Intrinsic $DX$ centers in ternary chalcopyrite semiconductors

“Why metastable intrinsic defects cause open-circuit-voltage limitation and how they can be avoided”

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$V_{OC}$ saturation in CIGS

$V_{OC} = E_g - 0.5 \text{ eV}$

Higher $V_{OC}$:
- Higher $\eta$ for single-junction
- Needed for TF tandem
- Reason: Recombination due to deep defects \[3\]


Defects levels (I) – Example: Orbital interaction in the H$_2$ molecule

- **Superposition**
  - $\rho_1$ and $\rho_2$
  - $\psi_1$ and $\psi_2$

- **Anti-bonding**
  - $+ -$

- **Bonding**
  - $+ +$

The diagram illustrates the overlap of orbitals $\psi_1$ and $\psi_2$ leading to superposition, anti-bonding, and bonding states.
Defects levels (II): Se-vacancy in CuInSe$_2$
Intrinsic DX centers in CIGS
**DX centers:** *Electron traps formed due to lattice relaxations*

In II-VI, **DX centers require** extrinsic impurities. In CIGS, **native defects** (In$_{Cu}$, Ga$_{Cu}$) exhibit **DX behavior**.

Evolvement of ionic structure, electron-level, and energy during the transition into the deep DX state
Critical Fermi levels for electron-trapping

$\text{In}_{\text{Cu}} \ (\text{Ga}_{\text{Cu}})$ exists isolated or in complexes, e.g., $(\text{In}_{\text{Cu}}-2\text{V}_{\text{Cu}})$ [1]

Transition

\[
\begin{align*}
\text{In}_{\text{Cu}}^{2+} + 2e & \rightarrow \text{In}_{\text{DX}}^0 & 0.9 \text{ eV} \\
(\text{In}_{\text{Cu}}-\text{V}_{\text{Cu}})^+ + 2e & \rightarrow (\text{In}_{\text{DX}}-\text{V}_{\text{Cu}})^- & 1.1 \text{ eV} \\
(\text{In}_{\text{Cu}}-2\text{V}_{\text{Cu}})^0 + 2e & \rightarrow (\text{In}_{\text{DX}}-\text{V}_{\text{Cu}})^2^- & 1.3 \text{ eV}
\end{align*}
\]

Electron-trapping due to DX centers occurs mainly in wider-gap CuIn$_{1-x}$Ga$_x$Se$_2$ alloys with $x \geq 0.3$

**VOC limitation by In$_{Cu}$, Ga$_{Cu}$, V$_{Se}$ and their complexes with V$_{Cu}$**

**In$_{Cu}$, Ga$_{Cu}$:** VOC is limited by the transition that causes atomic reconfiguration.

**V$_{Se}$-V$_{Cu}$:** The negative (acceptor) configuration exhibits deep trap level. Both types of defects limit VOC below ~1 eV.

How to avoid $V_{OC}$ limiting metastable defects?
Formation energies vs growth conditions

\[ \Delta H_{D,q}(\mu, E_F) = [E_{D,q} - E_{\text{host}}] + [\mu_{\text{host}} - \mu_D] + q \cdot E_F \]

CuInSe₂ stability condition
\[ \Delta \mu_{\text{Cu}} + \Delta \mu_{\text{In}} + 2\Delta \mu_{\text{Se}} = \Delta H_f(\text{CIS}) \]

Competing phases
e.g., \[ 3\Delta \mu_{\text{Cu}} + 2\Delta \mu_{\text{Se}} \leq \Delta H_f(\text{Cu₃Se₂}) \]

- Minimize \( \text{In}_{\text{Cu}}, \text{Ga}_{\text{Cu}}, \) \( (\text{In}_{\text{Cu}} - 2V_{\text{Cu}}) \)
- Minimize \( V_{\text{Se}}, (V_{\text{Se}} - V_{\text{Cu}}) \)
- Cu-rich / Se-rich growth
Trade-offs for minimizing $V_{OC}$ limiting defects

Minimizing defects: Se-rich / Cu-rich
e.g., phase-equilibrium with Cu$_3$Se$_2$

Type inversion: Se-poor / III-rich (Cu-deficient) [1]

Other causes of $V_{OC}$ limit. : band-offset [2], …?

Conclusions

- Intrinsic donor-type defects In$_{\text{Cu}}$, Ga$_{\text{Cu}}$, and V$_{\text{Se}}$, and their complexes with V$_{\text{Cu}}$ cause metastability, but also act to limit $V_{\text{OC}}$

- Growth conditions which minimize these defects (Cu-rich/Se-rich) are very different from those currently used

- Overcoming $V_{\text{OC}}$ limitation requires to address other issues and trade-offs

References

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