In the present day knowledge based society, Science transforms the Culture. This can be witnessed through the contemporary rationalized society that aroused with the advancement of science. Such revolutionised change leading to very fast modern-day walks of life can essentially be credited to the progression in light based technologies. However, in order to meet the continuously mounting demand for energy in this developed world, one has to look for the renewable energy resources and among all such resources most abundant one is the sunlight. In this context, an attempt has been made here to report a brief review on the development of solar cell, the simplest device that converts sunlight to electricity. Further, this article also presents the contributions of CSIR-CGCRI in this field.

Introduction

Apart from being one of the indispensible component of nature for existence of life on earth, the light, has widely been explored by mankind to meet with his basic needs in every stages of development. Light based technologies began to develop with the invention of incandescent bulb to meet with the requirement of vision during night. This then went through several stages of modification over centuries to ultimately evolve as the energy efficient compact fluorescent lamps (CFLs), high intensity discharge lamps and solid state lighting devices like Light Emitting Diodes (LEDs) and Organic LEDs (OLED) that serve to lit away the darkness in the present era. In addition to lightning applications, the discovery of lasers in 1960s brought about a revolution in the world of technology due to its immense applications in various sectors which include medical science, manufacturing industries, retail market, geology, atmospheric physics and optical communications, to name a few. The development of optical fibres enabled faster and easier communications leading to instantaneous data transfer within a fraction of second through internet connections across the world, thereby connecting people irrespective of their geographical locations. Thus in the present era, light based technologies have become vital for almost all human activities. And it is due to the immense societal benefits of these technologies that Nobel prizes have been awarded several times to encourage researchers in this sector.

However, as we all know, to every pro there is a con. In order to meet with the energy needs of these developing technologies, today mankind is exposed to one of the greatest threat of 21st century – the energy crisis. But here also, the ray of hope to overcome such crisis is the sunlight, which on the other hand is the most abundant renewable energy source, and the most common device for the purpose is – solar cell. When sunlight of suitable energy is incident on a solar cell which is basically a p-n junction, due to photovoltaic effect an electron–hole pair is produced. The presence of electric field across the junction of this device

---

In the present day knowledge based society, Science transforms the Culture. This can be witnessed through the contemporary rationalized society that aroused with the advancement of science. Such revolutionised change leading to very fast modern-day walks of life can essentially be credited to the progression in light based technologies. However, in order to meet the continuously mounting demand for energy in this developed world, one has to look for the renewable energy resources and among all such resources most abundant one is the sunlight. In this context, an attempt has been made here to report a brief review on the development of solar cell, the simplest device that converts sunlight to electricity. Further, this article also presents the contributions of CSIR-CGCRI in this field.

Introduction

Apart from being one of the indispensible component of nature for existence of life on earth, the light, has widely been explored by mankind to meet with his basic needs in every stages of development. Light based technologies began to develop with the invention of incandescent bulb to meet with the requirement of vision during night. This then went through several stages of modification over centuries to ultimately evolve as the energy efficient compact fluorescent lamps (CFLs), high intensity discharge lamps and solid state lighting devices like Light Emitting Diodes (LEDs) and Organic LEDs (OLED) that serve to lit away the darkness in the present era. In addition to lightning applications, the discovery of lasers in 1960s brought about a revolution in the world of technology due to its immense applications in various sectors which include medical science, manufacturing industries, retail market, geology, atmospheric physics and optical communications, to name a few. The development of optical fibres enabled faster and easier communications leading to instantaneous data transfer within a fraction of second through internet connections across the world, thereby connecting people irrespective of their geographical locations. Thus in the present era, light based technologies have become vital for almost all human activities. And it is due to the immense societal benefits of these technologies that Nobel prizes have been awarded several times to encourage researchers in this sector.

However, as we all know, to every pro there is a con. In order to meet with the energy needs of these developing technologies, today mankind is exposed to one of the greatest threat of 21st century – the energy crisis. But here also, the ray of hope to overcome such crisis is the sunlight, which on the other hand is the most abundant renewable energy source, and the most common device for the purpose is – solar cell. When sunlight of suitable energy is incident on a solar cell which is basically a p-n junction, due to photovoltaic effect an electron–hole pair is produced. The presence of electric field across the junction of this device
causes the electron-hole pair to drift apart to produce electricity provided recombination process is avoided. Fig.1 pictorially represents the working principle of a typical p-n junction solar cell. Efforts to convert sunlight to electricity using photovoltaic cells dates back to centuries. But the use of sunlight to generate fire, lighting for religious purposes, burning wooden ships of enemies in the war field, etc. was seen from as early as the 7th century B.C [1]. However, the photovoltaic effect was first experimentally observed in 1839 by a French scientist Edmond Becquerel who demonstrated an increment in electricity upon exposure to sunlight when two metal electrodes were immersed in an electrically conducting solution. Later in 1876, Adams and Day discovered photocurrent generation from selenium (Se) under exposure to sunlight. It was in 1905, Albert Einstein reported photoelectric effect along with his famous theory of relativity and subsequently he was bestowed with Nobel Prize in the year 1921. Photovoltaic effect in CdS was discovered in 1932 by Audobert and Stora. After two decades, in the year 1954 revolutionary progress in photovoltaic cell took place at Bell labs, USA with the development of Si-PV cell capable of converting solar energy into electricity suitable for running electrical equipment for daily usage. Production of silicon solar cell with 4% efficiency.

Table 1 lists historical advancements of photovoltaic technology in chronological order.  

<table>
<thead>
<tr>
<th>Year</th>
<th>Achievements/Milestones</th>
</tr>
</thead>
<tbody>
<tr>
<td>1839</td>
<td>Discovery of photovoltaic effect by Edmond Becquerel in electrolytic cell made up of two metal electrodes upon exposure of sunlight</td>
</tr>
<tr>
<td>1873</td>
<td>Demonstration of photoconductivity of selenium by Wiloughby Smith</td>
</tr>
<tr>
<td>1876</td>
<td>William Grylls Adams and Richard Evans Day discovered that illuminating a junction between selenium and platinum generates a photovoltaic effect.</td>
</tr>
<tr>
<td>1883</td>
<td>Development of first solar cells made from selenium (Se) wafers</td>
</tr>
<tr>
<td>1905</td>
<td>Publication of a legendary paper on “photoelectric effect” by Albert Einstein (Nobel Prize in the year 1921).</td>
</tr>
<tr>
<td>1932</td>
<td>Demonstration of photovoltaic effect in CdS by Audobert and Stora</td>
</tr>
<tr>
<td>1954</td>
<td>Realization of photovoltaic technology by Bell Telephone Laboratories with the development of Si-PV cell capable of converting solar energy into electricity suitable for running electrical equipment for daily usage. Production of silicon solar cell with 4% efficiency.</td>
</tr>
<tr>
<td>1958</td>
<td>Ted Mandelkorn of U.S. Signal Corps Laboratories produces n-on-p silicon PV cell by diffusing P-type layer on n-type layer.</td>
</tr>
<tr>
<td>1958</td>
<td>First PV-powered satellite, Vanguard I, was launched by United States Naval Research Laboratory.</td>
</tr>
<tr>
<td>1963</td>
<td>Production of practically viable silicon photovoltaic module by Sharp Corporation</td>
</tr>
<tr>
<td>1963</td>
<td>Installation of 242 watt PV array on a lighthouse by Japan which was world’s largest array at that time.</td>
</tr>
<tr>
<td>1966</td>
<td>Launching of first Orbiting Astronomical Observatory of 1 kilowatt PV array by NASA</td>
</tr>
<tr>
<td>1976</td>
<td>Development of first amorphous silicon PV cell by D. Carlson and C Wronski</td>
</tr>
<tr>
<td>1981</td>
<td>First solar-powered aircraft, the “Solar Challenger” built by Paul MacCready, flew from France to England across the English Channel.</td>
</tr>
<tr>
<td>1982</td>
<td>First solar powered car “the Quiet Achiever” developed by Hans Tholstrup</td>
</tr>
<tr>
<td>1985</td>
<td>Record breaking 20% efficiency for silicon solar cells under one sun conditions by the University of South Wales</td>
</tr>
<tr>
<td>1986</td>
<td>The first commercial thin film power module released by ARCO Solar</td>
</tr>
<tr>
<td>1994</td>
<td>Development of gallium indium phosphate and gallium arsenide solar cells which exceeded 30 % conversion efficiency.</td>
</tr>
<tr>
<td>2007</td>
<td>Research group at university of Delaware led by Allen Barnett achieved a record breaking 42.8% efficiency under standard terrestrial conditions</td>
</tr>
</tbody>
</table>
The developmental stages of solar cell can be classified into three generations. The first generation mainly includes the solar cells prepared from thick wafers of single crystalline semiconductors, mainly silicon (Si) and germanium (Ge). Especially, silicon wafers are most commonly used and are more reliable and efficient due to their chemical structure. Hence till now most widely used solar cells are based on silicon only which exhibit an efficiency of 20-24%. However growing large crystals of pure silicon is difficult as well as expensive. Therefore the production cost of this type of cells is exorbitantly high and ultimately resulting in a very high cost per unit of energy. Another issue with monocrystalline silicon cells is that their efficiency degrades with increase in cell temperature by about 25°C. To tackle these shortcomings, monocrystalline silicon wafers have been replaced with multi-crystalline silicon for the active material of solar cells. This resulted in a reduction of manufacturing cost but at the expense of reduction in efficiency to about 13-14%. With an aim to bring down the production cost of solar cell through reducing the amount of active material, second generation photovoltaics have evolved in the form of thin films of amorphous silicon (a-Si), CuIn(Ga)Se₂ (CIS), CdTe or CdS or polycrystalline Si deposited on low cost substrates. These cells utilise only 1-10 µm thick of active material and hence reducing the material cost substantially. However, in terms of energy conversion efficiency, it is still lower than that of c-Si. For CdTe cells, the efficiency is nearly 16.5% while for CIS cell it is about 12.5%. The third generation solar cell technology mainly targets at enhancing the conversion efficiency of solar cells by utilising maximum extent of incident solar energy to produce electron-hole pairs. This can be brought about by frequency conversion of incident photons which minimises two major loss processes in a solar cell, one being the thermalisation loss resulting from the excess energy of photons over the band gap energy and the other being the sub-band gap loss resulting due to non absorption of photons having lower energy than the band gap energy of the semiconducting material. This attempt witnessed the emergence of several new types of solar cells like organic solar cells, dye sensitized solar cells, hybrid solar cells as well as exploitation of band-gap engineering techniques by the utilisation of multi-junction systems like tandem cells. Use of different types of fluorophores, quantum dots, quantum wells in different host materials occupies the major areas of investigation in this generation of solar cells having high potential to provide the much required high performance, low-cost photovoltaic.

The proceeding sections address the routes that followed to improve efficiency of third generation photovoltaics and also highlight a part of such work that is presently being carried out at CSIR-CGCRI under the TAPSUN programme.

**Organic Solar Cell**

In this type of solar cells, low cost semiconducting polymers have been widely explored since the last three decades. The low weight, semi-transparent polymer material attracted the researchers mainly for its chemical flexibility towards modification which facilitated large scale production at a much cheaper cost. The 1st generation organic solar cells consisted of a single layer of polymer material sandwiched between two metal electrodes of different function. The polymers were mainly hole (h) conductors (p-type) with a band gap of nearly 2 eV. The difference in the work function of two metals brings about an asymmetry of e and h injection into the molecular \( \pi^* \) and \( \pi \) orbital along with the formation of schottky barrier between the p-type organic material and the metal with the lower work function. However, the power conversion efficiency of these devices was much poor (in the range 10⁻³ to 10⁻² %) due to very low charge carrier mobility and small diffusion lengths of the primary excitons. This can be improved by increasing the charge carrier concentration which can be achieved by doping with some n-type organic materials, like perylene and its derivatives through different wet processing techniques or by co evaporation of both the matrix and dopant. The bilayer heterojunction structure of the device containing a p-type and an n-type organic material stacked between two electrodes matching the donor HOMO and the acceptor LUMO, exhibited effective transfer of charge carriers between the two layers under illumination. Reduced rate of recombination due to repulsive interaction between the interface dipoles and free charge resulted in greater charge extraction and hence enhancement in efficiency. Power conversion efficiency of about 3.6% is achieved under AM 1.5 illumination using a bilayer device of copper phthalocyanine and \( C_{60} \). The development of bulk heterojunction, however has significantly improved the efficiency of the device in the last ten years. Intimate blending of conjugated polymers with fullerene (and its derivatives) throughout the bulk showed enhanced photoconductivity due to photo induced charge transfer from the excited state of the polymer to the much more electronegative \( C_{60} \). However it requires percolated pathways for the electrons and holes to reach the contacts and thus this device structures are much sensitive to the nanoscale morphology in the blend. Till now an efficiency of nearly 9% has been achieved in this device for single junction and about 10% in tandem cells. Continuous
efforts are being made through different routes to bring about an enhancement of efficiency up to 15% for large scale applications.

**Dye Sensitized Solar Cells**

Dye Sensitized Solar Cell (DSSC) can be assumed as a mesoscopic heterojunction solar cell or a mesoscopic electron-injection solar cell having significant advantages over other PV technologies in terms of the shorter energy payback time, performance under diffuse light conditions, cost effectiveness and novel architectures.

**Advantages of DSSCs**

- Low production cost and particularly interesting much lower investment costs compared with conventional PV technologies.
- Feedstock availability to reach terawatt scale.
- Enhanced performance under real outdoor conditions mainly at diffuse light and higher temperature.
- Bifacial cells capture light from all angles.
- Cell voltage does not decrease so much under low light intensity appropriate for use indoors and in poor weather conditions.
- Performance is stable over a long life-time.
- Materials used in DSSC are relatively non toxic.
- Short energy payback time (Â 1 year).
- Design opportunities such as transparency and multi- colour options.
- Flexibility and lightweight.

**Disadvantages of DSSCs**

- Difficulties with sealing the cell causing leakage and evaporation of the electrolyte.
- Lower efficiencies compared with conventional solar cells.
- The corrosive nature of the iodide/triiodide redox mediator.
- Difficulties in scaling up the production to large modules.

A DSSC is in essence a photochemical cell which contains two electrodes and an electrolyte and generates electrical current by redox reactions. The working electrode or photoanode of the cell which consists of nanostructured, porous semiconducting oxide layer, deposited on a transparent conducting oxide (TCO) glass or plastic substrate. The glass coated with fluorine-doped tin oxide (FTO) or indium-doped tin oxide (ITO) has commonly been used for this purpose. A monolayer of the light-sensitive charge transfer dye has been further attached to the semiconducting oxide film. Similarly the electrically conducting glass substrate coated with a thin layer of platinum catalyst acts as the counter electrode. This has been placed parallel with a face to face configuration to the working electrode. The interspacing has been filled with the liquid or solid electrolyte that plays a role of conducting media. The model structure of a complete DSSCs device including the principal components namely the TCO, photoanode semiconductor, light sensitizing dye, electrolyte, Pt electrode along with the basic electron transport processes among them have been illustrated in Fig. 2.

**Components of DSSC Device**

**Photosensitzers** : The most widely used photosensitzers are Ru (II) polypyridyl dyes where the light absorption originates due to MLCT process with molar extinction coefficient ($\varepsilon$) of 10,000-20,000 M$^{-1}$cm$^{-1}$. Functionalizing the ancillary polypyridyl ligand by the substituents including alkyl, aryl, alkoxy, phenyl, heterocycle etc., or by replacing the chelating anions many
popular dyes such as N719, N3, N749 (black dye), Z907, K51, K60, N886, C103, JK56 etc. have been synthesized. A maximum of 11.7% efficiency have been reported to be achieved with these Ru(II) dye based DSSCs till 2010\textsuperscript{12-15}. The structure of three extensively used dyes N3, N719 and black dye are illustrated in Fig. 3.

Besides the Cu(II) and Zn(II) porphyrins and Zn(II) phthalocyanines dyes, metal free coumarin dyes, indoline dyes, triarylamine dyes, carbazole dyes, squarines, perylene dyes are quite mentionable. The cadmium chalcogenite QDs including CdS, CdSe, CdTe and their different alloys, the lead-chalcogenite QDs such as PbS, PbSe and the antimony sulphide QDs have also been frequently studied. The organolead halide or perovskite CH\textsubscript{3}NH\textsubscript{3}PbX\textsubscript{3} (X= Cl, Br, I) photosensitizers have been spotlighted most in recent years owing to their outstanding light harvesting properties with \( E_g \) of \( \sim 1.5 \) eV, optical absorption edge of \( \sim 820 \) nm and \( \varepsilon \) of \( \sim 150,000 \) M\textsuperscript{-1}cm\textsuperscript{-1}\textsuperscript{16}. Based on the promising improvement of the ongoing researches the conversion efficiency of 20% is being expected in near future from the perovskite solar cell device\textsuperscript{15-18}.

**Electrolytes**

The most extensively used electrolyte is the iodide- triiodide (I\textsuperscript{3-}/I\textsuperscript{-}) electrolyte exhibiting superior performance constantly and an efficiency of 11% have been achieved from the I\textsuperscript{3-}/I\textsuperscript{-} electrolyte based DSSCs yet\textsuperscript{19,20}.

**Counter Electrodes**

Platinized conducting glass is mostly used. The carbon materials such as porous carbon, single wall carbon nanotubes, graphene, conductive polymers such as PANI, PEDOT, PPy and the sulfide inorganic compounds such as CoS\textsubscript{2}, CuInS\textsubscript{2}, CuZnSnS\textsubscript{4} are also being explored recent times\textsuperscript{10,15}.

**Photoanodes**

The R & D on DSSC promoted further based on the

### Table 2. Properties of commonly used photoanodes in DSSC.

<table>
<thead>
<tr>
<th>Material</th>
<th>Isoelectric point</th>
<th>Band gap(eV)</th>
<th>ECB = 0.0 V Vs NHE</th>
<th>Electron affinity (eV)</th>
<th>Highest reported efficiency (( \eta ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase TiO\textsubscript{2}</td>
<td>5-6</td>
<td>3.3</td>
<td>0.5 V</td>
<td>3.9</td>
<td>14.1%</td>
</tr>
<tr>
<td>ZnO</td>
<td>4-9</td>
<td>3.3</td>
<td>Close to TiO\textsubscript{2} higher than SnO\textsubscript{2}</td>
<td>4.5</td>
<td>6.5%</td>
</tr>
<tr>
<td>SnO\textsubscript{2}</td>
<td>2.5-4.0</td>
<td>3.5</td>
<td>Lower than TiO\textsubscript{2}</td>
<td>4.8</td>
<td>6.02%</td>
</tr>
<tr>
<td>In\textsubscript{2}O\textsubscript{3}</td>
<td>7.1</td>
<td>3.6</td>
<td>Lower than TiO\textsubscript{2}</td>
<td>4.45</td>
<td>2.37%</td>
</tr>
<tr>
<td>Nb\textsubscript{2}O\textsubscript{5}</td>
<td>2.6-4.5</td>
<td>3.4</td>
<td>0.2-0.3 V</td>
<td>2.34</td>
<td>4.10%</td>
</tr>
</tbody>
</table>
pioneer work of Michael Gratzel group in 1991 based on mesoporous TiO₂ nanoparticles as photoanode. Incessant research establishes TiO₂ as the ideal photoanode material exhibiting the highest efficiency of over 12% so far. The basic properties and performances of some commonly used materials as photoanode are exhibited in Table 2.

**Performance Measurement**

The overall solar-to-electrical energy conversion efficiency, \( \eta \), for a solar cell is given by the photocurrent density measured at short-circuit (\( J_{sc} \)), the open-circuit photo voltage (\( V_{oc} \)), the fill factor of the cell (\( FF \)), and the intensity of light (\( P_{in} \)).

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}
\]

Another fundamental measurement of a solar cell is the external quantum efficiency, which in the DSC community is normally called the incident photon to current conversion efficiency (IPCE). The IPCE value corresponds to the photocurrent density produced in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the cell.

\[
IPCE = \frac{J_{sc}(\lambda)}{\epsilon \phi(\lambda)}
\]

As far as the objective of our work was concerned, we have given emphasis exclusively in fabricating various photoanodes by economically viable and effective techniques and studying on their performance in N719 dye based DSSC. We have also focussed our attention on identifying alternative photoanodes to replace the existing TiO₂ and SnO₂ based oxides. In this respect, we have synthesized different microstructures of ZnO including 1D-rod, 3D-flower and particle through solution processed sonochemical method. The nature of structural defects in ZnO rods, nanoparticles and flowers have been investigated by several spectroscopic studies such as photoluminescence, Raman and EPR. An overall conversion efficiency of 1.38% was achieved for the DSSCs fabricated with ZnO rods, whereas the particles and flowers exhibited lower efficiencies of 1.004% and 0.63%, respectively. The higher efficiency exhibited by the rods has been attributed to the minimum oxygen vacancy defects along with favourable one dimensional structure for providing direct pathway of electron conduction. Correlating all the experimental evidences, it has been confirmed that the nature and concentration of structural defects are quite decisive than shape in monitoring the overall performance of ZnO based DSSCs. The effect of post annealing temperatures on the native defects of ZnO rods have been studied in detail to understand and its ambience on DSSC performance. The as prepared rods and that annealed at 600 °C exhibited the conversion efficiency of 1.38% and 0.63%, respectively. The J-V characteristics of the ZnO rods are exhibited in Fig. 4.

![Fig. 4. J-V characteristics of (a) as prepared ZnO rods and that annealed at (b) 300 ° and (c) 600 °C, respectively.](image)

Attempts were also made to synthesize alternative photoanodes such as spinel Zn₂SnO₄ and BaSnO₃. Such systems are expected to increase the stability and photo conversion efficiency of the device further. Efforts also being made to utilize the synthesized porous photoanodes as scaffold layer in the newly emerged perovskite systems.

**Multi Junction Solar Cell**

In general, more the extraction of incident solar energy by active material in a solar cell higher the electric power produced. However, any active material will have definite band gap energy that defines its extraction capacity. Hence in order to increase absorbance of solar energy over a wider wavelength range, different semiconductor materials with different p–n junctions could be utilized in multi-junction solar cell which brings in a significant enhancement in the conversion efficiency. While crystalline silicon solar cell efficiency is practically limited maximum up to 25.6 %, the multi junction cell with GaInP/GaInAs/Ge concentrator cell, demonstrated a record 46 % efficiency. Most interestingly, multi-junction solar cells based on III–V semiconductors, II–VI compounds and polymers exhibit highest efficiencies over any other present day photovoltaic devices due to the considerable reduction of thermalization and transmission losses unlike other PV materials owing to the presence of multiple p-n junctions with various band gap energies. Though it is possible to achieve very high in these tandem cells, implementation of various costly semiconducting oxides causes a significant enhancement in the manufacturing cost. Thus very high price-to-performance ratio of these cells has limited their market in
PV industry. However, the high power to weight ratio has opened up unique application fields towards aerospace and terrestrial applications. The futuristic approaches in tandem cells include integrating III-V compound semiconductor materials on Si substrate addressing the critical issues with the material growth, quality of grown crystals as well as reproducibility.

**Silicon Solar Cell**

Despite the advances in different types of solar cells, till date the solar cell market is dominated by silicon photovoltaics. Although silicon solar cells provide the highest energy conversion efficiency amongst all, still it falls much short to be compared to that of commercial grid electricity. Two main reasons for this are, (1) greater cost per unit of electricity and (2) its low conversion efficiency due to intrinsic or extrinsic losses in addition to restricted utilisation of incident solar energy. Three factors that contribute to the fabrication cost for solar modules are, cost of the silicon substrate (50%), cell processing (20%) and module processing (30%)\(^2\). Thus, reducing the cost of silicon substrate remains one of the most important issues in the PV industry which led to the emergence of low cost multi-crystalline silicon wafers or thin films. As it was discussed earlier, monocrystalline Si PV are the most popular with its maximum efficiency of 24.7% followed by 20% for multi-crystalline Si PV and 14% for thin film Si PV. With continued efforts in lowering the cost per unit solar power all over the globe, usage of solar energy is increasing exponentially for both industrial and domestic purposes over two decades. The global cumulative photovoltaic power is reported to be from just around 100 MW in 1992 to around 178,391 MW in 2014 with projected target of 233,000 MW by 2015\(^3\). Worldwide in many countries, governments even have taken initiatives in providing economic incentives for investments in solar PV. European countries were the pioneers along with Japan in this solar PV production. However, United States was topping the list for installed photovoltaics for many years up to 1996 after which Japan ousted US and remained leader until 2005. Later, Germany took the world’s lead in producing solar power and recently approaching 40,000 MW mark. Interestingly, cost of solar also declined significantly due to improvements in technology and last year, 2014 has seen a steep increase in production of solar cells and modules together with more deployment of photovoltaics in Asia particularly in China and India. China is expected to continue its rapid growth and enhance its PV capacity to 70,000 megawatts by 2017\(^3\). In national scenario, the installed grid connected solar power capacity is 4,229.36 MW and India expects to install an additional 10,000 MW by 2017, and a total of 100,000 MW by 2022\(^3\). At present, Rajasthan with its installed power of 1170 MW tops the state-wise list followed by Gujarat (1000 MW), Madhya Pradesh (603 MW) and other states are ramping up their solar capacity.

However in this attempt another major bottleneck is the efficiency of a Si photovoltaic cell, which is limited due to three loss mechanisms:

i) Recombination loss of the photo generated minority carriers in the silicon bulk and at the surface.

Attempts to minimise the thickness of cell material tends to increase the chances of recombination of the photo generated carriers. But the implementation of a passivation layer at the front and rear surfaces can enhance the effective lifetime of these minority carriers. Normally, this passivation is achieved either by reducing the surface defects (surface passivation) or by using a technique of band bending at Si surface creating electric field (field effect passivation). Deposition or growth of dielectric films like amorphous silicon nitride (SiN\(_x\)) containing high positive charge density or alumina (Al\(_2\)O\(_3\)) with high negative fixed charge density can provide not only chemical passivation but also field effect passivation. Field effect passivation can also be obtained by introducing high-low junction with the same type of impurities (p\(^+-\)p or n\(^+-\)n) or p-n junction with opposite doped types. The p\(^+-\)p combination is commonly employed at the rear side of p-type silicon solar cells thus creating ‘Back surface Field’ (BSF). However, the conventional Al (BSF) yields a maximum V\(_{OC}\) of about 630 mV, corresponding to rear surface recombination velocity (S\(_{eff}\)) ranging from 200-600 cm/sec, which is insufficient for high efficiency Si solar cells. Recent investigations revealed thermal and plasma ALD deposited Al\(_2\)O\(_3\) films can provide a very high passivation effect with very low surface recombination velocities S\(_{eff}\)\(\leq\) 5 cm/s on p-type and n-type Si(typically 1-4\(\Omega\)cm) after annealing at moderate temperatures\(^3\). The ALD synthesized Al\(_2\)O\(_3\) films can limit the emitter saturation current density to -10 and -30 fA/cm\(^2\) thereby producing a V\(_{OC}\) up to 700 mV which indicates that the level of passivation achieved by Al\(_2\)O\(_3\) is higher than that obtained by thermal SiO\(_2\), a-Si:H and SiN\(_x\)\(^3\).
ii) Heating loss arising due to series resistance in the gridlines and bus bars and also at the interface between the contact and silicon.

A metallic top contact is necessary to collect the photo-generated carriers. But the front metal grid of a conventional solar cell consisting of horizontal fingers and vertical bus bars are associated with three major loss mechanisms: one being the resistive loss due to lateral conduction of majority carriers in the emitter to the metal fingers, second being the resistive loss in the metal fingers and busbars, and third is the loss of light due to shading effect of metal fingers. To minimize these losses, grid spacing and designing should be optimized. Since the power loss from the emitter depends on the cube of the lone spacing, short distance between the fingers and multiple bus bars is desirable\textsuperscript{34}. Fingers of low resistivity material having higher height to width aspect ratio, is observed to be highly beneficial to reduce the power losses in a solar cell. According to HB Serreze, a tapered busbar has lower losses than a busbar of constant width. Smaller the unit cell, finger width and finger spacing, lower the losses. Also, optimum width of busbar ($W_b$) occurs when resistive loss in busbar equals its shadowing loss\textsuperscript{35}.

iii) Photon losses due to surface reflection

The reflection losses occurring at the top surface of a solar cell can be arrested by application of single or double layer anti reflection coatings deposited through chemical vapour deposition, spray, spin-on or screen printing techniques. Plasma enhanced chemical vapour deposition (PECVD) enables deposition of these layers of uniform and controlled thickness. TiO$_2$, Si$_3$N$_4$, SiO$_2$, Al$_2$O$_3$, Ta$_2$O$_5$ are most commonly used as ARC material. Recently a-SiNx:H and a-Si:C:H have proved to be a promising material for ARC and has been observed to enhance the efficiency of mc-Si solar cells from 9.84% to 14.25% while in c-Si, a double layer SiO$_2$-TiO$_2$ ARC has resulted in 37% improvement in efficiency\textsuperscript{36,37}. The reflection loss can also be minimised by texturing the front surface with pyramid or inverted pyramid like structures through different chemical etching and vapour deposition techniques.

Apart from above three conventional losses in a solar cell, another factor which limits the conversion efficiency of solar cell is the incomplete utilisation of the incident solar energy that mainly arises due to the fixed bandgap of Si. Photons having energy less than the band gap of Si passes through the cell unabsorbed while photons with energy greater than the bandgap causes heating of the cell resulting in thermalisation losses. This can be overcome by modulating the incident spectrum in such a way that photons having energy on either side of the band gap of silicon is converted to fall within the frequency range which Si-PV can absorb. Such spectral conversion can be attained by three possible phenomena, namely Upconversion, Downconversion and Downshifting of photons. The following sections present a detailed study of the role of UC, DC and DS mechanisms on the efficiency of solar cells.

**Spectral Conversion**

Up/Down conversion and down shifting: Upconversion is a non-linear anti-stokes luminescence process where two or more low energy photons are required to generate one high energy photon. This phenomenon was first discovered by Auzel in the 1960s\textsuperscript{38}. The phenomenon was usually observed in rare earth based materials. Up-converting materials have applications in diverging areas such as display, solid-state lasers, biomarkers, temperature sensors etc. The application of upconverting materials for Si based solar cells to enhance its efficiency has been proposed by Trupke et al.\textsuperscript{39}, and theoretically demonstrated that the upper EQE limit of UC- silicon solar cell systems can be enhanced to 47.6 % for single junction cells. In this concept, with an up-converting layer integrated with solar cell, sub band gap light could be converted to high energy photons that can be absorbed by active material. Fig. 5 presents implementation of an upconverting later on
the rear side of a bifacial solar cell along with possible energy level transitions. The same figure also represents the concepts of frequency down conversion and down shifting with respective layers placed on front side of the solar cell. The first up-converter on a silicon solar cell has been demonstrated by Shalav et al., in the year 2005 which shows enhancement in the photo-current much less than 1%.

So far, upconverting materials used for Si solar cells were based on phosphors which are not transparent and only applicable on the rear side of the bifacial Si-PV. In this regard CSIR-CGCRI has developed some of rare earth doped transparent glass systems which show efficient upconversion properties under IR (1550 nm) light excitation. The advantage of these materials is that they have minimum scattering losses compare to phosphors and are transparent in UV-Vis-NIR region which can be potentially utilised on either side of the Si-PVs for its efficiency enhancement.

Down-conversion is a process where one high energy photon will cut into two or more low energy photons. Initially, the Down converting mechanism has been explored decades back while working with phosphors which convert Vacuum Ultra Violet light to visible light for lighting applications. Trupke et al., showed that, using a silicon solar cell with an ideal DC, a conversion efficiency of 38.6% could be achieved under unconcentrated sunlight which will potentially reduces the thermalization losses encountered in Si-PVs. Fig. 3 describes the proposed configuration of single junction, bifacial solar cell integrated with down converting, down shifting and upconverting glass layers. So far there is no practical demonstration of efficiency enhancement using DC material on Si-PVs. CSIR-CGCRI has developed some of the materials which show DC phenomenon. Rare earths such as Pr/Yb co-doped low phonon fluoro-tellurite glass systems were developed which shows efficient downconversion emission from Pr ions to Yb ions (theoretical DC efficiency ~180%) near the bandgap of Silicon under UV-Vis excitation where the response of Si-PVs are very poor. Also, Eu/Eu-Yb co-doped silicate based oxyfluoride glass and glass-ceramics samples have been developed and frequency down-conversion has been demonstrated from Yb ions near 1 µm under broad UV excitation which is attributed to the cooperative energy transfer from Eu/ Eu defect centres to Yb ions. Several other rare earth ion pairs in glass or glass ceramic hosts were under examination for potential application of down converting materials to improve the efficiency of Si-PVs.

Frequency downshifting involves the conversion of one high energy photon, which is inefficiently absorbed by the active material of the solar cell to one low energy photon that it can absorb. This phenomenon obeys Stokes Law and the change in wavelength is known as the Stokes shift. Ideal luminescent materials used for downshifting should exhibit the following properties: unity quantum efficiency; a wide absorption band in the region where the radiation is required to be absorbed; high absorption coefficient; a narrow emission band, corresponding to a region where the cell quantum efficiency is high; and good separation between its absorption and emission bands to minimize losses due to recombination. Not only in solar cells, downshifting of luminescence has been widely explored in different systems for several applications like lasers, production of white LEDs etc. Hoevel et al., first applied the concept of luminescent downshifting on top of PV cells and studied its effect on spectral response of solar cell which showed that this system has the potential to enhance the efficiency of the device. Thereafter it has been studied widely on different types of solar cells. For LDS encapsulated e-Si solar cells, an enhancement of about 40% has been reported by Richards et al. Since transition metals exhibits broad absorption band, they are

![Figure 6](image_url)

Fig. 6. Solar spectrum and its modulation by application of UC, DC or DS layer on single junction, bifacial solar cell.
used as sensitizers to rare earth ions and thus helps to bring about effective downshifting of photons as observed in Cr\textsuperscript{3+}-Yb\textsuperscript{3+} and Cr\textsuperscript{3+}-Nd\textsuperscript{3+} pairs\textsuperscript{44,45}. Such downshifting of photons from UV to visible has been effectively realised in Ce\textsuperscript{3+}-Eu\textsuperscript{3+} and Ce\textsuperscript{3+}-Tb\textsuperscript{3+} doped metaphosphate glass prepared in CSIR-CGCRI. A part of the UV energy absorbed by Ce\textsuperscript{3+} is efficiently transferred to Tb\textsuperscript{3+} and Eu\textsuperscript{3+} which exhibits strong luminescence in the green and red region where EQE of c-Si solar cell is high. Also the quantum yield of the dopant ions is much higher than that reported in other host matrices. Further doping the Ce\textsuperscript{3+}-Tb\textsuperscript{3+} metaphosphate glasses with Mn\textsuperscript{2+} resulted in a broad luminescence covering almost the entire visible portion of the spectrum ranging from 320-750 nm. This proves to be highly promising since the EQE of c-Si solar cell is high in the visible region. These glasses have been tested for their performance on solar cell under solar simulator equipped with Xenon arc lamp as illuminator fitted with AM 1.5 filter to get 1 sun test condition. This is the conventional procedure to test solar cell performance in the laboratory condition as illustrated in Fig. 7 along with test result and the picture of the glass sample exhibiting luminescence under light exposure in the inset. Currently efforts are being carried out to integrate luminescent glass layers onto Si-solar cells for improved conversion efficiency. As a consequence of exertions towards lowering production costs of photovoltaics along with improvements in their conversion efficiencies, solar power is becoming affordable and Solar PV is progressively contending with conventional energy sources in many countries. India also going towards this by undertaking many strategies. So, we have entered in an era where Sun (solar power) would be illuminating dark nights.

References


