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Electronic properties of the iron-boron impurity pair in silicon

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We report results for the electronic structure of the interstitial-iron–substitutional-boron nearest-neighbor pair complex in silicon. Self-consistent one-electron state calculations, which are carried out here for the first time, yield a covalent microscopic model for the pair, in contrast with the currently accepted ionic model. The pair EPR parameters ($J=\frac{3}{2}$ and $g \simeq 2$) arise from our model, which ascribes an orbital singlet and a spin triplet to the ground state of the neutral Fe-B complex.

It has been known for a long time that 3*d* transition metals (TM's) form pair complexes with both shallow and deep-level impurities in silicon.[1] A class of TM-related pair complexes which has deserved a great deal of attention from the experimental point of view is the one that involves a group-III *A* acceptor (*A*) impurity, such as B, Al, Ga, In, or Tl. The *M*-*A* complexes (where *M* represents a TM atom) have been characterized by several experimental techniques.[1-15] Electron paramagnetic resonance (EPR) data[1-4] and measurements of photoluminescence (PL) correlated to stress and Zeeman effects[14] have shown that the pairs display a ⟨111⟩ axial symmetry, indicating that they may consist of a substitutional acceptor with a TM atom placed at a nearest-neighbor interstitial site. The Fe-In pair was pointed out as an exception to this rule since it shows a ⟨100⟩ symmetry, consistent with the assumption that the Fe impurity may be placed at the next-nearest-neighbor interstitial site.[1] However, recent EPR experiments ascribe both the ⟨111⟩ and ⟨100⟩ configurations to the Fe-Al pair.[3] The bistable behavior of the pairs of Fe with Al, Ga, and In has also been recently detected by using deep-level transient spectroscopy (DLTS).[11,12]

The energy levels induced in the silicon band gap by the *M*-*A* pairs in the ⟨111⟩ configuration, as obtained by various techniques, have been summarized by Feichtinger *et al.*[9] Recently, additional results for the donor activation energies of the pairs of Fe with Al, Ga, and In in the ⟨100⟩ configuration, and for the Fe-In pair in the ⟨111⟩ configuration, have been obtained from DLTS experiments.[12] Formation and dissociation reactions around room temperature have been investigated for the pairs of Fe with B, Al, and Ga as well as for the Cr-B pair, by carrying out DLTS measurements.[4-7] The role played by the bistable behavior of the Fe-Al pair on the pairing reactions has been recently monitored by DLTS.[11] The Fe-B pair[7,8] and the Cr-B pair[4] binding energies, the local vibrational modes associated with the Fe-B, Fe-Tl, and Cr-B pairs,[14] and the behavior of the electronic impurity levels induced by the pairs of Fe with B, Al, and Ga under hydrostatic pressure,[10] have also been investigated.

Although there has been considerable progress, from an experimental point of view, in understanding the properties of the *M*-*A* pairs in silicon, our knowledge of these complexes, as originated from a theoretical approach, is at an early stage. Up to now the only theoretical tool which has been used to deal with such systems is the so-called ionic model.[1] According to this model the pair stable configuration corresponds to a classical system consisting of a M_i^+ ion electrostatically bound to a nearest or next-nearest A_s^- impurity, embedded in a dielectric medium. In this Rapid Communication, we report for the first time rigorous self-consistent one-electron state calculations for the $\mathrm{Fe}_i\mathrm{B}_s$ nearest-neighbor pair in silicon. The theory used here is based on the multiple-scattering (MS) $X\alpha$ molecular-cluster model, the same approach that has been used in our previous calculations for the Au-Fe pair in silicon.[16] A $25\mathrm{Si}+\mathrm{B}_s\mathrm{Fe}_i$ cluster is adopted, comprising a central Fe atom at the *T* site, a nearest-neighbor substitutional B impurity, and eight shells of Si atoms classified according to a C_{3v} symmetry.

The energy spectrum of the $25\mathrm{Si}+\mathrm{B}_s\mathrm{Fe}_i$ cluster, simulating the electronic structure of the $\mathrm{Fe}_i\mathrm{B}_s$ pair, is shown in Fig. 1. In order to better characterize the impurity levels induced by the pair complex, we are selecting the Fe 3*d*- and B 2*s*- and 2*p*-derived levels from the complete spectrum, shown in Fig. 1(a), and locating them relatively to the band edges in Fig. 1(b).

Based on the calculations reported here and on the results obtained previously[17-19] for the isolated B_s and Fe_i neutral atoms in silicon, we are now able to describe the formation of the impurity levels induced by the $\mathrm{Fe}_i\mathrm{B}_s$ pair from the interaction between the molecular orbitals (MO's) of the isolated impurities. This effort gives rise to the microscopic model for the pair, schematically shown in Fig. 2. There, the (a), (b), and (c) labels indicate the one-electron impurity levels for the B_s, for the $\mathrm{Fe}_i\mathrm{B}_s$ pair, and for Fe_i, respectively. The charge distribution inside the B and Fe impurity spheres (radii = 1.18 Å) as well as the level positions, relative to the band edge, with which these impurity states are associated, are shown in Table I. The charge *Q* evaluation includes the occupancy of the levels.

According to a $16\mathrm{Si}+\mathrm{B}_s$ MS cluster model calculation, the relevant effect of introducing a B_s impurity into the silicon lattice is the appearance of a t_2 acceptor level slightly above the top of the valence band.[18] Our calculations for the $\mathrm{Fe}_i\mathrm{B}_s$ pair indicate that there are strong covalent interactions between the MO's of the isolated impurities. As a result, the B_s acceptor level is pulled down

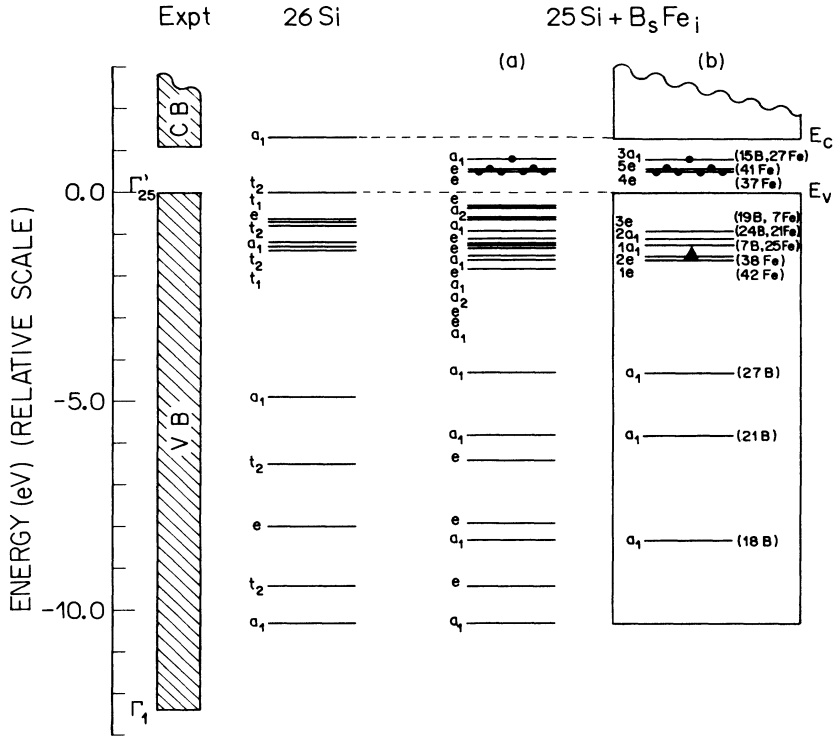

FIG. 1. Self-consistent one-electron energy spectra of the $25\mathrm{Si}+\mathrm{B}_s\mathrm{Fe}_i$ cluster simulating the electronic structure of the substitutional-B–tetrahedral-site interstitial-Fe pair in silicon. (a) All the electronic states are shown. (b) Only the Fe $3d$- and B $2s,2p$-derived energy levels, relative to the band edges [conduction band (CB) and valence band (VB)] are indicated. The results for a perfect 26-Si-atom cluster as well as the experimental values for the silicon valence-band width and band gap are also shown. The filled circles indicate the occupancy of the gap levels, and the filled triangle shows the Fe_i-derived dt_2 and de resonances quoted from Ref. 17. The numbers between parentheses denote the percentage of charge, normalized to one electron, within the Fe or B impurity spheres (radius 1.18 Å).

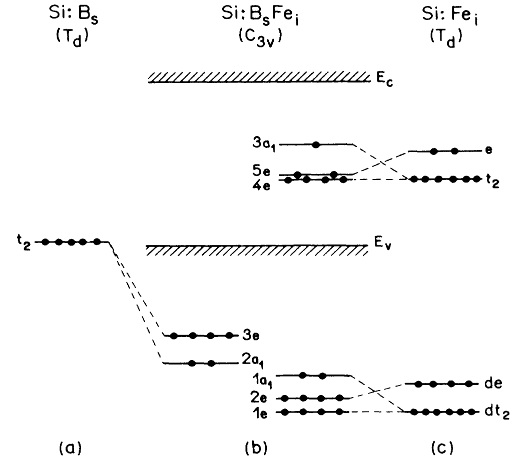

FIG. 2. Schematic representation of the $\mathrm{Fe}_i\mathrm{B}_s$ impurity levels, relative to the silicon band edges, as derived from the interactions between the impurity states of the isolated impurities. The filled circles indicate the occupancy of the levels. (a) Indicates the B_s shallow acceptor level. (b) Indicates the Fe-B resonances and gap levels, labeled according to Fig. 1. (c) Shows the Fe_i-derived dt_2 and de resonances and t_2 and e gap levels.

TABLE I. Energy levels, E, measured from the top of the valence band and charge, Q, within the impurity spheres (in units of one electron), relative to the impurity states induced in silicon by B_s, Fe_i, and $\mathrm{Fe}_i\mathrm{B}_s$. The levels are labeled according to Fig. 2.

Impurity	Level (occupancy)	E (eV)	Q (B)	Q (Fe)
B_s [a]	$t_2(5)$	0.04	0.70	· · ·
$\mathrm{Fe}_i\mathrm{B}_s$ [b]	$1e(4)$	−1.61	· · ·	1.68
	$2e(4)$	−1.48	· · ·	1.52
	$1a_1(2)$	−1.25	0.14	0.50
	$2a_1(2)$	−1.12	0.48	0.42
	$3e(4)$	−0.88	0.76	0.28
	$4e(4)$	0.50	· · ·	1.48
	$5e(2)$	0.54	0.12	0.82
	$3a_1(1)$	0.83	0.15	0.27
Fe_i [c]	$dt_2(6)$	−1.68	· · ·	2.40
	$de(4)$	−1.41	· · ·	1.80
	$t_2(6)$	0.64	· · ·	1.80
	$e(2)$	0.68	· · ·	0.76

[a] Reference 18.

[b] This work.

[c] Estimated from Ref. 17.

into the valence band and splits into a nondegenerate σ-like and a doubly degenerate π-like pair state. They are labeled as $2a_1$ and $3e$ in Fig. 2(b). The t_2 acceptor state of B_s interacts primarily with the dt_2 resonance of the Fe_i impurity. The t_2 acceptor level of B_s is shifted by about twice the value predicted by the ionic model, 0.55 eV, which corresponds to a shift caused by the Coulombic field created by the Fe_i^+ ion at the B_s^- site.[11]

The ionic model establishes that one electron is transferred from the Fe_i donor level in the gap to the B_s acceptor level. In order to analyze this assumption, we start by first taking into consideration the amount of charge which is transferred to the B_s sphere in the pair through the B_s t_2-derived $2a_1$ and $3e$ states. According to the entries shown in Table I, the difference between the charge associated with the t_2 hole state induced by B_s and the charge associated with the $2a_1$ and $3e$ states induced by the Fe_iB_s pair is $-0.54e$. On the other hand, an isolated Fe_i impurity in silicon gives rise to dt_2 and de resonances within the valence band [filled triangle in Fig. 1(b)] and t_2 and e levels within the band gap, schematically shown in Fig. 2(c).[17,19] The Fe_i $3d$-derived resonances give rise to the $1e$, $2e$, and $1a_1$ resonances for the pair, as indicated in Fig. 2(b). The dt_2 resonance interacts with the t_2 state of B_s and splits into σ-like $(1a_1)$ and π-like $(1e)$ levels. The de resonance is shifted down slightly, being labeled as $2e$ in Fig. 2(b). The entries in Table I show that the difference between the total charge associated with the dt_2 and de resonances induced by the Fe_i impurity and the total charge associated to $1e$, $2e$, and $1a_1$ resonances induced by the pair complex is $+0.5e$. Thus, the Fe_i impurity loses about the same amount of charge which is transferred to the B_s impurity when the pair is formed.

One important feature of our calculations is finding that the gap states of the Fe_iB_s pair are Fe_i-like states. The gap levels induced by the pair, labeled as $4e$, $5e$, and $3a_1$ in Fig. 2(b), originate from the t_2 and e gap states of the Fe_i impurity. The interactions with the B_s MO splits the t_2 state, by about 0.33 eV, into the $4e$ and $3a_1$ levels, with the latter crossing the $5e$ level and becoming the highest gap level for the pair. This splitting is mostly due to the upwards displacement of the σ-like $3a_1$ level. A similar conclusion was reached by Feichtinger *et al.* in their analysis of the electronic structure of the Mn-B pair.[9] By using perturbation theory, the authors have shown that the π-like state $(4e)$ is pushed apart by approximately 0.1 eV, whereas the σ-like state $(3a_1)$ is split by an amount of the order of 1 eV. The strong localization of the Fe_iB_s gap states within the cluster central atomic sphere emphasizes the Fe_i $3d$ character of these impurity states.

The analysis of the charge distribution shown in Table I for the Fe_i and Fe_iB_s gap states leads to an interesting conclusion related to the pair electronic structure. The eight electrons occupying the t_2 and e gap levels lead to the value $2.56e$ for the charge associated with these states within the Fe_i sphere of the isolated impurity. On the other hand, the seven electrons occupying the Fe_iB_s gap levels give the value $2.57e$ for the charge within the Fe_i sphere. Thus, the same amount of charge within the Fe_i atomic sphere is obtained in both cases. This result contradicts the assumption that a Fe_i^+ ion is created by transferring one electron from the donor level of the isolated iron to the B_s impurity. Here the Haldane and Anderson mechanism, which is operative if covalent effects play a role, prevents charge transfer out of the Fe_i impurity sphere by compensating the decrease in one unit of the gap-level occupancy.[19]

Although our calculations show that the interaction between the t_2 acceptor state of B_s and the dt_2 resonance of Fe_i causes a transfer of about 0.5 electronic charge from Fe_i to B_s, we do not conclude that some ionic character can be ascribed to the stabilized pair. This fact can be confirmed in a straightforward way by analyzing the total electronic charge within the impurity atomic spheres. According to the $16Si+B_s$ cluster model calculation, simulating the electronic structure of an isolated neutral boron substitutional impurity, the value $5.61e$ is found for the electronic charge within the B_s impurity sphere.[18] Our calculations show that this value is reduced to $5.34e$ when the pairing between B_s and Fe_i occurs. On the other hand, the Fe_i atomic sphere contains $26.13e$ when the neutral impurity is isolated, whereas this value changes to 26.07 when the pairing takes place. Therefore, there is no clear indication from the calculations that there is a transfer of one electron from Fe_i to B_s, as is assumed in the ionic model.

In spite of the fact that the calculations reported here were not carried out to the spin-polarized limit, we can infer from the significant localization of the pair gap states on the Fe_i impurity sphere that the exchange interactions drive the complex to a high-spin configuration. If the calculations are performed with three electrons filling the $5e$ gap level and with the $3a_1$ level empty, we obtain the $3a_1$ level placed at about 0.15 eV above the $5e$ level. In this case, the value 31% is found for the percentage of charge within the Fe sphere corresponding to the $3a_1$ state. The strong localization of the $3a_1$ state in the Fe sphere and its proximity to the $5e$ level indicate that a high-spin configuration is likely.[19] Within the framework of the spin-restricted calculations carried out in the present work, the high-spin configuration is simulated by promoting one electron from the $5e$ to the $3a_1$ level. We point out that the C_{3v} crystal-field effects are strong enough to push the $3a_1$ level above the $5e$; however, these levels are close enough to favor spin alignment.

In conclusion, the donor and acceptor transitions observed for the pair are related to the $3a_1$ state. The Fe_iB_s pair ground state is a ^4A orbital singlet, implying that the values $L=0$ and $S=\frac{3}{2}$ are ascribed to the angular momentum and spin eigenvalues of the complex, respectively, in agreement with EPR measurements. This conclusion indicates that the pair complex does not undergo Jahn-Teller distortions, therefore it is stable in a trigonal symmetry as has been detected.

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[1] G. W. Ludwig and H. H. Woodbury, Solid State Phys. **13**, 223 (1962).

[2] W. Gehlhoff and K. H. Segsa, Phys. Status Solidi (b) **115**, 443 (1983).

[3] J. J. van Kooten, G. A. Weller, and C. A. J. Ammerlaan, Phys. Rev. B **30**, 4564 (1984).

[4] H. Conzelmann, K. Graff, and E. R. Weber, Appl. Phys. A **30**, 169 (1983).

[5] K. Wünstel and P. Wagner, Appl. Phys. A **27**, 207 (1982).

[6] K. Graff and H. Piepper, J. Electrochem. Soc. **128**, 669 (1981).

[7] L. C. Kimerling and J. L. Benton, Physica B **116**, 297 (1983).

[8] H. Lemke, Phys. Status Solidi (a) **64**, 215 (1981).

[9] H. Feichtinger, J. Oswald, R. Czaputa, P. Vogl, and K. Wünstel, J. Electron. Mater. **14a**, 855 (1985).

[10] K. Wünstel, O. Kumagai, P. Wagner, and W. Jantsch, Appl. Phys. A **27**, 251 (1982).

[11] A. Chantre and D. Bois, Phys. Rev. B **31**, 7979 (1985).

[12] A. Chantre and L. C. Kimerling, in *Proceedings of the 14th International Conference on Defects in Semiconductors, Paris, 1986* [Mater. Sci. Forum **10-12**, 387 (1986)].

[13] M. Kittler, W. Seifert, K. Schmalz, and K. Tittelbach-Helmrich, Phys. Status Solidi (a) **96**, K133 (1986).

[14] R. Sauer and J. Weber, Physica B **116**, 195 (1983).

[15] C. A. J. Ammerlaan and J. J. van Kooten, Mater. Res. Soc. Symp. Proc. **46**, 525 (1985).

[16] L. V. C. Assali, J. R. Leite, and A. Fazzio, Phys. Rev. B **32**, 8085 (1985).

[17] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **23**, 1851 (1981).

[18] M. A. Bunin, Yu. A. Matveev, N. A. Petrov, and Yu. V. Sukhetskii, Fiz. Tekh. Poluprovodn. **17**, 2025 (1983) [Sov. Phys. Semicond. **17**, 1291 (1983)].

[19] A. Zunger, Solid State Phys. **39**, 275 (1986).