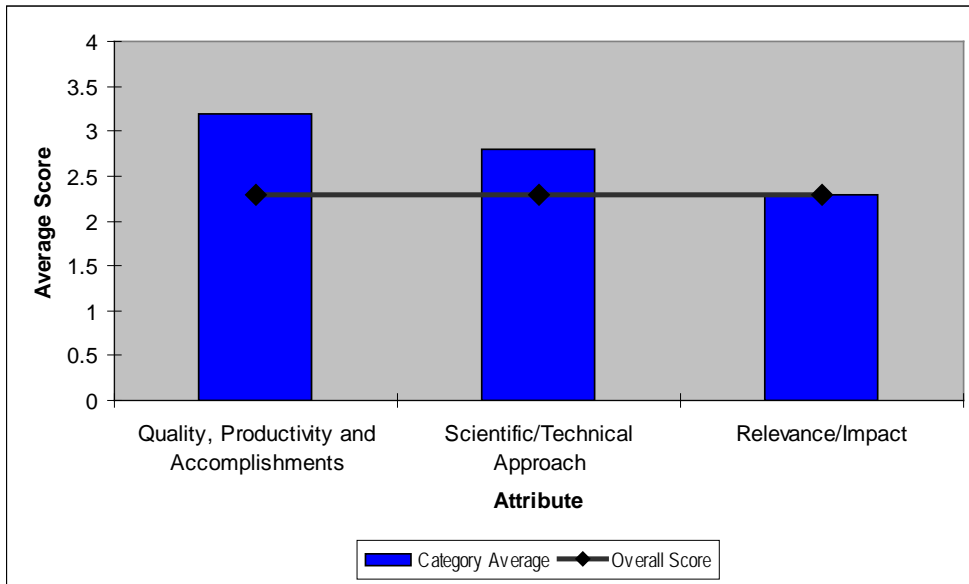


**Earth-Abundant Semiconductors**

**Principal Investigator: Harry Atwater, California Institute of Technology**



This project is investigating the possibility of multi-junction solar cells composed of earth-abundant semiconductor materials such as Si, Cu<sub>2</sub>O, Zn<sub>3</sub>P<sub>2</sub>, and FeS<sub>2</sub>. The research is designed to exploit recent advances in plasmonics to realize high-efficiency solar cells, based on enhanced absorption and carrier collection in optically thin film and quantum dot absorber layers.

**Quality, Productivity and Accomplishments (Average Rating 3.2)**

**Rating      Comments**

2.0      Slow - Mostly a theoretical study based on the idea that earth abundant materials are necessary. Productivity limited by diffuse approach. There are two projects here in one; the plasmonic work and the Zn<sub>3</sub>P<sub>2</sub> and CuO<sub>x</sub> work. The goal and scope is commendable, but the focus should be narrowed so that meaningful results can be obtained in the timeframe of the project. It is going to be clear in a few experiments, combined with some very basic economic modeling, which pathway is going to have the highest likelihood of success. This should be done in the next 6 – 9 months. Given the technical challenges and the limitations on personnel and equipment, this is the only logical course of action for project management.

3.0      Objectives: 1) Synthesis of two-junction solar cells with top subcells composed of earth-abundant compound semiconductors including quantum dots, 2) Design plasmonic structures to enhance solar light absorption in ultrathin film Si and wide bandgap earth-abundant Zn<sub>3</sub>P<sub>2</sub> and Cu<sub>2</sub>O films and low-dimensional semiconductor structures, and 3) Cost-based targets for the final materials based upon SAI guidelines. These are appropriate objectives, and to his credit, the researcher does not default to the generic descriptions.

Accomplishments: 1) Fabricate high purity CVT Zn<sub>3</sub>P<sub>2</sub> wafers; characterize via PL, 2) Deliver plasmon-enhanced absorber design for Si thin film cell, and 3) epitaxial growth of Cu<sub>2</sub>O on MgO. Accomplishments are consistent with the outlined program objectives; however, there are additional concerns regarding the overall performance of the two junction cells. Prof. Atwater should provide estimates of projected efficiencies of the earth abundant semiconductors within the context of currently existing technologies and future efficiency goals needed for SETP targets.

Qualifications of Research Team and Available Resources: The researcher and his team are well-qualified for the proposed tasks with a demonstrated record of achievement in the areas of

technology. The resources available to the research team are appropriate to task.

- 4.0 Atwater and Lewis are an excellent team, there is clearly no issue with resources here. For  $\frac{3}{4}$  of a year's worth a funding, they have made good progress towards their goals.
- 3.0 Quite a few new projects started, not all interconnected. Very good team assembled, and at the top of their fields. Good progress in all of the proposed projects, given the amount of time that has passed. I would prefer to see them separated, and separately funded. Are these really "out of the box" concepts? Earth abundant, maybe. Plasmonics, probably yes.
- 4.0 The PI has multiple other programs, and this has aided the quality of the resources involved. This team got a lot done compared to other programs.

### Scientific/Technical Approach (Average Rating 2.8)

Rating	Comments
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| 2.0 | Not focused. There are two projects (earth abundant and plasmonic). Neither shows any real promise as of yet. Efficiency of $\text{Cu}_x\text{O}/\text{Zn}_3\text{P}_2$ is low in literature. These materials are already well known. The approach is only minimally innovative for these. $\text{Zn}_3\text{P}_2$ was studied as a Schottky barrier solar cell in the mid 1980s. Moderate efficiencies of 4 – 6 % have already been obtained. Although the present PI has gone a long way in terms of the characterization of its basic material properties (L, PL etc.) he has failed to address the limitations that pushed this material to the sidelines in previous decades (stability and reactivity). It is applaudable to make a heterojunction, but the PI has failed to consider lattice constancy and interface recombination for that approach. A band diagram, as was shown, simply does not paint a realistic picture. |
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The story for  $\text{Cu}_x\text{O}$  is much the same. One simply cannot throw it together with another oxide and think that it is going to be a new solar cell. The literature is extensive for this material since it was one of the world's first rectifier and studied semiconductor material. Attempts to make heterojunctions have resulted in copper metal at the interface due to redox potential considerations. All of these aspects and histories should be reported on during the next report or review. Plasmonics is interesting, but a cost structure should be put in place to see if additional costs are offset by expected efficiency gains for earth abundant materials that can be used for plasmonics (e.g. Si, Ag etc.).

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| 3.0 | Prof. Atwater's presentation and report demonstrated good accomplishment towards his project objectives; however, the approach to these goals was difficult to ascertain as there are two distinct research projects contained within a single program. The choice of $\text{Zn}_3\text{P}_2$ and $\text{Cu}_2\text{O}$ materials is interesting; especially since each material had been previously considered as a candidate solar material. Long term chemical stability of $\text{Cu}_2\text{O}$ will present a challenge. The temperature dependence of the $\text{Zn}_3\text{P}_2$ electronic characteristics is also a concern. The plasmonic component of this program is well underway, and methods to generate uniform, dense arrays of quantum dots are under development. Scale-up of these methods while controlling size and structural dispersion will become keys to future implementation of this technology.                        |
| 2.0 | I am not optimistic for the materials systems chosen for the semiconductor work. Neither $\text{Zn}_3\text{P}_2$ nor $\text{Cu}_2\text{O}$ are new materials so the project's novelty relies on their ability to synthesize better (i.e. more higher purity) samples for characterization. The strong temperature dependence of the $\text{Zn}_3\text{P}_2$ bandgap measured thus far does not seem to bode well for device applications, however, especially since the initial target was for a bandgap of 1.7 – 1.8. The $\text{Cu}_2\text{O}$ would seem to have potentially disastrous stability problems, particularly in the presence of any amount of moisture (however, it should be noted that $\text{Cu}_2\text{O}$ nanoparticles have been demonstrated as stable in water so perhaps we should not hurry to naysay the potential here). It is unclear how the epitaxial layers, grown on $\text{MgO}$ , will be integrated into a device. |

Frankly, the title of the project somewhat turns me off- if “earth abundance” were the important issue we would all be burning hydrogen and there would be no energy problem. The relevant questions are how easy is it to get the material in the right form, does it work and for how long? Getting some device results from these materials (planned in '09) is absolutely critical in order to maintain faith in their ability to achieve worthwhile goals. The plasmonic coupling piece is much more exciting but has not yet passed beyond the modeling and simple fabrication stage. The results look promising but there will clearly be scale-up issues to be addressed eventually. I will be very interested to see what results come out of this side of the project, however.

- 4.0 Interesting approach to exploring earth-abundant materials – the problem that I see is that most of the easy to use earth abundant materials are in use, those that are left are problematic in one form or another. Is Zn3P2 going to be sufficiently stable? Cu2O is notorious already for its instability. Need answers to these questions for DOE. Plasmonics is more out of the box and exploratory.
- 3.0 There are really two projects here:
1. New large bandgap semiconductors
  2. Plasmonic enhancement of absorption
    1. Zn3P2 has only 1.3-1.5 eV bandgap, compares to 1.7-1.8eV optimal for double junction on Si. Need to calculate benefit in efficiency on crystalline Si. Maybe would work better on low efficiency u-c Si. Or, could work better as a single junction. Also, what about the cost of epitaxy – does this make economic sense?
    2. The plasmonic incoupling scheme can be thought of as a solar concentrator. If it doesn't track the sun then it should follow the limits that govern all solar concentrators, i.e.  $2x(\text{index})^2$ . The PI suggested that the plasmonic approach can exceed the performance of optical concentrators. This needs more support. It is essential to see data here showing high optical concentrators independent of incidence angle, otherwise many will not believe the claims.

### Relevance/Impact (Average Rating 2.3)

Rating	Comments
1.0	Too little accomplished for too diffuse goals. One can throw 10 times the number of funds and researchers at the approach and not have it yield anything in 3 years. It is suggested that the project quickly screen approaches and focus on the one that is most promising in terms of cost and efficiency. Devices should be made within the next 6 – 9 months and from that work the most promising single pathway should be explored. If that line is exhausted, or blocked, the most promising path can be undertaken.
2.5	This effort provides evidence that there is more than pure efficiency issues that need to be addressed by the SETP program. Prof. Atwater's research examines two relevant and essential issues for the widespread deployment of solar technology; are there other means to increase efficiency other than conventional materials re-configurations, and will there be sufficient materials supply. Both of these issues are topical, and the materials availability issue has not been addressed sufficiently in previous work. However, the concept of plasmonic design has already been adopted by other solar researchers, suggesting that the 'new-ness' factor of this approach may be past. At some level, it is difficult to confirm the progress of this work. As prototypical junctions have been prepared or are currently in preparation, this reviewer expected to see more complete experimental characterization of these new materials, possibly in the form of I-V curves.
2.0	The plasmonic coupling work, if proven and scaled to large areas, could be extremely impactful. Perhaps even without the ability to aggressively scale, there could be applications in

concentrator geometries. The novel semiconductor research has laid good groundwork and, indeed, both parts of the research have made good progress but it is not yet obvious whether it represents good progress toward DOE goals and objectives.

- 3.0 Two quite different project areas – very big vision, but is there enough money in this effort to make adequate progress on both? I would focus on the plasmonics approach, which I think has a bigger impact, and is more in keeping with the “Exploratory” nature of this program. IF there is sufficient funding and IF success is achieved in both areas, impact would be high.
- 3.0 The lack of high quality widegap semiconductors is a very important problem that has limited the opportunities for higher efficiencies via multijunctions. Crystalline Si + a widegap semiconductor should push easily past 30% (theoretical max is 42% if I remember). Without sacrificing VOC, the only proven 1.7-1.8eV semiconductor is GaInP. But this material seems destined to cost >>\$10k/m<sup>2</sup> for the foreseeable future. So the ZnP, CuO project is a high risk, but potentially high return project. The risks include poor stability, and growth difficulties - can it be lattice matched on Si? I am concerned, however, that the data already demonstrates that these materials won't make it; see previous comments. It might be time for the PI to re-justify this work in light of the current results. The plasmonic approach is novel and a strength of the PI. I'm concerned about the cost of fabricating the antennas/incouplers and also the compatibility of this approach with realistic PV structures.

### Overall (Average Rating 2.3)

Rating	Comments
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| 1.0 | This was the least focused of all the projects reviewed in this track/session. See comments above. Project is 2 projects in one. Goals for next 2 years should already have been done. The Zn <sub>3</sub> P <sub>2</sub> PL work should differentiate direct and indirect bandgap possibility from the possibility of an optically active defect. This could perhaps be done by correlating PL and absorption spectrum work and plotting absorption with the appropriate power law (1/2, 2).   |
| 2.7 | This presentation described two separate and distinct programs, each performing at an almost good level, with the combination detracting attention to achievement on a single topic. The plasmonics works described by Prof. Atwater is an important research area with a sound fundamental basis provided by the combination of his work within this program, but also from his Office of Science funding. The overall impact of this work should be categorized as an emerging and undergoing technology transition. Other solar technologies have noted the potential improvement in efficiency offered by this approach, and the researcher should have acknowledged their contributions and/or the limitations that these approaches would face without his current investigation. |

The selected materials systems ZnP and CuO were interesting choices considering their past histories as solar materials. While Prof. Atwater acknowledged previous ZnP efforts by Catalano and Barnett, he needs to address how his current efforts will address the exploratory aspects for future technology spanning the next 5-10 years. He should not be satisfied by merely reaching comparable efficiencies to current technologies, especially considering the escalating efficiency and cost objectives of the Solar America Initiative.

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| 2.0 | My scores are dragged down somewhat by the difficulty of reviewing what is essentially two entirely independent projects in one unit. Both halves have merit but the zinc phosphide and copper oxide semiconductor work seems to have a relatively low probability of success. While there is a very urgent need to search for new novel semiconductors, it might perhaps be more appropriate to make such an effort in a hypothesis driven fundamental science portfolio such as BES should be funding rather than a milestone-driven applied initiative like SETP. The plasmonic coupling work, in contrast, has demonstrated real improvements on a GaAs cell and |
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could easily be a high-impact project independent of the whole “Earth Abundant” project.

- 3.0 Is  $Zn_3P_2$  stable with respect to environment? Is this going to be one of the key limitations to such materials? As with many of the research programs funded by this DOE money, seems to be too many issues being addressed at once? Is this by design? Hard to see relationship between these efforts. Good work in both areas, but tie them together, or work on one of them!
- 3.0 This project should be commended for its ambition.