Invited

Theoretical Results on Dopability in Large Band Gap II-VI Semiconductors

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The difficulties in the *p*-type doping of ZnS and the *n*-type doping of ZnTe are well known phenomena in the II-VI semiconductor community. We find extremely strong evidence from the results of parameter-free firstprinciples calculations that the major source of doping difficulties in II-VI semiconductors is the formation of self-compensating centers resulting from bond rearrangement at dopants. The most important self-compensating center is identified. When the formation energy of this center is endothermic, there is no problem with doping but when it is exothermic, low resistance doping is not possible. The theoretical results on formation energies and dopability are in excellent accord with experimental data.

The ability to dope semiconductors n- or ptype by the incorporation of suitable impurities is at the heart of the semiconductor industry. The relative ease of both n- and p-type doping of III-V semiconductors is for the most part absent in II-VI semiconductors. The latter show ease of doping for either n-or p-doping but not for both. Small changes in chemical composition sometimes lead to large variations in doping. In the common cation compounds ZnS, ZnSe, and ZnTe, good p-type doping has not been achieved in ZnS and occurs only for N impurities in ZnSe. However, ZnTe can be pdoped to extremely high levels with most Column V impurities. In contrast, ZnTe cannot be doped low resistance *n*-type, whereas both ZnS and ZnSe are easily n-doped with Al.

The understanding of doping problems in II-VI semiconductors is not yet as advanced as in III-V semiconductors, especially in $Al_xGa_{1-x}As$ alloys. There is as yet no theory that unambiguously predicts the differences in the doping behavior of ZnS and ZnTe, for example. Experimental data on persistent-photoconductivity in *p*-doped ZnMgSSe alloys similar to that seen in *n*-type $Al_xGa_{1-x}As:Si$ suggests very strongly the presence of stable deep acceptor centers (i.e., *AX* centers similar in properties to the deep donor *DX* centers in III-V semiconductors) that can be optically excited into metastable effective-mass states

In this paper we identify the structure of the AX center in II-VI semiconductors and show that its formation can unambiguously account for all the observed experimental trends in the *p*-type doping of ZnS, ZnSe, ZnTe, and CdTe with N, P, As, and Sb. From the results of our calculations we find that substitutional fourfold coordinated dopants in II-VI (and III-V) semiconductors always give rise to shallow (i.e., effective-mass, hydrogenlike) electronic states. If a substitutional tetrahedrally coordinated state is stable against other possible bonding configurations, then there will be no problem with doping. The most important result from the calculations is, however, that dopants often have other configurations that are more stable than the tetrahedral configuration. It is the existence of such structures in which there is a "large-lattice-relaxation" (LLR) away from tetrahedral bonding that leads to deep impurity states and to self-compensation.

A projection of the atoms in a ZnS crystal (with a substitutional P impurity) onto a (110) plane is shown schematically in Fig. 1a. All atoms are fourfold and tetrahedrally coordinated. In this configuration, the P dopant is a *shallow* acceptor impurity. The substitutional tetrahedral state is found to be always present, either as the ground state of an impurity or as a metastable state. A very low energy structure with a LLR is shown in Fig. 1b. In this structure *two* anion-cation bonds are broken and an anionanion bond between second-neighbor atoms is formed. The lattice-relaxation and rebonding have the effect of transforming the *shallow* P *acceptor* impurity into a compensating *donor* center. Self-compensation occurs by the reaction,

$$a^- + 2h \rightarrow AX^+$$
 (1)

in which a negatively charged P dopant in a tetrahedrally coordinated state (as in Fig. 1a) captures two holes and is transformed into a positively charged AX state which we identify with the structure in Fig. 1b. To maintain overall charge neutrality in the system, only half of the P atoms transform into the AX^+ state while the other half remain in "normal" a^- acceptor states.

The AX structure in Fig. 1b above is the lowest energy self-compensating center in p-doped II-VI semiconductors. The calculated sign of the formation energy for this defect relative to the substitutional donor state in Fig. 1a is strongly correlated with whether a dopant gives a shallow or a deep state. When the formation energy of the AX center is exothermic, a dopant gives a deep acceptor state whereas when the formation energy is endothermic, the shallow acceptor state is the dominant dopant species.

(1a)



Shallow acceptor state d(P-S) = 3.82 Å

(1b)



AX deep acceptor state d(P-S) = 2.22 Å