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Brief Reports

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Electronic structure of S and Sn impurities in InP

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Sulfur is an unavoidable contaminant in InP. Recent experiments indicate that the ionization energy of InP:S is very close to that of InP:Sn. We have performed a fully self-consistent discrete-variational linear-combination-of-atomic-orbitals method to study the electronic structure of S and Sn substituted at the In site in InP. Calculated results indicate S to be an acceptor in contrast to donorlike behavior observed in Sn. It is concluded that S occupies the P site and/or forms defect complexes in InP. Comparison with experimental results is made wherever available.

INTRODUCTION

Proper identification of the residual impurities in undoped semiconductors and their control is important in producing high-purity material. In order to suppress the effects of these contaminants, doping with other atomic species is found to be beneficial. For example, Ge doping at 10^{19} cm^{-3} in InP is utilized in fabricating dislocation-free devices.[1] The major problem posed by InP is in its preparation of high-purity defect-free samples. Vacancies, antisite defects, defect complexes, and impurities are often detected, and sulfur seems to be an unavoidable contaminant[2] in InP. It is also known that heavy doping of Sn in InP causes gap shrinkage, which affects the characteristics and performance of laser devices. Recent experimental studies indicate that (i) nearly 100% of the tin atoms occupy the In site in InP, and (ii) the ionization energies of S- and Sn-doped InP are very close to each other. This closeness in ionization energies motivated us to perform theoretical electronic-structure calculations of InP doped with S and Sn at the In site and to make a detailed comparison of impurity charge distributions, defect levels introduced in the gap region, and the densities of states. The calculated electronic structures show an acceptorlike behavior for S, contrary to the experimental results, and a donorlike behavior for Sn, in agreement with experiments. This rules out the possibility of S occupying the In site. Rather, it suggests the possibility of S occupying the P site and/or forming various defect complexes.

METHOD

The ground-state electronic structure of "ideal" and "defected" (a centrally located defect) clusters extracted from the solid are obtained self-consistently using the discrete-variational linear-combination-of-atomic-orbitals (DV-LCAO) method[3–6] in the embedded scheme within the local-density framework. In other cluster approaches, such as the multiple-scattering (MS $X\alpha$) method, hydrogen atoms are often used as surface-dangling-bond saturators. Proper charges are promoted to the Watson sphere to neutralize the cluster. Often better results are obtained by relaxing the hydrogen-ligand bond length by a few percent. This may introduce the task of identifying and eliminating troublesome and spurious levels due to hydrogen termination. In our present calculations, we generate a microcrystal extending out to 17–20 a.u. from the center of the cluster and consisting of 250–300 atoms around the cluster to simulate the solid. The main idea is to suppress surface and cluster-size effects by making the peripheral atoms sense a potential similar to that found in the bulk crystal. Earlier calculations suggest[6,7] that this embedding leads to a better approximation to the local environment in treating impurities in semiconductors successfully. In the discrete-variational method, the Hamiltonian and the overlap matrices are calculated as weighted sums over a set of sampling points r_k rather than integrals, thereby avoiding multicentered integrals and hence reducing the computational space and time. The Hamiltonian and the overlap matrix are written as

$$H_{ij}=\sum_k W(r_k)\varphi_i^{\beta *}(r_k)H\varphi_i^{\beta}(r_k)\ , \tag{1}$$

$$S_{ij}=\sum_k W(r_k)\varphi_i^{\beta *}(r_k)\varphi_i^{\beta}(r_k)\ . \tag{2}$$

The variational basis functions assigned to In and P are [Pd]$5s^2 5p^1$ and [Ne]$3s^2 3p^3$, while those due to S and Sn are [Ne]$3s^2 3p^4$ and [Pd]$5s^2 5p^2$, respectively. These are generated by numerical atomic procedures. The truly nonlocal Hartree-Fock exchange-correlation potential is approximated in the $X\alpha$ form, dependent only on the local charge density

$$V_{\text{ex}} = -\alpha(3/4\pi)[(3\pi^2/4)\rho(r)]^{1/3} \tag{3}$$

for α varying between $\frac{2}{3}$ and 1. The total nonspherical potential due to all the atoms in the microcrystal is the sum of each of the spherically symmetric contributions written as an Ewald[8]-type summation. Finally, the partial densities of states are obtained by broadening the discrete one-electron-cluster energy levels with a Lorentzian of constant width.

RESULTS AND DISCUSSIONS

We chose a cluster of 17 atoms in the form InP_4In_{12} to constitute our ideal host or a "perfect" cluster. The In and P atoms in this cluster are placed in a tetrahedral configuration and hence the energy levels obtained self-consistently as a solution of the one-electron Schrödinger equation are designated according to the irreducible representation of the tetrahedral point group. The effect of the contaminants and intentionally doped impurities are taken into account by considering the "defected" cluster obtained by replacing the central In atom with the desired impurity, thereby maintaining the symmetry of the original "perfect" cluster. With the embedding used in the DV method, there is no appreciable band-gap shrinkage or enhancement in changing the cluster size. It also considers the associated impurity wave functions that extend beyond the second neighbor shell through total charge-density (cluster and crystal charge-density) calculations.[7] The 17-atom cluster, however, ensures the interaction of the impurity with the host atoms explicitly and at the same time optimizes the computational time.

Table I, column (a) shows the volume charges and Mulliken populations for pure InP. The volume charges are obtained by integrating over the Wigner-Seitz volumes. The net charges on the cations and the anions are not of equal magnitude because of the nonstoichiometric nature of the cluster chosen. Sulfur, when substituted at the In site in InP, behaves as a shallow acceptor [see Table I, column (b)] as only 0.12 electrons are taken up by the impurity. This is surprising since one would expect sulfur to donate three of its six valence electrons and become a donor while the other three electrons would rebuild the broken bonds that were created in removing the central In atom with three valence electrons. The net charge on the distant In atoms does not change much, but the four neighboring P atoms become less ionic compared to the host. Sn, on the other hand, is a donor with a net charge of eight-tenths of an electron [Table I, column (c)]. The ionicities of In and P atoms in InP:Sn are not very different from the host. Looking at the individual free atomic states we see that the 3*s* state of S is 0.38 eV lower than the atomic Sn 5*s* state and the S 3*p* state nearly coincides with the Sn 5*s* state ($\sim$0.01 eV higher). Also, the first ionization energy of S (10.36 eV) is higher than that of Sn (7.36 eV). The deep-lying, somewhat localized states of S in the valence band suggest why a S atom collects more charge around itself as compared to Sn, which has a more delocalized 5*p* state.

The partial density of states for P 3*s* and P 3*s* is shown in Figs. 1(a) and 1(b), respectively. The solid, long-dashed, and short-dashed lines correspond to pure InP, InP:S, and InP:Sn, respectively. It is seen that the 3*s* and the 3*p* states of P are pulled down into the valence band in introducing the S impurity at the In site but they are again pushed back towards the Fermi energy (indicated by the vertical line) for the Sn impurity. It may be pointed out here that the Fermi energy in our calculations is pinned at the last filled or partially filled level. Figures 2(a) and 2(b) show the In 5*s* and In 5*p* states in the three cases stated above. These states show behavior similar to the 3*s* and 3*p* functions of P. There is, however, a strik-

TABLE I. Charge distribution in the different atomic regions of the pure InP semiconductor, InP:S, and InP:Sn.

	(a) InP		(b) InP:S		(c) InP:Sn
In	48.83		48.61		48.65
P	15.30		15.34		15.47
		S	16.19	Sn	49.13
Mulliken charge distribution:					
In 5*s*	1.83		1.90		1.89
In 5*p*	0.82		0.76		0.81
Net charge	0.35		0.34		0.30
P 3*s*	1.79		1.84		1.78
P 3*p*	3.61		3.41		3.56
Net charge	−0.40		−0.25		−0.34
		S 3*s*	1.94	Sn 5*s*	1.55
		S 3*p*	4.18	Sn 5*p*	1.66
Net charge			−0.12		0.78

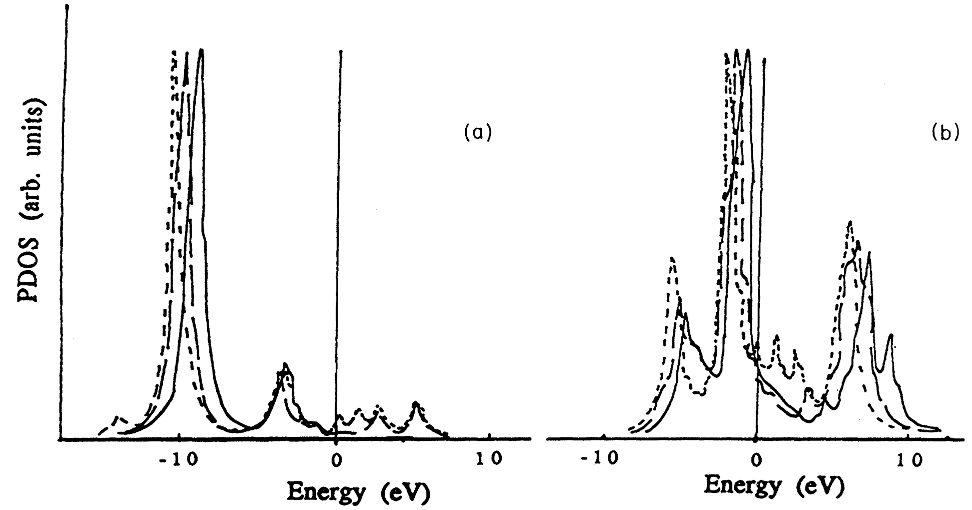

FIG. 1. Partial density of states for the (a) P 3*s* state and (b) P 3*p* states. The solid, long-dashed, and short-dashed lines correspond to the pure semiconductor, InP:S, and InP:Sn, respectively.

ing agreement among the valence states of In for pure and InP:Sn. They both look very similar and almost overlap each other. These features are correctly reflected in the charge distribution shown in Table I. In Fig. 3(a) we see that the S 3*p* peak lies deep in the valence band at -14.6 eV. The Sn 5*s* states show a small peak at -10.9 eV and a larger peak at -6.4 eV. The major part of the S 3*p* states lies below the Fermi energy in contrast to Sn 5*p* peaks, which are much more delocalized and show multiple humps in the conduction band.

From the self-consistently obtained one-electron energy spectrum, we obtain the last filled t_1 and the first empty a_1 levels leading to a band gap for pure InP of 1.44 eV, in excellent agreement with the experimental value of 1.41 eV. Our calculation technique may not give a good description of the conduction states, which are rather delocalized, but the deep levels produced by localized perturbation of the lattice can be identified by taking the valence-band edge as the reference point. With S doping, we find a level a_1 character containing two electrons at $E_c-0.68$ eV, while a level of t_2 character with one electron grazes the conduction band. The defect level at $E_c-0.68$ eV is indeed a deep level in contrast to the experimentally observed[9] shallow donorlike states. However, when Sn is substituted at the central In site, a level of a_1 character with one electron appears at $E_c-0.19$ eV. Clearly, the calculated defect levels for InP:S and InP:Sn are not close to each other as reported experimentally.[2] The disagreement between calculated and experimental results could arise due to two major reasons: (a) relaxation of the lattice around the impurity and (b) proper choice of site selection and/or formation of defect complexes for InP:S. Relaxation of the lattice occurs only around the impurity and, in principle, reduces the symmetry of the system, thereby making computations tedious. In our calculations, we freeze the crystal lattice

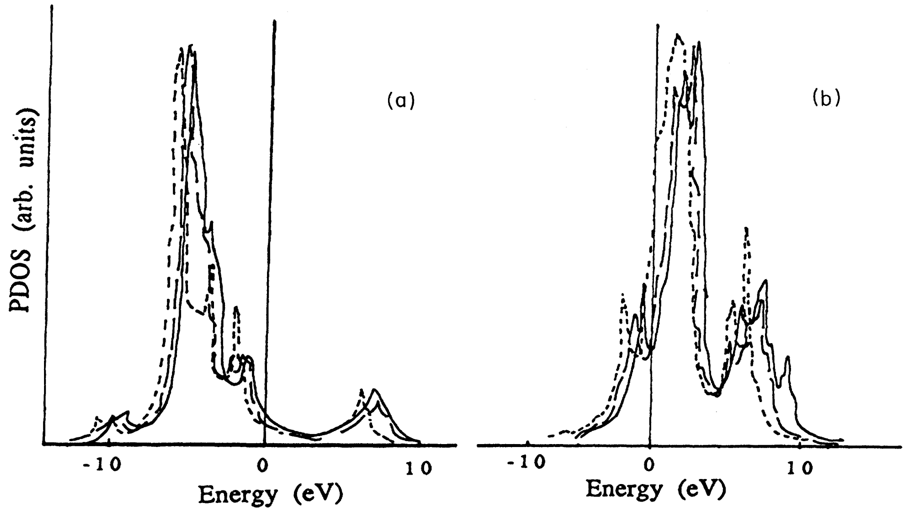

FIG. 2. Partial density of states for the (a) In 5*s* state and (b) In5*p* states. The solid, long-dashed, and short-dashed lines, correspond to the pure semiconductor, InP:S, and InP:Sn, respectively.

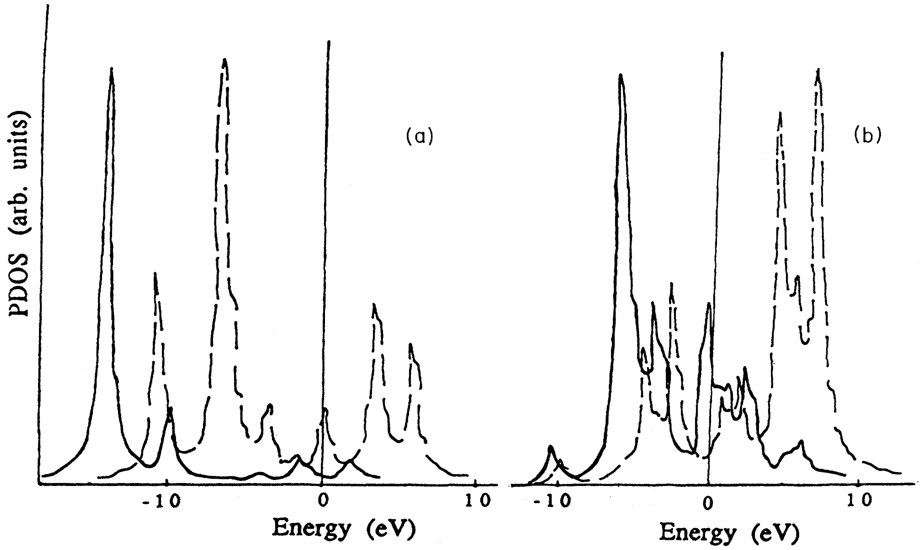

FIG. 3. Partial density of states for (a) S $3s$ in InP:S (solid line) and Sn $5s$ (dashed line) in InP:Sn and (b) S $3p$ in InP:S (solid line) and Sn $5p$ (dashed line) in InP:Sn.

structure at the experimental value of the pure InP as is done for most of the state-of-the-art calculations. The site selected by the impurity [point (b) above] can be reinvestigated from radius considerations. The atomic radii of In and P atoms are 1.44 and 1.10 Å, respectively. Sulfur with a smaller radius of 1.04 Å could, in principle, substitute for either the In or the P site in InP. Due to the smaller size of sulfur, one expects a larger relaxation of the lattice when sulfur is substituted at the In site. The magnitude of this relaxation again depends on the charge state of the impurity. For example, in the case of S-doped Si, it has been reported[10] that the relaxation of the S^{2+} center is larger than S^{+} but smaller than S^{0}. Again, S being the first neighbor to P in the Periodic Table, it would still be expected to behave as a donor with one extra valence electron, if substituted at the P site in InP. It would be interesting to repeat the calculation by substituting S at the P site and find the deep and shallow defect levels. More appropriate would be an energy calculation at both sites to identify conclusively the site occupied by the impurity, but this is beyond the scope of the present work. On the other hand, the atomic size of Sn (1.40 Å) is close to that of In and much larger than that of P. Therefore, from radius considerations, Sn would prefer to substitute the In site only in InP. Recent experimental studies[11] show that almost 100% of the Sn atoms occupy the In site. This is in accordance with the size effects of the atoms discussed above.

To summarize, we have used the fully self-consistent discrete-variational method in the embedded scheme within the local-density framework to study the electronic structure of InP doped with S and Sn impurities at the In site. From our theoretical calculations we obtain a band gap of 1.44 eV, in excellent agreement with the experimental value of 1.41 eV. For S, the charge distribution and the defect levels indicate that it is an acceptor with a level, deep in the gap, at $E_c - 0.68$ eV in contrast to donorlike behavior observed experimentally. It is therefore concluded from our theoretical calculations and radius considerations that S does not occupy the In site in InP. Instead it prefers the P site or forms various defect complexes, such as $\mathrm{In}_V\mathrm{P}_S$. On the other hand, Sn is a donor with a net charge of 0.78 electrons, in agreement with experimental results. We conclude with a hope to study in the future the effect of local relaxations around the impurity on the electronic structure.

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