PHYSICAL REVIEW B VOLUME 46, NUMBER 4 15 JULY 1992-II

Effect of local relaxation on the binding energy of group-V donors in silicon

D. Sasireka* and E. Palaniyandi
School of Physics, Madurai Kamaraj University, Madurai 21, India

(Received 29 October 1991)

With use of a first-principles pseudoimpurity theory and a variational method, the binding energies of the shallow donors P, As, Sb, and Bi in Si are estimated; a multivalley effective-mass equation, incorporating the effect of local relaxation due to the difference in sizes between the host and impurity atoms, has been used. The extent of this relaxation is compared with results available in the literature. The substitutional donors As, Sb, and Bi are found to occupy nearly the same volume of the Si atom in the lattice. The model of the lattice-relaxation effect as proposed by Pantelides and Sah [Phys. Rev. B **10**, 638 (1974)] is used.

I. INTRODUCTION

The problem of donor states in multivalley semiconductors is of fundamental importance in semiconductor physics. When a group-V element enters a Si lattice substitutionally, localized energy levels are formed in the otherwise forbidden energy gap. Experiments reveal that the ground-state energies of these donors depend markedly on the specific impurity, while the excited-state energies are almost impurity independent. On the theoretical side, it is well known that there is excellent agreement between the Kohn-Luttinger effective-mass theory[1] (KL-EMT) and experiment for the excited states where the bound-electron wave function has vanishing amplitude at small r. The limited success for the ground state is due to the wave function having a large amplitude at small r. Many attempts have been made to go beyond the hydrogenic model and to account for the chemical shifts—the large discrepancies between the experimental ground-state energies and those given by KL-EMT—which arise due to the central-cell correction. Most of the attempts failed either because of an improper choice of the impurity potential[2] or because of the neglect of the intervalley mixing.[3] Though Ning and Sah[4] were quite successful with their phenomenological two-parameter model potential, first-principles calculations were lacking. Pantelides and Sah[5] reformulated the EMT in the framework of the pseudopotential theory and reproduced the ground-state energies of shallow donors in Si in excellent agreement with experiment except for a small discrepancy. One of the reasons for this discrepancy has been attributed to the large size of the cores of the substitutional impurities[5,6] and the local relaxation which results. Attempts have been made through laser annealing techniques[7] and x-ray diffraction techniques[8] to estimate the local strain field and lattice relaxation due to the size difference between the impurity and the host atoms. A spectroscopic investigation of Pajot and Stoneham[9] provides information on the local volume change produced when a group-V atom replaces a Si atom. In the absence of a simple and direct method to include the effect of lattice relaxation in the calculations of donor binding energies and wave functions, Manimahalai and Palaniyandi[10] have introduced an impurity-dependent effective mass to represent the effect of lattice relaxation, which depends strongly on the specific impurity.

In the present paper, an attempt is made to study systematically the effect of local relaxation on the donor binding energies and to compare the local volume change with those available in the literature. Atomic units are used throughout.

II. DONOR BINDING ENERGIES

The energy spectra of donors in a multivalley semiconductor are obtained by solving the effective-mass equation of Twose[11] within the framework of pseudopotential theory.[5] It is necessary here to justify the use of the Twose multivalley effective-mass equation (MVEME), the validity of which was sometimes questioned.[6] Palaniyandi and Vasantha Malliga[12] have shown that the MVEME of Twose could predict the shallow donor spectrum of Si reasonably well, over a wide range of the impurity potential.

It can be shown that the donor energies with respect to the conduction-band minimum are given by[5]

$$E_d=\frac{\sum_i\sum_j \alpha_j^*\alpha_i[T_{ij}+(U_{\rm PC})_{ij}+W_{ij}+(U_R)_{ij}]}{\sum_i\sum_j \alpha_j^*\alpha_i N_{ij}}\ , \tag{1}$$

where T_{ij}, $(U_{\rm PC})_{ij}$, W_{ij}, $(U_R)_{ij}$, and N_{ij} are the various matrix elements and α's are the numerical coefficients determined from symmetry considerations. For Si, the conduction band has six equivalent minima along the $\langle 100\rangle$ directions at a distance of $0.85\mathbf{k}_{\rm max}$ from the center of the Brillouin zone. The matrix elements are given by

$$T_{ij}=\langle \exp\{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}\}f_j(\mathbf{r})|T(-i\nabla)|f_i(\mathbf{r})\rangle\ , \tag{2}$$

$$N_{ij}=\langle \exp\{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}\}f_j(\mathbf{r})|f_i(\mathbf{r})\rangle\ , \tag{3}$$

$$(U_{\rm PC})_{ij}=\langle \exp\{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}\}f_j(\mathbf{r})|U_{\rm PC}(r)|f_i(\mathbf{r})\rangle\ , \tag{4}$$

$$W_{ij}=\langle \exp\{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}\}f_j(\mathbf{r})|W(r)|f_i(\mathbf{r})\rangle\ , \tag{5}$$

$$(U_R)_{ij}=\langle \exp\{i(\mathbf{k}_i-\mathbf{k}_j)\cdot\mathbf{r}\}f_j(\mathbf{r})|U_R|f_i(\mathbf{r})\rangle\ , \tag{6}$$

where $U_{PC}(r)$ is the screened point-charge Coulomb potential, $W(r)$ is a short-range core potential, and U_R is the reorthogonalization potential.[5] By making use of the atomic core wave functions of Herman and Skillman,[13] the first-principles pseudoimpurity potentials are constructed. With a hydrogenic trial function for the 1s ground state

$$f_i(\mathbf{r})=\exp\{-r/a\}/(\pi a^3)^{1/2} \tag{7}$$

the above matrix elements are calculated and Eq. (1) is solved variationally. The values of the parameters used in the present work are the same as those used by Pantelides and Sah.[5] The energy minimum is located for P, As, Sb, and Bi in Si.

III. EFFECT OF SQUEEZING

When substitutional impurities like P, As, Sb, and Bi enter the Si lattice, one of the following two situation may occur:[5] (i) Due to lattice relaxation, the core states of these impurities may extend out appreciably and push away their nearest neighbors; and (ii) the core wave functions of the impurity may get distorted by the local environment of the host crystal. In the present study, the latter case is prescribed.

From the atomic core wave functions available at 96 points (r), the distorted core wave functions for various impurities at the new points (r') are calculated by the prescription

$$\mathbf{r}'=\mathbf{r}-\eta\mathbf{r}/100\ , \tag{8}$$

where η is the percentage of squeezing. The distorted core wave functions are renormalized and are used to recalculate the donor ground-state energies as a function of η. From Fig. 1, the values of η for which the experimental ground-state energies are reproduced are found and given in Table I. Assuming that Pauling's tetrahedral covalent atomic radii[14] of the impurity atoms undergo the same extent of squeezing as that of the core wave functions, the modified values of the tetrahedral covalent radii of the impurity atoms in Si lattice are determined and given in Table II. Similarly, the changes in volume of the

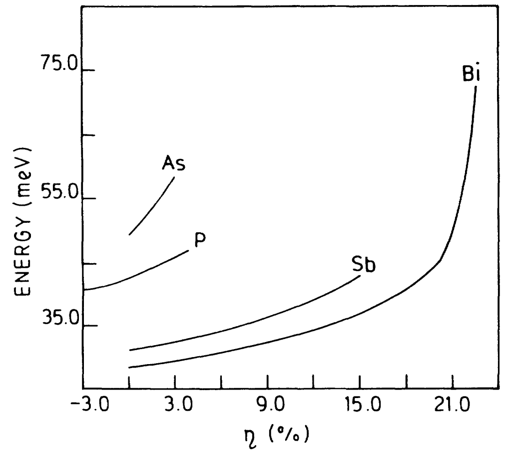

FIG. 1. Effect of squeezing on $1s(A_1)$ state energies.

TABLE I. Effect of squeezing on the $1s(A_1)$ ground-state energies of donors in silicon.

Donor	Extent of squeezing η(%)	Binding energy Present calculation (meV)	Experiment (meV)
P	0.00	−42.5	−45.5
	2.80	−45.5	
As	0.00	−49.31	−53.7
	1.67	−53.7	
Sb	0.00	−31.03	−42.7
	14.83	−42.7	
Bi	0.00	−28.26	−70.9
	22.52	−71.03	

TABLE II. Effect of squeezing on Pauling's tetrahedral covalent radii and on the volumes of the impurity atoms.

Donor	Extent of squeezing η (%)	Squeezed radii (Å)	Change in volume $\Delta V/V_0$ a	b	c
Si					
P	2.80	1.07	0.023	−0.08	−0.17
As	1.67	1.16	0.017	0.04	0.03
Sb	14.83	1.16	0.233	0.17	0.57
Bi	22.52	1.13	0.438	0.30	0.94

[a] Present study.

[b] Spectroscopical data of Pajot and Stoneham, Ref. 9.

[c] Derived from a comparison of Pauling's tetrahedral covalent radii.

TABLE III. Effect of squeezing on the binding energies of donors in silicon.

Donor	State	Extent of squeezing η (%)	Variational parameter (a.u.)	Binding energy Present study (meV)	Expt. (meV)
P	$2s(A_1)$	0.00	32.0	−8.83	−8.95[a]
		2.80	31.3	−8.99	
	$1s(T_2)$	0.00	37.8	−31.26	−33.9
		2.80	37.8	−31.28	
	$1s(E)$	0.00	38.9	−30.58	−32.6
		2.80	38.8	−30.62	
As	$2s(A_1)$	0.00	30.5	−9.08	−9.26[a]
		1.67	30.0	−9.19	
	$1s(T_2)$	0.00	40.2	−29.97	−32.6
		1.67	40.2	−30.00	
	$1s(E)$	0.00	40.8	−29.54	−31.2
		1.67	40.8	−29.58	
Sb	$2s(A_1)$	0.00	38.5	−7.79	−8.79[a]
		14.83	32.0	−8.77	
	$1s(T_2)$	0.00	42.2	−28.95	−32.9
		14.83	41.6	−29.21	
	$1s(E)$	0.00	43.0	−28.39	−30.5
		14.83	41.9	−29.99	

[a] Ning and Sah's theoretical estimate, Ref. 4.

impurity atoms P, As, Sb, and Bi when they get squeezed in the Si lattice are determined and given in Table II, together with the $\Delta V/V_0$ values reported in the literature[9] for the above impurities. For the above η values the $2s(A_1)$ state energies of P, As, and Sb are calculated and are found to be in good agreement with Ning and Sah's theoretical estimates, as can be seen from Table III.

IV. DISCUSSIONS

From Table I it is seen that the substitutional impurities P, As, Sb, and Bi seem to undergo squeezing due to local relaxation. The effect of this squeezing is to make the levels deeper. From Table II it is seen that the substitutional impurities As, Sb, and Bi assume more or less the same radii of the Si atom in the lattice. Table II shows that there is good agreement between the $\Delta V/V_0$ values obtained for As and Sb in the present work and those from the spectroscopic data of Pajot and Stoneham.[9] This suggests that the observation made by Pajot and Stoneham[9] that the volume changes are definitely smaller than the estimates derived from Pauling's tetrahedral covalent radii is corroborated and that the forced hybridization of the atomic orbitals could be the origin of the apparent shrinking of the free atom when tetrahedrally bound in the Si lattice.

The positive volume change observed for P contradicts the concept of the tetrahedral covalent radii. In addition to the negative volume change (-0.08) due to P diffusion reported by Pajot and Stoneham,[9] Cohen,[15] and McQuhae and Brown[16] have also reported a negative change in the overall volume of -0.11 and -0.15, respectively, for As and Sb. But, recent x-ray measurements[8] of the Si lattice expansion indicate a small increase of the lattice parameter, or a positive $\Delta d/d_0$ value (≤ 0.14), for Si if the impurity (any one of B, P, As, and Sb) is introduced in low concentrations. This supports the positive parameter change of $\Delta d/d_0$ (0.026) observed for P in the present work. Again, the trend in the x-ray measurements[8] for As and Sb in low concentrations is in agreement with the results of the present work.

The effect of squeezing on the donor ground-state energy is much more pronounced in the case of Bi in Si, as expected. However, the effect of squeezing on $1s(T_2)$ and $1s(E)$ state energies of substitutional donors in Si (Table III) is found to be negligible when compared with that for the $1s(A_1)$ or $2s(A_1)$ state energies, as the wave functions for these states have vanishing amplitude in the immediate vicinity of the impurity site.

Thus the effect of squeezing makes the levels deeper. As the group-V impurities enter the Si lattice substitutionally, due to local relaxation As, Sb, and Bi tend to occupy more or less the same volume of the Si atom they replace. However, P seems to contradict this observation. The substitutional donors P, As, Sb, and Bi, irrespective of their Pauling tetrahedral covalent radii, undergo a contraction as a local relaxation as they enter the semiconductor lattice in low concentrations.

ACKNOWLEDGMENTS

The authors thank the Department of Computer Science, Madurai Kamaraj University, where the computations were carried out on a Cyber 180/830 A computer.

---

*Present address: Standard Fireworks Rajaratnam College for Women, Sivakasi 626 123, India.

[1] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).
[2] A. Baldereschi, Phys. Rev. B **1**, 4673 (1970).
[3] M. Jaros, J. Phys. C **4**, 1162 (1971).
[4] T. H. Ning and C. T. Sah, Phys. Rev. B **4**, 3468 (1971).
[5] S. T. Pantelides and C. T. Sah, Phys. Rev. B **10**, 621 (1974); **10**, 638 (1974).
[6] K. Shindo and H. Nara, J. Phys. Soc. Jpn. **40**, 1640 (1976).
[7] A. M. Stoneham, Phys. Lett. **70A**, 55 (1979).
[8] P. Becker and M. Scheffler, Acta Crystallogr. Sect. A **40**, 341 (1984).
[9] B. Pajot and A. M. Stoneham, J. Phys. C **32**, 5241 (1987).
[10] K. Manimahalai and E. Palaniyandi, J. Phys. Chem. Solids **46**, 831 (1985).
[11] W. D. Twose, as quoted in the Appendix of H. Fritzsche, Phys. Rev. **125**, 1560 (1962).
[12] E. Palaniyandi and T. Vasantha Malliga, Phys. Rev. B **38**, 13 197 (1988).
[13] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
[14] C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1968), p. 105.
[15] B. G. Cohen, Solid State Electron. **10**, 33 (1967).
[16] K. G. McQuhae and A. S. Brown, Solid State Electron. **15**, 259 (1972).