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Hybrid Solar Cells Based on Silicon

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1. Introduction

Human need for renewable energy resources leads to invention of renewable energy sources such as Solar Cells (SCs). Historically, the first SCs were built from inorganic materials. Although the efficiency of such conventional solar cells is high, very expensive materials and energy intensive processing techniques are required. In comparison with the conventional scheme, the hybrid Si-based SC system has advantages such as; (1) Higher charging current and longer timescale, which make the hybrid system have improved performances and be able to full-charge a storage battery with larger capacity during a daytime so as to power the load for a longer time; (2) much more cost effective, which makes the cost for the hybrid PV system reduced by at least 15% (Wu et al., 2005). Thus, hybrid SCs can be a cheap alternative for conventional SCs.

One type of hybrid SCs is a combination of both organic and inorganic materials which combines the unique properties of inorganic semiconductors with the film forming properties of conjugated polymers. Organic materials are inexpensive, easily processable, enabling lightweight devices and their functionality can be tailored by molecular design and chemical synthesis. On the other hand, inorganic semiconductors can be manufactured as nanoparticles and inorganic semiconductor nanoparticles offer the advantage of having high absorption coefficients, size tunability and stability. By varying the size of nanoparticles the bandgap can be tuned therefore the absorption range can be tailored (Günes & Sariciftci, 2008). These kinds of hybrid SCs based on organic-inorganic materials are fabricated by using different concepts such as solid state dye-sensitized SCs and hybrid SCs using Bulk Heterojunction (BHJ) concept such as TiO_x (Hal et al., 2003), ZnO (Beek et al., 2006), CdSe (Alivisatos, 1996; Huynh et al., 2002), Cds (Greenham et al., 1996), PbS (McDonald et al., 2005), and CuInS₂.

Another generation of hybrid SCs are silicon-based modules due to the direct bandgap and high efficiency of Si. This system includes SC module consisting of crystalline and amorphous silicon-based SCs. The methods for enhancing the efficiencies in these types of hybrid SCs such as applying textured structures for front and back contacts as well as implementing an intermediate reflecting layer (IRL) between the individual cells of the tandem will be discussed (Meillaud et al., 2011). This chapter brings out an overview of principle and working of hybrid SCs consisting of HJ SCs which is itself divided into two groups, first organic-inorganic

module and second, HJ SCs based on single crystalline, amorphous and microcrystalline Si and SCs in dye-sensitized configuration. Afterward, material characterization of these kinds of SCs will be investigated. Precisely, Crystalline Si thin film SCs and later amorphous and microcrystalline Si SCs and the recent works are discussed.

2. Principle and working of hybrid solar cells

One of the methods to build hybrid SCs is Bulk Heterojunction (BHJ) SCs, composed of two semiconductors. Excitons created upon photoexcitation are separated into free charge carriers at interfaces between two semiconductors in a composite thin film such as a conjugated polymer and fullerene mixtures. One of these materials of an HJ obviously must be an absorber. The other may be an absorber, too, or it may be a window material; i.e., a wider-gap semiconductor that contributes little or nothing to light absorption but is used to create the HJ and to support carrier transport. Window materials collect holes and electrons, which function as majority-carrier transport layers, and can separate the absorber material from deleterious recombination at contacts. The interface they form with the absorber is also used for exciton dissociation in cells where absorption is by exciton formation. Absorber and window materials may be inorganic semiconductors, organic semiconductors, or mixtures (Fonash, 2010, as cited in Khalili et al. 2010; Sohrabi et al. 2011). For applying HJ structure (HJS) for hybrid SCs, the blends of inorganic nanocrystals with semiconductive polymers as a photovoltaic layer should be employed.

Schematically, the HJ hybrid SCs consist of at least four distinct layers, excluding the substrate, which may be glass. These four layers are anode, cathode, hole transport layer and active layer. Indium tin oxide (ITO) is a popular anodic material due to its transparency and glass substrate coated with ITO is commercially available. A layer of the conductive polymer mixture PEDOT:PSS may be applied between anode and the active layer. The PEDOT:PSS layer serves several functions. It not only serves as a hole transporter and exciton blocker, but it also smoothens out the ITO surface, seals the active layer from oxygen, and keeps the anode material from diffusing into the active layer, which can lead to unwanted trap sites. Next, on the top of the PEDOT:PSS, layer deposited is the active layer. The active layer is responsible for light absorption, exciton generation/dissociation and charge carrier diffusion (Chandrasekaran et al., 2010). The so-called two materials are inserted in active layer namely donor and acceptor. Polymers are the common donors whereas nanoparticles act as common acceptors. On the top of active layer is cathode, typically made of Al, Ca, Ag and Au (Chandrasekaran et al., 2010).

BHJ hybrid SCs attracts much interest due to these features:

- a. HJs allow the use of semiconductors that can only be doped either n-type or p-type and yet have attractive properties which may conclude their absorption length, cost, and environmental impact. The existence of concentration gradient of the n-type nanoparticles within the p-type polymer matrix may allow optimization of the topology of the HJ network.
- b. HJs allow the exploitation of effective forces.
- c. HJs of window-absorber type can be used to form structures that shield carriers from top-surface or back-surface recombination sinks (Fonash, 2010).
- d. The affinity steps at HJ interfaces can be used to dissociate excitons into free electrons and holes.
- e. HJs can also permit open-circuit voltages that can be larger than the built-in electrostatic potential.

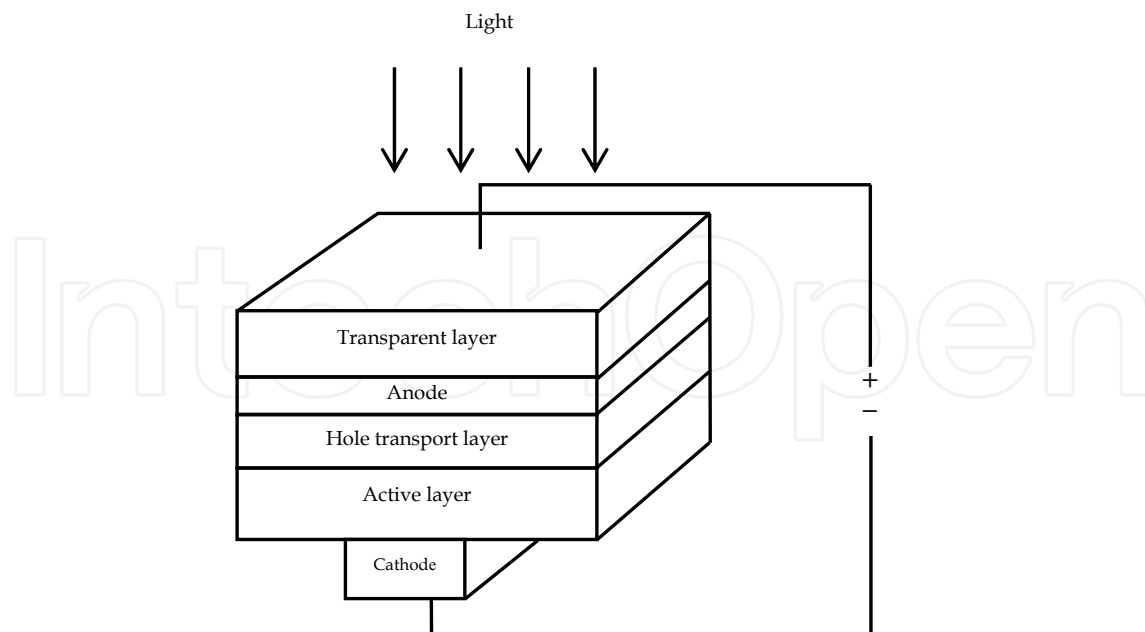


Fig. 1. Structure of HJ hybrid SCs

f. Inorganic semiconductor materials can have high absorption coefficients and photoconductivity as many organic semiconductor materials (Günes & Sariciftci, 2008). Typically, inorganic semiconductors in macroscopic dimensions, irrespective of their size, will absorb all electromagnetic radiation with energy greater than the bandgap. However, if the particles become smaller than that of the exciton in the bulk semiconductor (typically about 10 nm), their electronic structure has changed. The electronic properties of such small particles will depend not only on the material of which they are composed, but also on their size, the so-called quantum confinement effect (Arici et al., 2004, as cited in Weller, 1993; Steigerwald & Brus, 1990; Alivisatos, 1996; Empedocles & Bawendi, 1999; Murphy & Coffey, 2002; Movla et al. 2010a). The lowest energy of optical transition, among others, will increase significantly due to the quantum confinement with decreasing size of the inorganic clusters. Since the energy levels of the polymers can be tuned by chemical modification of the backbone chain and the energy levels of the nanoparticles can be tuned through the size-dependent quantum confinement effects, blends of the two materials offer the possibility of tailoring optimal conditions for a solar cell, including energy gain from charge transfer for the efficient charge separation and the spectral range of the absorbing light (Arici et al., 2004). Therefore, in order to obtain hybrid polymer SCs with high current and fill factor, both electron and hole mobilities must be optimized and most importantly balanced (Chandrasekaran et al., 2010). However, diffusion of nanoparticles into the polymer matrix takes place with the penetration depth controlled by temperature, swelling of the polymer layer, and not at least by the size and shape of the nanocrystals.

Another module of HJ hybrid SCs consists of crystalline and amorphous silicon-based SCs which is the main discussion in this chapter. The present PV market is dominated by three kinds of Si-based solar cells, that is, single-, multi-crystalline or amorphous Si-based solar cells (for short, marked hereafter as Sc-Si, Mc-Si and a-Si solar cells, respectively). The conventional PV system in general uses Sc-Si or Mc-Si solar cell module as the element for solar energy conversion, which have comparatively higher conversion efficiency. However, it is not only the module efficiency that decides whether a PV system is cost effective but

also the timescale during which the module works efficiently in a daytime of use and the cost the module itself requires. At this point, a-Si solar cell comes with its advantages of broader timescale and lower cost (Wu et al., 2005, as cited in Goetzberger et al., 2003).

The broader timescale merit of a-Si solar cell arises from its high absorption of light with wavelength around 300–800nm, no matter if it is scattered or not, and no matter if it is weak or blazing. The Sc-, Mc- and a-Si solar cells, therefore, reinforce each other in performances, which could be exploited to construct a hybrid PV system with lower cost in view of the well balanced set of system performance (Wu et al., 2005). The last efficiencies reported for c-Si, Mc-Si and a-Si are approximately 25%, 20% and 10%, respectively (Green et al., 2011).

The newest configuration for hybrid SCs is dye-sensitized SC developed by O'Reagan and Graetzel in 1991. This class of cell has reached efficiencies of over 11%. The basic structure of a dye-sensitized SC involves a transparent (wide-band-gap) n-type semiconductor configured optimally in a nanoscale network of columns, touching nanoparticles, or coral-like protrusions. The surface area of the network is covered everywhere with a monolayer of a dye or a coating of quantum dots, which functions as the dye (Fonash, 2010). A monolayer of dye on a flat surface can only harvest a negligibly small fraction of incoming light. In this case it is useful to enlarge this interface between the semiconductor oxide and the dye. As mentioned above, it is achieved by introducing a nanoparticle based electrode construction which enhances the photoactive interface by orders of magnitude (Grätzel, 2004). The dye sensitizer is the absorber. An electrolyte is then used to permeate the resulting coated network structure to set up a conduit between the dye and the anode. The dye absorbs light, producing excitons, which dissociate at the dye-semiconductor interface, resulting in photogenerated electrons for the semiconductor and oxidized dye molecules that must be reduced and thereby regenerated by the electrolyte (Fonash, 2010).

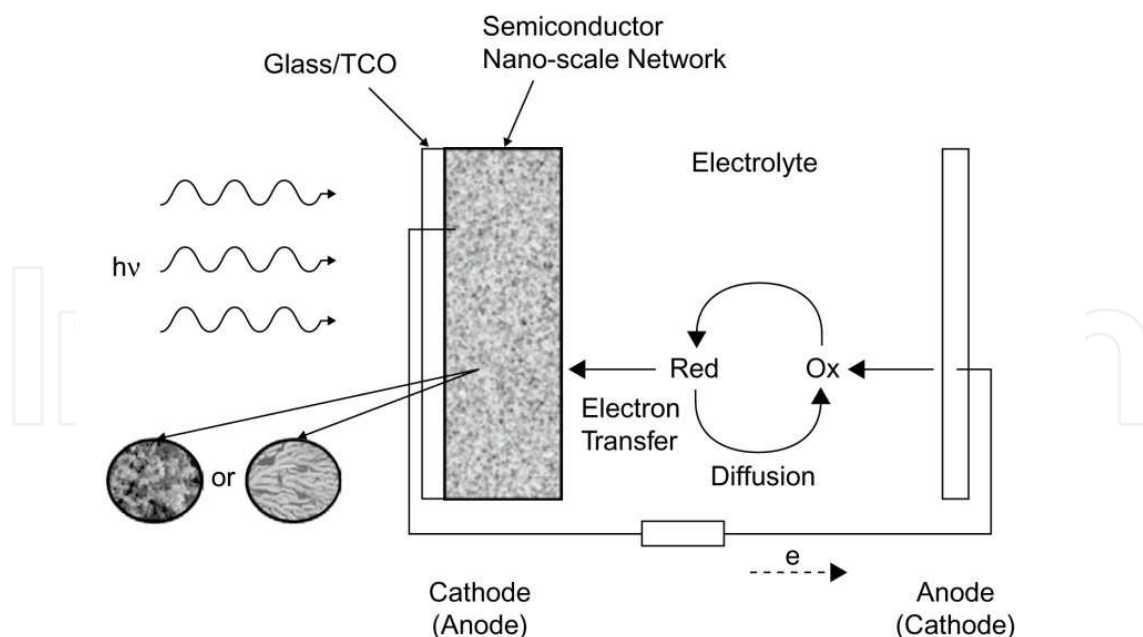


Fig. 2. Schematic of a dye-sensitized SC

A dye-sensitized SC of Graetzel type comprises of several different materials such as nanoporous TiO_2 electrodes, organic or inorganic dyes, inorganic salts and metallic catalysts (Grätzel, 2004, 2005, as cited in Nogueira et al., 2004; Mohammadpour et al., 2010) which

will be discussed more in next section. The dye sensitization of the large band-gap semiconductor electrodes is achieved by covering the internal surfaces of porous TiO_2 electrode with special dye molecules which absorb the incoming photons (Halme, 2002). Alternatives to the liquid electrolyte in dye-sensitized SCs are a polymer gel electrolyte or solid state dye-sensitized SCs which can contain organic hole conductor materials, inorganic p-type semiconductors or conjugated polymers (Fonash, 2010). The impetus for this effort is the increased practicality of an all-solid-state device and the avoidance of chemical irreversibility originating from ionic discharging and the formation of active species (Fonash, 2010, as cited in Tennakone et al., 2000). And also this method avoids problems such as leakage of liquid electrolyte. In solid state dye-sensitized SCs, the sensitizer dye is regenerated by the electron donation from the hole conductor (Wang et al., 2006). The hole conductor must be able to transfer holes from the sensitizing dye after the dye has injected electrons into the TiO_2 . Furthermore, hole conductors have to be deposited within the porous nanocrystalline (nc) layer penetrating into the pores of the nanoparticle and finally it must be transparent in the visible spectrum, or, if it absorbs light, it must be as efficient in electron injection as the dye. (Günes & Sariciftci, 2008)

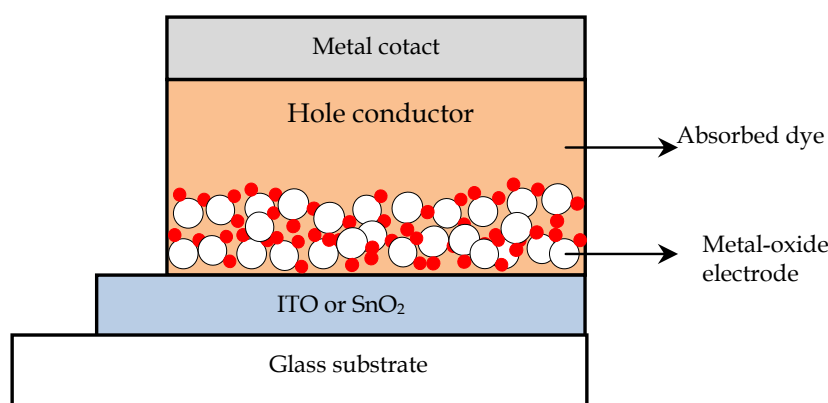


Fig. 3. Schematic of solid state dye-sensitized SC

Other quasi-dye sensitized SCs are nanoparticle sensitized SCs and extremely thin absorber (ETA) SCs. Nanoparticle sensitized SCs are prepared by replacing the dye with inorganic nanoparticles or quantum dots. They can be adsorbed from a colloidal quantum dot solution (Zaban et al., 1998; as cited in Günes et al., 2006; Guenes et al., 2007) or produced in situ (Liu & Kamat, 1993; as cited in Hoyer & Könenkamp, 1995). Inorganic nanocrystals instead of organic dyes could imply tunability of the band-gap and thereby the absorption range. Nanocrystals have large extinction coefficients due to quantum confinement and intrinsic dipole moments, leading to rapid charge separation and are relatively stable inorganic materials (Alivisatos, 1996). To embed the particles into porous TiO_2 films and to use those modified layers as light converting electrodes, the incorporated nanoparticles need to be much smaller than the pore sizes of the nanoporous TiO_2 electrodes (Shen, 2004).

ETA SCs are conceptually close to the solid state dye-sensitized solar cells. In the ETA SCs, an extremely thin layer of a semiconductor such as CuInS_2 or CdTe or CuSCN replaces the dye in TiO_2 based SCs. The ETA SCs has the advantage of enhanced light harvesting due to the surface enlargement and multiple scattering. Similar to the solid state dye sensitized SCs, the operation of the ETA SC is also based on a heterojunction with an extremely large interface (Nanu et al., 2005).

3. Material characterization of hybrid solar cells

Relating to the configuration of hybrid SCs like HJ SCs or dye-sensitized SCs, various materials have been suggested by research groups. The BHJ devices were characterized by an interpenetrating network of donor and acceptor materials, providing a large interface area where photo-induced excitons could efficiently dissociate into separated electrons and holes. However, the interpenetrating network cannot be easily formed in the blended mixture. In addition, the organic materials are not good in carrier transport. Thus, the power conversion efficiency is still limited by the low dissociation probability of excitons and the inefficient hopping carrier transport (Huang et al., 2009, as cited in Siringhaus et al., 1999; Shaw et al., 2008). Semiconductor nanostructures are used to be combined with the organic materials to provide not only a large interface area between organic and inorganic components for exciton dissociation but also fast electron transport in semiconductors. Therefore, many research groups combined organic materials with semiconductor nanostructures to overcome the drawbacks of the organic solar cells. Many inorganic nanowire (NW) had been experimented for this purpose, including CdTe, CdS, CdSe, ZnO, and TiO₂ NWs (Huang et al., 2009, as cited in Kang & Kim, 2006). Totally, BHJ hybrid SCs itself have been demonstrated in various inorganic materials such as CdSe nanodots, nanorods and tetrapods, TiO₂, ZnO, ZnS nanoparticles, CuInS₂, CuInSe₂, CuPc, CdS, SnS, CIS, PbSe or PbS nanocrystals, HgTe ncs, Si NWs, Si ncs (Chandrasekaran et al., 2010 as cited in Kwong et al., 2004, Arici et al., 2004 Greenham et al., 1996 Qi et al., 2005; Choudhury et al., 2005), etc. which act as acceptors and polymer materials acting as donors are P3HT, PPHT, P3OT, P3BT, P3MeT (Lin et al., 2006), MDMO-PPV, MEH-PPV, MOPPV, etc. (Chandrasekaran et al., 2010). However, CdTe, CdS, and CdSe materials are harmful to the environment, while ZnO and TiO₂ have a bandgap higher than 3eV and so cannot effectively absorb the solar spectrum. To overcome this, SiNWs are suitable for this application because they are environmental friendly and have high absorption coefficient in the infrared region (Huang et al., 2009).

J. Haung et al. (2009) reported the fabrication of the SiNW/P3HT:PCBM blend hybrid SCs using the SiNW transfer technique.

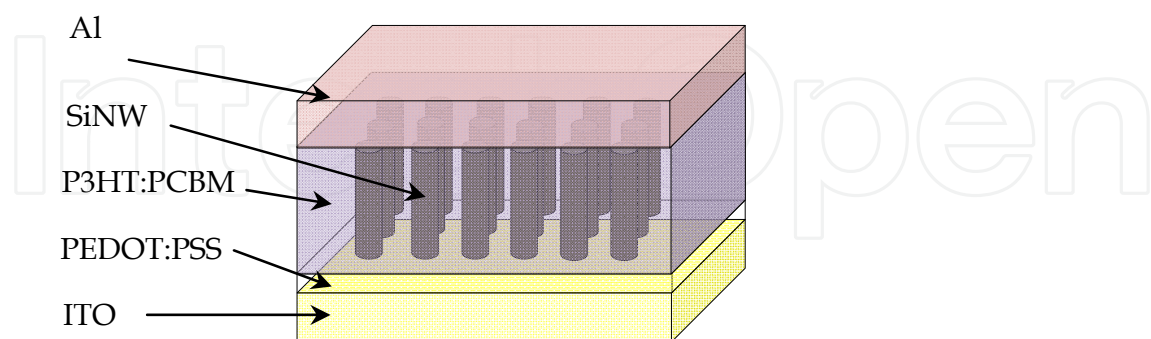


Fig. 4. A schematic of the hybrid SC using SiNWs and P3HT:PCBM blend

Their investigation showed that after introducing the SiNWs, the J_{sc} increases from 7.17 to 11.61 mA/cm² and η increases from 1.21% to 1.91% (Haung et al., 2009). This increase is due to this fact that the NWs act as a direct path for transport of charge without the presence of grain boundaries. (Movla et al., 2010b).

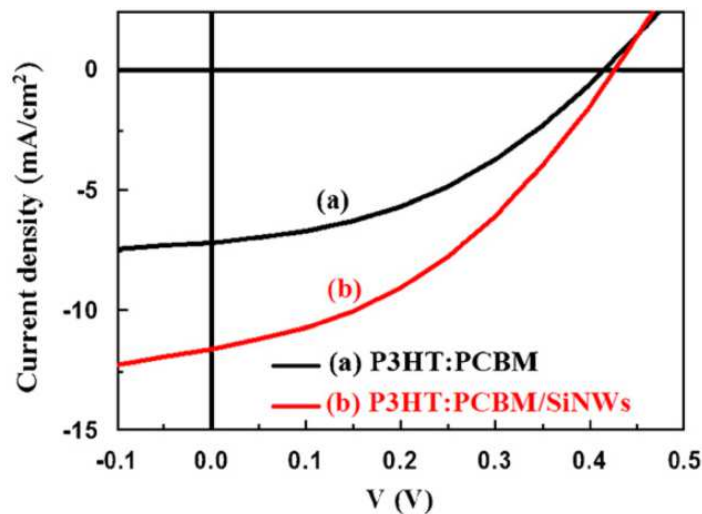


Fig. 5. The current density–voltage characteristics for the SCs with and without the SiNWs under simulated AM1.5 illumination. Reprinted with permission from *Solar Energy Materials & Solar Cells* Vol.93, Huang, J. et al. Well-aligned single-crystalline silicon nanowire hybrid solar cells on glass, pp. 621–624 © 2009, Elsevier.

More precisely, the results clearly indicate that combination of the SiNWs and P3HT:PCBM blend is an attractive route to obtain high J_{sc} and efficiencies by improving the optical absorption, dissociation of excitons, and the electron transport. Silicon wafer is commercially available and cheap. SiNWs can be fabricated at low temperature from solution processing without any vacuum equipment or high-temperature processing. In addition, this transfer method for SiNWs is simple and fast. It is not a laborious way. This method is suitable for plastic SCs because it can be processed fast, is cheap and simple (Haung et al., 2009).

Similar work was done by G. Kalita et al. (2009) for demonstrating hybrid SCs using Si NWs and polymer incorporating MWNTS. This fabricated device with the structure of Au/P3OT+O-MWNTS/n-Si NWs marked a conversion efficiency of 0.61% (Bredol et al., 2009). Another study was done by C. Y. Liu et al. (2009) about fabricating the hybrid SCs on blends of Si ncs and P3HT (Liu et al., 2009). Also, V. Svrcek et al. (2009), investigated the photoelectric property of BHJ SC based on Si-ncs and P3HT. They came into conclusion that I–V characteristic enhanced when BHJ was introduced into TiO_2 nanotube (nt). The arrangement of Si-ncs/P3HT BHJ within ordered TiO_2 nt perpendicular to the contact facilitated excitation separation and charge transfer along nts (Chandrasekaran et al., 2010, as cited in Svrcek et al., 2009).

A new approach for hybrid metal-insulator-semiconductor (MIS) Si solar cells is adopted by the Institute of Fundamental Problems for High Technology, Ukrainian Academy of Sciences. In this technique, the porous silicon layers are created on both sides of single crystal wafers by chemical etching before an improved MIS cell preparation process. The porous Si exhibits unique properties. It works like a sunlight concentrator, light scattering diffuser and reemitter of sunlight as well as an electrical isolator in the multilayer Si structure. The most important advantage of using porous Si in SCs is its band gap which behaves as a direct band gap semiconductor with large quantum efficiency and may be adjusted for optimum sunlight absorption. Employing a specific surface modification, porous Si improves the PV efficiency in UV and NIR regions of solar spectra (Tuzun et al.,

2006, as cited in Tiris et al., 2003). In this approach, due to high quality starting materials and rapid low-temperature (<800 °C) processing a high minority carrier life time is attainable; this, in turn, gives rise to a high photogenerated current collection. Therefore, the SCs with efficiencies above 15% have been obtained under AM1.5 condition (under 100 mW/cm² illumination at 25 °C) (Tuzun et al., 2006).

Another study was reported by J. Ackermann et al. (2002) about the growth of quaterthiophene (4T), a linear conjugated oligomer of thiophene behaving as a p-type semiconductor, on n-doped GaAs and Si substrates to form hybrid HJ SCs. This study shows that in the case of Si as substrate there is almost defect-free high ordered films with grain sizes of several micrometers up to a film thickness of 250 nm (Ackermann et al., 2002). K.Yamamoto et al. (2001) investigated a-Si/poly-Si hybrid (stacked) SC paying attention to the stabilized efficiency, since a-Si has photo degradation, while a poly-Si is stable. This tandem cell exhibited a stabilized efficiency of 11.3%. Also, this research group prepared three-stacked cell of a-Si:H/poly-Si/poly-Si(triple), which will be less sensitive to degradation by using the thinner a-Si. This triple cell showed a stabilized efficiency of 12% (Yamamoto et al., 2001). Their reasons for applying poly-Si are (i) high growth rate (ii) large area and uniform deposition at the same time and (iii) monolithic series interconnection. In addition, for enhancing the absorption, they suggested natural surface texture and a back reflector (See Fig .6.) (Yamamoto et al., 2001).

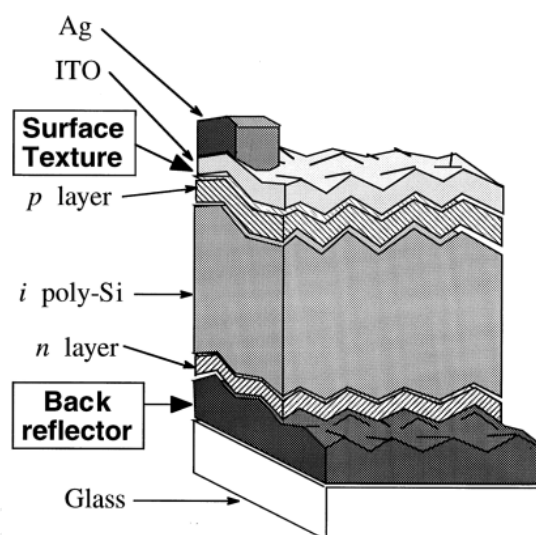


Fig. 6. Schematic view of thin film poly-Si solar cell with natural surface texture and enhanced absorption with back reflector structure. Reprinted with permission from Solar Energy Materials & Solar Cells Vol.93, Huang, J. et al. Well-aligned single-crystalline silicon nanowire hybrid solar cells on glass, pp. 621–624 © 2009, Elsevier.

Apart from BHJ SCs, solid state dye-sensitized SCs can experience various materials. CuI, CuBr, CuSCN, MgO (Tennakone et al.,2001) can be replacements for liquid crystals as inorganic p-type semiconductors. Also, 2,2',7,7'-tetraakis(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (OMETAD) can replace the liquid crystals as organic p-type semiconductor due to their low cost processability (Bach et al.,1995). Poly (3 alkylthiophenes) were used to replace the liquid electrolyte by Sicot et al. (Sicot et al., 1991) and Gebeyehu et al. (Gebeyehu et al.,2002a,2002b) as conjugated polymers although high molecular weight polymers cast from solution, do not penetrate into the pores of the

nanoparticles. A polymeric gel electrolyte is considered as a compromise between liquid electrolytes and hole conductors in quasi solid state dye-sensitized SCs (Günes & Sariciftci, 2008, as cited in Nogueira et al., 2004; Murphy, 1998; Megahed & Scosati, 1995). A mixture of NaI, ethylene carbonate, propylene carbonate and polyacrylonitrile was reported by Cao et al. [55]. Poly (vinylidene fluoride- co-hexafluoropropylene) (PVDF-HFP) used to solidify 3-methoxypropionitrile (MPN) was utilized by Wang et al. (Wang et al., 2004). The last efficiency for dye-sensitized reported by Sharp Corporation is about 10.4 which stands in lower rank in comparison with crystalline Si showing efficiency of approximately 25% (Green et al., 2011).

3.1 Crystalline silicon thin film solar cells

Silicon is the leading material used in microelectronic technology and shows novel photoelectrochemical properties in electrolyte solutions (Wang et al., 2010). Now and before Si-based cells especially crystalline Si has shown higher efficiencies. The last efficiency reported by UNSW PERL is 25% which exceeds other types of Si-based SCs (Green et al., 2011, Zhao et al., 1998).

Crystalline silicon (c-Si) is an extremely well suited material for terrestrial photovoltaics (PV). It is non-toxic and abundant (25% of the Earth's crust), has excellent electronic, chemical and mechanical properties, forms a simple mono-elemental semiconductor that has an almost ideal bandgap (1.1 eV) for terrestrial PV, and gives long-term stable SCs and modules. Furthermore, it is the material of choice in the microelectronics industry, ensuring that a large range of processing equipment exists and is readily available. Given these properties of c-Si, it is not surprising that almost all (>90%) terrestrial PV modules sold today use Si wafer SCs. However, the fabrication of Si wafers is both material and energy intensive. Therefore, there is a need for a less material intensive c-Si technology calling a thin-film technology. Besides cost savings on the materials side, thin-film technologies offer the additional benefits of large-area processing (unit size about 1 m²) on a supporting material, enabling monolithic construction and cell interconnection. The recent c-Si thin-film PV approaches can broadly be classified as follows: (i) fabrication of thin, long stripes of c-Si material from thick single crystalline Si wafers ("ultrathin slicing"); (ii) growth of c-Si thin-films on native or foreign supporting materials (Aberle, 2006).

Recently photoelectrochemical (PEC) SCs based on 1D single crystalline semiconductor micro/nanostructures have attracted intense attention as they may rival the nanocrystalline dye-sensitized SCs (Wang et al., 2010, as cited in Law et al., 2005; Peng et al., 2008; Baxter & Aydil, 2005; Jiang et al., 2008; Mor et al., 2006; Hwang et al., 2009; Dalchiele et al., 2009; Goodey et al., 2007; Maiolo et al., 2007). Therefore, X. Wang et al. (2010) proposed single crystalline ordered silicon wire/Pt nanoparticle hybrids for solar energy harvesting. In this configuration, wafer-scale Si wire arrays are fabricated by the combination of ultraviolet lithography (UVL) and metal-assisted etching. This method emphasizes that the etching technology forms SiNWs non-contaminated by catalyst material while SiNWs by vapor-liquid-solid (VLS) is generally contaminated by gold (Wang et al., 2010, as cited in Allen et al., 2008). It is found that PtNPs modified Si wire electrochemical PV cell generated significantly enhanced photocurrents and larger fill factors. The overall conversion efficiency of PtNPs modified Si wire PEC solar cell is up to 4.7%. Array of p-type Si wire modified with PtNPs also shows significant improvement for water splitting (Wang et al., 2010).

3.2 Amorphous (protocrystalline) and microcrystalline silicon solar cells

The use of thin-film silicon for SCs is one of the most promising approaches to realize both high performance and low cost due to its low material cost, ease of manufacturing and high efficiency. Microcrystalline silicon (μc) SCs as a family of thin film SCs formed by plasma CVD at low temperature are assumed to have a shorter carrier lifetime than single-crystal cells, and it is common to employ a p-i-n structure including an internal electric field in the same way as an amorphous SC. These cells can be divided into p-i-n and n-i-p types according to the film deposition order, although the window layer of the SC is the p-type layer in both cases. A large difference is that the underlying layer of a p-i-n cell is the transparent p-type electrode, whereas the underlying layer of an n-i-p cell is the n-type back electrode. Light-trapping techniques are a way of increasing the performance of mc-SCs. This is a core technique for cells made from μc -silicon because—unlike a-silicon—it is essentially an indirect absorber with a low absorption coefficient. That is, the thickness of the Si film that forms the active layer in a mc-silicon SC is just a few μm , so it is not able to absorb enough incident light compared with SCs using ordinary crystalline substrates. As a result, it is difficult to obtain a high photoelectric current. Light trapping technology provides a means of extending the optical path of the incident light inside the SC by causing multiple reflections, thereby improving the light absorption in the active layer (Yamamoto et al., 2004). Light trapping in this method of categorizing the SCs according to p-i-n or n-i-p types, can be achieved in two ways: (1) by introducing a highly reflective layer at the back surface to reflect the incident light without absorption loss, and (2) by introducing a textured structure at the back surface of the thin-film Si SC (see Fig.7.) (Komatsu et al.,2002; Yamamoto et al.,2004).

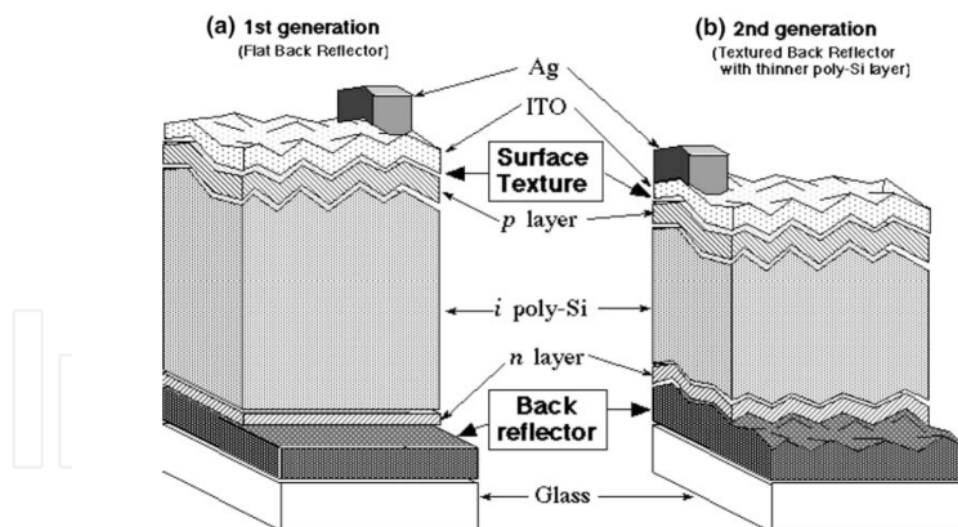


Fig. 7. Cross-sections through light-trapping μc -silicon SC devices: (a) first generation (flat back reflector); (b) second generation (textured back reflector, thinner polycrystalline silicon layer). Reprinted with permission from Solar Energy Vol. 77, Kenji Yamamoto et al., A high efficiency thin film silicon solar cell and module, pp. 939–949 © 2004, Elsevier.

Although the μc -silicon cells formed at low temperature have a potential for high efficiency, their efficiency in single-cell structures is currently only about 10%, which is much lower than that of bulk polycrystalline cells. In order to achieve high efficiencies, Yamamoto et al.(2004) investigated the use of two-and three-stacked (hybrid) structures in which multiple

cells with different light absorption characteristics are stacked together. This approach allows better characteristics to be obtained with existing materials and processes. The advantages of using a layered structure include the following: (1) it is possible to receive light by partitioning it over a wider spectral region, thereby using the light more effectively; (2) it is possible to obtain a higher open-circuit voltage; and (3) it is possible to suppress to some extent the rate of reduction in cell performances caused by photo-degradation phenomena that are observed when using a-silicon based materials. Therefore, they have engaged in thin film amorphous and microcrystalline (a-Si/ μ c-Si) stacked solar cell (Yamamoto et al., 2004).

The advantage of a high J_{sc} for our μ c-Si Sc as mentioned before was applied to the stacked cell with the combination of a-Si cell to gain stabilized efficiency as the study done by K.Yamamoto et al. (2001) since a-Si has a photo-degradation while a μ c-Si cell is stable. They have also prepared three stacked cell of a-Si:H/ μ c-Si/c-Si (triple), which will be less sensitive to degradation by using the thinner a-Si and they have investigated the stability of a-Si:H/ μ c-Si/ μ c-Si (triple) cell, too (Yamamoto et al., 2001, 2004). Some other three stacked Si-based SCs can be named such as a-Si/a-SiGe/a-SiGe(tandem) and a-Si/nc-Si/nc-Si (tandem) SCs. The last efficiency reported for a-Si/a-SiGe/a-SiGe(tandem) is about 10.4% and for a-Si/nc-Si/nc-Si (tandem) is approximately 12.5% (Green et al., 2011).

As a next generation of further high efficiency of SC, the new stacked thin film Si SC is proposed where the transparent inter-layer was inserted between a-Si and μ c-Si layer to enhance a partial reflection of light back into the a-Si top cell (see fig.8.). This structure is called as internal light trapping enabling the increase of current of top cell without increasing the thickness of top cell, which leads less photo-degradation of stacked cell (Yamamoto et al., 2004).

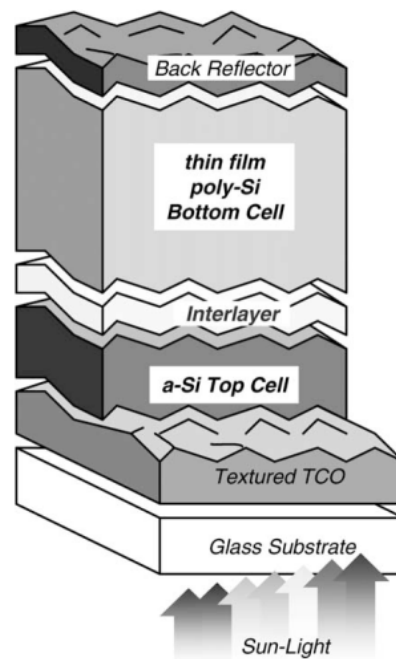


Fig. 8. Schematic view of a-Si/poly-Si (μ c-Si) stacked cells with an interlayer. Reprinted with permission from Solar Energy Vol. 77, Kenji Yamamoto et al., A high efficiency thin film silicon solar cell and module, pp. 939–949 © 2004, Elsevier.

By introduction of this interlayer, a partial reflection of light back into the a-Si top cell can be achieved. The reflection effect results from the difference in index of refraction between the interlayer and the surrounding silicon layers. If n is the refractive index and d is the thickness of inter-layer, the product of $\Delta n \times d$ determine the ability of partial reflection. Namely, the light trapping is occurred between the front and back electrode without inter-layer, while with inter-layer, it is also occurred between inter-layer and back electrode. This could reduce the absorption loss of TCO and a-Si:H (see Fig.9.) (Yamamoto et al., 2004).

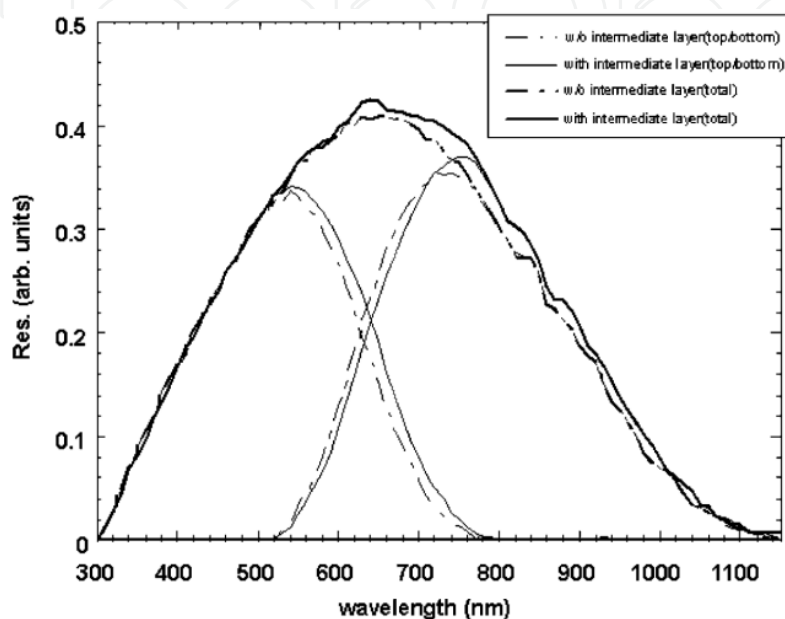


Fig. 9. Spectral-response of the cell with and without interlayer. Bold and normal line shows the spectral-response of the cell with and without inter-layer. Reprinted with permission from Solar Energy Vol. 77, Kenji Yamamoto et al., A high efficiency thin film silicon solar cell and module, pp. 939–949 © 2004, Elsevier.

Some of the advantages of thin film SCs are being characterized to low temperature coefficient, the design flexibility with a variety of voltage and cost potential. Therefore, the thin film Si SCs can be used for the PV systems on the roof of private houses as seen in Fig.10. (Yamamoto et al., 2004).

Another similar work was done by F. Meillaud et al.(2010). They investigated the high efficiency (amorphous/microcrystalline) "micromorph" tandem silicon SCs on glass and plastic substrates. High conversion efficiency for micromorph tandem SCs as mentioned before requires both a dedicated light management, to keep the absorber layers as thin as possible, and optimized growth conditions of the $\mu\text{c-silicon}(\mu\text{c-Si:H})$ material. Efficient light trapping is achieved in their work by use of textured front and back contacts as well as by implementing an intermediate reflecting layer (IRL) between the individual cells of the tandem. The latest developments of IRLs at IMT Neuchâtel are: SiO_x based for micromorphs on glass and ZnO based IRLs for micromorphs on flexible substrates successfully incorporated in micromorph tandem cells leading to high, matched, current above $13.8\text{mA}/\text{cm}^2$ for p-i-n tandems. In n-i-p configuration, asymmetric intermediate reflectors (AIRs) were employed to achieve currents of up to $12.5\text{mA}/\text{cm}^2$ (see fig.11.) (Meillaud et al., 2011).



Fig. 10. KW system at the top of the building Osaka (HYBRID modules). Note that modules are installed at low angle (5 degree off from horizontal).

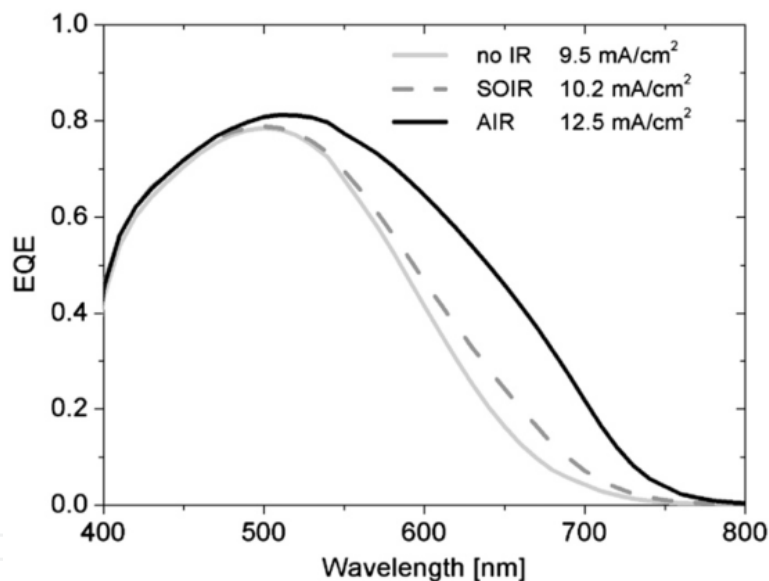


Fig. 11. External quantum efficiency of the top cell in an n-i-p/n-i-p micromorph on flexible substrate (i-layer thickness:200nm). Reprinted with permission from Solar Energy Vol. 95, Meillaud et al., Realization of high efficiency micromorph tandem silicon solar cells on glass and plastic substrates: Issues and potential, pp. 127-130 © 2010, Elsevier.

The last efficiency reported by Oerlikon Solar Lab, Neuchatel for a-Si/ μ c-Si (thin film cell) is about 11.9% (Green et al., 2011, as cited in Bailat et al., 2010). More precisely talk about tandem cells will be done in following sections.

3.3 Tandem cell

The tandem junction cell is a high-performance silicon solar cell, which is best suited for terrestrial solar power systems. The most distinctive design feature of this device is the use

of only back contacts to eliminate the metal shadowing effects because of lower conversion efficiency and steady-state bias requirement. Here we discuss tandem devices consisting of the a-si:H with other forms of silicon:

3.3.1 Tandem cell with multicrystalline Si

In the tandem cell configuration in 1983, Hamakawa reported the structure that a-Si: H/ μ c-Si heterojunction cell has been investigated as a bottom cell (Hamakawa et al. 1982). Its advantage is that it does not require high temperature processing for junction formation, and the top a-Si:H cell can be fabricated continuously. A heterojunction cell that is reported in 1994 by Matsuyama consisting of a-Si:H as p-type and μ c-Si as n-type, with a 10 nm thick μ c-Si film fabricated by solid phase crystallization yielded an efficiency of 8.5%. By using a p- μ c-Si: C/n- μ c-Si/n-pc-Si heterojunction bottom solar cell a conversion efficiency of 20.3% and good stability can be gained. At least in this type of devices the highest efficiency reported up to now is 20.4% (Green et al., 2011)..

3.3.2 Tandem cell with microcrystalline Si

Microcrystalline silicon (μ c-Si) has been studied extensively for three decades and has been used for doped layers in a-Si solar cells for over 15 years. Microcrystalline silicon is a complex material consisting of conglomerates of silicon nanocrystallites embedded into amorphous silicon. It can be more easily doped than a-Si:H; but, on the other hand, it is also more sensitive to contaminants than a-Si:H. The nucleation and growth of μ c-Si:H are determinant for device quality; a certain amount of amorphous material is needed for the passivation of the nanocrystallites and for the reduction of defect related absorption. During the growth of the layer, the formation of crystallites starts with a nucleation phase after an amorphous incubation phase. During continued layer deposition, clusters of crystallites grow (crystallization phase) until a saturated crystalline fraction is reached. These processes are very much dependent on the deposition conditions. In general, crystalline growth is enhanced by the presence of atomic hydrogen, which chemically interacts with the growing surface.

Much research effort has been put worldwide into the development of both fundamental knowledge and technological skills that are needed to improve thin film silicon multijunction solar cells. The research challenges are:

1. To enhance the network ordering of amorphous semiconductors (leading to protocrystalline networks), mainly for improving the stability;
2. To increase the deposition rate, in particular for microcrystalline silicon;
3. To develop thin doped layers, compatible with the new, fast deposition techniques;
4. To design light-trapping configurations, by utilizing textured surfaces and dielectric mirrors.

The first report on practical microcrystalline cells is given in 1992 by Faraji that reported a thin film silicon solar cell with a μ c-Si: H: O i-layer by using VHF PECVD and the first solar cell with a μ c-Si: H i-layer was fabricated with 4.6% power efficiency (Meier et al., 1994).

In 1996, Fischer reported that microcrystalline (pc) Si: H p-i-n junctions have an extended infrared response, and are entirely stable under photoexcitation with an efficiency of 7.7% (Fischer et al., 1996). The tandem arrangement of an a-Si: H solar cell with a μ c-Si: H solar cell also appears promising a remaining problem of the insufficient deposition rates for the

$\mu\text{-Si:H}$ layers. In 2002, Meier published a micromorph tandem cell with efficiency of 10.8% in which the bottom cell was deposited at a rate of $R_d = 0.5 \text{ nm/s}$ with the thickness of $2 \mu\text{m}$ (Meier et al., 2002). At least in this type of devices the highest efficiencies reported to date are 15.4% (tandem cell consisting of microcrystalline silicon cell and amorphous silicon cell) (Yan et al., 2010).

Further development and optimization of $\text{a-Si:H}/\mu\text{-Si:H}$ tandems will remain very important because it is expected that in the near future, its market share can be considerable. For example, in the European Roadmap for PV R&D, it is predicted that in 2020, the European market share for thin film silicon (most probably $\text{a-Si:H}/\mu\text{-Si:H}$ tandems) will be 30%. This shows the importance of thin film multibandgap cells as second-generation solar cells.

4. Conclusions and outlook

Although conventional SCs based on inorganic materials specially Si exhibit high efficiency, very expensive materials and energy intensive processing techniques are required. In comparison with the conventional scheme, the hybrid Si-based SC system has advantages such as; (1) Higher charging current and longer timescale, which make the hybrid system have improved performances and be able to full-charge a storage battery with larger capacity during a daytime so as to power the load for a longer time; (2) much more cost effective, which makes the cost for the hybrid PV system reduced by at least 15% (Wu et al., 2005). Therefore, hybrid SCs can be suitable alternative for conventional SCs. Among hybrid SCs which can be divided into two main groups including HJ hybrid SCs and dye-sensitized hybrid SCs, HJ hybrid SCs based on Si demonstrate the highest efficiency. Thus, the combination of $\text{a-Si}/\mu\text{-Si}$ has been investigated. These configurations of SCs can compensate the imperfection of each other. For example, a-Si has a photo-degradation while a $\mu\text{-Si}$ cell is stable so the combination is well stabilized. Furthermore, applying textured structures for front and back contacts and implementing an IRL between the individual cells of the tandem will be beneficial to enhancement of the efficiencies in these types of hybrid SCs. Due to recent studies; $\text{a-Si}/\mu\text{-Si}$ (thin film cell) has an efficiency of about 11.9%. Another study is done over three stacked cell of $\text{a-Si:H}/\mu\text{-Si}/\text{c-Si}$ (triple), which will be less sensitive to degradation by using the thinner a-Si . The last efficiency reported for $\text{a-Si}/\text{a-SiGe}/\text{a-SiGe}$ (tandem) is about 10.4% and for $\text{a-Si}/\text{nc-Si}/\text{nc-Si}$ (tandem) is approximately 12.5%.

Furthermore, Si based SC systems are being characterized to low temperature coefficient, the design flexibility with a variety of voltage and cost potential, so it can be utilized in large scale. In near future, it will be feasible to see roofs of many private houses constructed by thin film Si solar tiles. Although hybrid SCs are suitable replacements for conventional SCs, these kinds of SCs based on inorganic semiconductor nanoparticles are dependent on the synthesis routes and the reproducibility of such nanoparticle synthesis routes. The surfactant which prevents the particles from further growth is, on the other hand, an insulating layer which blocks the electrical transport between nanoparticles for hybrid SCs so such surfactants should be tailored considering the device requirements. Therefore, there is an increased demand for more studies in the field of hybrid SCs to find solutions to overcome these weak points.

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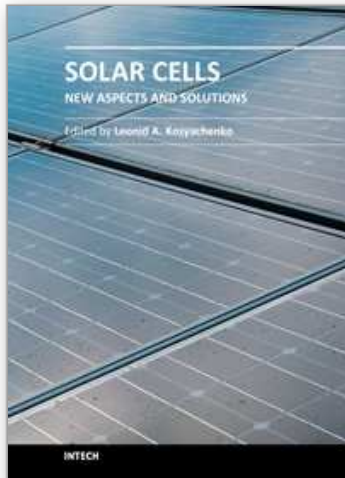
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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AlSb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

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