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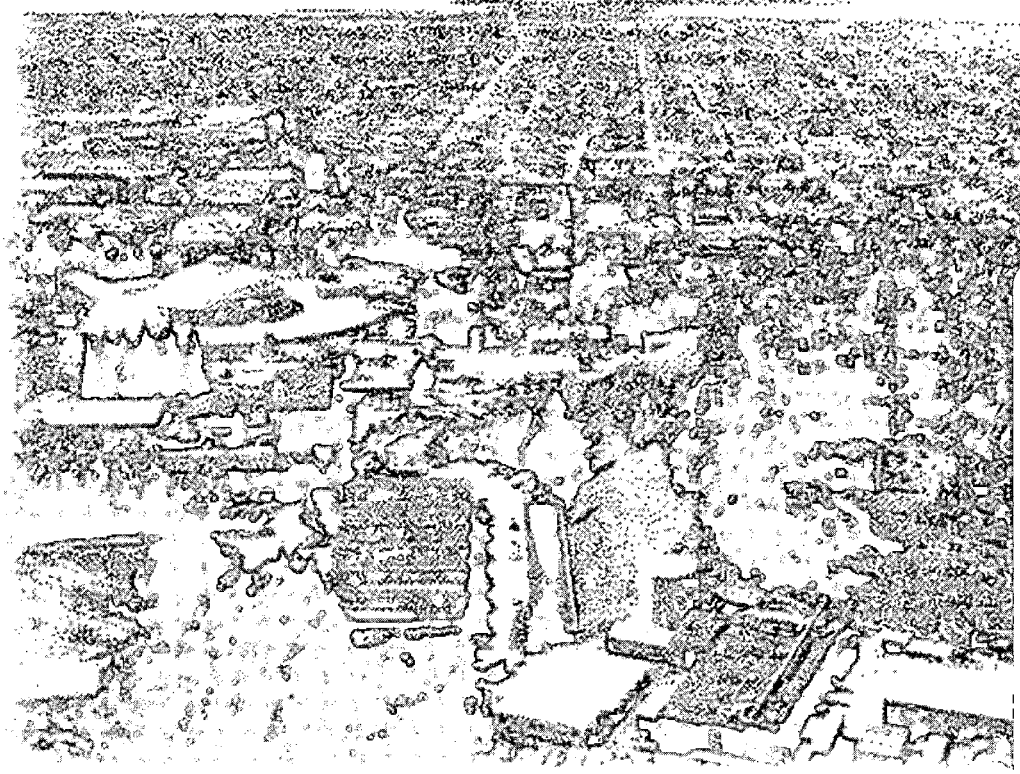

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FERMI LEVEL STABILIZATION, BAND OFFSETS AND MAXIMUM DOPING LIMITS IN WIDE-GAP II-VI SEMICONDUCTORS

by W. Walukiewicz

A. INTRODUCTION

Band offsets at semiconductor heterointerfaces play a critical role in a variety of electronic devices. Although a large variety of theoretical and experimental methods have been employed to determine the location of the band edges, the actual band offsets are far from being firmly established in II-VI semiconductors [1]. One of the phenomenological methods to determine the band offsets is based on the observation that the levels of highly localized defects align across semiconductor interfaces [2 - 4]. Thus it has been demonstrated that the known positions of the transition metal energy levels can be used to find the band offsets among different group III-V and II-VI semiconductors [2].

It has been shown recently that the notion of the material independent location of highly localized energy levels The fact that the energy levels of highly localized defects align across semiconductor interfaces has important consequences for understanding of the thermodynamic properties of the native defects in compound semiconductors [5-7]. Native defects are known to introduce deep, highly localized levels in semiconductors. In wide gap semiconductors those levels are frequently located in the band gap and compensate intentionally introduced shallow dopants. In some instances the compensation is so severe that a certain type of doping cannot be achieved at all. This review addresses the

issue of the relationship between the band offsets and the maximum free carrier concentrations in wide-gap II-VI semiconductors.

B. BAND OFFSETS AND THE FERMI LEVEL STABILIZATION ENERGY

Incorporation of native defects leads, in most instances, to changes in the electrical and optical properties of semiconductor materials. Depending on the location of the Fermi energy, acceptor- or donor-like native defects are predominantly formed. The amphoteric nature of native defects is now quite well established. Extensive studies of compound semiconductors irradiated with high energy particles have shown that at high enough irradiation doses the Fermi energy, E_F, is stabilized at $E_F = E_{FS}$. For this position of the Fermi energy the formation energies and thus also the formation rates for the acceptor- and donor-like defects are the same. The existing data on the location of the E_{FS} shows that it aligns across semiconductor heterointerfaces [5]. This indicates that the stabilization of the Fermi energy is accomplished by charge states of highly localized defects.

The stabilization energy, E_{FS}, plays the important role of an energy reference for the determination of the Fermi level dependent formation energy of native defects. When a semiconductor is doped with shallow donors or acceptors the Fermi energy E_F is shifted towards the conduction or the valence band. Fermi level induced change in the formation enthalpy of the native defects is given by

$$H_f = H_{fo} - m(E_F - E_{FS}) \qquad (1)$$

where H_{fo} is the formation enthalpy for $E_F = E_{FS}$ and m is the charge state of the defect. The sign of m is negative for acceptors ($E_F > E_{FS}$) and positive for donors ($E_F < E_{FS}$). The maximum doping concentration limit is set by the position of the Fermi energy at which concentration of the compensating native defects, as determined from the formation enthalpy, is becoming comparable to the concentration of the dopants. This leads to a saturation of the free carrier concentration and defines a range of allowed Fermi energies in a given semiconductor.

The band offsets and the location of E_{FS} in different wide-gap II-VI semiconductors are shown in Figure 1. Extensive studies have shown that a maximum free electron concentration of about 10^{19} cm^{-3} [8] and a maximum free hole concentration of 10^{18} cm^{-3} [9] can be achieved in ZnSe. These concentrations correspond to $E_F^{max} = E_{FS} + 1.3$ eV and $E_F^{min} = E_{FS} - 1.3$ eV. Using the same values of E_F^{max} and E_F^{min} one can find the maximum free carrier concentrations for the other II-VI semiconductors. The carrier concentration limits given in Figure 1 have been obtained assuming a hole effective mass of $0.6m_0$ for all compounds. For most of the compounds the electron effective masses were adopted from Rode [10]. For MgSe and MgTe an electron effective mass of $0.3m_0$, i.e. , the same as that for ZnSe was assumed.

As is seen in Fig. 1 the locations of E_F^{max} and E_F^{min} with respect to the conduction and the valence band edges vary dramatically among II-VI materials. Consequently, large differences in the maximum electron and hole concentrations are predicted for these materials. The free carrier concentrations given in Figure 1 well account for the experimentally observed trends among II-VI semiconductors. Also, it has been shown that one can use the band offsets to

predict the maximum doping levels in ternary and quaternary alloys of II-VI compounds [11- 17] . The above method can be especially useful in predicting doping limits in new materials with known band offsets. For example, it is expected that BeTe with the valence band at E_{FS} - 0.8 eV [18,19] can be very heavily doped with acceptors. However, since the conduction band is located at E_{FS} + 1.9 eV the maximum electron concentration should be limited to about 4×10^{15} cm^{-3}.

Since the band offsets are known only with a limited accuracy, the doping concentration limits given in Figure 1 are approximate and in most cases can be treated only as order of magnitude estimates. More accurate calculations would require incorporation of the effects of temperature on the location of the valence and the conduction band edges as well as temperature dependent density of states. Also in the cases where very high limits, exceeding 10^{20} cm^{-3}, are predicted the actual concentration of free carriers can be limited by the dopant solubility limits rather than compensation by the native defects.

C. CONCLUSIONS

The concept relating semiconductor band offsets to the location of the Fermi level stabilization energy has been reviewed and applied to wide gap II-VI semiconductors. It provides a simple method to estimate the maximum carrier concentrations that can be achieved by doping of the binary compounds and their alloys

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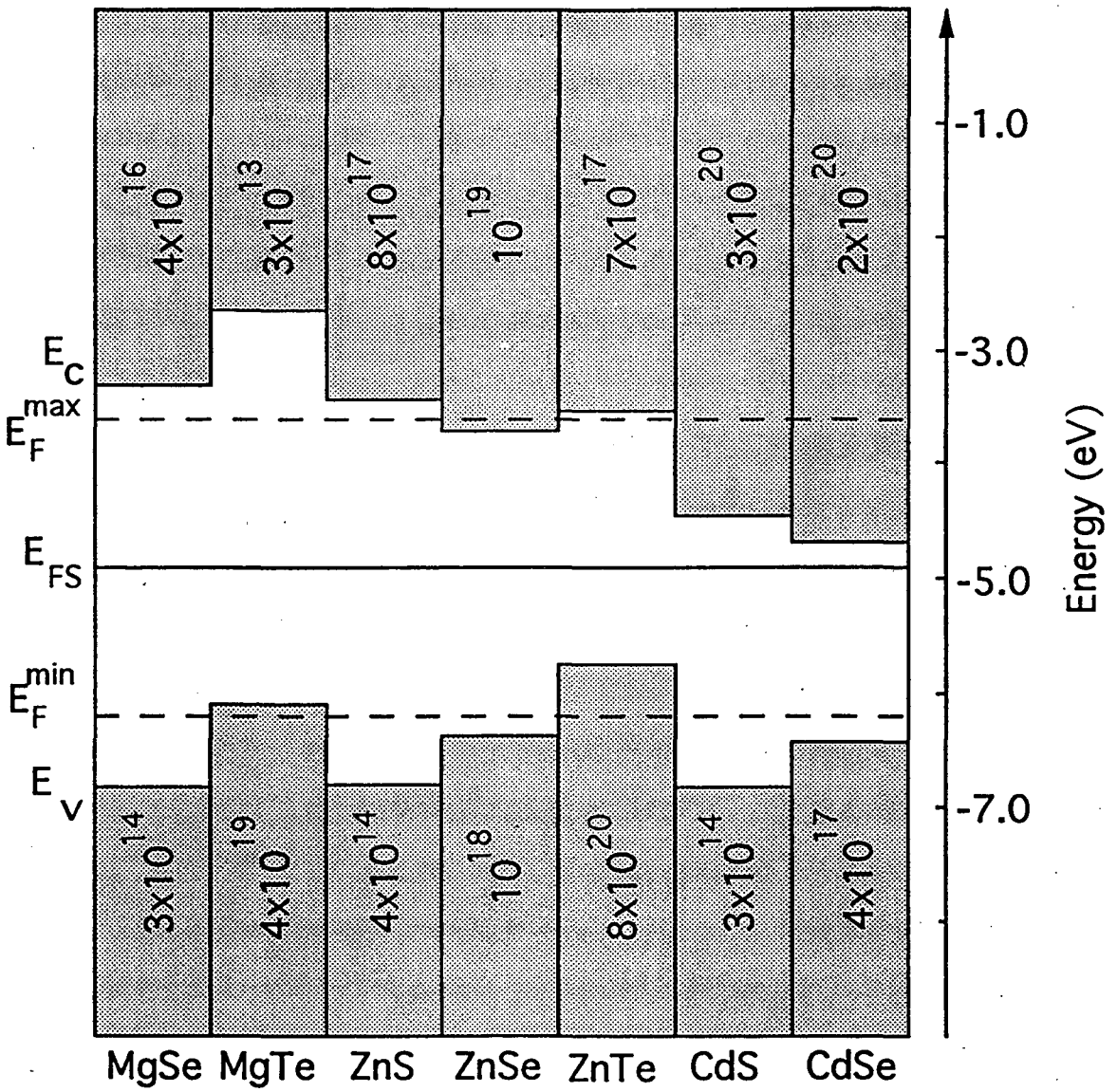
Figure caption

Figure 1 The band offsets in II - VI wide gap semiconductors. The energy scale shows the position of the band edges with relative to the vacuum level. The maximum electron and hole concentrations achievable by doping were calculated for the temperature of 620 K.


E_C
E_F^{max}
E_{FS}
E_F^{min}
E_V
4×10^{16}
3×10^{13}
8×10^{17}
10^{19}
7×10^{17}
3×10^{20}
2×10^{20}
3×10^{14}
4×10^{19}
4×10^{14}
10^{18}
8×10^{20}
3×10^{14}
4×10^{17}
-1.0
-3.0
-5.0
-7.0
Energy (eV)
MgSe
MgTe
ZnS
ZnSe
ZnTe
CdS
CdSe

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