Simulations of Deep-Level Defects in Semiconductors

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Abstract
Experimental and theoretical investigations into divacancies in Si are reviewed. The results of EPR, DLTS and theoretical modelling are described in detail.
Talk overview

The lattice divacancy in silicon

☐ How is this native defect created?
☐ What techniques are used to detect and study it?
☐ What are its structural and electrical properties?
☐ Recent advances in theory
The lattice divacancy in silicon

The lattice divacancy ($V_2$) is one of the most important native defects in irradiated and/or implanted silicon...

It can be defined as two nearby monovacancies sharing a unpaired ‘dangling-bond’.

- $V_2$ defects are unavoidably created during any of the following processing steps:
  - ion-implantation, electron-beam lithography or plasma etching
- Intentionally, by irradiation or implantation at room-temperature of: electrons ($e^-$), protons ($H^+$), $\alpha$-particles ($He^{2+}$), heavier ions, neutrons ($n$) or $\gamma$-rays
- Appears in both Czochralski (O-rich) and float-zone Si, irrespectively of the dopant type

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Experimental tools

$V_2$ is known to:

- be immobile and stable at room temperature
- anneal out $\sim 200$–$300$ °C

Its properties have been studied over the last 3 decades by:

- Electron-paramagnetic resonance (EPR)
- Electron-nuclear double resonance (ENDOR)
- Photoluminescence (PL)
- Infra-red (IR) absorption
- Photoconductivity measurements
- Deep-level transient spectroscopy (DLTS)
- Positron-annihilation spectroscopy
The “defect-molecule” model

One-electron model for the single vacancy in Si (LCAO-MO):

\[ \Psi = \sum_{i} \eta_i \left( a_i (\psi_s)_i + b_i (\psi_p)_i \right) \quad \text{with} \quad a_i^2 + b_i^2 = 1 \]

Eigenvalue problem: \( \hat{\mathcal{H}} \Psi = E \Psi \)

\[ \det |\hat{\mathcal{H}} - E \hat{S}| = 0 \quad \text{with} \quad <\psi_i|\hat{\mathcal{H}}|\psi_i> = 0 \]
\[ <\psi_i|\hat{\mathcal{H}}|\psi_j> = \beta \]
\[ S_{ij} = <\psi_i|\psi_j> \equiv \delta_{ij} \]

- Diagonalization of

\[
\begin{pmatrix}
-E & \beta & \beta & \beta \\
\beta & -E & \beta & \beta \\
\beta & \beta & -E & \beta \\
\beta & \beta & \beta & -E \\
\end{pmatrix}
\]

\( E(A_1) = 3\beta \)
\( E(T_2) = -\beta \)

\[
v = \frac{1}{2} \{ \psi_1 + \psi_2 + \psi_3 + \psi_4 \};
\]
\[
t_x = \frac{1}{2} \{ \psi_1 + \psi_2 - \psi_3 - \psi_4 \}
\]
LCAO-MO model of $V_2$ from EPR

$D_{3d}$

Jahn-Teller distortion

$C_{2h}$
The divacancy is a perfect example of the power of EPR. From the experiments of Watkins and Corbett...

It is known that...

\[ G6 \left( V^+_2 \right) \& G7 \left( V^-_2 \right): \; S = \frac{1}{2} \]

From...

\[ \vec{g}, \text{ fine structure} \]

\[ ^{29}\text{Si hf satellites vs. } \vec{B} \]

\[ \langle 4.7\%, \; I = \frac{1}{2} \rangle \]

\[ \vec{A}_b = \vec{A}_{b'} \]

\[ \vec{A}_i & \vec{g} \text{ shifts with } \vec{B} \]

Low-\( T \) stress studies

\[ \text{hf interaction analysis via } a_i^2, b_i^2 \text{ and } \eta_i^2 \]

Low-\( T \) stress studies

\( C_{2h} \) symmetry at \( T < 40 \) K

60\% of \( w_f \) localised on \( b \& b' \)

\( \sim 70\% \) on the 6 atoms

\[ E_{\text{Jahn-Teller}} \left( V^+_2 \right) \sim 1.3 \text{ eV} \]

\[ E_{\text{Jahn-Teller}} \left( V^-_2 \right) \sim 2.4 \text{ eV} \]

‘bond switching’ \( \Delta E \sim 0.06 \text{ eV} \)

Motional narrowing: \( C_{2h} \rightarrow D_{3d} \)

\( T \)-activated reorientation

\[ \Delta E \text{ for diffusion: } \sim 1.3 \text{ eV} \left( V^0_2 \right) \]

High-\( T \) stress studies
Structural manifestation of the Jahn-Teller effect

A “Mexican Hat”...

The potential surface $V$ for a doubly degenerate state and a contour map of $V(Q_2, Q_3)$ including anharmonic terms.
Electrical activity

EPR and DLTS studies have provided two slightly different pictures for the level structure of the lattice divacancy in Si:

\[
\begin{align*}
\text{EPR} & \\
\text{N-EPR} & = E_c - 0.4 \\
\text{G7} & \quad ? \\
\text{N-EPR} & = 0 \\
\text{G6} & + E_v + (~0.25) \\
\text{DLTS} & \\
& = E_c - 0.23 \\
& = E_c - 0.42 \\
& = 0 \\
& = E_v + 0.25
\end{align*}
\]

It is important to note that:

- For \( T \leq 40 \text{ K} \) (EPR), the unpaired electron is trapped in one of its 3 equivalent JT distortion directions
  \( \Rightarrow C_{2h} \) symmetry.

- In DLTS, \( 80 < T < 250 \text{ K} \), the electronic jump rate between equivalent Jahn-Teller directions and the rate for electron emission relate as follows:

\[
\frac{1}{\tau} (\text{jump EPR}) \gg \frac{1}{\tau} (\text{emission DLTS})
\]

\( \Rightarrow \) "Motionally average" state \( D_{3d} \)

The Poole-Frenkel effect

Electron emission enhancement under an electrical field

\[ g_e \propto \exp \left\{ -\frac{E_t - \Delta E_m}{k_B T} \right\} \]

\[ V_{\text{defect}} = -\frac{e^2}{\epsilon_c r} \Rightarrow \Delta E_m = 2e \sqrt{\frac{eF}{\epsilon_c}} \]

The study of the \( \Delta E_m \) vs. \( F \) (\( \Delta E_m \propto F^{1/2} \)) is a possible way of determining the donor or acceptor character of the centre!
DLTS results

There is still some debate on the assignments of the charge states $2-, -$, and $0$, of $V_2$ to the peaks observed by DLTS...

- The reported electron-capture cross-sections ($\sigma_n$) have not confirmed a double acceptor character for the $E_c - 0.23$ eV DLTS trap ($H^+$-irradiated samples), e.g.

$$\sigma_n(=/-) = 2.6 \times 10^{-15} \text{ cm}^2 : E_c - 0.23 \text{ eV}$$

$$\sigma_n(-/0) = 1.7 \times 10^{-15} \text{ cm}^2 : E_c - 0.43 \text{ eV}$$

- $\sigma_n$ for a (=/-) level is typically $\sim 10^{-18}-10^{-21}$ cm$^2$; unexpectedly, no Poole-Frenkel was ever reported for $V_2(=/-)$!

- From depth profiling studies, it was observed that:
  - MeV-e irradiation
  - $H^+$, $He^{2+}$ or heavier ions

$$\frac{[V_2(-/0)]}{[V_2(=/-)]} = 1 \quad \frac{[V_2(-/0)]}{[V_2(=/-)]} \gg 1$$

- It has been argued$^2$ that the formation of $V_2^{2-} (D_{3d})$ is improbable in highly damaged regions of the sample – the high-$T$ bond-switching does not occur, with the distortion acting to relief the strain around the defect.

Modelling

The common denominator to all the recent theoretical studies on $V_2$ is...

**Density Functional Theory (DFT):**

Electron density is a quantity of fundamental importance

The Kohn-Sham scheme allows a description of the many body-problem as a set of self-consistent one-electron equations:

\[
\left\{ -\frac{1}{2} \nabla^2 + V_{\text{eff}}(\vec{r}) \right\} \psi_j(\vec{r}) = \varepsilon_j \psi_j(\vec{r})
\]

\[V_{\text{eff}} = v_{\text{i-c}} + v_{\text{Hartree}} + v_{xc}\]

\[n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2\]

- $v_{xc}$ (exchange-correlation term) assumed to be something simple – Local density approximation (LDA): electron-gas of slow-varying density

- Core electrons are removed by using norm-conserving pseudopotentials: only valence electrons come into play

- Write $\psi_i$s as sum of plane-wave or Cartesian Gaussian orbitals

- The crystalline environment of the defects is simulated by: periodic super-cells or H-terminated atomic clusters
Simulating bulk silicon

Clusters vs. Supercells

128-atom fcc supercell  bond-centred Si_{148}H_{98} cluster

The spatial extent of the divacancy wavefunction is of particular importance. The system size has to be large enough to avoid:

- defect-defect interactions (supercells)
- defect-surface interactions (clusters)
Calculation of electrical levels

In order to understand the electrical properties of $V_2$, the prediction of its electrical-level structure is of great importance...

▷ A donor level with respect to $E_v$ is the difference between the ionization energy of bulk Si and that of the defect, i.e.

$$E(0/+)_{d} = I_b - I_d$$

▷ To overcome difficulties on calculating the ionization energy of bulk Si, we compare the ionization energies of the defect and a standard defect with well-known electrical levels

$$E(0/+)_{d} = (I_s + (E(0/+)_s)) - I_d$$

$E(0/+)_s \equiv$ observed donor level of the standard defect.

▷ The affinity and ionisation potentials are calculated by applying Slater’s “transition state” scheme.
Previous theoretical studies: A. Saito & Oshiyama

Recently, Saito and Oshiyama\(^3\) have proposed a new model for the structure of \(V_2\), and in particular \(V_2^-\)...

\(\Delta\) For \(V_2^-\), the sense of the Jahn-Teller (JT) distortion is the inverse of that proposed by Watkins & Corbett (pairing model)

\[ C_{2h} \]
Pairing model (P)
\[ l_{ac} < l_{ab} = l_{bc} \]

\[ D_{3d} \]
Breathing model (B)
\[ l_{ab} = l_{ac} = l_{bc} \]

\[ C_{2h} \]
“resonant-bond” model (R)
\[ l_{ab} = l_{ac} > l_{bc} \]

According to this model, the one-electron configurations of \(V_2\) in its paramagnetic charge states are:

\[ V_2^+ : (a_u)^1 (b_u)^0 \] and \[ V_2^- : (a_u)^2 (b_u)^1 \]

\(\Delta\) Note that the \(a_u\) level has no amplitude on the mirror plane!

Previous theoretical studies: B. Pesola, von Boehm, Pöykkö and Nieminen

Pesola et al.\textsuperscript{4} have suggested that the distortion exhibited by $V_2^-$ is mixture between a "rebonding-by-pairs" distortion and a "resonant-bond" one.

This group was able to predict the electrical structure of $V_2$ by first principles...

Table I. Calculated and electrical levels of $V_2$ for different supercell sizes.

<table>
<thead>
<tr>
<th>supercell</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>216</td>
</tr>
<tr>
<td>(=/−)</td>
<td>$E_c - 0.73$</td>
</tr>
<tr>
<td>(−/0)</td>
<td>$E_c - 0.78$</td>
</tr>
<tr>
<td>(0/+ )</td>
<td>$E_v + 0.04$</td>
</tr>
</tbody>
</table>

* Positron annihilation spectroscopic studies

The structure proposed by Saito and Oshiyama was found to be unstable, relaxing spontaneously to a metastable “rebonding-by-pairs”-like structure: weak pairing.

**Table II.** Differences in total energies (eV) for the several competing configurations of $V_2$ in four difference charge states.

<table>
<thead>
<tr>
<th>Energy diff.</th>
<th>$V_{2}^{2-}$</th>
<th>$V_{2}^{-}$</th>
<th>$V_{2}^{+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>strong pairing</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$D_{3d}$</td>
<td>+0.5</td>
<td>+0.4</td>
<td>+0.3</td>
</tr>
<tr>
<td>weak pairing</td>
<td>+0.4</td>
<td>+0.3</td>
<td>+0.6</td>
</tr>
</tbody>
</table>
Results: B.
Structural parameters

Table III & IV. Calculated distances (Å) for Si atoms surrounding a $V_2^-$ defect, for two different charge states.

<table>
<thead>
<tr>
<th>Type</th>
<th>Symm.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>$C_{2h}$</td>
<td>[1]</td>
</tr>
<tr>
<td>$V_2^+$</td>
<td>3.75 3.75 3.61</td>
<td></td>
</tr>
<tr>
<td>$V_2^-$</td>
<td>3.60 3.60 3.69</td>
<td>R</td>
</tr>
<tr>
<td>M(P)</td>
<td>$S_2$</td>
<td>[2]</td>
</tr>
<tr>
<td>3.55 3.52 3.45</td>
<td></td>
<td>\</td>
</tr>
<tr>
<td>3.71 3.71 2.76</td>
<td>P</td>
<td>$C_{2h}$</td>
</tr>
</tbody>
</table>

(64-atom supercells; 8-Ry cut-off)

(64-supercell; 15-Ry cut-off)
Results: C.
Spin density localisation

One-electron picture for $V^{-}_2$

**CONDUCTION BAND**

\[ \begin{align*}
  b_g &- a_u \\
  a_g &- b_u \\
  e_g &- e_u
\end{align*} \]

**VALENCE BAND**

\[ \begin{align*}
  C_{2h} &\rightarrow D_{3d} &\rightarrow C_{2h}
\end{align*} \]

- **inwards distortion**
- **undistorted**
- **outwards distortion**

"Rebonding-by-pairs Model"  Breathing Model  "Resonant-bond" Model

**Below:** Projection of the wavefunction of the 2 highest occupied states onto the defect's mirror plane – **inwards distortion**.
Results: D.

Electrical levels

Table V. Calculated & observed electrical levels of V₂ in two different configurations: distorted (P) and undistorted (B). Values in eV.

<table>
<thead>
<tr>
<th>Levels</th>
<th>C₂h</th>
<th>D₃d</th>
<th>Obs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(=/-)</td>
<td>E_c - 0.36(^{(a)})</td>
<td>E_c - 0.33(^{(a)})</td>
<td>E_c - 0.23</td>
</tr>
<tr>
<td></td>
<td>E_c - 0.59(^{(b)})</td>
<td>E_c - 0.56(^{(b)})</td>
<td>E_c - 0.23</td>
</tr>
<tr>
<td>(-/0)</td>
<td>E_c - 0.63</td>
<td>E_c - 0.61</td>
<td>E_c - 0.43</td>
</tr>
<tr>
<td>(0/+ )</td>
<td>E_v + 0.31</td>
<td>E_v + 0.46</td>
<td>E_v + 0.25</td>
</tr>
</tbody>
</table>

The standard defect levels (markers) were the following:

▸ (=/-): \(\text{(a) Au–H}_1\) at \(E_c - 0.19\) eV

▸ (b) Pt–H₂ at \(E_c - 0.18\) eV

▸ (-/0): interstitial-carbon (C\(_i\)) level at \(E_c - 0.1\) eV

▸ (0/+): C\(_i\) level at \(E_v + 0.28\) eV