Title
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Publication Date
1987-07-01

LBL-23785 c.2
Preprint

Center for Advanced Materials

CAM

Submitted to Physical Review B

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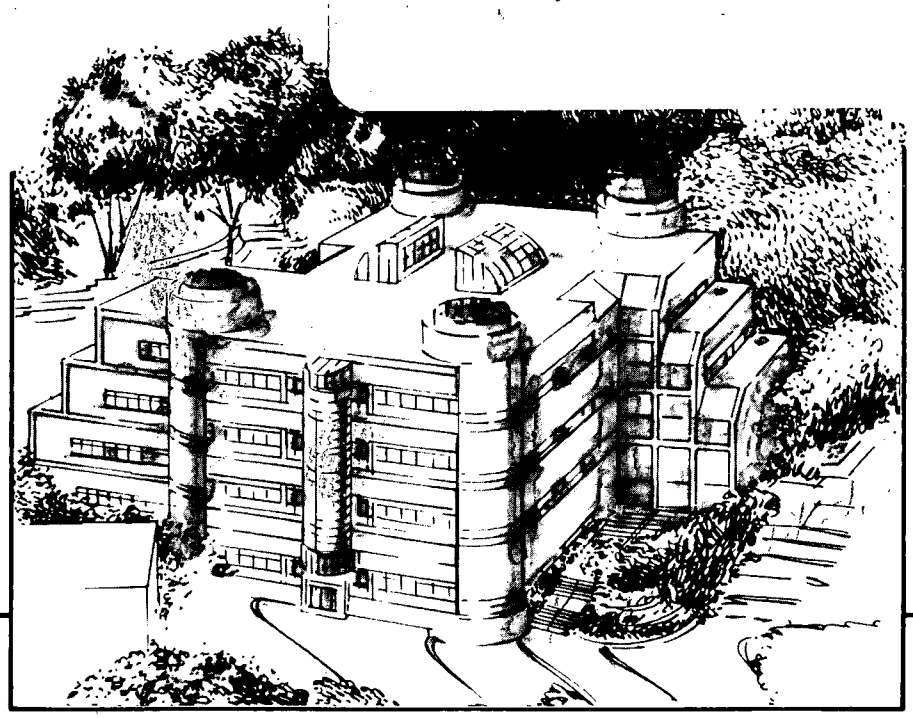
July 1987



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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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ABSTRACT

A striking correlation between the Fermi level in heavily radiation damaged semiconductors and at metal-semiconductor interfaces is presented. The correlation provides critical evidence supporting the defect model for Schottky barrier formation. The Fermi level energy for both situations corresponds to the average energy of the sp^3 hybrid. In the case of GaAs, a detailed description of the Fermi level stabilization caused by amphoteric dangling bond-like defects is given.

The location of the Fermi level with respect to the semiconductor band edges determines the electronic characteristics of the semiconductor. In general, the understanding of the physical processes affecting the Fermi energy is a complex issue which requires an extensive knowledge of mechanisms leading to the introduction of electrically active impurities and/or native defects.

In this paper we report on a remarkable correlation found between the Fermi level position at metal-semiconductor interfaces deduced from Schottky barrier heights and the Fermi energy in heavily irradiated III-V and column IV semiconductors. The correlation strongly suggests that a similar microscopic mechanism is responsible for the Fermi level behavior in both cases. In a detailed analysis for GaAs we propose that very specific thermodynamic properties of native defects are responsible for the stabilization of the Fermi energy. The finding has important consequences for the understanding of the mechanism of Schottky barrier formation. It also sheds a new light on heretofore unexplained trends in implant activation efficiency in semiconductors.

It is well known that the intentional generation of native defects affects the Fermi energy.[1] This phenomenon has practical applications and is widely used in particle irradiation experiments to change the electrical conductivity of semiconductors. This effect is caused by radiation generated, electrically active native defects or defect complexes.[1] Since the identity of these defects as well as their concentrations are in the general case not known, it is not possible to predict the effect of irradiation on the Fermi level behavior. However, it has been found in a series of recent experiments[2] that room temperature irradiation of covalent or weakly ionic semiconductors induces a Fermi level shift towards an "ultimate" position, characteristic for

the particular semiconductor, which is not affected by further irradiation. This characteristic Fermi level stabilization energy (E_{FI}) corresponds to the situation in which radiation defects do not affect the charge balance and thus also the Fermi level position. The stabilization energy is independent of the type of doping and the doping level. It therefore can be treated as an intrinsic property of a semiconductor.

A stabilization or "pinning" of the Fermi level position is also observed in the apparently unrelated physical process of room temperature metalization of a semiconductor surface. The stabilized Fermi level at the metal/semiconductor interface is responsible for the observed Schottky barrier heights which only very weakly depend on the choice of metal. A number of physical mechanisms which could cause such stabilization at the metal/semiconductor interface have been proposed.[3-8] In particular, it has been argued that native acceptor- and donor-like defects created at the interface during metal deposition can stabilize the Fermi energy.[5] However, lack of convincing experimental evidence for the existence of native defects with the very specific properties required for the Fermi level pinning has left this proposal in a speculative state.

In Table I we list values of the Fermi level stabilization energies E_{FI} in heavily irradiated III-V and group IV semiconductors, along with the range of Fermi level pinning positions E_{FS} deduced from the Schottky barrier heights for metal/semiconductor contacts. The data in Table I demonstrate that for all the semiconductors for which irradiation data are available there exists a very distinct correlation between stabilization energies in irradiated semiconductors and at metal/semiconductor interfaces. In all cases E_{FI} lies within or very close to the energy range of E_{FS} found for various metals. Further experimental support for the correlation is provided by the

experimental data shown in fig. 1, where the Fermi energy evolution with increasing irradiation dose for GaAs[9] is presented and compared with a typical dependence of the surface Fermi energy on the metal layer thickness for very low metal coverages.[8] The choice of the metals is not critical since it has been shown that a very similar behavior of the Fermi level is observed for all metals studied.[10]

The great similarity of the Fermi level dependence on the metal layer thickness and irradiation dose is quite unexpected because of the very different mechanisms of defect generation in the two cases. At a metal/GaAs interface the defects are related to chemical reaction induced nonstoichiometry whereas in irradiated semiconductors the stoichiometry is preserved and vacancy-interstitial pairs are the primary defects. A presence of dangling bond-like defects is a common feature in both instances. When such defects are created at room temperature they undergo transformations and interact with each other in such a manner that a minimum of the total energy of the defect system in equilibrium with the lattice and the free electron or hole gas is achieved.

The total energy required to form a native defect consists of the energy of structural change in the lattice and the electronic energy associated with charging of the defect. The electronic part of the energy depends on the location of defect levels relative to the Fermi level. For defects with multiple charge states in the bandgap the electronic energy can be quite large and therefore it can affect defect abundances and reactions.[11] A very well-known example of a phenomenon where the electronic part of the total defect energy plays a critical role is the effect of self-compensation.[11] This effect, which is very often observed in wide-gap ionic semiconductors, does not seem to play a significant role in strongly bound, III-V

semiconductors. We will show, however, that in these weakly ionic semiconductors the dependence of the electronic part of defect energy on the Fermi level position considerably affects defect reactions and controls the compensation mechanism leading to the Fermi level stabilization at low temperatures.

In order to demonstrate how this mechanism operates we shall consider the case of GaAs. Recent progress in the understanding of defect thermodynamics allows for a detailed analysis of the behavior of simple defects in this semiconductor. It has been shown[12,13] that large contributions of the electronic energy to the total energy of Ga and As vacancies results in a Fermi level-dependent stability of these defects. Thus, it has been found that V_{Ga} is a stable acceptor in n-type GaAs, but it transforms to a donor complex $As_{Ga}+V_{As}$ in p-type material. Similarly, V_{As} is a stable donor in p-type, whereas $G_{As}+V_{Ga}$ is a stable acceptor in n-type crystals. This characteristic amphoteric behavior of stoichiometric native defects lies at the heart of the recently proposed Schottky barrier formation mechanism.[14] Here we will show that a very similar mechanism explains Fermi level stabilization in irradiated GaAs.

Recent positron anihilation studies[15] have shown that electron irradiation of III-V semiconductors leads to the formation of a large concentration of simple vacancies. Here, we shall assume that the primary defects in irradiated GaAs are Frenkel (vacancy-interstitial) pairs on the As and Ga sublattices. Depending on the Fermi level position, V_{Ga} and V_{As} retain their character or undergo transformation to $As_{Ga}+V_{As}$ and $Ga_{As}+V_{Ga}$, respectively. Therefore, for n-type GaAs, irradiation induced

defect reactions on Ga and As sublattices are:

$$Ga_{Ga} + As_{As} \rightarrow V_{Ga} + Ga_i + As_{As} \quad (1a)$$

$$Ga_{Ga} + As_{As} \rightarrow (Ga_{As}+V_{Ga}) + As_i \quad (1b)$$

Similarly, for p-type

$$Ga_{Ga} + As_{As} \rightarrow (As_{Ga}+V_{As}) + Ga \quad (2a)$$

$$Ga_{Ga} + As_{As} \rightarrow V_{As} + As_i + Ga_{Ga} \quad (2b)$$

where $(Ga_{As}+V_{Ga})$ and $(As_{Ga}+V_{As})$ are close defect pair complexes. Using results of refs. 12 and 13 one can construct a diagram of the defect reaction energy as a function of the Fermi energy position in the bandgap. The diagrams illustrating the defect reactions described by eqs. (1) and (2) are shown in fig. 2. The numbers assigned to different parts of the curves indicate the total net charge transfer from the free electron or hole gas to a defect pair. Thus, for conductive n- or p-type GaAs the effect of irradiation created defects is to compensate the original electrical activity of the material. The compensation induces a Fermi level shift away from the band edges. Eventually, at sufficiently high defect concentrations, the Fermi energy reaches the stable position. This position is characterized by the condition of zero net charge transfer between the Fermi sea and the defects. In such a case, introduction of further defects does not affect the charge balance any longer, i.e. the Fermi energy position is stable. This, as seen in fig. 2, occurs at E_v+0.6eV for As, and in the energy range E_v+0.8eV to E_v+1.0eV for Ga sublattice defects. Combining these two results for the case when these two types of defects are present we find that the Fermi level is stabilized in the energy range E_v+0.6eV to E_v+0.8eV. A final Fermi

level position in this energy range depends on the concentration ratio of the defects on As and Ga sublattices. Bearing in mind the limited accuracy of the theoretical calculation of the defect energy levels we find these predictions to be in very satisfactory agreement with experimentally observed stabilization energies in the range E_v+0.5eV to E_v+0.7eV.

We have shown previously that the amphoteric behavior of the nonstoichiometry induced native defects very well accounts for the Fermi level "pinning" at metal-GaAs interfaces[14]. Here we have demonstrated that also in the case of irradiated GaAs the same properties of native defects lead to Fermi level stabilization. Hence, for GaAs there is a unique mechanism leading to Fermi level stabilization in both cases.

We can now examine trends in the Fermi level stabilization energy among different semiconductors to find out if there exists any relation between this energy and the intrinsic properties of the crystals. We find from Table I that the experimentally observed stabilization energy correlates quite well with the midgap energy[16] or charge neutrality level E_B [17] which has been postulated to be a reference point for metal induced gap states pinning of the Fermi energy at metal-semiconductor interfaces. Furthermore, it has been shown[18] that E_B is very closely related to the average hybrid energy E_h, i.e. the energy where the Fermi level would be located in the absence of a coupling between sp^3 hybrids in the bonds. In covalent or weakly ionic semiconductors it is the presence of this coupling which opens the "optical" bandgap separating bonding from antibonding states. Introduction of dangling bond type defects to the crystal pulls bonding and antibonding states towards the middle of the gap.[19] If, as it is the case for GaAs, the defect can change its character from bonding (donor) to antibonding (acceptor), an equilibrium for the system with a large concentration of native defects will

be reached when the formation rates of acceptor- and donor-like states are equal, i.e. when the Fermi energy is located close to E_h or E_B. Therefore, this Fermi level position corresponds to the minimum of the total energy for the crystal with native defects.

The strong correlation between the Fermi level stabilization energy and the charge neutrality level E_B has important consequences for the understanding of the relation between defect[5,14] and the Metal Induced Gap States (MIGS)[13] model of the Schottky barriers. One of the strongest arguments in favor of the MIGS model was its ability to approximately predict Schottky barrier heights for a large number of semiconductors.[17] Here we have shown that the same Fermi level stabilization is observed in irradiated semiconductors in which metal induced gap states do not exist. Thus, native defects provide as good an explanation for the observed Schottky barrier heights as the MIGS model. A detailed analysis of a large variety of experimental data on metal/semiconductor interfaces along the lines of ref. 14 will be required to determine which model provides a more realistic description of the processes occurring at metal/semiconductor interfaces.

Additional evidence for a fundamental role played by the stabilization energy, E_{FI}, is provided by ion implantation experiments. We have found that semiconductors with E_{FI} located close to the conduction (valence) band in general exhibit higher implant activation efficiency for donor (acceptor) type impurities. An especially interesting and extreme case is InAs, which shows n-type conductivity independently of the type of implanted impurities.[20] This is a consequence of the fact that in InAs E_{FI} is located deeply in the conduction band.

In summary, we have shown that there exists a universal mechanism of Fermi level stabilization in covalent and weakly-ionic semiconductors. The mechanism is responsible for formation of Schottky barriers at metal-semiconductor interfaces, as well as compensation of semiconductors during irradiation. A strong correlation between the stabilization energy and the average hybrid or charge neutrality point energy explains the relationship between different existing Schottky barrier models. We postulate that the stabilization energy plays a role of reference level for physical processes in which native defects are involved.

The author wishes to acknowledge stimulating discussions with Prof. E.E. Haller. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

TABLE I. Fermi level stabilization energy in irradiated semiconductors (E_{FI}) and at metal/semiconductor interfaces (E_{FS}). E_B represents charge neutrality level. All energies are measured with respect to the valence band edges.

	E_{FI} (eV)	E_{FS} [i] (eV)	E_B [k] (eV)
Ge	0.07 [a]	0.16 [j]	0.18
Si	0.4 [b]	0.3 - 0.4 [j]	0.36
GaAs	0.5 - 0.7 [c]	0.5 - 0.7	0.5
InAs	~0.42 [d]	0.46	0.5
InP	1.0 [e]	0.8-1.1	0.76
GaP	0.9 - 1.34 [f]	0.75 - 1.2	0.81
GaSb	0.12 - 0.2 [g]	0.1	0.07
InSb	0.06 [h]	~0.04	0.01

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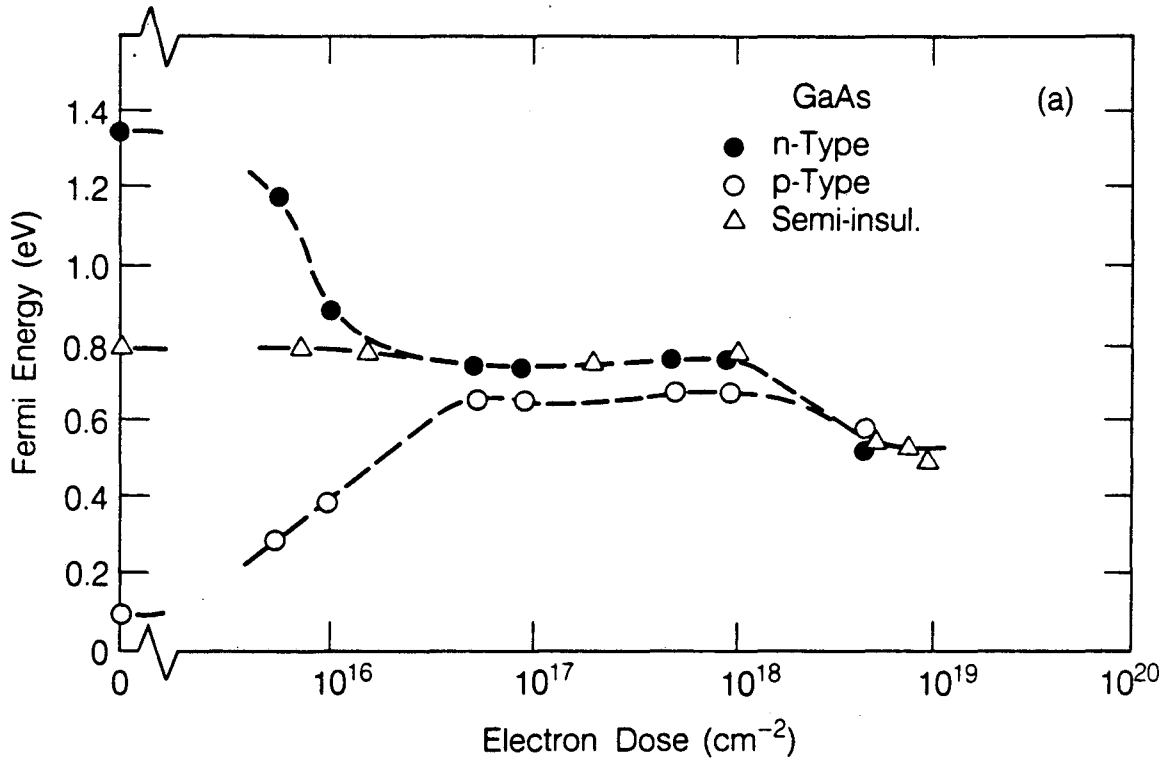
FIGURE CAPTIONS

Fig. 1 Comparison of Fermi level behavior in (a) electron irradiated GaAs (deduced from data of ref. 9) and (b) at Ti/GaAs interface for submonolayer Ti coverage (after ref. 8).

Fig. 2 Defect reaction energy for As (broken line) and Ga sublattice (solid line) defects. The vertical lines represent defect energy levels .



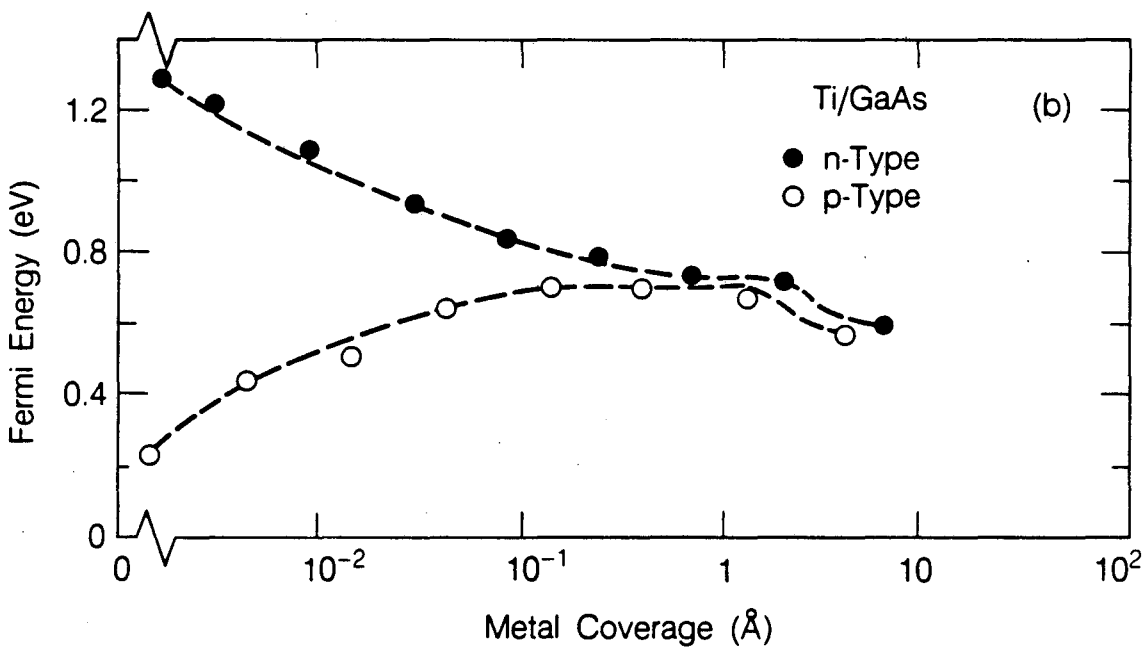


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Figure 1.

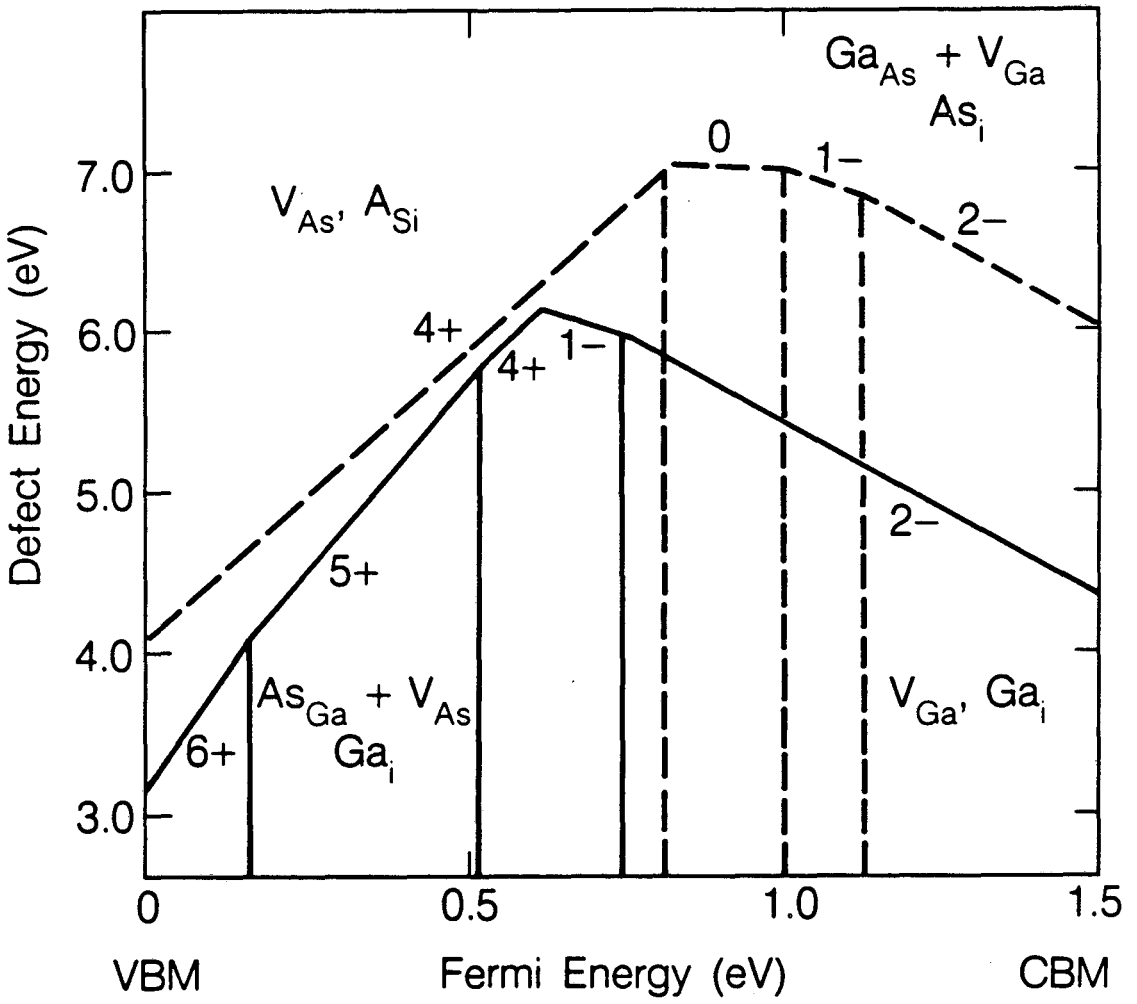

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Figure 2.

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