

THEORETICAL INVESTIGATION OF THE LEVEL ENERGIES FOR IDEAL Ga AND As VACANCIES IN GaAs

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The bound state energies of ideal Ga and As vacancies in GaAs have been studied in the Green's-function framework in conjunction the tight-binding method. Using existing data for band structures, the Koster-Slater parameters have been estimated, the energy levels at critical points and the density of states in perturbed and unperturbed crystal have been calculated. The unrelaxed vacancy of Ga and As introduces bound state at 0.05 eV and 1.46 eV respectively above the valence band edge. These results provide justification to experimental data based on irradiation of GaAs by energetic neutrons.

I-Introduction

In the last decades, remarkable progress have been made toward accurate calculations of vacancy levels of impurity states in semiconductors [1-4]. These studies are of crucial interest in the understanding of optical and electrical properties of this class of materials which is of major importance in most fields of pure and applied solid state physics.

Two types of important calculations have provided means for progress to understand the electronic structure of defect states in semiconductors. The molecular cluster approach, which is a faster and less complicated method, has been applied to the electronic states of isolated vacancies and substitutional impurities [5-8]. It has shown that the size of the cluster and the choice of the boundary conditions can affect the existence of the localized states [9]. Moreover, the calculations do not always provide reliable results both for the perfect and the imperfect clusters especially for many-valley direct-gap semiconductors [10].

The second category of methods are based on the well-known Green's function [11-16]. These methods provide qualitative description of the deep level in semiconductors.

The purpose of the present work is the determination of the position of bound state energies of ideal Ga and As vacancies in the GaAs. For this study, the Green's function method, in conjunction with the tight-binding approximation has been used.

This work is motivated by experimental results obtained by the irradiation of GaAs by energetic particles. The primary effect of energetic neutron irradiation is to displace atoms and create vacancies and interstitial particularly at higher fluences [17]. The Ga Vacancy has been also observed by electron paramagnetic resonance (EPR) in electron-irradiated p-type GaAs [18]. GaAs is a direct-gap semiconductor whose gap at the Γ point is 1.5192 ± 0.0002 eV [19]. In such a material, the point defects are the vacancies,

interstitial and antisites. Among these point defects, the arsenic vacancy (V_{As}) is a donor and its energy is thought to be at 0.045 eV below the conduction band [20,21]. The arsenic and gallium interstitials are also expected to be donors, but the gallium vacancy (V_{Ga}) is expected to be an acceptor and its energy is at 0.0424 ± 0.003 eV above the valence band [17,22-26].

In this work, we have obtained, for the Ga vacancy a bound state in the gap of GaAs at 0.05 eV above the valence band. For As vacancy the obtained level is at 1.46 eV above the valence band. These values are in good agreement with the experimental results [17] and with the self-consistent calculation [2,11,12].

The paper is organized as follows: in sec II we recall the method of calculation based on the Green's-function outlined in the tight-binding framework; in sec III we present the result obtained for both type of vacancies in GaAs and some discussions.

II - Theoretical considerations

a - Tight-binding description of energy bands.

The electronic band structure of GaAs in the blend structure has been obtained by a fitting of the pseudopotential energy bands calculated by Chelikowsky and Cohen [27] with the empirical tight-binding (ETB) method. the electronic states were modeled with a tight-binding Hamiltonian, which includes the s and p orbital for Ga and As.

Because of the presence of two Ga and As atoms in the unit cell, the resulting ETB Hamiltonian is 8×8 matrix. The fitting has been performed starting from the universal form of the interaction parameters proposed by Froyen and Harrison [28]. The final parameters entering our GaAs empirical TB Hamiltonian are identical to those given by Talwar and Al [4]. Taking into account all first and second -nearest-neighbor interaction, we obtained the energy levels at Γ , X, L critical points given in Fig I. The fitting

error was less than 0.2 eV for the valence band and about 0.4 eV for the lowest conduction band.

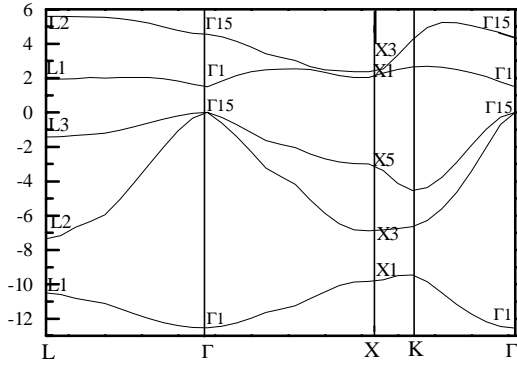


Figure 1: Calculated band structure for GaAs with the second-neighbor tight-binding parameters .

b-calculation of the ideal neutral vacancy levels in GaAs.

The defect states in GaAs were calculated by the Green's function method. We here only recall the basic features of this approach, more details can be found in ref [29]. The point defect is represented by a potential $U(r)$, which vanishes at large distance. The corresponding Schrodinger equation for the perturbed crystal:

$$(H^0 + U) |\Psi\rangle = E |\Psi\rangle \quad (1)$$

Where H^0 is the unperturbed Hamiltonian of perfect crystal.

Integral information about perturbed crystal can be obtained from the knowledge of the function $D(E)$ defined as:

$$D(E) = \det \|1 - G^0(E)\| \quad (2)$$

where G^0 is the perfect crystal Green's operator:

$$G^0(E) = (E - H^0 + i\eta)^{-1}, \eta \rightarrow 0 \quad (3)$$

The energies of the bound states are determined by:

$$D(E) = 0 \quad (4)$$

In the case of an ideal vacancy, the defect potential is obtained by removing from the periodic solid the corresponding atom . This removal was accomplished by shifting to infinity the on site energies of this atom. Due to the nature of the symmetry group of the vacancy, which is C_{3v} in the GaAs structure , s and p

orbital induce the irreducible representation (I.R) A and T(E) of this group, s being basis partners of the one dimensional (I R) A and p_x, p_y, p_z basis functions of three dimensional (IR) T(E). The matrix element of the Green's function

$G_{\mu\mu'}^0(E)$ have been calculated as:

$$G_{\mu\mu'}^0(E) = P \int \frac{A_{\mu\mu'}(E')}{E - E'} dE' - i\pi A_{\mu\mu'}(E) \quad (5)$$

μ is s, p_z or any p_x and p_y orbital at the vacancy site.

P stands for principal part and the spectral density of states $A_{\mu\mu}(E)$ is given by:

$$A_{\mu\mu}(E) = \sum_{\vec{n}(\vec{k})} \left| \langle \mu | \vec{n}\vec{k} \rangle \right|^2 \delta(E - E_n(\vec{k})) \quad (6)$$

$|\vec{n}\vec{k}\rangle$ are the unperturbed eigenstates of the crystal with energies $E_n(\vec{k})$. These spectral densities of states were obtained by the Gilat-Raubenheimer method [30] summing over 248 \vec{k} points in the irreducible 1/12 Brillouin zone using a high speed computer. However, in the case of A and T symmetry, it was found that the coupling between the s and p_z states was negligibly small which allowed us to treat these two states separately. Equation (4), which determines the position of the bound states now simplifies as:

$$G_{\mu\mu}^0(E) = 0 \quad (7)$$

The relation who binds the local density of states to the spectral density of states is:

$$N^0(E) = \sum_{\mu} A_{\mu\mu}(E) = \sum_{\vec{n}\vec{k}} \delta(E - E_n(\vec{k})) \quad (8)$$

To determinate $A_{\mu\mu}(E)$ we evaluate the local density of state $N^0(E)$ and ponderate each state $E_n(\vec{k})$ to $N^0(E)$ by the weight $\left| \langle \mu | \vec{n}\vec{k} \rangle \right|^2$ of the considered orbital μ .

III - Results and discussions

In this work we have studied the electronic structure of ideal vacancies in Zinc blend structure GaAs. We have first constructed an empirical tight-binding Hamiltonian describing the energy bands in the vicinity of the fundamental gap. This hamiltonian involves first and second nearest neighbor interactions of the s and p orbital of the constituent ions and reproduces reasonably accurately the band structure obtained by the pseudopotential method. The densities of states were determined by Green's function method using the Gilat-

Raubenheimer method. The state density curves corresponding to the imaginary part of the Green's functions presented in Fig 2-5 show the contribution of s, p states of the cation (anion) to the total state density of states in GaAs. The valence band is basically due to the p states of the anion (As) (Fig 5). The s state of the cation (Ga) is mainly responsible of the formation of states at the bottom of the conduction band (Fig 2); whereas the p state forms states at the upper conduction band (Fig3). We observe that each band is principally formed by one type of orbital; this confirms the ionic character of GaAs. It can be seen from these figures that the contribution of the p_x and the p_y and p_z orbital to the total density of states is almost the same.

Our calculation shows that, in the case of GaAs, the neutral cation and anion vacancy induce bound state inside the fundamental gap. The position of the bound states in the gap can be determined from the zero of the real part of the Green's function. This real part being obtained as the Hilbert transform of the imaginary part and presented in figs 6-9. The position of our calculated energy levels with respect to the top of the valence band are given in Table I.

	$A_I(s)$	$T(p_x, p_y, p_z)$
V_{Ga}	-1.59	0.05
V_{As}	0.0001	1.46

Table I: Energies of the states induced by ideal neutral vacancies in GaAs. Energies (in eV) are measured from the top of the valence band.

The value of energy level of the cation vacancy V_{Ga} is estimated to be 0.05(eV). The energy of the arsenic vacancy V_{As} is thought to be 1.46 eV above the valance band. These results corroborate with precedent finding results [2, 4] and are in good agreement with the experimental data based on the identification of the vacancies by the photoluminescence spectroscopy [17] in the case of V_{Ga} . In this work, the vacancies are

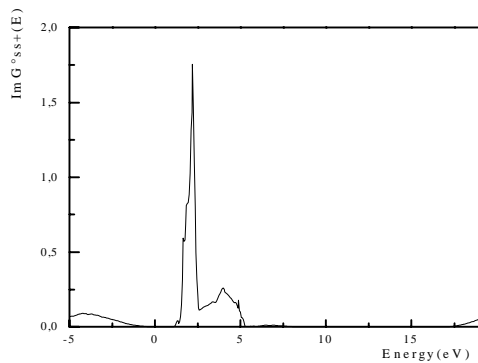


Figure 2: Imaginary part of the Green's function for an ideal cation vacancy: symmetry A(s) (a.u).

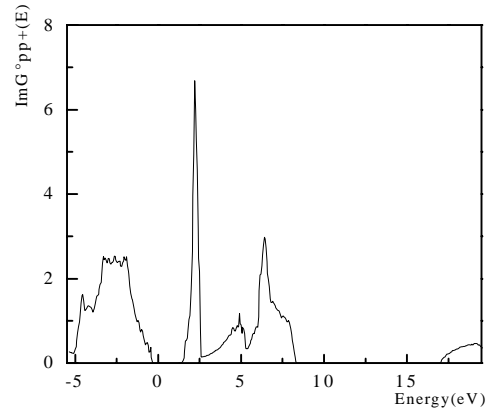


Figure 3: Imaginary part of the Green's function for an ideal cation vacancy: symmetry $T(p_x, p_y, p_z)$ (a.u).

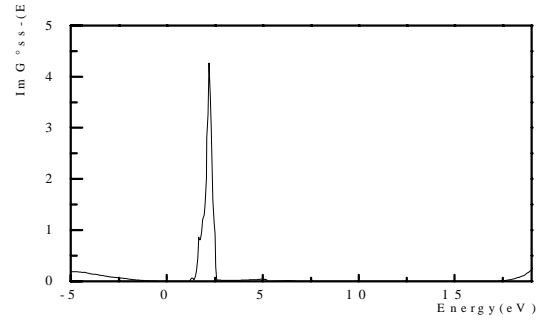


Figure 4: Imaginary part of the Green's function for an ideal anion vacancy: symmetry A(s) (a.u).

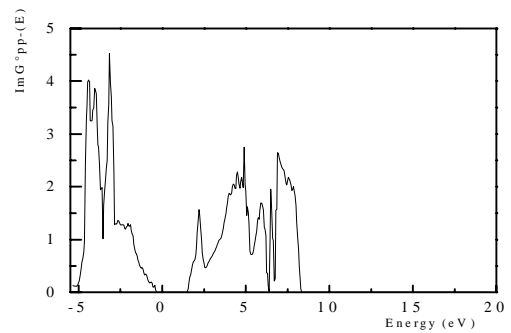


Figure 5: Imaginary part of the Green's function for an ideal anion vacancy: symmetry $T(p_x, p_y, p_z)$ (a.u).

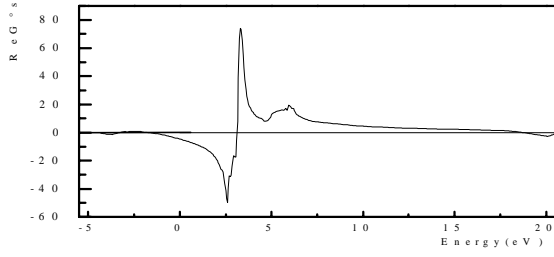


Figure 6: Real part of the Green's function for an ideal cation vacancy: symmetry A(s) (a.u).

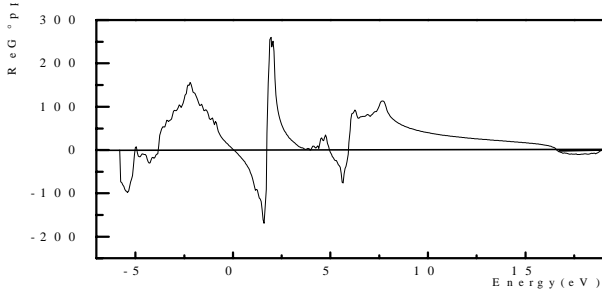


Figure 7: Real part of the Green's function for an ideal cation vacancy: symmetry T(p_x , p_y , p_z) (a.u).

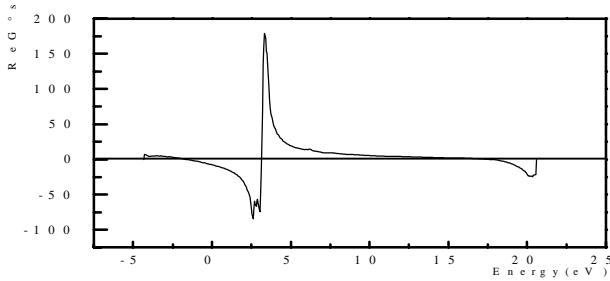


Figure 8: Real part of the Green's function for an ideal anion vacancy: symmetry A(s) (a.u).

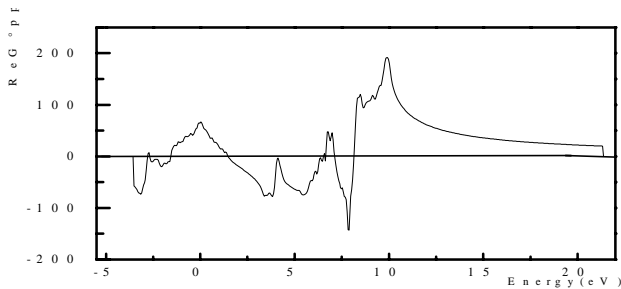


Figure 9: Real part of the Green's function for an ideal anion vacancy: symmetry T(p_x , p_y , p_z) (a.u).

created by the energetic neutron irradiation at higher fluences. One could confirm that the transition observed at 1.4745 ± 0.0003 eV in [17] is the V_{As} . It is to be mentioned that the lattice surrounding a vacancy will undergo Jahn-Teller distortions which have been completely neglected here. This study is under consideration.

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