Electronic structure of hydrogen- and alkali-metal-vacancy complexes in silicon

Gary G. DeLeo, W. Beall Fowler, and George D. Watkins
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015
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We have applied the self-consistent-field scattered-wave $X\alpha$ cluster method to the substitutional group-I impurities (X) H, Li, Na, K, H_4, and Li_4 (T_d symmetry) in silicon using the cluster XSi_4H_{12}. We find that for the neutral alkali-metal impurities the electronic structure of the vacancy is essentially preserved except that the t_2 gap state is now occupied by the appropriate number of alkali-metal-atom valence electrons plus the normal neutral-vacancy complement of two electrons. This means that the Li_4 impurity, for example, is better described as a vacancy V^{4-} charge compensated by four Li^+ ions. Hence this suggests that alkali-metal impurities do not passivate vacancy dangling bonds. The electronic structures of the H and H_4 impurities, on the other hand, are found to be quite different from those of their alkali-metal-impurity counterparts. The single-hydrogen impurity (on-center substitutional hydrogen) is found to have vacancylike t_2 states but crystalline siliconlike a_1 states. Four hydrogen atoms in a vacancy *do* appear to passivate the vacancy dangling bonds; thus in this case the electronic structure of crystalline silicon is recovered.

The interaction of the hydrogen and alkali-metal impurities with defect dangling bonds in silicon is a subject of current interest and controversy. The importance of understanding the hydrogen-vacancy interaction is clearly suggested by simple chemical reasoning: The vacancy or other-defect dangling bonds, associated with the defect electrical activity, could be passivated by appropriately located hydrogen impurities. In fact, there is experimental evidence for the neutralization by atomic hydrogen of dangling-bond-related electrical activity in silicon.[1] This effect is clearly important in solar-cell and electronic device technology. Such chemical reasoning and observations therefore suggest the following question: Can other group-I impurities, with their characteristic single unpaired s electrons, also passivate defect-related dangling bonds in silicon?

Lithium, for example, is normally observed in silicon at the tetrahedral interstitial site, and when located there it is well understood.[2] In irradiated material, however, lithium impurities could be trapped at lattice vacancies. Therefore, one might expect to find a variety of lithium-vacancy complexes with perhaps other alkali-metal impurities exhibiting similar characteristics. Many experiments suggest the existence of alkali-metal-vacancy and other alkali-metal-defect complexes in silicon.[3] There has been, however, no clear experimental evidence for any particular alkali-metal-vacancy configuration until perhaps just recently. From luminescence versus stress studies, Canham *et al.*[4] have tentatively identified the "Q" luminescence line in silicon with a Li_4-vacancy complex which has C_{3v} symmetry. This identification has interesting implications since it suggests a model in which four lithium atoms are located in a single lattice vacancy, off-center in the [111] directions toward the near-neighbor silicons. A spontaneous asymmetric displacement could then account for the C_{3v} (as opposed to T_d) symmetry.

We proceed here to explore these questions of electrical activity and dangling-bond passivation by calculating the single-particle electronic structures of substitutional H, Li, Na, and K. We then consider the complexes consisting of four hydrogen or four lithium impurities in a single lattice vacancy, with each atom off-center in a different [111] direction (i.e., toward each of the near-neighbor silicons). Tetrahedral symmetry is preserved in all cases in these calculations.

In this treatment, we employ the self-consistent-field scattered-wave $X\alpha$ (SW$X\alpha$) cluster technique.[5,6] This method has been well documented in the literature; so we describe it here only briefly. The impurity X and its environment are simulated by a finite fragment of crystalline silicon ("cluster method") which is terminated by hydrogen atoms at normal silicon sites[7] to tie up the surface dangling bonds and to simulate the missing, more distant part of the crystal. The small substitutionally centered cluster, XSi_4H_{12}, which has been used successfully in previous defect studies,[6] is used here. The cluster $X_4Si_4H_{12}$ is employed in the corresponding H_4 and Li_4 defect calculations. The electronic structures of these molecular clusters are calculated by the self-consistent-field SW$X\alpha$ method.[5] Here, the cluster is partitioned into three regions: atomic, interatomic, and extramolecular. The potential, in the statistical exchange approximation, is spherically averaged in the atomic and extramolecular regions and volume averaged in the interatomic region (i.e., a muffin-tin approximation is made).

The electronic structure computed for the cluster Si_5H_{12}, which represents our model for crystalline silicon, is shown in Fig. 1(a). The state $1t_1$ is the last occupied state, and $3a_1$ is the first unoccupied state, representing, respectively, the top of the valence band and the bottom of the conduction band in our model system. The band gap then corresponds to the energy region between these two states. The electronic structure of the lattice vacancy is shown in Fig. 1(c) (cluster Si_4H_{12}). Here, the states labeled $2a_1$ and $3t_2$ are the defect states normally associated with the vacancy dangling bonds. These resonance ($2a_1$) and

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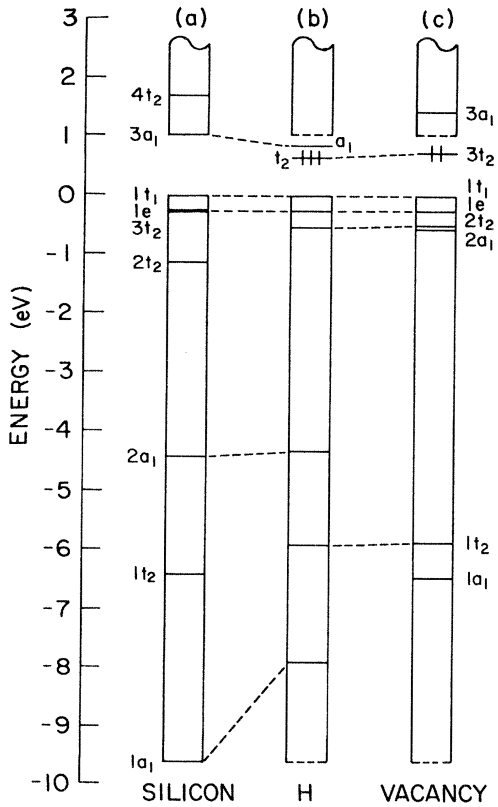

FIG. 1. Single-particle electronic structures of (a) Si_5H_{12}, (b) HSi_4H_{12} (note that $\alpha=0.978\,04$ [K. Schwarz, Phys. Rev. B 5, 2466 (1972)] is used for the hydrogen impurity, but the silicon value of 0.727 51 is used for the hydrogen terminators), and (c) Si_4H_{12}. The dashed lines demonstrate the similarity between substitutional hydrogen and vacancy t_2 states and between substitutional hydrogen and crystalline silicon a_1 states.

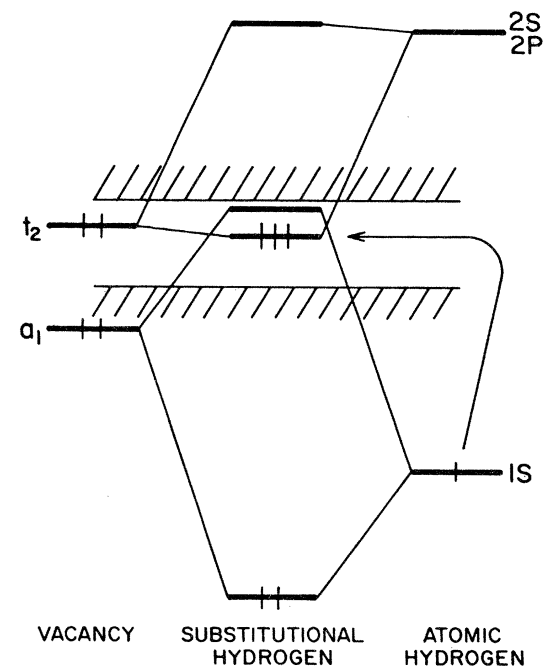

FIG. 2. Ligand-field model for the electronic structure of substitutional hydrogen in terms of the interactions between the vacancy orbitals and the atomic hydrogen orbitals.

gap ($3t_2$) states are reproduced by most modern electronic structure calculations.[6,8] The "on-center" (impurity at origin) substitutional hydrogen electronic structure is shown in Fig. 1(b). We see from the figure that the a_1 states of the hydrogen substitutional most closely resemble those of the model calculation appropriate to pure crystalline silicon [Fig. 1(a)], while the t_2 states are vacancylike [Fig. 1(c)], with the t_2 gap state now occupied by three electrons. These computational results are similar to those of Bernholc *et al.*,[9] who find a triply occupied state in the gap and only a small change in the a_1 valence-band density of states from that of silicon.

Bernholc *et al.*[9] have interpreted their computational results in terms of a model for the group-I substitutional impurities in silicon. According to their model, the group-I valence "*s*" states tend to repair the broken a_1-symmetry dangling-bond combinations associated with the lattice vacancy. Lacking a "*p*" valence electron, however, the t_2 electronic structure of the vacancy will tend to remain intact. We show in Fig. 2 the model which we propose to explain the computational results shown in Fig. 1. It appears that the atomic hydrogen 2*s* and 2*p* states play, at best, only a small role in altering the electronic structure of the lattice vacancy into which the impurity is inserted. The hydrogen 1*s* state, however, seems to interact strongly with the vacancy $2a_1$ state, pushing it up, near, or into the conduction band, as shown in the figure. This state also provides the extra electron which is accommodated by the vacancylike t_2 state in the gap. This interpretation is consistent with the Bernholc model for group-I substitutional impurities.

The electronic structures for the substitutional alkali impurities, Li, Na, and K, as shown in Fig. 3, are quite different. We find here a vacancylike t_2 state in the gap which is occupied by three electrons. This therefore is similar to the case of substitutional hydrogen as just described (Fig. 1). The a_1 states, however (with the possible exception of potassium), are also found to resemble those of the lattice vacancy. This is in contrast to the case of substitutional hydrogen, where the a_1 states are crystalline-silicon—like (Fig. 1).

For these alkali-metal-impurity systems, we propose the simple model shown in Fig. 4, in contrast to the substitutional hydrogen model of Fig. 2. The computational results suggest that here there is only a very weak interaction between the atomic valence *ns* and *np* states of the impurity and the vacancy electronic structure. These interactions are, therefore, similar to those of the vacancy dangling-bond and hydrogen 2*s* and 2*p* states. The alkali-metal core states, being considerably deeper and more compact than the hydrogen 1*s* state, also play only a small role in the alkali-metal-vacancy interaction. The extra electron in the t_2 gap state is provided by the atomic valence state which is now in the conduction band. This physical interpretation is in the spirit of Hjalmarson *et al.*;[10] hence we say that the defect state has been "pinned" at the vacancy level. If the impurity had introduced a near-band-gap "*p*" state, then we would have ex-

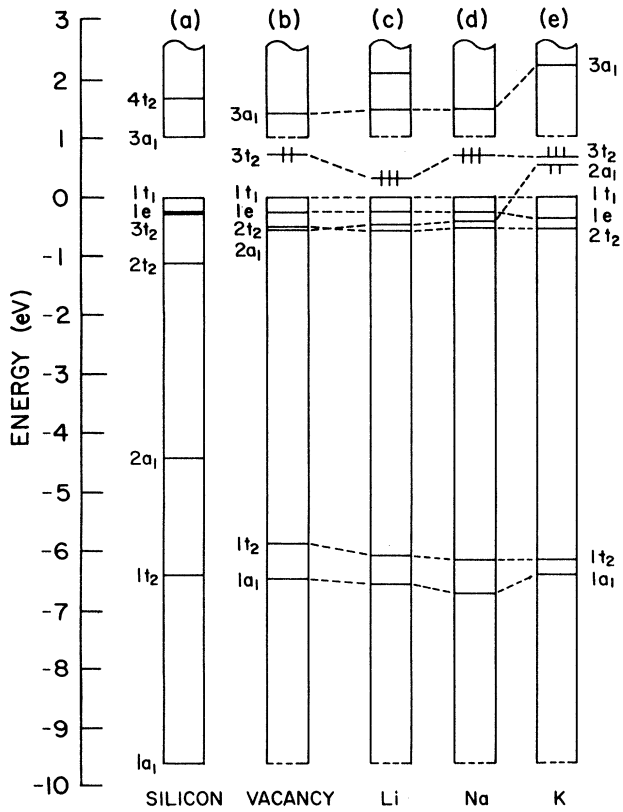

FIG. 3. Single-particle electronic structures of (a) Si_5H_{12}, (b) Si_4H_{12}, (c) $LiSi_4H_{12}$, (d) $NaSi_4H_{12}$, and (e) KSi_4H_{12}.

pected to find the gap swept clean of t_2 states as the impurity "p" and vacancy t_2 states interacted. Instead, we find that the vacancy t_2 state remains intact.

These arguments suggest an alternative description of the substitutional alkali-metal impurity. The alkali-metal-atom valence electron appears to be trapped in an orbital associated with the lattice vacancy [$3t_2$ state of Fig. 3(b)]. Therefore, this system is perhaps better described as a negative vacancy (V^-), charge compensated by a positively charged alkali-metal ion.

We now consider a tetrahedral arrangement of either four hydrogen or four lithium impurities in a single lattice vacancy. Both impurities are placed a distance of 0.65 Å from the vacancy center, which corresponds to 1.70 Å from each of the near-neighbor silicon atoms. This location allows us to use the largest possible nonoverlapping impurity muffin-tin spheres, having radius 0.53 Å. In addition, this represents a reasonable Li-Si distance since the diatomic molecules, LiN, LiO, and LiF, have interatomic distances from experiment of 1.71, 1.62, and 1.56 Å, respectively. The Li-Li separations do, however, turn out to be rather small (1.06 Å compared with 2.67 Å from experiment for Li_2), and we comment on this later. In this Li_4 calculation, the lithium cores are not frozen as in the typical cluster-SW$X\alpha$ defect calculations, but rather they are treated on an equal footing with the other valence states. This was found to be necessary as a consequence of the small lithium sphere sizes which are used.

The electronic structures for the H_4 and Li_4 systems are shown in Fig. 5. We find that the H_4 electronic structure most closely resembles that of our model for pure crystalline silicon, both for the a_1 and the t_2 states. The physical interpretation of this can be considered as an extension of the model shown in Fig. 2, where now, both a_1- and t_2-symmetry states may be constructed from the tetrahedral arrangement of the four hydrogen 1s orbitals. These a_1 and t_2 combinations appear to interact with the vacancy

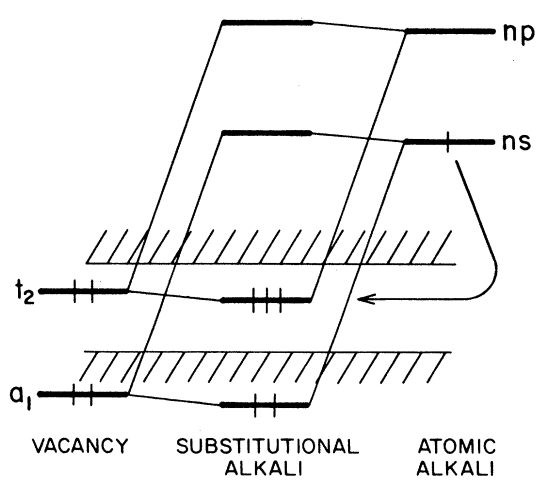

FIG. 4. Ligand-field model for the electronic structure of the substitutional alkali-metal impurities in terms of the interactions between the vacancy orbitals and the alkali-metal-atom orbitals.

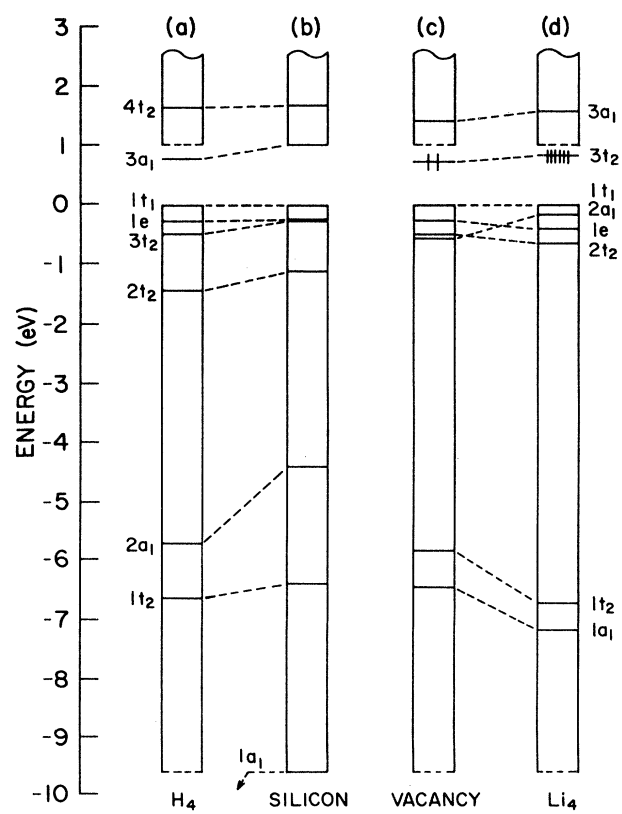

FIG. 5. Single-particle electronic structures of (a) $H_4Si_4H_{12}$, (b) Si_5H_{12}, (c) Si_4H_{12}, and (d) $Li_4Si_4H_{12}$. See Fig. 1 for description of "alpha" used for the hydrogen impurities.

a_1 and t_2 ligand states, just as would a single silicon atom located at the origin. In other words, the vacancy dangling bonds are passivated by the presence of the four hydrogen impurities. These results are consistent with those of similar calculations by Pickett[11] using the self-consistent pseudopotential method with a supercell configuration, by Economou and Papaconstantopoulos[12] using a Green's-function approach with a Koster-Slater Hamiltonian, by Singh *et al.*[13] using an extended-Hückel-theory cluster approach, and by Corbett *et al.*[14] using a modified neglect of diatomic overlap (MNDO) cluster approach.

The electronic structure for the Li_4 system is seen from the figure to be quite unlike that of the corresponding hydrogen configuration. Here, the electronic structure most closely resembles that of the lattice vacancy, just as it does for a single alkali-metal impurity located at the origin. It appears, therefore, that the vacancy electronic structure is insensitive to lithium $\langle 111 \rangle$ displacement. It also appears to be insensitive to the close proximity of the lithiums to each other, since we find no evidence of Li-Li interactions. The only significant difference between the four-lithium and single-lithium complexes [Figs. 5(d) and 3(c)] is the occupancy of the t_2 gap state, which now contains six electrons. This occupation represents the normal vacancy complement of two electrons plus the four lithium-atom valence electrons. Hence we suggest that such a system is best described as V^{4-}, charge compensated by four Li^+ ions.

These electronic structure calculations suggest that, unlike hydrogen, lithium impurities would not passivate vacancy dangling bonds. In fact, the impurity system remains electrically active as a multiple donor. The acceptor levels of the vacancy, however, are removed by the presence of the lithium impurities since the t_2 gap state is fully occupied.

Since the lithium atoms do not appear to passivate the silicon dangling bonds, it is not clear that lithium impurities would be stable in a silicon lattice vacancy. The stabilizing bonding which is present in the hydrogen system is absent for lithium. With this point in mind, we have performed preliminary total energy versus displacement calculations for these systems using the MNDO electronic structure method,[15] which provides reliable relative total energies. These calculations indicate that although the hydrogen impurities would remain in the lattice vacancy and passivate the dangling bonds, the lithium impurities (even isolated lithium impurities) would be ejected into the neighboring interstitial regions. This suggests that the Li_4 defect observed by Canham *et al.*[4] may involve a V^{4-} charge compensated by *four adjacent interstitial* Li^+ ions. These total energy results contradict the extended-Hückel-theory study by Singh *et al.*,[16] which indicates that the Li impurities could be stable in the [111] directions in the lattice vacancy. Our hydrogen-impurity results *are*, however, consistent with those of Singh *et al.*[13] and Corbett *et al.*[14] Our MNDO calculations are still tentative, and we will publish a more complete treatment at a later time.

In summary, our cluster-SW$X\alpha$ calculations indicate that the substitutional alkali-metal impurities (X and X_4) exhibit vacancylike electronic structures, and are best described as negatively charged vacancies, charge compensated by positively charged alkali-metal impurities. This is in sharp contrast to the electronic structures of the corresponding hydrogen configurations, where a single on-center hydrogen impurity restores the crystalline silicon a_1 states, and an H_4 impurity restores both the a_1 and t_2 states. These results therefore suggest that an alkali-metal impurity cannot passivate (i.e., neutralize in a direct way the electrical activity of) a silicon dangling bond.

We can apply these results not only to the vacancy, but also to studies of grain boundaries in polycrystalline silicon. Here, it has been shown experimentally that minority-carrier lifetimes and conductivity increase with the addition of lithium.[17] We would tentatively conclude from our theoretical treatment that this effect is not a consequence of direct dangling-bond passivation at the grain boundary as one might be led at first to believe. A similar argument applies to the observation of a reduced minority-carrier cross section associated with the presence of lithium in silicon which contains defect clusters.[18,19] This effect has been attributed to cluster charge neutralization by the lithium impurities.[19]

The single-particle electronic structure for the Li_4 complex suggests that the lithium atoms would not be stable in the vacancy region and perhaps would be ejected into the neighboring interstitial regions. We would then have a vacancy V^{4-} charge compensated by four adjacent interstitial Li^+ ions. The locations of the lithium atoms are of no consequence, however, since they do not alter the single-particle electronic structure even when they are located in the vacancy. We suggest that this configuration or some variation of it could be related to the lithium-vacancy complex which has been tentatively identified by Canham *et al.*[4]

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