1.   Project Title: Solid State Theory of PV Materials and Devices

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5. & 6. Statement of Problem and Objectives: Whereas Si-based, or III-V based solar cell R&D has benefited from the pre-existence of a broad base of basic research on these materials, chalcopyrite based solar cell R&D has had to develop its own basic material research. The present task represents ongoing research aimed at establishing the scientific basis for the materials science of chalcopyrites $CuInSe_2$ (CIS), $CuGaSe_2$ (GGS) and related II-VI compounds. Over the years, this involved theoretical modeling of the following categories: (a) *Bulk materials:* band structure, chemical bonding and stability, density of states vs. photoemission, predicted band gaps of yet unmade chalcopyrites, ordered vacancy compounds; (b) *Defects and impurities:* energy levels and transition energies for intrinsic defects and impurities; (c) *Alloys:* optical bowing and heat of solution of chalcopyrite-chalcopyrite and zincblende-chalcopyrite alloys; (d) *Surfaces:* reconstructed surface structures of polar and nonpolar surfaces; (e) *Interfaces:* band offset for chalcopyrite-chalcopyrite and chalcopyrite-zincblende contacts; (f) *Doping:* identification and prediction of p-type and n-type dopants; (g) *Electronic metastability:* persistent photoconductivity and other defect-induced deep-shallow transitions; (h) *Grain boundaries:* electronic and transport properties. The project objectives for FY04-05 involved mostly items (f) – (h) above, aimed at future high performance tandem cells.

7. Project History & Relationships: Over the years, the project involved different subjects under the same "Solid State Theory of PV Materials and Devices" task including: (i) **Si PV** [defects, transition metal impurities, Si-Ge superlattices, PV-nanostructures]; (ii) **III-V PV** [GaP/InP ordering; III-V nitrides; GaAsP alloys]; (iii) **II-VI PV** [alloys; defects; interfaces; schotcky barriers]; (iv) **chalcopyrite PV** [listed above]; and, (v) **nanostructures for PV** [auger multiplication in dots]. In FY04 and FY05 the emphasis was on item (iv). The PI has an independent project with the Office of Science (SC), which does not involve PV materials, but is centered around (1) development of computational techniques for nanostructures and alloys (cluster-expansion; inverse-band structure; genetic algorithm; solving huge matrixes and (2) quantum dot nanostructures. Computer codes developed by us under SC sponsorship have been made available to our EERE funded project at no cost sharing.

8. & 9. Technical Approach and Work Plan:
(I) Doping of CIS and CGS [1]-[4]: CIS can be grown both *p*- and *n*-type, while CGS is always obtained *p*-type. This poses a serious limitation to making cells that incorporate a wide-gap CGS component. In order to address these questions we calculated recently [1]-[4] the defect concentrations and equilibrium Fermi level at different growth conditions. This involved computing the defect and compound formation energies of intrinsic defects (all vacancies, anti-sites and defect pairs) and extrinsic (F, Cl, Bc, Mg, Cd, Zn) doping and competing compounds, which we obtained from first-principles total-energy calculations. We identified maximally Se-poor and Cu-, In-rich growth as being the optimal condition for obtaining *n*-type conductivity by halogen-, and Cd-doping. We found that extrinsic doping by halogen is overwhelmed by the high concentrations of intrinsic defects [3]. This explains why in recent experiments in CIS the electron concentration after Cl-doping did not exceed levels that are frequently obtained without extrinsic dopants. The problem of *n*-type doping in the larger-gap CGS was traced back to the exceedingly low formation energy of compensating acceptor-like Cu vacancies V_{Cu} which form spontaneously even under Cu-rich growth when the Fermi level raises in the band gap [1], [4]. Thus, a Fermi level near the conduction band minimum, which is required for successful *n*-type doping, cannot be obtained in CGS under equilibrium conditions. Therefore, we suggested that *n*-type CGS may only be obtained under non-equilibrium conditions where the formation of Cu vacancies is kinetically inhibited. This will be a crucial step in designing future cells with a CGS layer.

II. Light and bias-induced metastability in CIS and CGS [5]-[7]: Solar cells based on CIGS frequently show metastability effects, i.e. a persistent change in the junction capacitance and the open-circuit voltage. Such metastability occurs either upon illumination with photon energies equal or higher than the band-gap or after

application of a voltage bias. It is important to figure this out for establishing stable cells. Using first-principles electronic structure calculations, we investigated metastability caused by anion vacancies in II-VI and chalcopyrite semiconductors Refs. [5]-[7]. For $CuInSe_2$ and $CuGaSe_2$, we found that the formation of $(V_{Se}-V_{Cu})$ vacancy complexes is thermodynamically favorable at room temperature, and that this complex can exists in two charge states $q = +1$ and $q = -1$, resulting in a donor and an acceptor configuration, respectively. The calculated energy barriers between these configurations exhibit metastable behavior. Both the presence of light-induced carriers, and the change of Quasi-Fermi levels that occurs when a voltage bias is applied, can trigger a switching between the two charge states explaining the experimental observation of persistent changes in the capacitance of the solar cell junction and in the charged defect distribution (Ref. [5]). Thus, the $(V_{Se}-V_{Cu})$ vacancy complex is identified as the source of both light- and bias-induced metastability. Based on the calculated optical transition energies, we further predict that the vacancy complex will produce a *recombination center* in the light-induced metastable configuration, highlighting its detrimental affect on solar cells. We concluded that the sometimes observed small beneficial effects of light-soaking relies only on a feeble balance between the detrimental effect of recombination centers and the beneficial effect of increased space charge density which occurs when the complexes change persistently their charge state upon illumination.

III. Grain-Boundaries in CIS and CGS [8]-[10]: Whereas the *polycrystalline* form of conventional semiconductors (Si, GaAs) have poor transport and electronic properties relative to their *crystalline* counterparts, surprisingly, poly-crystalline alloys of CIS with CGS has excellent properties, manifested among others by nearly 20% solar cell conversion efficiency, outperforming even its crystalline counterpart! We have explained theoretically [8,10] why, despite the existence of many defects and impurities at the GBs of $CuInSe_2$, there appears to be a negligible recombination of electrons and holes there. Our conclusion was based on the analogy between the structure of GB "internal surfaces" and the surface structure of CIS films. Total-energy minimization of the surface structure of CIS showed that in contrast with conventional semiconductors such as GaAs, in CIS the *polar* surface is more stable than the non-polar surface. Polar CIS surfaces must reconstruct to remove the electrostatic dipole created by the alternation of pure cation and pure anion planes along the polar axis. This reconstruction involves creating rows of either Cu vacancies or In-on-Cu antisites. Unlike conventional bulk vacancies, this surface Cu vacancy is charge-neutral because its negative (acceptor-like) charge has been used to cancel the electrostatic dipole. Furthermore, unlike GaAs, this reconstruction in CIS costs little energy because the creation of Cu vacancies is much less costly than the creation of Ga vacancies in the strongly covalently bonded III-V's. Thus, the GB in CIS is intrinsically Cu-poor while the GI is closely Cu stoichiometric. Indeed, our study of the electronic structure of the interface between the GB and the GI has shown a valence band offset ΔE_v of ~0.5 eV due to the lowering of the valence band maximum (VBM) at the Cu-poor GB. This offset causes all photogenerated holes to be repelled from the GB into the GI. Thus, although the GB has numerous defect recombination centers, the electrons there have no holes to recombine with. Two dimensional device simulations (W. Metzger et al., NREL) of our model of neutral offset at the GB/GI interface indicate a strongly reduced recombination at the GB (on account of a reduced $n \cdot p$ product), leading to a significant increase in solar cell efficiency relative to a cell having no band offset at the GB/GI interface. Our model of GB/GI *charge-neutral* band offset hole reflector was recently validated experimentally [9].

10. Technical Problems/Barriers: NREL removed all funding of this project in mid FY-05. Expect renewal in FY06.

11. Status/Milestones: "Perform Theory of Defects, Doping and Metastability in High-Performance Chalcopyrites." Milestones accomplished.

15. Budget: 85% coverage of PI (A. Zunger) from PVA5.2001 and 100% of one postdoc (first, Clas Persson, then replaced by S. Lany) out of PVA5.0002. No other support for this program. Budget was zeroed in mid FY05.

16. Principal Project Personnel: A. Zunger (PI), alex_zunger@nrel.gov, (303) 384-6672; Postdocs (C. Persson & S. Lany, consecutively).

17. Website link: http://www.sst.nrel.gov

Attachment I:
14. Project Output:
(A) Articles Published in Refereed Journals:

I. **Doping of chalcopyrite photovoltaic semiconductors:** (1) C. Persson, Y.J. Zhao, S. Lany and A. Zunger, "***n-type doping of CuInSe$_2$ and CuGaSe$_2$***," Phys. Rev. B **72**, 035211 (2005); (2) S. Lany, Y.J. Zhao, C. Persson and A. Zunger, "***Halogen n-type doping of chalcopyrite semiconductors***," Appl. Phys. Lett. **86**, 042109 (2005); (3) Y.J. Zhao, C. Persson, S. Lany and A. Zunger, "***Why can CuInSe$_2$ be readily equilibrium-doped n-type but the wider-gap CuGaSe$_2$ can not***," Appl. Phys. Lett. **85**, 5860 (2004); (4) A. Zunger, "***Practical doping principles***," Appl. Phys. Lett. **83**, 57 (2004).

II. **Metastability of anion vacancies in II-VI and chalcopyrite semiconductors:** (5) S. Lany and A. Zunger, "***Light and bias induced metastability in Cu(In,Ga)Se$_2$ caused by the V$_{Se}$-V$_{Cu}$ vacancy complex***," submitted to Appl. Phys. Lett. (2005); (6) S. Lany and A. Zunger, ***Anion vacancies as a source of persistent Photoconductivity in II-VI and chalcopyrite semiconductors***, Phys. Rev. B **72**, 035215 (2005); (7) S. Lany and A. Zunger, ***Metal-dimer atomic reconstruction leading to deep donor states of the anion vacancy in II-VI and chalcopyrite semiconductors***, Phys. Rev. Lett. **93**, 156404 (2004).

III. **Grain Boundaries in polycrystalline solar cells:** (8) C. Persson and A. Zunger, ***Compositionally Mandated Valence Band Offset at the Grain-Boundary of Polycrystalline Chalcopyrites Create a Hole Barrier*** , submitted to Appl. Phys. Lett. (2005); (9) M.J. Hetzer, Y.M. Strzhemechny, M. Gao, M.A. Contreras, A. Zunger, and L.J. Brillson, ***Direct observation of copper depletion and potential changes at copper indium gallium diselenide grain boundaries*** , Appl. Phys. Lett. **86**, 162105 (2005); (10) C. Persson and A. Zunger, ***Anomalous Grain Boundary Physics in Polycrystalline CuInSe$_2$: The Existence of a Hole Barrier***, Phys. Rev. Lett. **91**, 266401 (2004).

(B) Invited Talks: Five in 8/04 to 8/05.