se-$Zn_{4-n}Ga_n$, where the bond increases with increasing Ga content in the cluster. Table II shows analogous results for the Ga-centered Ga-$As_{4-n}Se_n$ cluster in ZnSe and the As-centered cluster As-$Ga_{4-n}Zn_n$ in ZnSe.

A. Formation enthalpies for *p*-type doping of GaAs by Zn+Se

For

ter doping $(\text{Zn-Se}_4)^{3-}$ and $(\text{Zn-Se}_3\text{As})^{2-}$, monodoping of Se (denoted as $(\text{Se-Ga}_4)^{+}$), and codoping $(\text{Zn-Se}_2\text{As}_2)^{-}$], which promote an *n*-type behavior, have lower formation enthalpies than the acceptor dopant clusters. Actually, the formation enthalpies of the donor dopant clusters are negative under Se-rich conditions, which means that the donor dopant clusters can reach a very high concentration, even higher than the available sites, if the dopants are available. These

doping of Ga] generate free electrons and promote *n*-type doping. (ii) From the intermediate chemical potential range to the very As-rich limit, the acceptor dopant clusters cluster doping $(\text{Ga-As}_4)^{3-}$ and $(\text{Ga-As}_3\text{Se})^{2-}$, codoping $(\text{Ga-As}_2\text{Se}_2)^{-}$, and monodoping of As] have lower formation enthalpies than the donor dopant-clusters, which means a strong compensation to *n*-type doping for this chemical potential range. So in order to obtain *n*-type doping it is necessary to keep very Se-rich conditions.

Again, we see that when the Fermi energy is shifted from the CBM to the middle of the gap, the chemical potential range for which the donor dopant clusters are more stable than the acceptor dopant clusters is increased see Fig. 4(b) for $E_F = E_{midgap}$]. Therefore, it is favorable to form donor dopant-clusters at the Fermi energy $E_F = E_{midgap}$.

We conclude that doping ZnSe by Ga+As is done most effectively by *cluster doping* for ''Se-rich *n*-type'' conditions, whereas cluster doping cF3 1m4(donTJ 0 TD (.TD [(0 TD 5359[(0 lgs /F10g3963 -0 lgs /F10g3969((. f 6.270 1 Tf 6.2777 485.2(ra

positely charged isolated dopants leads to a minimum in $\delta^{(n)}$ for pairs, and implies that a significant concentration of dopant pairs will exist in such alloys. The charge neutrality of such pairs may explain the surprisingly high carrier mobility[7] in nonisovalent alloys in terms of weak dipolar (rather than charged-ion) scattering. Note that neutral clusters ($n=3$) do not contribute to doping, whereas charged clusters (e.g. $n=4$ and 0) which contribute to doping also contribute to enhance scattering.

The greater tendency for clustering of the small gap Ga+As in ZnSe than for the large-gap Zn+Se in GaAs (Fig. 6) may also explain the fact[1,2] that dissolving Ga+As in ZnSe leads to the creation of a smaller band gap, akin to GaAs-like clusters, while dissolving Zn+Se in GaAs does not change the host crystal band gap.

C. Thermodynamic instability of codoping

The formation enthalpies of triatomic co-doping are shown in Figs. 3 and 4 by dashed lines. We see that the *p*-type codoping $(\text{Se-Zn}_2\text{Ga}_2)^-$ and the *n*-type codoping $(\text{Zn-Se}_2\text{As}_2)^+$ in GaAs are never the ground state structures for any value of (, E_F). The same is true for the *n*-type codoping $(\text{As-Ga}_2\text{Zn}_2)^+$ and the *p*-type codoping $(\text{Ga-As}_2\text{Se}_2)^-$ in ZnSe (Fig. 4). Codoping becomes even less favorable when using dilute dopant sources (see Fig. 5). Thus, if codoping is the dominating form of doping in this system,[18–22] it is not mandated by thermodynamics. This conclusion focuses attention on the possibility of nonequilibrium metastable species, since stable species do not lead here to codoping.[23] The instability of codoping reflects the balance of two competing interactions.[24] In *p*-type codoping we have two acceptors and one donor; we find that the repulsive acceptor-acceptor interaction overwhelms the attractive donor-acceptor interaction, resulting in a lower stability relative to monodoping.

D. Thermodynamic stability of cluster-doping

Unlike triatomic codoping which is unstable, some tetrahedral pure-dopant clusters are predicted to be thermodynamically stable (see Figs. 3 and 4 and Table III). Figure 3 shows, for example, that in GaAs the Zn-Se_4 cluster is the stablest structure under Se-rich conditions, whereas Se-Zn_4 is the stablest structure under As-rich conditions for dopant rich sources ($K=0$). These dopant clusters are stabilized under extreme chemical potentials because of the stronger dependence of their formation enthalpies on the chemical potential (see Figs. 3 and 4 the corresponding slopes). We estimate that the configurational entropy contribution at room temperature is about 0.2 eV in favor of stabilizing the monodoping (the vibrational entropy has even a much smaller contribution). But ignoring the entropy contributions as we have done in the present study will not affect our conclusion that the cluster doping can be stabilized under extreme chemical potentials. The predicted thermodynamic stability and carrier production of tetrahedral clusters in GaAs and ZnSe implies that the ratio between incorporated cation and anion dopants will not be 2:1 (as in the proposed[18] *n*-type codoping of GaAs by Zn+2Se), but rather higher, e.g., Zn+4Se *n* doping in GaAs. So cluster doping may be realized in experiments by working with a high (3:1 or 4:1) ratio of acceptor-to-donor for *p*-type doping (and a high ratio of donor-to-acceptor in *n*-type doping), and pushing the chemical potential conditions to the extreme limits.

Cluster doping may also prevent a spontaneous, symmetry-lowering deformation, turning a shallow defect into a deep one.[25] This is because in the tetrahedral pure-dopant clusters3.3(sr)2.4(ad)-1.3(ja)-0.2(cen)-0.2(t)-0.2(Se)-0.2(-)-0.2(Se)-0.2(4)-0.2(Sh)-0.2(as)-0.2(T)-0.2(9)-0.2(ad)-0.2(ru)-0.2(a)-0.2(1)-0.2(3)-0.2(3)-0.2(3)-0.2( )-0.2(0)-0.2(0)-0.2(2)-0.2(\()-0.2(po)-0.2(.)-0.2(47)-0.2(e)-0.2(4)-0.2(GT)-0.2(D)-0.2( )-0.2([)-0.2(()-0.2(e)-0.2(.)-0.2(g)

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