SPECIAL POINTS AND IDEAL-VACANCY-INDUCED DEEP LEVEL IN Si AND SOME III—V SEMICONDUCTORS

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We show that the special points average technique is a suitable computational scheme to calculate the Green's function in the gap and we give a tight binding parameter set for Si.

Introduction

Vacancy induced localized defects in semiconductors have been the subjects of experimental and theoretical investigations for over two decades. Though not unambiguously identified experimentally, this simple lattice defect has attracted significant theoretical interest, mainly because of its conceptual simplicity as a prototype system to study localized defects. The knowledge of the deep level in the gap caused by localized defects in semiconductors is important in the understanding of many properties of a class of materials of major importance in most fields of pure and applied semiconductor physics.

To study the ideal vacancy induced levels in Si and in III—V compound semiconductors we have used an empirical tight binding scheme with linear combination of atomic orbitals in conjunction with the Green's-function technique [1]. As it was shown in [2], the levels caused by the vacancy in the gap, calculated by this method, are sensitive to the choice of the tight binding parameters. With different sets of parameters all of which give comparably good fits to the bulk band energies, the levels can vary through the whole range of the band gap. Clearly then, additional constraints on the fitting procedure are required to reduce ambiguity of the choice of the tight binding parameters.

A possibility to find a unique set of tight binding parameters [2] relied upon the established correlation between photothreshold and ionicity of the III—V compound semiconductors. The levels, obtained by these parameters provide trends as one goes from one material to another.

However the tight binding method with Green's function technique can be applied not only to vacancy induced deep levels in the gap but also to determining the surface and interface states [3] and in these cases finding a unique set of tight-

binding parameters is very important as well. In addition for the unrelaxed vacancy in some semiconductors there exist self-consistent Green's function calculations also [4], so it is natural to fit the TB parameters to these best results.

This fact, *i.e.* the knowledge of the "best" level would be a criterion to determine the tight-binding parameter system which might be useful for other calculation. But the calculation of the level induced by vacancy is rather cumbersome because of the time consuming integration over the Brillouin zone.

In this paper we will show that this integration can be reduced with the so-called special points average technique [5]. With this reduction we are able to determine a tight-binding parameter set which satisfies the requirement that the resulting level should agree with the level obtained from a self-consistent calculation and reproduce the bulk band structure.

I. The method for calculation of vacancy states

The basis of the Green's function method is the early work of KOSTER and SLATER [6], who showed that the electronic energy levels introduced in the band gap by a localized perturbation could be calculated from the knowledge of the Green's function for the perfect crystal and the matrix elements of the potential, both calculated in the Wannier representation.

LANOO and LENGLART [7] observed that the Green's function method is not limited to employing Wannier functions as a basis, but can be applied using a set of atomic orbitals and performing an LCAO band structure calculation. With this observation BERNHOLC and PANTELIDES [1] extended the method and showed that in an arbitrary localized representation the gap states introduced by the vacancy are given by the solution of

$$\det G^0_{\alpha\alpha}(E) = 0$$

where the matrix elements of the perfect-crystal Green's function are given by

$$G^0_{\alpha\alpha'}(E) = \sum_{n,\vec{k}} \frac{\langle \alpha | n\vec{k} \rangle \langle n\vec{k} | \alpha' \rangle}{E - E^0(n, \vec{k})}$$

where $|n\vec{k}\rangle$ are the Bloch states of the perfect crystal and $E^0(n, \vec{k}) - s$ are the corresponding energy bands and the $\{\varphi_\alpha\}$ is the set of orbitals which are localized about the site of the atom to be removed.

If the bulk solid electronic structure is sought within the LCAO approximation with s and p atomic basis set then the condition for the existence of a bound state can be rewritten as

$$\sum_{n,\vec{k}} \frac{|c_{\alpha j}(n, \vec{k})|^2}{E - E^0(n, \vec{k})} = 0$$

where $\{c_{\alpha j}\}$ are the coefficients of the expansion of the perfect crystal wave function, α, j refer to the αth-type (s, p_x, p_y, p_z) orbital located on the jth atom, n is the band index and $E^0(n, \vec{k})$ is the nth band energy at the wave vector $\vec{k}$.

The integration over $\vec{k}$ is carried out over the Brillouin zone of the material and the sum over n over all bands.

II. Average over Brillouin zone and results

As we have seen in Sec. I. the calculation of the vacancy-induced level in the gap requires an integration over Brillouin-zone. One of the most widespread methods is the so-called GILAT—RAUBENHEIMER [8] method, were used at first to calculate the frequency-distribution function in solids.

At this method we have to solve for the energy eigenvalues at evenly spaced points in reciprocal space and then to find other solutions in between by means of a TAYLOR expansion about each such point for each eigenvalue. By choosing the points for diagonalization sufficiently close together, all of the eigenvalues can be reached by linear extrapolation. In the application of the extrapolation method, the irreducible section of the first Brillouin zone is divided into a uniform simple cubic mesh of points $\vec{k}$, separated by a distance. Every $\vec{k}$ is at the center of a small cube throughout which extrapolation is carried out. In order to reach a reasonable result with this method a number of $\vec{k}$ is needed.

As it was shown in [9], a considerable simplification can be reached by introducing the mean value point or some special points [4], which are dictated by crystal symmetry, to calculate the approximate average values over Brillouin zone. The coordinates of these points were given for some lattices and possible applications of the method were suggested in the calculation of the electronic valence charge density and of the average one-electron valence-band energy [9]. The mean value point technique was also useful in evaluating the element of the dielectric matrix [10].

In this paper we have studied the possibility of the application of the method mentioned later to calculate the levels caused by the ideal vacancy in Si and some III—V semiconductor.

Since the question in this part is the applicability of the method therefore we have tested on the wellknown Si vacancy. We accepted for the tight binding parameter system given by PANDEY and PHILLIPS [11] which retains first and second nearest-neighbour interactions. Fig. 1 shows the function $G^0_{ss}(E)$, calculated with the mean value point and the two,- and ten special points. The zeros of $G^0_{ss}(E)$ in the regions of the band gap correspond to bound states of A_1 symmetry. As it can be seen there is no bound state in agreement with the calculation of Bernholc and Pantelides [1]. The Fig. 2 shows the function $G^0_{pp}(E)$ similar to $G^0_{ss}(E)$. The zeros of $G^0_{pp}(E)$ in the regions of the band gap correspond to bound states of T_2 symmetry. From this figure we can see that the $G^0_{pp}(E)$, obtained by ten points average becomes zero at $E=0.31$ eV (compared with 0.27 eV of [1]) and the other two do not give bound state. We have repeated this calculations using the parameters proposed by KAUFFER *et al.* [12]. We have obtained the same results, *i.e.* bound state is only in T_2 state ($E=0.25$ eV) with the help of ten representative points.

In Table I. the results of calculations for some III—V semiconductors are shown. The tight binding parameters are the same as in [2], and we compare the position of the levels in the fundamental gap region to the same levels previously calculated by hundred $\vec{k}$ point integration [2]. All energies are in eV and measured from the valence-band edge.

From the results we can establish that the one point and the two points average is not suitable, the ten point average agrees very well with the test data.

In particulary in the case of Ga series using the ten points good approximation can be reached. In the case of In series the gaps are so narrow for InSb and InAs

(0.24 eV and 0.38 eV, respectively) that there is no level in the gap, therefore the results are not informative, but for InP the agreement is suitable. Since from the calculations it was turned out that the ten points average over Brillouin zone is a succesful computational tool to determine the level caused by vacancy in the gap we tried to use this fact.

Knowing the position of the levels from other calculation (self-consistent calculations), we were able to determine the tight-binding parameters which gave a good

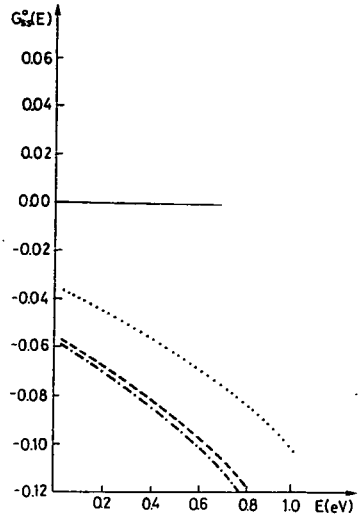

Fig. 1. The function of $G^0_{ss}(E)$, calculated by one point (dotted line), two points (dashed line), ten points (dashed dotted line) for Si.

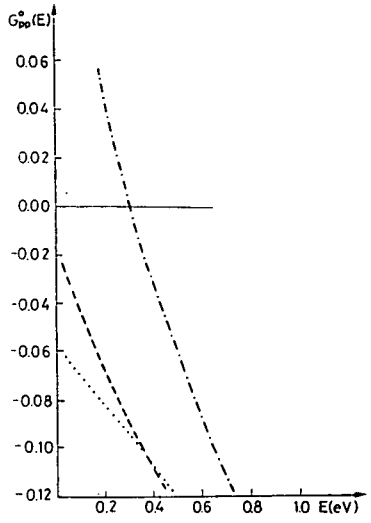

Fig. 2. The function of $G^0_{pp}(E)$ similar to Fig. 1

Table 1

A_1 and T_2 levels in the gap for anion vacancies (the energy zero is at the top of the valence band) as obtained with different calculations. A: mean value point; B: two points; C: ten points; D: from Ref. [2]. Energy in eV

	A_1				T_2			
	A	*B*	*C*	*D*	*A*	*B*	*C*	*D*
GaSb	—	0.67	0.49	0.56	—	0.39	0.59	0.76
GaAs	—	1.50	1.22	1.3	0.58	1.28	1.54	1.53
GaP	2.02	1.96	1.84	1.75	0.87	1.49	1.93	1.93
InSb	—	—	—	—	—	0.05	—	—
InAs	—	—	—	—	—	—	—	—
InP	—	—	1.29	1.35	0.33	1.06	1.37	1.47

Table II

Tight binding parameters for Si and the energies in the symmetry points. (The energies are in eV)

$E_{ss}(0, 0, 0)$	−4.24		−12.56
$E_{pp}(0, 0, 0)$	0.39		0.0
$E_{ss}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$	−2.08	Γ	3.59
$E_{xx}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$	0.428		3.92
$E_{xy}\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$	0.95		−8.11
$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\Big)$	1.375	X	−3.2
$_s(1, 1, 0)$	0.00		2.54
$E_{xx}(1, 1, 0)$	0.19		4.54
$E_{xy}(1, 1, 0)$	0.34		−10.22
$_x(1, 1, 0)$	0.00		−7.79
$E_{xx}(0, 1, 1)$	−0.05	L	−1.0
			2.37
			2.50
			4.30

band structure and the energy level in the gap agrees with the level of self-consistent calculation [4].

We have generated such a parameter set for Si, shown in Table II., where the energies in symmetry points are also shown. This parameter system may be useful to solve other (for example vacancy system) problems.

III. Summary

In this paper using a linear combination of atomic orbitals description of the electronic structure of the perfect solid in conjunction with the Green's function technique we have shown that the ten points average over the Brillouin zone is a good approximation to determine the vacancy induced levels in semiconductors. Furthermore using this fact we have given a tight binding parameter set for Si.

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СПЕЦИАЛЬНЫЕ ТОЧКИ И ГЛУБОКИЕ УРОВНИ НАВЕДЕННЫЕ ВАКАНСИЯМИ В Si И В НЕКОТОРЫХ ПОЛУПРОВОДНИКАХ ТИПА III—V.

Г. Папп и Ф. Белезнаи

Показано, что техника усреднения в специальных точках является подходящим ме
тодом для вычисления функции Грина в запрещенной зоне, и задается множество параметро
сильной связи для Si.