

APPROACHING THE 29% LIMIT EFFICIENCY OF SILICON SOLAR CELLS

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ABSTRACT

The so-called "limit efficiency" of a silicon solar operating at one-sun is well established at approximately 29%, and laboratory cells have reached 25%. The efficiencies of commercially available silicon solar cells have been increasing over time, however, only recently have the highest performance commercial cells reached 20% efficiency. This presentation discusses the prospects of how the limit efficiency may be approached more closely in practical cells. Surprisingly, presently available silicon has sufficient minority carrier lifetime to achieve the goal. In fact, all aspects are in place for approaching 29% except for the existence of a suitable passivated contact technology.

A BRIEF HISTORY OF LIMIT EFFICIENCIES

Since shortly after the announcement of the first silicon solar cell, whose efficiency was around 6%, there has been an ongoing sport of calculating how efficient a solar cell can potentially be. This has become known as the "limit efficiency." Two parallel tracks have been followed in this endeavor. The first tack exercises semiconductor device models to see how best to make the cell, and how efficient it could be if various losses were eliminated or reduced as much as possible. The first stab at predicting the limit efficiency using cell models was done by Prince only one year after the original cell announcement[1]. He calculated a limit efficiency of 21.6% for silicon using a cell model that would be familiar to workers today. A problem with this approach is that it is dependent on assumed material parameters, particularly the minority carrier lifetime. A cursory observation of the solar cell modeling equations reveals that if one assumes infinite carrier lifetime, the voltage and efficiency also become infinite. Clearly there are limits on carrier lifetime, but what are they?

The second approach uses thermodynamics to provide bounds on potential efficiency. This approach avoids getting mired in device details, and answers the question much in the manner that Carnot did when he calculated how efficient a steam engine could be. Shockley and Queisser did the job for solar cells in their seminal 1961 work[2]. They calculated the maximum efficiency of a single band-gap photovoltaic converter to be 30%. The optimum band-gap was 1.2 eV (Quite close to silicon's 1.12 eV). The Shockley and Queisser approach is easy to describe. They used a detail balance approach in which they

calculated the flux of blackbody photons at room temperature impinging on the cell that have an energy greater than the band-gap. For silicon's 1.12 eV band-gap this turns out to give a current of 0.27 fA/cm² per side of the cell. Each of these photons is assumed to generate an electron-hole pair. In thermal equilibrium, an equal number of photons must be emitted by recombining electron-hole pairs, balancing the above generation. A little arguing and one can see that this current is the saturation current, J_0 , of the cell, if one assumes that all recombination and generation is radiative. In addition, the radiative recombination will increase as the pn product is enhanced by application of an exterior terminal voltage, so that the net cell recombination is

$$J_r = J_0 \left(\frac{pn}{n_i^2} - 1 \right) = J_0 \left(e^{qV/kT} - 1 \right).$$

Cell modeling and efficiency calculation then proceeds as usual. Shockley and Queisser assumed that the sun's spectrum is that of a 6000K blackbody. This gives the efficiency of 30%. If they had assumed that it was the AM1.5 spectrum, they would have obtained about 10% higher efficiency, or 33%.

The above J_0 for silicon of 0.27 fA/cm² gives an open circuit voltage of 0.845 V. Readers will recognize that this is a rather high V_{oc} and low J_0 compared to the usual silicon values. The difference comes from non-radiative recombination. The above argument sets voltage and J_0 limits which cannot be surpassed. This is because the radiative recombination process cannot be eliminated by the detail balance argument, as it is the inverse of the radiative generation process. At the time of the Shockley & Queisser paper, the typical silicon cell J_0 was about 5 orders of magnitude greater than this. Today, the gap has closed to about 2 to 3 orders of magnitude, giving open circuit voltages of up to 0.720 V. The limit efficiency question boils down to how close this gap can become. Interestingly, Shockley and Queisser conjectured in their 1961 paper that practical silicon cells could reach 26%. The conclusion of this paper is that they were correct; that we will someday see 26% efficient laboratory cells, followed eventually by commercial cells of similar performance.

Tiedje, Yablonovitch, and Cody extended the analysis to include an AM1.5 spectrum[3]. They obtained a limit efficiency of 33.2% for a band-

gap of 1.15 eV. (More about their work below). The seminal work of Shockley and Queisser has been examined and extended by many authors, but the calculated limit efficiency has remained the same at 33% AM1.5. The interested reader is referred to the literature, for example reference [4]. Instead, we move to the device modeling approach.

Following Prince, workers continued to refine the device modeling approach to calculating the limit efficiency. Many models predicted that a cell with a band-gap around 1.4 eV would be optimum. This set off hopes that CdTe cell would be more efficient than silicon cells. What was neglected is the high lifetime obtained in silicon because of its indirect band-gap. Figure 1 illustrates the progress for silicon cell projections. Martin Wolf presented a series of papers in 1960[5], 1970[6] and 1980[7] that captured the then-current thinking. Limit efficiencies were relatively constant, going from that period from 24% to 25%, AM1.5. One reason for the rather constant result is that some factors improved over time with increased understanding and some deteriorated. For example, the negative impact of band gap shrinkage due to heavy doping effects became recognized in the 1980s; however the

ability to limit surface recombination by surface passivation was also recognized. In Wolf's 1980 paper he posited for the first time that surfaces could have zero recombination velocity by using hetero-junction contacts, as was emerging in the GaAs material system. These became known as minority carrier mirrors. At present, a perfect minority carrier mirror contact for silicon is still a dream; however, it is being approached by the amorphous silicon contacts used in Sanyo's HIT cells and the localized contacts used in the 24.7% record cell from UNSW[8]. By 1980, the limit efficiency was getting dangerously close to the best laboratory cells, which were begging to improve rapidly. Loferski came to the rescue, by developing a new cell design that included light trapping, as well as minority carrier mirrors[9]. He calculated a limit efficiency of 27%. This represents the first emergence of more modern models that generally assume light trapping, passivated surfaces, and nearly flat quasi-Fermi levels. Loferski's 1980 concept of light trapping assumed wedge-shaped solar cells. In 1982 the modern theory of light-trapping from diffuse reflectors was developed, giving improved accuracy[10]. After that, it was just a matter of refining the assumed material parameters.

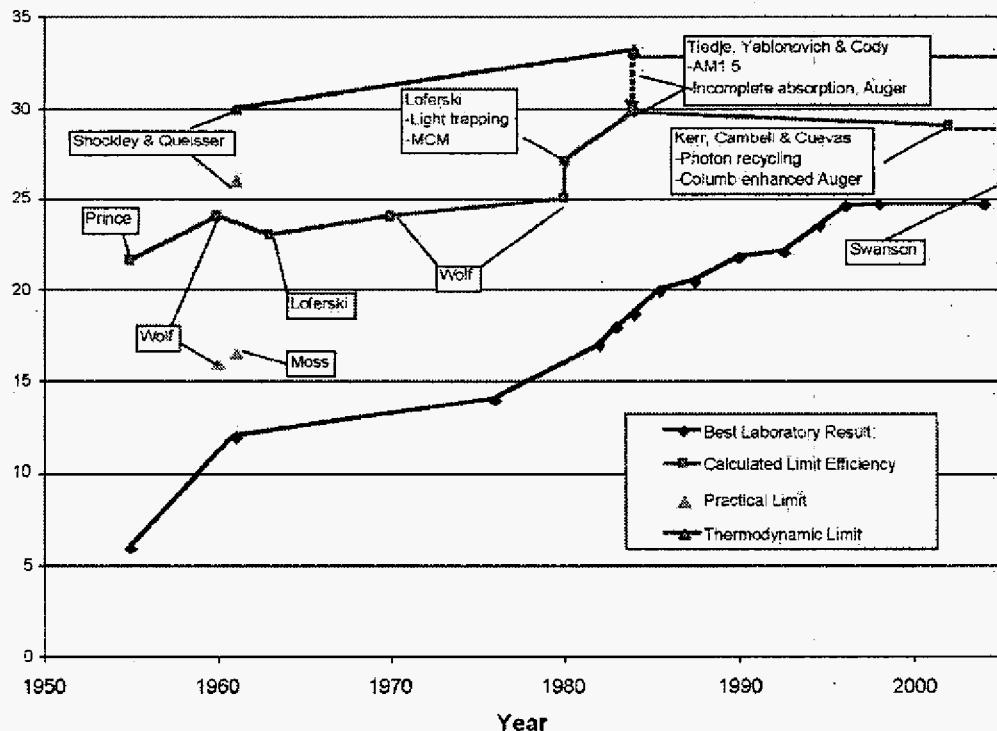


Figure 1. Progress in calculated limit efficiencies. AM0 efficiencies have been adjusted to AM1 by adding 10% relative.

As mentioned above, Tiedje, Yablonovitch and Cody calculated a maximum thermodynamic efficiency for a perfect absorber at 33.2%. This occurred at a band-gap of 1.15 eV. Going to silicon's 1.12 eV band-gap dropped this to 32.7%. In the same paper, they made a significant connection between thermodynamic and cell modeling analysis[3]. They computed the actual photo absorption for silicon cells with finite thickness and used the result to find the detailed balance saturation current. In this manner, cell thickness was incorporated into the thermodynamic analysis. This yielded a limit efficiency of 31.6% for silicon, and for the first time revealed the impact of silicon's rather weak band-edge absorption. They also incorporated a non-radiative recombination process, three particle Auger recombination, into the analysis. This is fair, as Auger recombination is intrinsic to silicon and cannot be eliminated. In so doing, they obtained a new device limit of 29.8%. The optimum cell thickness was found to be 80 μm .

As higher quality silicon and better lifetime measurements became available, it became clear that the commonly accepted Auger recombination coefficients extracted from highly doped silicon were not correct for doping in the range used in solar cells. In particular, they predicted higher lifetime than experiment. This was rectified by Kerr, Campbell and Cuevas in 2002, where they incorporated their work on coulomb enhanced Auger recombination into the limit efficiency calculation[11]. They went further than this, however. It had also become clear that the actual radiative recombination rate that must be used in device models was impacted by photon recycling. They showed how this effect can be included by using an "effective" radiative recombination coefficient[12]. When Auger recombination is turned off, they find the limit efficiency to be 31.6%, in agreement with Tiedje, et al. above. This occurs for thick cells. Including Auger recombination with the new coulomb-enhanced parameters drops the efficiency to 29%, and the optimum thickness once again shrunk to 80 μm . This is where it stands today, and it is unlikely to change in the future. The theory seems complete, and finally ties device analysis nicely with the original Shockley and Queisser result. Interestingly, the highest efficiency was obtained with undoped silicon. Incorporating either n or p-type dopant lowers the calculated result.

MODEL RESULTS FOR PRACTICAL CELLS

In order to explore how efficient practical cells can become, we need to begin by adding additional losses over which we have no control. For example, the limit calculations of Tiedje, et al, and Kerr, et al. assume constant quasi-Fermi

levels, which is equivalent to assuming infinite mobility. These days it is easy to do limit calculations using PC1D. (To include photon recycling, one needs to adjust the radiative coefficient to $2 \times 10^{-15} \text{ cm}^3/\text{s.}$) Using PC1D, if one sets: a) a very high bulk SRH lifetime, b) a very low surface recombination velocity, c) a perfect reflector at the back of the cell, d) sets the electron and hole mobilities to high values, and so forth to simulate a limit cell, the calculated efficiency is 28.8%. This is tolerably close to the 29% found by Kerr, et al. Transitioning to the default mobility models lowers this to 28.7%. Put bluntly, constant quasi-Fermi levels is a pretty good approximation.

Optical Losses

The first losses we explore are optical. The front surface reflectance can't be zero, but it can be small. Textured surface with a single layer ARC will have a weighted reflectance of around 2%. This lowers the efficiency to 28.2%. In addition, the back surface reflectance won't be 100%, but it can easily be 90%. This lowers the efficiency to 27.8%. The corresponding short circuit currents are: 42.5 mA/cm² for perfect optics, 41.6 mA/cm² when including 2% front reflectance, and 41.1 mA/cm² by decreasing the back reflectance to 90%. In all, going from ideal optics to readily achievable optics has resulted in a 3% relative efficiency penalty.

Excess Bulk Recombination

The previously considered radiative and Auger recombination are intrinsic to silicon, and nothing can be done to reduce their effect. Additional recombination mechanisms are generally associated with silicon crystal defects. Defect mediated recombination has historically dominated over radiative and Auger, and thereby been much more important in determining the performance of solar cells. Over time, the prevalence of crystalline defects has decreased as crystal growth technology improved. Figure 2 shows the computed impact of increasing the recombination due to defects. Here the efficiency is plotted versus one over the lifetime associated with such defects (often called the SRH lifetime after the authors who originally studied the kinetics of defect recombination, Shockley, Read and Hall.) The right hand end of the x-axis then corresponds to an SRH lifetime of 1 ms, and the left hand end to infinite SRH lifetime, i.e., no defects. In Figure 2, the realistic optics of the above section is assumed.

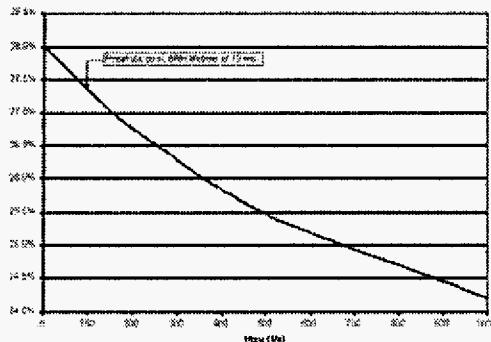


Figure 2. Impact of defect mediated bulk recombination on limit efficiency.

Ingots lifetime measurements from production 2 ohm-cm n-type material have yielded an average lifetime around 6 ms. The Auger lifetime in this case is 25 ms and the radiative lifetime 43 ms. This means that the SRH lifetime is around 10 ms. This corresponds to 100 sec⁻¹ on the x-axis of figure 3, which gives an efficiency of 27.3%. The rather surprising result is that the cell efficiency using practical and available silicon material is over 27%, providing that contacts with sufficiently low recombination can be found.

Passivating and Contacting the Surfaces

Up to now, the cell surfaces have been treated assuming that have ideal minority carrier mirrors, i.e., there is no recombination. It is when incorporating real-world contacts and surface passivation that big losses beyond 27% obtain. Figure 3 shows the impact of adding top and bottom surfaces that have a J_0 behavior. By this it is meant that the recombination at the surface is proportional to the pn product, specifically $J_{rec} = J_0(pn/n_i^2 - 1)$. This is generally the case when the surface is sufficiently doped that it is in low-level injection.

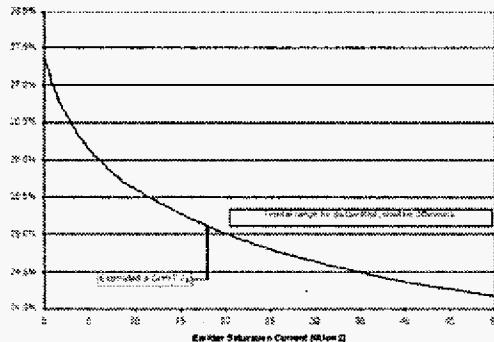


Figure 3. Impact of contact saturation current on limit cell efficiency.

Already there is significant effect with a J_0 of only 1 fA/cm². This is not surprising, recalling that the radiative limit J_0 is 0.27 fA/cm² and the cell performance is not terribly far from the thermodynamic limit. Unfortunately, no contacts with such low J_0 are known. Shallow diffusions that are passivated with high quality thermal silicon dioxide have J_0 over 20 fA/cm², and this drags the efficiency to under 25%. To make matters worse, these diffusions have no contacts, so current cannot be withdrawn from the cell. Diffusions with contacts tend to have a J_0 of over 1000 fA/cm², which reduces efficiency to values around 16%. The only way to limit the impact of contacts in this case is to have very small, localized contacts, but this increases the cell resistance.

Another approach to contacts is to put a heterojunction with a band-gap larger than silicon between the metal and silicon. If the conduction and valence bands are properly aligned to silicon's, this has the effect of creating a minority carrier mirror. The best developed such contact uses hydrogenated amorphous silicon, such as in the Sanyo HIT cell. Modeling the HIT cell performance reveals that they have a front and back average J_0 of around 18 fA/cm². This is despite the presence of metal contacts. It is interesting to note that that intrinsic efficiency of HIT cells is thus over 25%. The difference between that and the reported 21.4% comes mainly from grid obscuration, grid series resistance, lower base lifetime, ITO series resistance, and light absorption in the ITO. All of these losses are subject to reduction through process and design improvements.

NEEDED—NEW CONTACTS

None of the above discussed contacts permit cell efficiency over 25%. What is needed is a new contact that has J_0 less than 5 fA/cm² and makes good majority carrier contact. Two such contacts are needed, one for electrons and one for holes. There are many possibilities to explore that may be hiding such contacts. a-Si may improve to meet the goal. On another front, the author supervised a PhD student in 1985 who developed oxygen doped poly silicon emitters (SIPOS) with J_0 less than 10 fA/cm². (This value has been corrected to the "new" n_i of 1×10^{10} cm⁻³ at 300K.) In addition, there are many heterojunction candidates that can be explored, including poly crystalline materials such as InP, and amorphous materials such as a-Si_xC_{1-x}. Even organic semiconductor contacts are a possibility. The author is quite confident that a practical emitter with J_0 less than 5 fA/cm² will be found if sufficient effort is expended.

THE REMAINING LOSSES

If an emitter with a J_0 of 2 fA/cm^2 is developed the intrinsic cell efficiency will be 26.7%. That leaves 0.7% for additional losses (2.6% relative). These losses are:

1. Grid reflection. This can be eliminated by using backside contacts.
2. Grid resistance. Grid resistance losses can be reduced to less than 1% relative using backside contacts.
3. Lateral transport. This is the additional loss incurred from two-dimensional effects as current transports laterally between grid fingers. This can be made arbitrarily small by shrinking lateral dimensions.

All of the above losses are shown together in Figure 4. It is seen that a backside contact cell with sufficiently fine features will closely approach the intrinsic cell performance. 26% is indeed a realistic performance goal; but as the above analysis shows, the processing technology must be under very good control. So it is a goal to be steadily approached over time, but at least we know where we can eventually arrive if we pursue it diligently. First, of course, 25% cells that exceed the current laboratory best will become available. To put a rough timeline on all this, I will go out on a limb and posit that 25% cells will be commercially available within 5 years, followed by 26% cells within 10 years.

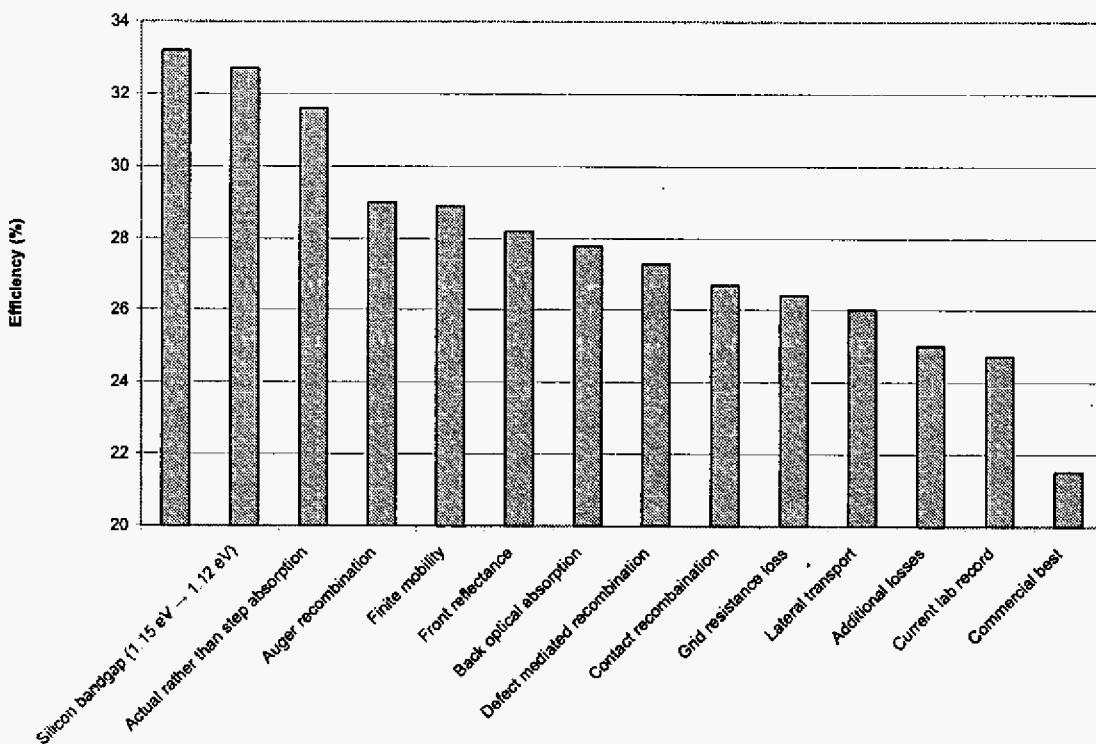


Figure 4. The loss waterfall in going from the thermodynamic limit to future practical cells.

¹ M. B. Prince, "Silicon solar energy converters," *J. Appl. Phys.*, vol. 26, May, 1955, pp. 534-540.

² W. Shockley and H. J. Queisser, "Detailed Balance Limit of Efficiency of p-n Junction Solar Cells," *J. Appl. Phys.*, Vol. 32, No. 3, March 1961, pp. 510-519.

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⁶ M. Wolf, "A New Look at Silicon Solar Cell Performance," *Proc. 8th IEEE Photovoltaic Specialists Conference*, Seattle, August 1970, pp. 360-371.

⁷ M. Wolf, "High Efficiency Silicon Solar Cells," *Proc. 14th IEEE Photovoltaic Specialists Conference*, San Diego, January 1980, pp. 674-679.

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⁹ M. Spitzer, J. Shewchun, E. S. Vera and J. J. Loferski, "Ultra High Efficiency Thin Silicon P-N Junction Solar Cells Using Reflecting Surfaces," *Proc. 14th IEEE Photovoltaic Specialists Conference*, San Diego, January 1980, pp. 375-380.

¹⁰ E. Yablonovitch and G. D. Cody, *IEEE Trans. Electron Devices*, vol. ED-20, p. 300, 1982.

¹¹ M. J. Kerr, P. Campbell, and A. Cuevas, "Limetime and Efficiency Limits of Crystalline Silicon Solar Cells," *Proc. 29th IEEE Photovoltaic Specialists Conference, New Orleans*, May 2002, pp. 438-441.

¹² Bulk radiative recombination is a bi-molecular process, and thus its volume rate, R_{rad} , is proportional to the electron-hole product. The proportionality constant is usually written as B, so that $R_{rad} = B(pn - n_i^2)$. The detailed balance measurements of Tiedje, et al., give $B = 2.1 \times 10^{-15} \text{ cm}^3/\text{s}$. This number already includes photon recycling by the thermodynamic nature of the calculation. Device models often

use $B = 9.5 \times 10^{-15} \text{ cm}^3/\text{s}$; however, photon recycling reduces the impact of radiative recombination, and a lower effective B is appropriate depending on the fraction of photons that are recycled. This fraction depends mainly on cell thickness. With thin cells, photons are more likely to escape and recycling is less effective, but for thin cells the volume for recombination is less. The net impact is that radiative recombination is somewhat independent of cell thickness. This analysis closes the gap between thermodynamic detailed balance calculations, which give a result that is independent of cell thickness, and device models, which decidedly do.