The defect challenge of wide-bandgap semiconductors for photovoltaics and beyond

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The optoelectronic performance of wide-bandgap semiconductors often cannot compete with that of their defect-tolerant small-bandgap counterpart. Here, the authors outline three main challenges to overcome for mitigating the impact of defects in wide-bandgap semiconductors.

Visible-light harvesting materials with bandgaps in the range of 1.6–2.5 eV are gaining increasing significance across a range of emerging technologies, such as indoor and tandem photovoltaics (PVs), but feature inferior optoelectronic performance compared to their small-bandgap (<1.6 eV) counterparts. Charge-carriers tend to have shorter diffusion lengths, along with higher trapping and recombination rates. We outline the critical challenges for achieving defect-tolerant wide-bandgap crystals, and suggest promising routes forward.

Efficient, low-cost devices through defect tolerance

Defects are ubiquitous in crystalline semiconductors. Managing their influence on electronic properties is critical for high performance across a range of technologies, including PVs, photovoltaic cells and radiation detectors. Of particular importance are point defects—such as vacancies, anti-sites or interstitials—which lead to the introduction of electronic states that fall within the bandgap (Eg), resulting in irreversible losses in charge-carriers through trapping and non-radiative recombination. Historically, the effects of defects were mitigated by minimising their concentration through careful (and often expensive) fabrication methods, such as the case for Si1. More recently, new classes of semiconductors have been discovered that can maintain high light conversion efficiency despite high concentrations of point defects. Such defect tolerance can arise in several ways. Defects can pair together to form electronically benign complexes (e.g., in CuInSe2)2,3. Defects can also be less harmful if: (i) the dominant traps within the bandgap are energetically close to the valence or conduction band edges (i.e., shallow), or (ii) have low capture cross-sections (see ref. 4 for details). These effects have been found in metal-halide perovskites, and are an important factor behind their rapid achievement of PV efficiencies comparable to those of Si2,4, despite being processed at significantly lower temperatures that enable lower levelised cost of energy and CO2eq footprint5.

Wide-bandgap challenge

Semiconductors that have both been demonstrated to be defect tolerant and also realised in efficient PV (i.e., CuInSe2 and iodide-based perovskites) have only been achieved for materials with <1.6 eV bandgap2,3. Wider-bandgap semiconductors, with Eg in the range of 1.6–2.5 eV, have had less success, but are now becoming increasingly important for a range of clean energy and healthcare applications. These include indoor PV (optimal Eg of 1.9 eV) to sustainably power the Internet of Things6, photovoltaic chemical cells (~2 eV) for single-junction solar-to-hydrogen water splitting7, X-ray detectors (1.4–2.5 eV) for medical imaging and security8, and top-cells (>1.7 eV) for tandem PV with silicon9. There are a number of obstacles to overcome. Below, we discuss the critical challenges to achieving defect tolerance in wide-gap semiconductors, and inspiration on how these challenges could be overcome.

Harder dopability. Many materials can be doped by either electrons (n-type) or holes (p-type) but not both. Such doping asymmetry is a feature of wide-bandgap systems. One example is the field of transparent oxide electronics where n-type doping is possible (e.g., in ZnO, SnO2, In2O3), yet effective p-type doping is much more challenging. This type of behaviour is often rationalised by using the doping limit rules5 (and sometimes explained by the concept of Fermi level pinning), which state that the lower the ionisation potential (valence band energy), the easier it is to make a material p-type, and the higher the electron affinity (conduction band energy), the easier it is to make it n-type. The limit itself is imposed by the spontaneous formation of charge compensating point defects. As such, wide-gap semiconductors with low electron affinity and/or high ionisation potential generally have lower dopability to one or both carriers. This can be seen in Fig. 1a, in which there is an overall decrease in the predicted dopability (Eg) as the bandgap increases (especially for the case of n-type dopability shown). Whilst the correlation between band-edge position and dopability is established, the link between dopability and defect tolerance is still unresolved.

Increased ionicity. Ionic materials typically have larger bandgaps than their covalent counterparts, which can be seen, for example, in comparing NaCl (8.5 eV) to silicon (1.12 eV), or LiF (14 eV) to diamond (5.5 eV). As charge transfer increases, a stronger Coulomb potential separates the valence and conduction bands. For example, the bandgap of CH3NH3PbI3 can be continuously increased from 1.59 to 3.04 eV by changing the halide species to the more electronegative Br or Cl, or using mixtures thereof (Fig. 1b). The established defect tolerance of CH3NH3PbI3 is not preserved across the entire halide composition range. The halide vacancy (0/) donor level becomes deeper through the series (Fig. 1b), due to the lower electron affinity, as well as the smaller lattice constant of CH3NH3PbCl3 leading to greater overlap between Pb dangling bonds when halide vacancies form. The electrostatic potential at the vacancy site becomes sufficiently large to localise an unpaired electron to form a deep state with large structural relaxation energy. For the case of ZnO1–xSx, a nitrogen acceptor is deep above the valence band for small values of x, but becomes shallower for S-rich materials. Increased ionicity can lead to stronger carrier trapping and activate
the exceptional 9000 cm$^2$ V$^{-1}$ s$^{-1}$ electron mobility for GaAs ($E_g$ = 1.5 eV, $m_e = 0.07$, $\varepsilon_\infty = 10.9$) is reduced to 900 cm$^2$ V$^{-1}$ s$^{-1}$ for GaN ($E_g$ = 3.5 eV, $m_e = 0.22$, $\varepsilon_\infty = 4.9$)\textsuperscript{14}.

**Future opportunities**

A promising avenue to enhance dielectric screening is to identify host materials with large ionic (vibrational) contributions to the static dielectric constant. This component is sensitive to the underlying structure and vibrations, which can be tuned through crystal engineering. The net ionic screening (defined as $\varepsilon_\infty - \varepsilon_0$) is decoupled from the bandgap (Supplementary Fig. 1). Instead, large ionic contributions are found in materials containing polarisable cations (such as Bi or Pb) and in materials close to a polar phase transition (such as SrTiO$_3$ and other perovskite structured crystals). These factors are realised in the emerging absorber SbSI which, despite its relatively wide bandgap of 1.86 eV, possesses a giant room temperature dielectric constant >10$^4$ (along the $c$ axis) due to a ferroelectric Curie temperature around 291 K. This route has also recently been exploited in the development of ferroelectric oxide PVs, such as KNbO$_3$–Ba Nb$_3$O$_9$O$_3$ solid solutions\textsuperscript{13}. Here, spontaneous electric polarisation promotes the separation of photoexcited carriers and enables the generation of above-bandgap photovoltages. As oxides typically possess larger bandgaps, this approach may prove especially fruitful for the identification of wide-gap defect-tolerant candidates.

Inspiration on how to achieve shallow traps in wide-gap materials can be found in bismuth oxyiodide (BiOI) and BaZrSi$_3$ ($E_g$=1.8–1.9 eV). In BiOI, the Bi-I bonds are comparatively long (3.4 Å [Fig. 2a] vs. 3.7 Å for Pb-I in CH$_3$NH$_3$PbI$_3$)\textsuperscript{16}. When I vacancies form, the neighbouring Bi atoms are sufficiently far apart to avoid significant orbital overlap, leading to small energy splittings in the
bonding-antibonding combinations formed from the dangling bonds. This, coupled with the moderate electron affinity of 4.1 eV, results in the $V_I$ (0+/+) donor transition level being resonant within the conduction band (Fig. 2b). The inert nature of I vacancies has been verified experimentally. Preliminary defect chemistry analysis indicates that BaZrS$_3$ benefits from the flexible perovskite structure (Fig. 2c), similar to the metal halides, which ‘cleans up’ deep traps from the bandgap (Fig. 2d). These recent results further motivate efforts at overcoming the challenges of growing high-quality thin films of chalcogenide perovskites at low temperatures to exploit these properties in PV devices.

In conclusion, defect tolerance has allowed select low-bandgap semiconductors to achieve efficient device performance when processed by low-temperature, cost-effective methods. As a new generation of wide-bandgap semiconductors gain increasing technological significance, overcoming their unique defect challenges is of paramount importance. Promising strategies include identifying materials with high ionic dielectric constants but weak Fröhlich coupling, translating the defect chemistry of halide perovskite semiconductors.

Fig. 2 | Wide-bandgap semiconductors with non-harmful traps. a Crystal structure and b band diagram of BiOI, showing the (0+/+) transition level of iodide vacancies (V)$_I$. c Crystal structure and d band diagram of BaZrS$_3$, showing the deep donor (0+/+) and shallow acceptor (0-/+) transition levels of zirconium vacancies (V)$_Zr$.

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