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Photovoltaic Efficiency Improvement: Limits and Possibilities

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Abstract

Solar cells based on the photovoltaic effect are the source of energy which compete with known fossil fuel sources and another renewable energy sources. According to the Plank's law, estimated efficiency of solar energy conversion may reach in the ideal case up to 93%. However, many physical and technical restrictions significantly decrease this perfect value. The Shockley-Queisser limitations show the possible boundaries for energy production using photovoltaic effect. At the same time, many researchers in the world are looking for the ways to circumvent these limitations. Various possible ways for improvement of solar cells efficiency are considered in this review. Specific attention was applied to plasmon enhanced solar cells.

Keywords: Solar cell efficiency; Improvement ways; Plasmonic enhancement

Introduction

Last time, the photovoltaic cells came as a significant source of renewable energy which compete with known fossil fuel sources and another renewable energy sources. Usually, solar cells are built from the semiconductor materials with well-known properties, in general silicon. Unfortunately, the conversion efficiency of usually applicated solar cells is limited both physical reasons and due to technical losses resulted from imperfections of fabrication and usage. The trials to use other semiconductor materials with the goal to increase the photovoltaic conversion efficiency show that all changes are in the narrow limits. For example see the last chart of NREL, presented in **FIG. 1** [1].

It can be seen that maximum conversion efficiency for one-junction photovoltaic converters is no more than ~29% independent on the type and material of applied semiconductor. This claim is proved by the known calculation provided by Shockley and Queisser [2]. The calculation places maximum solar conversion efficiency around 33.7% assuming a single p/n junction with a band gap of 1.4 eV (using an AM 1.5 solar spectrum).

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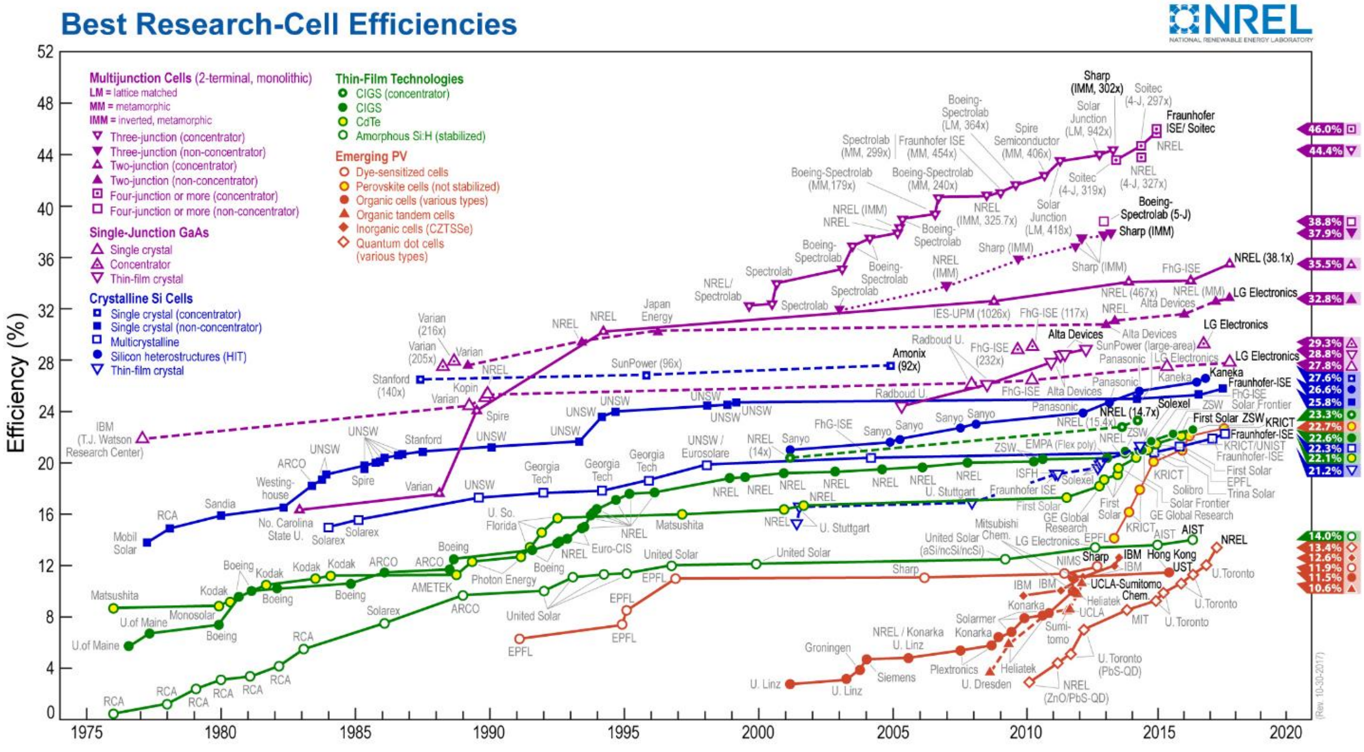


FIG. 1. Best Research-Cell Efficiency [1].

FIG. 2. Presents the maximum efficiency dependence on the band gap of the applied semiconductor.

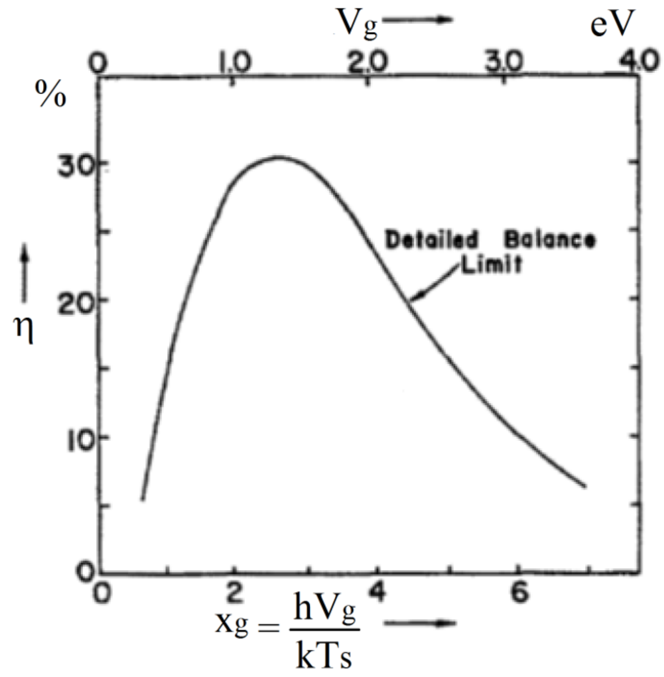


FIG. 2. The maximum efficiency of a single-junction solar cell [2].

This dependence was returned and calculated for maximum achievable solar call efficiency made of various semiconductor materials characterized by different values of the energy band gap, as shown in **FIG. 3** [3]. The curves were calculated for various solar spectra and ambient temperatures. Calculations were normalized to maximum value that may be theoretically achieved for the material with the band gap of about 1.39 eV. As can be seen from **FIG. 3**, variation of semiconductor materials cannot provide increasing of the efficiency.

Thus, the maximum efficiency of solar cells based on the photovoltaic effect are limited by physical reasons such as transparency of the semiconductor material for photons with an energy more the band gap and thermalization of the semiconductor material under absorption of high energy photons. Evidently, there are pluralities of electrical and optical losses which prevent possibility to obtain extremely high conversion efficiency. Detailed analysis of these losses was done by previous researches [4,5]. Therefore, to leave the framework outlined by the Shockley-Queisser limit, we must consider the various ways which can promote the high efficiency conversion of solar cells. In this review, we go to compare various methods for increasing the photovoltaic conversion efficiency.

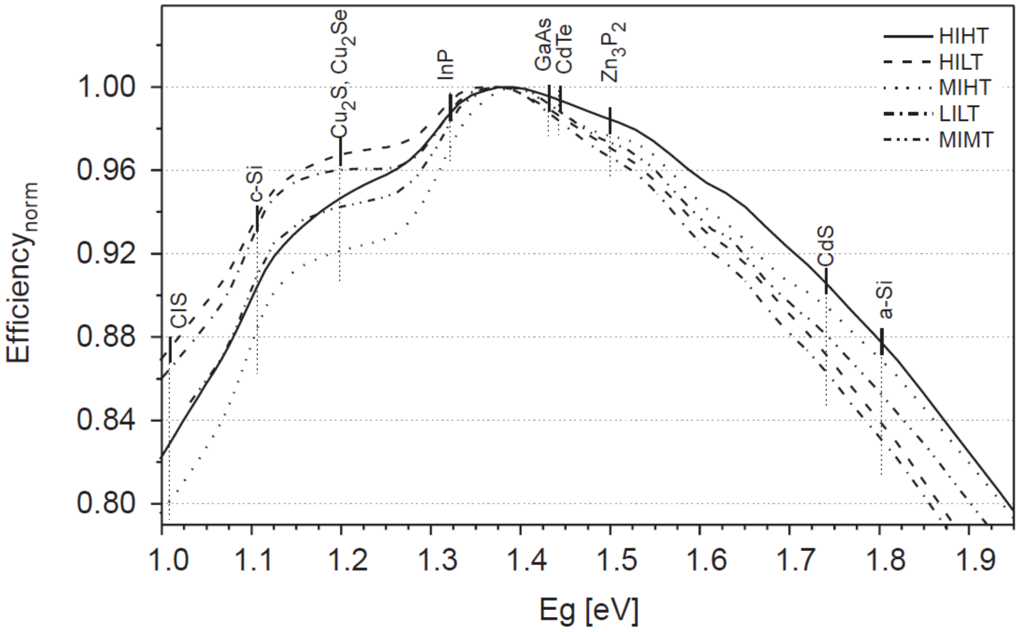


FIG. 3. Maximum efficiency of single junction solar cell versus absorber energy band gap [3].

Ways to the High-efficiency Conversion

There are several roads for increasing the efficiency more the Shockley-Queisser restriction. First of them is to integrate a semiconductor photovoltaic converter with suitable heat absorbing bodies, for example with water or oil for heat them and use this thermal energy together with electrical energy. Second way is in creation of multi-junction systems. Application the multi-junction devices and hetero-junction devices can reach larger spectral efficiency by capturing different parts of the solar spectrum. The third way is in application the low-dimensional structures such as quantum dots or quantum wells which can increase efficiency by using high-energetic photons through their multi-step absorption and low-energetic photons using various up-conversion processes.

The solar cells related to third way, known also as the third-generation devices, use different advanced strategies for solar energy conversion. These strategies are symbolically presented in **FIG. 4** [6]. Theoretically, the solar cells built using these novel principle, can have higher limiting conversion efficiency by bypassing one of the assumptions of the Shockley-Queisser analysis and recovering either some of the energy lost via thermalization or providing pathways to harvest those photons not absorbed in a standard solar cell [7]. In addition to the efficiency considerations, a third-generation solar cell must have low manufacturing costs.

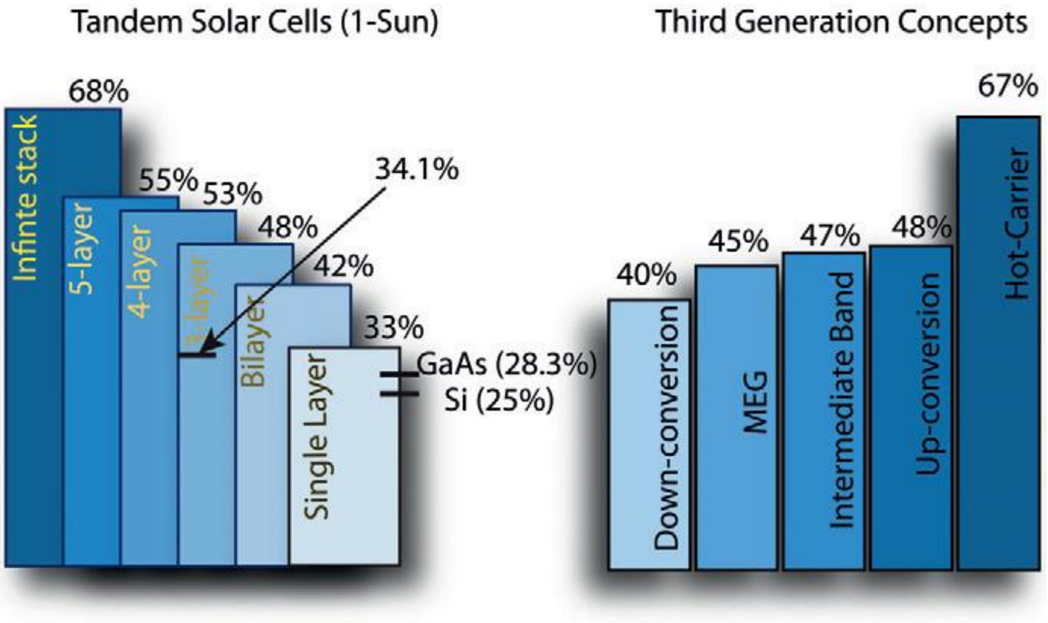


FIG. 4. The detailed balance-derived maximum allowable power conversion efficiency for a range of advanced solar conversion strategies. The original Shockley-Queisser calculation for a traditional single-junction solar cell is also shown, as well as a few record-certified values for single layer and triple junction cells [6].

Multi-junction solar cells

One of the well-known approaches is to combine together several semiconductor junctions with different bandgaps with the goal to absorb different parts of solar spectrum. This is known as a multijunction or heterojunction or stacking solar cells. Arrangement of several single junctions in descending order of bandgaps from top to bottom provides absorption larger spectrum and leads to increasing of the cell's efficiency. It was theoretically proven that consecutive combination of 36 junctions may attain an ideal efficiency of 72% [8]. As shown in **FIG. 1**, the world record presented here is 46% efficiency obtained for the four-junction device. Unfortunately, this approach is very expensive such as the multilayer system grown to obtain high efficiency is very complex technologically. **FIG. 5** illustrates, for example the triple-junction photovoltaic cell [9].

The first layer of this cell is composed of GaInP (1.85 eV), converting short wavelength portions of spectrum, such as blue and UV, the second GaAs-layer (1.42 eV) captures near-infrared light, and the third layer is made of Ge, effectively absorbs the lower photon energies of the IR radiation that are above 0.67 eV. In this structure, each upper junction filters the low-wavelength photons and transmits only these photons that have long wavelength.

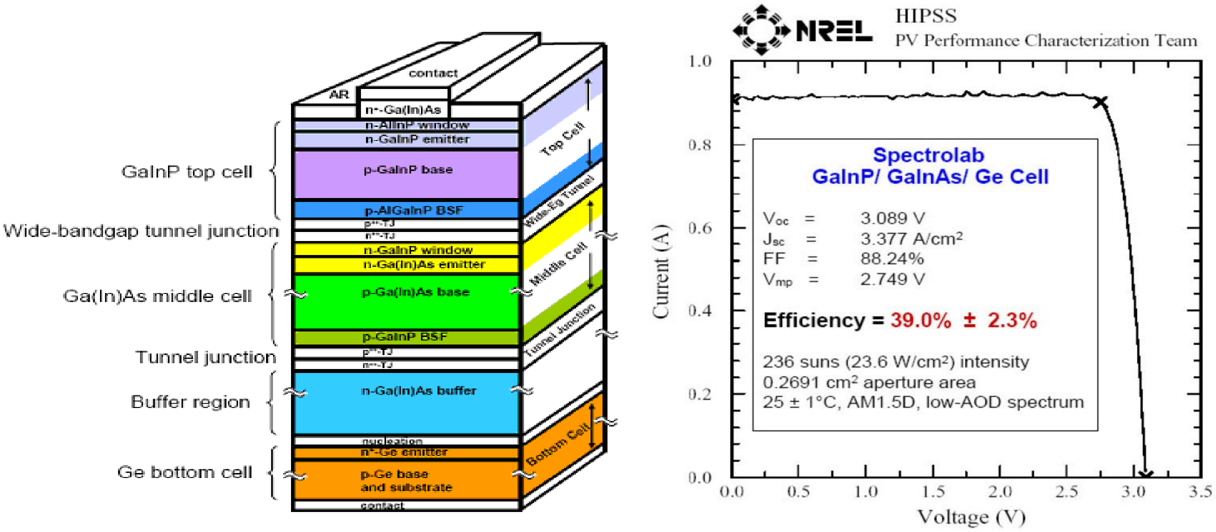


FIG. 5. Structure and performance characteristics of Spectrolab's triple-junction solar cell [9].

The main problem in fabrication the multijunction cells is in their complication, in matching of adjacent layers, in producing all included thin films with very precise thickness which all together result in high final cost.

Up-conversion solar cells

One of significant problems in utilization of solar energy is that the substantial part of solar spectrum consists of low-energy photons. Thus, the near infrared light (700-2500 nm) constitutes approximately 52% of the energy of the entire solar spectrum. For example, crystalline silicon photovoltaic cells are the most used among all types of solar cells on the market, representing about 90% of the world's total PV cell production in 2008 [10]. These cells also cannot use solar energy with the wavelength more than ~1080 nm and as a result, more than 20% of the sun's energy stills not applicable.

Photon up-conversion provides a way to circumvent transmission loss by converting two sub-band-gap photons into one above-band-gap photon, where the photovoltaic cell has high light responsivity [11]. **FIG. 6** illustrates schematic the solar cell structure which includes the solar up-converter [12]. As shown in the **FIG. 6a**, an up-converter represents a separated device integrated with the conventional solar cell.

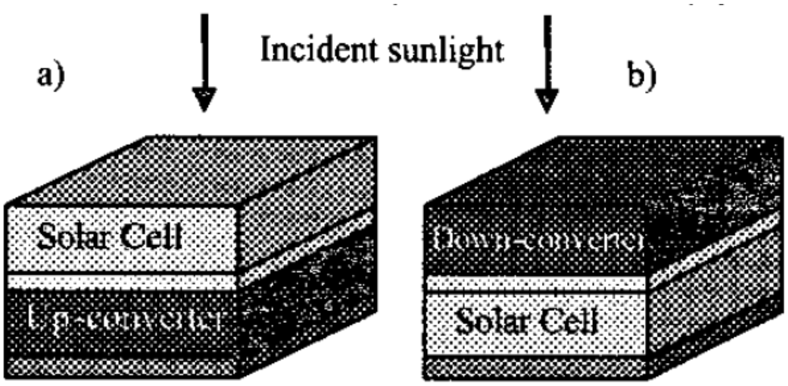


FIG. 6. Schematically presentation of an up-converter (a) and a down-converter (b) in combination with the conventional photovoltaic cell. In both cases a reflector is located at the rear surface and the converter and the solar cell are electronically isolated from each other (possibly, but not necessary by a separate insulating layer, as shown) [12].

For preparation the up-converters, the specific materials are used. These materials consist of rare-earth elements which include all lanthanide elements (from La to Lu) and two additional elements, scandium (Sc) and yttrium (Y). The main property of up-conversion materials is ability to emit visible light under near infrared irradiation. Such behavior is provided by possibility of the material to intra-band electron transition under near infrared illumination. Excited electrons recombine in the up-converter with emission of the visible range photons by the luminescence process. Usually, the up-conversion material is distributed in the suitable host material. To obtain the highest up-conversion luminescence efficiency, it is critical to choose an appropriate host material with lower phonon energy (high phonon frequencies of the host lattice lead to nonradiative relaxation) [13]. Such host materials include fluorides, bromides and chlorides. However, the metal oxides such as Y_2O_3 or ZnO also may be applied as the host materials [14,15]. Theoretical estimation shows that the conversion limit for a single-junction crystalline up-converter could to be as high as 40.2% under non-concentrated sunlight irradiation, that beyond the Shockley-Queisser limit [16].

FIG. 7 schematically illustrates the up-conversion process based on the two-photon excited-state absorption. Here, E_0, E_1 and E_2 represent ground state, intermediate, and excited state respectively and ω_0, ω_1, and ω_2 are suitable photon's frequencies. When the electron in the ground state absorbs one photon, it will be excited to the intermediate state characterized by the transfer E_0 --> E_1. The consequent absorption the second photon transfers this electron to the excited state E_2. This excited electron after follows collision comes back to the ground state with emission of the photon of higher energy.

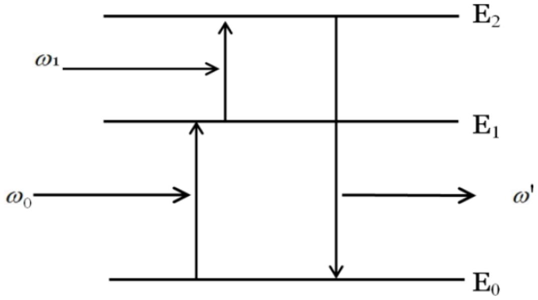


FIG. 7. Schematic presentation of the two-photon absorption and luminescence process in the up-converter [13].

Down-conversion solar cells

Another significant problem preventing high conversion efficiency of photovoltaic cells is the thermalization effect appearing under absorption of high energetic photons. Each photon, regardless their energy can generate only one pair of charged carriers. Energy exceeds the bandgap value is going to increase the energy of electron and hole up to level much higher than the Fermi level. These high-energetic particles anneal the solar cell by thermalization process which consists in the transfer of additional energy to the heat under collisions of particles. This leads to decreasing of the cell's efficiency.

One way to decrease influence of the thermalization process is apply a down-converter whereupon the high energy photons will split into two photons with lower energy, by this way increasing the number of generated charged pairs. This down-converting process also known as a quantum cutting. A principal scheme of the down-conversion application shown in **FIG. 6b**. The down-converter separated from the solar cell by a dielectric thin layer, filtrates the high energy photons and transfers additional photons with decreased energy into the solar cell active regions. It was shown that the possible efficiency improvement for a perfectly efficient down-converting material can reach 7% [17].

FIG. 8 illustrates the principal behavior of a down-converter arranged together with a solar cell. The down-converter transmits the photons with low energy and absorbs the high energy photons. Down-converting material splits these photons on the photons with lower energy and emits them to the solar cell, by this way increasing the number of generated charged carriers.

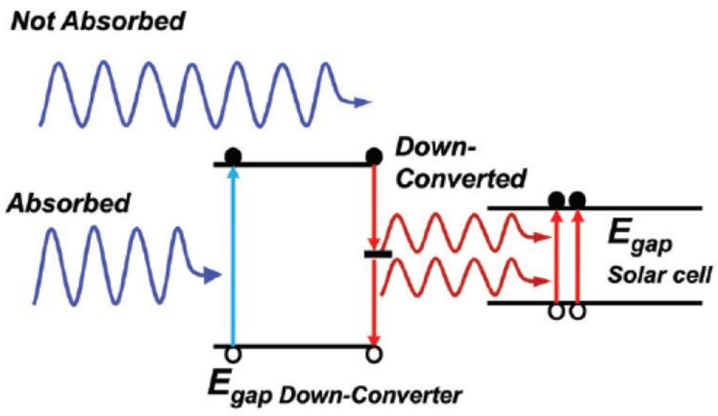


FIG. 8. Principal scheme of a down-converter working together with a solar cell [17].

There is another similar mechanism called down-shifting whereby a conventional photoluminescence process converts a high energy photon into another with lower energy [18]. The down-shifting process behaves similar to the down-converting however the quantum efficiency of both processes differs. **FIG. 9** illustrates both mentioned processes. Evidently, the quantum efficiency of the down-shifting process is lower due to thermalization process occurring in the material as shown in **FIG. 9**.

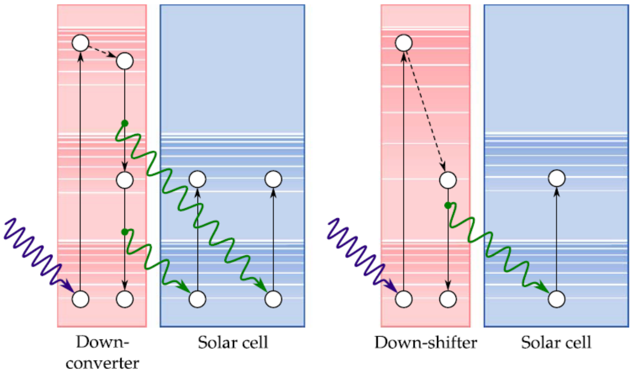


FIG. 9. Energy diagram that shows schematically difference between two similar processes: down-converting and down-shifting [18].

The lanthanide ions spreaded out in the various host materials were used for down-conversion goals. The main idea behind this application is possibility for intraband transitions in the lanthanides due to not-filled 4f-orbitales and filled 5s and 5p orbitales. Like this, the transition metals as Sc and Y also can be applied for the same goals. First materials used for down-conversion were single-ions doped fluorides od Pr+, Tm+, Er+ and Gd+. Typical materials used are lanthanide phosphors doping a host material [19]. The host materials such as ZnS, Y_2O_5, YVO_4, $Zn2SiO_4$ etc. doped by suitable ions have provided quantum efficiency from 125% to 200% [20].

Solar cells with intermediate bands

One of the ways to improve the solar cells efficiency and circumvent the Shockley-Queisser limitation is introducing intermediate bands within the energy gap of the solar cell. This idea relates to the possibility absorb the low-energy photons which cannot be absorbed by the solar cell. Intermediate band introduced within the bandgap of the applied semiconductor will allow the excited electrons and promotes them on the level normally forbidden. Then these electrons will be transferred to the conductive band under absorption additional low-energy photons. Estimation of the converting efficiency provided for ideal case shows that the maximum efficiency can reach 63.2% for one intermediate band and 74.4% for two intermediate bands [21].

FIG. 10 illustrates the absorption process in the photovoltaic cell with the intermediate band. Here, photons with high wavelength are absorbed through two-step process and additional electrons obtained from it increase the total photocurrent from the cell [22].

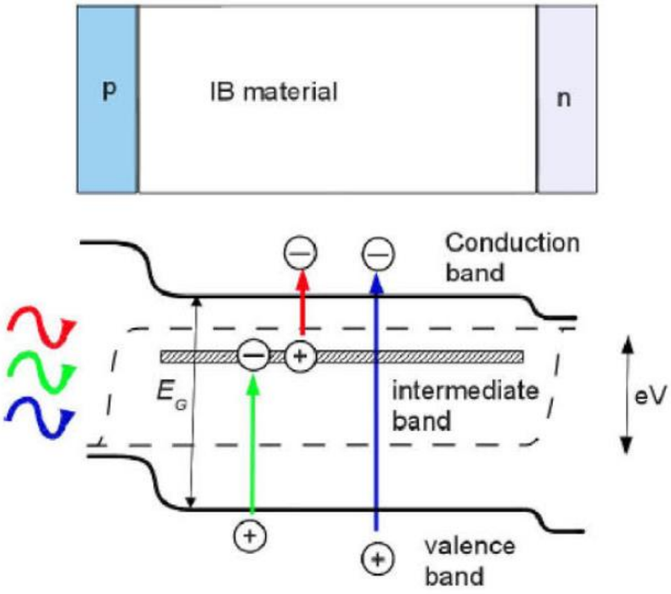


FIG. 10. The principal arrangement structure of the intermediate band solar cell (top) and the simplified band diagram of this structure under operation [22].

Intermediate band application resembles the possibility of using low-energy photons in up-converters, but unlike them, here there is no separate up-converters and the intermediate band producing material should be introduced into the structure of the hosting solar cell. So, the intermediate-band material should be sandwiched between emitter and base of the solar cell as shown in **FIG. 10**. A main requirement for intermediate band materials is absorption of sub-bandgap photons. In other words, the absorption coefficient of these materials should exhibit possibility to absorb the photons into all three bandgaps coexisting together. The promising candidates for the role of intermediate band materials represent transition metals. For example, the titanium with s^2d^2 configuration may be considered as a good entrant for GaAs or GaP matrices [23]. Additional examples which were described are Si doped with Ti, ZnS doped with Cr or the complex alloys such as ZnOMnTe or Ga_4TiAs_3. Unfortunately, many such alloys are thermodynamically unstable. Usually, intermediate band materials are applied in the form of quantum dots which will be considered hereafter.

Hot carrier solar cells

As it was mentioned above, the charge carriers generated under absorption of high-energetic photons thermalize the solar cells and thus decrease their efficiency. Another way to use these hot carriers instead of the down-conversion is to slow the rate of their cooling or to extract rapidly the initial hot carriers from the semiconductor to the external circuit. This method enables to collect photoexcited carriers whilst they are still at elevated energies. This requires an absorber material in which carrier cooling is reduced from the picosecond timescale towards the radiative recombination timescale of nanoseconds [24].

To provide essential properties of the absorber material, it must to meet following requirements: it is necessary to prevent the transfer of the photon's energy into acoustic phonons and the solar cell must extract the hot charge carriers into an external circuit using energy selective contacts. These contacts should prevent the energy transfer from hot carriers to another and not cool them. So, the hot carriers will be collected by selective energy contacts and cold carriers using lower-energy contacts. **FIG. 11** illustrates a principle of operation of a hot carrier solar cell.

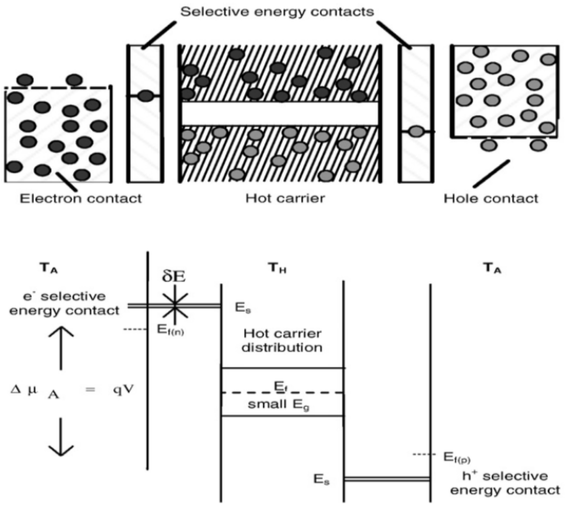


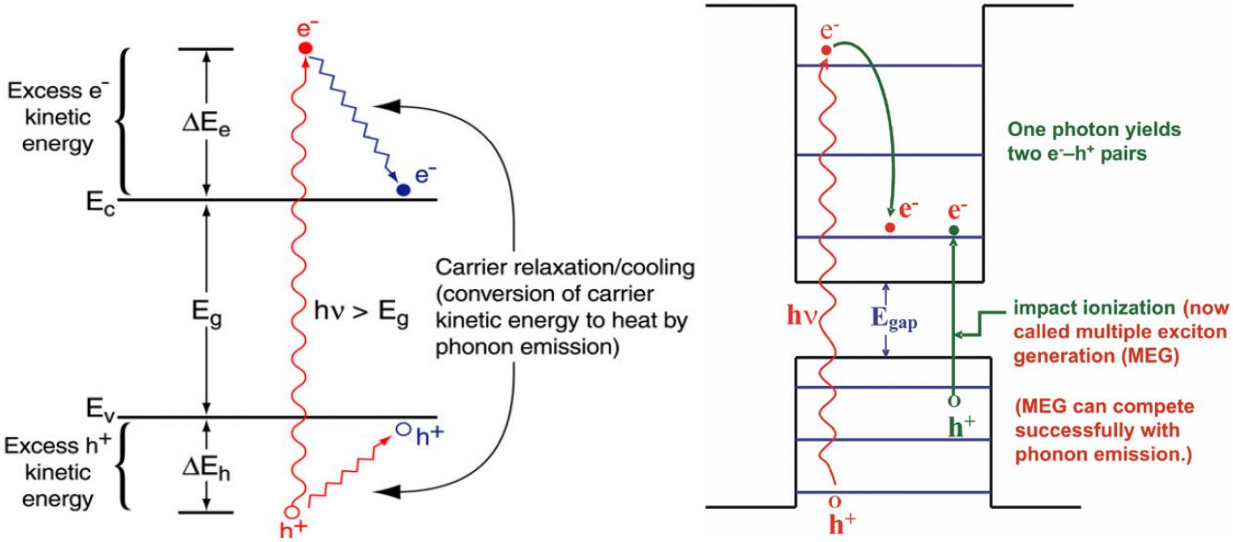
FIG. 11. Band diagram of an ideal hot carrier solar cell [25].

Here, hot carriers with temperature T_H are collected by the specific energy selected contacts at ambient temperature of T_A and all other carriers are collected by usual contacts. Resulted generated voltage here will be defined by difference of energy selected contacts for hot electrons and holes. By this way, the hot carrier solar cells performance is enhanced by converting the excess carrier's kinetic energy. In usual solar cells, this energy goes to the thermal lost. The limiting efficiency of an ideal hot carrier solar cell with the bandgap of 0.7 eV should reach up to 65% [7,26].

The investigation of hot carriers relaxation which was provided with different materials showed that the hot-carrier cooling rate increases when instead the bulk semiconductor, the quantum wells were applied [27,28]. This result show that successful enhancement of the solar cell efficiency increasing may be obtained by using the low-dimensional structures. Thus, the enhancing structure dimensions should provide quantum confinement properties at least in one dimension. So, such structures as quantum wells, quantum wires or quantum dots must be used to enhance the required properties.

Multiple exciton generation solar cells

Multiple exciton (electron-hole pairs) generation is a photocurrent enhancing mechanism in quantum dot-based photovoltaic elements. Here, the energy of a high-energy photon is going to generation of multiple carrier pairs with lower energy. This method devoted to increase the solar cell efficiency above the Shockley-Queisser limit using the impact ionization [29]. It was shown that the effect of impact ionization is not significant in bulk semiconductors, however in the case of quantum confinement, the bulk material restrictions reduce and generation of additional charge-carrier pairs comes to be substantial [30]. **FIG. 12** illustrates two possible thermalization ways.

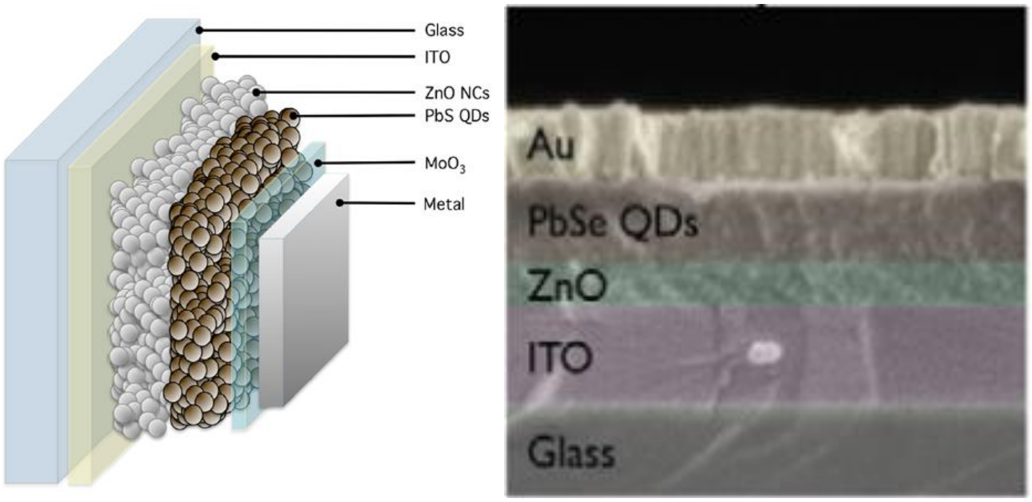


(a) Bulk semiconductor (b) Quantum dot

FIG. 12. Thermal loss of hot carriers in a bulk semiconductor (a) and in quantum dot (b) [31].

In a bulk semiconductor (**FIG. 12a**), the absorbed high-energetic photon generates one charged pair electron-hole (the exciton) when these high energetic particles, electron and hole, reduce their energy due collisions in the material with generation of many phonons thus increasing the semiconductor temperature. In a quantum dot (**FIG. 12b**), due to high concentration of excited electrons and holes, the impact ionization occurs thus producing two excited electrons instead one in the bulk semiconductor. This process looks as the inverse Auger recombination process [32].

Typical structure of heterojunction solar cell using quantum dots shown in **FIG. 13**. The scheme of such solar cell [33] and the implementation of the structure [6] are presented in this figure.



(a) (b)

FIG. 13. A schematic presentation of a heterojunction quantum-dots solar cell (a) [33] and a cross-section SEM of the device structure (b) [6].

Here, the quantum dot PbSe layer forms a heterojunction with ZnO nanocrystals. Electrons are extracted through the ITO electrode and holes are collected through the transition metal oxide or metal electrode. ZnO represents the large-bandgap semiconductor (3.37 eV) and PbSe is a narrow bandgap semiconductor (0.28 eV) [34]. Thus, the relation between these materials enables to successfully apply the quantum dots of PbSe for the charge carriers multiplication. The bandgap value in the quantum dots may be tuned by change of the nanodots dimensions [6].

Application of Metal Nanoparticles for Solar Cells Efficiency Enhancement

Another type of nano-dimensional structures is the metal nanoparticles. As known, small metal particles made of gold or silver have an interesting property: in response to light exposure in a certain spectral range, in these particles occurs resonant absorption of light. This phenomenon is explained by the appearance of localized plasmons-polaritons with intensity and frequency that are relative to the size of the particles. The localized surface plasmons represent collective behavior of free electrons confined to the small metal particles. In other words, surface plasmons are coherent fluctuations in electron density, occurring at a “free-electron” metal–dielectric or metal–air interface [35]. There are another metal island films appearing the same properties. The main requirement for these materials is the forbidden intraband transition [36]. Noble metals, alkali metals and several transition metals such as palladium, when penultimate electron shell is fully filled can appear the localized surface plasmon resonance or plasmon [37].

Many researchers have tried to use the surface plasmon resonance to increase efficiency of solar cells. For this purpose, the nanoparticles of such metals as Au, Ag, Cu and Al were deposited on the surface of solar cells with the goal to increase the light trapping. Unfortunately, all these efforts were not successful. Also, the silver nanoparticles were embedded into thin photovoltaic structures with the goal to increase the light absorption in ultrathin media, see **FIG. 14** [38]. Simulation shows enhanced light trapping. Unfortunately, the efficiency growth upper the Shockley-Queisser limit was not demonstrated for this energy-conversion scheme.

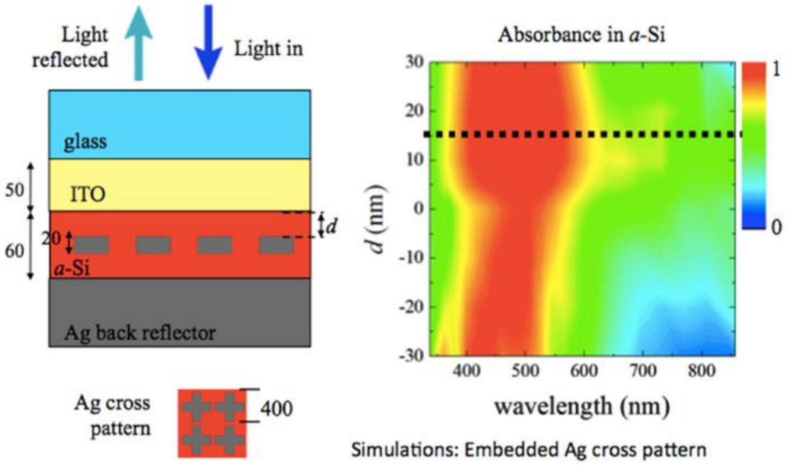


FIG. 14. Plasmonic metal nanopattern embedded in the silicon [38].

The specific pattern of silver deposited on the cell's surface was prepared to use the high-energetic electrons excited under absorption of hot photons for transfer their additional energy to metal nanoparticles instead of usual thermalization process. Technological scheme and simulation results of this project shown in **FIG.15** [39]. Such construction is devoted to protect the photovoltaic structure from electron-phonon scattering due to absorption of excess energy in the silver nanopatterns deposited on the surface of the devices. Simulation predicts slight increasing of the photocurrent.

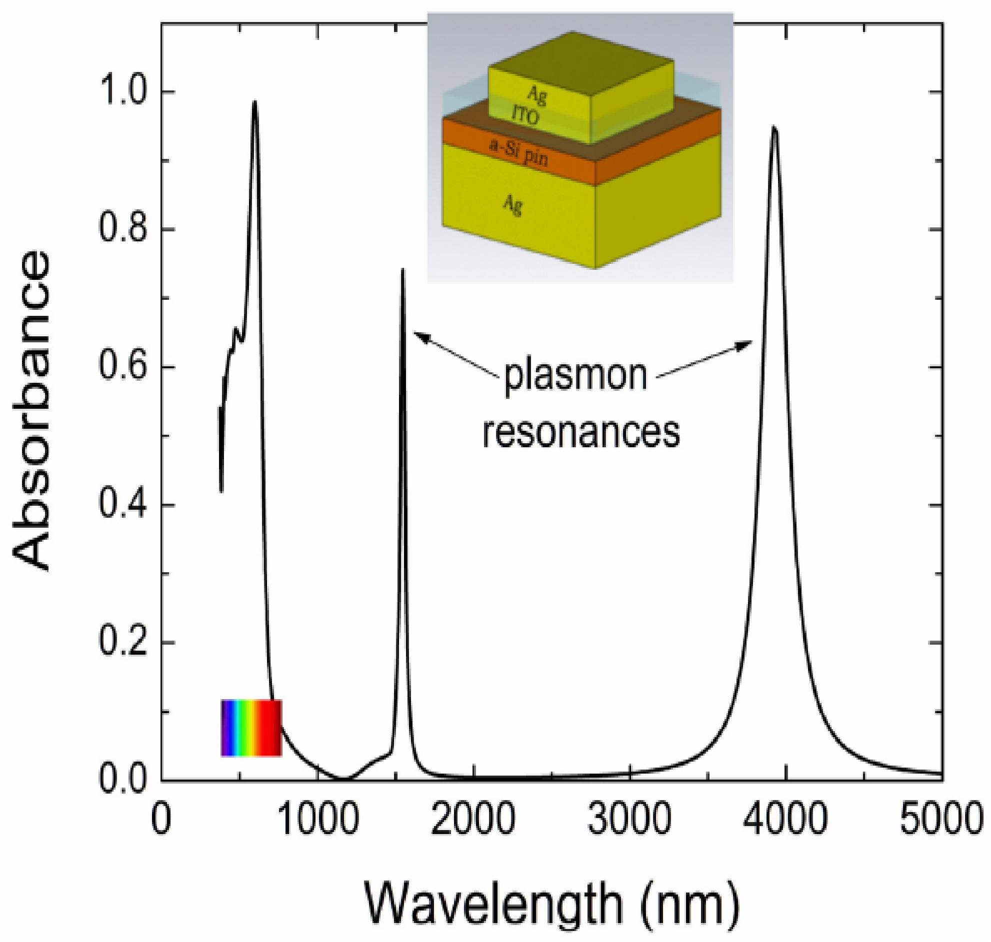


FIG. 15. Plasmonic metal-insulator-metal structure for utilization the excess energy [39].

Influence of the location of the silver nanoparticles on the efficiency of PIN heterostructure solar cells was studied using simulation technique as shown in **FIG. 16** [40]. Here, the silver nanoparticles were embedded in various parts of the heterostructure.

As shown using 3D multiphysics modeling tools, the presence of metal nanoparticles might be helpful to enhance light absorption, although it would not guarantee improving the sola cell's efficiency. These results were also confirmed by experimental measurements [40]. On our opinion, the main problem of this work is that the nature of the applied metal and the contact properties of the metal-surrounding material have not been taken into account.

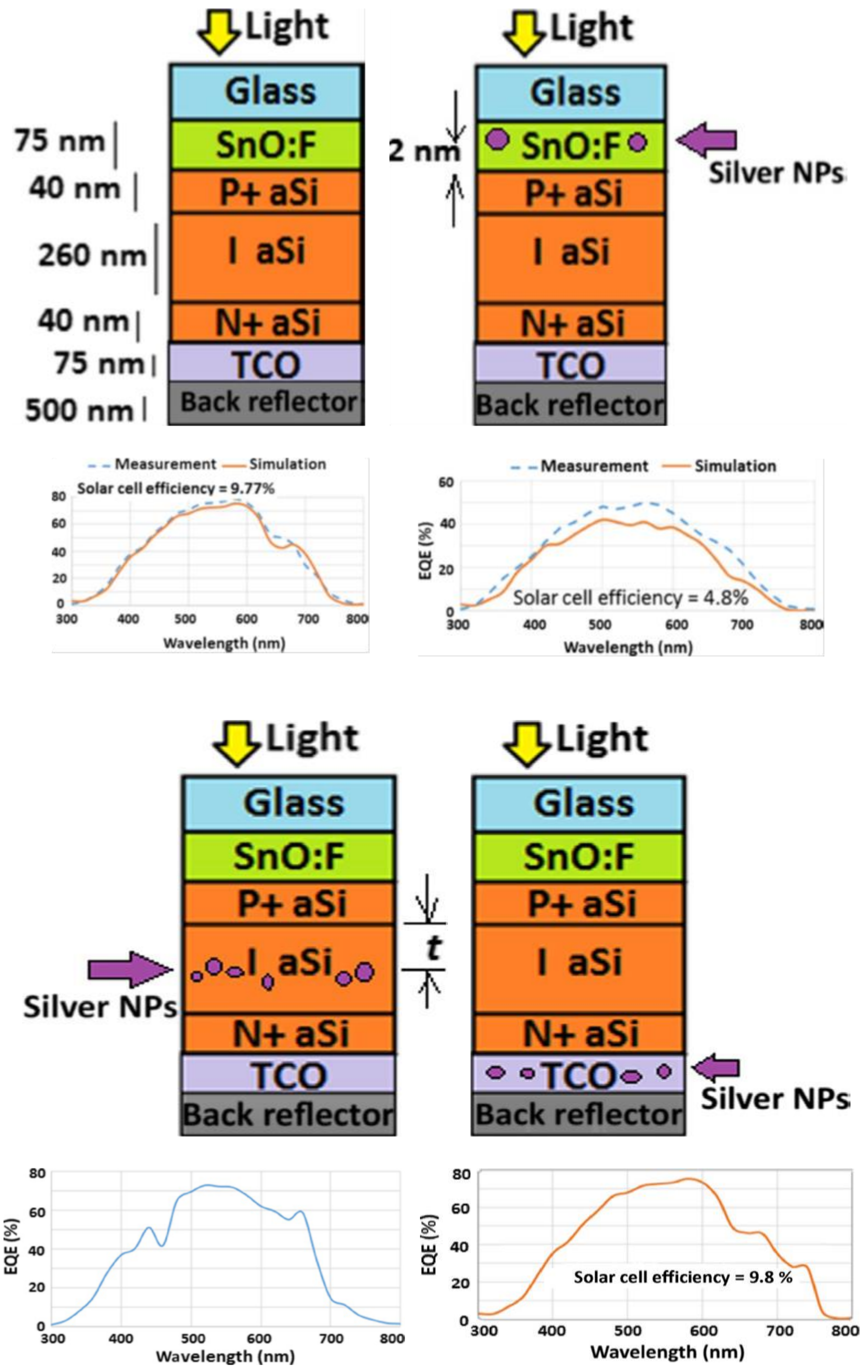
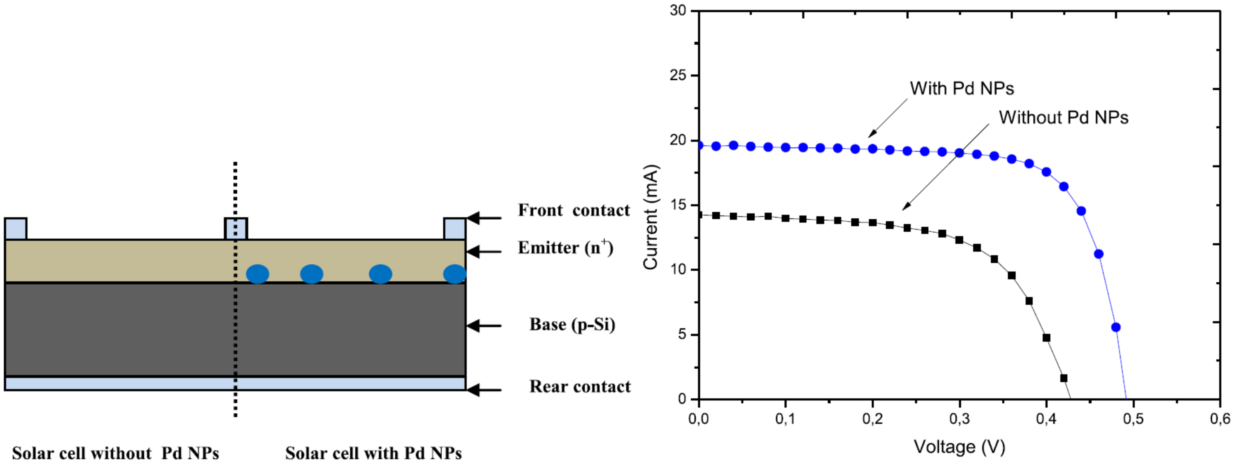


FIG. 16. Structure of heterojunction photovoltaic cells with embedded silver nanoparticles and external quantum efficiency simulated and measured curves: (a) the basic reference structure, (b) silver nanoparticles located above the absorber layer along the windows film, (c) silver nanoparticles embedded inside an intrinsic layer, (d) silver nanoparticles arranged inside the ITO back-side coating [40].

Another, very promising result was shown by incorporation of palladium nanoparticles into the semiconductor junction based on silicon with the goal to improve the solar cell efficiency [37]. In this work, the Pd nanoparticles, prepared by the wet chemical process, were deposited on the [100] surface of the boron-doped p-type single-crystalline silicon wafer used as the base of the photovoltaic cell. Then, to form a thick n+ (emitter) region and to achieve the required junction, a phosphorous diffusion at 950^{0}C through 30 min was provided. **FIG. 17a** represents the schematic view on the solar cells with and without palladium nanoparticles.



(a) (b)

FIG. 17 A schematic presentation of the studied photovoltaic structures (a) and measured I-V characteristics [37].

An almost twofold increase in the efficiency of the solar cell, from 3.79% to 7.02% was obtained in this work. This result was explained by appearing an enhanced electromagnetic field in vicinity of palladium nanoparticles or by appearing the localized surface plasmons. This additional field was absorbed by the emitter and base layers and thus contributing additional charge carriers in the conductive and valence bands of the photovoltaic structure.

Additional explanation may be done on the base of contact properties of the metal nanoparticle with the surrounding materials. As known, a metal forms a Schottky contact with the semiconductor of N-type and the Ohmic contact with the semiconductor of P-type if the metal work-function is more than that of the semiconductor [41]. For example, the gold forms the Schottky contact with the silicon of N-type and the aluminum forms the Ohmic contact with the same material. Palladium has the work-function enough high to forms the Schottky contact with the N-type silicon. Therefore, each palladium nanoparticle represents a Schottky contact with the N-type silicon an Ohmic contact with the P-type base. Between the base and emitter, the built-in potential exists. So, all palladium nanoparticles represent the Schottky diodes under forward bias which enables them to transfer generated inside the plasmon electrons to the conductive band of the emitter. Theoretical analysis of similar structure included gold nanoparticles shows that maximum generated current of the solar cell will take following form [42]:

$$I_m = (I_L + I_{ad})\left(\frac{V_t}{V_m} - 1\right) \quad (1)$$

where I_L is the generated current, $V_t = kT/q$ is the thermal voltage, k is the Boltzmann's constant, T is the absolute temperature of the environment in K, q is the electron charge, V_m is the maximum voltage producing by the solar cell, and I_{ad} is the full additional current produced by the plurality of built-in Schottky nano-diodes, presented by the following relation:

$I_{ad} = A \sum_{j}^{N} S_j J_{nj}$ (2)

where J_{nj} is the current from the metal nanoparticle, j is an index, N is an average number of metal nanoparticles per unit area, S_j is an average contact surface area between metal nanoparticle and emitter, and A is the active surface area of the photovoltaic cell.

Experimental verification of this theory was done using gold island film embedded into the heterojunction silicon-ITO photovoltaic structure which presented in **FIG. 18** [35].

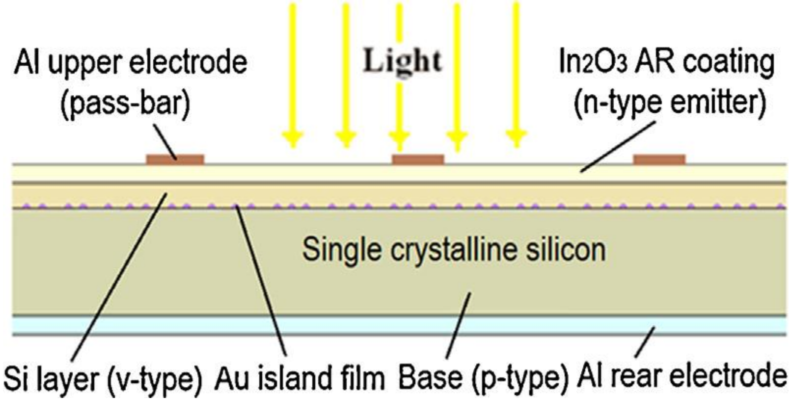
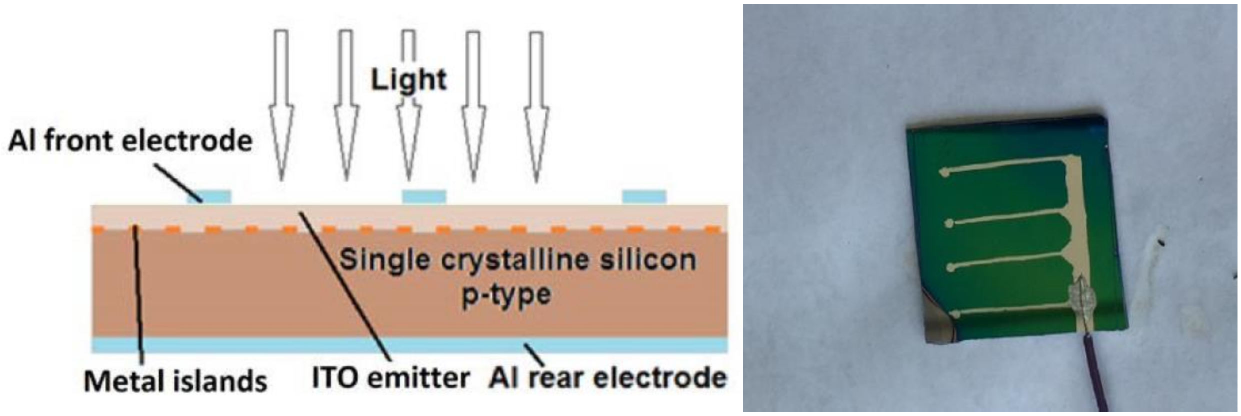


FIG. 18. A side view of the heterojunction photovoltaic system based on silicon [35].

The experimental solar cell, as shown in **FIG. 18**, represents a multilayer structure included a P-type single crystalline silicon substrate, an aluminum rear continuous electrode, thin gold island film with calculated thickness of ~2 nm, deposited on the substrate by sputtering method, a ν-type silicon buffer layer with thickness of ~500 nm, transparent conductive In_2O_3 thin film, playing both roles: anti-reflecting coating and emitter layer, and upper aluminum electrodes. To verify an influence of gold nanoparticles embedded into the P-N junction on the properties of solar cells, the I-V characteristics were measured on the samples with and without gold interlayer. Measurements show that both short circuit current and open circuit voltage grow approximately to ten times in the samples with Gold Island interlayer.

To verify influence of island metal films embedded into the P-N junction on the efficiency of a photovoltaic structure, different metals, gold and silver were applied. It is known that both these metals appear similar plasmonic behavior [43]. The semiconductor heterojunction structures based on the single crystalline silicon were grown and studied. A schematic presentation of the studied structures and an external view of one of samples are shown in **FIG. 19** [44].



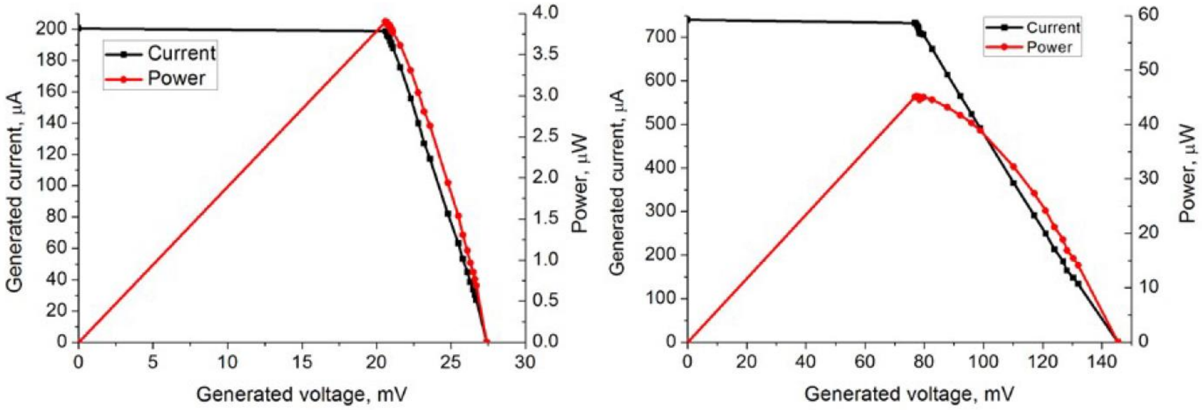
(a) (b)

FIG. 19. A schematic presentation of the experimental photovoltaic structure (a) and an external view on the prepared sample (b) [44].

The simplest heterostructure shown in **FIG. 19** represents a multilayer system grown on the single crystalline silicon of P-type. The front surface of the substrate is coated in series by gold or silver island interlayer with thickness of approximately 2 nm and transparent conductive In_2O_3-SnO_2 (ITO) thin film with thickness of about 200 nm. Metal interlayer and ITO film were deposited by sputtering and front and rear aluminum electrodes were prepared by thermal vacuum evaporation.

To obtain the I-V and P-V characteristics of our PV-structures, they were measured at the same conditions at constant temperature of 20°C under illumination of an incandescent lamp (its radiation spectrum significantly biased in the IR range) on the distance of 10 cm providing maximum light intensity of ~1800 Lx that relates to approximately 15 W/m^2.

The I-V characteristics were measured using a variable load resistor. The load resistance was varied in the interval from 1 Ω up to 900Ω. **FIG. 20** present I-V characteristics measured for samples with two different structures: (a) Al/ITO/Si/Al and (b) Al/ITO/Au/Si/Al. The P-V characteristics were calculated on the base of measured I-V characteristics. As shown in this figure, the generated power in the structure with embedded gold interlayer is in 10 times more than in the structure without it. In the sample with gold islands, the gold forms diverse types of contact with ITO emitter and the p-type silicon base [41]. This is due to the difference in the work functions between contacting materials. The work function of the gold is higher than the work function of the ITO. Therefore, the gold islands create Schottky contacts with the emitter and Ohmic contacts with the base of the heterojunction P/N structure.



(a) (b)

FIG. 20. I-V and P-V characteristics measured on the Al/ITO/Si/Al structure (a) and Al/ITO/Au/Si/Al structure (b) [44].

For explanation of the results shown in **FIG. 20**, the schematic energy band diagram (not to scale) based on calculation of substantial parameters of the photovoltaic structure was designed. It presented in **FIG. 21**.

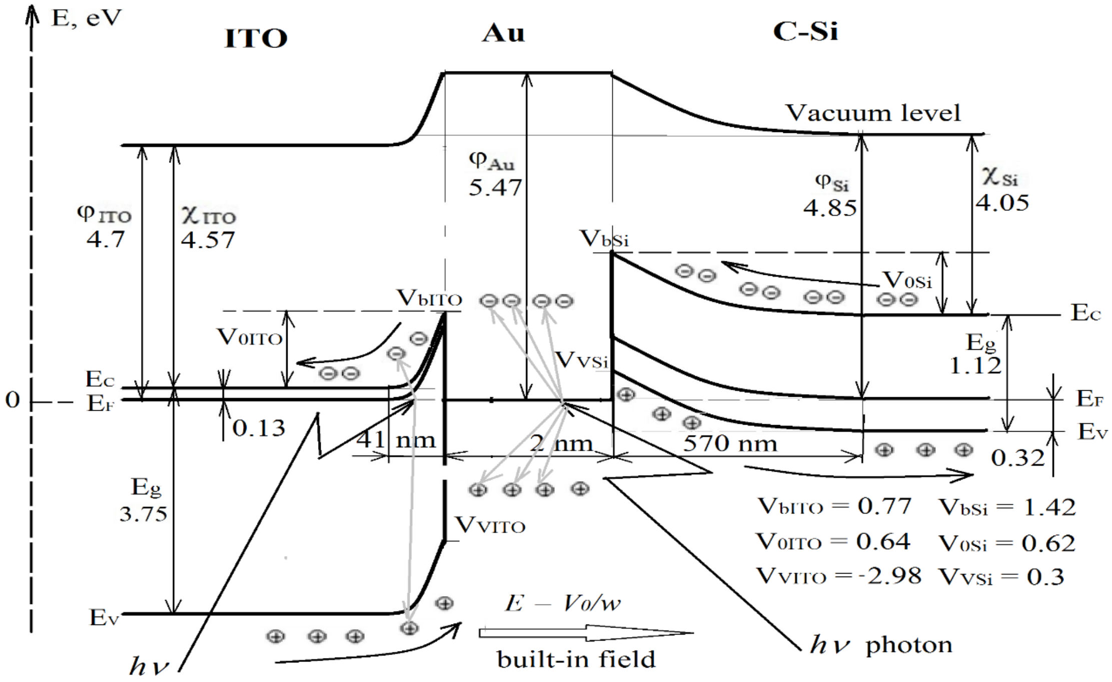


FIG. 21. A schematic energy diagram for the experimental photovoltaic cell [44].

Calculation of a built-in potential, V_{0Si}, on the junction Si-Au and V_{0ITO} on the junction Au-In_2O_3 were provided by the same way as it was done by E.M. Nasir [45]. This diagram illustrates the behavior of p-n heterojunction with embedded gold island film under illumination. The metal (gold) particle with a work function greater than the work function of the emitter ITO layer of n-type and greater than that of p-type base crystalline Si is embedded inside the depletion region with width w. This width is a sum of depletion regions in the ITO-Au contact and in the Au-Si contact: $w = w_{Si} + w_{ITO}$. Therefore, it forms a Schottky contact with the emitter ITO layer and an Ohmic contact with the base (p-type silicon). This particle is subjected to a strong electric field $E = V_b/w$ produced by the built-in potential, V_b, in the depletion region. Thus, all the gold particles form a set of forward-biased nano-diodes Schottky.

Under solar light irradiation, *hv*, one can see two mechanisms of absorption: first one is a usual absorption of the photon in the active part of the solar cell producing one pair electron-hole, second mechanism is an absorption by the gold particle producing localized surface plasmon resonance in gold particles. Excited electrons from the metal particles-islets are injected into the conducting band of the semiconductor due to the resonance energy exceeding the Schottky barrier. These additional electrons are collected by the emitter electrode of the photovoltaic cell, thus increasing the load current. So, each photon absorbed by the gold particle produces a group of charged carriers due to polarization of the gold and injects them into the conductive (electrons) and valence (holes) bands of the ITO and silicon. Therefore, the amplification effect or the photon amplifier generating additional charged carriers utilized in the grown structure appears here. Parallel connection of a plurality of nano-diodes Schottky to the silicon p-n junction leads to increase in the voltage generated by the system. Also, additional charged carriers generated within the gold particles and injected into the semiconductor environment, increase the generated photocurrent.

Now, we can return to consideration the question, what kind of plasmon-generating metal should be used in the solar cell. Evidently, this metal should be chosen according to the applied semiconductor structure. **FIG. 22** presents measured short-circuit currents for various photovoltaic structures [44]. Three different structures were compared: the system with embedded silver island film, the system without an interlayer, and the system with the gold interlayer embedded into the P-N junction. Insert in **FIG. 22** illustrates a principal measuring scheme. As shown in **FIG. 22**, the silver layer prevents to the spread of the generated charged carriers and promotes their rapid recombination. Authors of the work explain this effect by the formation of Ohmic contact between the silver particles and ITO emitter and Schottky contact with the P-type silicon base.

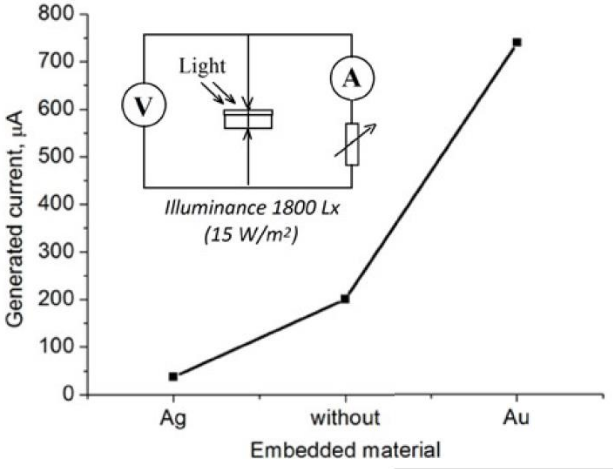


FIG. 22. Comparison of the short-circuit current in various photovoltaic structures [44].

Conclusion

The most efficient photovoltaic cell that got up to day 46% efficiency consists of four-junction structure and is used with the concentrator. This structure is very complex and expensive; however, it shows a way to approach to the maximum theoretical efficiency 86.8% [46]. By the contrast, efficiencies of single-junction solar cells are almost reached their potential limit. Presented review devoted to methods enabling circumvent the Shockley-Queisser limit and increase efficiency of single-junction solar cells. Most likely, the right way to reach high efficient low-cost photovoltaic devices will be based on integration of various approaches mentioned in the review. For example, combination of up-converter with the plasmon enhanced photovoltaic structure looks as a very promising solution. Here, the up-converter will enable to utilize the long wavelength photons, and the plasmon structure will use the high energy photons for generation multiple charged carriers under absorption of one photon. In any case, the use of solar energy for the electricity production is a major task that will be solved with the help of the described here and novel ideas.

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