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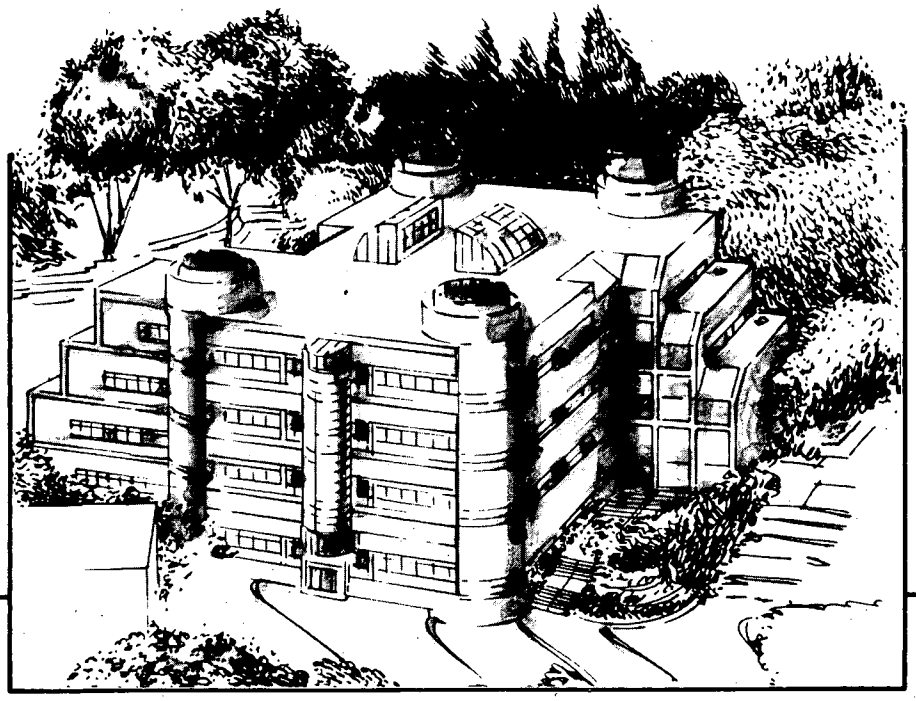

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ACTIVATION OF SHALLOW DOPANTS IN II-VI COMPOUNDS

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Abstract

The amphoteric native defect model is applied to the understanding of the variations in the dopant activation efficiency in II-VI compounds. It is shown that the location of the common energy reference, the Fermi level stabilization energy, relative to the band edges can be used to determine the doping induced reduction of the formation energy and the enhancement of the concentration of compensating native defects. The model is applied to the most extensively studied compound semiconductors as well as to ternary and quaternary alloys. The effects of the compound ionicity on the dopant activation are briefly discussed.

1. Introduction

The low doping activation efficiency is one of the major problems impeding device applications of many of semiconductor materials. The importance of this problem has been recognized very early [1] and the recent progress in applications of the wide gap II-VI compounds for the short wavelength light emitters has led to renewed interest in this long standing and controversial issue . There were numerous experimental and theoretical attempts to understand the mechanism responsible for the reduced activation efficiency of intentionally introduced donors and/or acceptors [2]-[9]. In an "ideal" doping experiment the impurities are introduced on the proper substitutional sites with the rest of the crystal

remaining unaffected by this procedure. Unfortunately, since the incorporation of the dopants changes the electrochemical potential, the ideal experiment can be realized only for a limited dopant concentration. At the concentrations approaching these limits the system is becoming unstable to formation of intrinsic defects compensating the intentionally introduced dopants or, in order to lower their chemical potential, the dopants precipitate and/or form chemical compounds with the atoms of the host crystal lattice.

The doping problem is not limited to any specific sub-group of semiconducting materials. It is found in elemental semiconductors as well as in a large variety of compound semiconductors. Among group III-V semiconductors GaAs and GaSb, can be easily and efficiently doped with acceptors however very stringent limits on the maximum n-type doping are found in these materials. On the other hand InP, GaN and InN show much higher activation efficiencies for donors than for acceptors. Compound II-VI semiconductors also exhibit a wide range of doping behaviors. For example ZnSe, CdSe and CdS are routinely n-type materials and can be heavily doped with donors whereas doping with acceptors is very difficult to achieve. In contrast it is very easy to activate high concentrations of acceptors in ZnTe although only a very lightly doped n-type ZnTe has been reported in a recent study [10].

It has been an accepted notion that doping problems occur only or most severely in wide-gap semiconductors. This is not necessarily true. A good example is HgSe, a semiconductor with a zero-gap, inverted band structure. As grown HgSe is always n-type typically with electron concentration in high 10^{17} to low 10^{18} cm^{-3}[11]. It can be heavily doped with donors but so far no p-type conductivity has ever been reported in this material.

The earliest efforts to understand the reduced electrical activity of dopants were based on the fact that the formation energy of charged defects depends on the location of the Fermi energy which in turn is determined by the electron or hole concentration [1]. Therefore, any attempt to increase the carrier concentration decreases the formation energy and increases the concentration of compensating defects. This results in a saturation of the free carrier concentration at high doping levels. This explanation however could not provide an answer to the question why some of the semiconductors exhibit good n-type conductivity whereas others, with a similar band gap are good p-type conductors. These trends in the dopant activation efficiency of different compound III-V semiconductors have been recently explained in terms of the amphoteric native defect model [12]-[14]. In this paper we will apply this concept to address the issue of dopant activation in II-VI compounds [15]-[17]. We will then show similarities and differences between III-V and II-VI materials and discuss the effects of ionicity on the activation efficiency.

2. Fermi Level Induced Formation of Defects

The concentration of defects under equilibrium conditions is determined by the Gibbs free energy. In the cases where the change in the crystal volume can be neglected the expression for the defect concentration takes a form:

$$C = C_o \exp[(S_f T - E_f)/kT] \qquad (1)$$

where S_f and E_f are, respectively, the formation entropy and the formation energy of the defect. For charged defects the formation energy E_f depends on the location of the Fermi energy relative to the charge transition state of the defect. Thus for a donor which can support charge m+ the formation energy is given by,

$$E_f = E_{f0}' + \Sigma (E_F - E^{m+}) \quad (2)$$

where E^{m+} is the energy of (m+1/m) charge transition state, E_F is the Fermi energy and E_{f0}' is the structural part of the defect formation energy that is independent of the Fermi energy.

Calculations of the electronic part of the formation energy given by the second term in Eq. (2) require a detailed knowledge of the defect energy levels. Unfortunately for most defects such information is not readily available. We have argued previously that based on general properties of highly localized defects one can define a universal energy reference that is constant on an absolute scale and does not depend on the semiconductor material [14]. Using this energy reference one can evaluate the change in the formation energy of the same type of defects in different semiconductors. In III-V compounds the energy reference, known as the Fermi level stabilization energy, E_{FS}, can be determined from the known Fermi level pinning position at a metal-semiconductor interface or from the stabilized position of the Fermi level in semiconductors heavily damaged with high energy particles [12], [14].

The Fermi level stabilization energy plays an important role as it divides the whole range of available energies into two regions. For $E_F < (>) E_{FS}$ donor (acceptor) like defects are predominantly formed. Such an amphoteric behavior of native defects lies at the heart of the model which has been applied to explain a variety of phenomena in semiconductors including formation of Schottky barriers [12], doping induced diffusion [14] suppression of dislocation formation [18] and trends in surface recombination velocities [19].

Using E_{FS} as an energy reference the formation energy of the donor defect given by Eq. (2) takes the form,

$$E_f = E_{f0} + m(E_F - E_{FS}) \qquad (3)$$

A great advantage of using E_{FS} as an energy reference is that since E_F can be related to the carrier concentration E_f is fully determined by the known position of E_{FS} relative to the band edges. This approach is especially valuable in an analysis of the trends in defect formation in similar materials and has been successfully applied to explain differences in the doping efficiency in different III-V compounds. Thus it has been shown that in GaAs and InP the Fermi energy cannot be separated from E_{FS} by more than about ± 0.8 eV[13]. Any attempt to move E_F further away by increased doping results in an enhanced formation of compensating defects that deactivate the intentionally introduced dopants. Therefore, as a rule, it is easier to dope a material with donors (acceptors) when E_{FS} located close to the conduction (valence) band edge.

3. Application to II-VI compounds

Successful application of the amphoteric defect model to variety of defect related phenomena in III-V raises the question whether the model is also applicable to other semiconductor systems. There were several reports indicating that the concept of the common energy reference can be also used in this case[15]-[17]. Here we will examine this issue in more detail and show similarities and difference between those two material systems.

Since the position of E_{FS} can be determined from the known band offsets, one can find the location of E_{FS} relative to the band edges of different II-VI compounds. As is

seen in Fig. 1 the location of E_{FS} relative to the band edges varies very significantly in different II-VI compounds. It is located in the upper half of the band gap in ZnSe and in the lower half of the band gap in ZnTe. The location of E_{FS} explains the experimentally observed propensity of ZnSe to be n-type and ZnTe to be a p-type material. Proximity of E_{FS} to the conduction band edges in CdSe and CdS accounts for the fact that both materials are good n-type conductors and are very difficult to dope with acceptors.

Extensive doping studies of II-VI compounds have shown that the maximum concentration of free holes in N doped ZnSe is close to 10^{18} cm^{-3} [2],[4],[5] whereas ZnTe can be efficiently doped to a level higher than 10^{20} cm^{-3} [20]. It has been demonstrated most recently that CdSe can also be doped p-type [21]. However the hole concentration is limited to about 10^{17} cm^{-3}. So far there has been no report on p-type doping of CdS. A quite different behavior is found for the activation efficiency of donors. Electron concentration exceeding 10^{19} cm^{-3} were reported in ZnSe but, so far the highest electron concentration of in ZnTe does not exceed $4x10^{17}$ cm^{-3}[10].

The positions of the Fermi level corresponding to the maximum doping levels are shown in Fig. 1 with the dashed lines. The calculations were performed for a temperature T=600 K, typical for the epitaxial growth of thin films of II-VI compounds. It is quite evident that there is a correlation between the extreme positions of the Fermi level in different semiconductors. In ZnSe the limits for the Fermi level are located approximately at E_{FS} - 1.3 eV in p-type and at E_{FS} + 1.3 in n-type. The energy range between those two limits represents an allowed Fermi energy band. Assuming that the minimum Fermi level position in CdS lines up with other materials at E_{FS} -1.3 eV we can expect that CdS can be doped p-type only to a concentration of about 10^{14} cm^{-3}. It also appears that ZnTe could be doped to the level of about 4 to $5x10^{20}$ cm^{-3} which 2 to 3 times higher than the highest hole concentration reported [20].

As mentioned before a very interesting case is represented by HgSe. In this zero-gap material both conduction and valence band edges are located at about E_{FS} -1.2 eV. This indicates that for any position of the Fermi energy donors are the dominant point defects and that it should be very difficult to dope it with acceptors. Indeed HgSe is always n-type and the lowest reported electron concentration of mid 10^{16} cm^{-3} [11] corresponds a Fermi energy close to the conduction/valence band edge which as is seen in Fig. 1 is located at E_{FS} -1.2 eV. In HgTe, another zero-gap semiconductor the conduction and valence band edges are located much higher at E_{FS} - 0.5 eV, i.e., well within the range of the allowed Fermi energies. This again is consistent with the fact that n- and p-type doping can be easily attained in HgTe.

So far we have considered the binary II-VI compounds with discrete band offsets. For many applications however ternary or quaternary alloys are used. Therefore it is important to be able to predict electrical activity of dopants in those materials. Among the group II-VI alloys ZnMgSSe quaternary compounds, lattice matched to GaAs, play a special role as materials for blue-green light emitters. It has been found recently that the efficiency of p-type doping is dramatically decreasing with increasing energy gap, controlled by the Mg and S contents [5]. The effect was explained in terms of the amphoteric native defect model. Using the analysis previously proposed for acceptors in III-V compounds the authors show that the compensation of nitrogen acceptors can be explained by the Fermi level induced formation of donor defects [22]. Later the reduced activation of N acceptors in ZnMgSSe was confirmed by another study [23]. The main assumption of the model is that the donors compensating N acceptors are highly localized with their charge transition states pinned to E_{FS}. In such a case the acceptor to donor concentration ratio is,

$$[N^+]/[D^-] = \exp[2(E_F - E_{SI})/kT] \quad (4)$$

where $[N^+]$ is the concentration of N acceptors, $[D^-]$ is the concentration of compensating donors and E_{SI} is the energy reference which is equal to the lower limit of the allowed Fermi energies. In ZnSe $E_{SI} = E_{FS} - 1.3$ eV. In ZnMgSSe lattice matched to GaAs the valence band offset $\Delta E_v = 0.4\ \Delta E_g$, where ΔE_g is the change of the band gap. Adopting a constant, composition independent value of the hole density of states effective mass $m_h = 0.6m_0$ one can calculate the maximum hole concentration, n_h as a function of the energy gap in ZnMgSSe. For a non-degenerate hole gas, to good approximation, n_h is given by the simple expression [14],

$$n_h = N_v \exp[(E_{SI} - E_v)/kT] \quad (5)$$

where N_v is the density of states in the valence band, E_v is the valence band edge energy and E_{SI} is the lower limit for the allowed Fermi energy band. The calculated n_h along with available experimental data are shown in Fig. 2. The agreement with the experiment is reasonably good. The deviation found for the highest band gap could be attributed to other compensation mechanisms which are becoming increasingly important at very low hole concentrations.

Similar reductions in the activation efficiency of shallow acceptors have been observed in other alloys including $Zn_xSe_{1-x}Te$ where, as expected, a rapid increase in the activation efficiency of N acceptors is observed with increasing Te content [24]. Again the trend can be attributed to the Te induced shift of the valence band edge towards E_{FS}.

Numerous studies have also demonstrated that the concept of the universal energy reference can be also applied to n-type doping of group II-VI alloys. Thus it has been

shown recently that the doping efficiency of Cl donors in $Zn_{1-x}Mg_xSe$ is decreasing with increasing x [16]. The calculated maximum hole concentrations as a function of x for two different conduction band offsets between ZnSe and MgSe are shown in Fig. 3. In the same Figure the experimental data of Ref. 16 are also shown. It appears from Fig. 3 that the limits on the band offsets required to explain the experimental results are ΔE_c(ZnSe/MgSe) = 0.6 ± 0.1 eV. This value is higher than ΔE_c = 0.36 ± 0.07 eV deduced from the measurements of the band valence band offsets in $MgSe/Cd_{0.54}Zn_{0.46}Se$ [25]. On the other hand a rapid reduction of the electron concentration with increasing Mg content in Br doped $Cd_{1-x}Mg_xTe$ [26] can be explained assuming a large conduction band offset of ΔE_c(MgTe/CdTe) = 1.55 eV which is a good agreement with a value of 1.57 + 0.11 eV determined from the valence band offset in $MgTe/Cd_{0.88}Zn_{0.12}Te$ [25].

The above examples demonstrate that one can use the common energy reference to evaluate trends in dopant activation efficiency in different compound semiconductors. Although the same concept applies to III-V and II-VI semiconductors it should be noted that the range of allowed Fermi energies is different in those two material systems. For example in GaAs E_F changes by about 1.5 eV from E_{FS} - 0.7 eV to E_{FS} + 0.8 eV. However as is seen in Fig. 1 in the isocoric II-VI compound, ZnSe, E_F varies by about 2.6 eV from E_{FS} - 1.3 eV to E_{FS} +1.3 eV. This large difference of 1.1 eV in the allowed Fermi energy band is comparable to the energy gap difference of 1.3 eV between GaAs and ZnSe and can be attributed to the ionic contribution to the semiconductor band gap or equivalently to the difference between energies of sp^3 hybrids for anion and cation sites in these two materials. The difference between III-V and II-VI compounds resembles the situation found for the Fermi level pinning at metal semiconductor interfaces where a wider range of Schottky barrier heights and a much stronger dependence on the electronegativity of metals is observed in ionic II-VI compounds [27]. This again points

at the common origin of the defect induced Fermi level stabilization in semiconductors and the Fermi level pinning at metal-semiconductor interfaces.

4. Conclusions

The concept of amphoteric native defects and the common energy reference provides a simple guiding principle to evaluate trends in the dopant activation efficiency in different semiconductors. It does not require any detailed knowledge on the microscopic nature of the compensating defects. We show that the concept applies to a large variety of II-VI materials including some extreme cases of zero gap semiconductors. Compound II-VI materials with more ionic nature of the cation ion bonds exhibit a much larger width of the allowed Fermi energy band than III-V semiconductors.

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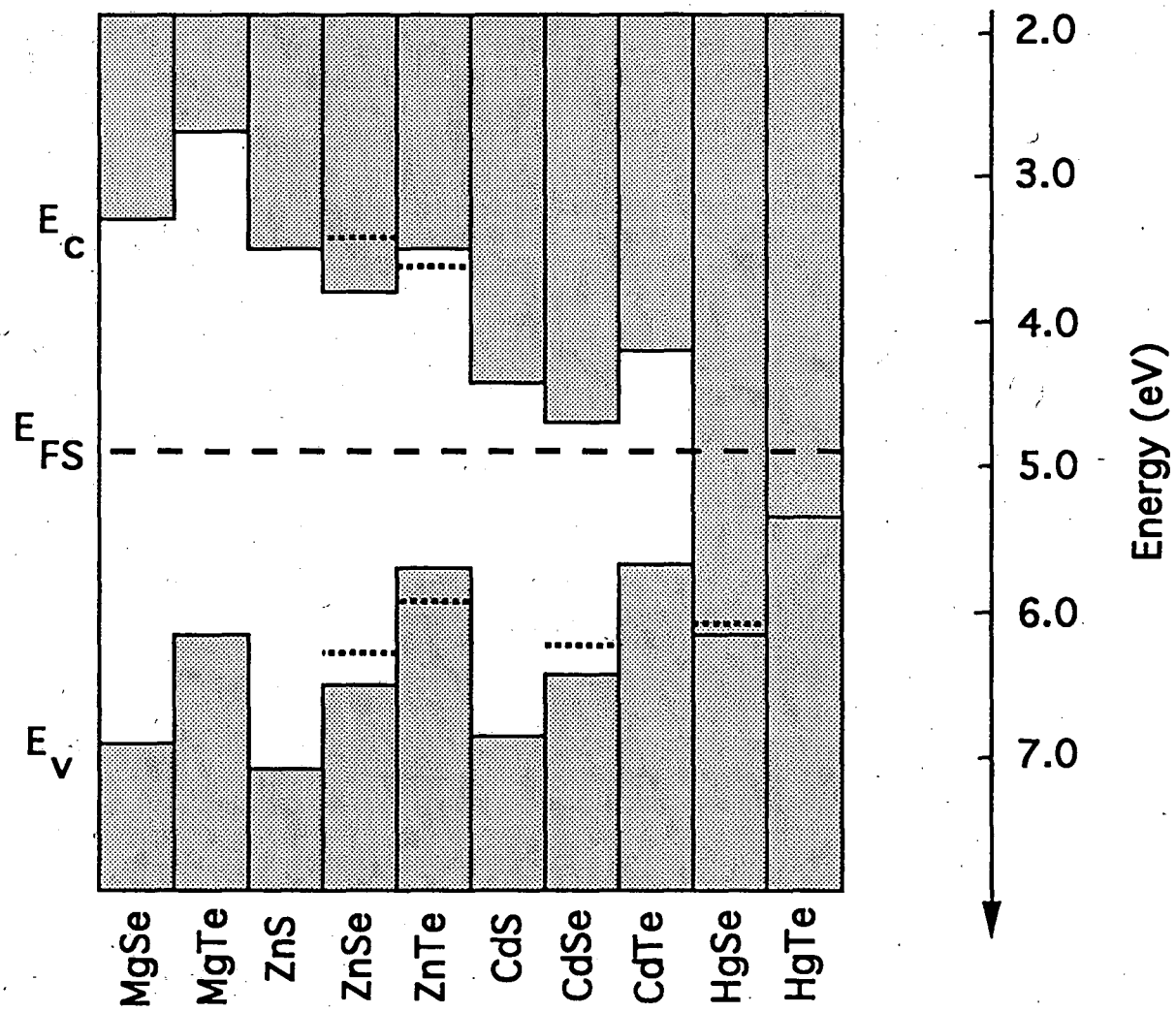
Figure captions

Fig. 1 Band offsets for II-VI compounds. E_{FS} represents the Fermi level stabilization energy at about 4.9 eV below the vacuum level. The limiting positions for the maximum doping levels are shown by the dashed lines.

Fig. 2 Calculated dependence of the concentration of electrically active acceptors as function of the band gap in ZnMgSSe. Experimental results of Ref. 5 and Ref. 23 are also shown.

Fig. 3 Calculated maximum electron concentration as a function of composition in $Zn_{1-x}Mg_xSe$ along with the data of Ref. 26.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CdS
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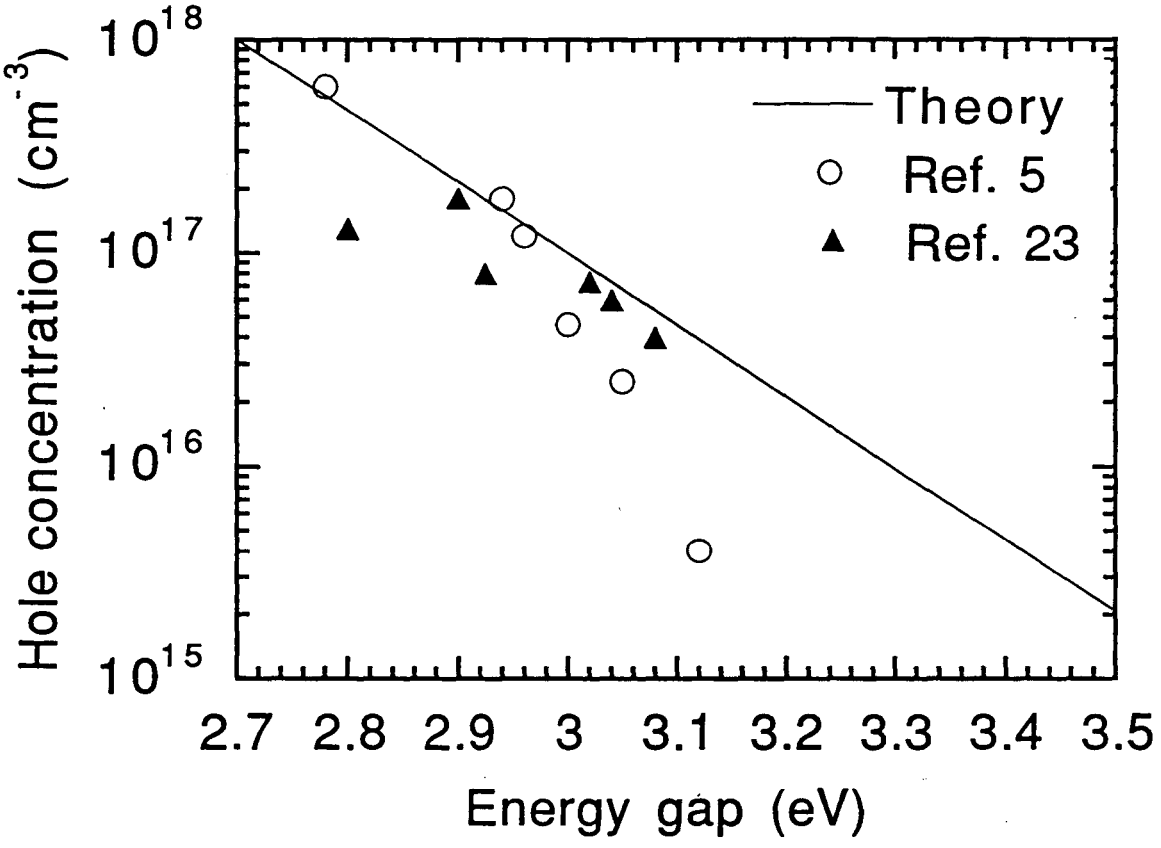
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Ref. 23
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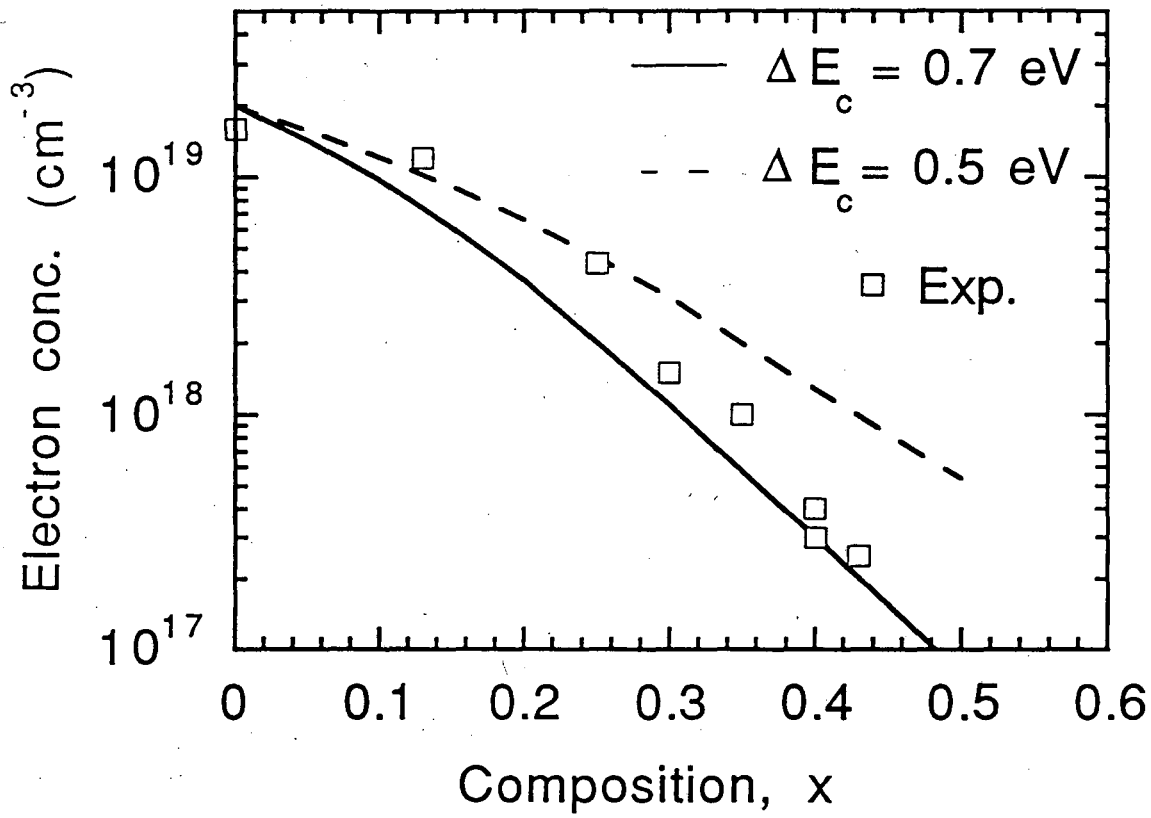
Energy gap (eV)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Composition, x
ΔE_c = 0.7 eV
ΔE_c = 0.5 eV
Exp.

Fig. 3

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