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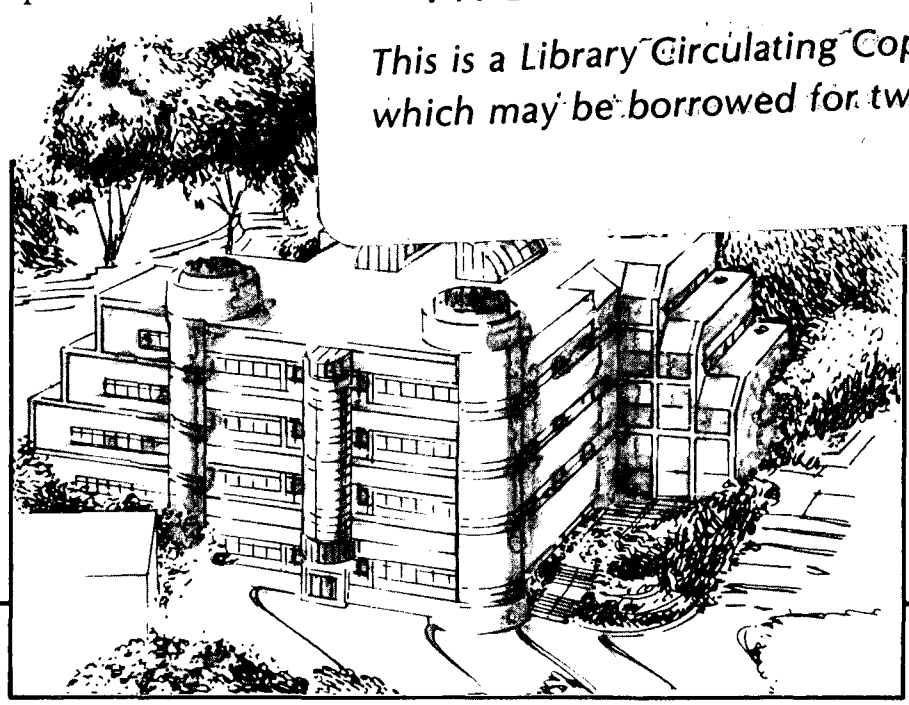

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DEFECT REACTIONS AT METAL-SEMICONDUCTOR AND SEMICONDUCTOR-SEMICONDUCTOR INTERFACES

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ABSTRACT

A recently proposed, new approach to the problem of native defect formation in compound semiconductors is presented. The approach is based on the concept of amphoteric native defects. It is shown that the defect formation energy as well as structure and properties of simple native defects depend on the location of the Fermi level with respect to an internal energy reference: the Fermi level stabilization energy. The known location of the stabilization energy determines the electronic part of the defect formation energy and allows for a quantitative description of a variety of phenomena including: the formation of defects at metal-semiconductor interfaces, doping induced superlattice intermixing and limitations of free carrier concentrations in semiconductors.

I. INTRODUCTION

It has long been recognized that identification of the physical processes which control the formation and the abundances of native (intrinsic) defects is essential for understanding of the structural and electronic properties of semiconductors [1]. This problem has become especially important in compound semiconductors in which, in principle, a large variety of different native defects can exist. In these materials the native defects were implicated to play a crucial role in a variety of phenomena in bulk crystals as well as at the metal-semiconductor (M-S) and semiconductor-semiconductor (S-S) interfaces. Thus, it has been proposed that a number of effects observed in semiconductors, such as saturation of electrical activity of impurities [2], formation of Schottky barriers [3] and doping-induced superlattice intermixing [4] are direct consequences of the presence of native defects. However, the well-known difficulties with the identification of native defects in compound semiconductors have left these proposals in a speculative stage.

It will be shown in this paper that recent developments in experimental defect studies, as well as higher accuracy of theoretical methods to calculate defect energies, provide the basis for identification of the defects which play a pivotal role in the determination of structural and electronic properties of semiconductors. It will be argued that many of the properties of semiconductors can be understood within a single unifying concept of amphoteric native defects (AND) [5]. The most important factor controlling defect incorporation and defect abundances is the location of the Fermi level measured with respect to the internal energy reference, the Fermi level stabilization energy [6]. Therefore, structural properties as well as electronic identity (donor or acceptor) of the defects depend on the type of doping, doping concentration and temperature. We will demonstrate how this novel approach to the problem of defects can be applied to quantitatively understand the formation of the Schottky barriers, superlattice intermixing and limitations of free carrier concentrations in semiconductors.

II. DEFECT INDUCED STABILIZATION OF FERMI ENERGY

It has been demonstrated in numerous photoemission experiments that the deposition of a metal on cleaved (110) surfaces of weakly ionic III-V semiconductors results in stabilization of the Fermi energy [7]. The position of the stabilized Fermi level is only very weakly dependent on the metal, and agrees very well with the position of the Fermi level at the interface determined from the Schottky barrier heights measured for thick metal coverages [7,8]. These experimental results indicate that deposition of metal stabilizes (or pins) the Fermi level at the interface. There were several attempts to understand this phenomenon in terms of screening [9], formation of new phases [10,11], or formation of localized states at the M-S interface. [3,12-16] The nature of

possible localized states and the mechanisms of their formation have been hotly debated issues. Thus it has been proposed that the presence of a high density electron gas in the metal in intimate contact with a semiconductor induces localized states in the semiconductor band gap [13-16]. These so-called metal induced gap states (MIGS) stabilize the Fermi energy at the neutrality point E_B, which is determined by the semiconductor band structure [16].

Another very actively pursued concept uses the assumption that the stabilization or pinning of the Fermi energy is caused by native defects created in the semiconductor in the immediate vicinity of the surface [3]. The attractiveness of this proposal lies in the fact that it could, in principle, explain the pinning of the Fermi energy caused by oxidation, surface damage, or deposition of submonolayers of metals, i.e., the cases to which the MIGS concept is not applicable. The problem of the defect model, however, was that at the time when the model was proposed the properties of native defects in compound semiconductors were very poorly understood. Therefore one could only speculate on the identity of the native defects responsible for the Fermi level pinning [3]. Lack of a solid proof of the existence of native defects with properties required to explain the Fermi level behavior was considered to be a strong argument against the defect model [17].

In the defect model of Schottky barriers one assumes that electrically active native deep donor and/or acceptor-like defects stabilize the Fermi energy. If these defects can be associated with intrinsic properties of the semiconductors rather than with the metal-semiconductor interface one can expect that they should be observable in other experiments in which native defects are intentionally introduced into the semiconductor.

The experimental situation in which electronic properties of a semiconductor are determined by native defects is realized in semiconductors heavily irradiated with high energy particles. In such a case the primary damage takes the form of simple native defects: vacancies and interstitials. Since such defects can be electrically active they can also affect the position of the Fermi energy. It has been demonstrated in recent experiments that the introduction of a high concentration of native defects leads to stabilization of the Fermi energy [18-20]. Figs. 1(a) and 2(a) show the dependence of the Fermi energy on the electron irradiation dose in GaAs [18] and InP [20]. It is seen that independently of the type of conductivity of the original material the native defects produced by high energy electrons lead to the same stable position of the Fermi energy at $E_{FS} \cong E_V + 0.7$ eV and $E_{FS} \cong E_V + 1.0$ eV for GaAs and InP, respectively. There is a striking similarity between the Fermi level stabilization induced by irradiation and by the deposition of a metal on GaAs [21] (Fig. 1b) and InP [22] (Fig. 2b). The stabilization energy caused by the metal deposition is in excellent agreement with the ultimate position of the Fermi energy in heavily irradiated samples.

For both GaAs and InP, E_{FS} is located in the band gap. It means that the native defects compensate intentionally introduced donor or acceptor impurities leading to high resistivity materials. This is not generally true since as is shown in Fig. 3, in InAs [23], irradiation produces low resistivity n-type material. From measurements of electron concentration in neutron irradiated InAs one finds that E_{FS} is located in the conduction band at $E_V + 0.45$ eV. The condition $E_F = E_{FS}$ corresponds to the electron concentration of $n \cong 3\times10^{18}$ cm^{-3}. The location of E_{FS} in neutron irradiated InAs agrees quite well with the Fermi level position determined from the Schottky barrier height measured on p-type

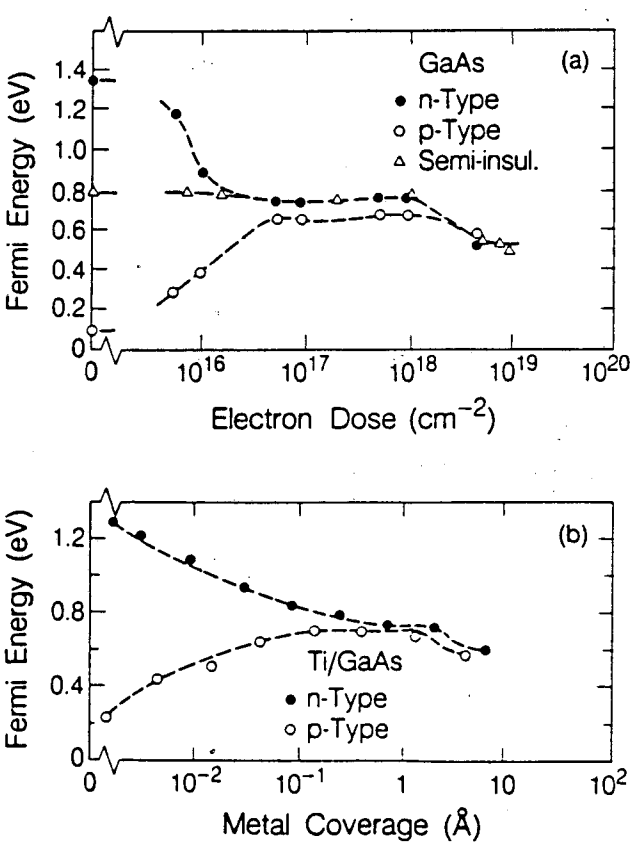

Fig. 1. The Fermi level dependence on electron irradiation dose in bulk GaAs (a) (Ref. [18]) and on metal thickness at metal-GaAs interface (b) (Ref. [21]).

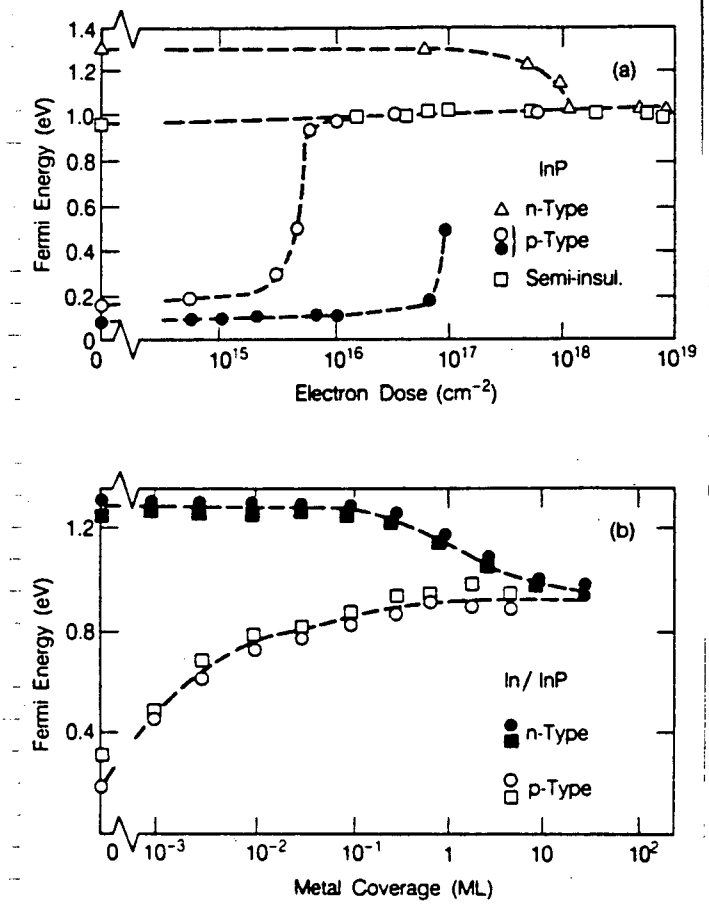

Fig. 2. The same as Fig. 1 but for InP. (Refs. [20] and [22]).

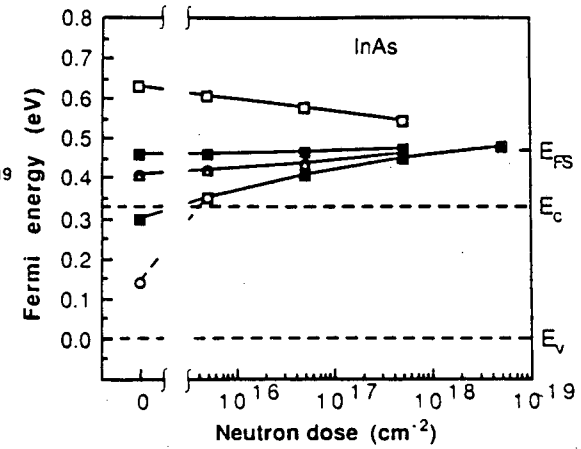

Fig. 3. Fermi level position in neutron irradiated InAs (after Ref. [43]). E_{FS} represents the Fermi level position determined from the Schottky barrier height in p-type InAs.

InAs [24]. The fact that E_{FS} is located in the conduction band indicates that the electronic states of the native defects are associated with a higher lying conduction band rather than with the low density of states conduction band minimum at Γ point. The donor-like nature of the native defects introduced in p-type or in low electron concentration ($n < 3\times10^{18}$ cm^{-3}) n-type InAs has been confirmed by ion implantation experiments which have shown that the implantation of acceptors (Mg) leads to n-type conductivity in this material [25].

The effects of irradiation have been much less extensively studied in other III-V semiconductors. On the basis of existing data compiled in Fig. 4 one finds, however, that in all the semiconductors for which experimental results are available there is a good agreement between the value of E_{FS} observed in heavily irradiated semiconductors and the Fermi energy position determined from the Schottky barrier heights at M-S interfaces [6,26]. One can conclude from the above experimental data that the same class of native defects is responsible for the defect induced Fermi level stabilization at metal semiconductor interfaces and in irradiated semiconductors.

The position of the neutrality point energy E_B [16] which has been postulated as the Fermi level pinning energy in the MIGS model of M-S interfaces is also shown in Fig. 4. Reasonably good agreement between the experimental values of E_{FS} and E_B is found. This is not surprising since it can be shown that E_B corresponds to an average energy of neutral vacancies [27,28]. Therefore, this energy is intimately related to the properties of native defects in semiconductors.

III. AMPHOTERIC NATIVE DEFECTS

In general, a quantitative description of defect abundances in semiconductors requires a full knowledge of the energetics of native defects. Recently a theoretical calculation of total energies of simple native defects in GaAs has been reported [29,30]. Based on this calculation it

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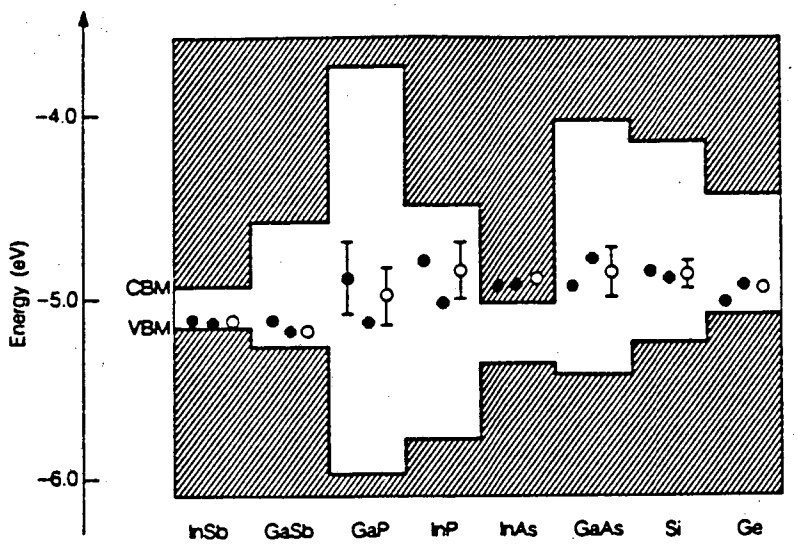

Fig. 4. Position of the Fermi level stabilization energy (Ref. [26]) deduced from the Fermi energy position in heavily irradiated semiconductors (•) and from the Schottky barrier heights of metal-semiconductor interfaces (o). The positions of the neutrality point energy E_B is also given (+).

has been shown that the abundances of simple nonstoichiometric defects are controlled by the following defect reactions [26]

$$As_{As} + V_{Ga} \leftrightarrow As_{Ga} + V_{As} \tag{1a}$$

and

$$Ga_{As} + V_{Ga} \leftrightarrow V_{As} + Ga_{Ga} \tag{1b}$$

The transformation from acceptor-like defects on the left hand side of 1(a) and 1(b) to the donor-like defects on the right hand side is accomplished by a single jump of an arsenic or gallium atom between the nearest neighbor sites. Since the donors and acceptors can support multiple changes their formation energy strongly depends on the location of the Fermi energy [29,31]. The formation energy of the donors (acceptors) is reduced in p-type (n-type) material. This is illustrated in Fig. 5 where total energies of the defects as functions of the Fermi level are shown. It is seen that in p-type GaAs donors $As_{Ga}+V_{As}$ and V_{As} have lower formation energies and are stable defects. On the other hand, in n-type material acceptor-like defects V_{Ga} and $Ga_{As}+V_{Ga}$ are stable. Therefore, when simple native defects are intentionally introduced into n- or p-type GaAs, acceptor or donor-like defects are formed. These defects compensate the electrical activity of the impurities and the Fermi energy shifts towards the mid-gap until it reaches the energy at which formation energies for donor- and acceptor-like defects are equal. At this point, further introduction of defects will not affect the Fermi level position. One finds from Fig. 5 that the the stable Fermi level is located at E_v+0.6 eV and E_v+0.8 eV for the reactions (1a) and (1b), respectively. The theoretical values of E_{FS} are in good agreement with the experimental Fermi level stabilization energies determined from the Fermi level position in heavily irradiated GaAs and also determined from the Fermi level pinning at the metal-GaAs interface.

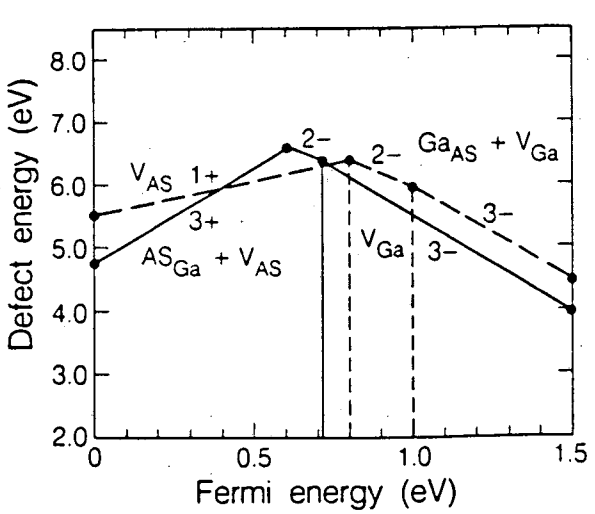

Fig. 5. Defect formation energies for V_{Ga}, V_{As} and related $As_{Ga}+V_{As}$, $Ga_{As}+V_{Ga}$ defects. The numbers at the graphs represent net charge transfer from the Fermi sea to the defects. The stabilization energy corresponds to zero net charge transfer.

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In our discussion of defect reactions in GaAs we have neglected arsenic and gallium interstitials. This is a good approximation for the present considerations since interstitials are fast diffusing species and do not exist as isolated defects at room or higher temperatures. However, the interstitials have to be included at low temperatures when their diffusion is suppressed [26]. It has to be emphasized that incorporation of the interstitials does not significantly affect the value of E_{FS} obtained for the reactions (1a) and (1b) [6].

IV. DEFECT FORMATION AT METAL-SEMICONDUCTOR INTERFACE; SUBMONO-LAYER COVERAGE

In order to consider the formation of defects during metal deposition on a semiconductor surface one has to identify a source of energy which is required for the defect generation. A perfectly cleaved (110) surface of a group III-V semiconductor undergoes a relaxation which removes the dangling-bond-like localized states from the energy gap. In such a system the Fermi energy at the surface is determined by bulk doping. There are several sources of additional energy released during metal deposition on a relaxed (110) surface:

a) Energy of condensing metal atoms.
b) Energy of exothermal chemical reactions between the deposited metal and host semiconductor atoms.
c) Energy released during formation of metal clusters [32].
d) Energy of the surface back-relaxation (un-relaxation) [33,34].

The energy of condensing metal atoms is small and cannot lead to the formation of defects by itself, however, it can initiate the other processes which can provide much more energy. In general, all the other three processes (b - d) can contribute to the formation of defects. However, here in our model calculations we will limit ourselves to the case when the energy for the defect formation is provided by surface back-relaxation. It has been shown in recent calculations that a substantial energy of about $E_0 = 0.35$ eV/surface atom is released in the process of back-relaxation of cleaved (110) GaAs surface [33,34].

To model the process of defect formation we assume that the number of back-relaxing surface atoms is given by the Poisson distribution,

$$p(N) = e^{-\langle N\rangle}\left(\langle N\rangle^N / N!\right) \tag{2}$$

where $\langle N\rangle$ is the mean value of the distribution. The probability of creating a defect with formation energy $E_{def}(E_F)$ is given by

$$G(E_F) = P(N \geq N_0) = \int_{N_0}^{\infty} p(N)\, dN \tag{3}$$

where $N_0(E_F) = E_{def}(E_F)/E_0$. The change of the defect concentration is related to the change in the concentration of metal atoms via the equation

$$dN_{def} = G(E_F)\, dN_{at} \tag{4}$$

Using standard electrostatic considerations one obtains

$$dN_{at} = \left(\varepsilon N_i / 4\pi |Q| \left|E_{Fb} - E_F\right|\right)^{1/2} dE_F / G(E_F) \tag{5}$$

where Q is the charge transferred from the defects to the Fermi gas.

Equation 5 has been solved for the defect reaction (1a) corresponding to the case of the As rich interface [35]. The results are presented in Fig. 6. A most important feature of the Fermi level behavior is a slow pinning extending over more than two orders of magnitude of the metal

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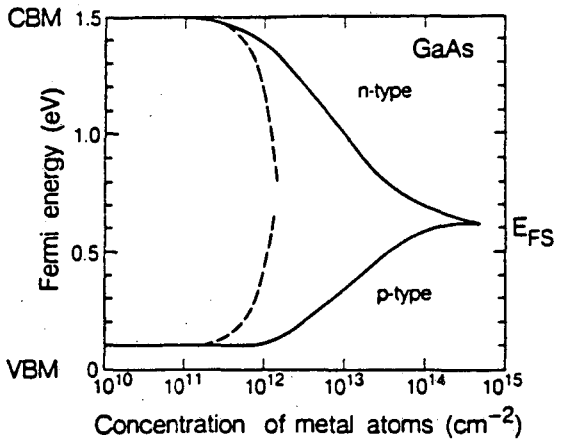

Fig. 6. Room temperature Fermi level pinning in n- and p-type GaAs obtained from the model calculations for $\langle N \rangle = 10$. The broken curves represent the pinning for defects with Fermi level independent defect formation energy.

coverage. This slow pinning is a direct consequence of the strongly Fermi level dependent defect formation energy. Such experimental behavior of the Fermi level is always observed for metal deposited at room temperature. Thus, as is seen in Fig. 1(b), in the case of Ti deposited on GaAs the full pinning of the Fermi energy extends over almost three orders of magnitude of metal coverage. This result can be contrasted with the Fermi level pinning predicted for the case of the defects with constant formation energy. As is seen in Fig. 6 for $G(E_F) = \text{const}$, a very fast pinning is found. Such dependence of the Fermi level pinning on the metal layer thickness is clearly inconsistent with the experimental data.

V. DOPING INDUCED SUPERLATTICE INTERMIXING

All the considerations of the preceding sections have been limited to the cases where the defects are intentionally introduced at low (room) temperature. Such defects form supersaturated systems and are not in equilibrium with the crystal lattice. It is well known that native defects play a crucial role in many phenomena observed at elevated temperatures during crystal preparation and/or processing. A phenomenon which has lately attracted considerable attention is so-called doping-induced superlattice intermixing [4]. It has been found that annealing leads to a very rapid destruction of GaAs/AlAs superlattices doped with donor impurities [4]. The effectiveness of the intermixing strongly depends on the doping level [36]. Also, it has been found that co-doping with acceptors suppresses the intermixing [37]. All these facts were interpreted as an indication that the concentration of the defects facilitating the interdiffusion of Ga and Al atoms depends on the Fermi energy [4,38,39]. A more complex situation has been found in the case of acceptor impurities where it has been demonstrated that doping with Be to very high levels of 4×10^{19} cm^{-3} does not lead to any significant intermixing [37]. On the other hand, very fast intermixing is promoted by diffusion of Zn into a GaAs/AlGaAs superlattice [40]. Here we will show how the process of donor induced intermixing of a GaAs/AlAs superlattice can be understood in terms of the properties of amphoteric native defects.

The diffusion coefficient for intermixing at the $GaAs/Al_xGa_{1-x}As$ heterointerface is given by,

$$D(x,T) = D_o(T) \exp(A(T) \cdot x) \tag{6}$$

where

$$A(T) = \left(E_{Ga} - E_{Al}\right)/kT \tag{7}$$

$$D_o(T) = C \exp\left(-E_{Ga}/kT\right) \tag{8}$$

E_{Ga} and E_{Al} is the formation energy of Ga and Al vacancies, respectively. One finds from these equations that the diffusion coefficient is proportional to the vacancy concentration

$$D_o(T) \sim [V_{Ga}] \tag{9}$$

As has been discussed in previous sections, the formation energy of V_{Ga} depends on the Fermi level. For n-type doping ($E_F > E_{FS}$) one has

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$$[V_{Ga}] = C' \exp\left(\frac{-E^{o}_{Ga} - 3\left(E_F - E_{FS}\right)}{kT}\right) \tag{10}$$

or

$$[V_{Ga}] = C'' \exp\left(3E_F/kT\right) \tag{11}$$

where E^{o}_{Ga} is the formation energy of V_{Ga} for E_F=E_{FS}. The Fermi level is determined by free carrier concentration

$$n = N_c F_{1/2}\left(\left(E_F - E_c\right)/kT\right) \tag{12}$$

where $F_{1/2}$ is the Fermi-Dirac integral. Since V_{Ga} are triply ionized acceptors they compensate intentionally introduced donors and

$$n = N_D^{+} - 3[V_{Ga}] \tag{13}$$

where N_D^{+} is the total concentration of shallow donors.
From eqs. (11), (12) and (13) one obtains

$$[V_{Ga}] = C''\left(\left(N_D^{+} - 3[V_{Ga}]\right)/N_c\right)^3 \tag{14}$$

Typical experiments on superlattice intermixing are performed in the temperature range ~ 700°C to 900°C. Therefore, to solve eq.(14) one has to know the temperature dependence of the position of conduction band-edge measured with respect to E_{FS}. There are two contributions to the temperature dependence of the band edges: the lattice dilation and electron-phonon interaction. The dilation contribution to the temperature shift of (E_c-E_{FS}) is

$$\frac{\partial\left(E_c - E_{FS}\right)}{\partial T} = 3\frac{\Delta a}{a} \cdot a_c \tag{15}$$

where $\Delta a/a$ is the relative temperature dependent change of the lattice parameter, and a_c is the conduction band deformation potential. Using the value $\Delta a/a = 6\times10^{-6}$ K^{-1} and recently determined value of a_c = 9.3 eV for the deformation potential [41], one obtains $\partial(E_c-E_{FS})/\partial T$ = 1.7×10^{-4} eV/K. Here we neglect the electron-phonon interaction contribution to the band-edge shift since it depends on the effective mass and is small for the conduction band. Eq. (14) is solved numerically. The results of the calculations are shown in Fig.7. It is seen that the diffusion coefficient increases very rapidly at low donor concentrations $D \sim N_D^3$. A much slower dependence $D \sim N_D$ is found for the doping levels exceeding ~3×10^{18} cm^{-3}. These results are in very good agreement with experimentally observed trends on the Si-doped GaAs/AlGaAs superlattice intermixing. A rapid decrease of the diffusion coefficient for $N_D<3\times10^{18}$ cm^{-3} was interpreted as a threshold for Si-induced intermixing.[42] The threshold concentration corresponds to $E_F-E_{FS} \cong 0.7$ eV at 1000 K. This location of the Fermi energy leads to the reduction of the V_{Ga} formation energy by 2.1 eV.

According to our present considerations the efficiency of intermixing is determined by the separation of the Fermi energy from E_{FS}. This indicates that the effectiveness of the doping induced superlattice intermixing will be reduced in systems with the conduction band edge lying closer to E_{FS}. An example of such a system is the lattice matched $In_{0.53}Ga_{0.47}As/In_{0.47}Al_{0.52}As$ superlattice. In InAs E_{FS} is located in the conduction band, therefore the primary effect of

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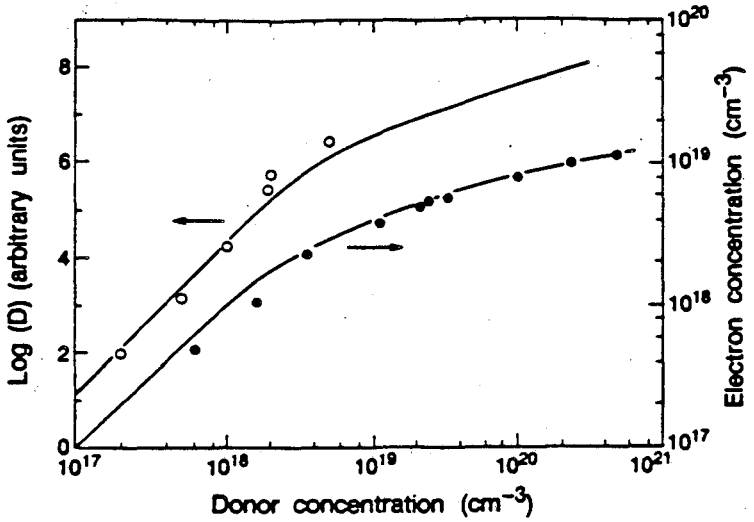

Fig. 7. Diffusion coefficient, D, in n-type GaAs/AlAs and electron concentration in GaAs as functions of donor concentrations. Experimental data from Si-doped GaAs/AlAs superlattice intermixing (o) [36] and from Hall measurements of electron concentration in Se doped GaAs (•) [46] is also shown.

addition of ~ 50% of In to GaAs and AlAs is to reduce E_c–E_{FS}. In GaAs at ~ 1000 K, E_c-E_{FS} = 0.7 eV, whereas it is only ~ 0.4 eV in $In_{0.53}Ga_{0.47}As$. In InGaAs the value of E_F–E_{FS} = 0.7 eV is achieved for electron concentrations of about 2×10^{19} cm^{-3}, which is much higher than the threshold concentration of 3×10^{18} cm^{-3} found in GaAs. Recently, Si-doping-induced intermixing of In GaAs/InAlAs superlattice has been studied [43]. It has been observed that the donor doping to the level 7×10^{18} cm^{-3} does not produce any intermixing. Much higher doping of 1.3×10^{19} cm^{-3} is required to substantially intermix the superlattice. This value of the critical doping agrees quite well with our theoretical estimate, providing additional support for the proposed mechanism of superlattice intermixing.

In its simplest form the present mechanism of the doping induced intermixing does not depend on the nature of donors. Intermixing efficiency depends only on the location of the Fermi level which in turn is determined by the carrier concentration. The most recent study of a Te-induced intermixing of GaAs/AlAs superlattice has shown that the interdiffusion is a linear function of Te concentration for the doping level in the range 2×10^{17} cm^{-3} to 5×10^{18} cm^{-3}. This is a much slower dependence than that reported for the case of Si doping. Assuming that all Te atoms are electrically active this result indicates that a different, more efficient interdiffusion process is operational in this case. However, if for some reason the electron concentration in the MOCVD grown superlattice is a sublinear function of the Te doping level, then it could explain the slower dependence of the interdiffusion on the Te atom concentration. Only direct measurements of the electron concentration in Te doped samples could resolve this issue.

It should be noted that the present model does not predict any intermixing of the GaAs/AlAs superlattice by p-type doping. For $E_F<E_{FS}$ the stable defects are V_{As} and $As_{Ga}+V_{As}$. These defects do not lead to interdiffusion of Ga and Al. This conclusion is in agreement with experiments which indicate that there is no universal intermixing of GaAs/AlAs interfaces by p-type doping. A very efficient intermixing caused by Zn in-diffusion finds an explanation consistent with the substitutional-interstitial mechanism of acceptor diffusion in GaAs [40,45] The explanation of superlattice intermixing in terms of the Fermi level dependent defect formation has been proposed before[38,39]. However, without the concept of the Fermi level stabilization energy the authors of this proposal were not able to account for the difference between n- and p-type doping or between superlattices based on different materials.

VI. LIMITATIONS OF MAXIMUM FREE CARRIER CONCENTRATIONS IN SEMICONDUCTORS

Many of the applications of compound semiconductors require preparation of low resistivity and high free carrier concentration materials. It is well recognized that in some cases one cannot achieve a high carrier concentration by either doping, implantation, or diffusion. Thus, in bulk grown GaAs the highest electron concentration which can be achieved by the doping does not exceed ~ 10^{19} cm^{-3} [46]. The highest electron concentration obtained by donor implantation is in the range 3 to 5×10^{18} cm^{-3} [47,48].

The situation is much different for p-type dopants in GaAs. In this case a very high concentration of holes, exceeding 10^{20} cm^{-3}, can be obtained [49]. Also, there is a one to one correspondence between the acceptor concentration and the concentration of holes, indicating that all acceptor atoms are electrically active and that the concentration of compensating donors is low. A semiconductor which shows a behavior similar to GaAs is GaSb. Again, in this case one finds that the maximum reported hole concentration is much higher [50] than the maximum electron concentration [51].

In striking contrast to GaAs and GaSb, one can obtain n-type InP with high electron concentrations approaching 10^{20} cm^{-3} [52]. Whereas doping of this material with acceptors is very inefficient and the highest reported hole concentrations lie in the range 3 to 5×10^{18} cm^{-3} [53]. The low carrier saturation concentrations in n-type GaAs and GaSb and in p-type InP are not dependent on the chemical identity of the donors or acceptors and are not associated with the solubility limits of the impurities which can be one to two orders of magnitude higher than the maximum carrier concentrations.

All these findings indicate that the electrical activity of shallow impurities is compensated by native defects, acceptors in GaAs and GaSb, and donors in InP. In order to quantitatively describe the compensation process we consider n-type GaAs. In this case the Fermi energy is above E_{FS} and the formation energy of V_{Ga}^{3-} is reduced. The concentration of free electrons is given by eq. (13) with $[V_{Ga}]$ determined by the solution of eq. (14). The calculated free carrier concentration is shown in Fig. 7. The value of the parameter $C'' = 3\times10^{18}$ cm^{-3} has been used in the calculations. It is seen that for low doping levels, $N_d < 3\times10^{18}$ cm^{-3}, the concentration of the compensating V_{Ga} acceptors is low and $n = N_D^+$. For $N_d > 3\times10^{18}$ cm^{-3}, a much weaker dependence of the electron concentration on N_D is found, $n \propto (N_D)^{1/3}$. This characteristic 1/3 power dependence is related to the fact that the compensating V_{Ga} are triply charged acceptors. As is seen in Fig. 7 the results of the calculations are in a good agreement with experimental data on Se doped GaAs [46]. It should be noted that very similar $n(N_D)$ dependencies were observed for other donors in GaAs [54]. We find from Fig. 7 that a critical concentration of electrons at which the effects of the compensation are becoming significant is $\sim 3\times10^{18}$ cm^{-3}. This corresponds to the value of $|E_F-E_{FS}| = 0.7$ eV for T = 1000 K. In p-type GaAs the same condition $|E_{FS}-E_F| = 0.7$ eV is satisfied for the hole concentration of $p \cong 9\times10^{20}$ cm^{-3}. This indicates that in p-type GaAs the limit for the free hole concentration set by the native defect compensation is very high. This is in agreement with the experiments which consistently show a high activation efficiency for acceptors in GaAs.

We infer from the above considerations that the donor-induced GaAs/AlAs superlattice intermixing is intimately related to the problem of saturation of free electron concentration in GaAs. Also, we find that the most important parameter controlling generation of compensating native defects is the separation of the Fermi energy from E_{FS}. From known locations of E_{FS} we can predict the trends in doping activation efficiency for different III-V semiconductors. In InP $E_{FS} \cong E_v + 1.0$ eV is located close to the conduction band. Therefore one expects that it should be easier to activate donors in this material than in GaAs. On the other hand, even moderate hole concentrations will result in a large value of the energy difference $(E_{FS}-E_F)$ leading to the formation of native defects and compensation of intentionally introduced acceptors. This is exactly what is observed experimentally where it has been found that it is much easier to obtain heavily doped n-type InP while the maximum hole concentration is limited to ~ mid 10^{18} cm^{-3} [53].

By virtue of the same qualitative argument one can expect that in GaSb, in which E_{FS} is located at $\sim E_v + 0.1$ eV, i.e. very close to the valence band, doping with donors will be much less efficient than doping with acceptors. Systematic studies of donor doping in GaSb have shown that for $n > 10^{18}$ cm^{-3} the electron concentration very weakly depends on the donor concentration $\left(n \propto N_D^{1/3}\right)$ [51]. This is the same dependence as that found for n-type dopants in GaAs. Therefore, we conclude that the native acceptor defects compensating the electrical activity of donors in heavily doped n-type GaSb occur in a triply ionized charge state. The highest electron concentration reported in GaSb does not exceed 3×10^{18} cm^{-3} [51]. On the other hand, doping with acceptors can provide material with the hole concentrations in excess of 10^{20} cm^{-3} [50].

Although the case of GaSb is, in many respects, similar to GaAs there is one important aspect which makes GaSb a unique material. It is well known that undoped, as-grown GaSb shows p-type conductivity with the hole concentration of the order of 10^{17} cm^{-3}. It has been proposed, based on thermodynamical analysis of the defect formation, that $Ga_{Sb} + V_{Ga}$ native acceptors are responsible for this high hole concentration [55]. It is interesting to note that this finding is in full agreement with the conclusions one can draw from the AND model. In Sb-deficient GaSb the amphoteric defect reaction corresponding to the reaction (1b) is,

$$Ga_{Sb} + V_{Ga} \leftrightarrow V_{Sb} + Ga_{Ga} \qquad (16)$$

Since, in GaSb E_{FS} is closer to the valence band than in GaAs, therefore, in intrinsic material the condition $E_F \gg E_{FS}$ is always satisfied and the $Ga_{Sb} + V_{Ga}$ acceptor is the stable defect.

VII. CONCLUSIONS

We have presented a new approach to the understanding of native defects in semiconductors. The approach is based on the concept of amphoteric native defects. It has been shown that the relative abundance, as well as structural and electronic properties of simple native defects, are controlled by the location of the Fermi level. The strongly Fermi level dependent electronic contribution to the total defect formation energy is proportional to the energy separation between the Fermi level and an internal energy reference: Fermi level stabilization energy. The location of the Fermi level stabilization energy with respect to the conduction and valence band edges is the single most important parameter controlling defect abundances at the metal-semiconductor and semiconductor-semiconductor interfaces, as well as in bulk semiconductor crystals. We have employed the amphoteric native defect model to show that apparently unrelated phenomena such as Schottky barrier formation, doping induced superlattice intermixing, and limitations of free carrier concentrations in semiconductors can have a simple common explanation.

The concept of amphoteric native defects finds application going beyond the effects discussed in this paper. It has been demonstrated recently that the very extensively studied and practically very important effect of doping-induced suppression of dislocation formation finds an explanation within the same basic concept [56,57]. Further, experimental and theoretical studies of defects in different semiconductors will be necessary to test the universality and applicability of this concept to other phenomena in semiconductors.

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