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1992 J. Phys.: Condens. Matter 4 1459

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## Theory of Li- and Br-saturated vacancies in radiation damaged silicon

Eugen Tarnow

Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA

Received 26 September 1991

**Abstract.** The atomic configuration, electronic states and a local vibrational mode of the Li-saturated vacancy in Si are determined using *ab initio* calculations. We find, in agreement with an earlier theoretical suggestion, that this defect consists of a tetrahedral combination of a negatively charged vacancy and four positively charged Li interstitials. A  $C_{3v}$  configuration is found to be higher in energy. This confirms recent experimental suggestions that a symmetry lowering, which is found in the luminescence spectrum, is due to excitonic effects. The geometric simplicity of this defect complex suggests that it may be universal for irradiated Si doped with column I and (from chemical symmetry) column VII elements. As an example of the latter we consider the structure of the Br-saturated vacancy.

Li has two interesting properties as an impurity in Si. Firstly, the presence of Li can increase the stability against radiation damage of c-Si solar cells [1]. Secondly, it diffuses in as a positively charged interstitial and exactly compensates donors in Si [2]. A Li-related defect in Si that has both of those properties is the ‘Li-saturated vacancy’ (LiSV). Firstly, one finds experimentally that it can heal Si vacancies resulting from irradiation and transform them into electrically neutral centres. In this paper we will identify the corresponding relaxed microscopic geometry and confirm that the LiSV is, secondly, a Li-compensated donor, where the donor is the Si vacancy with a charge of  $-4$ .

Much of the experimental knowledge about the LiSV comes from studies of the luminescence lines of the corresponding excited state. The first near-bandgap luminescence line reported was the Q line [3]. The line occurred when Li was diffused into Si and the crystal subsequently subjected to room temperature radiation damage [4]. It was thought that the radiation damage would create Si vacancies, and that the Li atoms would then come and heal it by capping the dangling bonds [5]. This capping of dangling bonds is known to occur for H [6] and may occur also for F impurities [7]. Measurements of the photoluminescence for different isotope concentrations, indeed established the presence of four Li atoms [8].

However, it turned out that perturbative effects on the luminescence lines from uniaxial stress show that the point group of the centre is not tetrahedral but trigonal ( $C_{3v}$ ,  $D_{3d}$ ) [9]. Furthermore, the isotope studies also established that one of the Li atoms is in a unique position [5, 8].

Properties of reorientation, and the presence of forbidden crossings in luminescence under uniaxial perturbation [9], implied to Davis ‘that the trigonal symmetry

arises from the centre being slightly perturbed from a tetrahedral complex' [4]. The perturbation has been considered to be due to dynamical effects of the different Li isotopes involved [10] or a spontaneous symmetry breaking [11]. Jahn–Teller effects were excluded due to the absence of a Ham effect and because the excited states resulting in the luminescence were found to consist of 'only slightly perturbed valence and conduction band extrema' [9]. Recently, Davies argued that the symmetry breaking can be understood as an excitonic effect, in which the conduction band minima are mixed in such a way so as to obtain a trigonally symmetric state [4].

The electronic structure of the defect has been considered by both experiment and theory. From the experimental side it was found that the defect was neutral [5, 8, 10]. Furthermore, Zeeman data suggests that the neutral centre is donor-like (there are two types of isoelectronic centres—donor-like and acceptor-like, depending upon whether the hole, or electron, respectively, is the more tightly bound particle of the corresponding exciton) [10].

From the theoretical side, the electronic structure of one unrelaxed geometry of the LISV has been calculated using the self-consistent field scattered-wave  $X\alpha$  (SWX $\alpha$ ) cluster technique [11]. Each of the Li atoms was placed inside the vacancy, 0.65 Å off-centre in a different direction, while at the same time preserving the tetrahedral symmetry. The authors found that the electronic structure closely resembled that of the vacancy, and extrapolated it so that it should be insensitive to the exact distance of the Li atoms away from the vacancy centre. This implied that 'unlike hydrogen, lithium would not passivate vacancy dangling bonds'. The authors further cautioned that the configuration considered might not be stable. Semi-empirical MNDO calculations indicated that Li atoms (one or four of them) would never enter the vacancy but 'be ejected into the neighbouring interstitial regions'. They suggested that the LISV might consist of four adjacent interstitial Li<sup>+</sup> ions. 'The location 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', the authors concluded, and accordingly the proposed structures of the LISV would not passivate the vacancy.

The electronic structure of a single substitutional Li atom has been considered before [11]. It was found that the  $3t_2$  states are partially occupied and lie about 0.3 eV above the valence band maximum.

The purpose of the present paper is threefold. Firstly, we will show that *ab initio* calculations on the LISV indeed give a  $T_D$  symmetric configuration in which the Li atoms are *outside* the vacancy, in agreement with the MNDO calculations. Secondly, we are able to exclude a configuration not previously considered, in which one Li atom is substitutional and three Li atoms are interstitial. This configuration would be analogous to Be pair configurations found in Si, in which one of the Be atoms is substitutional while the second Be atom is interstitial [12], and it would also have the  $C_{3v}$  symmetry seen in experiment. The electronic states are considered and a local vibrational mode is calculated. Finally, the work is extended to column VII elements, which, by chemical symmetry, should behave similarly to column I elements.

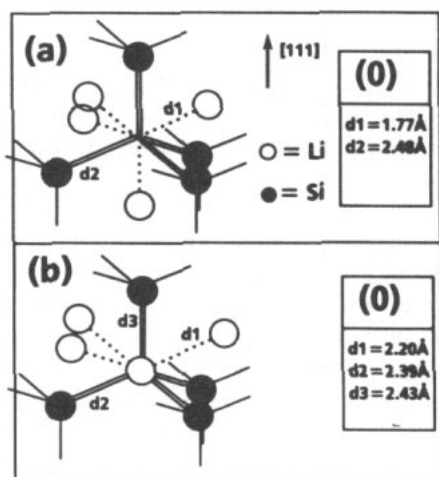
The calculational details of the present work were as follows. The computations were performed within the framework of density-functional theory using the local-density approximation combined with pseudopotentials and the supercell method [13]. A relativistic pseudopotential was used for Br, while Li was represented by a pseudopotential with a non-linear core correction [14]. A 32 atom supercell was used with one special  $k$  point of  $(1/4, 1/4, 1/4)$ . All Si and Br atoms in the supercell were allowed

to relax according to their forces. The forces on the Li atoms were not calculated, due to the complication of the core correction. Instead, they were relaxed by finding the minimum of the total energy curve for different configurational coordinates. In the  $C_{3v}$  geometries, the central Li and Br atoms were frozen at the substitutional site. A plane wave cutoff of 7 Ryd was used.

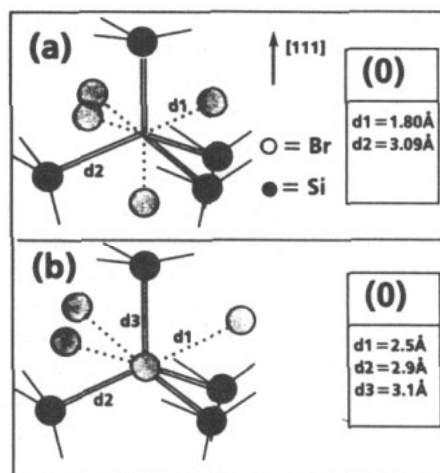
**Table 1.** Calculated total energies of different candidates for the Li-saturated vacancy in Si. The zero of energy is taken to be the  $T_D$  configuration.

Configuration	Four capping Li atoms	Four interstitial Li atoms	One substitutional and three interstitial Li atoms
Energy (eV)	9	0	0.7

Table 1 shows the energies calculated for three different types of LiSV configurations measured with respect to the lowest energy complex. As we see, the configuration consisting of four capping Li atoms is at 9 eV. Our proposed geometry of one substitutional and three interstitial Li atoms is seen to be at about 0.7 eV, and may not be stable towards decay to the lowest energy configuration—the configuration consisting of four Li atoms in nearest interstitial positions.



**Figure 1.** Geometries considered for the configurations of the Li-saturated vacancy. The filled circles represent Si atoms, and the open circles represent Li atoms. (a)  $T_D$  configuration; (b)  $C_{3v}$  configuration.



**Figure 2.** Geometries considered for the configurations of the Br-saturated vacancy. The filled circles represent Si atoms, and the open circles represent Li atoms. (a)  $T_D$  configuration; (b)  $C_{3v}$  configuration.

Let us compare the two lowest-energy geometries (figure 1). The equilibrium distance of the Li atoms from the centre of the vacancy (calculated for the  $T_D$  symmetric configuration Li atoms) is  $1.77 \text{ \AA}$ . As we go to the  $C_{3v}$  configuration (figure 1(b)), the Li atoms are  $0.43 \text{ \AA}$  further out. The surrounding Si atoms in either geometry relax only slightly away from their bulk positions (relaxations of the

interstitial Li atoms away from the  $\langle 111 \rangle$  directions were found to be small, yielding an energy gain of only about 0.1 eV).

In the  $T_D$  configuration of the LiSV we find that there is a triply degenerate state at the top of the valence band reminiscent of the  $t_2$  vacancy states, and each of the states is about 40% localized on the four Si atoms surrounding the vacancy. It is about  $0.11 \pm 0.02$  eV above the top of the valence band (where the error bar comes from the difference in estimates from 1 to 2 special  $k$ -point calculations). Note that the finite size of the supercell increases the energy of the defect states, and our estimates are accordingly upper bounds. Thus our result is not inconsistent with a passivation of the vacancy gap states. There is no localized state near the bottom of the conduction band. For the  $C_{3v}$  configuration, the triply degenerate vacancy state is about 0.1 eV lower in energy.

The local breathing mode associated with the four Li atoms was considered. We assumed that the Si lattice would stay fixed (which is a good approximation according to experiment: they find an isotope-dependent energy separation of 1.058, close to the ideal 1.08 [8] which would occur for a completely decoupled Li mode). We found a frequency of 47 meV for a complex with four Li atoms which compares favourably with 50.7 meV from experiment [4] (the line was identified as a breathing mode in [5]).

There should be metastable states associated with the LiSV: one or more of the interstitial Li atoms could move from the  $\langle 111 \rangle$  first nearest-neighbour interstitial site to the  $\langle 100 \rangle$  second nearest-neighbour interstitial site. This is known to occur for  $Al_i-Fe_i$  pairs in Si [15–17] and has been proposed for the  $Be_s-Be_i$  system in Si as well [12]. From the Coulomb interaction alone one can estimate an energy cost for moving a single Li atom to the  $\langle 100 \rangle$  interstitial configuration of 0.25 eV (modelling the system with a single negative charge at the centre of the defect, and assuming that the Li interstitial moves from the relaxed LiSV position to the perfect second nearest-neighbour interstitial site).

Our result supports the possibility that the lowest energy state of the Li saturated vacancy is of  $T_D$  symmetry. The discrepancy between the theoretically predicted tetrahedrally symmetric ground state and the experimentally predicted axial symmetry in the excited state should therefore be due to the difference between the ground and excited states. This is in agreement with the work of Davies [4]. It is possible that the discrepancy with the isotope splitting of the zero-phonon line, indicating a trigonal symmetry, could have an alternate explanation: the symmetry breaking might result from *symmetry of the vibrational mode* responsible for the isotope splitting, and not the symmetry of the defect itself.

Other column I elements may behave similar to Li [18], the only difference being in the size of the atoms, which may expand the lattice around the vacancy further. Recently, there are also reports of column IB elements (for example Cu) passivating vacancies [19]. Once we have considered the column IA and IB elements that are three steps to the left of Si in the periodic table, it is natural to consider atoms three steps to the right, i.e. column VIIA and VIIB elements. We already know that there may be a symmetric situation for H and F atoms [6, 7, 20]. In this work we chose to study Br as a representative of column VII elements [20].

We performed two calculations on the Br-saturated vacancy (BrSV), determining the energy difference between the  $C_{3v}$  and the  $T_D$  symmetry configurations analogous to the Li configurations considered (see figure 2). We found, again that the lowest energy geometry was the  $T_D$  configuration. Surprisingly, however, it was lower by

**Table 2.** Calculated total energies of different candidates for the Br-saturated vacancy in Si. The zero of energy is taken to be the  $T_D$  configuration.

Configuration	Four interstitial Br atoms	One substitutional and three interstitial Br atoms
Energy (eV)	0	8

8 eV (see table 2)! This is to be compared with the much smaller energy difference of 0.7 eV for the  $Li_{SV}$ . The energy difference here is too large to be of Coulomb origin in the screened Si environment, but rather must come from either bonding or stress effects. To investigate which of the two effects dominates, the charge density was examined. Although there were overlaps between the charge of Br and Br atoms and the charge of Br and Si atoms, no clear bond charge was found. Indeed, the Br-Br distance is about 2.94 Å, which is large compared to the Br-Br covalent bond length of 2.28 Å. Furthermore, the relative geometries of the Si and Br atoms prohibit the formation of strong Si-Br bonds.

We then examined the stress effects. The Br ions are large, and may prefer to stay as close to the open vacancy as possible. This behaviour is possible only in the  $T_D$  configuration. To study this stress effect we calculated the energy of the Si lattice of the two configurations with the Br ions removed, and the energy of the Br configurations with the Si atoms removed. We found that the energy difference for the Si lattice, in the +4 (+2) charge state, was about 1.7 eV (1.5 eV). For the Br configuration, having compensated for the difference in Coulomb interaction using a model of four point charges, we found a large stress effect of about 8 eV. This is consistent with the Br-Br distance being significantly smaller than the van der Waals distance of 3.9 Å.

Thus we see that the  $T_D$  configuration is strongly favoured when the passivating atomic species becomes large and stress effects become important. While we expected the  $Li_{SV}$  to have several low-energy metastable states, we would not expect this to occur for the  $Br_{SV}$ . Another speculation that results is that the Si vacancy in general might have an affinity for large atoms.

The  $Br_{SV}$  electronic states in the supercell were sufficiently different from Si bulk that we did not attempt to identify the top of the valence band or the bottom of the conduction band. The highest filled state was not significantly localized either on the Br atoms or the four Si atoms nearest to the vacancy. The lowest unfilled state was very roughly 40% localized on the Br atoms and had equal amounts of s and p character, each directed along a line from the Br atom to the vacancy.

Finally, we may speculate on the passivation of vacancies by F and H atoms in diamond. The ratio of the Si-H bond (of  $SiH_4$ ) to the crystalline Si-Si distance is 0.63, while the ratio of the C-H (of  $CH_4$ ) bond to the C-C distance is somewhat larger, 0.71. For F, the ratio of the C-F bond (of  $CF_4$ ) to the C-C distance is even larger, 0.86. Thus H and especially F are less likely to go inside the vacancy in C than in Si.

### Acknowledgments

Discussions with Dr Robert Street and Dr John Northrup are acknowledged, as is a critical reading of the manuscript by Dr John Northrup. This work was supported by

the Office of Naval Research through contract no N00014-82-C-0244.

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