

The formation, dissociation and electrical activity of divacancy-oxygen complexes in Si

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Abstract

Density functional calculations are carried out on divacancy-oxygen (V_2O and V_2O_2) complexes in silicon, paying particular attention to their formation and dissociation mechanisms as well as their electrical activity. The formation of V_2O around 220°C is controlled by the diffusion of V_2 to immobile oxygen traps, while it dissociates around 300°C into VO and V. V_2O and V_2O_2 are found to possess deep single and double acceptor levels as well as deep donor levels similar to those of V_2 .

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1. Introduction

Unlike single vacancies, the divacancy (V_2) in Si is a highly stable radiation-induced defect, and anneals out at $\sim 220^\circ\text{C}$ when it starts to diffuse with a migration barrier of ~ 1.3 eV [1]. This complex can appear in four charge states (+, 0, – and =), and deep-level transient spectroscopy (DLTS) measurements established a (0/+) state at $E_v + 0.20$ eV [2] and (–/0) and (= /–) acceptor levels at 0.42 and 0.23 eV below the conduction band bottom [3], respectively. Despite

a large effort to understand the properties of V_2 , several unanswered questions remain. Among these are its products formed after annealing and the asymmetry between the DLTS (–/0) and (= /–) peak intensities under heavy ion bombardment [3].

V_2^+ and V_2^- are paramagnetic, and from electron paramagnetic resonance (EPR) measurements, Watkins and Corbett [1] arrived at the atomic and electronic models depicted on the left-hand side of Fig. 1. Positively and negatively charged defects have b_u^\uparrow and $b_u^\uparrow a_g^\uparrow$ occupancy, giving rise to large hyperfine signal shoulders from ^{29}Si atoms on the symmetry plane. The anti-bonding a_u and b_g states are localized on $\text{Si}_a\text{--Si}_d$ and $\text{Si}_{a'}\text{--Si}_{d'}$ pairs.

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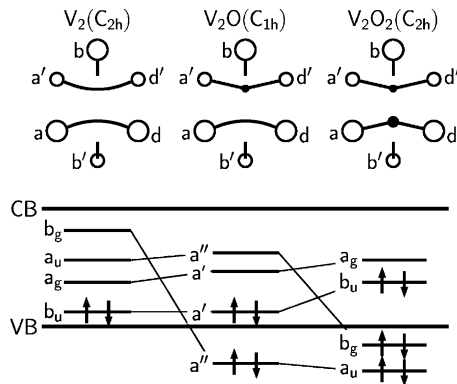


Fig. 1. Atomic structure of V_2O and V_2O_2 viewed along a $\langle 111 \rangle$ direction, and their one-electron states at Γ compared with the divacancy (see Ref. [1]). Si and O are represented as white and black circles, respectively.

Interstitial oxygen (O_i) is an effective trap for vacancies in Czochralski-grown silicon (Cz-Si). It seems therefore logical to hypothesize O_i as the main sink for mobile V_2 defects at $T > 200^\circ\text{C}$ in this material. Early EPR measurements in e-irradiated Cz-Si led to the assignment of $S = 1$ signals A14 and P2 to neutral V_2O and V_2O_2 , respectively [4]. From the ^{29}Si hyperfine structure it was concluded that the defects possess C_{1h} and C_{2h} symmetry, and that they are stable to around $\sim 320^\circ\text{C}$ and $\sim 400^\circ\text{C}$, respectively.

Recently, interest in V_2O has increased following suggestions that this defect may produce a deep level close to mid-gap that is responsible for an enhancement of the leakage current in Si-based radiation detectors [5]. DLTS measurements have been carried out by several groups, but unfortunately the location of the levels produced by V_2O is still a matter of dispute [6–8]. While Pintilie et al. [6] attributed a level at $E_c - 0.55$ eV to $V_2O(-/0)$, other authors [7,8] assigned $(-/0)$ and $(= /-)$ levels at $E_c - 0.46$ eV and $E_c - 0.20$ eV, respectively, to the defect (labeled X), which in agreement with the EPR data, anneals at $T \sim 320^\circ\text{C}$.

Previous density functional cluster methods have been used to successfully explore the structure and electronic properties of V_2 [9] and V_2O [10,11]. However, supercell methods have found difficulty in treating the Jahn–Teller distortion in V_2 [12]. In spite of the difficulties experienced for V_2 , the structures and vibrational modes of V_2O

are reasonable although the calculated binding energy of V_2 with O_i at 0.5 eV is too low [11]. The $(-/0)$ and $(= /-)$ levels of V_2O were placed at $E_c - 0.83$ eV and $E_c - 0.78$ eV, respectively [11].

The purpose of this work is to investigate the electrical properties of divacancy-oxygen complexes in silicon, as well as their formation and dissociation mechanisms. We employ a density functional method briefly described below but evaluate the electrical activity of the defects by using empirical corrections.

2. Method

We utilize a local spin density-functional supercell code (AIMPRO) [13], together with a Perdew–Wang exchange-correlation energy parameterization [14], and the pseudopotentials by Bachelet et al. [15]. The basis is composed of a set of Cartesian–Gaussian functions centered on each atom. Defects were introduced in 216 Si atom cubic supercells, and full relaxation was attained using the 8 special \mathbf{k} -points by Monkhorst and Pack (MP-2³) [16]. To calculate energy levels we use the *marker method* [17,18]. Accordingly, we compare ionization energies and electron affinities of V_2O and V_2O_2 complexes with the same quantities for a marker defect, here chosen to be VOH [19] and SnV [20] defects in Si. Modeling details of VOH and SnV defects are reported elsewhere [19,20]. Formation and dissociation mechanisms were investigated using Γ only. However, the MP-2³ scheme was chosen to calculate relevant stable structures and saddle point energies. These calculations were accomplished by evaluating the energy at intermediate positions along chosen mechanism trajectories, and energies were found by relaxing the system at each intermediate point in a hypersurface perpendicular to the mechanism path. The resulting energy barriers from this calculations are in principle high bounds of the real barrier.

3. Results

Ground state structures of V_2O and V_2O_2 are shown in Fig. 1. This figure shows that these

defects are obtained by placing O atoms between the $\text{Si}_a\text{--Si}_d$ and $\text{Si}_{a'}\text{--Si}_{d'}$ reconstructions in V_2 . Therefore, and in agreement with the EPR data, V_2O and V_2O_2 are monoclinic defects and transform according to the C_{1h} and C_{2h} point groups, respectively. A metastable C_2 symmetry V_2O_2 structure was also found at about 0.1 eV above the ground state. This defect forms $\text{Si}_a\text{--O--Si}_d$ and $\text{Si}_{b'}\text{--O--Si}_{d'}$ units, also leaving two Si unsatisfied radicals at b and a' (see Fig. 1). The Si–O bond lengths are 1.69 and 1.68 Å for V_2O and V_2O_2 , respectively, and the $\text{Si}_a\text{--Si}_d$ length in V_2O is 3.07 Å.

The one-electron band structures associated with the defective supercells strongly indicate donor and acceptor activity for V_2O and V_2O_2 . The levels at Γ are depicted in Fig. 1 and compared with those from V_2 according to Ref. [1]. Inspection of these states lead us to conclude that the interaction between oxygen and V_2 , results in the partial or full removal of the a_u and b_g anti-bonding gap states. These were lowered into the valance band. From Fig. 1 we also conclude that except for the a'' gap state in V_2O , donor and acceptor activity arrives from states with amplitude at the mirror plane. From a plot of the wavefunctions we conclude that a' , b_u and a_g are mostly localized at the Si_b and $\text{Si}_{b'}$ dangling bonds, whereas the a'' state in V_2O is localized at the $\text{Si}_a\text{--Si}_d$ reconstruction. Spin-1 electronic configurations for V_2O^0 and V_2O_2^0 have also been investigated. These were found at 0.06 and 0.01 eV above the spin-zero ground states, respectively. This appears to be in conflict with assignments to the A14 and P2 EPR spin-1 centers although the energy differences are small [4].

Comparing ionization energies of V_2O , V_2O_2 and VOH complexes, we place $(0/+)$ levels at $E_v + 0.15$ eV and $E_v + 0.22$ eV for V_2O and V_2O_2 , respectively. These are close to the $\text{V}_2(0/+)$ hole trap, and could explain its shift toward $E_v + 0.24$ eV observed by DLTS during anneals at $T > 200^\circ\text{C}$ [2]. On the other hand, comparing electron affinities of V_2O , V_2O_2 and VOH complexes, we arrive at acceptor states at $E_c - 0.43$ eV and $E_c - 0.42$ eV for V_2O and V_2O_2 , respectively. These are very close to the measured $\text{X}(-/0)$ and

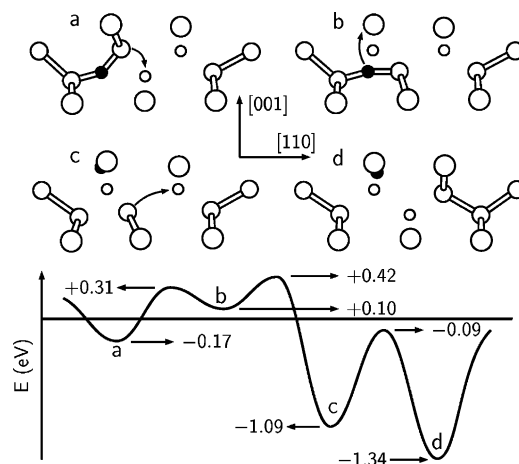


Fig. 2. Four-step formation mechanism of V_2O in silicon. Si, O and vacant sites are represented as large white, small black and small white circles, respectively. The overall barrier (relative to isolated V_2 and O_i defects), is the ~ 1.3 eV diffusion barrier of V_2 . The horizontal line in the configuration coordinate diagram represents the zero energy, i.e., two separated V_2 and O_i defects.

$\text{V}_2(-/0)$ states, and hence we support an assignment of X to V_2O .

Now using SnV as marker we find $\text{V}_2\text{O}(0/+)$ and $\text{V}_2\text{O}_2(0/+)$ donor states at $E_v + 0.08$ eV and $E_v + 0.15$ eV, respectively. Second donor levels fall below the valance band top. We also place $\text{V}_2\text{O}(-/0)$ and $\text{V}_2\text{O}_2(-/0)$ levels at $E_c - 0.65$ eV and $E_c - 0.64$ eV, and second acceptor states $\text{V}_2\text{O}(= /-)$ and $\text{V}_2\text{O}_2(= /-)$ at $E_c - 0.35$ eV and $E_c - 0.40$ eV, respectively. The SnV-marked $(-/0)$ levels are about 0.2 eV deeper than those obtained using VOH as marker. This discrepancy is likely to arise from the different character of the SnV and VOH related gap states.

Now we turn to the formation mechanism of V_2O . We assume that at $T \sim 220^\circ\text{C}$, O_i is immobile and serves to trap a diffusing neutral divacancy. We found a class of mechanisms with low-energy barriers. Such mechanisms can be divided into four main steps [(a), (b), (c), and (d)], exemplified in Fig. 2. In step (a), V_2 approaches an O_i defect producing a weakly bound precursor with an energy of -0.17 eV with respect to the infinitely separated $\text{O}_i + \text{V}_2$ pair. Now, the displacement of a Si atom into the vacant site [Fig. 2(a)] must overcome a barrier of 0.48 eV. In step (b) the

complex starts at +0.10 eV. During this step the O atom reorients inside the vacancy cage with an overall barrier of 0.32 eV. This is close to the measured 0.38 eV reorientation barrier for the isolated VO defect [21]. Step (c) starts with a structure at –1.09 eV, and again, the Si atom moves toward the second vacancy with a 1.0 eV barrier, arriving at step (d) with the formation of a V₂O complex at –1.34 eV. Remarkably, we do not find a barrier higher than for V₂ diffusion. This can be explained by the fact that at every step the number of dangling bonds is kept constant. This result suggests that V₂O formation kinetics should be a diffusing limited process with a ~ 1.3 eV barrier. The analysis does not support the conjecture that there is an additional barrier to be overcome at the final stage of formation of V₂O [7].

Two dissociation mechanisms were considered, (i) $V_2O \rightarrow V_2 + O_i$, or (ii) $V_2O \rightarrow V + VO$. In reaction (i) the binding energy 1.34 eV, which together with the diffusion barrier of V₂ gives a dissociation barrier of about 2.6 eV. On the other hand, reaction (ii) has a binding energy of 1.30 eV. Considering the diffusion barrier of the vacancy [22], we arrive at dissociation barrier, W , of only 1.5–1.6 eV. This figure suggests a dissociation temperature $T \sim W/k \ln \nu \sim 300^\circ\text{C}$ when $\nu \sim 10^{13} \text{ s}^{-1}$, which is consistent with the $\sim 320^\circ\text{C}$ thermal stability of the A14 defect [4].

4. Conclusions

We have investigated the properties of V₂O and V₂O₂ complexes in Si. Their electrical levels were compared with those of VOH and SnV defects. Accordingly, V₂O(–/0) and V₂O(0/+) states are predicted at $E_c - 0.43$ eV and $E_v + 0.15$ eV, and V₂O₂(–/0) and V₂O₂(0/+) levels are placed at $E_c - 0.42$ eV and $E_v + 0.22$ eV, respectively. Second acceptor states are also predicted for both defects. These lie about 0.2–0.3 eV above (–/0) levels. The closeness to the acceptor and donor levels of V₂ is explained from the fact that in all these defects the electrical activity arises from similar Si dangling bonds. These results support the assignment of X to V₂O.

A formation mechanism for V₂O is proposed, according to which no relevant barrier is found apart from that for diffusion of V₂. The defects dissociate around 300°C, according to $V_2O \rightarrow V + VO$ with a barrier estimated between 1.5 and 1.6 eV. It is suggested that V₂O₂ is then formed by the pairing of A-centers.

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