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Solid State Theory of Photovoltaic Materials: Nanoscale Grain Boundaries and Doping CIGS

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Solid State Theory of Photovoltaic Materials

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ABSTRACT

We use modern first-principles electronic structure theory to investigate (1) why are grain boundaries in chalcopyrites passive; (2) can chalcopyrites be doped by transition metals, and; (3) can hot electrons and carrier multiplication be efficient in quantum-dot solar cells.

1. Objectives

The objectives are:
- Theory of grain boundaries in CIGS
- Doping chalcopyrites by transition metals
- Quantum-dot solar cells.

2. Technical Approach

We use first-principles electronic structure theory.

3. Results and Accomplishments

3.1 Theory of grain boundaries in CIGS [1]

Photovoltaic solar cells and other optoelectronic devices often necessitate the use of (rather expensive) *single-crystalline* active materials, because the analogues, low-cost *poly-crystalline* substances have grain boundaries (GB's) into which many defects and impurities segregate. In polycrystalline Si and GaAs these GB defects form effective recombination centers for the optically generated electrons and holes, thus diminishing and even eliminating carrier transport. However, polycrystalline $CuInSe_2$ solar cells outperform (20% efficient) the best single-crystal devices (~13%), even though no deliberate passivation of the GB's is attempted. This puzzle in polycrystalline $CuInSe_2$ and related polycrystalline materials attracted recently considerable attention because the understanding of the natural GB passivity in ternary chalcopyrites could lead in the future to the deliberate design of optoelectronic devices based on low-cost polycrystalline materials which could not only approach (viz Si, GaAs, etc.) but also surpass (viz $CuInSe_2$) their crystalline counterparts.

We performed detailed first-principles calculations on the density of states and wavefunction localization of various models of GB in CIS, including surface-like GB's [1]. Such first principles modeling of grain boundaries in $CuInSe_2$ semiconductors revealed that an energetic barrier exists for holes arriving from the grain interior (GI) to the GB. Consequently, the absence of GB holes prevents electrons from recombining at the GB defects. At the same time, the GI is purer in poly materials than in single crystal, since impurities segregated to the GB's. This explains the puzzle of the superiority of polycrystalline $CuInSe_2$ solar cells over their crystalline counterpart.

We identify a simple and universal mechanism for the barrier, arising from reduced *p-d* repulsion due to Cu-vacancy surface reconstruction. This discovery opens up for future design of superior polycrystalline devices.

3.2 Doping of chalcopyrites by transition metals [2]

We were wondering if chalcopyrites can be doped by 3d elements. We have now predicted the site preference of Mn in $CuAlS_2$, $CuGaS_2$, $CuInS_2$, $CuGaSe_2$, and $CuGaTe_2$, using first-principles total-energy calculations. We found that:

(1) The energetic preference of Mn on the Cu site is enhanced by growth condition with high chemical potential for the column III element, whereas the preference of Mn on the M^{III} site is enhanced by Cu-rich, III-poor growth conditions.

(2) When the Fermi energy E_F is near the valence band maximum (VBM), Mn_{III} is charge neutral and Mn_{Cu} is positively charged. Both defects are in the negative charge state when E_F is close to the conduction band minimum (CBM).

(3) The Fermi energy position affects the Mn site preference: as E_F moves toward the CBM (*n*-type behavior), the solubility of $Mn-$ on the column-III site increases. The solubility of Mn^+_{Cu} decreases when E_F moves from the VBM toward the CBM; it vanishes when E_F passes the mid-gap. Chalcopyrites are *n*-type when they are grown anion-deficient. In this case we expect mostly Mn_{III} if the sample is also Cu-rich. On the other hand, chalcopyrites are *p*-type when grown Cu-deficient. Then we expect Mn_{Cu}.

(4) *For Mn on the M^{III} site* (Cu-rich, anion-poor samples), a hole exists in the highest occupied state. So the system is p-type. The ferromagnetism stability is reduced in the sequences $CuAlS_2$ $CuGaS_2$ $CuInS_2$, and $CuGaS_2$ $CuGaSe_2$ $CuGaTe_2$. When Mn is negatively charged (by excessive donor doping), the hole is filled, and AFM replaces FM.

(5) *For Mn on the Cu site* (Cu-poor anion-rich samples), also introduces ferromagnetism. The ferromagnetic stability for Mn on the Cu site is generally lower than for Mn on the III-site, with minor exceptions. The order of ferromagnetic stability (for Mn atoms being fourth neighbors) is reduced in the series $CuGaSe_2$ $CuGaS_2$ $CuGaTe_2$ $CuAlS_2$ $CuInS_2$.

(6) The strongest tendency for hole doping and thus ferromagnetism occurs when the Mn ions are located along the <110> chain connecting in III-V's the atoms Ga-As-Ga-As-…, and in I-III-VI_2 the atoms Cu-Se-Ga-Se-… In III-V's, the strength of ferromagnetism (e.g., for the first-neighbor Mn atoms) decreases along the series GaN GaP GaAs GaSb, whereas in chalcopyrite it decreases

along the series CuGaS$_2$ CuGaSe$_2$ CuGaTe$_2$. Finally, comparing all compounds, the FM stability decreases along GaN   GaP   GaAs   CuGaS$_2$ GaSb   CuGaTe$_2$. This work was done in collaboration with ONR support.

3.3 Quantum-dot solar cells [3,4]

Many optoelectronic devices could achieve much higher efficiencies if the excess energy of electrons excited well above the conduction band minimum could be used to promote other valence electrons across the gap rather than being lost to phonons. It would then be possible to obtain two electron-hole pairs from one. This will possibly lead to high-efficiency solar cells. In bulk materials, this process is inherently inefficient due to the constraint of simultaneous energy and momentum conservation. We calculated the rate of these processes, and of selected competing ones in CdSe colloidal dots, using our semi-empirical non-local pseudopotential approach. (This methodology was developed over the past seven years via BES-SC support). We find much higher carrier multiplication rates than in conventional bulk materials for electron excess energies just above the energy gap Eg. We also find that in a neutral dot, the only effective competing mechanism is Auger cooling, whose decay rates can be comparable to those calculated for the carrier multiplication process. Figure 1 shows our results. We find that: (1) the DCM rates are of the order of 10^{10} s^{-1}, whereas in the usual bulk materials, rates of this magnitude are obtained only for excess energies about 1eV above Eg; (2) the lifetime of the competing Auger cooling (AC) mechanism is of about the same order of magnitude as that of the DCM process. For higher excess energies, the presence of an energy gap within the hole manifold slows DCM considerably compared to AC, which is unaffected by it, leading to inefficient DCM in an energy window of the size of such a gap. As in the case of Auger multi-exciton recombination rates, the main contribution to the DCM rates is found to come from the dot surface. We conclude that hot-electrons can live for only picoseconds-v-relaxing by at least six orders of magnitude faster than the "phonon bottleneck" will suggest. Furthermore, direct carrier multiplication is not an efficient process, having Auger cooling as a strong competitor.
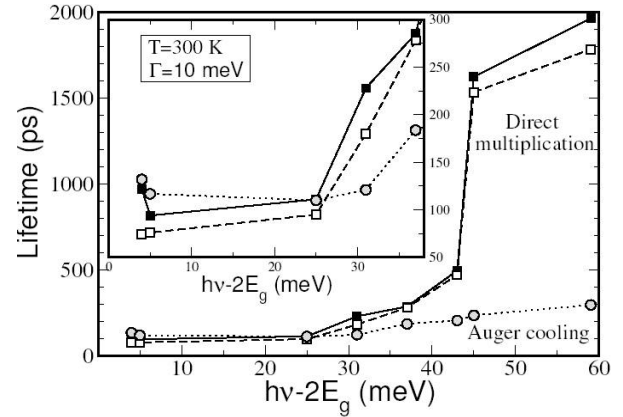

Fig. 1. DCM lifetimes with (filled squares and solid line) and without empty squares and dashed line) a hole present, compared to AC lifetimes (filled circles and solid line), for different (initial) impacting electron levels eth+1 as a function of the photon energy hv-2E$_g$ at room temperature. Inset: detail of the curve crossings in the low-energy region of the graph.

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