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Published in:
Physical Review B

DOI:
10.1103/PhysRevB.57.12164

Published: 15/05/1998

Please cite the original version:
Chlorine-impurity-related defects in ZnSe

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(Received 15 October 1997)

Defect complexes formed by chlorine-impurity atoms and native defects in ZnSe are studied by first-principles electronic-structure calculations. The strong tendency for the formation of vacancy-impurity pairs is shown. The chlorine-impurity–zinc-vacancy complex is shown to be the most important source of donor compensation. The results presented are compared with recent experimental results. [S0163-1829(98)02519-3]

I. INTRODUCTION

The wide-band-gap semiconductor ZnSe has received considerable attention during the last ten years. The large and direct band gap makes ZnSe a potential material for many optoelectronic applications. Since $p$-$n$ junctions are needed for most of these applications, controllable doping methods to achieve both $n$- and $p$-type material are required. For ZnSe, an effective $p$-type doping has been extremely difficult to obtain. The highest hole concentrations have been achieved by the incorporation of active atomic nitrogen. Chlorine has turned out to be the most successful donor concentration saturates and eventually begins to decrease in uniformly doped samples. Using planar-doping methods even higher free-electron concentrations have been achieved. In the case of ZnSe, the interest has mainly been directed towards the problems with the $p$-type doping. In spite of numerous theoretical studies of doping in ZnSe, there exist only a few theoretical studies of the effect of chlorine in ZnSe. In fact, to our knowledge, chlorine has been studied using modern electronic structure calculations only by Chadi. In his paper, Chadi shows that chlorine does not form a DX center in ZnSe.

We have made first-principles electronic-structure calculations of the formation energies and lattice relaxations for various chlorine-related defects in ZnSe. The defects studied here include the most feasible defect complexes formed by a chlorine-impurity atom and a native point defect. In this paper only the most interesting Cl-related defects from an extensive set of studied defects are discussed in detail. The aim of the present paper is to shed light on the question of the actual fate of Cl in ZnSe. Our calculations are based on the density-functional theory with the electron exchange correlation treated in the local-density approximation. In our calculations we have employed supercells containing 32 and 64 zinc-blende lattice sites. The Brillouin-zone sampling consists of a $2 \times 2 \times 2$ Monkhorst-Pack k-point mesh in the case of the 32-atom supercell. For the larger supercell the $2 \times 2 \times 2$ Chadi-Cohen k-point mesh has been used. For the chlorine ion a Vanderbilt-type ultrasoft pseudopotential has been employed. The use of ultrasoft pseudopotentials decreases the kinetic energy cutoff needed to describe the heavily peaked electronic states of Cl and a good convergence is obtained already with a 27 Ry cutoff energy. Further computational details can be found in our earlier study of nitrogen-related defects in ZnSe. The defect formation energies given in this work have been calculated using a standard method. We use neutralizing uniform background charge in order to avoid long-range Coulomb interactions between supercells. The energy bands of the defect supercells are aligned with those of the perfect lattice using an average-potential correction.

The organization of the paper is as follows: In Sec. II a detailed analysis of possible isolated chlorine impurities at different lattice sites is given. The analysis of the defect complexes is given in Sec. III. Section IV summarizes the paper.

II. ISOLATED CHLORINE IMPURITIES

We have investigated all possible substitutional and interstitial sites for an isolated chlorine atom. For every site full ionic relaxation without any symmetry restrictions has been performed. The formation energies and ionization levels, if any, are given in Table I. The chemical potential for the chlorine ion has been taken from the chlorine dimer ($\text{Cl}_2$). The absolute values given in Table I are thus not unambiguous, but the differences between them are. In other words, the values cannot be used to estimate the solubility of chlorine to ZnSe, but the numbers are intended to be used to predict the effect of incorporated chlorine. From the values listed in Table I it is evident that most of the incorporated chlorine ions occupy selenium sites. This is also the experi-

<table>
<thead>
<tr>
<th>Defect</th>
<th>Formation energy</th>
<th>Ionization level</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_{\text{Zn}}^{1+}$</td>
<td>$-1.13 + \Delta H + \mu_e$</td>
<td>(+/-) 0.04</td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Se}}^{1+}$</td>
<td>$5.38 - \Delta H + \mu_e$</td>
<td>(+/-) 0.02</td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Se}}^{-}$</td>
<td>$5.46 - \Delta H - \mu_e$</td>
<td>(+/-) 1.46</td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Zn}}^{-}(\text{Se})$</td>
<td>$3.71 + \mu_e$</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Se}}^{-}(\text{Zn})$</td>
<td>$3.75 - \mu_e$</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Se}}^{-}(\text{Se})$</td>
<td>$2.01 + \mu_e$</td>
<td></td>
</tr>
<tr>
<td>$\text{Cl}_{\text{Se}}^{-}$</td>
<td>$4.92 - \mu_e$</td>
<td></td>
</tr>
</tbody>
</table>
The only isolated Cl-impurity defect, which has states deep in the band gap is the chlorine interstitial in the tetrahedral selenium site \([\mathrm{Cl}(\mathrm{T\text{Se}})]\). Its possible charge states are the singly positive, the neutral, and the singly negative one. The neutral charge state is metastable and the negative-\(U\) transition level between the positive and negative charge states is located \(\sim 1.46\ \text{eV}\) above the valence-band maximum. Ionic relaxations of the surrounding lattice are extraordinary: the nearest-neighbor selenium ions move away from the chlorine ion while the next-nearest-neighbor zinc ions move towards it. As a result, in the positive charge state the chlorine ion bonds to three neighboring zinc ions and to one selenium ion. In the negative charge state the chlorine ion pushes all four selenium nearest-neighbor ions further away from itself and all the six next-nearest zinc ions are closer to the chlorine ion than any of the original nearest-neighbor selenium ions. These relaxation patterns reflect a strong ionic character in the interactions between the chlorine interstitial and the neighboring zinc and selenium ions.

### III. CHLORINE-IMPURITY NATIVE-DEFECT COMPLEXES

According to the previous section, the formation energy for the substitutional chlorine donor is much lower than the formation energies of any possible compensating center formed by an isolated chlorine impurity. Therefore the compensation observed\(^1\) has to be due to native defects or due to complexes formed by the chlorine impurity bound to some native defect. Among the native defects in \(n\)-type ZnSe the doubly negative zinc vacancy has been shown to be energetically the most favorable one.\(^4\) Thus the compensation in \(n\)-type ZnSe is due to the formation of isolated zinc vacancies, to some other impurities, or to the presence of defect complexes. Recently, Saarinen \textit{et al.} have identified zinc vacancies in \(n\)-type ZnSe:Cl using positron annihilation experiments.\(^1\) The defect complex \(\mathrm{Cl}_{\text{Se}}\mathrm{V}_{\text{Zn}}\) has been suggested to be formed in high-dose Cl implantation into ZnSe.\(^6\) We have studied possibilities for the creation of defect complexes formed by the zinc interstitial and by selenium or zinc vacancies with the substitutional or interstitial chlorine. Our results for the formation energies of the most feasible of such complexes are listed in Table II.

The stabllest defect complex formed by the chlorine impurity and a native defect in \(n\)-type ZnSe is \(\mathrm{Cl}_{\text{Se}}\mathrm{V}_{\text{Zn}}\). This nearest-neighbor pair is tightly bound: in the negative charge state the binding energy relative to the isolated \(\mathrm{V}_{\text{Se}}\)\(^2\) and \(\mathrm{Cl}_{\text{Se}}\)\(^1\) defects is 1.44 eV. Although we do not find any other stable charge states for this defect complex, there is a possibility for the formation of a triply negative defect. This is because just above the conduction-band minimum there is an electronic state with localized character. The occupancy of that state could be possible under certain circumstances. As a matter of fact, the recently found emergence of a defect state as hydrostatic pressure is applied to \(n\)-type, chlorine-doped ZnSe (Ref. 18) is probably related to this state. The ionic relaxations around the Cl-impurity Zn-vacancy pair shown in Fig. 2 conserve the \(C_{3v}\) symmetry of the defect. The negative charge state (favoring positron trapping at the defect) and the low formation energy of the \(\mathrm{Cl}_{\text{Se}}\mathrm{V}_{\text{Zn}}\) complex give
The chlorine-antisite–selenium-vacancy pair is in fact two small vacancies (V Se and V Zn); halfway between them is a Se-Cl pair. The binding energy of this quite distant pair is surprisingly high: 1.3 eV in the negative charge state. The barrier towards the re-creation of the Cl Se V Zn defect is low, since both of its constituents are, in principle, positively charged. The effect of the chlorine-impurity end of the defect three neighboring zinc ions stay almost at their ideal lattice sites and their relaxations do not depend strongly on the charge state. The detailed structures of defect in positive and negative charge states are visualized in Fig. 4. The formation energy for the selenium-vacancy–substitutional-chlorine pair is in any case so high that it is not a good candidate for the compensating center. Recent positron annihilation experiments by Saarinen et al.17 show, in good agreement with our results, that vacancy-type defects in ZnSe:Cl are created in the zinc sublattice, not in the selenium sublattice.

The defect formed by a chlorine interstitial at the tetrahedral site surrounded by selenium ions Cl(T Se) and a zinc vacancy located at two bond lengths away from the interstitial is depicted in Fig. 5. The ionic relaxations are very strong for this defect complex. Interstitial chlorine and the selenium atom between Cl i and Zn vacancy move as a pair towards the vacancy, so that in the relaxed structure there are in fact two small vacancies (V Se and V Zn); halfway between them is a Se-Cl pair. The binding energy of this quite distant pair is surprisingly high: 1.3 eV in the negative charge state. The high binding energy makes this defect complex a promising candidate for the compensating center in n-type ZnSe.

The chlorine-antisite–selenium-vacancy pair is in fact a metastable state of the substitutional-chlorine–zinc-vacancy pair. The barrier towards the re-creation of the Cl Se V Zn defect is low even for the positive charge state. The chlorine ion does not stay at a fourfold coordinated zinc sublattice site, but moves towards the selenium vacancy by about 50% of the ideal-lattice bond length. A similar metastable behavior connected to the change in the charge state of a complex has previously been found even in an even more pronounced way for defect complexes in GaAs.19,20

<table>
<thead>
<tr>
<th>Defect</th>
<th>Formation energy</th>
<th>Ionization levels</th>
</tr>
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<tbody>
<tr>
<td>(Cl i Se V Zn i ) 1−</td>
<td>2.11 + μe</td>
<td></td>
</tr>
<tr>
<td>(Cl i Se Zn i ) 1+</td>
<td>0.73 + λΔH + μe</td>
<td></td>
</tr>
<tr>
<td>(Cl i Se V Se 3) +</td>
<td>−0.82 + 2λΔH + 3μe</td>
<td>(3+/1+) 0.97</td>
</tr>
<tr>
<td>(Cl i Se V Se 4) +</td>
<td>1.11 + 2λΔH + μe</td>
<td>(1+/−) 1.41</td>
</tr>
<tr>
<td>(Cl i Se V Se 5) −</td>
<td>3.92 + 2λΔH − μe</td>
<td></td>
</tr>
<tr>
<td>[Cl i (T Se ) V Zn i ] 3+</td>
<td>2.03 − λΔH + 3μe</td>
<td>(3+/1+) 0.65</td>
</tr>
<tr>
<td>[Cl i (T Se ) V Zn i ] 4+</td>
<td>3.32 − λΔH + μe</td>
<td>(1+/−) 0.93</td>
</tr>
<tr>
<td>[Cl i (T Se ) V Zn i ] 5−</td>
<td>5.18 − λΔH − μe</td>
<td></td>
</tr>
<tr>
<td>[Cl Zn i Se V Se ] 1+</td>
<td>4.30 + μe</td>
<td></td>
</tr>
</tbody>
</table>

The chlorine antisite–selenium-vacancy pair is in fact two small vacancies (V Se and V Zn); halfway between them is a Se-Cl pair. The binding energy of this quite distant pair is surprisingly high: 1.3 eV in the negative charge state. The high binding energy makes this defect complex a promising candidate for the compensating center in n-type ZnSe.
The formation energy of the substitutional chlorine impurity attains its lowest values if the material is grown under Zn-rich conditions, whereas the formation energy of the most probable compensating center, i.e., that of Cl\_Se V\_Zn, does not depend on the stoichiometry. Thus, the increase in the parameter λ', dictating the stoichiometry, favors the generation of the compensating centers instead of the formation of substitutional chlorine donors. Therefore the best growth conditions for obtaining the highest effective donor concentrations are Zn-rich conditions. Figure 6 shows, as a function of the electron chemical potential, the formation energies for those chlorine-related defects that have the lowest formation energies in ZnSe grown under Zn-rich conditions (λ = 0). As the Fermi level rises, for example, due to chlorine doping, the formation energy of the donor impurity increases, and the formation of compensating defect complexes becomes more favored. Thus these chlorine-related defect complexes are formed and further chlorine incorporated into ZnSe decreases the doping efficiency.

IV. CONCLUSIONS

We have shown that most of the chlorine incorporated in ZnSe occupies selenium lattice sites indicating an effective donor doping. The chlorine-induced lattice relaxations are shown to be generally small, but in the case of defect complexes the softness of the ZnSe lattice manifests itself as large distortions. Our calculations show that the donor compensation observed in n-type chlorine-doped ZnSe is due to the creation of defect complexes. The most promising candidate for the compensating center is the substitutional-chlorine–zinc-vacancy complex. Since in every good candidate for the compensating center there is a zinc vacancy as a part of the complex or as an isolated defect, these results are in excellent agreement with the recent positron annihilation measurements by Saarinen et al.\textsuperscript{17}

ACKNOWLEDGMENTS

The authors wish to thank P. Hautojärvi, K. Saarinen, K. Laasonen, and T. Mattila for many valuable discussions. This work has been supported by the Academy of Finland through a MATRA grant. We also acknowledge the generous computing resources of the Center for the Scientific Computing (CSC), Espoo, Finland.