Overcoming the Shockley-Queisser Limit: Novel Approaches in Multi-Junction and Hot-Carrier Solar Cells

Dr. Anita Sagar
Assistant Professor, Department of Physics
College of Commerce, Arts and Science, Patna, India

Abstract - **The Shockley-Queisser (SQ) limit imposes a theoretical maximum efficiency of approximately 33.7% on conventional single-junction solar cells, primarily due to transmission and thermalization losses. To meet global renewable energy targets, photovoltaic (PV) technologies must transcend this thermodynamic barrier. This article presents a comparative analysis of two leading strategies: Multi-Junction Solar Cells (MJSCs), which spatially partition the solar spectrum, and Hot-Carrier Solar Cells (HCSCs), which attempt to harvest excess kinetic energy before thermal relaxation. We review recent milestones, including the 34.85% efficiency record for perovskite-silicon tandems and the breakthrough 27.3% efficiency achieved by a perovskite hot-carrier device in 2024. The analysis highlights that while MJSCs are entering commercial maturity with established techno-economic viability, HCSCs have recently graduated from theoretical concepts to high-efficiency prototypes, offering a complementary pathway to ultra-high efficiency.**

Keywords: **Shockley-Queisser (SQ) limit, Multi-Junction Solar Cells, Hot-Carrier Solar Cells, ultra-high efficiency, commercial maturity**

I. INTRODUCTION

The efficiency of standard single-junction solar cells is fundamentally constrained by the Shockley-Queisser (SQ) limit, first formulated in 1961. This limit dictates that for a material with an optimal bandgap of 1.34 eV, the maximum power conversion efficiency (PCE) is roughly 33.7% under standard illumination. As silicon photovoltaics approach their practical limit of 29.4%, further cost reductions in solar energy require device architectures that can manage the two dominant loss mechanisms responsible for the SQ limit:

1. Transmission Losses: Photons with energy less than the bandgap ($E < E_g$) pass through the absorber unutilized.
2. Thermalization Losses: Photons with energy greater than the bandgap ($E > E_g$) generate "hot" carriers. In conventional devices, these carriers rapidly relax to the band edges via phonon emission, dissipating the excess energy ($E - E_g$) as heat within picoseconds.

By addressing these losses, "Third Generation" PV technologies aim to approach the thermodynamic Carnot limit of solar energy conversion (~86% for infinite junctions or ideal hot-carrier extraction). This article examines the physical principles, recent experimental breakthroughs, and commercial prospects of Multi-Junction and Hot-Carrier architectures.

II. MULTI-JUNCTION SOLAR CELLS: SPECTRAL PARTITIONING

Multi-junction (tandem) solar cells stack multiple sub-cells with decreasing bandgaps to absorb specific segments of the solar spectrum, thereby minimizing thermalization losses in the top cells and transmission losses in the bottom cells.

2.1. III-V Multijunction Records

III-V compound semiconductors (e.g., GaInP, GaAs, GaInAs) have historically set the benchmark for PV efficiency.

- Current Record: As of 2025, the world record for solar cell efficiency stands at 47.6%, achieved by Fraunhofer ISE using a four-junction concentrator photovoltaic (CPV) cell under 665-sun illumination.
- Device Structure: This milestone was reached using a wafer-bonded architecture that combines diverse lattice constants, along with a newly developed four-layer anti-reflection coating to minimize optical losses across the broad absorption spectrum.

2.2. Perovskite-Silicon Tandems: The Path to Commercialization

While III-V cells are efficient, their high cost limits them to space and concentrator applications. The terrestrial market is currently focused on Perovskite-Silicon (PK/Si) tandems, which pair a low-cost, tunable perovskite top cell with a standard silicon bottom cell.

- Efficiency Milestones: Progress in this field has been rapid. In April 2025, LONGi Solar set a new certified efficiency record of 34.85% for a perovskite-silicon tandem cell, surpassing their previous 2024 record of 34.6%.
- Techno-Economic Viability: A 2025 techno-economic analysis (TEA) indicates that PK/Si tandems are becoming cost-competitive. The Levelized Cost of Electricity (LCOE) for these modules is projected to be between 1.47 and 1.66 ¢/kWh (assuming a 25-year lifetime), which is comparable to, and potentially lower than, standard crystalline silicon modules.
- Challenges: The primary hurdles remain the operational stability of the perovskite layer (particularly under moisture and heat stress) and the complexity of current matching between the two sub-cells. Current matching requires precise tuning of the perovskite bandgap and thickness; any mismatch results in the total current being limited by the weaker sub-cell.

III. HOT-CARRIER SOLAR CELLS: KINETIC ENERGY HARVESTING

Unlike MJSCs, which avoid thermalization, Hot-Carrier Solar Cells (HCSCs) actively exploit it. They aim to extract photogenerated carriers while they are still at an elevated electronic temperature ($T_e > T_{lattice}$), utilizing the excess kinetic energy to boost the open-circuit voltage (V_{OC}).

3.1. Fundamental Requirements

For an HCSC to function, two conditions must be met:

1. Slowed Thermalization: The carrier cooling rate must be slower than the extraction rate. This is often achieved via the "hot phonon bottleneck" (HPB) effect, where the decay of optical phonons into acoustic phonons is restricted, keeping the carrier population hot.
2. Energy Selective Contacts (ESCs): Carriers must be extracted through a narrow energy window. Broad-energy contacts would allow hot carriers to thermalize with cold carriers in the metal leads, destroying the voltage gain. The ESC acts as an "entropy filter," allowing isentropic extraction.

3.2. Recent Breakthroughs (2024-2025)

Historically, HCSCs were theoretical concepts with low practical efficiencies. However, 2024 marked a pivotal turning point.

- The 27% Efficiency Breakthrough: Researchers demonstrated a single-junction perovskite solar cell that effectively operates as a hot-carrier device. By utilizing a Phthalocyanine (SMePc) Hole Transport Layer (HTL), they achieved an ultrafast extraction velocity of 78,900 cm/s. This allowed hot holes to be collected within ~79 nm, competing with the thermalization timescale.
    - Performance: The device achieved a certified efficiency of 24.43% under 1-sun illumination and a record 27.30% under 5.9-sun concentration.
    - Mechanism: Under concentration, the device exhibited a V_{OC} exceeding the theoretical limit for cold carriers, providing definitive experimental evidence of hot-carrier extraction.
- Organic HCSCs: A separate 2024 study revealed that common organic bulk heterojunction cells inherently function as hot-carrier devices. The static energetic disorder in these materials acts as a natural energy filter, slowing thermalization and providing a "thermovoltage" boost of up to 0.2 V.

IV. DISCUSSION: TECHNOLOGY COMPARISON

Feature	Multi-Junction (MJSC)	Hot-Carrier (HCSC)
Primary Mechanism	Spectral Separation (Multiple Bandgaps)	Kinetic Extraction (Non-equilibrium)
Theoretical Limit	~68% (1-sun) / ~86% (conc.)	~66% (1-sun) / ~85% (conc.)
Record Efficiency	47.6% (4-Junction CPV)	27.3% (Perovskite HCSC)
Key Challenge	Lattice matching & Current matching	Femtosecond extraction & Contact design
Maturity	Commercial / Pre-commercial	Emerging / Lab-scale

V. CONCLUSION

The quest to overcome the Shockley-Queisser limit has bifurcated into two successful distinct pathways. Multi-junction cells have established themselves as the efficiency kings, with perovskite-silicon tandems poised to bring >30% efficiency to the mass market by 2030, provided stability challenges are resolved. Simultaneously, hot-carrier photovoltaics have achieved a "zeroth-to-one" moment in 2024, proving that kinetic carrier management can yield silicon-beating efficiencies in real-world devices. The convergence of these technologies—potentially using hot-carrier perovskites as the top cell in a tandem stack—represents the next frontier in photovoltaic research.

REFERENCES

[1] Shockley, W., & Queisser, H. J. (1961). Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. Journal of Applied Physics, 32(3), 510–519.

[2] Green, M. A., et al. (2024). Solar cell efficiency tables (Version 64). Progress in Photovoltaics: Research and Applications, 32(7), 430-441.

[3] Conibeer, G., et al. (2015). Hot carrier solar cell absorber prerequisites and candidate material systems. Solar Energy Materials and Solar Cells, 135, 124-129.

[4] Feng, Y., & Aliberti, P. (2012). Theoretical efficiency of hot carrier solar cells with non-ideal energy selective contacts. Journal of Applied Physics, 111(12), 123108.

[5] National Renewable Energy Laboratory (NREL). (2024). Best Research-Cell Efficiency Chart. Washington, DC: U.S. Department of Energy.

Works cited

[6] Stability Issues of Perovskite Solar Cells: A Critical Review - ResearchGate, https://www.researchgate.net/publication/354667530_Stability_Issues_of_Perovskite_Solar_Cells_A_Critical_Review

[7] Recent Trends and Challenges in Lead-Free Perovskite Solar Cells: A Critical Review, https://pubs.acs.org/doi/10.1021/acsaem.3c02327

[8] Quantum dot solar cell - Wikipedia, https://en.wikipedia.org/wiki/Quantum_dot_solar_cell

[9] Multiple exciton generation in quantum dot-based solar cells - ResearchGate, https://www.researchgate.net/publication/320448909_Multiple_exciton_generation_in_quantum_dot-based_solar_cells

[10] Multiple Exciton Generation in Colloidal Nanocrystals - PMC, https://pmc.ncbi.nlm.nih.gov/articles/PMC5304609/

[11] Multiple exciton generation in | Phys. Rev. B - Physical Review Link Manager, https://link.aps.org/doi/10.1103/PhysRevB.108.125133

[12] Perovskite-Silicon Tandem Solar Cells Achieve Record-Breaking 33.1% Efficiency, https://scitechdaily.com/perovskite-silicon-tandem-solar-cells-achieve-record-breaking-33-1-efficiency/

[13] Best Research-Cell Efficiency Chart | Photovoltaic Research - NREL, https://www.nrel.gov/pv/cell-efficiency

[14] NREL Best Research-Cell Efficiencies Chart, https://www.nrel.gov/docs/libraries/pv/cell-pv-eff.pdf?sfvrsn=26e2254e_14

[15] Popular NREL Cell Efficiency Chart Shines in New Interactive Version, https://www.nrel.gov/news/detail/program/2022/popular-nrel-cell-efficiency-chart-shines-in-new-interactive-version

[16] Perovskite solar cell - Wikipedia, https://en.wikipedia.org/wiki/Perovskite_solar_cell 12. Developments of Highly Efficient Perovskite Solar Cells | Accounts of Materials Research, https://pubs.acs.org/doi/10.1021/accountsmr.3c00068

[17] Non-fused ring acceptors for organic solar cells - OAE Publishing Inc., https://www.oaepublish.com/articles/energymater.2021.08

[18] Quantum Dot Solar Cells: Small Beginnings Have Large Impacts - MDPI, https://www.mdpi.com/2076-3417/8/10/1867

[19] Advancement on Lead-Free Organic-Inorganic Halide Perovskite Solar Cells: A Review, https://www.mdpi.com/1996-1944/11/6/1008