

### Multi-Bandgap Semiconducting Materials Boost Solar-Cell Efficiency

The most impressive improvements in the efficiency of solar cells have been realized by using the full spectrum of solar photon energies. The highest power-conversion efficiencies, up to ~37%, have been achieved with multijunction, tandem solar cells with Ge, GaAs, and GaInP junctions with energies ranging from 0.7 eV to 1.9 eV. Researchers at Lawrence Berkeley National Laboratory have recently used a novel ion-beam and laser-melting technique to synthesize a new class of semiconductor alloys—three-band semiconductors with an intermediate band within the energy gap. The three absorption edges of these alloys absorb photons from virtually the entire solar spectrum. They are potentially suitable for the fabrication of photovoltaic devices with power conversion efficiencies above 50%.

The alloys are II–VI semiconductors (ZnMnTe) in which a small fraction (a few percent) of the Group VI constituent (Te) in the host is replaced by O atoms. Oxygen is much more electronegative than the Group VI element it replaces. Such compounds are referred to as highly mismatched alloys (HMAs). HMAs have become an important class of materials because their electronic properties (e.g., their bandgaps) are unusually sensitive to small changes in alloy composition. For example, the bandgap is reduced by as much as 180 meV per mole percent of N (i.e., for  $x = 0.01$ ) in  $\text{GaN}_x\text{As}_{1-x}$  HMAs. This effect has been used to make commercial near-infrared, vertical-cavity surface-emitting lasers based on this alloy.

The unusual properties of HMAs have been explained by the band-anticrossing (BAC) model. According to this model, the anticrossing interaction between the localized states of the foreign electronegative element and the extended states of the host semiconductor matrix splits the conduction band into higher ( $E_+$ ) and lower ( $E_-$ ) energy subbands. The BAC model predicts that a dilute oxide of binary or ternary ZnMnTe will possess a three-band structure with a narrow intermediate band.

It is not possible to grow HMAs under equilibrium conditions because the solubility of O in II–VI compound is too low ( $\sim 10^{-5}$ ). Instead, nonequilibrium synthesis conditions are used—oxygen implantation followed by pulsed laser melting (PLM). The PLM process involves the melting of the implanted layer induced by the near surface absorption of a single pulse of intense laser radiation and the subsequent rapid epitaxial regrowth from the liquid

on a time scale between  $10^{-8}$  s and  $10^{-6}$  s. Due to the rapid melting and solidification process, the O atoms are trapped in the crystal lattice, forming a thin layer (~200 nm) of homogeneous ZnMnOTe.

Using this technique, ~2% of Te atoms in a ZnMnTe crystal were replaced by O, resulting in a dilute oxide layer. Photoreflectance measurements revealed that this material exhibits two optical transitions, at ~1.8 eV and 2.6 eV, that are distinctly different from the fundamental bandgap transition of the matrix  $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{Te}$  ( $E_M = 2.32$  eV) (see Figure 1). These transitions are from the valence band ( $E_v$ ) to the two conduction subbands,  $E_+$  (~2.6 eV) and  $E_-$  (~1.8 eV) formed as a result of the hybridization of the localized O states and the extended conduction band states of ZnMnTe. Three optical transitions cover nearly the entire solar spectrum.

This dilute II–VI oxide is a practical realization of a semiconductor with a narrow intermediate energy band, and therefore is a promising candidate for the multi-bandgap semiconductors envisioned for high-efficiency, intermediate-band solar cells (IBSCs). Theoretical evaluation shows that a single-junction solar cell fabricated from this material could achieve an ideal power conversion efficiency of 56%.

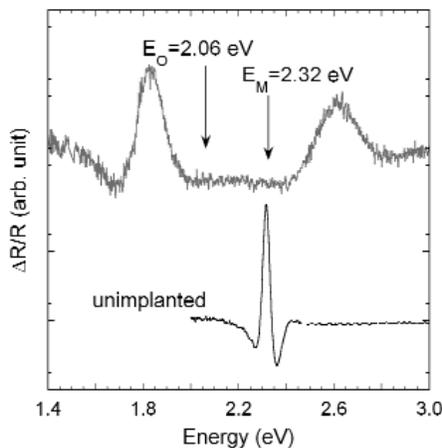


Figure 1. Photoreflectance spectra obtained from  $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{Te}$  samples as-grown and as-implanted with 3.3%  $\text{O}^+$  followed by pulsed laser melting (PLM) with energy fluence of 0.15  $\text{J}/\text{cm}^2$ . Two optical transitions from the samples implanted with O followed by PLM at ~1.8 eV and 2.6 eV occur that are distinctly different from the fundamental bandgap transition of the matrix  $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{Te}$  ( $E_M = 2.32$  eV).

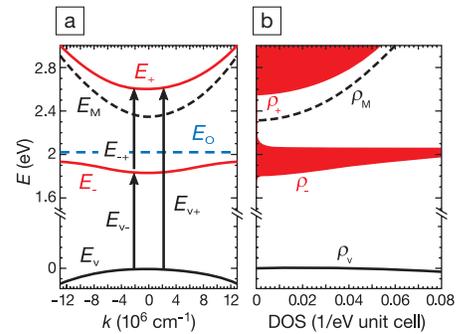


Figure 2. (a) Calculated energy-band structure and (b) density of states for 0.15  $\text{J}/\text{cm}^2$  synthesized  $\text{Zn}_{0.88}\text{Mn}_{0.12}\text{O}_x\text{Te}_{1-x}$  (with  $x \sim 0.023$ ). The three possible optical transitions are shown in (a).

Other HMAs are also potentially suitable candidates for IBSCs, provided that the localized level (O in II–VI or N in III–V) lies below the conduction band of the matrix. This is realized in  $\text{GaAs}_{1-y}\text{P}_y$  with  $y$  in the range of 0.3–0.5 and  $\text{Zn}_{1-y}\text{Cd}_y\text{Te}$  with  $y$  below 0.3. For example, a  $\text{Zn}_{0.8}\text{Cd}_{0.2}\text{O}_x\text{Te}_{1-x}$  HMA with  $x \sim 0.05$  has absorption edges at ~1 eV, 1.5 eV, and 2.5 eV. This band structure is expected to result in an ideal power conversion efficiency of ~60%.

#### Opportunities

The researchers are seeking collaborators interested in the development of practical high-efficiency multi-bandgap solar cells. Lawrence Berkeley National Laboratory is seeking industry partners interested in licensing this technology for developing such high-efficiency solar cells.

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