A HISTORY OF THE SOLAR CELL, IN PATENTS

Karthik Kumar, Ph.D.,
Finnegan, Henderson, Farabow, Garrett & Dunner, LLP
901 New York Avenue, N.W., Washington, D.C. 20001
karthik.kumar@finnegan.com

Member, Artificial Intelligence & Other Emerging Technologies Committee
Intellectual Property Owners Association
1501 M St. N.W., Suite 1150, Washington, D.C. 20005
info@ipo.org

Introduction

Solar cell technology has seen exponential growth over the last two decades. It has evolved from serving small-scale niche applications to being considered a mainstream energy source. For example, worldwide solar photovoltaic capacity had grown to 512 Gigawatts by the end of 2018 (representing 27% growth from 2017)[1]. In 1956, solar panels cost roughly $300 per watt. By 1975, that figure had dropped to just over $100 a watt. Today, a solar panel can cost as little as $0.50 a watt. Several countries are edging towards double-digit contribution to their electricity needs from solar technology, a trend that by most accounts is forecast to continue into the foreseeable future. This exponential adoption has been made possible by 180 years of continuing technological innovation in this industry. Aided by patent protection, this centuries-long technological innovation has steadily improved solar energy conversion efficiency while lowering volume production costs. That history is also littered with the names of some of the foremost scientists and engineers to walk this earth. In this article, we review that history, as captured in the patents filed contemporaneously with the technological innovation.

---

[1] Wiki-Solar, *Utility-scale solar in 2018: Still growing thanks to Australia and other later entrants*, https://wiki-solar.org/library/public/190314_Utility-scale_solar_in_2018.pdf (Mar. 14, 2019).

The Early Years: Selenium, Heat, and Thermopiles

The story of the solar cell began in 1839 with French scientist Edmond Becquerel's discovery that platinum electrodes coated with silver halides generates electricity when illuminated with blue or ultraviolet light.[2] Following English electrical engineer Willoughby Smith's discovery in 1873 that selenium demonstrates this photovoltaic effect,[3] Charles Fritts in 1883 developed and installed the world's first solar panel from selenium cells in New York City. Although Fritts argued that his solar cells would soon compete with the coal-fired plants that Thomas Edison had built just three years earlier, his work was met by skepticism in the United States. Fritts' selenium cells achieved an energy conversion rate of less than 1 percent.[4] Although others continued to develop and patent photovoltaic cells based on selenium,[5] it eventually fell out of favor. Even by the 1980's, selenium cells had achieved no more than a 5.0% energy conversion rate.[6] Fritts applied for but never received a patent on his work.

Research continued, centered in France and spreading elsewhere, on thermal energy generation from solar radiation. In 1860, Augustin Mouchot, a French mathematics professor, began working on solar energy after becoming gravely concerned about France's dependence on coal. In 1861, he filed for a French patent on the use of concentrated solar radiation to heat water, and continued registering patents through the 1870's. Backed by Emperor Napoleon III's financial assistance, Mouchot

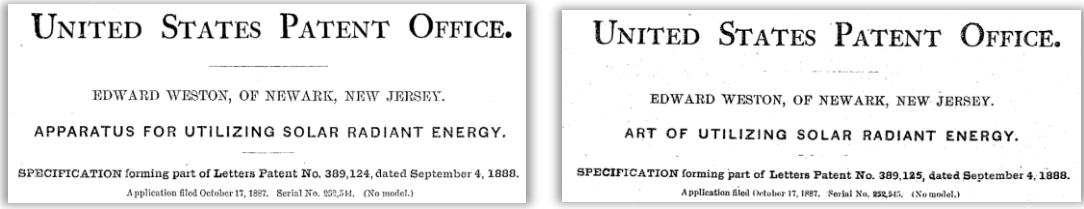
---

[2] E. Becquerel, *Mémoire sur les effets électriques produits sous l'influence des rayons solaires*, 9 Comptes Rendus 561–567 (1839).
[3] W. Smith, *The action of light on selenium*, 2 J. Soc. Tel. Eng'rs 27-29 (1873).
[4] C.E. Fritts, *On a new form of selenium cell, and some electrical discoveries made by its use*, 26 Am. J. Sci. 465-472 (1883).
[5] *See, e.g.*, A.H. Lamb, U.S. Patent No. 2,000,642 (May 7, 1935)
[6] M. A. Green, *Silicon photovoltaic modules: a brief history of the first 50 years*, 13 *Prog. Photovolt. Res. Appl.* 447–55 (2005).

developed a “Sun Engine” to operate a small, conventional steam engine, and wowed the public by making a block of ice from the sun’s rays at the Paris World Fair of 1878. But at that same fair, the internal combustion engine was also unveiled. The United States had discovered oil in 1859 and was supplying fuel to meet global energy needs. Moreover, coal deposits had been discovered in eastern France, making coal abundant and less expensive. Unlike gasoline and coal-based systems, Mouchot’s system could not store energy for later use. Concluding that solar energy was not economically viable, the French government withdrew support for Mouchot’s research.

Across the Atlantic, in 1888, Edward Weston was awarded perhaps the first two United States patents on solar cells based on thermopiles. A thermopile converts thermal energy into electrical energy based on the Seebeck Effect, a phenomenon originally discovered in 1794 by Italian scientist Alessandro Volta[7] (for whom the photovoltaic effect is named), but named after German physicist Thomas Johann Seebeck who independently rediscovered it in 1821.[8] Weston, an England-born American chemist, was himself a prolific inventor, garnering 334 United States patents on various electromagnetic instruments over his lifetime. He invented U.S. Patent Nos. 389,124 and 389,125, claiming an apparatus and method, respectively, for converting solar radiation into electrical energy using thermopiles.

[7] C. Goupil *et al.*, *Thermodynamics and thermoelectricity*, in *Continuum theory and modeling of thermoelectric elements* 2-3 (Wiley-VCH 2016).
[8] T.J. Seebeck, *Magnetische Polarisation der Metalle und Erze durch Temperatur-Differenz*, Abhandlungen der Königlichen Akademie der Wissenschaften zu Berlin 265–373 (1822).


UNITED STATES PATENT OFFICE.

EDWARD WESTON, OF NEWARK, NEW JERSEY.

APPARATUS FOR UTILIZING SOLAR RADIANT ENERGY.

SPECIFICATION forming part of Letters Patent No. 389,124, dated September 4, 1888.

Application filed October 17, 1887. Serial No. 252,544. (No model.)

UNITED STATES PATENT OFFICE.

EDWARD WESTON, OF NEWARK, NEW JERSEY.

ART OF UTILIZING SOLAR RADIANT ENERGY.

SPECIFICATION forming part of Letters Patent No. 389,125, dated September 4, 1888.

Application filed October 17, 1887. Serial No. 252,545. (No model.)

Fig. 1. Edward Weston's U.S. Patent Nos. 389,124 and 389,125 for utilizing solar radiant energy.

Contrasting Mouchot's earlier work as "directly utilizing solar heat to produce steam or hot air," Weston explained that his invention could store solar energy in a chemical battery cell so that "energy accumulated during hours of sunshine may be utilized during night or periods of cloudy weather." In Weston's apparatus, sunlight concentrated by a lens F heat up the junctions D of a thermopile A made of dissimilar metal bars B and C. The thermopile converted thermal energy into electrical energy, which was stored in a secondary cell H, and then deployed to run motor K. Weston's stored-energy concept is today the generally accepted approach for deploying solar energy.

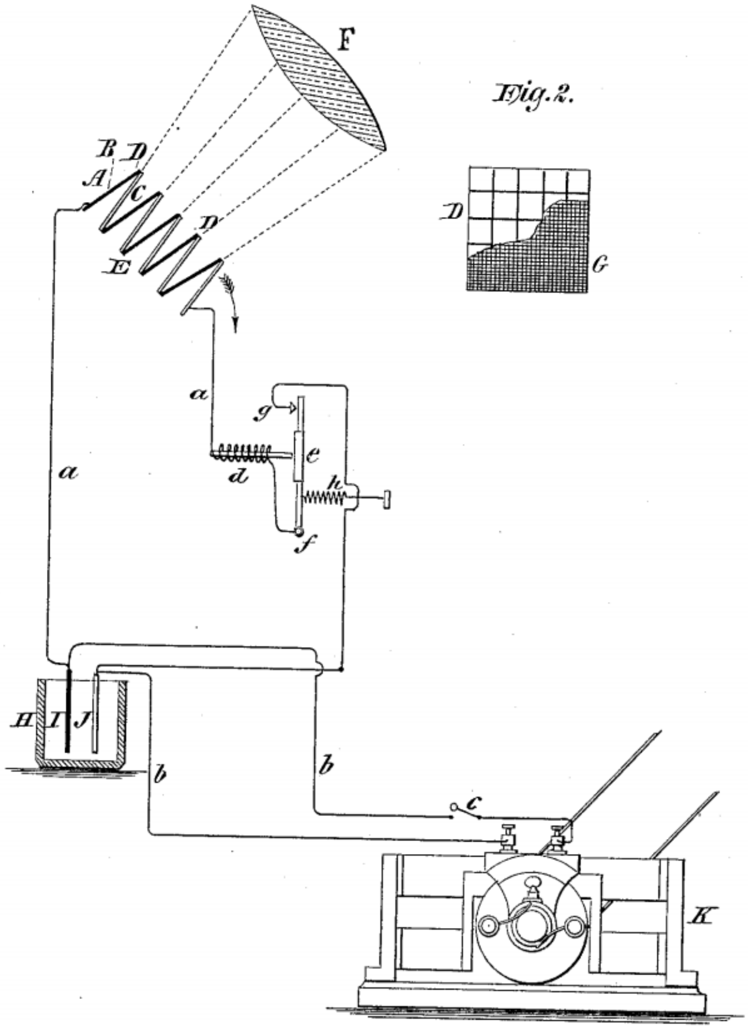


Fig. 2. Edward Weston's thermopile-based apparatus for utilizing solar radiant energy

Research on improvements in thermopile-based solar cells continued into the 1890's. For example, in 1894 American musician and artist Melvin L. Severy secured two patents on optimizing the orientation of thermopiles to sunlight. In U.S. Patent No. 527,377, Severy arranged thermopiles 1 in a semi-circular frame 25, on a line running east-west, and at an angle that is a mean between the winter and summer declination of the sun. The frame revolved in synchrony with a clock 21 keeping solar time.

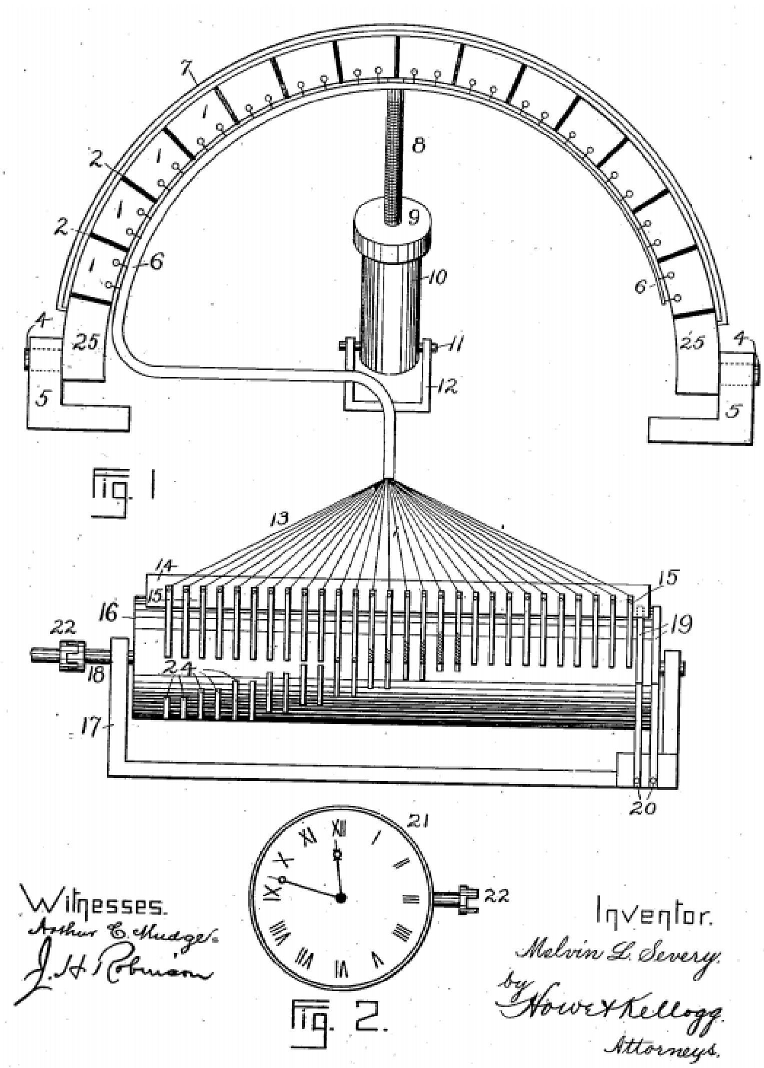


Fig. 3. Severy's thermo-pile orientation system in U.S. Patent No. 527,377.

In U.S. Patent No. 527,379, he pivoted a case 10 containing a thermopile upon a vertical standard 24, and supported it on a horizontal turn-table 26. By the combination of these components, the thermopile could be oriented such that "the face of the pile can be maintained opposite to the sun at all times of the day and at all seasons of the year."

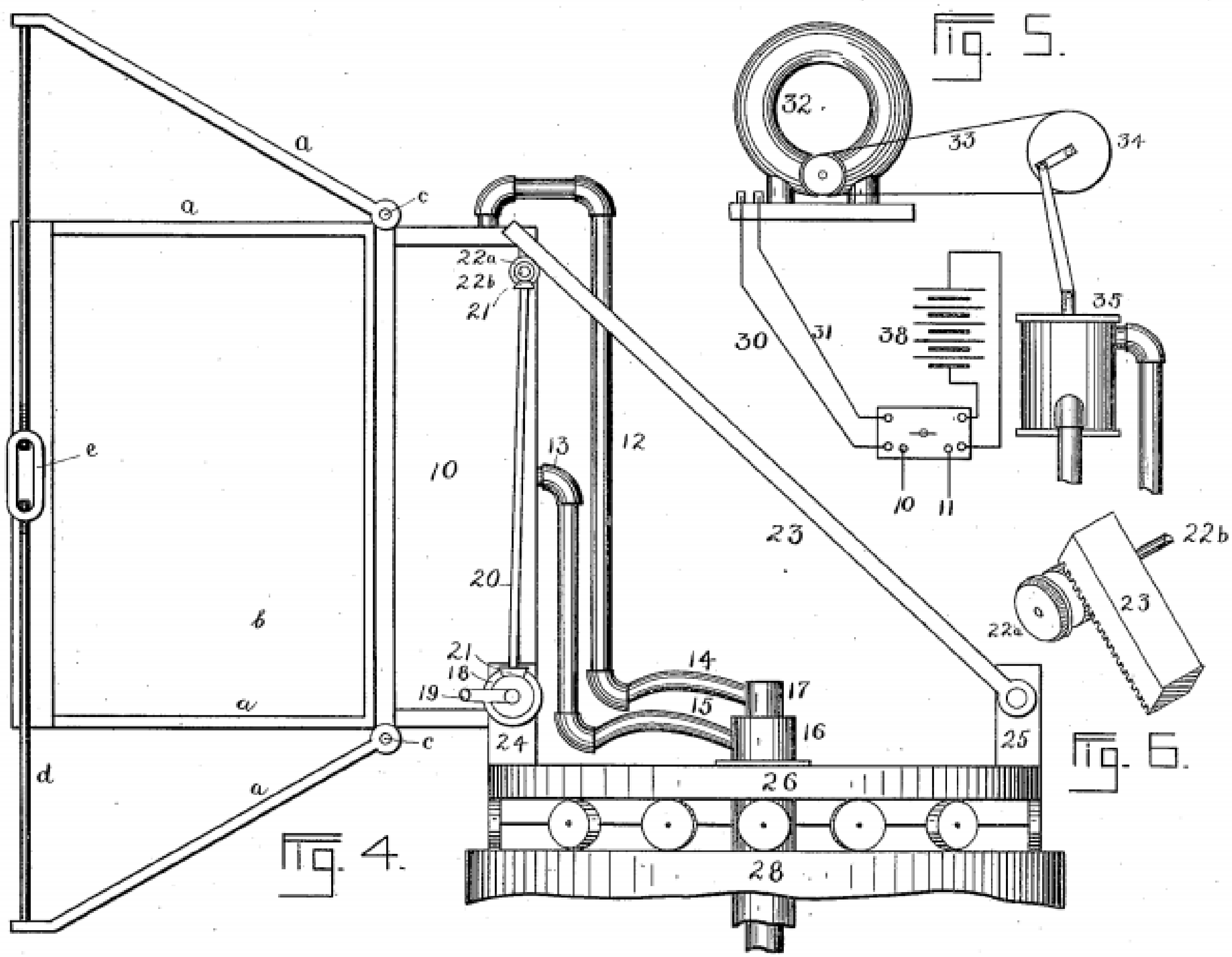


Fig. 4. Severy's thermo-pile orientation system in U.S. Patent No. 527,379.

In 1897, Philadelphia resident Harry C. Reagan Jr. secured U.S. Patent No. 588,177 on a thermo-pile based "thermo-battery." In Reagan's invention, a series of thermo-couples L were placed at the focus of a set of adjustable mirrors K, which concentrated the sun's rays onto the thermo-couples L. One side N of the junctions of the thermo-couples L was cooled by liquid in tank B', and the other side M heated due to the sun's rays. Electrical energy generated at the thermo-couples could be taken away and utilized where convenient.

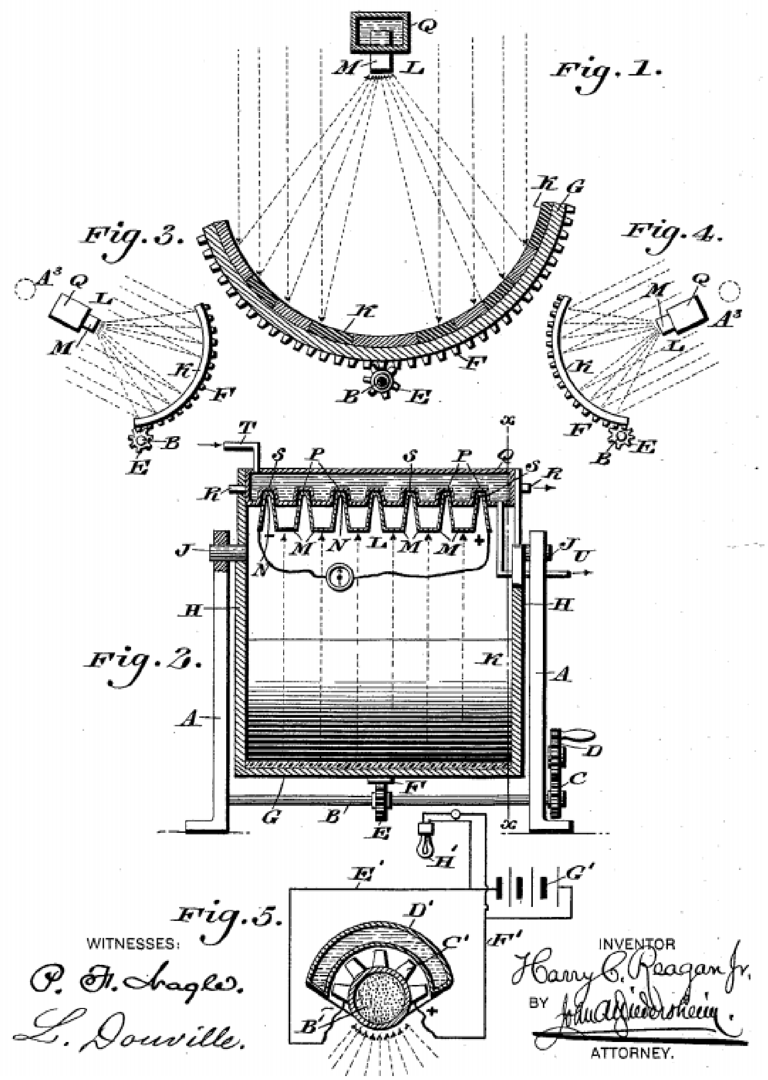


Fig. 5. Reagan's "thermo-battery" in U.S. Patent No. 588,177.

<u>The Rise of Semiconductors</u>

As the 20th Century approached, scientists across the globe gained a deeper understanding of the forces of nature, in the process laying the theoretical and practical foundations for the rise of semiconductor solar cells. In 1887, German physicist Heinrich Hertz discovered the photoelectric effect, which refers to the emission of electrons when light hits a material. In 1905, Albert Einstein explained the quantum basis of the photoelectric effect, for which he won the 1921 Nobel prize in physics.[9] Between 1888 and 1891, Russian physicist Alexander Stoletov published six works on the photoelectric effect and built the first solar cell based on the effect.[10] In 1904, Hertz's one-time assistant Wilhelm Hallwachs—the photoelectric effect was previously called "Hallwachs-Effekt"—made a semiconductor-junction solar cell based on the photoelectric effect, using copper oxide as a semiconductor. In 1918, Polish scientist Jan Czochralski produced a method to grow single crystals of metal.[11] The Czochralski method would later be adapted to produce single-crystal silicon. In 1928, Swiss physicist Felix Bloch set out a band theory to explain quantum behavior based on a single crystal periodic lattice.[12] In papers published in 1931-1932, British mathematician Sir Alan H. Wilson developed a theory explaining how energy bands of electrons determine whether a material is a conductor, semiconductor, or insulator.[13] In 1948, Gordon Teal and John Little adapted the Czochralski method to produce single-crystalline germanium and silicon.[14]

These and other scientific works set the stage for Bell Laboratories' monumental advances in silicon solar cells. Bell Labs realized that semiconductor materials like

---

[9] A. Einstein, *Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt*, 322 Annalen der Physik 132-148 (1905).

[10] A. Stoletow, *Sur une sorte de courants electriques provoques par les rayons ultraviolets*, Comptes Rendus CVI:1149 (1888); A. Stoletow, *Sur les courants actino-electriques au travers deTair*, Comptes Rendus CVI:1593 (1888); A. Stoletow, *Suite des recherches actino-électriques*, Comptes Rendus CVII:91 (1888); A. Stoletow, *Sur les phénomènes actino-électriques*, Comptes Rendus CVIII:1241 (1889); A. Stoletow, *Актино-электрические исследования*, 21 J. Russian Physico-chem. Soc. 159 (1889); A. Stoletow, *Sur les courants actino-électriques dans l'air raréfié*, 9 J. de Physique 468-473 (1890).

[11] J. Czochralski, *Ein neues Verfahren zur Messung der Kristallisationsgeschwindigkeit der Metalle*, 92 Zeitschrift für Physikalische Chemie 219-221 (1918).

[12] F. Bloch, *Über die Quantenmechanik der Elektronen in Kristallgittern*, 52 Zeitschrift für Physik 555-600 (1928).

[13] A.H. Wilson, *The Theory of Electronic Semi-Conductors*, 133 Proc. Roy. Soc. A 458-491 (1931); A.H. Wilson, *The Theory of Electronic Semi-Conductors II*, 134 Proc. Roy. Soc. A 277-287 (1932).

[14] D.C. Brock, *Useless no more: Gordon K. Teal, Germanium, and Single-Crystal Transistors*, 24 Chem. Heritage Mag. 1-2 (2006)

silicon were more efficient than previously used materials like selenium. In 1941, Russell S. Ohl at Bell Labs invented the first silicon solar cell, securing U.S. Patent No. 2,402,662 on his invention. In the '662 Patent, Ohl described a process of forming a silicon ingot using silicon of a high degree of purity, ideally around 99.85 per cent. He formed the ingot by fusing metallic silicon in powdered form in a silica crucible in an electric furnace and slowly cooling it until it solidifies. The resulting ingot included a light-sensitive barrier portion 9 in between a top region 7 ("p" zone) which developed a positive potential with respect to an attached copper electrode, and a bottom region 8 ("n" zone) which developed a negative potential with respect to an attached copper electrode.

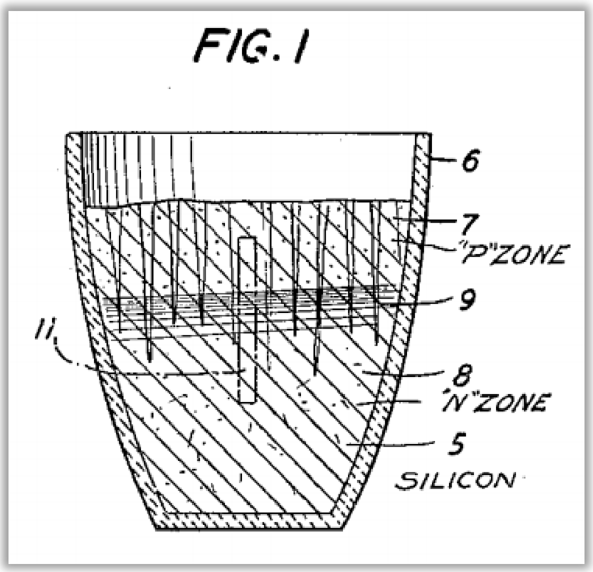


Fig. 6. Ohl's silicon ingot with P and N zones, in U.S. Patent No. 2,402,662.

Ohl cut a section from the ingot including the top, barrier, and bottom portions, and attached electrodes to the top and bottom portions, yielding the first silicon solar cell.

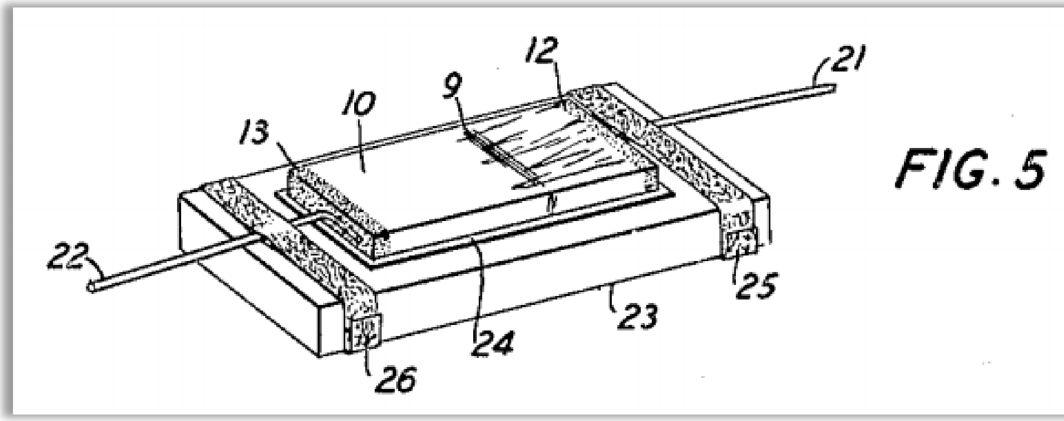


Fig. 7. Ohl's silicon P-N photo-E.M.F. cell, in U.S. Patent No. 2,402,662.

In 1954, Bell Labs' Daryl Chapin, Calvin Fuller, and Gerald Pearson created a silicon single-crystal photovoltaic (PV) cell capable of about 6 per cent conversion efficiency with direct sunlight, enough to power an electric device for several hours of a day.[15] Their patent, U.S. Patent No. 2,780,765, issued in 1957. In it, they describe creating a light-sensitive p-n junction by diffusing boron into a 40 mil thickness[16] n-type silicon wafer 11. This forms a thin and highly transparent boron-doped surface p-type layer 13 that is only 0.1 mil thick. They treated the light-exposed top surface 14 with a thin polystyrene coating 20 to minimize losses from reflection of sunlight. They also etched away portions of the p-type layer 13 on the back surface 15 and electroplated rhodium contacts 17, 18, 19 to create electrical connections to the p-type and n-type layers.

---

[15] D. M. Chapin, C. S. Fuller, and G. L. Pearson, *A New Silicon p-n Junction Photocell for Converting Solar Radiation into Electrical Power*, 25 J. App. Phys. 676-677 (1954).
[16] 1 mil is 1 millionth of an inch, or 25.4 micrometers.

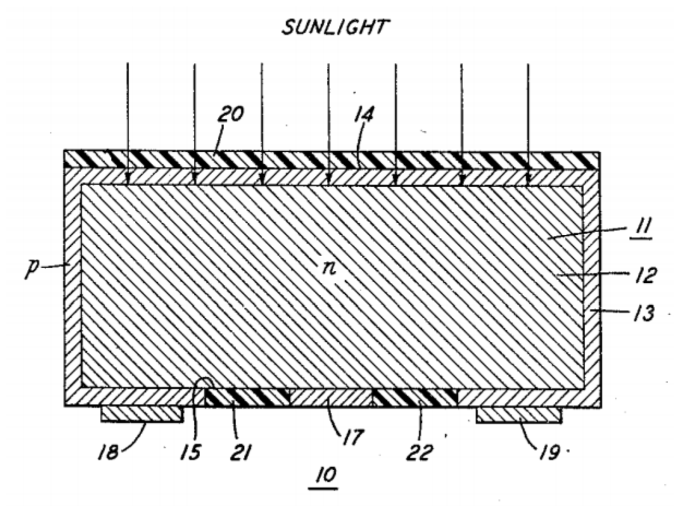


Fig. 8. Chapin, Fuller, and Pearson created a single-crystal silicon p-n junction solar cell, in U.S. Patent No. 2,780,765.

Chapin, Fuller, and Pearson also described chaining multiple such solar cells together to form a solar panel.

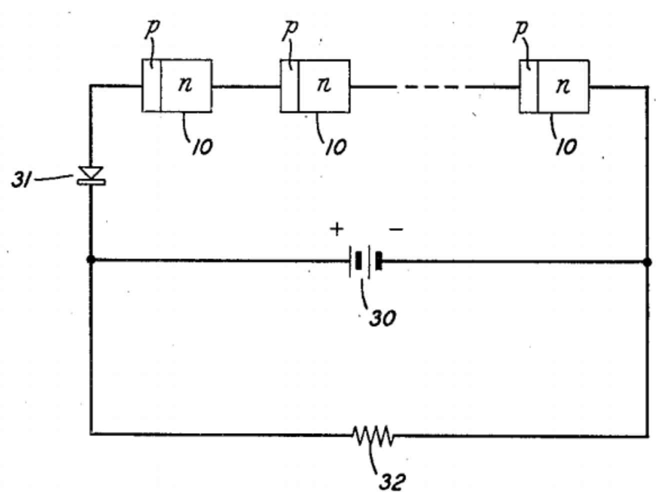


Fig. 9. Chapin, Fuller, and Pearson chained together multiple single-crystal silicon p-n junction solar cells to form a solar panel, in U.S. Patent No. 2,780,765.

Chapin, Fuller, and Pearson's work in the 1950's is the foundation for much of today's solar cell technology. For their work, Chapin, Fuller, and Pearson were inducted into the National Inventors Hall of Fame in 2008.[17]

The Modern Age of Solar Cells

Today, there are thousands of issued patents, both U.S. and worldwide, on various solar cell technologies. Accompanying this explosion in green technological innovation, cumulative solar photovoltaic installed capacity worldwide has soared due to improved conversion efficiency and lowered volume production costs. For example, worldwide solar photovoltaic capacity had grown to 512 Gigawatts by the end of 2018 (representing 27% growth from 2017)[18], accompanied by a steady decrease in system and installation costs. Besides single-crystal technologies, research has also focused on polycrystalline silicon, organic, and thin-film technologies. While cheaper, these technologies do not provide the high conversion efficiency of single-crystal technologies. For example, in addition to silicon, which is in Group IV of the periodic table, researchers have developed solar cells from Group III and Group V (or even Group VI) materials. By 1972, IBM had developed an aluminum-gallium-arsenide based solar cell with between 18% and 20% conversion efficiency.[19] Others have since demonstrated over 35% conversion efficiency for such cells.[20] Continued innovation, incentivized by strong intellectual property protection regimes, will only bring further improvements in

---

[17] National Inventors Hall of Fame, *Daryl Chapin: Silicon Solar Cell*, https://www.invent.org/inductees/daryl-chapin (last visited April 23, 2020).
[18] Wiki-Solar, *Utility-scale solar in 2018: Still growing thanks to Australia and other later entrants*, https://wiki-solar.org/library/public/190314_Utility-scale_solar_in_2018.pdf (Mar. 14, 2019).
[19] H. J. Hovel and J. M. Woodall, *High Efficiency AlGaAs-GaAs Solar Cells*, 21 Appl. Phys. Lett. 379-381 (1972).
[20] *See, e.g.*, L. Fraas *et al.*, *Over 35% Efficient GaAs/GaSb Stacked Concentrator Cell Assemblies for Terrestrial Applications*, 21st IEEE PV Specialist Conference 190 (1990).

efficiency and costs, making green solar technology more accessible to consumers everywhere.