The state-of-the-art and future development of the photovoltaic technologies – the route from crystalline to nanostructured and new emerging materials

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Abstract. Photovoltaic technology has received raising attention as one of the most promising approach to environment friendly energy production. The main efforts in the PV technologies are focussed on increasing of the efficiency and decreasing of the price of the solar cells and modules. Solar cells made applying nanostructured and new emerging materials are being investigated to address this challenge. In this paper an overview of the present state of knowledge of material aspects of photovoltaic cells is given, and new materials, including nanomaterials, with the potential for using in photovoltaic devices are presented.

1. Introduction
Electricity from the Sun (Photovoltaics - PV) is considered as one of the most prospective and clear source of energy. Because of universal availability of solar energy and immense potential of direct conversion of solar radiation into electricity to use, it was predicted that photovoltaic will become a very serious alternative for fossil fuels in the nearest future. PV-generated electricity is totally environmental-friendly. As mankind will probably have to face energy crisis, factors such as energy independence, energy security, stability of energy supply and variety of energy sources become much more vital these days.

Different semiconducting inorganic and organic materials are used to prepare solar cells and modules. In this work, an overview of the present state of knowledge of the materials aspects of photovoltaic cells will be given, and new materials, namely nanomaterials, with the potential for application in photovoltaic devices will be introduced.

2. World’s PV market
From the first space applications to the GW planned systems, more than 50 years have passed. The last decade has seen PV technology emerging as a potentially major technology for power generation in the World (figure 1). By the end of 2008, the World cumulative PV power installed was approaching 16 GW and today, almost 23 GW are installed globally which produce about 25 TWh of electricity on a yearly basis. Europe is leading the way with almost 16 GW of installed capacity in 2009, representing about 70% of the World cumulative PV power installed at the end of 2009 while Japan (2.6 GW) and the USA (1.6 GW) are following behind. The 2010 World PV market could reach up between 8.2 and 12.7 GW of new installations under the Moderate scenario and the Policy-Driven scenario, respectively [1]. In a policy Driven scenarios, the World annual PV market could reach up to
30 GW in 2014, based, of course, on favorable conditions established by policy makers, regulators and the energy sector at large. The announced world-wide PV production capacity would also be sufficient to cover the expected evolution of the market in the coming five years. The PV market forecasts demonstrate a bright future for the PV market and industry in the coming 5 years.

3. Photovoltaic materials - state-of the-art

Solar cells are in fact large area semiconductor diodes (figure 2). Due to photovoltaic effect energy of light (energy of photons) converts into electrical current. At p-n junction, an electric field is built up which leads to the separation of the charge carriers (electrons and holes). At incidence of photon stream onto semiconductor material the electrons and holes are generated, if the energy of photons is sufficient. Contact to a solar cell is realized by metal electrodes. If the circuit is closed, meaning an electrical load is connected, and then direct current flows.

A number of properties are required for candidate PV materials and device structures. The most essential ones concern optical and electrical conditions:

i) Strong light absorption over a large spectral range. This property implies that a tunable band gap is desirable. The peak of absorption should be at 1.4–1.5 eV, for optimal efficiency.

ii) Good carrier collection properties for both - minority and majority carriers, a low carrier recombination loss (in the bulk, at grain boundaries and at the front and back surfaces).

iii) Low cost, so that the thin film structures are preferable.

iv) Stability as functions of both time and illumination conditions (stable active materials, stable metal contacts, resistance to corrosion);

v) High abundance of the source materials (for large-scale production);

vi) Environment friendly technology;

PV technologies presently fall into three categories:

i) **Crystalline silicon flat plates** (single crystalline and multicrystalline silicon wafers) - 1st generation solar cells;

ii) **Si-based thin films** (polycrystalline silicon, amorphous silicon and its tetrahedral alloys, protocrystalline and microcrystalline silicon) and **polycrystalline films of CdTe, CuIn(Ga)Se₂** - 2nd generation solar cells, and

iii) **GaAs** and a multijunction approach using **III-V alloy** material combinations; number of concentrator approaches (including Si, GaAs, GaAlAs) - 1st generation solar cells. This type of solar cells are suitable for installation in the regions with a high intensity of the solar radiation, under sunlight concentration and for space application, they will not be object of discussion in this review.

**Crystalline (c-Si) and multicrystalline (mc-Si) silicon** based technologies dominate today’s PV production. Si is presently the most mature and best studied candidate for terrestrial PV applications. It
offers several advantages over other PV materials, including abundance, an established technology base, high material quality and stability, and good surface passivation characteristics. The obvious disadvantages are the indirect band gap and the currently high processing cost for silicon material and devices. Hence, research continues both in improving silicon material and in studying and developing other Si-based technologies (e.g. thinner Si wafer -100-50 µm, metallurgical silicon, etc.).

Today, the most efficient c-Si solar cell is a “passivated emitter and rear locally diffused” (PERL) structure (figure 3), showing an efficiency of about 24.4% [2,3]. The main features of this cell are: front surface reflection loss reduced by inverted pyramids, high quality emitter-diffusion profile and high quality passivating thermal oxide on the front and back surfaces to reduce surface recombination losses, small front-contact fingers and localized rear p+ diffusion to reduce the contact contribution to total recombination losses. A similar approach has been applied for a multicrystalline silicon solar cell, where “honeycomb” front surface texturing is performed. As a result, multicrystalline Si solar cells with 19.8% efficiency have been produced [4].

Amorphous Silicon solar cells. a-Si:H is a non-crystalline solid, lacking long-range periodic ordering of its constituent atoms. However, it does have local order on an atomic scale. This short-range order is directly responsible for the observation of semiconductor properties such as an optical absorption edge and an activated electrical conductivity. A typical amorphous silicon cell employs a p-i-n design where an intrinsic layer (i-layer) is sandwiched between a p-layer and a n-layer (figure 4). The flexible solar cells are based on a sophisticated multi-layer amorphous silicon thin-film solar cell have been developed.

This spectrum-splitting cell, shown schematically in figure 5, is constructed of separate p-i-n type a-Si:H solar sub-cells, each with a different spectral response characteristic. This allows the cell to convert the different visible and near infrared wavelengths of sunlight with optimal efficiency. Amorphous cells with different light absorption properties and deposited continuously, one on top of another, to capture the broad solar spectrum more effectively. This increases the energy conversion efficiency of the multi-cell device and improves performance stability. The multi-junction approach has resulted in world record stabilised efficiencies for these cells of 15%.

Figure 2. Scheme of the solar cell and p-n junction.

Figure 3. Structure of PERL cell: c-Si with a pyramidal textured surface [4].

Figure 4. A typical a-Si:H solar cell employs a p-i-n design, in which an intrinsic layer (i-layer) is sandwiched between a p-layer and an n-layer.
A multijunction device is a stack of individual single-junction cells in descending order of bandgap ($E_g$).

**Chalcopyrite solar cells (figure 6).** Ternary chalcopyrite CuInSe$_2$ (CIS) and its modification Cu(In,Ga)Se$_2$ (CIGS) are the first thin film materials to achieve 10% efficient solar cells. The device stability, together with improvements of the cell efficiency, has attracted the interest of researchers and industry in CIS-based PV technology. The maximum efficiency reported to date is 19.19% 50 x 50 mm test cells [5]. For modules on flexible Ti foil substrate, the efficiency of 17.9% is reported [6] and 13.9% (for 90 cm$^2$) [7].

**Cadmium telluride solar cells (figure 7).** Many of the basic properties of CdTe make it an ideal material for use in thin film solar cells. For example: i) its energy gap is direct and its value of 1.45eV supports maximal conversion efficiency, ii) it may be doped n- or p-type, and the preparation of the stoichiometric compound may be achieved easily in the production process, iii) CdTe thin films can be deposited at high rates by various methods: sublimation/condensation, close spaced sublimation, chemical spraying, electro-deposition, screen printing, chemical vapour deposition and sputtering. A disadvantage of CdTe solar cells concerns environmental and safety problems, since the product contains Cd, a toxic element. It has been shown, however, that modules can be produced under normal industrial risk conditions, and suitable techniques for waste treatment and recycling of modules are available [8]. Maximal efficiency of solar modules with CdTe thin films is achieved of 18% in the laboratory conditions and 11.1% by industry [9].

4. Solar spectrum

Solar radiative energy has its origin in a nuclear fusion reaction in the sun. The resulting energy is emitted mainly as electromagnetic radiation in the spectral range 0.2–3 μm (figure 8). The spectral distribution of the solar radiation which reaches the earth can be approximated by that of a black body at a temperature of 5800K. However, there is a sufficient departure from this idealized spectrum and hence it is desirable to use more exact data.

The sunlight is absorbed and scattered when it passes through the atmosphere on its way to the earth’s surface. Basically, three sources of atmospheric absorption and scattering are important: atmospheric gases (O$_2$, N$_2$ etc.), aqueous vapour, and dust. The solar spectrum under different conditions is shown in figure 8 (left) [10]. The solar spectrum is very broad and contains significant power density.
both below and above the band gap of semiconductors applied for solar cells (figure 8). Figure 8 (right) illustrates the spectral sensitivity of different types of solar cells on the background of the solar spectrum at the earth surface. It is seen that different materials used for solar cells fabrication could transfer only part of the Sun spectrum into electricity.

Increasing the efficiency and decreasing the production cost of terrestrial photovoltaic devices is important for their widespread acceptance as a major power generation technology for the future. One of the main factor limiting the efficiency of solar cells is the spectral mismatch between the band energy (absorption spectrum) of the absorber material and the incident solar light. The solar spectrum is very broad and contains significant power density both below and above the band gap of the materials applied. Therefore the conversion efficiency limit, e.g. for a single-junction Si solar cell, according to the detailed balance analysis, yield a maximum of 31% under standard AM 1.5 solar spectrum radiation[11].

Several approaches have recently been proposed to increase the efficiency of single-junction solar cells above the theoretical limit. Within the category of high-efficiency approaches, a distinction is made between approaches that tailor the properties of the active layer to better match the solar spectrum and approaches that modify the incoming solar spectrum and function of the periphery of the active device, without fundamentally modifying the active layer properties. Advances in nanotechnology and nanomaterial are relevant to both approaches.

Another main factor, which limits large-scale use of solar energy, is the cost, which is still too high. The most advanced solar cell processes make extensive use of high temperature processes, vacuum processes, pattern definition steps, and/or expensive materials (including the silicon wafers). Therefore, not only the efficiency enhancement but also the cost reduction of solar cells has to be a target of innovative developments.

An analysis of current trends in the PV field shows that both improved efficiency and lowered cost can be obtained by implementing nanomaterials and nanotechnology to existing solar cells. Solar cells entirely based on nanostructured materials can ultimately be an alternative to the dominant bulk crystalline Si technology (1st generation) and thin film based PV technology (2nd generation) Thus, incorporation of nanostructured and new materials in 1st and 2nd generation solar cells to enhance conversion efficiency and lower cost per unit Wat, is required and will provide an evaluation process towards creation of new generation of advanced solar cells, the 3rd generation, which can produce efficiency greater than 20% yet at the same cost levels as thin film solar cells.

5. Nanomaterials and emerging technologies for PV application

Nanomaterials such as nanowires and nanoparticles have unique advantages that make them useful in photovoltaic devices. The nanometer size objects have very large surface areas per unit volume which offers the possibility to form very large interfacial area. The quantum confinement effects due to the
nanosize effect results in increasing of the band gap of materials that help to design materials with different band gap. Nanomaterial can be produced by non vacuum technologies on large area substrate. All these advantages offer the possibility to increase the efficiency of solar cells and modules and the reducing their price.

5.1. Silicon nanowires

While the 3rd generation imply use of new band structure concepts that allow for limiting efficiencies greater than 31% Shockley-Queisser limit, a first step taken toward such device is development of thin film-based concept with using Si nanowires [11,12]. Silicon nanowire carpets can be produced by Vapor Liquid Solid method (VLS) using metal (Au or Al) nanotemplate [12], galvanic wet etching process [13], Plasma Enhance Chemical Vapour Deposition (PECVD) [14] and arc discharge [15]. There are several potential advantages of silicon nanowire-based solar cells compare to conventional thin film. One of the key features of nanowire devises is the ability to design the structure such that optical absorption is effectively de-coupled from charge transport consideration. In the bulk Si solar cell it is necessary that the cell be greater than ~120 µm in thickness to absorb the light, which in turn may lead to recombination losses as minority carriers diffuse to the top of the p-n junction. In the nanowire device it is possible to build a so-called conformal p-n junction that is only 100’s of nanometers to a few microns width. Nanowire arrays possess excellent anti-reflection and light trapping properties that enable broadband absorption enhancement compared to solid thin films of the same thickness [14]. Nanowires also provide a direct path for charge transport resulting in lower series resistivity and lower probability of non-radiative recombination. Independent of the nanowire preparation method two designs of nanowire solar cells are under consideration with the p-n junction either radial or axial (figure 9).

Figure 10 shows a higher resolution SEM image, indicating the metal droplets on top of each wire deposited by VLS method. The optical reflection, transmission and absorption of a Si nanowire carpet are shown in figure 10 b. Typical is the very low reflectivity of about 5% up to a wavelength of 800 nm which demonstrates perfect antireflection properties. The I-V curves of the cell n-doped nanowires grown on p-type wafer are demonstrated in figure 10 c. The open circuit voltage is rather low. However the doping of the nanowire is not optimised. This result is one of the first demonstrations of possible application of the Si nanowires in a solar cell.

5.2. Silicon quantum dot

The radiative efficiency of the bulk Si solar cells is limited theoretically to 31% due to the incomplete utilization of high energy photons and transmission of the photons with less energy than the Si band gap. One way to enhance the efficiency is to use stack of solar cells in which each cell has band gap that is optimized for the absorption of a certain spectral region. The theoretical efficiency of tandem solar cells with a bulk Si bottom cell increases to 42.5 % when one additional cell with 1.8 eV band is used and to 47,5% with two other solar cells with band gaps of 1.5 and 2 eV placed on top of the bulk cell [16]. Promising materials for the fabrication of Si based high band gap solar cells are Si quantum dots (Si QD) in dielectrics. By restricting the dimensions of Si to less than Bohr radius of bulk crystalline Si (≈5 µm), quantum confinement causes its effective bandgap to increase. Heteroface
structures composed of Si QD deposited on p-i-n homojunction crystalline silicon are fabricated and studied [17]. Figure 11 demonstrates the scheme of the devices with Si QD, the dependence of the open circuit voltage of the device and the spectral response of internal quantum efficiency (IQE) of the cell with various sizes of p-type Si QD and n-type c-Si heteroface devices. The IQE in the case of 3 nm Si QD size shows higher values in the entire range wavelength. For the short wavelength response, the IQE is around 96% at 500 nm for 3 nm Si QD heteroface device and the efficiency of this solar cell is 13.01%. This result is an encouraging step towards application of Si QD in tandem Si solar cells. Further device optimization is required to improve photovoltaic efficiency, including not only process parameters (substrate resistivity, QD deposition conditions and thickness, etc.) but also device structure such as front metallization, base doping concentration, back-surface field, etc.

Figure 11. Scheme of the Si QD on c-Si substrate heteroface device (a), dependence of the $V_{oc}$ on the Si QD size (b) and internal quantum efficiency of the cell with different size of the SiQD(c) [17].

5.3. Nanowires of $A_2B_6$ semiconductors

Increased optical absorption and stability of thin film silicon solar cells is the main goal of all thin film silicon solar cell developments. This is possible to do by increasing the light scattering and subsequent light trapping due to the nano-rough interfaces.

The photovoltaic (PV) devices based on inorganic $A_2B_6$ semiconductor with vertically oriented nanowires and nanorods structure have been extensively investigated, such as ZnO [15,18-26], CdS [27], covered with a-Si:H heterostructures or filled with organic photo-active materials [35],
fullerences [26], etc. These solar cells with ordered or well-aligned nanowires or nanorods, in comparison with the bilayer structure, have the advantages of very large donor–acceptor (D–A) interface area, continuous and minimized carrier conduction path ways which can significantly increase the power conversion efficiency of cells. Light scattering and subsequent light trapping due to nano-rough interfaces of the TCO is generally applied, too. Figure 12 shows the scheme of 3-dementional a-Si:H solar cells on superstrate galss/TCO/nanocolumns, covered by ZnO serving as electrode [18].

Single-crystal ZnO nanowire arrays have attracted research interest because they may be used as building blocks for a new generation of devices. In the framework of photovoltaic applications, they are an interesting option to be applied as n-type wide band material in nanostructures solar cells. They show quantum confinement and direct path for electrons promoting higher electron diffusion coefficient of ZnO nanowired areas with respect to nanoparticles. ZnO nanowire could be prepared by different techniques such as chemical and electrochemical deposition, sol-gel processing, spray pyrolysis, Vapor Liquid Solid (VLS), arc discharge, etc.[15, 20-24].

Figure 13, 14a and 14b show the SEM images of ZnO nanostructures prepared by the method of arc discharge and electrochemical deposition, respectively. The high value of defuse reflection (figure 14 c) of ZnO nanostructured films demonstrate the possibility to be applied as a back contact for increased light trapping in thin film solar cells.

The ZnO nanowired films deposited on the glass/ITO electrode have been used in ZnO/organic hybrid solar cells [25]. It was found that fill factor (FF) was remarkably improved from 50% to 65% along with a small change in short circuit current and open voltage. The ZnO nanorods work as the electron collectors by shortening the average electron diffusion distance in the polymer PCBM network in the bulk heterojunction. The ZnO nanorods work also as direct paths to transport charge to the ITO electrode, resulting in a decreased charge recombination. Therefore, a large FF is observed.
Applying fullerene interlayer between the ZnO nanorod arrays of polymer/ZnO hybrid solar cells an enhancement in the efficiency, short-circuit current density, open circuit voltage and fill factor compare to the devices without the interlayer has been achieved (figure 15 and 16). This enhancement is due to the improved infiltration of the photoactive layer into ZnO nanorod spacing [26].

CdS has been proved to be an excellent photoactive and charge transport material in PV devices [25–28], and its direct band-gap of 2.4 eV is appropriate to be an acceptor in solar cells. Recently, the synthesis and application of CdS nanowire arrays or nanorod arrays have become an attractive research field. Hybrid solar cells based on one-step fabricated vertically aligned CdS nanorod arrays and poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene)(MEH-PPV) have been fabricated. The vertically aligned CdS nanorods provide the minimal electron transport path to reduce the charge carrier recombination at the heterojunction interface [27]. It is believed that the device performance of polymer/CdS nanorod composites can be improved further by improving the CdS nanorod arrays structure and introducing the higher mobility polymers.

To explore the potency of the proposed strategy, highly ordered, single-crystalline nanopillars of n-CdS directly on aluminium substrate and embedded them in a thin film of p-CdTe as the optical absorption material (figure 18) have been synthesized [28]. Conventional thin-film photovoltaics rely...
on the optical generation and separation of electron-hole pairs with an internal electric field, as shown in figure 2. Among different factors, the absorption efficiency of the material and the minority carrier lifetime often determine the energy conversion efficiency [29].

In this regard, simulation studies have previously shown the advantages of three-dimensional (3D) cell structures, such as those using coaxially doped vertical nanopillar arrays, in improving the photocarriers’ separation and collection by orthogonalizing the direction of light absorption and electrons-holes separation (Figure 18 b). This type of structure is particularly advantageous when the thickness of the device is comparable to the optical absorption depth and the bulk minority carrier lifetimes are relatively short. Under such circumstances, the optical generation of carriers is significant in the entire device thickness and the 3D structure facilitates the efficient electron-hole separation and collection [28]. Figure 19 shows the I-V characteristics of a typical cell under different illumination intensities, P, ranging from 17 to 100 mWcm$^{-2}$ (AM 1.5G). Specifically, an efficiency $\eta= 6\%$ is obtained with an open circuit voltage $V_{oc} = 0.62$ V, short circuit current density $J_{sc} = 21$mAcm$^{-2}$ and fill factor $FF= 0.43$ under AM1.5G illumination. The dependency of the performance characteristics on the illumination intensity is shown in figure 19 (down). As expected, $J_{sc}$ exhibits a near-linear dependency on the intensity because in this regime the photocurrent is proportional to the photon flux with a constant minority carrier lifetime. On the other hand, $V_{oc}$ increases only slightly from 0.55 to 0.62 V with a linear increase of $J_{sc}$, which we attribute to a slight thermal heating of the device. As the efficiency of a solar cell is expressed as $\eta = V_{oc}J_{sc}FF/P$ and FF slightly decreases with light intensity, the efficiency is about 6% and shows minimal dependence on the illumination intensity as shown in figure 19 (above). It should be noted that this modest efficiency is obtained without the use of an antireflective surface coating or concentrators.

6. Photon management concept

Photon management concept employed to the solar cells is based on the phenomena as i) by surface

![Figure 18](image1.png)

**Figure 18.** CdS/CdTe solar cell with nanoparticle: a) Energy band diagram of CdTe/CdS heterojunction, b) cross-sectional schematic diagram, illustration the enhanced carrier collection efficiency, c) fabrication processes flow [13].
Figure 20. AFM image of 12 monolayers Au nanoparticles on n-type a-Si:H/ p-type c-Si heterojunction,(a), spectrum of extinction coefficient of two nanoparticle Au layers and of a-Si:H thin film (b) and I-V characteristics of heterojunction without and with Au nanoparticle with 12 Mls (20 nm) and 18 Mls (30 nm) (c) [30].

Plasmon Resonance (SPR) effect and ii) spectral modification of the incident light - up- and down-conversion.

6.1. Surface plasmon resonance

SPR from noble metal nanoparticles (NPs) is a promising way to improve the efficiencies of silicon based photodiodes and solar cells. Exploitation of the localized absorption of metal Au nanoparticles via SPR and improvement of the characteristics of solar cells is demonstrated [30]. Methods of electroless plating, sputtering or thermal evaporation with post thermal treatment or ion irradiation, deposition from colloidal solution are used to prepare Ag or Au nanoparticles [30-32]. It is shown that a density of $1.3 \times 10^{11}$ cm$^{-2}$ of Au nanoparticles with an approximately 20 nm diameter (12 monolayers (Mls)) deposited by sputtering on the surface of n-type a-Si:H/p-type c-Si heterojunctions enhance performance (short circuit current) of solar cell due to the improved absorption of light by the SPR of Au NPs (figure 20)[30].

6.2. Up- and down- conversion

Up-down conversion can be regarded as one of the approach for development of the Third Generation Photovoltaics - to use the energy incident on a solar cell more effectively. Most of the attempts to improve of the solar cell efficiency to date have aimed at modifying the structure of the solar cells itself, by fitting its spectroscopic sensitivity to the fixed sunlight spectrum. A reverse concept, however, is to fit the sunlight spectrum to the solar cell sensitivity via a wavelength-shifting operation. This can be done e.g. by the inclusion of layers containing rare earth ions. Rare earth ion complexes absorb light of short (or long) wavelength, and then emit light with longer-down conversion, (or shorter – up-conversion) wavelengths. If the wavelength shifts for rare earth ion are applied to solar cells, the higher (or lower) photon energy component of sunlight can be shifted to the longer (shorter) wavelength, at which cells can produce electrical power with high efficiency. Candidate rare earth ions for improvement of the conversion efficiency are Ce$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Yb$^{3+}$, Nb$^{3+}$, Tb$^{3+}$, Er$^{3+}$, Dy$^{3+}$ embedded in different glass matrices.

The efficiency of thin film solar cells can be improved with the addition of a photon down-conversion top layer. This layer converts incident ultraviolet light of the solar spectrum to visible light, which transmits through the glass and is efficiently absorbed by the active layer of the solar cell.

In the case of down-conversion doping of the transparent antireflection coating of the solar cell with suitable rare earth elements, which have absorption bands in the UV region and emission bands in the visible region (in the best case at the spectral sensitivity peak of the solar cells), would results in increasing of the conversion efficiency. Not all rare-earth ions, however, are suitable for increasing the
efficiency via up-conversion. Several rare-earth ions satisfy these conditions: Ce$^{3+}$, Sm$^{3+}$, Eu$^{2+}$, Eu$^{3+}$, Yb$^{3+}$, Nb$^{3+}$, Tb$^{3+}$ [33]. It has to be considered that the position of the emission band of the rare earth, however, depends on the host material and the ambient temperature. The rare-earth ions can be involved in the antireflection coating by different methods: ion implantation, magnetron co-sputtering of the ion and AR coating, sol-gel [33-37]. A diagram of a PV module with a luminescent down-shifting (LDS) layer on top is presented in figure 21. An example of PL spectrum of a LDS material – a SiO$_2$ thin film with embedded Tb$^{3+}$ ions, deposited by magnetron co-sputtering on glass substrate is given in figure 22. The photoluminescence spectrum is exited by 488 nm line of Ar$^+$ line. Three characteristic bands were observed and identified as the following 4f-4f transitions: $^5$D$_4$ – $^7$F$_5$ ($\sim$ 546 nm), $^5$D$_4$ – $^7$F$_4$ ($\sim$ 586 nm) and $^5$D$_4$ – $^7$F$_3$ ($\sim$ 622 nm). The first transition was much stronger than the others because of the highest value of the corresponding transition matrix element according to the Judd-Ofelt theory [39]. It had a structure with two maxima at 542 nm and 549 nm, which was ascribed to Stark splitting and has been also observed for Tb$^{3+}$ in some glasses [40]. Such layer deposited on the front side of the glass substrate with solar cells on the back side will transmit the emitted light through the glass which will be efficiently absorbed by the active layer of the solar cell.

Application of the up-converters to the solar cells and modules could reduce the losses of the incident power. E.g. silicon solar cells lose about 35% of the incident power because of the thermalisation losses and 20% because photons with energy below the band gap are transmitted straight through the device. The theoretical efficiency limit is raised from near 30% [11] up to about 40% [40] for Si solar cells with upconverter illuminated by non-concentrated light.

**Figure 21.** A diagram of a PV module with an LDS layer on top. Light having $\lambda$ within the absorption band of the luminescent species 1 will be absorbed and re-emitted at longer $\lambda$.

**Figure 22.** PL spectra of an as-deposited 260 nm thin SiO$_2$:Tb film on a Si substrate with a Tb concentration of 4.61 at.% and annealed at 700 °C PL is exited by 488 nm line of Ar$^+$ line of Ar laser[37].

Figure 23. Spectral concentration and upconversion. The fluorescent material absorbs in a broad spectral range (green) and emits in the absorption range of the upconverter (red). The upconverter emits photons with energies above the bandgap $E_g$ of the silicon solar cell.

**Figure 24.** Potential setup of an advanced upconverter system.
Unfortunately, promising up-converting materials, such as erbium-doped \( \text{NaYF}_4 \), have only a narrow absorption range. More photons can be converted, when the upconverter is combined with a fluorescent material. The fluorescent material should absorb over a wide spectral range and emits in the absorption range of the upconverter (figure 23). \( \text{PbSe/PbS} \) core-shell nanocrystal quantum dots area promising fluorescence material for this application. An advanced upconverting system layout, which includes the combination of up-converter and fluorescent material, and the application of photonic structures for spectral management has been proposed [42, 43]. The experimental data demonstrate the effect of an UC material on the long-wave-length response of amorphous Si solar cells (figure 25 [42]). The I-V characteristics of a-Si:H solar cell with UC phosphor is a factor of three larger (figure 26 [42]. Up today the enhancement of the quantum efficiency of the real c-Si solar cells with \( \beta-\text{NaYF}_4:20\% \text{Er}^{3+} \) is very low (0.011%) [43].

![Figure 25](image1.png) **Figure 25.** Spectral response measurements for solar cells with 1 \( \mu \text{m} \) \( \text{ZnO:Al} \) 0.5% layer as the back contact and different back reflectors [42].

![Figure 26](image2.png) **Figure 26.** I-V curves of a-Si:H solar cells with and without UC layer attached at the back. The current in the cell with the UC phosphor is a factor of three larger [42].

7. Conclusion

The third generation of solar cells as low cost and high efficiency revolutionary technologies needs to be developed to make photovoltaic energy economically competitive. Nanostructured materials are likely to play important roles both in reducing the cost of second generation thin film solar cells and in the development of third generation photovoltaic devices because they offer some significant and unique advantages for solar-to-electric energy conversion. Proposed novel solar cell architectures that make use of nanomaterials have already been demonstrated but these are still not efficient and reliable enough to compete with first and second generation solar cells in the near future for generating electricity. Compared to the traditional solar cells the new technologies based on nanomaterials are still in their infancy. In some areas, progress from fundamental research to prototypes has been achieved. Future advances and the rate at which we can achieve them will depend entirely on the amount of resources the society chooses to invest in photovoltaics.

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