The effect of photonic bandgap materials on the Shockley-Queisser limit

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The limiting efficiency of photovoltaic energy conversion was determined by Shockley and Queisser using the theory of detailed balance, which described the balance between absorption and emission of photons. However, when a material is placed on top of a solar cell that modifies the transmission of photons (e.g., a photonic crystal), both the absorption and emission of photons are modified. Here, we show how the addition of a photonic structure can lead to an *effective modification* of the energy bandgap of the material and can subsequently change its maximum theoretical efficiency. We consider the effect of non-ideal photonic structures and the effect of non-radiative recombination within the cell and find that, with realistic materials, efficiency gains of several percent can be achieved with the addition of photonic structures. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4742983]

I. INTRODUCTION

In 1961, Shockley and Queisser developed a formalism to calculate the limiting efficiency of a pn-junction solar cell.[1] This method describes the detailed balance of absorption and emission of photons which occurs at open circuit[2–6] and lays the theoretical foundation for many advances that have been made in the decades that have followed their original calculations. In order to surpass this limit, one must consider the assumptions that are made and find systems that violate these assumptions. Such schemes are sometimes referred to as third generation photovoltaics[7] and are usually aimed at reducing thermalization losses through hot carrier collection,[8] multi-exciton generation,[9–11] intermediate band collection,[12–14] or by channeling photons into absorbing layers whose bandgap energies are more closely matched to the incident photon energies, e.g., spectrum splitting or tandem multijunction solar cells.[15–22] Other techniques aim to circumvent this limit by exploiting various aspects of the derivation, which do not violate the overall assumptions of detailed balance; for instance, the use of angularly or spectrally selective filters,[3,23–26] which have found uses in intermediate band concepts[26] and multi-junction designs.[3]

In this paper, we will reevaluate the detailed balance assumptions and consider how photonic bandgap materials can modify the absorption and emission spectra of a photovoltaic device.

II. THEORY OF DETAILED BALANCE

In its most basic sense, a photovoltaic device absorbs some fraction of the incident solar flux and converts this energy into work. The absorption event gives rise to an electron-hole pair, which in turn can either be extracted via an external circuit or recombine. If the pair recombines, it can do so either radiatively with the emission of another photon or non-radiatively as an unrecoverable loss mecha-

nism. Photons emitted via radiative recombination can be reabsorbed or can exit the cell, which represents an unavoidable consequence of detailed balance. Non-radiative (NR) recombination, on the other-hand, can generally be reduced by using high quality materials with few trap states. In high quality materials like GaAs, the fundamental lower bound on non-radiative processes is limited by Auger recombination.

To understand why radiative recombination is an unavoidable consequence of detailed balance, we consider the total current generated by the cell when non-radiative processes are absent,

$$I_{tot} = q(\text{absorbed photons} - \text{emitted photons}), \quad (1)$$

where q is the charge on an electron. At open circuit conditions, the total current is zero. Because the cell is still under illumination, the absorption rate must equal the emission rate, and hence the cell must emit.

The current generated by the absorption of the incident photons is

$$I_L = q \int_{E,\Omega,A} a(E)F_s \cos\theta \, dE d\Omega dA, \quad (2)$$

where $a(E)$ is the absorptivity (i.e., the probability of absorbing a photon of energy E) and F_s is the spectral photon flux (i.e., the number of photons per unit time, energy, area A, and solid angle Ω) incident on the surface of the cell. The integration extends over the surface of the cell for all photon energies and incident angles θ. The differential solid angle is given by its usual form, $d\Omega = 2\pi \sin\theta d\theta$, where θ is measured from the surface normal and goes from 0 to $\pi/2$.

If we treat the illumination as a blackbody, the spectral photon flux is given from Planck's law as

$$F_s = \frac{2n^2}{h^3 c^2} \frac{E^2}{e^{E/k_B T_s} - 1}, \quad (3)$$

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where h is Planck's constant, k_B is Boltzmann's constant, c is the speed of light, and n is the refractive index of the material surrounding the cell, which is generally taken as vacuum. Figure 1(a) shows the normalized power density of a blackbody emitter at temperature $T_s = 6000\,\mathrm{K}$ (thick black line) and the above bandgap absorption within the cell (light shaded region), which can lead to photocurrent. Under standard conditions, the total illumination is a combination of the sun's illumination and the illumination of the surrounding ambient, which is typically much smaller.

When the cell is not illuminated, it is in thermodynamic equilibrium with its surroundings; it absorbs and emits like a blackbody at the ambient cell temperature $T = T_c$. Assuming that the emission is from excited carrier recombination, emission only occurs for wavelengths above the semiconductor bandgap energy, as depicted in Fig. 1(a).

Upon illumination, the cell is no longer in thermal equilibrium with its surroundings. The additional charge carrier separation leads to a Fermi level splitting characterized by a chemical potential $\Delta\mu = qV$. This splitting leads to an increase in the spectral photon flux out of the cell,

$$F_c(V) = \frac{2n^2}{h^3 c^2} \frac{E^2}{e^{(E-qV)/k_B T_c} - 1}, \tag{4}$$

and the total photon emission rate from the cell becomes

$$\int_{E,\Omega,A} e(E) F_c(V) \cos\theta \, dE \, d\Omega \, dA, \tag{5}$$

where $e(E)$ is the emissivity (i.e., the probability of photon emission). At steady-state, the current densities must balance, and we get $e(E) = a(E)$. The current-voltage characteristic for the device can then be described by

$$I_{tot} = I_L + q \int_{E,\Omega,A} a(E) F_c(V=0) \cos\theta \, dE \, d\Omega \, dA$$
$$- q \int_{E,\Omega,A} a(E) F_c(V) \cos\theta \, dE \, d\Omega \, dA, \tag{6}$$

where the second term corresponds to illumination by the ambient at T_c. Note that the spectral photon flux from the ambient is the same as the photon flux out of the cell with $V = 0$. With the approximation $e^{(E-qV)/k_B T} \gg 1$, Eq. (6) becomes

$$I_{tot} = I_L - I_0 (e^{qV/(k_B T_c)} - 1), \tag{7}$$

where I_0 is the reverse saturation current. It is clear that I_0 depends on the absorptivity $a(E)$ and on the integration of θ. In order to calculate a maximum limiting efficiency, we will consider a solar cell with an ideal mirror back reflector that absorbs all above bandgap energy photons ($a(E) = 0$ for $E < E_g^{SC}$ and $a(E) = 1$ for $E \geq E_g^{SC}$). Without the mirror back reflector, the θ integration would be increased by a factor of 2 because emission could occur through both the front and back surfaces. The reverse saturation current is then

$$I_0 = Aq \frac{n^2 \pi}{h^3 c^2} [1 - \cos(2\theta_e)] \int_{E=E_g^{SC}}^{\infty} E^2 e^{-E/k_B T_c} dE, \tag{8}$$

where θ_e is the emission half angle for the cell, which is usually taken to be $\pi/2$ (other cases will be considered in Sec. III).

The current-voltage relationship defined by Eq. (7) can be used to determine the power conversion efficiency,

$$\eta = \frac{I_{SC} V_{OC}}{P_{in}} FF, \tag{9}$$

where I_{SC} is the short circuit current, V_{OC} is the open circuit voltage, FF is the fill factor, and P_{in} is the input illumination power. Figure 1(b) shows that for increasing semiconductor bandgap, I_{SC} decreases, but V_{OC} increases. This tradeoff between the current and the voltage leads to the well-known semiconductor bandgap dependency of the overall cell efficiency (Fig. 1(c)).
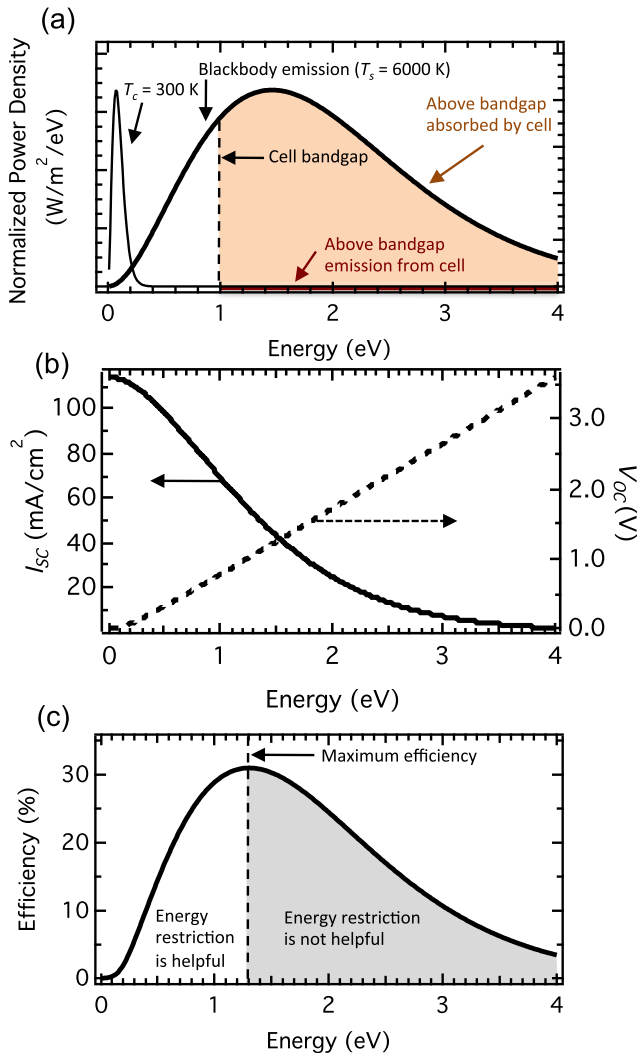
FIG. 1. Principles of detailed balance. (a) Normalized spectral power density showing above-bandgap absorption and emission from a solar cell. (b) Short circuit current and open circuit voltage as a function of semiconductor bandgap energy. Low bandgap semiconductors allow for higher currents but lower voltages. (c) Because of the tradeoff between current and voltage, the maximum efficiency occurs around 1.3 eV. For semiconductor bandgap energies below 1.3 eV, photon energy restriction is capable of improving efficiencies.
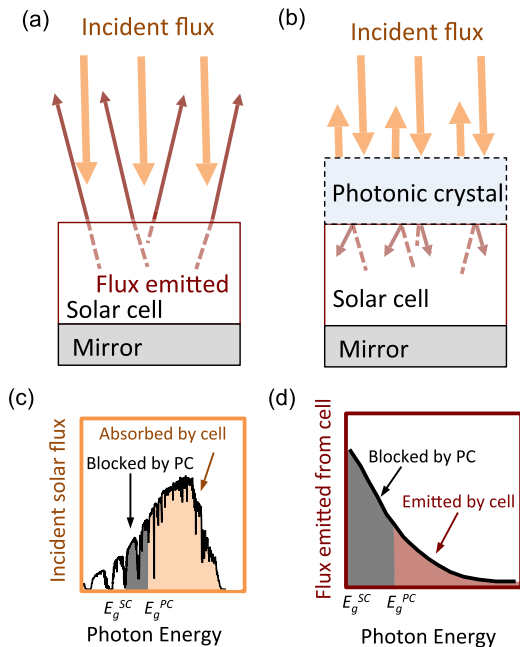
FIG. 2. Schematic depicting the effect of a photonic crystal on a solar cell. (a) At open circuit, a traditional solar cell both absorbs incident light and emits light by radiative recombination. (b) The addition of a photonic crystal causes reflection of both the incident solar flux and the flux emitted by the cell. (c) The photonic crystal blocks incident solar illumination with energies between E_g^{SC} and E_g^{PC} and hence reduces the absorption and short circuit current. (d) The photonic crystal also blocks the emission of photons with energies between E_g^{SC} and E_g^{PC}. The blocked emission improves photon recycling effects (see Fig. 3) and increases carrier concentrations, which lead to an improvement in the open circuit voltage.

III. PHOTONIC ASPECTS OF DETAILED BALANCE

There are several implicit assumptions that go into the analysis of Sec. II. (1) Each above bandgap photon incident on the cell is absorbed, and each below bandgap photon is transmitted, having no effect on the device. (2) Each absorbed photon creates exactly 1 electron-hole pair. (3) Each electron-hole pair either recombines radiatively with the emission of 1 photon or is separated and collected as current, implying that the mobility is infinite. With these assumptions, the semiconductor bandgap energy, E_g^{SC},

dictates which photons can be absorbed and emitted; however, a photonic structure can also be employed to further restrict the absorption and emission, as shown in Sec. III A and Sec. III B. In the calculations that follow, the illumination source will be taken as the AM 1.5 G solar spectrum, rather than the more simplified blackbody expression used in Sec. II.

A. Energy restriction

When a photonic crystal (PC) is placed on top of a semiconductor, both the absorption and emission are modified (Fig. 2). If the photonic crystal has a bandgap that extends from the semiconductor bandgap energy E_g^{SC} to the photonic bandgap energy E_g^{PC} (where $E_g^{SC} < E_g^{PC}$), any photons within this range will be reflected and will not reach the cell. This results in a decrease of I_L. Similarly, radiative recombination within the cell leads to emission of photons with energy greater than E_g^{SC}; however, only photons with energies greater than E_g^{PC} can escape the cell. Photons with energies between E_g^{SC} and E_g^{PC} will be blocked by the PC and will be continuously absorbed and re-emitted (photon recycling) at open circuit. The recycled photons lead to a high concentration of carriers and hence an increased open circuit voltage. The important effects of photon recycling are naturally included in detailed balance calculations;[4] however, they are neglected in many device-based models.

The increased carrier concentrations caused by photon recycling can increase the quasi-Fermi level splitting within the cell. For a typical solar cell, the quasi-Fermi level for the electrons resides within the semiconductor energy bandgap (Fig. 3(a)). When the cell is surrounded by a mirror and a suitable photonic crystal, the emitted photons are unable to escape the device. This effect leads to a high photon density, which further increases the carrier concentration. For an ideal photonic crystal with perfect reflectivity, the carrier concentration increases to the point that the lower level of the conduction band can become completely full. Thus, the electron quasi-Fermi level is pushed up into the conduction band (Fig. 3(b)). This leads to the possibility of an open circuit voltage that surpasses the semiconductor bandgap
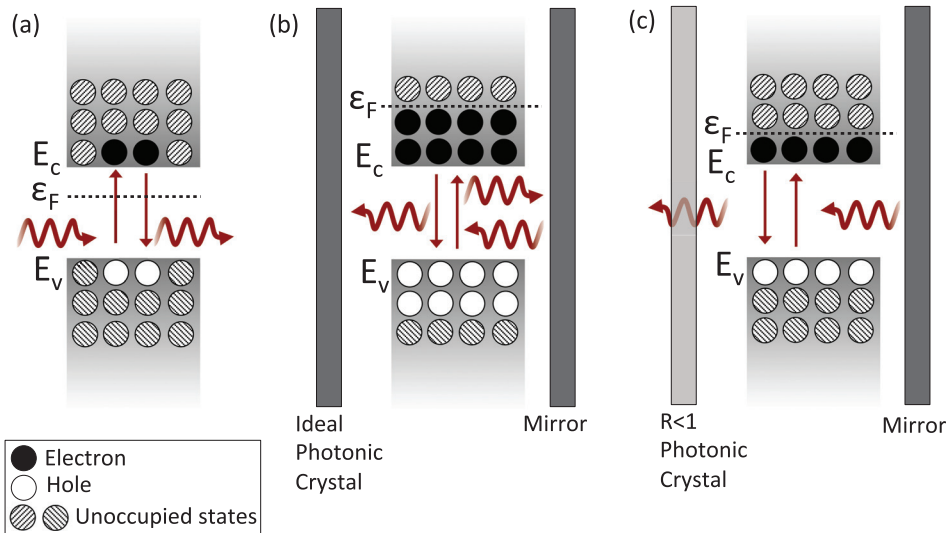

FIG. 3. Increase of the quasi-Fermi level splitting upon photonic structuring. (a) For a typical cell, the electron quasi-Fermi level resides within the semiconductor bandgap. (b) A photonic crystal and mirror back reflector results in an increase in photon recycling, which in turn increases the carrier concentration until the electron quasi-Fermi level is pushed into the conduction band. (c) Optical losses reduce the photon recycling and cause a reduction in the quasi-Fermi level splitting.

energy under ideal conditions. For a non-ideal photonic crystal, the light intensity inside the device is dramatically reduced. The reduction of the carrier concentration reduces the quasi-Fermi level splitting (Fig. 3(c)). Small amounts of emission out of the cell result in the electron quasi-Fermi level returning to below the conduction band.

In the absence of NR recombination, the equations of Shockley and Quesisser can be used, and the semiconductor bandgap energy is simply replaced with the photonic bandgap energy. Thus, for $E_g^{SC} < E_g^{PC}$, the addition of an ideal photonic crystal is equivalent to making a solar cell out of a material with an energy bandgap of E_g^{PC}. For a material like Ge that has a low bandgap energy (0.67 eV), the addition of a photonic crystal allows the effective bandgap to be increased and the efficiency improved (Fig. 1(c)). For semiconductors with bandgap energies equal to or great than $\sim$1.3 eV, restriction of higher energy photons decreases the cell's efficiency (Fig. 1(c)). A similar result was recently found for ideal selective reflectors.[33]

The total current in the cell without NR recombination is given by Eq. (7) and can be re-written as

$$I_{tot} = I_L - I_{dark}, \qquad (10)$$

where $I_{dark} = I_0[\exp(qV/k_BT) - 1]$. At open circuit, the absorbed solar photons create electron-hole pairs that subsequently recombine and re-emit photons. This causes an intensity buildup within the semiconductor because only photons within the critical angle of the escape cone will exit the material. Thus, the internal fluorescence is $4n^2/\sin^2\theta_e$ larger than the luminescence that escapes.[27] If some fraction of the recombination happens non-radiatively, we can define an additional term in Eq. (10), which corresponds to a NR current, I_{NR}. The internal luminescence efficiency can thus be written as

$$\eta_{int} = \frac{I_{dark}(4n^2/\sin^2\theta_e)}{I_{dark}(4n^2/\sin^2\theta_e) + I_{NR}}. \qquad (11)$$

Combining Eqs. (10) and (11), we get

$$I_{tot} = I_L - I_0\left(e^{qV/(k_BT_c)} - 1\right)\left[1 + \frac{4n^2}{\sin^2\theta_e}\left(\frac{1}{\eta_{int}} - 1\right)\right]. \qquad (12)$$

Non-ideal internal fluorescence yield reduces the overall efficiency of the photovoltaic device; however, the ability of the photonic crystal to improve the efficiency of low band gap semiconductors remains (Fig. 4(a)). It is also clear from the above arguments that the external emission is linked to the open circuit voltage. It has been rigorously shown that the inherent reciprocity between absorption and emission links the external quantum efficiency of a light emitting diode to the open circuit voltage of a solar cell.[28]

A non-ideal PC will also limit efficiency gains. Figure 4(b) shows the effect of a PC with varying amounts of reflectivity R for a solar cell with $\eta_{int} = 100\%$. A reflectivity of 90% means that 10% of the photons will not be restricted from absorption or emission over the range of energies from the semiconductor bandgap to the photonic bandgap. It can be seen from Fig. 4(b) that a high reflectivity is needed from the PC.
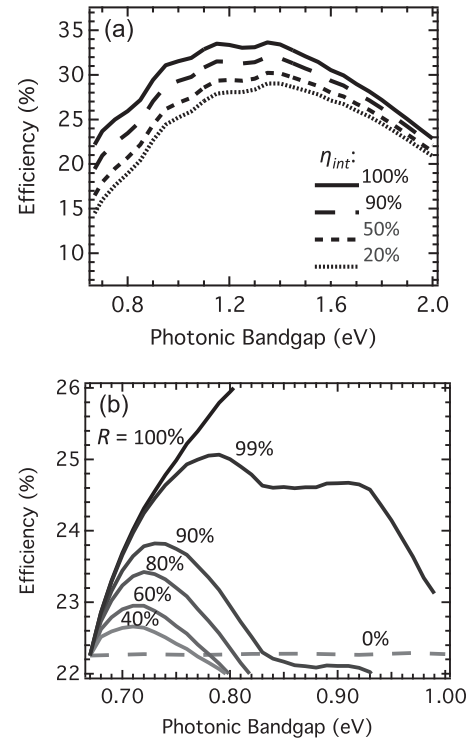

FIG. 4. PV efficiency of a low bandgap semiconductor ($E_g^{SC} = 0.67$ eV) can be improved with the addition of a photonic crystal. (a) Efficiency improves even for low internal fluorescence yield materials. (b) Efficiency for a low bandgap semiconductor as a function of photonic bandgap energy and different values of reflectivity, R. A highly reflective photonic crystal is needed to achieve significant efficiency enhancements.

For realistic material parameters, efficiency gains of several percent are possible. As a specific example, we consider a solar cell made from a material with a bandgap energy of 0.67 eV (e.g., Ge) and $\eta_{int} = 20\%$ (Fig. 5). The addition of an ideal photonic crystal with energy bandgap from 0.67 to 0.74 eV results in 2.8% absolute efficiency gain. For a PC with $R = 90\%$, the solar cell efficiency still improves by 1.8%. Note that the PC reduces the maximum current by limiting absorption; however, the overall cell performance improves because of an increase in the open circuit voltage (Fig. 5).
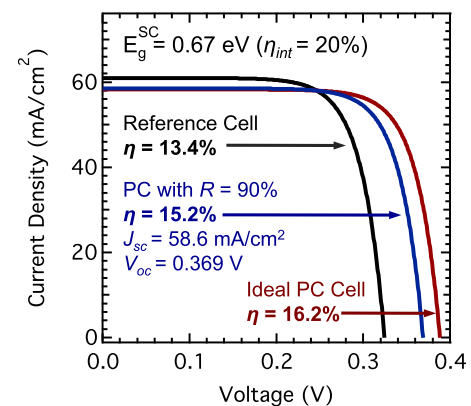

FIG. 5. The addition of an ideal photonic crystal with $R = 100\%$ (red curve) or a photonic crystal with $R = 90\%$ (blue curve) improves the efficiency relative to a cell with no photonic crystal (black curve) by 2.8% and 1.8%, respectively. The photonic crystal reduces the I_{SC} but increases the V_{OC}.

B. Angle restriction

Photonic crystals or other structures can also be used to tailor the angle of emission for photons exiting the cell. It is well known that restricting the emission angles can lead to an improvement in the V_{OC} (Refs. 4 and 29–31). This improvement is comparable to the improvement in the V_{OC} due to concentration of incident illumination and is caused by an increase of the carrier densities. When the emission half angle θ_e is limited to that of the sun $\theta_s = 0.267°$, the efficiency reaches that of maximum concentration, i.e., $> 40\%$ even under 1 sun illumination. When $\theta_e \neq \theta_s$, generation of *optical entropy* reduces the efficiency.[31]

While NR recombination is thought to limit the efficiency improvements possible by angle restriction,[4] there is experimental evidence[32] that GaAs has an internal florescence yield of 99.7%, making it an excellent case study. However, in order to achieve this improvement a photonic structure must be designed that is capable of fully restricting the emission of all photons. Previous studies have considered only these ideal photonic structures. Here, we show that angle restriction is only needed over a bandwidth of a few hundred meV to obtain a significant efficiency improvement.

Figure 6(a) shows schematically the emitted flux from the cell θ_e and the incident solar flux with possible concentration θ_x, where $X = \sin^2\theta_x/\sin^2\theta_s$ is the concentration factor. Efficiency improvements can be made by reducing the mismatch between θ_x and θ_e, which is accomplished by either increasing the concentration factor or reducing the emission angle (Fig. 6(b)). The introduction of NR recombination (red dashed lines) dramatically reduces the efficiency for small emission angles suggesting that a combination of angle restriction and concentration, as shown in Fig. 6(b), may provide the best option for high efficiencies.

If angle restriction is only possible over a range of wavelengths or the photonic structure only restricts some fraction of the photons, then the overall efficiency enhancement will be decreased. Suppose that the photonic structure that is constructed to restrict the emission angle is only effective from the semiconductor bandgap to an energy E_{rest} (Fig. 7(a)). Over this range of wavelengths, the photons are only emitted into the cone defined by $\theta_e = \theta_s$. For energies greater than E_{rest}, there is no restriction, $\theta_e = \pi/2$. Figure 7(b) shows that for a material with a semiconductor bandgap energy $E_g^{SC} = 1.43\,eV$, the emission angle only needs to be restricted over a few 100 meV to achieve a substantial improvement in the overall efficiency; however, a leaky structure ($R \neq 100\%$) makes the maximum achievable efficiency significantly lower. While a perfect photonic structure could allow for a solar conversion efficiency of near 42%, a photonic structure with $R = 99\%$ results in a solar conversion efficiency below 37% (Fig. 7(b)). Thus, the development of extremely high quality photonic structures is necessary. For a semiconductor with $E_g^{SC} = 1.43\,eV$ and $\eta_{int} = 99.7\%$ (e.g.,
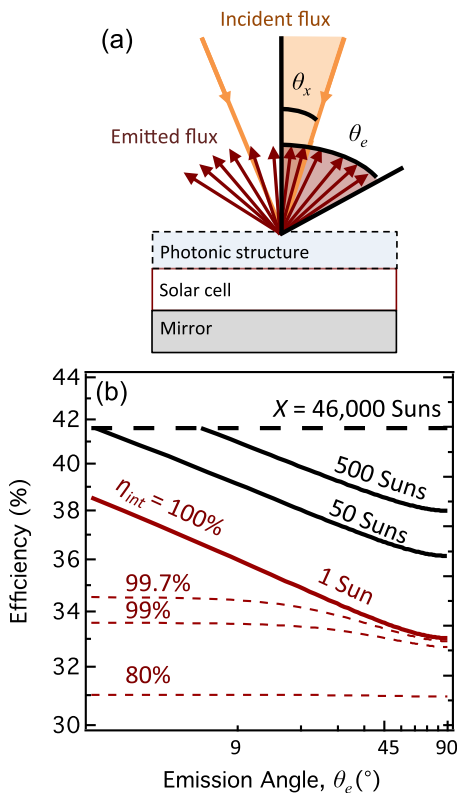

FIG. 6. Emission angle restriction. (a) Solar illumination, with possible concentration, has an incidence half angle θ_x. The solar cell has a restricted emission half angle of θ_e due to the photonic structure. (b) Efficiency improves as the emission angle is decreased. For larger concentration values, less angle restriction is needed to reach the maximum efficiency. However, small amounts of non-radiative recombination greatly reduce the efficiency enhancement due to angular restriction.
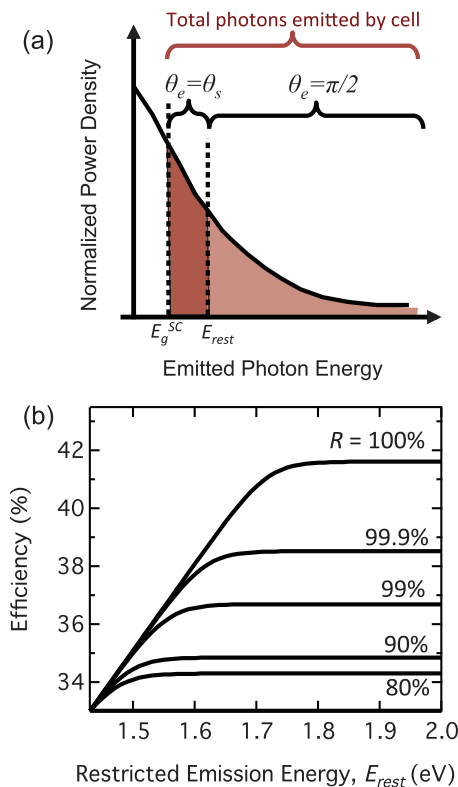

FIG. 7. A high quality photonic structure is needed for angle restriction. (a) Graphical representation of a photonic structure that restricts the emission angle θ_e of the cell to that of the sun's angle θ_s for a range of energies from E_g^{SC} to E_{rest}. (b) Rapid improvement in the efficiency can be achieved when a relatively narrow band of wavelengths is restricted in emission angle; however, for very high efficiencies, a nearly perfect photonic structure and a solar cell with almost no NR recombination are needed.

high quality GaAs) that is fully angle restricted ($\theta_e = \theta_s$ and $R = 100\%$), an absolute efficiency enhancement of 1.7% is found due to an improvement in the V_{OC}.

IV. CONCLUSIONS

The addition of a photonic structure to the top of a photovoltaic device is found to improve its efficiency by several percent. The improvement is based on restricting emission of specific energy photons, which in turn increases carrier concentrations and hence V_{OC}. Effects of non-ideal reflectivity and non-radiative recombination play an important role in determining the maximum achievable efficiency.

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