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Overcoming the bandgap limitation on solar cell materials

A. Niv,^{1,a)} Z. R. Abrams,^{1,2,a)} M. Gharghi,¹ C. Gladden,¹ and X. Zhang^{1,2,3,b)}

¹NSF Nanoscale Science and Engineering Center (NSEC), 3112 Etcheverry Hall, University of California, Berkeley, California 94720, USA

²Applied Science and Technology, University of California, Berkeley, California 94720, USA

³Materials Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA

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The thermodynamic efficiency of a single junction solar cell is bounded by the Shockley-Queisser detailed balance limit at $\sim 30\%$ [W. Shockley and H. J. Queisser, *J. Appl. Phys.* **32**, 510 (1961)]. This maximal efficiency is considered achievable using a semiconductor within a restricted bandgap range of 1.1-1.5 eV. This work upends this assumption by demonstrating that the optimal material bandgap can be shifted to lower energies by placing selective reflectors around the solar cell. This technique opens new possibilities for lower bandgap materials to achieve the thermodynamic limit and to be effective in high efficiency solar cells. © 2012 American Institute of Physics. [doi:10.1063/1.3682101]

The range of ideal photovoltaic materials is limited by the matching of the bandgap of the photovoltaic material to the solar spectrum, and lies within 1.1-1.5 eV.^{1,2} This range encompasses silicon (Si, 1.12 eV), gallium arsenide (GaAs, 1.42 eV), cadmium telluride (CdTe, 1.49 eV) and copper indium gallium selenide (CIGS, 1-1.7 eV), which are currently the primary materials for solar cells. The limit is imposed thermodynamically by the detailed balance model,^{3,4} in which a perfect solar cell will absorb light with energy above the bandgap and the only loss mechanism considered is radiative recombination. At open-circuit conditions, the flux of photons absorbed by the cell must equal the flux of photons emitted by the semiconductor encapsulated by the following equation:⁴

$$\Omega_S \int_{E_g}^{\infty} \frac{E^2 dE}{\exp[E/kT_S] - 1} = \Omega_o \int_{E_g}^{\infty} \frac{E^2 dE}{\exp[(E - qV_{oc})/kT_c] - 1}, \quad (1)$$

where Ω_S is the solid angle subtended by the sun (6.85×10^{-5} sr), Ω_o is the solid angle of emission out of the cell (2π for a flat plate, 4π for a sphere^{3,4}), k is Boltzmann's constant, q is the electronic charge, T_S and T_c are the sun (6000 K) and the cell (300 K) temperatures, respectively, E_g is the bandgap of the cell, and V_{oc} is the open-circuit voltage. Equation (1) can be used to isolate an approximate form for V_{oc}

$$qV_{oc}^{reg} \cong E_g \eta_C + kT_c \ln[(\Omega_S/\Omega_o)(T_S/T_c)(\alpha_{S1}/\alpha_{c1})], \quad (2)$$

where $\eta_C = (1 - T_c/T_S)$ is the Carnot efficiency,^{4,5} and $\alpha_{S1} = 1 + 2kT_S/E_g + 2(kT_S/E_g)^2$ and $\alpha_{c1} = 1 + 2kT_c/E_g + 2(kT_c/E_g)^2$ are small correction terms to the integral.^{6,7}

As can be seen from Eq. (2), V_{oc} is directly related to E_g , which is considered as the upper limit to the extractable

voltage from the cell.⁸⁻¹¹ While a larger bandgap gives rise to a higher voltage, it simultaneously reduces the absorption and thus the current. Therefore, the essential trade-off in solar cell engineering is to choose the material bandgap that maximizes the efficiency, $P = I \times V$. Increasing the efficiency can also be obtained by limiting the emission out of the cell,¹² or by controlling the spectral^{11,13,14} or angular^{15,16} emission from the cell. Here we analyze the thermodynamics of adding a selective reflector to a cell and show that the bandgap limitation can be surpassed.

A graphic depiction of the concept is given in Fig. 1: A selective reflector is placed in front of the solar cell, which blocks all photons with energy between the bandgap E_g and a reflector bandwidth of Δ . In this case, higher energy photons are transmitted (blue) and can be absorbed by the cell, while lower energy photons (red), including those that would match the bandgap, are reflected. The same mechanism also

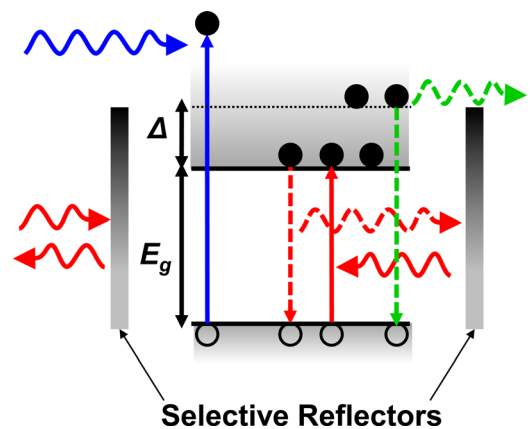


FIG. 1. (Color online) A spectrally selective reflector prevents photons with energies between the bandgap (E_g) and the reflector edge (Δ) to be absorbed (red lower left arrows), while allowing higher energy photons to be transmitted (blue upper left arrow). This reflector confines band-to-band recombination photons (dashed red line) from escaping, resulting in an accumulation of electrons (black dots) such that the Fermi level (dotted line) is shifted. At equilibrium, photons escape the cell (dashed green arrow, upper right) with energies above the bandgap, shifted by the reflector bandwidth.

^{a)}A. Niv and Z. R. Abrams contributed equally to this work.

^{b)}Author to whom correspondence should be addressed. Electronic mail: xiang@berkeley.edu.

confines the re-emitted photons from radiative recombination (dashed red) within the cell/reflector system. Since the band edge emitted photons (red) are fed back into the device by the reflectors, the effective Fermi level of the electrons will build up (dotted line) to allow emission above the threshold of the reflector (dashed green). Eventually, photon flux equilibrium⁴ is reached when photons are re-emitted with energies above $E_g + \Delta$ (dashed green).

To describe the thermodynamics of this system from the flux equilibrium perspective, Eq. (1) must be modified to include the feedback re-emission on the absorption side as well as the decreased absorption of solar flux from the threshold of the selective reflector:

$$\begin{aligned} \Omega_S \int_{E_g+\Delta}^{\infty} \frac{E^2 dE}{\exp[E/kT_S] - 1} + \Omega_o \int_{E_g}^{E_g+\Delta} \frac{E^2 dE}{\exp[(E - qV_{oc})/kT_c] - 1} \\ = \Omega_o \int_{E_g}^{\infty} \frac{E^2 dE}{\exp[(E - qV_{oc})/kT_c] - 1}. \end{aligned} \quad (3)$$

Here, the limits of integration of the second term coincide with the bandwidth of the selective reflector, Δ . By rearranging the limits of integration of the semiconductor emission we obtain

$$\Omega_S \int_{E_g+\Delta}^{\infty} \frac{E^2 dE}{\exp[E/kT_S] - 1} = \Omega_o \int_{E_g+\Delta}^{\infty} \frac{E^2 dE}{\exp[(E - qV_{oc})/kT_c] - 1} \quad (4)$$

Solving Eq. (4) for V_{oc} , we can isolate the approximate form of V_{oc} for the selective reflector system

$$qV_{oc}^{SR} \cong (E_g + \Delta)\eta_C + kT_c \ln[(\Omega_S/\Omega_o)(T_S/T_c)(\alpha_{S\Delta}/\alpha_{c\Delta})], \quad (5)$$

where $\alpha_{S\Delta} = \alpha_{S1} + 2\Delta/E_g + (\Delta/E_g)^2 + 2kT_S\Delta/E_g^2$ and $\alpha_{c\Delta} = \alpha_{c1} + 2\Delta/E_g + (\Delta/E_g)^2 + 2kT_c\Delta/E_g^2$. Comparing Eqs. (2) and (5) reveals the increase in V_{oc} of the system with the selective reflector by a factor of $\Delta\eta_C$

$$\begin{aligned} V_{oc}^{reg} &\propto E_g, \\ V_{oc}^{SR} &\propto E_g + \Delta. \end{aligned} \quad (6)$$

Equation (6) thus states that a selective reflector may result in V_{oc} larger than E_g without violating *thermodynamic* considerations. Since the photons are retained within the cell there is no significant entropic loss due to the reflector, assuming perfect reflectance and no non-radiative losses.

Using this formalism, the thermodynamic efficiency of cells with the selective reflector can be calculated numerically for varying bandgaps and reflector bandwidths, as shown in Fig. 2(a). The maximal efficiency remains $\approx 30\%$, which is the Shockley-Queisser limit and is independent of the selective reflector design. From the *thermodynamic* perspective, this efficiency can even be reached for bandgaps

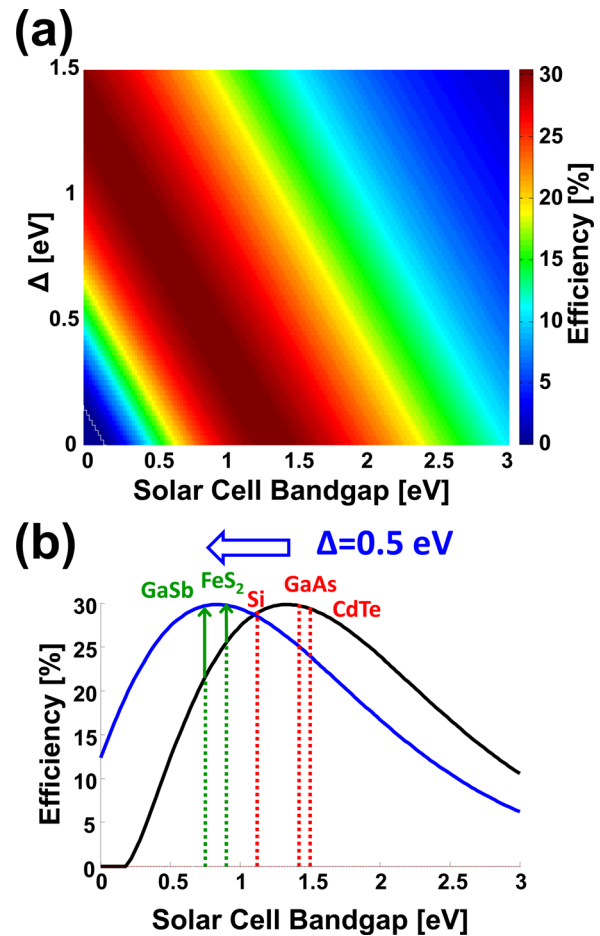


FIG. 2. (Color online) (a) Total thermodynamic efficiency calculation for varying bandgaps (E_g) and reflector bandwidths (Δ). The $\approx 30\%$ efficiency peak shifts to the left for larger values of bandwidth. (b) A reflector bandwidth of 0.5 eV will shift the regular detailed balance curve (black curve, right) to the left (blue curve, left), allowing non-optimal semiconductors to achieve maximal thermodynamic efficiency. Overlaid are the bandgaps of some semiconductors traditionally used in solar cells (Si, GaAs and CdTe; red), as well as some potentially new solar cell materials (GaSb and FeS₂; green).

approaching zero. Fig. 2(b) emphasizes the importance of the result: using a reflector with a bandwidth of $\Delta = 0.5$ eV, the traditional Shockley-Queisser curve (black) can be shifted to the left (blue), thereby enabling the consideration of materials that would have otherwise been non-optimal for use as high efficiency solar cells.

Real materials will restrict the desired rise in voltage due to losses.¹⁷ In particular, small bandgap devices suffer from increased Auger recombination,^{10,18} free-carrier absorption, and non-linear effects due to high intrinsic carrier concentrations.^{19,20} This high carrier and photon concentration may induce refractive index changes¹⁹ as well as band gap renormalization,²⁰ which may counter the desired effect described here. Furthermore, non-radiative recombination via trap centers (Shockley-Read-Hall) severely limits the efficiency of indirect bandgap devices^{18,21} requiring pristine crystalline materials to be used. From the *semiconductor* perspective, the voltage shift will be limited to the bandgap of the material, $qV_{oc}^{max} \leq E_g$,^{8,11} with increased carrier concentration affecting the stimulated emission.⁹ However, from the *thermodynamic* perspective this limitation of the bandgap is not fundamental.

Considering Auger recombination as the most likely limiting mechanism, this loss can be modeled as an additional flux term on the right hand side of Eq. (4) using the expression $LC_{Aug}n_i^3\exp(3qV/2kT_c)$.¹⁸ Besides the operating voltage V , the Auger recombination is dependent upon the intrinsic carrier concentration, n_i ; sample thickness, L ; as well as the material's Auger coefficient, C_{Aug} , which can be averaged for n and p type carriers. From a fundamental perspective, these constants can be technologically improved upon. In particular, both bandgap engineering^{22,23} and nanostructures²⁴ having been shown to lower the Auger recombination rate. Therefore, the following analysis can be considered as an upper limit for Auger losses in the cell-reflector device.

Figs. 3(a) and 3(b) display the efficiency vs. cell thickness ($L=0.1\text{--}10\text{ }\mu\text{m}$) and varying reflector bandwidth

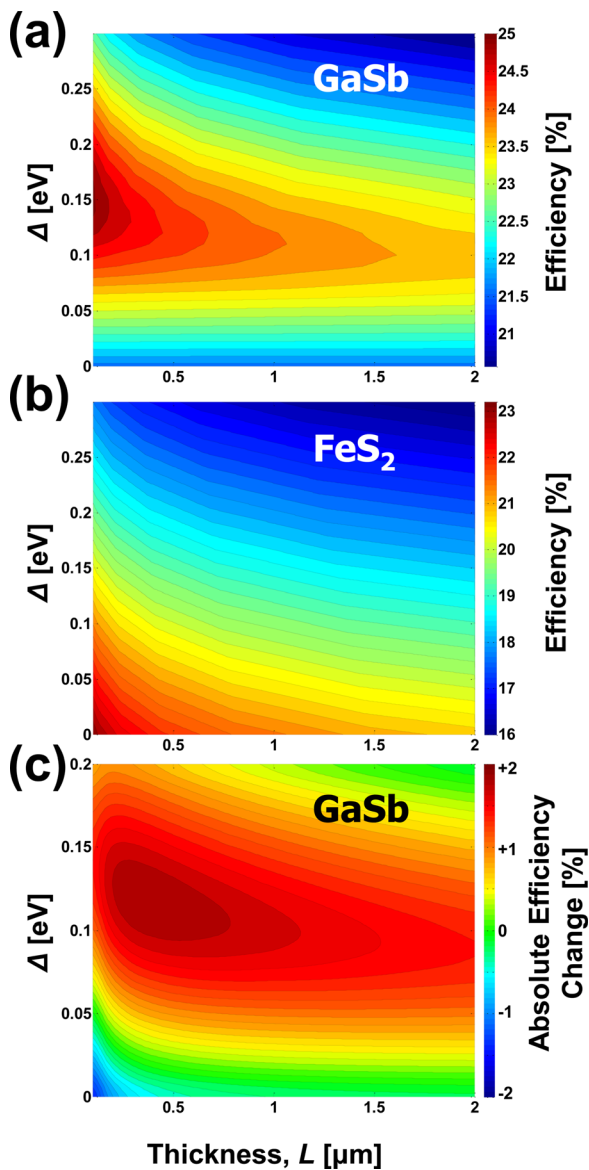


FIG. 3. (Color online) Efficiency increase per thickness (L) and reflector bandwidth (Δ) including Auger losses for: (a) GaSb, a direct bandgap material with $E_g=0.73\text{ eV}$, $n_i=1.5\times 10^{12}\text{ cm}^{-3}$ and $C_{Aug}=5\times 10^{-30}\text{ cm}^6/\text{s}$; (b) FeS₂ (Pyrite), $E_g=0.9\text{ eV}$, $n_i=2.78\times 10^{12}\text{ cm}^{-3}$ and $C_{Aug}\approx 10^{-29}\text{ cm}^6/\text{s}$. (Assuming Auger recombination as the dominant loss mechanism.) (c) The absolute efficiency change of GaSb, including the absorption coefficient dependence on the thickness (L), in addition to the Auger losses.

($\Delta=0\text{--}0.3\text{ eV}$) and including Auger losses for GaSb ($E_g=0.73\text{ eV}$), a direct bandgap semiconductor,^{25,26} and FeS₂ ($E_g\approx 0.9\text{ eV}$), an indirect semiconductor²⁷ that has recently attracted attention due to its strong absorption and elemental abundance.² In both examples, the cell absorption is taken as unity to represent the case of maximal efficiency. This assumption is acceptable if good anti-reflection coatings,¹⁸ light-trapping, or absorption-enhancement techniques are used.^{28,29} The increase in efficiency beyond the baseline without a selective reflector ($\Delta=0\text{ eV}$) is perceptible for GaSb, whereas the Auger recombination effectively curtails the increase in FeS₂. However, it is expected that decreasing the Auger recombination coefficient ($C_{Aug}<10^{-31}$, see Ref. 26) will give rise to higher efficiencies for FeS₂ as well.

We also include the efficiency calculation for GaSb including the absorption coefficient²⁵ in Fig. 3(c). Here, an absolute efficiency increase of $\sim 2\%$ appears ($21\% \rightarrow 23\%$) at $L=0.4\text{ }\mu\text{m}$ and $\Delta=0.12\text{ eV}$. This peak occurs at a smaller thickness than what would typically be required for a GaSb device and indicates yet another advantage of the selective reflector: a substantial material reduction while increasing the efficiency.¹³

The shifting of the effective bandgap as portrayed in Fig. 1 is reminiscent of the dynamic Burstein-Moss effect,^{30,31} with the feedback of re-emitted photons emulating the degenerate doping conditions in semiconductors. The Burstein-Moss effect is known to blue-shift the band-edge of the semiconductor effectively increasing E_g or inducing transparency by shifting the absorption edge.^{19,20,32} The Auger coefficient is also known to decrease under Burstein-Moss shifts effectively lowering this non-radiative recombination term,²² an effect that was not included in the calculation of Fig. 3. Although the shift in the apparent bandgap produced by the selective reflector is *thermodynamically* achievable, it is unknown to what extent real materials can support such large shifts.^{8–10} Experimental evidence of the dynamic Burstein-Moss shift has shown increases of up to 0.35 eV in CdSe³¹) and 0.16 eV in InSb.³³ These values surpass the bandgap by a relatively large amount in direct bandgap materials. The use of selective reflectors with indirect bandgap materials such as Ge ($E_g=0.67\text{ eV}$) has also been proposed.^{13,34} However, there are restrictions on the efficiency resulting from additional losses in these indirect bandgap materials, such as Shockley-Read-Hall recombination losses.²¹

In conclusion, we claim that the range of materials available for high efficiency solar cells can be extended by using a selective reflector system, thereby shifting the optimal bandgap to lower energies. This method does not aim to surpass the $\sim 30\%$ Shockley-Queisser efficiency limit but rather relaxes the restriction on available semiconductors. Since the selective reflector is an external modification to an otherwise standard cell, the proposed method presents only a small modification to the already intricate cell design and thus provides a novel route for improving single- and multiple-junction cell technologies.

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