

Thermodynamic Limits and Efficiency Strategies in Photovoltaic Technology

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Abstract

Photovoltaic (PV) cells convert sunlight directly into electricity without moving parts or producing emissions. Yet, even an idealized single-junction device converts only a fraction of the incident solar power: the ceiling is set by thermodynamics, not by engineering. This paper asks how efficiently a solar cell can in principle operate and which of the mechanisms that bound real devices can actually be relaxed. Following the Shockley-Queisser detailed-balance model, which assumes a single bandgap absorber at 300 K illuminated by the AM1.5G spectrum, complete absorption of all above-bandgap photons, and radiative recombination as the only loss channel, we obtain three quantitative results. First, the unavoidable losses of a perfect silicon cell are sub-bandgap transmission (about 19% of incident power), thermalization of hot carriers (about 33%), and a voltage deficit arising jointly from the cell-to-sun temperature ratio and from radiative recombination (about 18%). Second, the detailed-balance ceiling reaches about 33% for a single junction at the optimal bandgap near 1.34 eV, and approximately 29-30% for silicon under unconcentrated illumination. Third, real devices add avoidable losses from non-radiative recombination, series resistance, and optical reflection; passivation-based silicon technologies (PERC, TOPCon, HJT) have closed most of this gap, bringing commercial silicon cells within a few percentage points of their ceiling, while perovskite/silicon tandems exceed 34% by relaxing the single-bandgap assumption. The analysis is limited to a single spectrum and temperature and to the radiative-recombination idealization; concentrated, spectral-conversion, and multi-junction systems are discussed only qualitatively, since they correspond to different thermodynamic limits.

Keywords

photovoltaic technology, solar cells, thermodynamics, Shockley-Queisser limit, semiconductor physics, tandem solar cells, renewable energy

1. Introduction

In 2024, solar photovoltaic (PV) technology supplied roughly 7% of global electricity generation after more than 600 GW of new capacity was commissioned in a single year, and the cumulative worldwide total surpassed 2.2 TW [1, 2]. The remaining majority of the world's electricity is still produced by burning coal and natural gas, whose carbon dioxide emissions are the principal driver of climate change. Reducing those emissions by shifting generation toward renewable sources is therefore one of the defining engineering problems of this century, and PV is currently the fastest-growing solution to it.

Among the alternatives, solar energy is distinguished by its abundance and its simplicity. In a little over an hour, the sun delivers to the Earth's surface more energy than humanity consumes in a year, and a PV cell converts that light directly into electrical current with no moving parts and no emissions during operation. These properties make PV attractive across the entire scale range, from rooftop installations to utility-scale plants.

Nevertheless, no solar cell converts all of the sunlight that reaches it. The losses are not merely engineering imperfections; many are imposed by physics. Photons below the semiconductor bandgap pass through the cell unused; photons well above the bandgap dissipate their excess energy as heat; and the voltage a cell can sustain is bounded by a thermodynamic factor that no refinement in manufacturing can alter. Recent records illustrate how close engineering has come to these bounds: certified silicon cells now exceed 27% and perovskite/silicon tandems have surpassed 34%, already beyond any single-junction device [3]. Yet the underlying constraints are rarely examined systematically, and it is often unclear which losses are truly unavoidable, which can be engineered away, and what price each strategy pays in manufacturing complexity or stability. This paper addresses that gap.

The remainder of the paper is organized as follows. Section 2 reviews related work on efficiency limits and records. Section 3 introduces the physical fundamentals of photon absorption and current generation. Section 4 develops the detailed-balance model, quantifies the principal loss mechanisms, and identifies which of them are unavoidable. Section 5 surveys commercial and emerging technologies that approach or exceed the single-junction limit. Section 6 compares these strategies in terms of the theoretical gain, manufacturing cost, and stability they offer. Section 7 states the limitations of the analysis, and Section 8 concludes.

2. Related Work

The detailed-balance framework of Shockley and Queisser [4] established a ceiling of roughly 33% for a single junction at the optimal bandgap. Tiedje and Yablonovitch [5] extended the analysis to silicon, showing that luminescence extraction is required to approach the radiative limit and confirming that the silicon ceiling is lower, about 29–30%, and Rühle [6] tabulated the detailed-balance efficiency for every bandgap under standard spectra, providing the reference curves against which experimental cells are now compared.

On the technology side, crystalline silicon has progressively approached its detailed-balance ceiling. The record progression from the first cells above 25% to the 26.3% silicon heterojunction cell with interdigitated back contacts reported by Yoshikawa et al. [7] has been followed by certified cells above 27% [3], within a few percentage points of the roughly 29–30% radiative limit for a 1.1 eV absorber. The annually updated efficiency tables of Green et al. [8] and the NREL best-research-cell efficiency chart [3] document this trajectory.

Breaking the single-junction ceiling requires relaxing the single-bandgap assumption. Perovskites, introduced as visible-light sensitizers by Kojima et al. [9] and developed into efficient thin-film cells by Lee et al. [10], offer bandgaps tunable from roughly 1.2 to 2.3 eV that are well suited to tandem stacks; Snaith [11] and De Wolf et al. [12] mapped the path from lab cells toward tandems, and Polman et al. [13] compared photovoltaic materials broadly against the limit. Certified perovskite/silicon tandems now exceed 34% [3], surpassing every single-junction cell, but their long-term stability under heat, moisture, and illumination remains the principal open problem.

3. Fundamentals of Photovoltaic Energy Conversion

3.1 Photon Energy and Solar Radiation

Light behaves both as a wave and, in quantum mechanics, as a stream of discrete packets called photons, each carrying an energy $E = h\nu$ set by its frequency ν , where $h \approx 6.626 \times 10^{-34}$ J·s is Planck's constant. Using the relation $c = \lambda\nu$ between wavelength λ and frequency ν , this can be written as $E = hc/\lambda$.

Photon energy, therefore, grows as wavelength shrinks: a blue photon near 400 nm carries roughly three times the energy of a near-infrared photon near 1200 nm. The solar spectrum reaching the ground is not monochromatic; it spans the ultraviolet, the visible, and well into the infrared. The standard terrestrial spectrum

used to rate solar cells, AM1.5G, runs from about 300 nm to 2500 nm. Different parts of this spectrum interact with a photovoltaic material in different ways, which is why no single semiconductor can convert all of it efficiently.

3.2 Semiconductor Bandgap and Electron Excitation

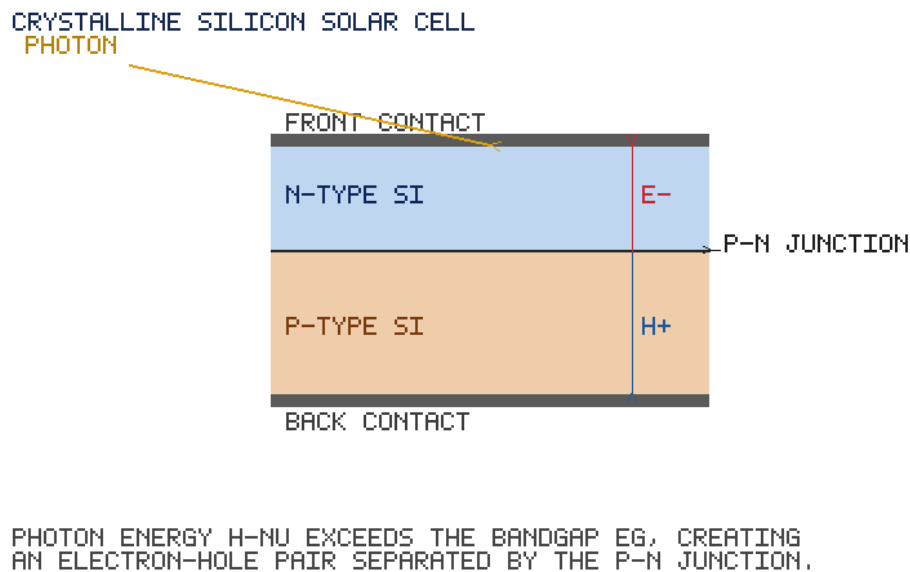
Solar cells are almost always made from semiconductors, and silicon dominates the market. Silicon is cheap, chemically stable, and its electronic properties are well-suited to the solar spectrum.

In a semiconductor, electrons normally sit in the valence band, bound to atoms. To contribute to electrical current, an electron needs enough energy to jump across the bandgap E_g into the conduction band. Three energy regions matter here: the valence band (where electrons normally reside), the bandgap itself (a forbidden region of width E_g), and the conduction band (where electrons are free to move). When a photon with energy $E \geq E_g$ is absorbed, it kicks an electron from the valence band into the conduction band, leaving behind a positively charged hole. The electron and the hole together form the electron-hole pair that ultimately becomes current.

3.3 Photovoltaic Current Generation

An electron-hole pair recombines within microseconds unless the carriers are separated quickly. To extract the carriers as electricity, the cell uses a p-n junction: doping the silicon n-type on one side and p-type on the other creates a built-in electric field that sweeps electrons toward the n-side and holes toward the p-side, separating the pair before recombination (Fig. 1). Metal contacts on each surface collect the separated carriers, so that when an external circuit is connected, electrons flow through the load and do useful work.

Figure 1: Schematic of a crystalline silicon solar cell. A photon with energy $h\nu \geq E_g$ is absorbed near the p-n junction, creating an electron-hole pair that the junction field separates before recombination—source: author's own figure



The power a cell delivers at its operating point is the product of current and voltage, and its efficiency is set by three quantities: the short-circuit current density J_{sc} , the open-circuit voltage V_{oc} , and the fill factor, which measures how closely the current-voltage curve approaches the ideal rectangle. None of these is set by manufacturing alone; each is bounded by fundamental physics, which is the subject of the next section.

4. Thermodynamic and Detailed-Balance Efficiency Limits

4.1 The Shockley-Queisser Framework

In 1961, Shockley and Queisser asked a simple question: if a solar cell were perfect except for the physics of light, how efficient could it be? Their detailed balance analysis assumed that the cell loses energy only

through the unavoidable emission of photons back into space and treated the sun as a 6000 K blackbody [4]. The result, now known as the Shockley-Queisser (S-Q) limit, sets a ceiling of about 33% for a single-junction cell with the optimal bandgap near 1.34 eV, and about 29–30% for silicon, whose 1.11 eV bandgap is not quite optimal.

Three idealizing assumptions make the calculation tractable. First, the cell is a single junction with one bandgap E_g that absorbs every photon with energy above E_g , so perfect antireflection and complete absorption are assumed. Second, radiative recombination is the only recombination channel: every absorbed photon either contributes to the photocurrent or is re-emitted as a photon, the thermodynamically unavoidable counterpart of absorption. Third, the cell is treated as a blackbody at room temperature (about 300 K) radiating into its surroundings. At the same time, the sun is approximated as a blackbody at about 6000 K. With these assumptions the only irreversible steps left in the conversion process are the mismatch between the broad solar spectrum and the single bandgap, together with the entropy cost of turning dilute, heat-like sunlight into electrical work; the resulting efficiency is therefore a genuine thermodynamic ceiling, not an engineering target.

The calculation rests on two currents that must balance. The cell absorbs photons with energy above E_g from the sun, producing a short-circuit current density

$$J_{sc} = qE_g \int \Phi_{sun}(E) dE \quad (1)$$

where $\Phi_{sun}(E)$ is the solar spectral photon flux and q is the elementary charge. At the same time, the cell unavoidably emits photons back, an effect equivalent to that of a diode in the dark. Setting absorption equal to emission in equilibrium defines an upper bound on the open-circuit voltage V_{oc} , and therefore on the efficiency

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (2)$$

with FF the fill factor and P_{in} the incident solar power. Pushing any one of these terms higher is what the rest of this paper is about.

The product structure of (2) also exposes the central trade-off of single-junction design. A smaller bandgap E_g allows more of the solar spectrum to be absorbed and raises J_{sc} , but it lowers V_{oc} : a cell with a smaller bandgap begins emitting photons at lower energies, and the equilibrium recombination current grows exponentially as E_g decreases. The optimum that balances these competing effects lies near 1.34 eV under unconcentrated sunlight, which is why the best single-junction absorber materials cluster in the 1.1–1.5 eV range and why tandem cells, discussed in Section 5, split the spectrum between two bandgaps to relax this constraint.

4.2 Principal Loss Mechanisms

Even a cell that achieves the S-Q limit loses most of the incident solar power. For silicon ($E_g \approx 1.11$ eV) under AM1.5G illumination, three unavoidable thermodynamic losses dominate, together leaving only about 29–30% of the incident power available as electricity.

The first unavoidable loss is transmission. Photons with energy below E_g lack sufficient energy to excite an electron across the bandgap; roughly 19% of the incident power lies in this sub-bandgap tail and passes straight through the cell. No single-junction absorber can use these photons, because a bandgap low enough to capture them would sacrifice even more voltage.

The second is thermalization. Photons well above E_g , particularly in the blue and ultraviolet parts of the spectrum, excite electrons high into the conduction band, and those hot carriers quickly relax to the band edge, releasing the excess energy as lattice heat. This is the largest single loss, accounting for about 33% of the incident power.

The third is the voltage deficit. Even in the radiative limit a cell cannot deliver the full voltage E_g/q : to preserve detailed balance it must re-emit a fraction of the absorbed photons, and the entropy cost of converting dilute, broadband sunlight into concentrated electrical work imposes a further Carnot-like factor. Together these unavoidable terms keep V_{oc} at roughly 70–75% of E_g/q . Non-radiative recombination at defects,

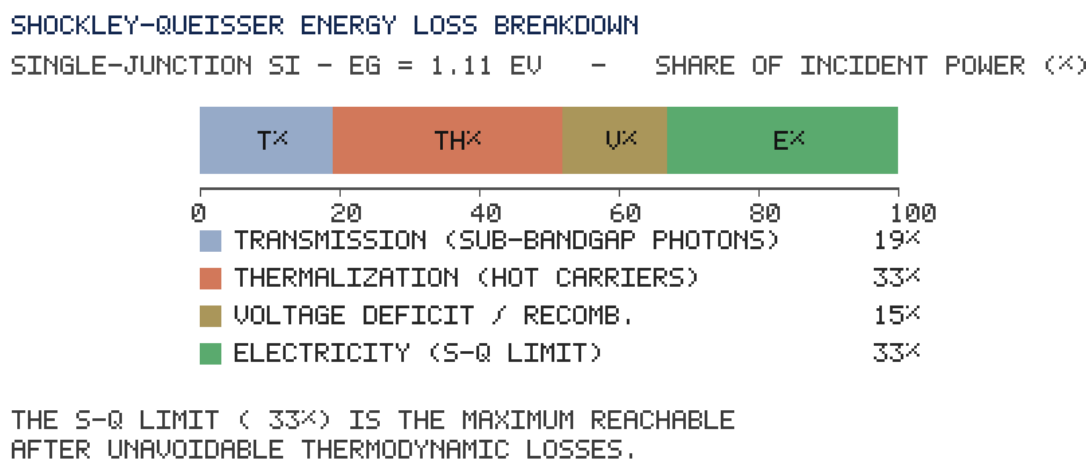
surfaces, and interfaces pushes the voltage lower still, but this part is not unavoidable: it is an engineering loss that improved materials and passivation can reduce.

What remains, roughly 29–30% of the incident power, is the maximum fraction a single-junction silicon cell can, in principle, convert into electricity, i.e., the S-Q limit for silicon. Real cells fall short of this ceiling because of additional avoidable losses, including front-surface reflection, incomplete absorption in a thin wafer, series resistance, and parasitic recombination. The distinction is central to this paper: the three mechanisms above are thermodynamic facts that no silicon cell can escape, whereas the avoidable losses are precisely what the technologies surveyed in Section 5 are designed to minimize.

4.3 Quantitative Breakdown for Silicon

The shares above are summarised graphically in Fig. 2. The exact split depends on the assumed spectrum (AM0 vs. AM1.5G) and on whether sunlight is concentrated, but the ordering is robust: thermalization is always the biggest loss, and the ceiling for silicon stays near 29–30% [5, 6].

Figure 2: Share of incident solar power lost to each mechanism for a single-junction silicon cell ($E_g \approx 1.11$ eV) under AM1.5G. The maximum reachable efficiency is the Shockley-Queisser limit for silicon, about 29–30% [5, 6]



5. Commercial Technologies and Efficiency Strategies

Strategies for approaching the S-Q limit can be grouped by the loss they attack. Passivation-based silicon technologies (PERC, TOPCon, HJT) cut recombination at surfaces and contacts. Tandems attack thermalization by giving high-energy photons a wider-bandgap absorber. Optical strategies reduce reflection and improve light trapping. Representative performance is summarised in Table I.

Table 1: Representative photovoltaic technologies and their reported record efficiencies. References are to peer-reviewed work and the NREL best-research-cell efficiency chart

Technology	Bandgap (eV)	Record eff.	Key idea	Main challenge
c-Si PERC	1.11	~24-25% [8]	Rear-surface passivation	Rear recombination
c-Si TOPCon	1.11	>26% [3]	Tunnel-oxide passivated contact [14]	Process cost
c-Si HJT	1.11	26.3% [7]	a-Si/c-Si heterojunction	Equipment cost
Perovskite (single)	~1.6	~26% [3, 11]	Bandgap-tunable absorber	Long-term stability
Perovskite/Si tandem	1.7 / 1.11	>33% [3]	Stacked bandgaps	Stability, scaling

5.1 Passivated Emitter and Rear Cell (PERC)

Passivated emitter and rear cell (PERC) technology, introduced in the late 1980s and scaled industrially in the 2010s, adds a dielectric passivation layer on the back of the cell. Without it, electrons that reach the rear surface recombine there; with it, more of them get reflected back into the bulk and collected. PERC pushes mainstream silicon cell efficiencies from roughly 19% to over 22%, and it can be manufactured on largely existing production lines, which is why it now dominates new module production.

5.2 Tunnel Oxide Passivated Contact (TOPCon)

Tunnel oxide passivated contact (TOPCon) cells take the passivation idea further. A thin silicon oxide layer, thin enough that electrons can tunnel through it, sits between the silicon absorber and a doped polysilicon contact. The oxide dramatically reduces recombination at the contact while still allowing carriers to pass, thereby causing the cell's voltage to climb. TOPCon has overtaken PERC in the highest-efficiency production lines, with module efficiencies regularly above 24% and lab cells above 26% [3, 14].

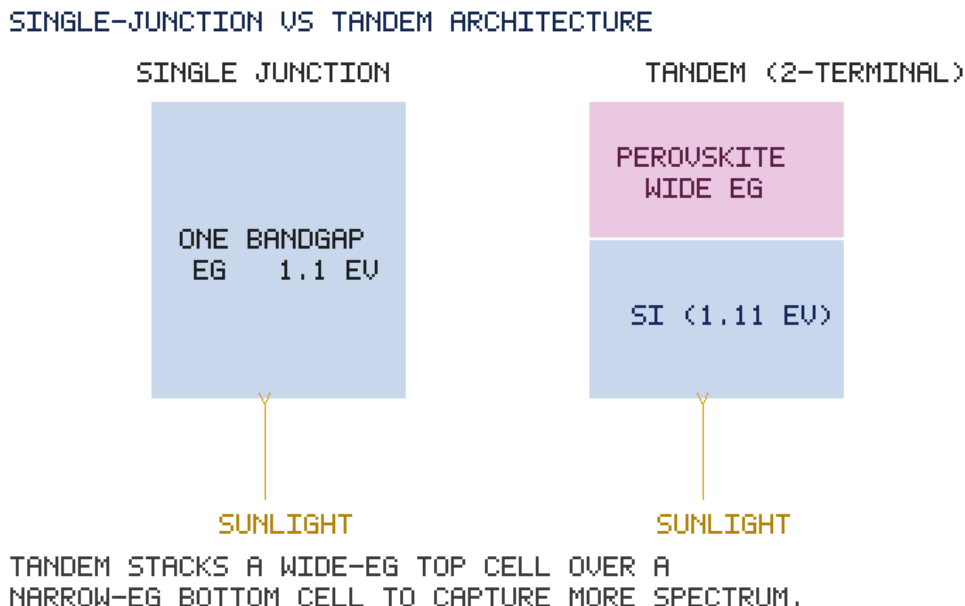
5.3 Heterojunction Technology (HJT)

Heterojunction technology (HJT) stacks amorphous silicon on top of crystalline silicon. The amorphous layer passivates the crystalline surface almost perfectly, since its defect density is much lower than that of the silicon-silicon interface, while the crystalline layer absorbs most of the light. The combination of very low recombination and a transparent conductive oxide front contact gives some of the highest open-circuit voltages of any silicon technology. The 26.3% Panasonic cell is the most famous HJT result [7], and commercial HJT modules are now competitive with TOPCon.

5.4 Perovskite and Tandem Architectures

Perovskite solar cells are made from a class of materials with the ABX_3 crystal structure, typically a methylammonium, formamidinium, or cesium lead halide. What makes perovskites interesting is that their bandgap can be tuned from about 1.2 to 2.3 eV simply by changing the chemistry. A cell with a wide bandgap on top of a narrow-bandgap silicon cell captures high-energy photons in the perovskite and lets lower-energy photons through to the silicon, which is exactly the strategy the Shockley-Queisser analysis suggests for beating the single-junction limit (Fig. 3) [9]-[12].

Figure 3: Single-junction vs. two-terminal tandem architecture. Stacking a wide-bandgap perovskite top cell over a narrower-bandgap silicon bottom cell captures more of the solar spectrum than a single-junction cell of either bandgap. Source: author's own figure



Two-terminal perovskite-on-silicon tandems have already exceeded 33% in certified measurements, surpassing any single-junction cell [3]. The main unresolved problems are long-term stability, since perovskites degrade under heat, moisture, and illumination, and the lead content of the most efficient compositions, though lead-free variants and improved encapsulation are under active study.

5.5 Optical Management Strategies

Optical strategies are cheaper than changing the absorber and are often complementary to the cell architectures above. It is useful to distinguish two families. Passive light-management techniques leave the

photon energy unchanged: anti-reflection coatings and surface texturing reduce the roughly 10% reflection loss at the air-glass interface, and light trapping, which uses the back surface as a diffuse reflector so that unabsorbed photons bounce back through the cell, lengthens the optical path inside the absorber and improves absorption near the bandgap, where the absorption coefficient is small. Spectral-conversion techniques, by contrast, deliberately change the photon energy before absorption: luminescent down-shifting layers convert high-energy photons into longer wavelengths that the cell absorbs more efficiently, upconversion materials attempt the reverse for sub-bandgap photons but remain experimental, and spectrum-splitting designs route different wavelength ranges to cells with matching bandgaps. None of these techniques changes the thermodynamic ceiling, but they let real cells get meaningfully closer to it.

6. Discussion

The technologies in Section 5 attack different terms in the loss breakdown of Fig. 2 and are therefore largely complementary. PERC and TOPCon reduce non-radiative recombination at the rear surface and contacts, directly raising V_{oc} and the fill factor, with TOPCon adding a passivating tunnel oxide that lowers contact recombination further. HJT replaces the crystalline-silicon surface with a passivating amorphous-silicon layer whose defect density is far lower, pushing recombination losses below what PERC and TOPCon achieve at the cost of more complex equipment. Perovskite/silicon tandems attack thermalization instead: the wide-gap perovskite top cell converts high-energy photons at high voltage while the silicon bottom cell handles the low-energy remainder, so each photon is converted at a voltage closer to its energy. Optical management is the cheapest and most universal lever but also the most incremental, recovering only a few percent of reflection and absorption losses. The choice among these routes is ultimately an engineering trade-off between efficiency gain, added complexity, and long-term stability.

The record-efficiency chart of the past decade [3] reveals two trends. First, single-junction silicon has essentially saturated: champion cells have advanced from roughly 25% to about 27% over the past fifteen years, and the remaining gap to the 29–30% S-Q limit can be closed only by eliminating the last recombination and optical losses. Second, the largest gains now come from stacking: perovskite/silicon tandems crossed the single-junction ceiling a few years ago and have since reached certified efficiencies above 34% [3], while all-perovskite and III-V/Si tandems are under active development. Comparing the technologies by the loss they target makes the picture coherent: PERC, TOPCon, and HJT recover a few percentage points in the recombination and voltage channels and are distinguished mainly by manufacturing cost and maturity, whereas tandems recover more than five points by attacking the largest single loss, thermalization, at the price of added complexity and stability risk. The open question is no longer whether tandems work, but whether they can sustain high efficiency over the 25-year lifetime expected of field modules.

7. Limitations and Future Work

This paper is a review-level analysis built from published records and standard thermodynamic models, not from original experimental data. The loss breakdown in Fig. 2 assumes AM1.5G and a single-junction silicon cell; for other spectra, materials, or under concentration, the numbers shift. The discussion of perovskite stability is necessarily incomplete because the field is moving quickly; published lifetimes in 2024–2026 are already longer than the numbers cited in most review articles.

Future work on this topic would benefit from a quantitative techno-economic analysis: at what module efficiency does a perovskite/silicon tandem pay back the extra manufacturing cost compared with a single-junction module? Coupling that to lifetime projections under realistic operating conditions is probably the most useful thing a student could add next.

8. Conclusion

Photovoltaic cells are limited, fundamentally, by how much of the sun's energy can be put to work under the laws of thermodynamics. The Shockley-Queisser detailed-balance calculation caps a single-junction cell at roughly 33% when the bandgap is optimally chosen, while silicon, because of its 1.11 eV bandgap, reaches only about 29–30%. The largest unavoidable loss is thermalization; the next largest is the inability to absorb sub-bandgap photons.

Improvements over the past two decades have come from reducing the avoidable losses: passivating contacts (PERC, TOPCon), better interfaces (HJT), and, more recently, stacking two absorbers with different bandgaps so that each photon finds a home closer to its own energy. Perovskite/silicon tandems have already passed the single-junction ceiling, and the research direction is clear even if the engineering problems, stability, lead content, scaling, remain real.

For a student looking at photovoltaics, the field is unusual: the physics is essentially settled, and progress is now an engineering and economics problem. That makes it one of the more tractable pieces of the energy transition to work on.

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Conflicts of Interest

The authors declare no conflict of interest.

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