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Identification of the hexavacancy in silicon with the B_{80}^4 optical center

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The ring hexavacancy (V_6) has been found by previous theoretical modeling to be a particularly stable defect, but it has not been identified with any observed center to date. Here, we use *ab initio* calculations to derive the structure and properties of two forms of V_6H_2 and identify these defects with the trigonal optical centers B_{41} and B_{71}^1, which are known to contain two hydrogen atoms in equivalent and inequivalent sites, respectively. It follows from the calculations that V_6 should also be optically active and we identify it with the B_{80}^4 (J line) center. This allows us to place the acceptor level of V_6 at $E_c - 0.04$ eV.

Electron paramagnetic investigation of multivacancy centers in Si have successfully identified V_1,[1] V_2,[2] V_3, V_4, and V_5.[3] The last has been correlated with the $P1$ center and is a nonplanar defect with C_{1h} symmetry. The larger vacancy centers are formed in irradiated material when subjected to a heat treatment. Thus V_5 is formed around 170 °C and is stable until ~450 °C.

Theoretical investigations have predicted that the ring hexavacancy (V_6) is a particularly stable defect.[4,5] There are several metastable configurations of V_6, but they are all at least 0.8 eV higher in energy than the ring structure.[5,6] Removing six atoms of a puckered hexagon in Si [Fig. 1(a)] leaves 12 broken bonds. However these can be rejoined in pairs, suggesting that the reconstruction can eliminate, or reduce, the electrical activity of the center. One would suppose that this defect would be formed after V_5 between 170 °C and 450 °C. It is tempting to argue that, among the various multivacancy defects, V_6 should be exceptionally numerous. Even if it is not electrically active, it should provide a trap for interstitial impurities such as transition metals,[7] oxygen, and hydrogen. Then evidence of a V_6 core could be found from an analysis of the spectra of impurity related defects. We argue here that the 1.107 eV photoluminescent (PL) center called B_{80}^4 (Ref. 8) or the J-line center,[9] arises from a reconstructed V_6 defect.

The evidence for this assignment comes from a study of the J-line defect and a family of hydrogen related PL centers with similar optical characteristics. The J-line defect is one of the most dominant luminescence systems formed in irradiated Si after a heat treatment between 300 and 500 °C (Refs. 8 and 9) (see Fig. 4). However, a number of other shallow luminescence centers have been observed in Si grown in a hydrogen atmosphere after thermal neutron irradiation and subsequent heat treatment at 400–480 °C (Ref. 8) which grow at the expense of the J-line defect, as shown in Fig. 4. These radiation-related defects have labels of the form B_{yz}^x, which specifies the exciton binding energy relative to the free exciton as $xy.z$ meV. So, for example, B_{71}^1 has an exciton binding energy of 17.1 meV, and a main PL line at 1.138 eV.

Isotopic analysis of Si samples saturated with hydrogen-deuterium mixtures have unambiguously established the direct involvement of hydrogen in the defects and have shown that they contain two or more H atoms.[10,11] High resolution spectroscopic studies involving uniaxial stress and magnetic field measurements reveal that each of the centers has a complex structure of bound exciton states arising from the interaction between a bound electron and a hole in a defect field of particular symmetry.[12,13] A detailed quantitative analysis of the optical transitions under external field perturbations has shown that, despite the apparent differences between these optical systems and their multiple transition structures, all of them have a similar origin. In each case the luminescence activity arises from a single (−/0) level in the vicinity of E_c.[14,11]

This suggests that these multihydrogen defects possess a common core. The symmetry of this core must allow the possible symmetries of the different hydrogen related centers and, in particular, B_{41} and B_{71}^1 which contain *equivalent* and *inequivalent* pairs of hydrogen atoms, respectively, arranged in trigonal symmetry. Other centers, such as B_{81}^1 and B_{18}^1 also contain two H atoms but have C_{1h} symmetry, while others like B_{80} and B_{19}^1 contain more H atoms without any symmetry.[10,11,13]

The high symmetry of B_{41} and B_{71}^1 strongly restricts possible structures of the defects, as the two equivalent hydro-

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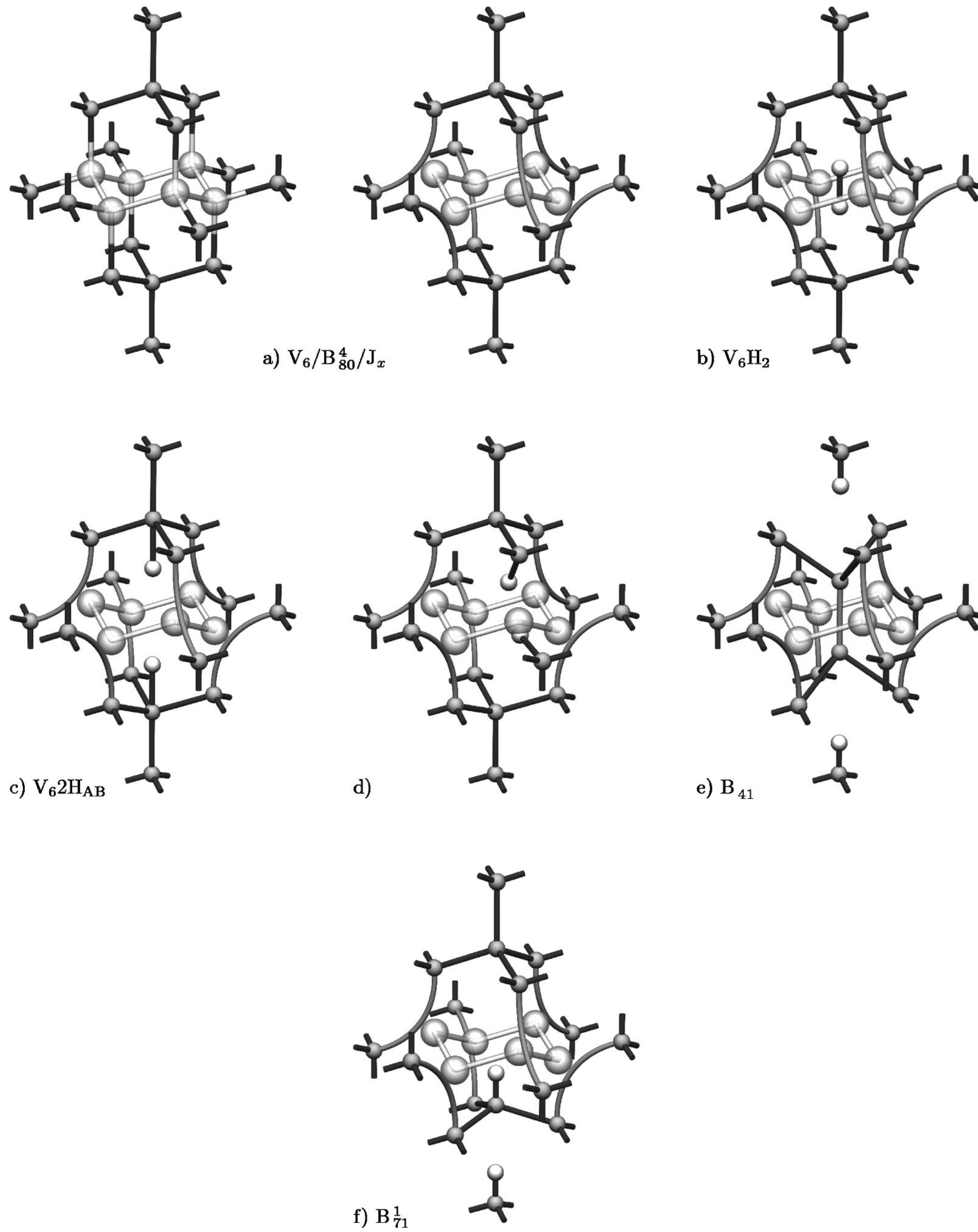

FIG. 1. Schematic diagrams of V_6 and related defects. (a) V_6 displaying the six vacancy sites, and the subsequent reconstruction caused by them. (b) V_6 plus two antibonding hydrogen atoms. (c) The structure formed by the dissociation of the H_2 molecule, which breaks one of the reconstructed bonds. (d) The proposed B_{41} structure is shown with the two equivalent hydrogen atoms that force the further reconstruction of the two axial silicon atoms across the center of the defect. (e) The second proposed B^1_{71} structure with the two inequivalent hydrogen atoms arranged as in H_2^*.

gen atoms in B_{41} must lie along a $C_3\langle 111\rangle$ axis and requires an additional C_2, S_2, or σ_h symmetry element. There are only two sites in the diamond lattice at which the center of this defect can lie. These are the bond-center and hexagonal lattice sites, which yield D_{3d} symmetry. The obvious structure, consisting of two antibonded hydrogen atoms attached to the pair of silicon atoms surrounding a bond-centered site must be discounted, since such a defect should be stable only at low temperatures.

The combined requirements of creation by irradiation and high thermal stability point towards a multi-vacancy-hydrogen complex. V_1–V_5 can be excluded either because they are not centered at these sites or do not possess trigonal symmetry. V_6 has D_{3d} symmetry, and thus the simplest candidate is a complex involving V_6 and hydrogen. As stated above, V_6 is expected to form in irradiated material which is heated between ~ 200 °C and 450 °C. If the material contains hydrogen molecules these will readily react with V_6 to form dimer structures. This has prompted investigations, using a first principles local density functional cluster method, into the structure of V_6 complexed with hydrogen.

The defects considered were each constructed in a $Si_{154}H_{108}$ cluster centered on the hexagonal site. The size of the cluster meant that there is at least two layers of Si-Si bonds separating the terminating H atoms and the H atoms in the defect.

The wave-function basis consisted of independent *s* and *p* Gaussian orbitals, with either four different exponents sited at each Si atom, or three at the H atoms of the dimers. A fixed linear combination of two Gaussian orbitals was sited

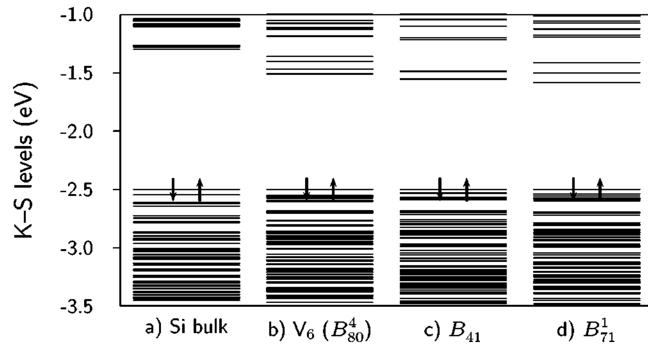

FIG. 2. The Kohn-Sham energy levels for clusters used in this work. (a) The $Si_{154}H_{108}$ ideal Si fragment, (b) cluster with reconstructed V_6, (c) and (d) clusters containing V_6H_2 as shown in Fig. 1. The arrows denote highest occupied levels. The levels are scaled by a factor of 0.53 to give a 1.2 eV band gap for (a). The other figures (b), (c) and (d) then demonstrate that the defects give only shallow unoccupied defect levels.

on the H atoms which terminated the cluster. In addition, the basis at each Si-Si bond and the Si-H bonds in the defects were augmented by placing two Gaussian functions of different widths at the center of each bond. The charge density was fitted with five independent Gaussian functions with different widths on each Si atom, and four (three) on the central (terminating) H atoms. Two extra Gaussian functions were placed at each bond center. All atoms, including the terminators, were allowed to relax by a conjugate gradient method. Full details of the method can be found in Ref. 15.

We firstly simulate V_6 itself by removing the six atoms nearest to the hexagonal site. The resulting structure possesses D_{3d} symmetry and strongly reconstructs on relaxation to form six new bonds of length 2.63 Å between the 12 dangling bonds, as shown in Fig. 1(a). The length of the two nearest Si-Si bonds along the trigonal axis is then 2.53 Å, demonstrating that tensile strain resides in this direction. The resulting electronic Kohn-Sham (KS) levels display a well defined band gap, which is consistent with previous calculations.[6] This defect possibly possesses states in the gap very near the conduction band (Fig. 2), but it is difficult to decide whether such near-conduction levels are localized on the defect in cluster calculations. The character of the deepest of these shallow states is a_{1g} (Fig. 3), this state is antibonding to both the six reconstructed bonds and the two nearby axial bonds in the defect.

We now investigate V_6H_2. There are several potential structures for B_{41} based on V_6 and one possible model would be a hydrogen molecule aligned along [111] and sited at the center of inversion of the defect. Alternately the H-H bond could be broken and the atoms placed at antibonding sites to the axial Si-Si bonds as in Fig. 1(b). A third possibility is that the hydrogen atoms are near the bond-centered sites within the axial Si-Si bonds. The second, antibonded structure is unstable and spontaneously relaxes back to the [111] aligned molecule structure, however we calculate that the molecule itself is only metastable at the defect's center of inversion, and will dissociate with a barrier of less than 0.23 eV. It does this by breaking one of the reconstructed Si-Si bonds shown in Fig. 1(a), to form two Si-H bonds, giving rise to a structure which is 1.76 eV lower in energy and of C_{1h} symmetry, as shown in Fig. 1(c). The third, bond-centered, structure causes a further reconstruction of V_6, by breaking the two axial Si-Si bonds and forming Si-H bonds.

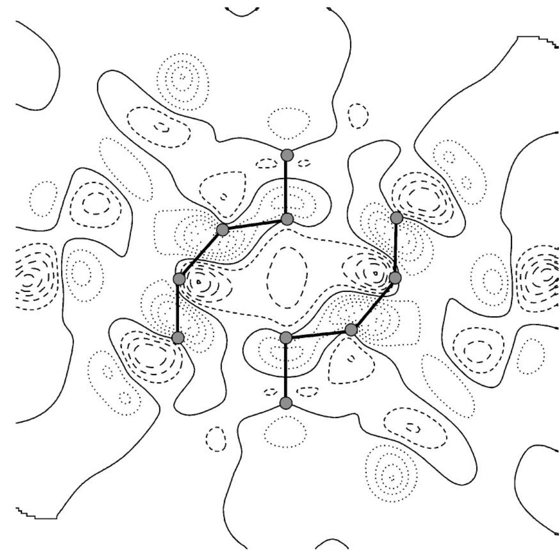

FIG. 3. Contour plot of the a_{1g} pseudowavefunction corresponding to the lowest unoccupied state of V_6, shown in one of the six equivalent mirror planes containing the three-fold axis of the defect shown in Fig. 1(a). The nodal surface is marked with a solid line, and shows that the state is antibonding between both the atoms in the six central reconstructed bonds, and also the two nearby axial Si-Si bonds. The silicon atoms at the center of the defect, which lie on this plane are marked with gray circles.

The two dangling Si bonds thus formed pair together in the middle of the defect, leaving the structure with D_{3d} symmetry shown in Fig. 1(d). This new bond is then 2.42 Å, and the six reconstructed bonds relax to a length of 2.58 Å—a lowering of 0.02 Å. The reconstruction is energetically very favorable, being 0.80 eV lower in energy than the C_{1h} structure in Fig. 1(c). Thus the most stable structure has D_{3d} symmetry.

The KS levels of this defect again show evidence for a very shallow $(-/0)$ level, of symmetry a_{1g}. There are two high-frequency modes related to the hydrogen in this structure of symmetries A_{1g} and A_{2u} (which is infrared active), which we find to lie at 2033 and 2021 cm^{-1}, respectively. It is clear that this structure possesses properties entirely consistent with B_{41}, although electrical field and stress alignment studies are necessary to verify this assignment.

We now consider potential structures for B_{71}^1. Again this structure requires a C_3 axis, but due to the inequivalent hydrogen atoms the symmetry of the defect must be of lower order, i.e., C_{3v}. If it is assumed that dangling silicon bonds

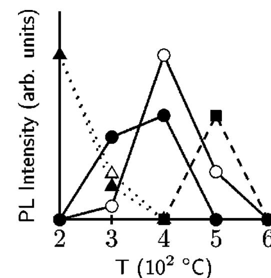

FIG. 4. Thermal stability of the $B_{80}^4(J)$ center (circles), the B_{71}^1 centers (squares), and the W center (triangles). The behavior of the centers is shown in non-hydrogenated (open symbols) and hydrogenated (filled symbols) silicon. Note that the W center is unaffected by hydrogen. The samples used were high resistivity (~ 1000 Ω cm) FZ Si with [C] $\sim 10^{17}$ cm^{-3} and [O]$< 10^{16}$ cm^{-3}.

are energetically unfeasible, there is an obvious structure which can be derived from the bond-centered model for B_{41}. This defect consists of one hydrogen atom lying at a bond-centered site, and the other atom directly passivating the silicon atom which is displaced by the bond-centered H. There are two locations on either side of the silicon atom at which the hydrogen might be positioned. If the hydrogen were placed on the side nearest the other H atom, this would bring the two atoms into close proximity and thus raise the energy of the defect; this suggests that the hydrogen is sited on the opposite side of the silicon atom, as shown in Fig. 1(e). The relative energies of these defects are 0.13 eV in favor of the structure with the hydrogen atoms on opposite sides of the silicon. The more stable structure, which is reminiscent of H_2^*,[16] is 0.09 eV higher in energy than the the C_{1h} defect formed by the dissociation a hydrogen molecule inside V_6. The KS levels again show evidence of a near conduction-band a_1 state localized on the defect in both cases. Both of these models possess two high-frequency A_1 vibrational modes, lying at 2149 and 2029 cm^{-1} for the structure with the two H atoms lying close together, or 2051 and 2010 cm^{-1} for the hydrogen on opposite sides of the silicon.

It is also clear that other, stable centers containing more H atoms could arise by inserting H pairs into the reconstructed bonds, as well as along the trigonal axis.

These investigations then favor V_6 to be a precursor for the family of H-related optical centers. It is clear that an unreconstructed V_6 defect has deep levels arising from the dangling bonds but these are pushed to the band edges on reconstruction. A greater degree of reconstruction results in increasingly shallow levels. As the effect of hydrogen is to reduce the strain in the defect, we expect the acceptor $(-/0)$ level of V_6 to be deeper than that of V_6H_2. The KS levels also suggest that V_6 itself should be optically active.

In nonhydrogenated Si, the B_{80}^4 center (J line) is observed after irradiation and subsequent heat treatment between 300–500 °C (Ref. 9) as shown in Fig. 4. Zeeman splitting studies have also shown that B_{80}^4 possesses trigonal symmetry.[9] However, in hydrogenated Si, the J-line intensity declines at a much lower temperature ~450° C, which coincides with the appearance of the hydrogenated related B centers. Figure 4 shows the variation in the J-line intensity and the intensity of B_{71}^1 in nonhydrogenated and hydrogenated Si respectively, after a 30 min isochronal anneal at different temperatures.[14] As one can see, there is an anticorrelation between B_{71}^1 and the B_{80}^4 centers with B_{71}^1 created at temperatures when the B_{80}^4 centers are disappearing. The figure also shows that B_{71}^1 is not related to the 1.018 eV $W(I_1)$ center, which is also known to be trigonal.[9,17]

The identification of B_{80}^4 with a vacancy aggregate is consistent with the strong preference for the defect to align under [111] stress during formation.[18] This is directly analogous with V_2, where stress alignment studies show that $V_2^{\pm}$ favors an orientation where the reconstructed bonds are parallel to the stress axis.[2] Uniaxial stress along the trigonal axis leads to a reduction in the exciton binding energy consistent with the idea that antibonding orbitals on the dilated reconstructed bonds are the origin of the gap acceptor level. Recent Zeeman and uniaxial studies demonstrate that the exciton consists of an electron in a deep $(-/0)$ level near E_c with a loosely bound hole in a similar way to B_{41}.[19] Thus this defect shares the properties expected for V_6 and we identify it with this center. However, in the absence of experiments performed in an electric field, the question of whether B_{80}^4 has a center of inversion has yet to be resolved.

The dependence of the intensity of the PL due to B_{80}^4 demonstrates that the exciton is thermally bound with an energy of 18 meV (Ref. 8) and this can be taken to be the ionization energy of the hole. The exciton binding energy relative to a free electron and hole is the sum of 48.0 meV and the free exciton binding energy of 14.3 meV. From these results, we place the $(-/0)$ level of V_6 at $E_c-44.3$ meV.

In conclusion, we have shown that complexes between V_6 and hydrogen have properties consistent with those of the photoluminescent B_{41} and B_{71}^1 centers formed in irradiated silicon. We also suggest the the B_{80}^4 (J-line) defect is the hydrogen-free hexavacancy and represents the largest electrically active vacancy complex found so far.

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