

The Shockley–Queisser limit and the conversion efficiency of silicon-based solar cells

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ABSTRACT

According to some estimates, every hour, Sun provides planet Earth with more energy than humankind consumes in a whole year. Part of this energy has been essential to ensure living conditions (warmth and food production, for instance) and, more recently, to generate electricity by means of atmospheric (aeolian) and/or geographical (hydropower) sources. In addition to these, the direct (photovoltaic PV) conversion of solar radiation into electricity represents a very elegant method of power generation that causes minimum (or no) environmental disturbance. As a result, numerous efforts have been dedicated to further advance the achievement of clean and sustainable electricity, as supplied by the PV science and technology. Within this scenario, the association of PV with the silicon (Si) semiconductor industry played a crucial role—either by introducing new scientific insights or by promoting successive costs reductions in the field of renewable energy conversion. Yet, the performance of these so-called (either crystalline or amorphous) Si-based solar cells was always a matter of concern. In fact, the subject gained attention with the seminal work by *Walter Shockley* and *Hans Queisser* that, in 1961, proposed a model according to which the maximum efficiency of a solar cell is determined by both the solar spectrum and the properties of the semiconductor material. Since then, the work by *Shockley* and *Queisser* (also known as the *Shockley–Queisser limit*) has experienced some improvements and became a reference in the field. Motivated by these facts, along with the main scientific–technological achievements they provided, the *Shockley–Queisser limit* and the conversion efficiency of the Si-based solar cells along the last 60 years form the basis of this paper.

1. Silicon & Silicon-based solar cells

As stated by literature, the French chemist *Antoine Lavoisier* identified the element silicon in 1787. At that time, it was not exactly pure and was called *silice* suggesting “earthy” or, in *Lavoisier*’s own words, *terre flûcieuse* or *terre vitrifiable* (*Lavoisier*, 1789). Afterwards, silicon received other names and various attempts of chemical refinement (see Supp-Mater_Part1 for further details and references). Comparatively better quality silicon was achieved only in 1823 (by *Jöns Jakob Berzelius*) and in 1854 (by *Henri Étienne Saint-Claire Deville*) by producing amorphous and crystalline silicon, respectively (*Weeks*, 1932). This period coincides with the birth of photovoltaics (PV) that includes the discovery of the effect in 1839 (at that time known as *Becquerel* effect (*Becquerel*, 1839) and the invention of the first solar cell device, made of selenium, in 1883 (*Fritts*, 1883)—see Fig. 1.

The following decades were characterized by extraordinary advances in the science and technology of silicon (Si)—and semiconductors and electronics in general—giving rise to the *Silicon Age* (also known as the *Digital* or *Information Age*) (*Hoddeson et al.*, 1992; *Orton*, 2009). In parallel with the many technological (social and economic) advances it provided, the so-called *Silicon Age* brought about important energy

production–consumption concerns that, ideally, are in accord with the concept of sustainability and involve strategies that are consistent with reduced (or no) environmental damage and long-term climate goals (*Righini and Enrichi*, 2020).

Accordingly, the Sun is at the center of this discussion by supplying the Earth’s surface with huge amounts of energy (daily average insolation $\sim 6 \text{ kWh/m}^2 = 21.6 \text{ MJ/m}^2$) essentially in the form of visible light and warmth. Since only a fraction of this energy is exploited to produce electricity—either by atmospheric (wind), geographical (hydropower), or radiation (PV) means—it is common sense that there is plenty of room to improve the field. Within this scenario, PV and Si occupy a privileged position. The former representing one of the most environmentally-friendly form of energy generation that, additionally, requires no severe atmospheric–geographical conditions. And the latter, corresponding to the second most abundant element (only after oxygen) occupying $\sim 27\%$ of the Earth’s crust.

The PV + Si association dates from the 1940–1950’s and, basically, originated at the *Bell Telephone Company*. During this period, the company made great progress in the science and technology of Si (Supp-Mater_Part1), and was looking for a replacement to its traditional (dry cell batteries) power source of telephones. A trio of Bell’s scientists

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(Daryl Chapin, Calvin Fuller, and Gerald Pearson) was assigned to find a new–alternative freestanding source of electricity, and the search started with wind and steam machines as well as with solar devices made of selenium. It was only in 1954 that the trio of scientists achieved what they called a “solar battery” – corresponding to several independent Si solar cells (~6% efficient each) linked together (Chapin et al., 1954; Chapin et al., 1954).

The production of this preliminary Si solar cell gave rise to the 1st PV Generation (*i.e.*, photovoltaic devices made of semiconducting *p-n* junctions) and, soon after, to the 2nd PV Generation (1st PV Generation associated with thin-film technology – Fig. 1). Combined, these two PV generations were responsible for great scientific progress (effective use of new semiconductors and device structures, advent of grid contacts, etc.) and lots of successful applications in photovoltaics (such as solar cell powered: outspace satellites, wristwatches, and pocket calculators, for example–see SuppMater_Part1). The 3rd (and current) PV Generation is based on novel concepts (materials properties, physical processes, and cell architectures) aiming at very low production costs and/or very high device efficiencies. Apart from all the success and progress these PV generations provided over the years, the efficiency of the solar cells was always a matter of great concern (Tsuda et al., 1993; Ehrler et al., 2020).

The efficiency of a solar cell is usually defined as the percentage of power converted from sunlight to electrical energy–under standard (or known) test conditions. It is from 1954 the first estimate of the maximum efficiency (around 22 %) a Si solar cell can exhibit, and it was made by the same scientists that invented the device (Chapin et al., 1954). The work was followed by others that, in addition to the solar radiation characteristics and the cells circuitry considerations, also took into account some empirical quantities (like the charge carriers lifetime, for instance) (Pfann and Van Roosbroeck, 1954; Prince, 1955; Loferski, 1956; Rappaport, 1959; Wolf, 1960). According to these approaches (usually referred to as semi-empirical), the efficiency of a solar cell depends on the optical bandgap (E_{gap}) of the semiconductor material indicating that, for crystalline Si ($E_{gap} \sim 1.1$ eV), the maximum efficiency stays in the ~ 15–22 % range.

These (semi-empirical) introductory efforts were further developed by Walter Shockley and Hans Queisser that, in 1961, applied the *Detailed Balance Model* to calculate the efficiency of solar cells (Shockley and Queisser, 1961). Since then, the work of Shockley and Queisser (also known as the Shockley–Queisser or SQ limit) has experienced some

improvements and received great attention of the PV community. The essentials behind the SQ limit and the main achievements in the efficiency of Si-based solar cells along the last 60 years represent the focus of this paper, that are presented and discussed in the following.

2. Detailed balance model & efficiency issues

The four most important parameters that define the operation of a solar cell (under specific illumination conditions) are (Goetzberger et al., 1998): the short circuit current I_{SC} (corresponding to the maximum electric current generated by the solar cell), the open circuit voltage V_{OC} (maximum voltage of the cell), the fill factor FF (ratio between the maximum power P_{max} and the product $V_{OC} \cdot I_{SC}$), and the efficiency η (defined as the ratio of the electrical power output to the total incoming sunlight power P_{Sun}). Put in numbers, the efficiency of any solar cell can be written as:

$$\eta = \frac{V_{max} \cdot I_{max}}{P_{Sun}} = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{Sun}} \quad (1)$$

Amongst the various factors that affect η one can mention: the materials properties and physical structure of the cell, their sensitivity to the different wavelengths of the solar spectrum, the intensity of the incident light, the working (local) temperature, the efficiency in generating electron–hole pairs, the ability of the cell to extract charge carriers (with minimum or no loss) and, more recently, the presence (or not) of anti-reflection coatings and/or of surface texturing. For comparison reasons, the experimental determination of η involves the analysis of the cell with standard solar radiation (SuppMater_Part2), and the use of Eq. (1) with the values supplied by a current *versus* voltage plot (Goetzberger et al., 1998).

The theoretical calculation of η follows a similar procedure, but depends on the assumption of certain criteria. Accordingly, in its simplest and most common version of the SQ limit (Shockley and Queisser, 1961), the theoretical η was based assuming that (Guillemoles et al., 2019): the solar cell is constituted by a single semiconductor and *p-n* junction, the sunlight is not concentrated (*i.e.*, “one Sun” source), the mobility of the charge carriers is infinite (imposing no spatial restrictions to electric charge collection), and that all incident photons with energy equal or above the semiconductors optical bandgap E_{gap} are absorbed by the cell. The original calculation by Shockley and Queisser

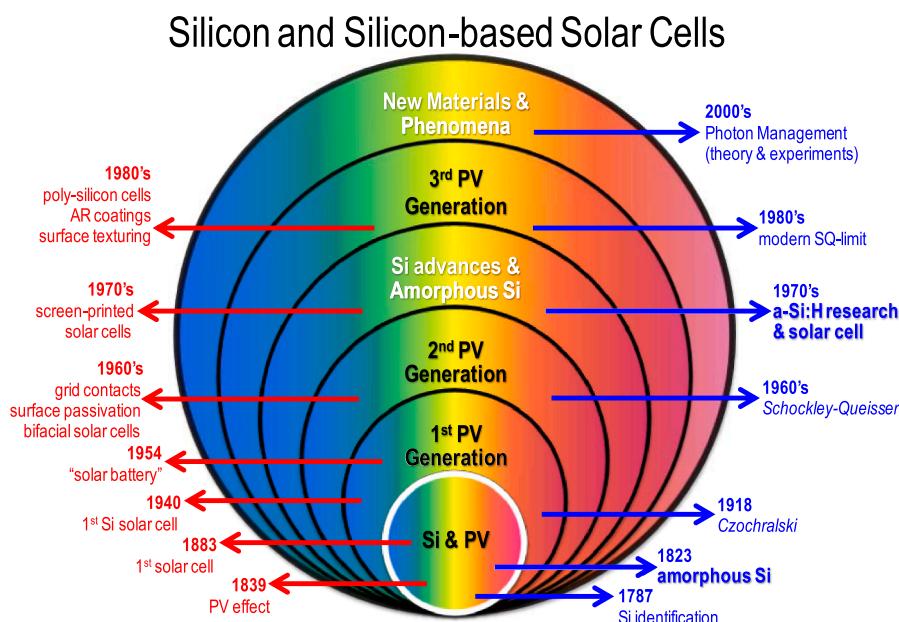


Fig. 1. Graphic overview highlighting some milestones regarding the silicon (Si) science and technology (right-hand side, blue text) and advances in the photovoltaic (PV) field (left-hand side, red text). See SuppMater_Part1 for further details and references.

estimated a maximum theoretical efficiency of $\sim 30\%$ for a crystalline Si solar cell, and showed that η_{\max} is a function of E_{gap} (see SuppMater_Part3 for details). In fact, along with the results provided by the semi-empirical approaches, the model by Shockley and Queisser clearly indicated that, under AM1.5 illumination conditions, the maximum cell efficiency is reached at about 1.1 eV (or ~ 1130 nm)—very close to the optical bandgap of crystalline Si (Zanatta, 2019). The idea of this original SQ limit was further developed by considering Si solar cells of different thicknesses (and real optical spectra), absorption due to free charge carriers, and Auger recombination processes (Henry, 1980; Tiedje et al., 1984). Also, in order to enhance the solar radiation absorption (by light trapping), the surfaces of the Si cells were assumed to be texturized (Goetzberger et al., 1998). According to this modern version of the SQ limit, the maximum theoretical efficiency of solar cells made of crystalline (amorphous) Si is $\eta \sim 33\%$ ($\sim 28\%$) that, nowadays, corresponds to the most accepted value.

The maximum theoretical efficiency values as provided by the semi-empirical (Pfann and Van Roosbroeck, 1954; Prince, 1955; Loferski, 1956; Rappaport, 1959; Wolf, 1960), original SQ (Shockley and Queisser, 1961), and modern SQ methods (Henry, 1980; Tiedje et al., 1984)—as obtained for crystalline Si solar cells ($E_{\text{gap}} \sim 1.1$ eV)—are presented in Fig. 2(a). The figure also shows the best experimental efficiency values reported between 1975 and 2021 (NREL, 2022).

The maximum theoretical and best experimental efficiency records of solar cells made of amorphous Si are presented in Fig. 2(b). In this case, however, it has been considered the optical bandgap of hydrogenated amorphous silicon a-Si:H $E_{\text{gap}} \sim 1.75 \pm 0.05$ eV (or ~ 710 nm) (Carlson and Wronski, 1976; Carlson, 1980; Morariu et al., 2012).

At first sight, it is evident from the data of Fig. 2 the comparatively lower efficiency values presented by the cells made of amorphous silicon, as well as the discrepancy between the maximum theoretical and

best experimental efficiencies—around 7% for the crystalline cells, and $\sim 16\%$ for the amorphous ones. In the first case, the differences arise essentially owing to the $\eta(E_{\text{gap}})$ dependence (SuppMater_Part3—Fig. S3). However, even lower efficiency values are expected because of the disordered atomic structure of amorphous silicon—that were not contemplated by the models—resulting in poor charge carrier mobility allied to severe non-radiative electron–hole recombination. Actually, to a lesser extent, this is the origin of the higher efficiency presented by mono-crystalline Si cells when compared to the performance of the polycrystalline Si wafer and film cells [Fig. 2(a)]. Regarding the theoretical–experimental efficiency differences, they originated from oversimplified (or not considered) assumptions during the theoretical modeling (Guillemoles et al., 2019).

Apart from these questions, it is clear the improvements that the (most simple, under non-concentrated AM1.5 illumination) Si solar cells experienced along the years: with the η values rising from $\sim 6\%$ to 26.7% (corresponding to single p - n junction, crystalline Si cells (Chapin et al., 1954; NREL, 2022), and in the ~ 0.5 –14% range (regarding approx. 1 μm thick p - i - n cell structures made of a-Si:H (Carlson and Wronski, 1976; Carlson, 1980).

Besides, one should remark the great technological achievements of the PV industry, in which case the typical cost per generated power of Si-based solar cell modules has been reduced from ~ 300 USD per Watt-peak (W_p) in the 1960's, to less than 0.35 USD/ W_p in the current days (Louwen et al., 2016; International Technology Roadmap for Photovoltaic – ITRPV, 2021).

Most of these figures are quite impressive but are not enough in view of the ever-increasing global energy needs and, specially, because the experimental η of the Si-based solar cells seems to be stationary for the last 20 years (Fig. 2). Even though such low—stagnated performance, the presence of Si in the PV industry is so influential that several approaches

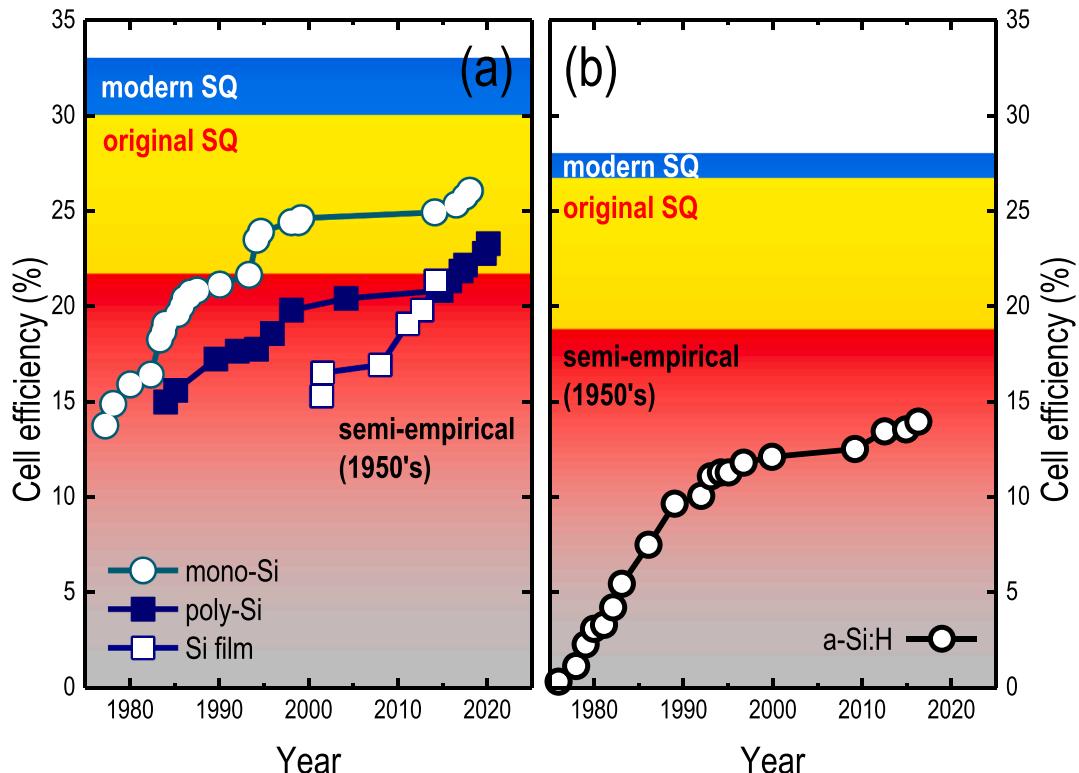


Fig. 2. Efficiency η of silicon-based solar cells in the 1975–2021 year period. (a) Maximum theoretical efficiency of crystalline Si solar cells: semi-empirical ($\eta \sim 22\%$), original SQ ($\sim 30\%$), and modern SQ ($\sim 33\%$) limits. (b) Same as in (a) but relating to hydrogenated amorphous Si solar cells: semi-empirical ($\eta \sim 19\%$), original SQ ($\sim 27\%$), and modern SQ ($\sim 28\%$) limits. The data points refer to experimental η values, as obtained (NREL, 2022): (a) from crystalline silicon (mono-, poly-, and in the form of films), and (b) from hydrogenated amorphous silicon a-Si:H films ($E_{\text{gap}} \sim 1.75$ eV). The figure is complemented by some ancient (not shown) data of mono-Si in 1954 ($\eta = 6\%$ (Chapin et al., 1954) and of a-Si:H in 1976 ($\eta = 2.4\%$ (Carlson and Wronski, 1976).

have been proposed to improve the above Si-based PV results. Some of these approaches have already been successfully implemented and considered the use of anti-reflection coatings (Sexton, 1982; Hsu et al., 2012), surface passivation (Boehme and Lucovsky, 2002; Panigrahi and Komarala, 2021) and/or light trapping (Tsuda et al., 1993; Lee et al., 2011; Isabella et al., 2012; Li et al., 2017) methods, as well as the construction of tandem or multi-junction cell designs (with new architectures and/or electrical contacts geometries–materials) (Smirnov et al., 2012; Wilson et al., 2020). In addition to these, it is of special interest the methods based on the so-called photon management concept, in which case the solar spectrum is modified to match the absorption profile of the Si solar cell. Along with other alternatives to improve η , the fundamentals and main results of the photon management approach applied to Si solar cells is the subject of the next section.

3. Advances & current status of Silicon-based solar cells

Traditionally, the efficiency of Si-based solar cells has been increased by means of light in-coupling and trapping approaches, as well as by improving charge carrier generation and collection (Goetzberger et al., 1998). More recently, the focus involves the idea of photon management (or spectral shaping) in which the solar radiation is customized to better match the cell response (Ehrler et al., 2020). It represents an alternative (and very convenient) method to increase η without modifying the original–basic structure of the cell. Accordingly, the photon management is based on the use of special (passive) layers—onto the front and/or rear faces of the solar cell—that are able to convert ultra-violet or infrared light into photons with energies that are effectively absorbed by the solar cell. The concept was originally proposed (Romagnoli, 1964; Weber and Lambe, 1976; Goetzberger and Greube, 1977) (and tested (Hovel et al., 1979) in the 1960–1970's and, since then, has received much attention and several names to make clear the physical processes involved (see SuppMater_Part4 for a detailed description). The most common of these designations refers to the conversion of high- into low-energy photons (luminescence down-shifting LDS and down-conversion DC) and vice versa (up-conversion UC) (van der Ende et al., 2009). The theoretical potential of these DC and UC photon conversion layers in

photovoltaic applications was investigated by Trupke et al. in 2002 (Trupke et al., 2002; Trupke et al., 2002). According to this study (see Fig. S5-C-SuppMater_Part5), under non-concentrated sunlight, the maximum efficiency of a Si ($E_{gap}=1.1$ eV) solar cell increases from ~ 30 % (corresponding to the original SQ limit) to ~ 37 – 40 % when covered with ideal DC and UC layers [Fig. 3(a)]. A slightly higher improvement was calculated for amorphous Si ($E_{gap}=1.75$ eV) under similar conditions: from ~ 27 % (original SQ limit) to ~ 30 – 46 % [Fig. 3(b)].

In spite of these exciting figures and lots of research, the pursuit of low-cost–high-gain solar cells (*via* photon management) is still under way (Ehrler et al., 2020; Taniguchi et al., 2019). Within them, one can mention a series of experimental works reporting the efficiency (under AM1.5G illumination conditions) of bare and modified crystalline Si solar cells: (1) from 20.1 % to 21.5 % (7.4 % relative increase of η) by LDS with water-soluble ZnSe/ZnS-related quantum-dot structures onto the cell (Nishimura et al., 2021), (2) from ~ 7 % to 7.5 % (7 % relative increase) by DC of Tb-doped tellurite glass (Florêncio et al., 2016), (3) from 14.1 % to 15.0 % (6.7 % relative increase) by LDS with perovskite quantum-dots (Meng et al., 2020), (4) from 16.9 % to 17.7 % (4.7 % relative increase) by applying a field-effect passivation (Al_2O_3) and up-converting (Er^{3+} – Yb^{3+} phosphor) layers (Ho et al., 2021) (see also (Fischer et al., 2015), (5) from 15.1 % to 15.4 % (~ 1.9 % relative increase) by LDS of a dye-containing EVA (poly-ethylene vinyl acetate) encapsulating layer onto multi-crystalline Si cells (Klampafitis and Richards, 2011), and (6) from 16.5 % to 16.7 % (1.1 % relative increase) by DC due to multi-layered ErYb-doped amorphous SiN layers (Dumont et al., 2019).

Research involving the photon management applied to amorphous Si solar cells has received less attention and, so far, the literature comprises a mix of proof-of-principle (Wild et al., 2010) and exciting experimental results (Meng et al., 2021).

In addition to the rather low efficiency enhancements achieved so far, the literature involving PV cells and photon management is so diverse as complex (Polman et al., 2016; Almora et al., 2021a; Almora et al., 2021b). At present, most of the reports in this field refer to the optical properties of (and physical processes taking place at) the photon converting layers, without applying them to practical cells. Others,

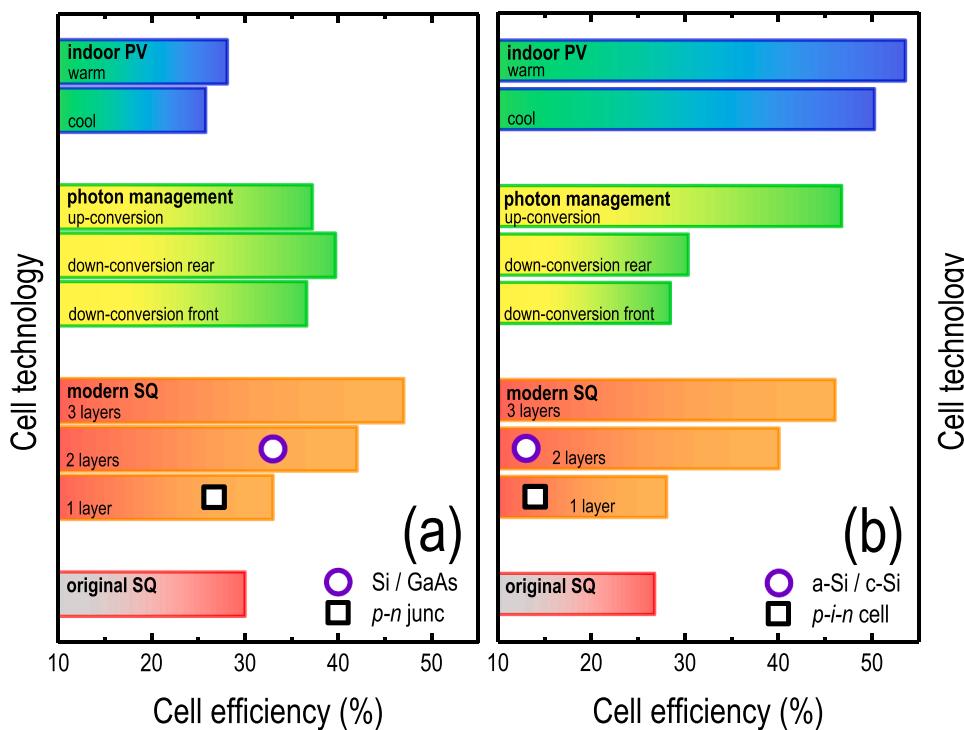


Fig. 3. Maximum efficiency of (a) crystalline and (b) amorphous Si-based solar cells, as obtained from different theoretical approaches–technologies: original Shockley–Queisser (SQ) detailed balance model (Shockley and Queisser, 1961), modern SQ (Henry, 1980) (including the results of single- and multi-layered cells), based on the photon management concept (Trupke et al., 2002; Trupke et al., 2002), and involving artificial lighting (indoor PV) (Jarosz et al., 2020). The highest experimental efficiencies (NREL Best Research-Cell Efficiency Chart. <https://www.nrel.gov/pv/cell-efficiency.html> (accessed July 2022) of single-junction (crystalline p - n & amorphous p - i - n) and double-junction (crystalline Si/GaAs & a-Si/c-Si) cells are also shown.

avoid direct comparison between the efficiency of bare and modified cells, and it is not rare to find results based on very high (narrow-band) light excitation intensities. Just to illustrate the point, whereas the full solar spectrum has an integrated intensity of $\sim 0.1 \text{ W/cm}^2$ (see SuppMater_Table S1), the typical light excitation applied to certain up- or down-conversion processes stay in the order of a couple of W/cm^2 , *i.e.*: it requires ~ 10 times more light intensity (just to observe the phenomenon)—without showing the real photovoltaic improvement. In short, the eventual advantages associated to photon conversion layers are still incipient, and future work in this field should concentrate on exploring/improving their interaction (*i.e.*, light in-coupling) with the solar cells to enable better overall performance (Taniguchi et al., 2019).

On the other hand, the results of multi-layered crystalline Si [Fig. 3(a)] and of amorphous Si cells [Fig. 3(b)] under indoor lighting seem to be very promising (Henry, 1980; Jarosz et al., 2020). In the first case, cell production costs are expected to be reduced with time, and an absolute efficiency increase of $\sim 6\%$ [from $\eta(1 \text{ layer}) = 26.7\%$ to $\eta(\text{Si}/\text{GaAs bi-layer}) = 33\%$] cannot be ignored. In the latter, higher efficiencies occur because artificial lighting mitigates the usual transparency and thermalization losses associated with the (broad-band) solar spectrum (Jarosz et al., 2020).

Albeit these emerging indoor–PV technologies cannot compete with the traditional solar–PV resources in terms of absolute power generation, they are based on the recycling of photons that would be wasted anyway. Besides: (1) many indoor environments are lit for the majority of the day, with typical light intensities on the 100 lx (homes), 500 lx (offices) to 1000 lx (warehouses or manufacturing lines) range (Kandilli and Ulgen, 2008)—*i.e.*, more than enough to supply mW power devices with either compact fluorescent lamp (CFL) or light-emitting diode (LED) sources (de Rossi et al., 2015), and (2) indoor–PV (instead of solar–PV) is compatible with minimum (or no) copper wiring grids and battery waste (Cutting et al., 2016). Yet, in order to be effective, indoor PV devices should be optimized for artificial lighting, but the results achieved thus far are very promising. In particular: under outdoor conditions (*i.e.*, 1 Sun and AM1.5G radiation) the typical $\sim 1\text{--}3\%$ conversion efficiency of some commercial cells based on amorphous Si increases to $\sim 7\text{--}8\%$ when illuminated with only 200 lx of either CFL or LED lighting (de Rossi et al., 2015). Regarding the cells made of crystalline Si, because of their optical bandgap and design to operate under solar radiation, their efficiencies behave differently: $\eta(\text{c-Si})_{\text{outdoor}} \sim 15\%$ and $\eta(\text{c-Si})_{\text{indoor}} \sim 4\%$ (de Rossi et al., 2015).

At this point, it would be interesting to compare most of the above figures (relating the Si-based cells) with those exhibited by other semiconductor materials. Table 1 presents a summary of the conversion efficiency η of various solar cells—as obtained according to different theoretical and experimental approaches.

In view of the results of Table 1, it is reasonable to assume that, whatever the semiconductor material and adopted photovoltaic cell design—*involving* single or multi-layered structures, based on photon management concepts, requiring solar or artificial lighting, for example—the best solution will be decided by future technological advances in the field. This is true for the PV industry in general (based on silicon or any other semiconductor material, requiring simple or complex processing, involving hybrid organic–inorganic compounds, etc.) and the decision should be made in close connection with the global economy and environmental demands. However, considering the influence and well-established S&T of silicon, it is clear from the previous discussion that the Si-based cells will continue to play a crucial role in photovoltaics.

4. Concluding remarks

For millions of years, the Sun has been an abundant (and essential) source of energy to humankind such that, more recently, part of this energy was used to produce electricity as well. In fact, considering its characteristics, the direct conversion of sunlight into electricity (by

Table 1

Maximum conversion efficiency, as obtained from various semiconductor materials—along with their typical optical bandgap E_{gap} values (and ranges in the case of compound materials)—and different theoretical approaches: modern SQ limit_{l modernSQ}, from artificial lighting η_{indoor} , and by photon management means η_{PM} —see also SuppMater_Part5. Whenever applicable, η_{modernSQ} , η_{indoor} , and η_{PM} were calculated by using the E_{gap} value that yields the highest efficiency. In parenthesis are given the best experimental η values regarding both the standard (as indicated by the NREL charts (NREL, 2022) and non-conventional indoor (Li et al., 2020) and photon management cell technologies (Goldschmidt and Fischer, 2015).

Semiconductor Material	E_{gap} (eV)	η modernSQ (%)	η_{indoor} (%)	η_{PM} (%)
		a	b	(exp ^{tal})
CZTS(Se) ^d (Deng et al., 2021)	1–1.6	33.3 (13)	49.1–45.4 (~8)	45.6–39.6 (–)
Organics (Wang et al., 2018; Xie et al., 2021; Chen et al., 2014; Svrcel et al., 2015)	1–2.3	33.3 (18.2)	53.6–51.6 (4–26)	47.6–39.6 (3–7)
CIGS ^d (Yang et al., 2011; Jeong et al., 2017; Khan and Kim, 2018; Xiong et al., 2020)	1–2.4	33.3 (23.4)	53.6–51.6 (2–10)	47.6–39.6 (14–19)
Si (Ghazy et al., 2021; Moon et al., 2019)	1.1	33.0 (26.1)	28.1–25.6 (4–10)	37.2–39.3 (7–21)
GaAs (Chen et al., 2012; Han et al., 2014; Ho et al., 2019; Mathews et al., 2020)	1.42	32.8 (29.1)	41.8–38.5 (~19)	43.6–36.2 (18–24)
CdTe (Michaels et al., 2020)	1.43	32.6 (22.1)	41.9–38.6 (~17)	43.7–35.8 (–)
DSSC (Devadiga et al., 2021; Haridas et al., 2021; Dutta et al., 2019; Li et al., 2018; Ghazy et al., 2021)	1.5	31.8 (13)	45.6–42.0 (5–29)	44.6–34.7 (8–22)
Perovskite (Jagadamma and Wang, 2021; Bi et al., 2020; Yu and Zunger, 2012)	1.6–3.2	30.2 (25.7)	53.6–51.6 (20–36)	47.6–33.1 (12–20)
a-Si (Meng et al., 2021)	1.75	28.0 (14)	53.3–50.4 (2–21)	46.7–30.2 (10)

In all cases, a typical $\eta \pm 0.5$ uncertainty applies.

^a Maximum theoretical solar cell efficiency (single *p*-*n* junction cells) as obtained from the modern SQ approach at standard testing conditions (1 Sun AM1.5 radiation) (Henry, 1980).

^b Maximum theoretical solar cell efficiency under indoor (warm and cool) lighting conditions (Jarosz et al., 2020).

^c Maximum theoretical solar cell efficiency according to (*up* and *down*–*rear* cell side) photon management processes (Trupke et al., 2002; Trupke et al., 2002).

^d Regarding the CZTS(Se)- and CIGS-based solar cells, more realistic theoretical η values (based on the spectroscopic limited maximum efficiency SLME method) can be found in (Yu and Zunger, 2012). In most of these cases $\eta_{\text{SLME}} < \eta_{\text{modernSQ}}$, except for CuAu-like CuInSe₂ films with thicknesses in the ~ 300 nm–300 μm range (Berck et al., 2016).

photovoltaic or PV means) is expected to provide clean and sustainable energy for the upcoming years. As a result, the interest in producing solar devices has experienced (together with the semiconductors industry) great advances along the last decades. However, since the beginning—whatever the material and technology considered—the efficiency of these so-called solar cells has always been an issue. The first efficiency estimate of a PV (solar cell) device dates from the 1950's and, since 1961, due to the work by *W. Shockley* and *H. Queisser*, it represents an important guideline toward the development of solar cell materials

and architectures. Therefore, the main aspects of the *Shockley–Queisser* limit were discussed in close connection with the evolution of the conversion efficiency presented by solar cells made of the silicon semiconductor. Within them, one should comment: a series of amendments to the theoretical model (use of real solar radiation and optical absorption spectra, corrections involving charge carrier mobility–recombination, etc.), as well as the advent of new–improved device features (involving light-trapping strategies, use of multi-layered cell structures, taking advantage of special photon conversion layers, etc.). Based on these aspects it became clear: the need of more rigorous–systematic reports (ideally based on solar-like broad-band light sources) and, where applicable, the direct comparison of the efficiencies attained by the photovoltaic devices with and without the new–proposed improvement. Most of the above remarks are not exclusive of the Si-based solar cells and can easily be considered with other (in) organic semiconductor junctions and types of PV devices—the final decision being determined exclusively by the conversion efficiency and the implementation costs aspects.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rio.2022.100320>.

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