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W. Walukiewicz

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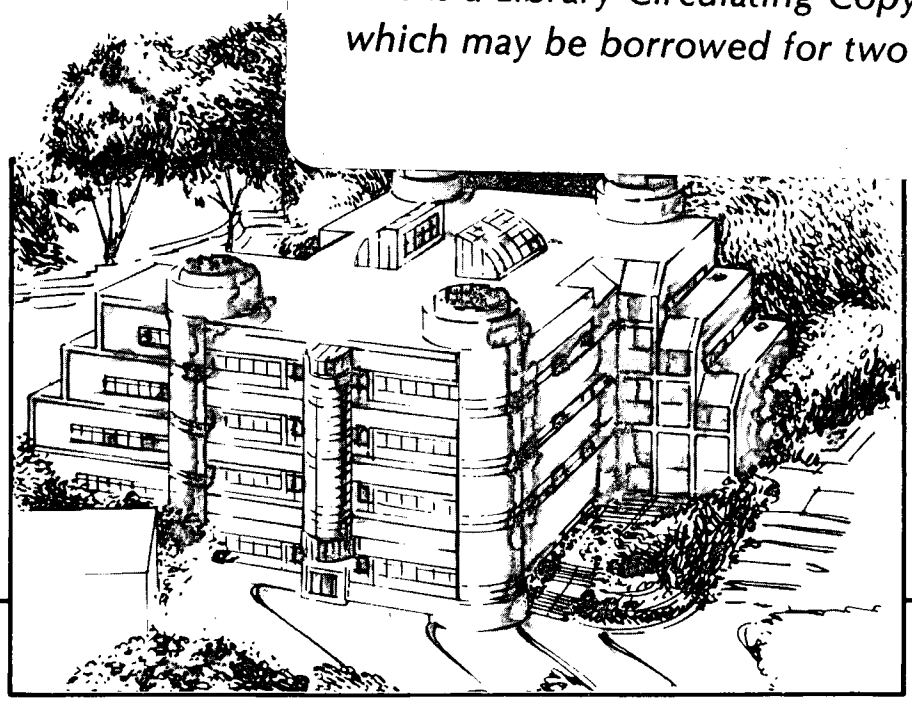

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

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FERMI LEVEL STABILIZATION IN SEMICONDUCTORS: IMPLICATIONS FOR IMPLANT ACTIVATION EFFICIENCY

W. WALUKIEWICZ
Center for Advanced Materials, Lawrence Berkeley Laboratory, University of California, 1 Cyclotron Road, Berkeley, CA 94720

ABSTRACT

We propose the existence of a Fermi level stabilization energy in III-V semiconductors which provides a reference level for the electronic part of defect annihilation energies. It is shown that the position of the stabilization energy with respect to the band edges determines the maximum free carrier concentration which can be obtained through doping. The proposed model accounts for previously unexplained trends in implant activation efficiency in III-V semiconductors.

Understanding of the processes leading to incorporation of impurities in semiconductors is a long-standing issue of great fundamental and technological importance. It is well-known that in III-V semiconductors the highest concentrations of free carriers which can be obtained by implantation or doping are limited. These limits are not related to the solubility limits of specific impurities since it has been demonstrated that the total impurity concentration can be much higher than the free carrier concentration [1,2]. Also, it has been shown recently [3] that in GaAs the limits are not caused by amphoteric behavior of group IV semiconductors. The saturation of the electron concentration was observed although LVM absorption measurements indicated that most of the Si atoms were located on Ga sites. Despite many years of extensive studies there is no commonly accepted explanation of the observed free carrier saturation phenomena. The most successful model which can account, at least partially for the existing data is based on the mechanism of auto-compensation [4]. However, in its current form this model does not provide any guidelines for an understanding of experimentally observed differences in maximum values of the free carrier concentrations in various semiconductors [5].

In this paper we propose that the processes which limit the free carrier concentrations in semiconductors are inherently related to the recently discovered mechanism of native defect induced Fermi level stabilization [6,7]. We show that the stabilization energy plays a fundamental role of an energy reference level for evaluation of the electronic part of the defect formation energy. It is, therefore, a key parameter determining native defect abundances and thus also electrical properties of semiconductors. The concept of the stabilization energy has been introduced in a context of a common Fermi level pinning energy at metal-semiconductor interfaces and in heavily irradiated semiconductors [6,7]. The stabilization energy, E_{FS}, is shown in Fig. 1 for a number of III-V and column IV semiconductors. It has been argued previously that the stabilization of the Fermi energy at E_{FS} corresponds to a minimum free energy of the defect system in quasi-equilibrium with the free carrier gas [7].

Stabilization of the Fermi energy is a direct consequence of amphoteric behavior of simple native defects which undergo transformations changing their electrical properties. Defect formation energy diagrams for simple native defects in GaAs are shown in Fig. 2. The diagrams are based on the total defect energy calculations of Refs. [9,10]. It is seen from this figure that the type of generated defects is determined by the Fermi energy position and that acceptor- or donor-like defects are preferentially

generated in n- or p-type material, respectively. The numbers at different segments of the curves represent the number of charges transferred from the Fermi sea to the defect. The stabilized Fermi energy is defined by the zero charge transfer condition. From Fig. 2 we find $E_V+0.6eV \leq E_{FS} \leq E_V+0.8eV$ which is in reasonable agreement with the experimentally observed range of $E_V+0.5eV \leq E_{FS} \leq E_V+0.7eV$ [7].

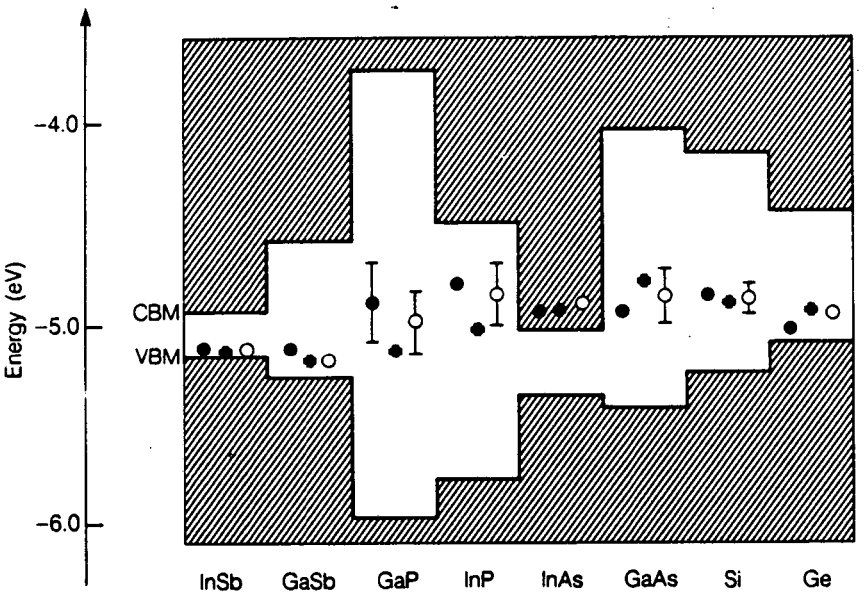

Fig. 1. Fermi level stabilization energy, E_{FS}, deduced from the Fermi level pinning at metal semiconductor interfaces (o) and from the position of the Fermi level in heavily irradiated semiconductors (•). The band edge offsets are taken from Ref. 8.

The Fermi level stabilization model postulates that the original electrical activity of a semiconductor is compensated by the generated native defects. A reverse process occurs during crystal growth or post-implantation annealing when intentionally introduced impurities are activated and damage is removed. The energy associated with the annihilation of a native defect is strongly dependent on the Fermi energy. However, since in the defect annihilation process charge is transferred from the defect to the Fermi sea the energy gained through annihilation decreases with increasing separation of the Fermi energy from E_{FS}. For example, it can be found from Fig. 2 that the energy gained during annihilation of a defect pair (V_{Ga},Ga_i) depends on net charge transfer from the pair to the free electron gas and decreases by ~1.7 eV with the Fermi energy shift from E_{FS} to the conduction band edge. This means that the process of the damage removal during post-implantation annealing or annihilation of native defects during the post-growth cooling is less efficient in the material with high free carrier concentration. In such a case the annealing process cannot eliminate residual defects which compensate the introduced donors or acceptors, limiting the maximum free carrier concentration. Introduction of more impurities will result only in higher concentrations of compensating defects and cannot lead to higher free carrier concentrations. For ion implantation this phenomenon will lead to lower implant activation efficiency for high implantation doses. Similar effects should be observed in the doping during crystal growth. Annihilation of equilibrium native defects at the growth temperature and/or during post-growth cooling is affected by the position of the Fermi level with respect to E_{FS}. For heavily doped samples annihilation of the compensating defects is not energetically favored. This again will lead to a saturation of the free carrier concentration.

It is clear from the above discussion that the energy determining

maximum carrier concentration is related to the energy separation $|E_F-E_{FS}|$. In order to predict implant activation efficiencies and/or maximum free carrier concentrations one needs to know $|E_F-E_{FS}|$ at high temperatures. In Fig. 3 $|E_F-E_{FS}|$ for p- and n-type GaAs and InP are shown as functions of free carrier concentrations. It is seen from this figure that for n-type doping E_F-E_{FS} is higher in GaAs than in InP. This suggests that a higher saturation level of electron concentrations can be expected in InP than in GaAs. On the other hand, in p-type material the reverse relationship is true $|E_F-E_{FS}|$ is larger for InP than for GaAs, indicating that higher concentrations of holes should be observed in GaAs. This is exactly what is observed experimentally. Implantation or doping of n-type InP easily provides concentrations in excess of 10^{19} cm^{-3} [11] with the highest reported concentration of close to 10^{20} cm^{-3} [12]. GaAs ion implantation can produce maximum concentrations of only 3 to $5x10^{18}$ cm^{-3} [1]. The highest reported n-type doping was limited to $2x10^{19}$ cm^{-3} and can be only obtained by elaborate MBE growth [13]. On the other hand the highest hole concentrations reported for InP are consistently in the range 3 to $4x10^{18}$ cm^{-3} [14] whereas in GaAs hole concentrations in excess of 10^{20} cm^{-3} can be obtained [15]. From Fig. 3 one can obtain approximate values of E_{FS} corresponding to the saturation levels of free carrier concentration experimentally observed for n- and p-type implants in GaAs and InP. It is found that in n-type GaAs (InP) $|E_F-E_{FS}|$ = 0.55ev(0.5eV) and in p-type GaAs (InP) $|E_F-E_{FS}|$ = 0.4ev(0.35eV). The energies are very similar for GaAs and InP. This is not surprising since the energy of bond is very similar for both materials.

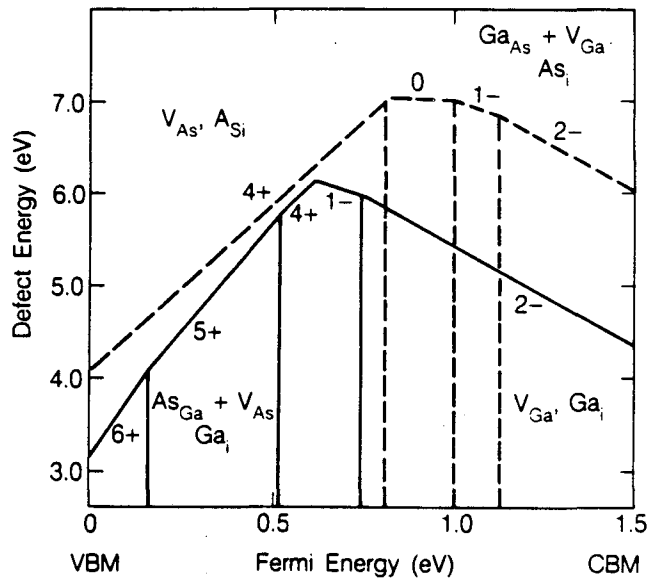

Fig. 2. Defect formation energies for simple native defects in GaAs.

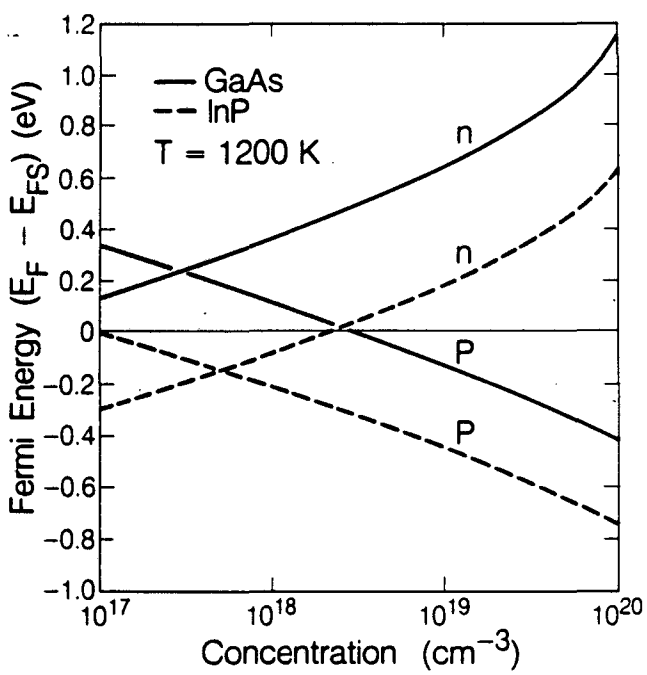

Fig. 3. Fermi level measured with respect to the stabilization energy E_{FS} in n- and p-type GaAs and InP.

The above discussion shows that our model finds excellent confirmation from existing experimental data on GaAs and InP. Such extensive

experimental results are not available for other III-V semiconductors. However, an interesting and extreme case is represented by InAs. It has been found that implantation of InAs with either donor or acceptor impurities always leads to an n-type conductivity [16]. Such behavior is predicted by the present model since, as we can see in Fig. 1, E_{FS} is located deeply in the conduction band and is well separated from the valence band. Thus in this system acceptor-like native defects are much more easily annealed than the donor-like defects which overcompensate implanted acceptor impurities.

The fact that the Schottky barrier heights and maximum doping levels are so intimately related has very important consequences for the Metal-Semiconductor Field Effect Transistor (MES FET) technology. In its simplest version this technology requires a possibility of producing metal-semiconductor contacts with the highest possible Schottky barrier as well as very low resistivity ohmic contacts. We have shown that it is not possible to meet both conditions since a large Schottky barrier means a large value of $|E_F-E_{FS}|$ which precludes the high doping levels necessary to produce low resistivity ohmic contacts by implantation or diffusion.

In summary, we have shown that many of the physical properties of III-V semiconductors such as Schottky barrier formation, irradiation induced resistivity changes and implant activation efficiency are different manifestations of the same basic mechanism of native defect induced Fermi level stabilization. Stabilization of the Fermi energy is a consequence of the strong dependence of defect formation energy on the Fermi level position with respect to the defect energy levels.

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