INTERACTION OF HYDROGEN WITH SECONDARY RADIATION DEFECTS

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ABSTRACT

The interaction of hydrogen with native defects formed in silicon by aggregation of primary radiation defects are studied using local density functional theory. The properties of both the V_6 "magic number" aggregate and its complexes with hydrogen are simulated and compared with the observed defects AA17 and the *B* centres.

Theoretical investigations have predicted that the ring hexavacancy (V_6) is a particularly stable defect [1, 2]. Removing six atoms of a puckered hexagon in Si 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 [3] between 170°C and 450°C. It is tempting to argue that, among the various multi-vacancy defects, V_6 should be exceptionally numerous. Even if it is not electrically active, it should provide a trap for interstitial impurities. Evidence of a V_6 core could then 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^4_{80} [4] or the *J*-line center [5], 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 [4, 5]. The formation of the *J* lines correspond to the loss of the divacancy [6]. 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 [4] which grow at the expense of the *J*-line defect [6, 7]. Loss of VH_4 in hydrogenated material has also been related to the growth of these hydrogen-containing *B* centres [6].

Isotopic analysis of Si samples saturated with hydrogen-deuterium mixtures have unambiguously established the direct involvement of hydrogen in these defects and have shown that they contain two or more H atoms [8, 9]. 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 [9, 10].

This suggests that these multi-hydrogen defects possess a common core. The symmetry of this core must allow the possible symmetries of the different hydrogen related centers and in particular the B_{41} centre which contains two *equivalent* hydrogen atoms, arranged with either D_{3d}, S_6 or D_3 symmetry. Such high symmetry strongly restricts possible structures of the defects. 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 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. If the material contains hydrogen molecules these will readily react with V_6 to form dimer structures.

There has been a recent observation of a trigonal hydrogen related $S = 1$ EPR centre, AA17 [11, 12], in silicon after white-light illumination of material which has been proton implanted. The two spins of this centre are mainly localised on two silicon atoms separated by ∼12 Å along the trigonal axis. It has been suggested that this defect is an excited form of V_6H_2. AA17 is thought to possess D_{3d} symmetry, and is correlated to two vibrational modes at 2070 and 2096 cm^{-1} [13]. It is perhaps strange that a structure with two hydrogen atoms and D_{3d} symmetry should display a pair of vibrational modes, since the stretch modes should form symmetric and antisymmetric combinations with only one of these, the *ungerade* combination, being IR active.

This has prompted investigations, using a first principles local density functional cluster method (AIMPRO), into the structure of V_6 complexed with hydrogen [14, 15].

The defects considered were each constructed in a $Si_{154}H_{108}$ cluster centered on the hexagonal site. The wave-function basis consisted of independent s and p Gaussian orbitals, with either four of three different exponents sited at each Si or H atom in the defect. A fixed linear combination of two Gaussian orbitals was sited on the H atoms which terminated surface of the cluster. In addition, the basis at each Si–Si bond and the Si–H bonds in the defects was augmented by placing two Gaussian functions of different widths at the center of the 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. [16].

We firstly simulate V_6 in its $S = 0$ state 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 twelve dangling bonds. 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 [17]. This defect possibly possesses states in the gap very near the conduction band, 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}, this state is anti-bonding to both the six reconstructed bonds and the two nearby axial bonds in the defect.

Models for the B_{41} centre based on V_6H_2 are now reported (other hydrogen related B-centres are discussed in Refs. [14, 15]). There are several potential structures, 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 anti-bonding sites to the axial Si–Si bonds. A third possibility is that the hydrogen atoms are near the bond-centered sites within the axial Si–Si bonds. The second, anti-bonded 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, to form two Si–H bonds, giving rise to a structure which is 1.76 eV lower in energy and of C_{1h} symmetry. 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. The two dangling Si bonds thus formed pair together in the middle of the defect, leaving the structure with D_{3d} symmetry. 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. 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.

These investigations then suggest that V_6 is a structural core of this 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.

The $S = 1$ excited forms of neutral V_6H_2 have also been investigated. Structures have been relaxed in the high-spin state after placing the two hydrogen atoms either within the axial Si–Si bonds of V_6, or anti-bonding inside the V_6 cavity itself. The structure with the hydrogen atoms placed within the axial Si–Si bonds relaxes in the same manner as the model presented for B_{41}, but with a slight Jahn-Teller distortion towards C_{3v} symmetry, leading to a reconstructed Si–Si bond in the centre of the defect and two axial Si–H bonds, with all of the atoms in the defect fully coordinated. This resulting structure is 1.57 eV higher in energy than B_{41}. The second form of the defect, with the two hydrogen atoms within the V_6 core, strongly Jahn-Teller distorts to C_{3v} symmetry, leading to the breaking of *one* of the axial Si–Si bonds and a resulting energy of 3.65 eV above B_{41}. Hence both models have properties inconsistent with AA17.

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 [19]. Uniaxial stress along the trigonal axis leads to a reduction in the exciton binding energy consistent with the idea that anti-bonding 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 a electron in a deep $(-/0)$ level near E_c with a loosely bound hole in a similar way to B_{41} [7]. 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^4_{80} has a center of inversion, as this model suggests, has yet to be resolved.

The dependence of the intensity of the PL due to B^4_{80} demonstrates that the exciton is thermally bound with an energy of 18 meV [4] 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.

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[1] D. J. Chadi and K. J. Chang, Phys. Rev. B **38**, 1523 (1988).

[2] S. K. Estreicher, J. L. Hastings, and P. A. Fedders, Appl. Phys. Lett. **70**, 432 (1997).

[3] Y. H. Lee and J. W. Corbett, Phys. Rev. B **9**, 4351 (1974).

[4] A. S. Kaminskii, B. M. Leiferov, and A. N. Safonov, Sov. Phys. Solid State **29**, 551 (1987).

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

[6] E. V. Lavrov, private comunication, 1999.

[7] A. N. Safonov, (unpublished).

[8] A. N. Safonov and E. C. Lightowlers, Mater. Sci. Eng. B **36**, 251 (1996).

[9] A. N. Safonov and E. C. Lightowlers, Mater. Sci. Eng. B **58**, 39 (1999).

[10] A. N. Safonov, E. C. Lightowlers, and G. Davies, Phys. Rev. B **56**, 15517 (1997).

[11] Y. V. Gorelkinskii, K. A. Abdullin, and B. N. Mukashev, Physica B **273–274**, 171 (1999).

[12] Y. V. Gorelkinskii, K. A. Abdullin, and B. N. Mukashev, Mater. Sci. Eng. B **71**, 249 (2000).

[13] S. Z. Tokmoldin, B. N. Mukashev, K. A. Abdullin, and Y. V. Gorelkinskii, Physica B **273–274**, 204 (1999).

[14] B. Hourahine *et al.*, Physica B **273–274**, 176 (1999).

[15] B. Hourahine *et al.*, to appear in *Phys. Rev. B* **61**, no. 19 (unpublished).

[16] R. Jones and P. R. Briddon, in *Identification of Defects in Semiconductors*, Vol. 51A of *Semiconductors and Semimetals*, edited by M. Stavola (Academic Press, Boston, 1998), Chap. 6.

[17] J. L. Hastings, S. K. Estreicher, and P. A. Fedders, Phys. Rev. B **56**, 10215 (1997).

[18] A. S. Kaminskii and E. V. Lavrov, Solid State Commun. **106**, 751 (1998).

[19] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).