

# Contents lists available at ScienceDirect

# **Comptes Rendus Physique**

www.sciencedirect.com



Demain l'énergie – Séminaire Daniel-Dautreppe, Grenoble, France, 2016

The new paradigm of photovoltaics: From powering satellites to powering humanity



# Le nouveau paradigme de l'énergie solaire photovoltaïque : de l'alimentation électrique des satellites à celle de l'humanité

# Daniel Lincot

CNRS, Institut photovoltaïque d'Île-de-France (IPVF), 30, route 128, 91120 Palaiseau, France

### ARTICLE INFO

Article history: Available online 2 October 2017

Keywords: Photovoltaic energy Climate mitigation Solar cells Silicon Perovskite New concepts

Mots-clés :

Énergie photovoltaïque Changement climatique Cellules solaires Silicium Perovskite Nouveaux concepts

## ABSTRACT

The photovoltaic effect has been discovered by Edmond Becquerel in 1839. Then it took 115 years to make the first efficient solar cell, with a few watts produced, about 50 years to deploy 3 GW of production capacity worldwide, and only 13 years to reach 300 GW in 2016. 500 GW are expected in 2020, and the TW within the next decade. How did this occur? How does photovoltaics work? What is the physical limit of conversion efficiency? What road map for photovoltaics in the energy transition? This paper aims at providing a review and discussion of these aspects, from the historical background to the state of the art and the emerging devices and concepts.

@ 2017 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

# RÉSUMÉ

L'effet photovoltaïque a été découvert par Edmond Becquerel en 1839. Il a fallu 115 ans pour fabriquer la première cellule efficace à hauteur de quelques watts, puis environ 50 ans pour atteindre 3 GW de capacité installée dans le monde, et seulement 13 ans pour atteindre 300 GW en 2016. 500 GW sont attendus en 2020, et plus d'un TW au cours de la prochaine décennie. Comment une telle accélération a-t-elle été possible? Quels sont les mécanismes de la conversion photovoltaïque? Son rendement maximum? Quels scénarios sont établis pour le futur dans le contexte de la transition énergétique? L'article examinera tous ces aspects, en partant du contexte historique jusqu'à l'état de l'art actuel, en incluant les cellules solaires émergentes et les nouveaux concepts.

© 2017 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

E-mail addresses: daniel.lincot@ipvf.fr, daniel.lincot@chimie-paristech.fr.

http://dx.doi.org/10.1016/j.crhy.2017.09.003

<sup>1631-0705/© 2017</sup> Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.



Fig. 1. Evolution of the global cumulated installed photovoltaic capacity, with regional subdivisions. From: Photovoltaic report 2017, ISE Fraunhofer [2].

#### 1. Introduction

The photovoltaic effect has been discovered by Edmond Becquerel in 1839 during the study of electrical effects occurring between two electrodes dipped in electrolytes [1]. At that time, the scientific community was fully engaged in exploring the new field of electricity opened in 1800 after A. Volta's discoveries. E. Becquerel reported the production of a photocurrent when electrodes covered by copper or silver halides salts were illuminated by solar light. He discovered also the effect of wavelength on the production of the electrical current, which is now explained by the semiconducting character of these salts with the existence of band gaps. It took 115 years to make the first efficient solar cell, with a few watts produced, about 50 years to deploy 3 GW of production capacity worldwide and only 13 years to reach 300 GW in 2016 (see Fig. 1 [2]), 500 GW are expected in 2020 and the TW within the next decade. How did this occur? How photovoltaics work? What is the potential for further development of photovoltaics in the energy transition? This paper aims to bring an overview and a discussion of all these aspects from an historical perspective.

#### 2. Historical survey

30 years later after Becquerel's discovery, during the course of establishing electrical communication networks around the world, the search for flaw detections led to both the discovery of photoductivity in selenium rods by W. Smith [3], and the premises of an operating solar cell by W. Adams and R. Days [4]. The first operating solar cell based on a copper/selenium film/gold junction was created by C. Fritts in 1883 [5] and adopted by W. von Siemens [6] and J. Maxwell [7]. These inventors already considered that photovoltaic solar energy could supply energy to the earth, and a first solar array was even installed on a roof top in New York in 1884 by C. Fritts. So was also the statement of A. Mouchot at about the same period for solar energy conversion with thermal machines [8]. However, the mechanism of photovoltaic action was not understood and these first cells were mostly considered with skepticism as "Fritts 'magic' plates, as perpetual motion machines" [9] since light was not perceived as a fuel. It came out in the following years that the photovoltaic effect had the same origin as the photoelectric effect: the quantum nature of light, chiefly introduced by A. Einstein in 1905 [10].

The poor performances of selenium cells and the development of coal- and petrol-based energy economy made this discovery restricted to limited use as exposure meters, but found regained applications in radio telecommunications rectifiers known as "cat-whiskers" during the First World War. The development of vacuum tubes electronics in the 1930s then replaced these solid-state rectifiers for radio telecommunications, but failed to be adapted for shorter wavelength applications needed for the development of radars in the period of World War II, creating a revival of interest for "old" cat whiskers solid-state rectifiers [11]. In the course of revisiting this area at Bell telephone's laboratories, Russel Ohl discovered the superior performances of silicon with reaching photopotentials up to 0.5 V, much more that selenium or copper oxide previous materials. He found that the photoeffect is maximum in specific zones of recrystallized silicon boules, leading to the discovery of the p–n junction, and incidentally of the doping phenomenon with Al (n type) and P (p type). The first application was silicon solar cells and modules based on his findings, that he patented in 1941 [12]. An intense research activity was then developed at Bell's laboratories to increase the efficiency of the solar cell, the best efficiency with Ohl's technology reaching 1% in 1952 [13] with limitations arising from the processing technologies (He bombardment). The introduction of Li diffusion wraparound led to 4.5% in 1953, then its substitution by boron diffusion led to a spectacular take off of the efficiency up to 6% in January 1954 and 11% in May 1955 (as reported in R. Bube's book [14]). The key milestone of efficiencies higher than 5% fixed by the Bell's management for industrial credibility was thus presented in the 6% efficiency famous paper authored in 1954 by D.M. Chapin, C.S. Fuller, and G.L. Pearson [15], which is considered worldwide as the birth of the modern silicon solar cell. The technology was then taken by Hoffman Electronics for applications, the efficiencies reaching 14% in 1959 with the introduction of contacting metallic grids, and 15.2% in 1961 with commercial applications. Then the record stagnated for more than 10 years [14]. This extraordinary jump in the efficiency from 1% to 15% in ten years was also a consequence of an external pressure. This pressure came from the space conquest and the cold war competition. Sputnik was launched by the USSR in 1957, but the first satellites were failing due the lack of sufficient stored energy. It was clear that photovoltaic solar cells could be the solution. As a result, only four years after Chapin and al.'s paper, the first satellite, Vanguard, powered by PV was launched by the USA, opening the still ongoing era of PV for spatial applications, with Spirit and Opportunity robots on Mars and Philae and Rosetta on and around Tchouri's comet as famous recent highlights. Thus developing the PV technology became a strategic priority for the USA, USSR and other spatial countries as France [16]. The French team led by M. Rodot at the CNRS reached 14% of Si solar cells in 1960 (footnote in [16]) at almost the same level as US teams. Note that at that time researchers were also considering solar energy conversion with thermoelectric devices and even considered it as more promising than PV [16].

The 10-year-stagnation plateau of record PV efficiencies, which was sometimes "abusively" considered as the demonstration of reaching the experimental limits of the technology, was broken in 1973 by a new record at 15.2%, but with a new technology for antireflection processes, known as the "violet cell". Thanks to this breakthrough, based by the texturing of the silicon surface by etching, the efficiency jumped to 17.2% in 1974 [14]. A new avenue was opened following these technological pillars and introducing step by step more and more sophisticated new architectures, new doping strategies and contact formations, with a new record efficiency at 25% achieved in 1985 with the PERL technology (Passivated Emitter, Rear Locally Diffused Cell). These tremendous improvements were leaded, from 1991, by Martin Green and his group in Australia, taking the relay of the US teams [17]. Fig. 2a shows the structure of record cells at that time. The wafer was p-type 100-oriented 250-µm-thick single crystalline silicon (100) oriented with n+ highly doped zones underneath the top grid contact to reduce the electrical resistance. On the back surface, the same approach was used with p+ zones locally diffused under the contacts. The heart of the electrical characteristic of an illuminated p–n junction solar cell is basically described by the equation:

$$J = J_0 \left( \exp\left(\frac{qV}{nkT}\right) - 1 \right) - J_L$$

where J and  $J_0$  are, respectively the current density (current I per unit area) and the saturation current density, V the voltage across the junction, q the charge of the electron, k the Boltzmann constant, and T the absolute temperature, leading to a q/kT value of 40 V<sup>-1</sup> at room temperature, n is the ideality factor of the diode, with values between 1 and 2 (1 for silicon). The first term on the right is thus the equation of a simple p-n junction in dark with the exponential behavior. Under illumination, the photons are absorbed at the junction and create electron-hole pairs that are separated by the electric field created at the interface between n and p zones. This gives rise to the addition of a photocurrent density term  $J_{\rm L}$  that is added to the diode current. The resulting  $J_{\rm L}V$  curve, if  $J_{\rm L}$  is constant, is a simple vertical translation of the  $J_{\rm L}V$ curve in the dark, making the device in "motor" conditions. All the efforts are thus devoted to reduce the saturation current and to increase the photocurrent! A key improvement of the record cell, shown in Fig. 2a was the use of ultrathin passivating silicon oxide layers on the outer surfaces on both sides. This allowed one to reduce markedly the loss of photocurrent by surface recombination of the electron-holes pairs generated by the absorption of photons in the bulk of the silicon. The surface texturing was used to trap the light and force the photons to enter the device increasing the photocurrent by minimizing the reflection losses. The bulk electronic quality of silicon (life times, diffusion lengths, doping concentrations), allowing one to reduce both the saturation current and to generate photocurrent all along the thickness, was also markedly improved with respect to previous cells generations thanks to continuous progresses in crystal pulling and purification techniques. Then a new plateau in record efficiencies occurred for about 15 years at the level of 25% efficiency. During this time, new approaches were investigated in research labs, with continuous progresses, and two key breakthroughs emerged, which led to new record breaking in the recent period. The first one is the removal of front contacts from the top surface to the bottom surface, leaving the front surface free of shading effects (a few percent of area) and processable only with surface passivation layers. To withstand this modification, it was necessary to create interdigitated contacts on the back side (named IBC), which has been made possible by the transfer of advanced microelectronic technologies to Si solar cells, and by improving silicon bulk properties allowing the collection on only one side of the cell. The associated diffusion lengths are able to reach several mm, which is an unbelievable value, as compared to the 100-200 microns available several years ago. This process was successfully developed by SunPower, reaching an efficiency of 25.2% in 2015, with commercial technologies and a record module efficiency of 24,1% [18]. The second breakthrough came from a change in surface processing of the silicon surfaces, using amorphous silicon intermediate layer instead of silicon oxide. By this way, surface recombination was further reduced. This technology, invented by Sanyo in Japan, named HIT, permitted also to reach the record-breaking value of 25% [19]. A key point is that it mixed for the first time different branches of PV research, namely crystalline silicon and amorphous silicon solar cells (introduced in 1976), favoring convergences between separated communities of researchers. The combination of both IBC and HIT technologies recently led to a new breakthrough in record efficiency at 26.6% by Kaneka's group [20]. The structure of the cell and its IV curves are reported in Fig. 2b. This result approaches the theoretical efficiency of silicon solar cells, i.e. 29.1%, and the authors estimate that they are in position to reach in the near future efficiencies as high as 27.1% by incremental improvements only. This shows that silicon solar cells have almost attained



From Essig et al. Nature Energy

**Fig. 2.** Evolution of record silicon solar cells devices and performances: a) 25% in 1994 from [17], b) 26.6% in 2017 [20] with cell cross section and IV and PV curve in darkness and under illumination for a record cell of 180.4 cm<sup>2</sup>, c) 32.8% in 2017 for a tandem junction combining a silicon bottom cell and a GaAs top cell [32].

their theoretical limit in efficiency after 60 years of research. The effort will now be to consolidate these results and to transfer them into module production at low cost. The other route is to use polycrystalline silicon, which suffers from grain boundaries recombination losses, but can be processed at lower costs. The record efficiency is 21.9% [19], which leaves room to efficiency improvements, especially thanks to grain boundaries passivation! The mean value of commercial crystalline silicon efficiencies is 16.3%, it increases more progressively than the record efficiency chart, since industrial transfer is based on a more conservative/incremental evolution. Both single crystalline and multicrystalline solar cells represented in 2016 about 94% of the annual production capacity [2]. The remaining 6% were shared by thin film technologies (CdTe, CIGS, silicon).

While silicon has been by far the most studied semiconductor for solar cell applications, great attention has been paid in parallel to other semiconductor materials since the 1950s and the early 1960s, in particular in the III–V family based on gallium arsenide and in the II–VI family based on cadmium sulfide and cadmium telluride families [21]. Gallium arsenidebased devices, with 6% efficiencies in 1956 [22], have reached even higher performances than silicon, with 28.8% efficient cells in 2015, which is the absolute record for a single junction solar cell. In addition to exceptional device quality, the key breakthrough developed by E. Yablonovitch and his team in Stanford was to introduce a mirror at the back side, allowing a new mechanism of photocurrent enhancement by photon recycling [23]. GaAs-based cells are much more expensive than silicon, but due to superior qualities, they are widely used in space applications, especially in multijunction configurations (see below). CdS/cuprous sulfide thin film solar cells, also introduced in 1954 [24], were first considered for light weight flexible modules for space applications [25], and then replaced in the 80's by CIGS (copper indium gallium diselenide) solar cells. CdTe cells were also introduced in mid 50's [20] and reached 7% efficiency in 1963 [26]. CIGS and CdTe are now established commercial thin film technologies.

### 3. Mechanism of photovoltaic conversion

At this stage, it is interesting to come back to a fundamental question: what is the theoretical limit of the conversion efficiency of photovoltaic solar cells? This question was present at the early stage of photovoltaic applications at the end of the 19th century, following a similar question for the efficiency of thermal machines since S. Carnot and the endeavor of thermodynamics. Fig. 3 illustrates the basic mechanisms taking place in a solar cell under operation. The photons are absorbed in the semiconductor by transferring their energy to electrons in the valence band, which are pushed to a higher energy level by a value corresponding to the photon energy  $h\nu$ . This process only occurs when the final energy level lies in the conduction band of the semiconductor and not in the forbidden energy gap. This creates an electron-hole pair, which thermalizes with holes reaching the top of the valence band and electrons reaching the bottom of the conduction



**Fig. 3.** Scheme of elementary mechanisms of photovoltaic conversion in a standard solar cell. Red arrows correspond to loss mechanism via thermalization (T) and Recombination (R) after photon absorption. Green arrows are transport and transfer processes (O) which lead to the extraction of photocarriers and power in the external circuit. (O) and (R) processes are in competition to fix the output power. (T) is too fast for any contribution. Red photons arrows correspond to non-absorbed photons.

band. Then they are transferred to the contacts with a potential difference corresponding in maximum to the band gap of the semiconductor. Part of them are reacting together by recombination processes via electronic defects, either in the semiconductor or on the surfaces, or via radiative recombination with the reemission of a photon, the first process being dominating for non-perfect crystals. Photons with energies lower than the band gap are lost and are able to cross the semiconductor without absorption. As a consequence, the maximum efficiency will correspond to that of the VI product, with V being at maximum the band gap value of the semiconductor and I the integral of electrons generated by the flux of photons from the solar light spectrum with energies higher than the band gap, assuming that the quantum efficiency (number of electrons per photon) is one. This gives rise to a bell-shaped curve (V increase with  $E_g$  and I decreases with  $E_g$ ), shown in Fig. 4 after theoretical calculations from [27]. We can observe that the maximum efficiency is about 31% for band gap values of about 1.5 eV. In the case of silicon, with a band gap of 1.12 eV, the value is about 29%, as indicated before. This bell curve was calculated in early publications from device properties as soon as 1954 by M. Prince from Bell [28], who predicted a maximum value of 24%, close to the silicon band gap and a possibility of 10% cells from the 6% efficient technology at this time, which was verified. In 1956, J. Loferski from RCA did the same with a maximum of 26,5% for 1,5 eV and only 20.3% for Si [29]. In 1961, a groundbreaking thermodynamic approach was presented by W. Shockley and H. Queisser [30], considering the ideal case of radiative recombination losses. The bell-shaped curve was peaking at about 30%, with a value of 26% for silicon, which is within a few per cent of recent calculations. This fundamental limit for simple p-n junctions is known as the Shockley-Queisser (QS) limit. It is valid for any PV device working on two levels as in Fig. 3 including recent organic PV devices based on molecular orbitals where BV and BV levels are replaced by HOMO and LUMO levels.

#### 4. Ultimate efficiency for PV conversion and devices

The question now is: is the Shockley–Queisser limit the ultimate one for PV converters? The answer is no. We can identify losses for photons having energies both higher and lower than the band gap in the basic behavior of a two-level device: at higher energy by partial thermalization (interaction with the phonons that are the vibrations modes of the lattice) and at lower energy by non-absorption (shown in Fig. 3 and quantified in Fig. 4 as a function of the band gap). In fact, the thermodynamic approach is again the right approach considering that the sun and the PV cell behave as a hot source and a cold source, respectively. Taking a value of 5800 °K for the sun and 298 °K for the cell leads to a crude estimation of Carnot efficiency as high as 95%! This means that the actual PV efficiencies are still far beyond the theoretical limit. Complete theoretical modeling has been performed, which confirms such high level as shown in Fig. 4 by adding SQ efficiency, high energy losses and low energy losses. Taking into account losses that were not present in the simplified Carnot efficiency leads to theoretically achievable efficiencies up to around 85%.

Would new device concepts allow us to cross the Shockley–Queisser limit? Yes. The PV research community started to address specifically these questions about the years 2000s under the "third-generation PV" flag, held by M. Green again [31]. The principles of some of them are presented in Fig. 5. The most advanced and already commercially present as a minor component of the market (<1%) is the concept of multijunctions (Fig. 5) which consists in placing several single junctions on the top of each other with decreasing band gap values from the top surface facing the sun and the bottom rear surface. Each junction working optimally for photons corresponding to the band gap, the combination of multiple junctions would lead to an increase in the efficiency limit. However, we can imagine the complexity of processing and cost of such devices... Hopefully, gains are already important for two junctions, three junctions, and four junctions with maximum values of about 43, 50 and 54%, respectively, as compared to 31% for a single junction [31]. An important renewed research activity is presently paid to the multijunctions approach, in particular in combination with existing silicon cells, to break the SQ limit



Fig. 4. Model of power distribution of incident light in a standard solar cell as a function of the band gap of the cell (1.12 eV for Si, 1.45 for GaAs for example). The bell curve corresponds to the upper conversion efficiency under the Shockley Queisser limit.



**Fig. 5.** Schemes of elementary mechanisms of high-efficiency devices, beyond the Shockley Queisser limit. A: Multijunction concept, already proven. B, C, D: new theoretical concepts, under fundamental study. B: hot carrier solar cells, which allow to compete with thermalization losses for high-energy photons. B: intermediate band solar cells which allow to collect the infrared photons. D: dow conversion solar cells, which use an active optical filter to convert high energy photons to several lower energy photons further absorbed standard single junction high efficiency cell (like Si, CIGS, CdTe...) without losses in energy. This is an example of a new concept based on photonics.

of single junctions. The goal would be to reach between 35 and 40% of record cells with either two (tandem) or three junctions, to bring the next generation at module efficiencies up to 30%. The record efficiency reached with tandem and triple junctions based on silicon bottom cells with top cells belonging to the III–V semiconductor family (GaInP, GaAs...) is now 35.6% for triple and 32.8% for tandem, which structure is shown in Fig. 2c [32]. Quadruple junctions based on III–V have reached efficiencies as high as 46% in 2014 with 400 concentration of light, in the frame of a work by a consortium led by Soitec in France and ISE Fraunhofer in Germany [19]. Concentration is a way to increase the efficiency of the cell due to the dissymmetric behaviors of photocurrent and tension with respect to light flux, as can be forecasted by multiplying  $J_L$  by the concentration factor ( $J_1$  is proportional to the incident light flux). The ultimate concentration factor from sunlight is 43,000, but typical concentration values are from 5 to 500. Achieving higher values need to manage stronger thermal effects and resistive losses. A recent concept has been introduced to reach higher values by using low-dimensionality devices (microcell concept) [33]. Upon concentration the one sun efficiency can be the SQ limit is increased by about 2% per decade, theoretically up to 10% for full concentration (31% to 41% at maximum of the SQ limit).

#### 5. Emerging PV devices and concepts

The full picture of the state of the art of PV research and its historical development is summarized in the well-known chart of PV record values of NREL, which also compares the different technologies, either commercial ones and emerging ones [19] established from 1976 to now. Beside the silicon technologies, the other commercial technologies are thin film technologies based on CdTe and on CIGS with efficiencies up to 22.1 and 22.6% respectively, beyond that of polycrystalline silicon. The evolution of the records as a function of time can be discussed in the same way as for silicon, as discussed for CIGS technology [34]. The improvements in the last period are impressive for both technologies. In the case of CIGS, new surface chemistry was introduced through doping with alkali metals (Na, K, Rb). Note that these solar cells are polycrystalline and with thicknesses of only a few microns, directly deposited on glass. This represents a potential cost advantage with respect to crystalline silicon. Note that non-vacuum-based elaboration processes like electrodeposition and printing are possible, like it has been developed in France by Nexcis with the electrodeposition of CIGS [35].

All these single junction technologies tend to reach the SQ limit of about 30% with non-concentration. Only multijunctions, as shown in [32] and shown in Fig. 2c for a tandem junction, are already able to cross this limit under standard illumination conditions. They reach 46% efficiency for quadruple junctions under concentration [19] which is the "champion value" ever achieved up to now for photovoltaic conversion.

Besides the established technologies dealing with inorganic semiconductors, we can observe the onset of emerging materials during the two last decades. The main breakthrough arises with the discovery of mesoporous report of efficient mesoporous dye sensitized solar cells in 1991 by B. O'Regan and M. Graetzel [36]. This approach is based on the use of a nanoporous titanium oxide matrix with a huge internal developed area (up to 500 times the flat area for a few micron-thick films) covered with a monolayer of a dye molecule, which is the active PV component, and then intimately impregnated with an electrolyte. This concept, which escaped for the first time the traditional p-n junction's ones (no need for internal electrical field), has revolutionized the PV research domain, by allowing breakthroughs in the stagnating organic PV domain, with introducing the intimate mixing of active components (bulk heterojunction concept). It was closer to the photovoltaic effect operating in photosynthesis with chlorophyll molecular PV centers, and a form of revival of the photo-electrochemical effect by E. Becquerel [1]. This resulted in a new era of PV research with nanoscale devices (quantum dots, nanorods, nanosheets...) based on oxides (like ZnO), nitrides, chalcogenides, carbon... However a breakthrough came in 2009 from a lapanese group [37] using as a sensitizer a completely new material for PV, that is an hybrid perovskite based on Lead Methyl ammonium iodide, with an efficiency of 3.8%. The perovskite solar-cell thin-film technology was born [38]. In only five years, this technology raised an efficiency from almost zero to 22.1% [19], under the combined efforts and competition between M. Graetzel group at EPFL, H. Snaith's group in Oxford and S. Seok's in Korea, and of many other groups! This incredible fast progress only compares to that of the early years of silicon solar cells. Research accompanying this technology is a multifront/multidisciplinary one ranging from fundamental studies of the mostly unknown properties of these materials, exploring new compositions for optimizing the properties and band gap engineering (for instance, replacing iodide by bromide allows one to increase the gap from 1.4 to 1.8), facing stability and large-scale processing issues, and at the same time trying to create functional devices and start commercialization [39]. Tremendous efforts are now paid at the international level to the application of perovskites for tandem junction as top cells on silicon bottom cells, as an alternative to using III-V top cells, which are more demanding in terms of cost and processing technologies (perovskites can be deposited by printing technologies without... vacuum, with superior efficiencies!). The irruption of perovskite and organic/dye solar cells (developing already in niche markets) also mark the irruption of cutting edge chemistry in the field of PV concepts and materials and shine new light on fundamental photosynthesis and self-assembly mechanisms as a source of inspiration for further progresses [40].

The 1990s and the beginning of the 2000s were also an exceptional period for new theoretical advances in PV research, which is known as "third-generation photovoltaics", the first generation being that of silicon and the second that of thin-film "two-level" single junctions, both "below Schokley Oueisser limit". The aim of "third-generation PV" was clearly to search for high "beyond-SQ" efficiencies, with revolutionary views beyond standard solar cell physics. While multijunctions were first considered, the merit of this research initiated as a whole by M. Green [31], who chiefly contributed to silicon solar cells progresses, was to propose new concepts were efficiencies higher than 50% could be obtained with simpler devices than multijunctions thanks to new electro-optical mechanisms, such as those shown in Fig. 5. The key point is to separate the opposite variations of photocurrent and potential with the band gap responsible for the SQ bell-shaped curve. To do this, the concept of "hot-carrier" solar cell (Fig. 5b) has been introduced where the generated electron hole pairs are collected before they thermalize to the band gap energy; this needs energy-selective contact with extremely fast charge transfer and low thermalization rates by engineering "electron-phonon interactions", in nanostructures for instance [41]. Another idea is to introduce intermediate bands (Fig. 5c) in the semiconductor to allow low-energy photons to be absorbed and contribute to the photocurrent, while maintaining the band gap value for open circuit voltage. The material behaves a bit like a "salmon ladder" for low-energy photons, and resembles an internal multijunction. Experimental proofs of these concepts are studied using superlattice devices [42]. The other concept is based on optics; it couples a standard single junction with active light filters, allowing to convert UV photons (down conversion) and infra red photons (up conversion) in visible photons optimally converted in the single junction (Fig. 5d for down conversion). This is like changing the sun light from polychromatic to monochromatic without energy losses! Another cutting-edge concept is to create locally a strong concentration of light in PV nanostructures by using plasmonic effects on metallic particles or local antenna effects. Light confinement in nanoscale



Notes: Orange dots indicate past module prices; purple dots are expectations. The oval dots correspond to the deployment starting in 2025, comparing the 2DS (left end of oval) and 2DS hi-Ren (right end).

**Fig. 6.** Price experience curve of PV modules since 1976 and projections [45]. The decrease is about 22% per doubling the installed PV capacity. This curve is known as Swanson's curve [46] but often called "the Moore's" law of photovoltaics. Similar lows are observed for other products like flat screens and computers. Actual prices (red rectangle) are indicated, they are already lower than projections.

layers or in microcells or nanocells (i.e. nanowires) is on the verge of first experimental demonstrations. The emergence of all these new concepts gives further momentum to the increased activity of PV in the recent years. It also creates the conditions to transfer some of these new knowledges to improve the present technologies (selective contacts, photon converting layers...).

#### 6. Photovoltaics in the main stream energy sector

Up to 2000, the contribution of terrestrial PV to the energy sector remained negligible. However, since the early years of the 1950s, and even sooner with the selenium cell, the objective of using PV for contributing to the energy supply on earth was present in most of PV researcher's minds, in public opinion, and was supported by specific programs and initiatives. As long as the cost was not an issue, PV could develop as a mature and reliable technology for space applications, and earth ones in isolated areas and special applications (like marine light and telecommunication spots, cathodic protection of pipes in the petroleum industry – explaining why petroleum companies were strongly involved at the beginning of PV). Coming to the earth was another story, because the costs were far too high to compete with fossil energy vectors (oil, coal). A first boost for accelerating PV deployment on earth came from the petroleum chock in 1973, but, after an increased attention, the political choices for an alternative to oil was to go to nuclear energy, releasing in many countries the efforts for terrestrial PV. However, after an increased attention, the political choices for an alternative to oil were to go to nuclear energy, releasing in many countries the efforts for terrestrial PV. However, the onset of concern about climate change, limitation of fossil fuel resources, and nuclear energy resulted in a new interest in PV with very important initiatives to consider PV and renewable energies in general in the economic context and competition, and to bring the debate at the political level. A pioneer of this mutation on PV thinking was Hermann Scheer with a first book in 1994 (a Solar Manifesto) and a second one devoted to the proposal of a solar economy in 1999 [43], which has strongly influenced the political sphere in Germany. Specific public programs to support PV implantations were launched in Germany, Japan, US, like roof tops projects, followed by the introduction of feed in tariffs in Germany, which proved to be very efficient to start the industrial endeavor. These supporting schemes have progressively spread in many countries, like in France in 2006, after the "Grenelle de l'Environnement". Then China entered the competition by deciding to force a strong industrial program. All this together created the right conditions for the endeavor of PV industry. These developments are remarkably recalled in the book published by W. Palz "Power from the sun", including contributions form worldwide solar pioneers [44]. The cost reductions arising from scale effects and technological improvements started to operate, allowing the cost of a watt to decrease from several dollars to less than one dollar, and now to less than 0.5 dollar within ten years (Fig. 6) [45]. This experience curve, precisely discussed in 2006 [46] by D. Swanson, founder of Sun Power corresponds to a decrease of about

22% of the price of a commercial module (in dollar per Watt) when the cumulated production doubles. This spectacular decrease of the costs of PV modules was accompanied by an exponential growth of the annual production of PV capacities, with a mean value of about 40%. From less than 1 GW per year in 2000, the 2016 production reached 75 GW in 2016, with a total cumulative installation reaching more than 300 GW at the world level (Fig. 1) coming from 1.4 GW in 2000 [2]. China shifted from being only a supplier to the foreign market to become the first installer now in the world, with 35 GW in 2016 and an objective to reach 100 GW cumulated in 2020. The electricity proportion coming from PV, estimated at the end of 2016 by IEA is reaching now 1.8% at the world level with about 7% in Germany, Italy, Greece, 1.7% in France, 1.5% in China, and 12.5% in Honduras, and is developing rapidly in many places around the world (India, Africa, America...) [47]. The price of PV electricity shifted accordingly from several tens of cents per kWh to values down to around 10 cents now and even 3 cents in recent calls [48]. This means that PV has reached the grid parity in many places and is now competing with other energy vectors in the open, non-subsidized, market. This is clearly a situation that was unexpected only a few years ago, even for PV specialists, making the evolution much faster than that predicted from many scenarios. This was pointed out in a 2015 analysis by the MIT [49]. In the IEA scenario of 2014 [45], PV was expected to reach 4.4 TW of installed capacity in 2040, but in more recent studies higher values up to about 10 TW or more are indicated from various scenarios [50]. It means that PV contribution is still in an infancy period. According to this scenario, the next decade will experience a dramatic acceleration of PV installations worldwide, with a rate of several hundreds of GW installed per year. Individual PV modules production plans are anticipated to reach capacity productions of more than 5 GW per year (i.e. approaching a 1 GW power plant in terms of energy output). R&D road maps, linking technological and cost aspects, are settled to pave the way for this development. For instance, IPVF with the support of leaders of main PV institutes worldwide, has issued the  $30 \times 30 \times 30$  white paper in COP21 in Paris (2015) aiming to reach 30% modules in 2030 at 30 dollar's cents per Watt [51], which should be possible by increased efforts on multijunction devices. See Figs. 5 and 6.

This represents a completely new paradigm for photovoltaics. On one side, this goes in the right direction to face the dramatic climate change issue by providing a new source of renewable energy able to contribute at a high level, with a strong potential, in supplying humanity with energy in the next decades. On the other hand, new aspects will have to be considered for increasing social and environmental benefits. PV has to support the economies of the different countries, and employment. It has to be inserted in the society with the support of the citizens. With this respect, a key advantage of PV is the distributed and abundant nature of solar energy, which delivers between 700 kWh·m<sup>-2</sup> per year and up to 2700 kWh·m<sup>-2</sup>·yr<sup>-1</sup> in most places of the world. Using PV systems with 15 to 20% efficiency currently and at expected levels up to 30% to be provided by the research sector in 2030, allows us to produce hundreds of kWh per square meter and per year all over the world. All possible sources can be considered, from individual installations on roofs, streets to large-scale installations in areas without space conflicts, PV on water can also be considered. This multiplicity of PV applications is a key advantage of PV. A clear positive evolution is also appearing around the convergence between PV production and storage technologies in self-consumption, smart grids, electrical mobility, hydrogen sector, and digital economy.

#### 7. Conclusions

The aim of this paper was to make a long trip within the historical development of photovoltaics, from the first silicon solar cells in 1954 to the most recent developments in this research field, characterized by booming activity since 2000. Attention was focused to recall how getting higher and higher efficiencies with more and more reliable technologies was the result of a form of "evolutionary" process like in biology with the alternation of scientific discovery steps and consolidation periods, and their relation to specific external accelerating contexts like the discovery of electricity, war efforts, space conquest, and recently climate change concern as well as energy transition issues. The potential of PV in terms of efficiency (up to 85%) was recalled paving the way for increased R&D effort to develop multijunction solar cells in the coming years and new concepts in the future [51]. The second part of the paper is devoted to analyze the fast development of PV in the main stream energy sector, which appears more and more as a pillar of the on going energy transition. Recent papers [52,53] provide extensive prospective studies of the potential of solar PV deployment up to 2050, up to 30–40% PV possible share in electricity generation in 2050 [53]. They point out the fact that PV is markedly underestimated in most scenarios and that there is an urgent need to convey such informations to the IPCC panel specialists and decision makers [53].

#### References

- [1] E. Becquerel, Mémoire sur les effets électriques produits sous l'influence des rayons solaires, C. R. Acad. Sci. Paris 9 (1839) 561.
- [2] https://www.ise.fraunhofer.de/content/dam/ise/de/documents/publications/studies/Photovoltaics-Report.pdf.
- [3] W. Smith, The action of light on selenium, J. Soc. Telegraph Eng. 2 (1873) 32.
- [4] W.G. Adams, R.E. Day, The action of light on selenium, Philos. Trans. R. Soc. Lond. 168 (1877) 341.
- [5] C.E. Fritts, On a new form of selenium photocell, Am. J. Sci. 26 (1883) 465.
- [6] W. Siemens, On the electromotive action of illuminated selenium discovered by Mr. Fritts of New York, Van Nostrand Eng. Mag. 32 (1885) 392.
- [7] C. Maxwell, letter, 31 October 1876, Archives of the Royal Society, London, RR, p. 429.
- [8] A. Mouchot, La chaleur solaire et ses applications industrielles, 1879, A. Blanchard (Ed.), Paris, 1980.
- [9] J. Perlin, in: From Space to Earth, the Story of Solar Electricity, AATEC Publications, 1999, p. 18.
- [10] A. Einstein, On a heuristic viewpoint concerning the production and transformation of light, Ann. Phys. (Berlin) 17 (1905) 132.
- [11] M. Riordan, L. Hoddeson, The origin of the PN junction, IEEE Spectr. (June 1997) 46, and references therein.
- [12] R. Ohl, Ligh sensitive electric device, US patent No. 2,402,662, priority date 1941.

- [13] E. Kingston, R. Ohl, Photoelectric properties of ionically bombarded silicon, Bell Syst. Tech. J. 31 (1952) 814; E.F. Kingsbury, R.S. Ohl, Bell Syst. Tech. J. 31 (1952) 8092.
- [14] R.H. Bube, Photovoltaic materials, in: Series on Properties of Semiconducting Materials, vol. 1, Imperial College Press, 1998, p. 36, and references therein.
- [15] D.M. Chapin, C.S. Fuller, G.L. Pearson, A new silicon P–N junction photocell for converting solar radiation into electrical power, J. Appl. Phys. 25 (1954) 676.
- [16] M. Rodot, La conversion de l'énergie solaire en énergie électrique par les semiconducteurs: thermopiles et photopiles, in: Proceedings of the International Congress "Thermal Applications of Solar Energy in Research and Industry", Montlouis, France, 23–28 juin 1958, CNRS editions, p. 697 (in French).
  [17] M.A. Green, K. Emery, K. Buecher, D.L. King, Prog. Photovolt. 3 (1995) 51.
- [18] Press release, Sun Power web site, 26 June 2016.
- [19] Record PV cell efficiencies chart, National Renewable Energy Laboratory, https://www.nrel.gov/pv/assets/images/efficiency-chart.png.
- [20] K. Yoshikawa, et al., Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%, Nat. Energy 2 (2017) 17032.
- [21] J. Loferski, The first 40 years: a brief history of modern PV age, Prog. Photovolt. 1 (1993) 67.
- [22] D.A. Jenny, J.J. Loferski, P. Rappaport, Photovoltaic effect in GaAs p-n junctions and solar energy conversion, Phys. Rev. 101 (February 1956) 1208.
- [23] E. Yablonovitch, O.D. Miller, S.R. Kurtz, The opto-electronic physics that broke the efficiency limit in solar cells, in: Proc. 38th IEEE Photovoltaic Specialists Conference, Austin, TX, USA, 2012, p. 001556.
- [24] D.C. Reynolds, G. Leies, L.L. Antes, R.E. Marburger, Photovoltaic effect in cadmium sulfide, Phys. Rev. 96 (1954) 533.
- [25] W. Palz, J. Besson, T. Nguyen, J. Vedel, New results on CdS solar cells, in: 9th EEE PV Specialist Conference, 1972, p. 91.
- [26] D.A. Cusano, CdTe Solar Cells and PV heterojunctions in II-VI Compounds, Solid-State Electron. 2 (1963) 217.
- [27] L.C. Hirst, N.J. Ekins-Daukes, Fundamental losses in solar cells, Prog. Photovolt. Res. Appl. 19 (2011) 286-293.
- [28] M.B. Prince, Silicon solar energy converters, J. Appl. Phys. 26 (1954) 534.
- [29] J.J. Loferski, Theoretical considerations governing the choice of the optimum semiconductor for photovoltaic solar energy conversion, J. Appl. Phys. 27 (1956) 777.
- [30] W. Shockley, H. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, J. Appl. Phys. 32 (1961) 510.
- [31] M. Green, Third Generation Photovoltaics: Advanced Solar Energy Conversion, Springer, 2003.
- [32] S. Essig, et al., Raising the one-sun conversion efficiency of III-V/Si solar cells to 32.8% for two junctions and 35.9% for three junctions, Nat. Energy 2 (2017) 17144.
- [33] M. Paire, et al., Toward microscale Cu(In, Ga)Se<sub>2</sub> solar cells for efficient conversion and optimized material usage: theoretical evaluation, J. Appl. Phys. 108 (2010) 034907.
- [34] D. Abou-Ras, et al., Innovation highway: breakthrough milestones and key developments in chalcopyrite photovoltaics from a retrospective viewpoint, Thin Solid Films 633 (2017) 2.
- [35] C. Broussillou, et al., Statistical process control for Cu(In, Ga) (S,Se)<sub>2</sub> electrodeposition-based manufacturing process of 60 × 120 cm<sup>2</sup> modules up to 14,0% efficiency, in: 2015 IEEE 42nd Photovoltaic Specialist Conference (PVSC), New Orleans, LA, USA, 2015, pp. 1–5.
- [36] B. O'Regan, M. Gratzel, Nature 353 (1991) 737-740.
- [37] A. Kojima, et al., Organometal Halide Perovskites as visible light sensitizers for photovoltaic cells, J. Am. Chem. Soc. 131 (2009) 6050.
- [38] N.G. Park, Perovkite solar cells: an emerging PV technology, Mater. Today 18 (2015) 65.
- [39] M. Saliba, et al., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency, Energy Environ. Sci. 9 (2016) 1989–1997.
- [40] D. Lincot, De la lumière à l'énergie : de la photosynthèse au photovoltaïque, in: Chimie et transition énergétique, Actual. Chim. 2016 (408–409) (2016) 54–60.
- [41] F. Gibelli, L. Lombez, J.-F. Guillemoles, Two carrier temperatures non-equilibrium generalized Planck law for semiconductors, Physica B, Condens. Matter 498 (2016) 7–14.
- [42] B. Behaghel, et al., Absorption enhancement through Fabry-Pérot resonant modes in a 430 ~ nm thick InGaAs/GaAsP multiple quantum wells solar cell, Appl. Phys. Lett. 106 (2015) 081107.
- [43] H. Scheer, Solare Weltwirtschaft, A. Kunstmann GmbH, Munchen, 1999; Le solaire et l'économie mondiale, Solin, Actes sud, 2001; The Solar Economy: Renewable Energy for a Sustainable Global Future, Earthscan, 2002.
- [44] W. Palz, The Emergence of Electricity from the Sun: Power for the World, Pan Stanford Publishing, 2011.
- [45] https://www.iea.org/publications/freepublications/publication/TechnologyRoadmapSolarPhotovoltaicEnergy\_2014edition.pdf.
- [46] D. Swanson, A vision for Crystalline Silicon photovoltaics, Prog. Photovolt. 14 (2006) 443.
- [47] http://iea-pvps.org/fileadmin/dam/public/report/statistics/IEA-PVPS\_-\_A\_Snapshot\_of\_Global\_PV\_-\_1992-2016\_\_1\_pdf.
- [48] http://www.irena.org/DocumentDownloads/Publications/IRENA\_REthinking\_Energy\_2017.pdf.
- [49] http://energy.mit.edu/wp-content/uploads/2015/05/MITEI-The-Future-of-Solar-Energy.pdf.
- [50] http://itrpv.net/Reports/Downloads/:ITRPV\_Seventh\_Edition\_including\_maturity\_report\_20161026.pdf.
- [51] http://www.ipvf.fr/wp-content/uploads/2016/03/Mid-term-technology-strategy-in-PV-EN.pdf.
- [52] C. Breyer, et al., On the role of solar photovoltaics in global energy transition scenarios, Prog. Photovolt.: Res. Appl. (2017), DOI: 10.1002.
- [53] F. Creutzig, et al., The underestimated potential of solar energy to mitigate climate change, Nat. Energy 2 (2017) 17140.