PHYSICAL REVIEW B VOLUME 15, NUMBER 8 15 APRIL 1977

Comment on the electronic structure of the neutral vacancy in silicon

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(Received 30 September 1976)

From a comparison of three calculations, we conclude that the unrelaxed vacancy in Si introduces a T_2 bound level in the gap and two A_1 resonances in the valence band. The lower one, in the first minimum of the density of states, is only weakly localized and the other, near the valence-band edge, corresponds to the symmetric combination of the dangling bonds. Preliminary results for the relaxed vacancy are also discussed.

Louie *et al.* have performed recently a self-consistent calculation of the electronic states for Si vacancy models.[1] As it has proved useful for calculating surface properties,[2] we have investigated the same problem using the tight-binding method.[3] Our starting point is a two-center tight-binding fit to the band structure of Herman *et al.*,[4] including second-nearest-neighbor interactions, using Green's-function formalism. This procedure is less elaborated than the self-consistent pseudopotential calculation of Louie *et al.*, but it is free of the dispersion introduced by their use of a cluster with periodic boundary conditions.

By comparing these two calculations and an earlier one by Callaway,[5] we draw some conclusions concerning the energy levels associated with the unrelaxed vacancy in silicon. Then we give some preliminary results in the case of the relaxed vacancy, obtained with the tight-binding method.

In Ref. 3, the Green's functions are calculated using the Haydock *et al.* procedure,[6] so that the gap is replaced by a region of low density of states and the bound states appear as resonant ones. However, from their position in energy with respect to band edges, one can easily separate bound from resonant levels. The energy levels are located by looking at the partial density of states of the A_1 and T_2 group orbitals of the atom which is removed to create the vacancy. This procedure insures that they correspond to the dangling bonds of the simple molecular-orbital picture of Watkins *et al.*[7] The unrelaxed vacancy is found to introduce a bound T_2 level at $+0.12$ eV and a resonant A_1 level at -0.88 eV (the top of the valence band being the origin of energies). As shown on Fig. 1 these levels can also be identified by looking at the phase shifts δ_{A_1} and δ_{T_2}; notice also that the A_1 phase shift exhibits a second resonance at -7.27 eV, in the first minimum of the valence-band density of states.

The general shape of these phase shifts is similar to that obtained earlier by Callaway.[5] However Callaway does not find any localized or resonant state of T_2 symmetry, even when he lets the perturbation potential increase arbitrarily by the factor 1.1 (only a A_1 level appears then in the gap). This result is rather difficult to understand as, the top of the valence band having a strong T_2 character, a repulsive potential should extract first a T_2 level. Moreover an A_1 level cannot account for the Jahn-Teller distortion observed in silicon. From Callaway's figure 1, it can be seen that two A_1 resonances are found at -0.4 and -8.6 eV, respectively. The lower A_1 resonance lies in the first minimum of the valence-band density of state of Callaway's band structure for the perfect crystal.

Louie *et al.* find a T_2 level at $+0.5$ eV; this figure is larger than our value of 0.12 eV but both calculations have built-in uncertainties. In particular our neglecting three-center second-nearest-neighbor interactions is difficult to justify, especially in the diamond structure, and Louie *et al.* have to correct their results for the dispersion introduced by their using a periodic cluster. They find only one A_1 resonance at -8.2 eV, which they interpret as the A_1 combination of the dangling bonds. Their Fig. 4 indicates however that there is another level introduced by the vacancy at about -1.8 eV (in a group of 25, instead of 24 for the perfect crystal). By comparison with our calculation, it seems that it is this level which must be associated with the dangling bonds.

We have looked at the localization of our two

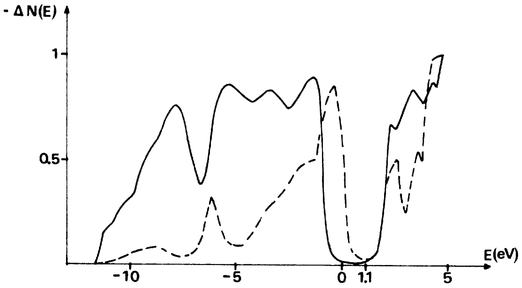

FIG. 1. A_1 and T_2 phase shifts of the vacancy in silicon $[\Delta N(E) = (1/\pi)\delta(E)]$. Solid line, A_1; dashed line, T_2.

resonant levels. Two linear combinations of A_1 symmetry can be built from the s and p atomic orbitals of the first neighbors: the symmetric combination of the p orbitals directed towards the vacancy and the symmetric combination of the s orbitals. We find that the -0.88-eV level is strongly localized on the first neighbors (~ 60% on the symmetric p combination and ~ 7% on the symmetric s) while the -7.27-eV level has only a weaker component on the symmetric s(~ 15%) and a negligible one on the symmetric p. Louie *et al.* also find that their -8.2-eV resonant level has a charge distribution mostly s like around the first neighbors but they find a high localization for this level. The low localization that we find may be due to the lack of self-consistency of our calculation but the high localization found by Louie *et al.* may as well be due to the periodic cluster method, which replaces the minimum of the density of states by a large gap in Γ.

In a preliminary analysis of the Jahn-Teller effect, we consider the same type of distortion as that of Louie *et al.* and the calculation is performed for $\delta = \pm 0.164 d_0$, using their notation. The Haydock *et al.* method for calculating the density of states is particularly useful as it does not appeal to crystal periodicity. Following Pandey and Phillips,[2] we assume an exponential variation of the two center parameter, with the same coefficient β as in Ref. 2. Our results for the dangling-bond levels, given in Table I, are very different from this of Louie *et al.* In particular, we find that the nearest neighbors must move pairwise towards each other ($\delta > 0$) in order that the nondegenerate B_2 level lie below the twofold-degenerate E level. For $\delta = +0.164 d_0$, a trial value smaller than that of Louie, (which seems large), the B_2 level falls in the valence band. We are currently performing more calculations on the relaxation problem. In particular, the distortion of the type described by Swalin is only one possible combination of symmetric and tetragonal displacements. An outward symmetric displacement (which rises the dangling-bond levels and stabilizes the back bonds) and a weaker tetragonal displacement (to account for the Jahn-Teller effect) would seem energetically more favorable.

TABLE I. Dangling-bond levels of the vacancy in silicon (in eV).

Levels	$\delta = -0.164 d_0$	$\delta = 0$	$\delta = +0.164 d_0$
A_1	-0.28	-0.88	-1.84
B_2	$+0.39$	$+0.12$	-0.21
E	$+0.28$	$+0.12$	$+0.08$

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