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A Review on Progresses and Developments in Solar cell Technologies

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ABSTRACT

To reduce the consumption of fossil fuels, mitigate climate change and meet the everincreasing energy demands, cost effective and everlasting renewable energy resources have been considered as promising alternatives. Among the renewable resources, solar energy is the most potential and clean energy resource. In this review paper, advancements and developments in different generations of solar cell technologies have been reviewed. Starting from silicon solar cells, solar cell technologies have passed through different stages of improvement regarding cost and efficiency. But in market, first generation solar cells are still dominating with global market share of over 90%. Thin film solar cell technology which comprises the second generation are economical as compared to traditional Si Solar cells but have relatively low efficiency. Third generation solar cells consist of DSSC, organic, perovskites and multijunction solar cells. The perovskites and tandem perovskites have achieved record breaking efficiencies of 34.6% and 36.1% in recent research. But the commercialization of these technologies is still a challenge due to stability related issues. The fourth-generation solar cells which combines the merits of organic and inorganic materials to give bulk heterojunction technology are emerging as future solar cell technologies.

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1. Introduction

Globally increasing energy needs for domestic and commercial purposes is the major factor of concern in modern era. At present about 80% energy demands are being fulfilled by the exhaustible fossil fuels. The production of energy from fossil fuels is causing depletion of ozone layer, global warming, environment related issues and many health hazards to living creatures [1]. The burning of fossil fuels are major contributors of toxic pollutants, carbon dioxide, sulphur dioxide, nitrogen oxides, carbon monoxide, particulate matter (PM_{2.5}) and mercury which are harmful to the living beings as well as their surroundings. The increased concentration of CO₂ and other greenhouse gases emitted during burning of fossil fuels has adverse impacts on the earth's climate. The report of "Intergovernmental Panel on Climate Change" has predicted a rise in global mean surface temperature from 1.4°C to 5.8°C by the end of 2100 [2]. The rise in temperature of earth is termed as global warming. Global warming will lead to melting of glaciers and will cause sea levels to increase. The "Intergovernmental Panel on Climate Change" has also reported an increase in global sea level by about 3.1 millimetres per year since 1993. The emission of particulate matter along with greenhouse gases cause multiple illnesses including respiratory problems, pneumonia, cancer, stroke, birth defects and premature death in humans. The developing foetus and children of age below 5 years are more prone to air pollution caused by burning of fossil fuels. In 2012, WHO projected that air pollution caused 169,000 global deaths among children younger than age of 5 [3]. Further it is estimated that fossil fuel pollution is contributor for one in five mortalities worldwide [4]. Generally, the developed nations are major consumers of fossil fuels and also major contributors of greenhouse gases. As per report of European Union's Joint Research Centre, total global CO₂ emissions have increased from 34.1 GT (Gigaton) in 2010 to 35.96 GT in 2020. In 2020, China released the highest carbon which is about 32% of total carbon emission [5]. Table 1 shows the list of top ten carbon emitting countries [5]. Also the present world fossil fuel reserves are unable to fulfil the global energy demands which are predicted to get double in upcoming decade due to increasing world population and technological advancements in developing nations [6]. To fulfil the growing energy needs, the developing nations are required to double their energy production. In the International Energy Outlook (IEO) 2009, the total consumption of

marketed energy worldwide is estimated to rise by 44% till [7]. As the existing fossil fuel reserves are depleting at fast rate and their prices are also continuously rising, the biggest challenge for developing nations is to explore some alternate resources to meet the increasing energy needs. Energy resources are mainly categorized into three groups: fossil fuels, nuclear energy resources and renewable energy resources [8]. The renewable energy resources are further categorized into mainstream and emerging renewable energy resources. Solar, wind, hydropower, fuel cell, geothermal etc are some of the mainstream renewable energy resources whereas marine energy, concentrated solar photovoltaics, geothermal energy, hvdrogen. bio energy and artificial photosynthesis are few promising potential renewable energy resources [1]. In the past decades, researchers and industrialists have shown their interest in the development of renewable energy resources due to their abundance and potential to provide energy free of pollutants and greenhouse gases [1]. This approach of diversity in energy resources can also provide sustainability, reduce pressure on existing resources and helps in maintaining the ecological balance [7]. Out of all these alternative resources, solar systems have shown significant improvement performance. Their associated capital and generation cost has also been decreasing gradually because of which these are emerging as cost-effective alternatives to fossil fuels. Further, solar energy is pollution free and sustainable source of energy. It has garnered the heightened attention due to its abundance and enormous potential to overcome the energy related issues [9]. Many countries are harnessing solar power as alternative to traditional non-renewable energy resources. A total of 629 GW capacities producing solar power plants were installed globally with China, United States and India as top solar power installers in 2019. China remains the leading country in 2020 with production of one third of total global solar power production. As per the renewable energy capacity statistics 2022 by International Renewable Energy (IRENA), 3063 GW energy was harnessed globally from renewable energy resources in 2021 out of which 849 GW is solar. Figure 1 shows contribution of leading countries in production of solar power [10]. Among all the renewable energy resources, solar energy is the one which is available everywhere on earth and is an inexhaustible source of energy. The harnessing of solar energy is very beneficial for remote locations. But there are some

limitations of solar energy also. The initial installation cost of solar system which includes solar panels, batteries, inverters, installation is quite high. Secondly, it occupies huge space and solar panels works effectively in sunlight only. In On-grid systems, energy can be taken from grid during night. For Off-grid systems solar energy can be stored in batteries to use during night and bad weather days. But the maintenance cost of these batteries is very high. Further its harness depends upon the geographical location and climatic conditions of that place. The tropical and sub-tropical region can take the most benefit of solar energy. But the poor infrastructure and high initial cost of installation is hindering the growth of solar installation in these regions as compared to developed countries. Due to warmer climate in tropical regions, dust rises higher and covers the solar panels leading to decreased efficiency of solar panels. The solar panels demand more maintenance and cleansing in these regions [11]. In spite of all these limitations, solar energy is still attracting scientific community to research in this field as it is a clean fuel and inexhaustible.

Table 1. List of top 10 carbon emitting countries [5]

Rank	Name of the	CO ₂ emission (in
	country	metric ton)
1	China	11680.42
2	United States	4535.30
3	India	2411.73
4	Russia	1674.23
5	Japan	1061.77
6	Iran	690.24
7	Germany	636.88
8	South Korea	621.47
9	Saudi Arabia	588.81
10	Indonesia	568.27

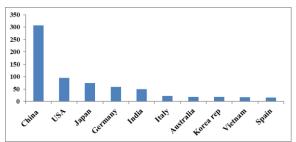


Figure 1. Contribution of different countries in solar energy production globally as per report of IRENA [10]

Solar energy can be converted into electrical energy using photovoltaic solar cell devices. The

photovoltaic devices are simple and easy to maintain and produces power from microwatts to megawatts. They have wide range of applications from being used in power plants, water pumps, remote buildings, solar home systems, communications, satellites and space vehicles etc [12]. Most of the solar radiations which reach earth's surface are in visible and infrared region with small amount of ultraviolet radiations. Sun emits 3.846 x 10²⁶ Watt energy. After suffering reflections and scatterings from earth's atmosphere about 48% of solar energy is absorbed by land and water. This percentage varies according to inclination of sun and cloud cover in atmosphere of earth. Solar energy reaching earth's surface per second per square meter (solar irradiance) is 1,360 watt/m² [13]. Figure 2 shows solar photon's flux at the surface of earth as a function of wavelength (AM 1.5 spectrum) [14].

A solar cell is basic unit of solar energy generating system which has one negative terminal and one positive terminal with semiconducting p-n junction in the middle. When light falls on the solar cell, some photons are absorbed and an electronhole pair is generated.

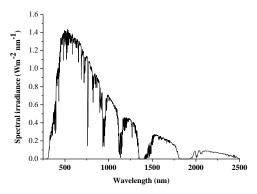


Figure 2. Solar photon's flux at the surface of earth as a function of wavelength (AM1.5 spectrum) [14]

Electrons are migrated to n-junction and holes are migrated to p-type side of the junction which establishes a potential difference. When solar cell is connected to external circuit, current starts flowing. Figure 3 shows the current–voltage characteristics under dark and illuminated conditions of a typical solar cell device

where I_{sc} is the short circuit current which is produced by solar cell without any external potential under illumination. V_{oc} is the open circuit voltage determined by potential difference between two terminals of solar cell when there is no current flowing through the terminal. V_{max} and I_{max} are the voltage and current at maximum power point of

solar cell. The ratio of maximum power to the product of short circuit current and open circuit voltage is called Fill factor (FF). The ratio of maximum power output to radiation power input to cell is called Efficiency (η) of the cell.

The materials which are non-toxic, have high absorption of sunlight, thermally stable, eco-friendly, band gap in optimum range are promising materials for photovoltaic applications. Band gap of a material is the minimum energy required for exciting an electron to higher energy state [15]. For maximum absorption of solar spectrum, low band gap material is suitable but for high efficiency and high fill factor, large built-in voltage is required which needs large band gap material. So, to accommodate both requirements, the materials with band gaps lying between 1.1eV- 1.7eV are best suited for solar cell applications. Table 2 depicts the band gap of some commonly used solar cell materials.

Based upon the type of material and technology, solar cells have been broadly classified into four generations.

- First Generation Solar Cells mono and poly-crystalline wafer-based Si solar cells
- 2. Second Generation Solar Cells- Thin film technology and semiconducting compound based amorphous Si (a-Si), CdTe, CIGS, GaAs
- 3. Third generation solar cells Based upon nano-technology DSSC, OPV, quantum dot, hybrid solar cells, perovskite solar cells
- 4. Fourth Generation Solar Cells- Bulk heterojunction

Table 2. Band gap of materials used in solar cells [15]

Materials	Band Gap (eV)
Silicon (Si)	1.11
Amorphous Silicon (a-Si)	1.75
Cadmium Telluride (CdTe)	1.44
Cadmium Selenide (CdSe)	1.73
Gallium Arsenide (GaAs)	1.42
Indium Phosphide (InP)	1.35
Aluminium Gallium	1.42-2.16
Arsenide (AlGaAs)	
Indium Gallium Arsenide	0.75
(InGaAs)	
Copper-Indium Gallium	1.06-1.7
Diselenide (CIGS)	

To increase the efficiency and reduce the cost of production, enormous research has been carried out in different materials and techniques to fabricate solar cells. Starting from crystalline silicon, group III-V materials to bulk hetero-junctions and multijunction a long journey has been travelled to achieve some significant performances which led to the development of various types of solar cells. But the first generation crystalline Si based solar cells are still dominating the market due to abundance of Si, its appropriate band gap, high power conversion efficiency and well developed processing techniques [16]. The few drawbacks of Si solar cells are its rigidity, high cost, presence of some light induced degradations etc. Among second generation solar cells, CIGS based solar cells have high efficiencies and can be fabricated by vacuum as well as solution processible techniques on glass as well as flexible polymer substrates.

The chemical and electronic structures of CIGS cells are very sensitive to growth techniques which limit their commercial applications. The secondgeneration solar cells also faced some problems related to toxicity of some materials such as cadmium. Hybrid perovskites, DSSC and organic promising third generation cells are technologies due to their advantage of being processible with wet chemical techniques on flexible substrates. Some of these devices such as DSSC have low production costs but the low absorption and photo sensitivity hinders their performance. In semiconducting generation solar cells, nanoparticles which are called quantum dots are incorporated to enhance the absorption. The bulk heterojunction are the recent developments in solar cells wherein the active layer is formed by blending conjugated polymer with electron acceptor. Table 3 shows highest efficiencies achieved by various types of solar cells and their efficiencies as reported in solar cell efficiency table (version 64) [17].

Table 3. Typical Solar cells with their reported

	efficiencies	5 [1/]	
Generation	Classification	Efficiency	Reference
		(%)	
1 st	Si (crystalline	27.4 ± 0.4	LONGi, n-
	cell)		type
			HTBC
			[18]
2^{nd}	Si (amorphous	10.2 ± 0.3	AIST [19]
	cell)		[19]
	Si	11.9 ± 0.3	AIST [20]
	(microcrystalline		
	cell)		
	GaAs (thin-film	29.1 ± 0.6	Alta
	cell)		Devices
	,		[21]
	InP (crystalline	24.2 ± 0.5	Wanlass,
	cell)		NREL

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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		` / `		Solar Frontier
Dye (cell) 11.9 ± 0.4 Sharp [25] Organic (cell) 15.2 ± 0.2 Fraunhofer ISE [26] 4^{th} III-V multi- 38.8 ± 1.2 Spectrolab junctions Five- [27]	$3^{\rm rd}$,	25.7 ± 0.8	UNIST
Organic (cell) 15.2 ± 0.2 Fraunhofer ISE [26] 4th III-V multi- 38.8 ± 1.2 Spectrolab junctions Five- [27]				
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junctions Five- [27]		Organic (cell)	15.2 ± 0.2	114411110101
J []	4^{th}	III-V multi-	38.8 ± 1.2	Spectrolab
		junctions Five-		[27]
junction cell		junction cell		
(bonded)		(bonded)		

2. Methodology

- 1. In this review, the development of various solar cell technologies from first generation to current generations were explored.
- 2. Historical milestones in the establishment of various generations were explored.
- 3. The achievements among various technologies were highlighted.
- The challenges among various technologies hindering their commercialization were also identified.

3 Developments in Solar Cells

3.1 First Generation Solar Cells (Wafer based)

First generation solar cells based upon silicon wafer is a mature solar cell technology and is contributing 90% to world market of photovoltaics. These are of two types: single crystal and polycrystalline Si solar cells. Single crystal is formed by doping the wafer of semiconductor with p-type impurities and then n-type impurities at high temperature. Due to high purity of single crystal, its efficiency is very high. Starting from 1954 to 2019, efficiency of single crystal Si solar cells has improved from 14% to 26.7 % [28]. First Si solar cell was reported by Ohl in 1941 with energy conversion efficiency less than 1 % [29]. Diffused pn junction solar cell fabricated on p-type Si substrate at Bell Laboratory by Pearson, Fuller and Chaplin in 1950's achieved efficiency of about 4.5% [30]. 14% efficiency was achieved by the end of 1950's for cells fabricated mainly on n-type Si substrates. As the Si solar cells were mainly used as power source for satellites and p-type substrates were found less affected by harmful effects of solar radiations, in

1960's cells were fabricated on p-type substrates. In 1980's cell development started with Passivated Emitter Solar Cells (PESC), Passivated Emitter and Rear Cell (PERC) and Passivated Emitter Rear Locally Diffused Cell (PERL). In these devices charge carrier recombination on surface was reduced by using surface passivation technique. In basic structure of c-Si, p -type Si wafer acts as absorber of light. On both sides of wafer, thin highly doped carrier selective contacts are developed. To reduce the front reflections, top surface is coated with antireflection layer (typically hydrogenated amorphous silicon nitride). Then, the metal contacts are provided at both ends[31]. Figure 3 shows a basic structure of c-Si solar cell. Abundance of Si in nature, non-toxic nature of Si, long-standing stability of PV modules with crystalline Si and high energy conversion efficiency makes the 1st generation solar dominate the market. But the high manufacturing cost of these solar cells is a challenge which needs attention and is the key area of research in this field. As the Si solar cells are close to their theoretical limiting efficiency of 33.7% it led the researchers to other solar cell technologies [32].

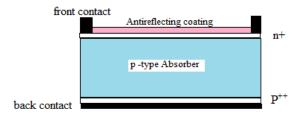


Figure 3. Basic structure of a c- Si solar cell

3.2 Developments in Second Generation Solar Cells

Second generation solar cells based on thin film technology are primary alternatives for first generation solar cells. Thin film technologies were introduced to provide cost reduction due to low consumption of raw material, scalability of mass production and development on light weight flexible substrates. The layers of thin films can be deposited on large area and cheap substrates such as glass, metal or polymer etc [33]. Some commercially developed thin film solar cells are Amorphous silicon (a-Si and a-Si/µc-Si); Cadmium Telluride (Cd-Te) and Copper-Indium-Gallium-Diselenide (CIGS) [33].

3.2.1. Amorphous Si based Solar cells

Hydrogenated amorphous Silicon (a-Si-H) was first prepared by Chittick and co-workers using glow discharge technique in 1969 [34]. Earlier, the research was also carried on unhydrogenated amorphous silicon but its high defect density made it unsuitable for further research [35]. In Amorphous Si based solar cells, films of thickness less than 1 um are required for absorption of sunlight due to high absorbance of amorphous Si. The amorphous silicon (a-Si:H) has 40 times high absorption rate as compared to mono-crystalline Si due to high bandgap of 1.75 eV. (a-Si:H) single junction solar cells have a p-i-n or n-i-p configuration as shown in figure 4 [36]. The major turning point in the development of a-Si: H based devices was the observations reported in 1975 by Spear and LeComber [37] [38]. The further improvements in these devices were observed when thin films were prepared by plasma deposition [39]. Due to ease of manufacturing and good performance at low light illumination, a-Si-H found practical applications in calculators. The first large-area a-Si:H modules was commercialized by Arco Solar in 1986. Japanese companies were pioneers to start mass production of amorphous silicon modules [40]. The intense research in these devices led to conversion efficiencies of 12-13% by 1989 [35; 41]. On exposure to light a degradation effect called Staebler -Wronski effect was observed by D. L. Staebler and C. R. Wronski [42] in amorphous silicon layers due to which these cells delivered low efficiencies. This light induced degradation was attempted to reduce by increasing the deposition temperature [43] or by using hydrogen dilution[40; 44]. The confirmed record stabilized efficiencies for a-Si is 10.2 % under the global AM1.5 spectrum [17].

To achieve high efficiencies and overcome the limitations of single junction amorphous cells, multi-junction cells were invented. The stacked cell approach in multi-junction devices not only enhanced the efficiency but also increased the light absorption as different components of cells absorb light in different regions of spectrum [36]. The record efficiencies 12.7% for dual-junction module and 14% for triple-junction cell were reported [17]. Due to Staebler-Wronski effect and low efficiencies as compared to other mature technologies, a-Si:H cells have limited market acceptance. The global market share of amorphous silicon PV technologies is 0.2% as reported in 2020 [45].

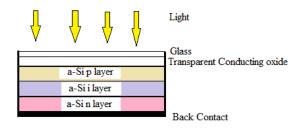


Figure 4. Basic structure of p-i-n a - Si solar cell

3.2.2. Hydrogenated microcrystalline silicon (µc-Si:H) based Solar cells

Hydrogenated microcrystalline silicon (µc-Si:H), is a heterogeneous material which consists of nanosized crystalline silicon grains (c-Si) surrounded by silicon tissues [46].The amorphous microstructure can be varied from highly crystalline to amorphous growth with small crystalline embeddings by varying the deposition parameters [47; 48]. As, µc-Si:H is obtained by diluting silane (SiH₄) in hydrogen (H₂), silane concentration plays role in determining the microstructure [49]. The deposition conditions near the transition to amorphous growth were proved to be most advantageous for solar cell properties [48]. μc-Si:H absorbs light in IR region due to its band gap of 1.1eV and is mostly deposited by plasmaenhanced chemical vapour deposition (PECVD) or hot-wire CV deposition techniques. μc-Si:H are also deposited using p-i-n or n-i-p configuration. µc-Si:H has several benefits over amorphous silicon such as wide spectral response, high carrier mobility and high tolerance to light soaking and is unaffected by the Staebler-Wronski effect. µc-Si: H is widely investigated as middle or bottom absorbing layer in dual and triple junction solar cells. The power conversion efficiencies have been increased steadily by improving the material quality and light utilization. The record reported efficiency of single junction µc-Si:H is 11.9 % [20]. Due to indirect band gap, the absorption of µc-Si:H is poor in infrared region which leads to poor efficiencies. To enhance the light absorption, textured surfaces were investigated. But the textured surfaces induce cracks in µc-Si:H films which again decreases the cell efficiencies [50].

3.2.3. Cadmium Telluride (Cd-Te) based solar cells

Cd-Te based solar cells are second most important class of solar cells with representation of 5% share in global photovoltaic market after crystalline Si. Cd-Te has direct band gap of 1.44 eV due to which very thin film of material is sufficient for high efficiency cells [51]. Cd-Te crystal was first synthesized in 1879 by Margottet and its p-type and *n*-type conductivity was reported by Jenny and Bube in 1954 [52; 53]. First Cd-Te solar cell was fabricated by diffusion of Indium into p-type CdTe crystals with efficiency of about 2% by Rappaport [54] [55]. Kodak developed Cadmium Telluride based solar cell with efficiency greater than 10% in 1982. The Research and Development cell of First Solar has reported the record efficiency of 21% in Cd-Te solar cells.

Mostly Cd-Te solar cells are fabricated in superstrate configuration as shown in Figure 5. Soda lime glass is most commonly used substrate on which transparent conducting oxide, buffer layer, Cd-Te and back contact are deposited [56]. However, the toxic nature of cadmium limits its commercial applications [51].

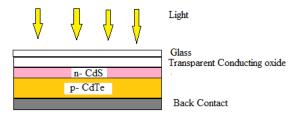


Figure 5. Basic configuration of Cd-Te based cells

3.2.4. Copper-Indium-Gallium-Diselenide (CIGS)

Chalcopyrite CuIn_{1-x}Ga_xSe₂ (CIGS) has become promising materials for flexible solar cells with efficiencies greater than 21% achieved by various research groups [57]. The band gap of most CIGS lies between 1.25 and 1.45 eV which can be increased above 1.50 eV by varying the proportion of its elements [58]. The performance of CIGS solar cells is comparable to c-Si with an added advantage of being low cost as only 2-2.5 nm absorber layer is required [59]. The CIGS solar cells can be fabricated on glass as well as flexible substrates with vacuum and non-vacuum deposition techniques. The typical CIGS solar cell structure consists of substrate, back contact, MoSe₂ layer, CIGS absorber layer, Buffer layer and window layer as shown in figure 6. The

fabrication method is major deciding factor in determining the efficiency of CIGS based solar cells. The record efficiencies are achieved with vacuum deposition of absorber CIGS layer due to better crystallinity of CIGS layer. The non-vacuum based methods provide the benefits of large scale production, high material utilization and low production cost [59; 60]. The cell efficiencies have been improved by band gap grading, doping and controlling morphology [59]. The introduction of Alkali elements such as lithium, sodium, potassium and cesium as post deposition treatment has significantly improved the cell efficiencies [61]. The efficiency of commercial modules is obtained to be much less than the lab based CIGS cells due to electronic inhomogeneities [59]. Although these thin film solar cells have a lower costs and good efficiencies, they have some drawbacks. Most of the material that these cells are made up of like indium or cadmium are either becoming increasingly scarce or are highly toxic [62].

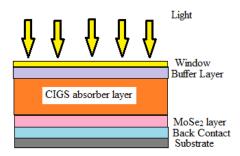


Figure 6. Structure of CIGS based Solar cells

3.3. Developments in Third Generation Solar Cells

The high manufacturing cost of first-generation cells and some limitations of second- generation cells paved way for third generation cells. The third-generation solar cells technologies are very different from previous technologies and have the potential to replace them commercially as well. The third-generation solar cells include organic photovoltaics, perovskites, Dye Sensitized Solar cells, nanostructured and multijunction technologies.

3.3.1 Perovskite Solar cells

Perovskite Solar cells are based on perovskite material having chemical formula ABX₃ where A is organic component, B is inorganic component and X is halogen. These materials have high optical absorption, tunable band gap, high charge carrier mobility which makes them suitable to harvest solar

energy from solar spectrum and also enables them to act as charge carriers [63]. The crystallinity and morphology of perovskite films depends to a large extent on method of deposition. The perovskite films can be deposited by solution based techniques as well as vacuum deposition method [64; 65]. The easy and cheap methods to fabricate these materials make them cheap alternatives as compared to traditional Silicon crystals. The commonly studied perovskite materials for solar cell applications are CH₃NH₃PbI₃, CH₃NH₃PbI_{3-x}Cl_x, $CH_3NH_3PbBr_3, CH_3NH_3Pb(I_{1-x}Br_x)_3, HC(NH_2)_2PbI_3,$ $HC(NH_2)_2Pb(I_{1-x} Br_x)_3$ and CH_3NH_3SnI [66]. The ni-p and p-i-n are two basic device architectures in perovskite solar cells which are further classified into mesoporous perovskite solar cell and planar perovskite solar cells. Mesoporous perovskite materials mostly employ n-i-p structure. In mesoporous perovskite architecture, perovskite material is deposited on mesoporous tiO2or mesoporous Al₂O₃ or znO followed by deposition of hole transport material. In a planar configuration, perovskite absorber layer is sandwiched between Electron Transport Material (ETM) and Hole Transport Material (HTM) without a meso-porous scaffold as shown in Figure 7 [69].

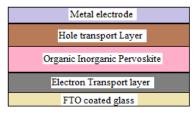


Figure 7. Schematic sketch of planar perovskite solar cell

Kojima et al have studied the photovoltaic properties of the organic-inorganic lead halide CH₃NH₃PbBr₃ perovskite compounds CH₃NH₃PbI₃ in liquid electrolyte based Dye Sensitized Solar cells and obtained power conversion efficiency of 3.8% for CH₃NH₃PbI₃ based solar cells [67]. Im et al have achieved an improved efficiency of 6.5 % in perovskite based quantum dot sensitized solar cells [68]. But in these liquid electrolytes based cells decomposition of perovskite materials leads to device degradation [69]. However, in 2012 the introduction of spiro OMeTAD as an organic hole transports material and (CH₃NH₃PbI₃) as solar absorber exceptionally improved the device efficiencies [64; 69]. Lead halide perovskite CH₃NH₃PbX₃ (X=Cl, Br, I) based solar cells have achieved a record efficiency of > 20%. But the commercialization and mass

production of perovskite solar cells is still a challenge due to stability related issues.

3.3.2. Organic solar cells

In Organic solar cells, organic semiconducting material is sandwiched between two electrodes. Low cost, intrinsic flexibility and processibility with easy techniques of organic semiconducting materials makes the organic solar cells potential alternatives to inorganic solar cells. The developments in organic solar cells instigated in 1980 with deposition of single active layer between electrodes. Later on in 1986, Tang et al successfully reported donor acceptor bilayer planar structure with power conversion efficiency (PCE) of around 1% [70]. In bilayer Organic solar cells, two layers of organic materials are sandwiched between electrodes. One layer of material which absorbs light to produce electron-hole pair is called a donor layer and second organic layer which accepts electrons from the donor layer is called the acceptor layer. This structure is also called a planar donor-acceptor heterojunction [71]. The charge generating interface between donor and acceptor in bilayer solar cells was limited within a small area which limits the performance of these devices. In 1995, Yu et al overcame this drawback by introducing polymer donor and fullerene acceptor based bulk hetero-junction organic solar cells. The blended active layer of donor and acceptor increased the interfacial area leading to an efficiency of 6% [72]. Now- a - days the PCE of organic solar cells has been significantly improved by exploring novel and inserting electron and hole materials transporting materials between active layers and electrode. The morphological optimization of active layer and improvements in device structure also leads to improved performance [73].

Regioregularpoly(3-hexylthiophene) dialkoxysubstituted poly(para-(P3HT), phenylenevinylene)s ME-PPV and MDMO-PPV, Benzodithiophene-based polymers (BDT). Benzotriazole-based polymers (BTA), Naphthobistriazole-based polymers (TZNT)are most investigated polymer donors [74; 75; 76]. Due to some merits of small molecules over polymers, small molecule-based donors (SMDs) are also investigated in addition to polymer-based electron donors. The well-defined molecular structure and pure synthesis have attracted the researchers in small molecule-based donors. Fused oligothiophenes and triphenylamine-based molecules are some of the small molecule donors. The thiophene ring is widely studied due to its

planar structure, easy availability, and ease of functionalization with several functional groups[75]. Heeger et al. in 2012, has demonstrated thiophene containing SMDOSC for the first time and achieved PCE of 6.7% for the DTS(PTTh2)2 :PC71BM (D:A=7:3) [77].

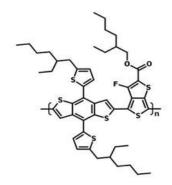
Fullerenes and their derivatives are most commonly used electron accepting materials. The efficiency of fullerene-based tandem solar cells has increased from 0.04% up to 17.3%. Due to some limitations of fullerene-based acceptors like weak absorption, limited tunability in structure, high synthetic costs, and morphological instability motivated the researchers in non-fullerene based organic solar cells [78] [79]. The optical properties and electronic energy levels of non-fullerene acceptors can be easily tuned as compared to fullerene based acceptors. PCE of 5.16% was achieved for P3HT as the donor and SF(DPPB)4 as the acceptor. SF(DPPB)4 is a diketopyrrolopyrrole (DPP) based small molecule with spirobifluorene as the core and benzene as the end groups [80]. Yong et al reported maximum PCE of 19.0% (certified value of 18.7%) for single-junction OPV cells using polymer donor named PBQx-TF and non-fullerene acceptor (NFA) named eC9-2Cl [81]. Some commonly used donors and acceptors are tabulated in table 4.

Table 4. Commonly used donors and acceptors in organic solar cells

Some Commonly used Donors

P3HT Poly(3-hexylthiophene)

MEH -PPV Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4phenylenevinylene]

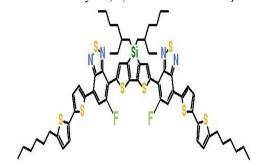


PTB7-Th

Poly([2,6'-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene]{3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}

PCDTBT

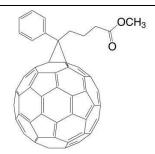
poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole]



DTS(FBTTh2)2

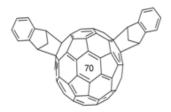
poly[2,5-bis(2-hexyldecyl)-3,6-diketopyrrolopyrrole-alt-5,5'-(2,2'-bithiophene-5,5'-diyl)bis(thieno[3,2-b]thiophene)]

Some Commonly used Acceptors



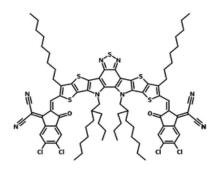
PCBM

Phenyl-C61-butyric acid methyl ester

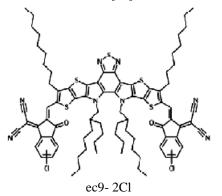


IC₇₀BA Indene-C70 Bisadduct

PDIs Perylene Diimides



BTP-eC9 Non fullerene acceptor with fused thienothienopyrrolo-thienothienoindole (TTP-TTI) core [82]



Non-fullerene acceptor with fused thienothienopyrrolo-thienothienoindole (TTP-TTI) core with two less chlorine than BTP-eC9 [82]

Despite the impressive advancements in organic solar cell technologies, there are still some challenges in the way of its commercialization. Heat, light, moisture, oxygen affects the stability of organic structures. By implementing effective encapsulating technology, this issue can be addressed. Pin-hole formation, non-uniform films and processibility are some key challenges in OSC.

3.3.3. Dye Sensitized Solar Cell

Dye-Sensitized solar cells (DSSCs) have attracted the researchers due to their various characteristics such as environment friendly, flexible fabrication process, light weight, low cost and highpower conversion efficiency. O'Regan and Gra"tzel were first reported a DSSC with record high PCE of 7.1% in 1991[83] [84]. The architecture of DSSC consists of semiconductor oxide coated glass transparent conductive substrate photoelectrode, monolayer of dye sensitizer covalently bonded to oxide layer, an electrolyte containing redox couple dissolved in an organic solvent and a counter electrode commonly made of platinum coated glass substrate (Table 5). The efficiency of constituent components determines the performance of DSSC. Figure 8 shows the basic structure of DSSC.

Table 5. Commonly used components in DSSC

Table 3. Commonly used components in DSSC		
Major Components of	Materials used	
DSSC		
Photoanode	TiO ₂ , ZnO, MgO and	
	Al_2O_3	
Dye Sensitizer	ruthenium (II) based dyes,	
	metal free organic dyes	
Electrolyte	Liquid electrolyte (I ⁻ / I ₃ -),	
	Solid Electrolyte (HTM),	
	quasi solid state	
	electrolyte	
Counter Electrode	Pt, Graphene or Carbon	

The wide bandgap mesoporous oxide which consist of nanoparticles sensitized by dye molecules act as photoanode. The nanoparticles in oxide layer increases the anchoring of dye molecules leading to increased absorption of light. Titanium dioxide (TiO₂) is widely investigated photoanode materials for DSSC [85]. ZnO, MgO and Al₂O₃ are another suitable semiconductors used in DSSCs. Dyes play an important role in DSSC. An efficient dye should get adsorbed to the surface of semiconductor oxide efficiently and exhibit absorption in visible region. It

should have anchoring groups such as carboxylate, phosphonate etc. for proper adsorption in photoanode layer. Since the discovery of DSSC, sensitization has been achieved using ruthenium (II) based dyes. (cis-bis(4,4'-dicarboxy-2,2'-bipyridine) disothiocyanato-ruthenium(II)) coded as N719 dye, cis-(SCN)2bis(2,2'-bipyridyl-4,4'

dicarboxylate)ruthenium(II) coded as N3 dye and N749 dye also called as black dye are few efficient sensitizers [86]. But their high cost, limited availability of noble metals, leads to the use of metal free organic dyes. The remarkable PCE of 13% for DSSCs was obtained by Mathew et al [87] using porphyrin based dye SM315 with Co(II/III) redox electrolyte. The photoexcitation of the dye molecules generates excitons. The electrons are injected to the conduction band of the oxide leaving the dye in its oxidized state. The electrolyte transfers the electron back to the dye and restores its ground state. The most popularly used electrolyte is redox in an organic matrix [88]. Due to corrosive nature of iodide/triiodide, pseduohalogen based electrolytes were explored by different research groups. Oskam et al reported selenocianate-based redox couple 2001 SeCN⁻/ $(SeCN)_2$ in [89]. Br^{-}/Br_{3}^{-} , SCN⁻/(SCN)₂, and S²⁻/S are some another inorganic redox couples used in DSSCs. 2,2,6,6-tetramethyl-1piperidinyloxy, phenothiazine, tetraphenyldiamine, quinones, and thiolate/disulfide are some organic redox couple alternatives of iodide/triiodide redox couple. In addition to inorganic and organic redox couples, transition metal comples based redox couples have also been investigated as iodine-free substitutes of redox couples for DSSCs [90; 91]. Efficiencies over 14% has been achieved by using the cobalt(III/II) complex redox electrolytes [92]. Due to some drawbacks of liquid electrolytes, room temperature ionic liquids, quasi solid and solid electrolytes have also been explored by researchers. Platinum is mostly used as counter electrode in high efficiency cells but it needs replacement due to its high cost and less availability. Graphene, graphene related materials, chalcogenides and p-type metal oxides are potential alternatives.

DSSCs are the most efficient solar cells which are easy to fabricate. They are most suitable for low scale applications like roof top solar collectors. DSSCs perform better than conventional solar cells in low illumination and diffused light. There are some disadvantages of DSSCs like the use of liquid electrolyte which has stability issues at low temperatures which may lead to physical damage of the cell. Another disadvantage is the expensive ruthenium dye, platinum and conducting glass which

is important parts of DSSC. The volatile organic component in the electrolyte solution is very hazardous for health.

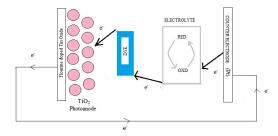


Figure 8. Basic structure of Dye Sensitized Solar Cell

3.3.4. Quantum dot solar cells

Quantum dot solar cells (QDSCs) have evolved as more advanced alternate to DSSCs in which the dye molecules are replaced by quantum dots (ODs) of suitable materials. ODs are tiny semiconductor particles having size of a few nanometres. These particles possess appealing optical and electrical properties which are different than the bulk particles, even of the same material. QDs possess a size tuneable band gap which increases with decrease in OD size. So, by using different sized QDs even of a single material, whole of the visible spectra of light can be utilized for power conversion in a solar cell. In addition, QDs have high extinction coefficient and exhibits multiple exciton generation (MEG). In conventional solar cells, light absorption results into the generation of an exciton (electron-hole pair) by exciting the electron from valance band of the absorbing material to conduction band and the excessive energy of photon is dissipated in the form of heat. On the other hand, if a photon of energy equal or more than double of the band gap is absorbed by a QD, two or even more electron-hole pairs may be generated [93; 94; 95].

Typical design of a QDSC is similar to DSSCs which includes a photoanode, suitable electrolyte and a counter electrode. The photoanode usually consists of deposition of a wide band nanostructured semiconductor like TiO₂, ZnO and SnO₂ etc. on a cleaned FTO or ITO substrate by doctor blading or tape casting technique followed by annealing at high temperature (450-500 °C). QDs are loaded into this film by successive ionic layer adsorption and reaction (SILAR), chemical bath deposition (CBD), adsorption of pre-synthesized

colloidal QDs using suitable linker molecules etc. The photoanode so prepared is assembled with a suitable counter electrode using some sealing materials. The space between the two electrodes is filled with a few drops of an electrolyte, usually sulphide/polysulphide redox couple. The working principle of QDSC is similar to DSSC. Exciton is generated on absorption of light photon by QDs. Conduction band of active layer material (TiO2, ZnO and SnO₂) lies lower in energy than conduction band of QD. So, electrons in the conduction band of QD drift towards active layer nanoparticles and further move through the conducting electrode and external circuit to reach the counter electrode. The holes in the valence band of the QDs enters into the electrolyte, where they got neutralized by gain of electrons from negative ions of the redox couple. The neutralized/oxidized ions of electrolyte are again reduced by the flow of electrons from the counter electrode [96].

The sensitizer material used for the deposition of active layer is a crucial factor in the performance of ODSCs. TiO2 is widely accepted and thoroughly investigated sensitizer material in DSSCs and QDSCs [97; 98; 99; 100; 101; 102]. But, TiO₂ possess some trap levels which leads to random charge transportation due to trapping and detrapping of electrons. A distinguished approach towards this is to improve the light harvesting and conduction properties of the photoanode by incorporating various types of nanostructures such as nanoparticles, nanorods, nanowires, nanotubes etc in the TiO₂ active layer by different methods. The one-dimensional nanostructures like nanorods, nanowires, nanotubes etc. effectively scatter light and improve the electron transfer properties. On the other hand, metallic nanoparticles (Mnps) especially of noble metals Au and Ag effectively harvest the light by inducing electrical and optical effects by localized surface plasmon resonance (LSPR) and convincingly improve the photo conversion efficiency[103] [104] [105][106].

Liu et al synthesized CdSe QD-sensitized Au/TiO₂ nanocomposite films by emulsion-based bottom-up self-assembly (EBS) method in a photo-electrochemical cell (PEC) [107]. This device shows a significant enhancement in the optical absorption caused by scattering of light from gold nanoparticles. Zhu et al used a different strategy by growing an interfacial layer of Au nanoparticles between FTO and TiO₂ active layer of CdS QD sensitized solar cell [108]. An 88% improvement in the device performance was observed due to easier transport and decrease in recombination rate of

photogenerated charge carriers in the photoanode due to the introduction of Au nanoparticle layer.

The second major approach to enhance the performance of sensitized solar cells is the use of graphene and its derivatives with different strategies. Graphene and its derivatives are widely studied in material science because of exceptional physical, chemical and mechanical properties which are proved to be a benchmark for continuous improvements in the performance of optoelectronic devices. Akilimali et al studied photoelectrochemical cell with GNR-TiO₂ hybrid photoanode sensitized with CdS/CdSe QDs [109]. Performance of the cell was improved with 20% increase in hydrogen generation and 30% increase in photocurrent density with addition of 0.02 wt% of GNR in TiO₂. GNR-TiO₂ hybrid photoanode based PEC device shows greater stability than the reference device. Kusuma et.al compared the effect of incorporating graphene oxide and graphene nanoribbons separately into the TiO₂ active layer in QDSC [110]. The high surface area of GNRs creates as many active sites for TiO₂ nanoparticles and act as interconnection between these nanostructures for improved electron transport.

3.3.5 Multijunction solar cells

Multiple junction solar cells consist of multiple semiconducting layers with varying band gaps stacked on a substrate. Due to tunable band gap and properties. efficient optoelectronic semiconductors from group III- V such as Indium gallium phosphide (IGaP), gallium arsenide (GaAs), gallium indium arsenide phosphide (GaIAsP) etc are most widely used as different layers in multijunction solar cells [111]. The layers of different semiconducting materials in multijunction solar cells lead to absorption of wide range of wavelength leading to higher efficiencies [112]. The theoretical limit of single junction solar cells is 31.1% whereas theoretical limit of infinite junctions is 86.8% [113]. Bedair et al demonstrated first multijunction solar cell with AlGaAs/GaAs two-junction cell in 1979 [114]. It also makes the choice of materials difficult along with increased complexity. Takamoto et al. achieved InGaP/GaAs tandem cells with an efficiency over 30% [115]. The developments in materials and advanced design techniques lead to triple junction, four junctions and six junction solar cells which make the best use of full solar spectrum to achieve high efficiencies. Dimroth et al reported four junction GaInP/GaAs//GaInAsP/GaInAs solar cell with a record efficiency of 44.7% at [116] [117].

The significant advancements in multijunction solar cells from two to six junction solar cells enhanced the PCE to 47.1% [111]. The multijunction solar cells are employed for space applications due to their high efficiencies, radiation resistance and reliable stability in space. The earlier multijunction solar cells suffered from lattice dislocations due to lattice mismatch during the epitaxial growth which deteriorates the device performance. This issue was resolved by wafer bonding technique [118]. Dimroth have reported four iunction GaInP/GaAs/GaInAsP/gaInAs wafer bonded solar cell with an efficiency of 46% [119]. The alternate way to resolve the lattice mismatching issue is metamorphic growth method in which a buffer layer is introduced between the mismatched layers. There are two kinds of metamorphic growth methods: inverted metamorphic growth method (IMM) and upright metamorphic growth method (UMM) [120]. IMM cells employs top to bottom approach with highest band gap layer at the top. IMM cells have the highest efficiencies among the multijunction solar cells. The substrate is removed in IMM cells by applying Epitaxial Lift-Off process which leads to increased power to mass ratio. The high efficiency, flexibility, light weight makes IMM cells promising candidate for space cell applications.

3.4 Developments in Fourth Generation Solar cells

Fourth generation solar cells also known as 4G solar cell technologies are hybrids of low cost and flexible organic polymeric materials and inorganic nanostructures which are designed to improve the efficiency by maintaining low cost. Inorganic semiconductors gives the advantage of absorbing broad range of photons and transporting the charge effectively however the organic materials have the potential for inexpensive processibility [121; 122]. In hybrid organic -inorganic bulk heterojunction cells, electron donating polymers are blended with inorganic semiconducting nano-particle. The photoinduced charge separation which is very critical step in hybrid solar cells generally takes place at the interfaces between inorganic semiconductors and organic materials. The nano-structured composites are widely studied hybrid photovoltaic materials because they offer large interfaces which are favourable for charge separation and leads to high efficiencies. There are many types of nanostructures, including nanoparticles, nanocrystals nanorods, nanotubes, tetrapods, sheets, needles, quantum dots, etc [123]. A blend of variety of nanomaterials such

GaAs. CdSe. PbS. and ZnO, carbon nanostructures, metal nanoparticles with different polymers have been investigated by the researchers [124]. In 1995, Yu et al. fabricated the first fully organic BHJ cell based on a mixture of poly(2methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and fullerenes [125; 126]. In 2012 Liu et al obtained 11.3%, efficiency with a c-Si/Zonyl-treated PEDOT:PSS heterojunction solar cells [127; 128]. An efficiency of 20% was reported by Sun et al on Mg/PCBM/p-type c-Si hybrid solar cells [129].

4.Evaluation and Future Prospect

Researchers are exploring the new ventures among the various solar cell technologies to improve the solar cell efficiencies. Researchers are making progresses in the established as well as developing technologies to achieve cost reduction and sustainability. Si based technologies continues to evolve through advancements in manufacturing technologies and materials. The introduction of nanomaterials has significantly enhanced the absorption in films. Perovskites and tandem perovskites are the future of solar cell technologies. They have the potential to offer cost reduction and high efficiencies. Table 6 and Table 7 depicts the manufacturing cost, levelized cost of energy (LCOE), advantage, disadvantages and current status of various generations of solar cells.

Table 6. Comparative analysis of different generations of solar cells from Cost perspective

Solar Cell Generation	Manufacturing Cost	LCOE
	The	High efficiency,
	manufacturing	long life span
1 st	cost is as low as	and stability
1	0.2 US\$/ Watt	lead to low
	[130] due to years	LCOE of 0.057-
	of refinement in	0.145 US
	technology.	\$/Kwh.
		Comparatively
	Due to lack of	higher LCOE
	commercialization	than c-Si solar
2^{nd}	high	cell technology
	manufacturing	due to low
	costs.	efficiencies and
		stability issues.
	The perovskites	The LCOE of
$3^{\rm rd}$	are most	perovskite based
	promising among	solar cell

	3 rd generation	technologies is
	solar cell	0.18-0.22 US
	technologies with	\$/KWh[132].
	manufacturing	
	cost of 0.57	
	US\$/Watt.	
$4^{ m th}$	High manufacturing cost.	Due to high manufacturing costs, LCOE is high.

Table 7. Advantages, Disadvantages and Current status of different generations of solar cells

Solar Cell Generati on	Advantages	Disadvantag es	Current status
1 st	High efficiency, established technology, abundant raw material.	High manufacturi ng cost and high precision in manufacturi ng process required.	Accounts for over 90% of global market share.
2 nd	Light weight, flexible design, building integrated (BIPV), curved surfaces [131].	Low efficiency, unstable.	Thin film technologi es accounts for small and growing share in global solar market.
3 rd	Abundant and cheap raw material, high lab efficiencies, Promising technology to achieve high efficiencies at low cost	Laboratory efficiencies compete with c-si but commercial yields, durability and stability are poor.	Negligible market shares but have the potential for significant market growth.
4 th	at low cost. Due to high efficiency used in space satellites and	High manufacturi ng cost and complexity.	Due to flexibility, durability and high efficiencies, fourth

terrestrial	generation
concentrate	solar cells
d	are
photovoltai	promising
cs.	technologi
	es for
	future
	growth.

The future of solar cell technologies depends upon overcoming the various challenges through innovations. Collaborations among researchers and engineers is essential for the development of sustainable photovoltaic technologies.

5. Conclusions

The solar cell technologies have evolved significantly through four generations and witnessed continuous advancement in materials and technologies. Extensive research has been conducted on various technologies by the academicians and researchers. This review highlighted the transition from early photovoltaic materials to modern multijunction, bulk heterojunction and quantum innovations. The developments and challenges in different solar cell technologies are also reviewed. The major findings of this review are as follows:

- Silicon solar cell technologies have achieved efficiencies above 26% and dominates the global market. The key research areas in this technology includes the development of new cell architectures like integrated back contacts. The application of artificial intelligence to optimise various parameters, to check quality and improve sustainability.
- Thin film solar technologies have witnessed reduced costs and good efficiencies. Thin film solar cells are more flexible than c-Si solar cells. Among the various thin film materials, CdTe and CIGS are the most promising materials. CdTe and CIGS based solar cells have achieved record lab efficiencies of over 20% but the efficiencies of commercially available modules are lower. The environment and stability related issues need to be addressed in thin film technologies.
- Among third and fourth generation solar cell technologies, perovskites, multijunction/tandem solar cells and hybrid solar cells are emerging as future solar cell technologies. Researchers must focus their efforts to address the issues related to instability and durability to commercialize Si/perovskite solar cells.

Nomenclature

I_{max} Current at Maximum Power Point

 I_{sc} Short Circuit Current η Efficiency of the Cell

V_{max} Voltage at Maximum Power Point

V_{oc} Open Circuit Voltage

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