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|  | Double Perovskite Solar Cells |  |
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|  |  |  |
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Contents

[Introduction 1](#_Toc135648815)

[Photovoltaic technology 2](#_Toc135648816)

[Types of PV cells 3](#_Toc135648817)

[Perovskite solar cell 4](#_Toc135648818)

[Perovskite material 4](#_Toc135648819)

[Perovskite material properties 5](#_Toc135648820)

[Historical background of PSCs 8](#_Toc135648821)

[Structural properties of hybrid organic-inorganic perovskite materials 12](#_Toc135648822)

[Device architecture 14](#_Toc135648823)

[Dye-sensitized structure 15](#_Toc135648824)

[Solid state mesoscopic structure 16](#_Toc135648825)

[Meso-superstructure structure 17](#_Toc135648826)

[Regular structure 18](#_Toc135648827)

[Planar n-i-p heterojunction structure 18](#_Toc135648828)

[Inverted planar structure 20](#_Toc135648829)

[Solar Cell Physics 22](#_Toc135648830)

[Solar Spectrum 23](#_Toc135648831)

[Solar cell working principle 24](#_Toc135648832)

[Solar cell I-V characteristics 27](#_Toc135648833)

[Solar cell materials and efficiency 30](#_Toc135648834)

[Materials and Methodology 37](#_Toc135648835)

[Introducing SCAPS 37](#_Toc135648836)

[The Basics 38](#_Toc135648837)

[Run SCAPS: 39](#_Toc135648838)

[Define the problem: 40](#_Toc135648839)

[40](#_Toc135648840)

[Define Working Point 40](#_Toc135648841)

[Shunt conductance and series resistance 41](#_Toc135648842)

[Select the measurement(s) to simulate 41](#_Toc135648843)

[Start the calculation(s): 41](#_Toc135648844)

[Display the simulated curves 42](#_Toc135648845)

[Batch calculations 42](#_Toc135648846)

[The batch set-up panel 42](#_Toc135648847)

[Varying entire definition files 42](#_Toc135648848)

[Varying parameters of the initial state work point 43](#_Toc135648849)

[Recorder calculations 44](#_Toc135648850)

[Solar cell definition 44](#_Toc135648851)

[Editing a solar cell structure 45](#_Toc135648852)

[Reference conventions for voltage and current 45](#_Toc135648853)

[Navigating to the analysis 47](#_Toc135648854)

[Results and Discussions 49](#_Toc135648855)

[SCAPS-1D Numerical Simulation. 49](#_Toc135648856)

[Cs2BiAgI6 Perovskite Solar Cell Structure. 51](#_Toc135648857)

[51](#_Toc135648858)

[Effect of Absorber, ETL and HTL Layers Thicknesses on PV Performance 53](#_Toc135648859)

[Absorber Layer Thickness 53](#_Toc135648860)

[ETL(TiO2) Thickness 54](#_Toc135648861)

[HTL Thickness 55](#_Toc135648862)

[Effect of Absorber Layer Properties. 57](#_Toc135648863)

[Absorber Layer Acceptor Density. 57](#_Toc135648864)

[The absorber layer defect density 58](#_Toc135648865)

[Effect of ETL properties. 59](#_Toc135648866)

[ETL Donor Density. 59](#_Toc135648867)

[Effect of ETL Defect Density. 60](#_Toc135648868)

[Effect of HTL properties. 61](#_Toc135648869)

[HTL Acceptor Density 61](#_Toc135648870)

[HTL Defect Density. 62](#_Toc135648871)

[Effect of Interface Properties. 63](#_Toc135648872)

[Defect Density at the Interface of HTL and the Cs2BiAgI6 Absorber Layer. 63](#_Toc135648873)

[Defect Density at the Interface of the Cs2BiAgI6 Absorber Layer and ETL. 64](#_Toc135648874)

[Effect of Temperature, Shunt, and Series Resistances 65](#_Toc135648875)

[Series Resistance 65](#_Toc135648876)

[Shunt Resistance 67](#_Toc135648877)

[Temperature 68](#_Toc135648878)

[Effect of Capacitance and Mott−Schottky. 69](#_Toc135648879)

[Effect of Generation and Recombination Rate. 70](#_Toc135648880)

[J−V and QE Characteristics. 71](#_Toc135648881)

[Results of SCAPS-1D Compared to Earlier Research. 72](#_Toc135648882)

[Conclusions 73](#_Toc135648883)

[Acknowledgments 75](#_Toc135648884)

[References 76](#_Toc135648885)

# Introduction

World's energy demand increasing significantly because of population growth and industrial evolution. It is important to note that the population has increased by 2 billion just in one generation and major contribution has been given by developing countries. Preventing an energy crisis in one of the most casual issues of the 21st century. Energy demand is therefore increasing fast as to meet the requirements of growing population in the world. Different countries in the world have their own strategies, plans, policies and control measures to establish themselves in the world. As of the population growth and development initiatives, resources available in the world are getting depleted [1]. Considering energy sources is therefore very important as they play a key role in satisfying the need of the world and living population. Accessible energy is not sufficient to people, because of several reasons such as developmental profile of a country, economic status of people and nature of technological advancements of the country. Ecosystem is polluted heavily because of the emission of various gases generated from burning of fossil fuel which are readily available and commonly used for satisfying energy demand of the world [2]. Developing countries are now put into pressure to search for the sources of energy as their population growth is high and they are seeking for economic development to become economically viable [3]. As economic development takes place, energy demand also increases since it is proportional to economic growth. Introducing non renewable energy sources would not definitely meet energy demand since they are exhaustible and limited source of energy [4].Many countries relay on exhaustible energy sources than renewable energy sources. Continuous use of non-renewable energy sources may lead to climate change, **soil degradation,** **destruction of the ozone layer,** **global warming, air pollution,** **acid rain, etc.** which may in turn end up with heavy natural disasters damaging ecosystems of the planet.[5] It is therefore vital to go for eco-friendly energy sources for the betterment of the future world.[6] Considering renewable energy sources such as solar energy, wind energy, hydropower and geothermal, is critically important in this sense as they are eco-friendly.[7]

However, solar energy could be a best option for the future world because of several reasons: First, solar energy is the most abundant energy source of renewable energy and sun emits it at the rate of 3.8 - 1023 kW, out of which approximately 1.8 - 1014 kW is intercepted by the earth[8]. Solar energy reaches the earth in various forms like heat and light. As this energy travels, majority of its portion is lost by scattering, reflection and absorption by clouds. Studies revealed that global energy demand can be fulfilled by using solar energy satisfactorily as it is abundant in nature and freely available source of energy with no cost [9]. Second, it is a promising source of energy in the world because it is not exhaustible, giving solid and increasing output efficiencies than other sources of energy [5].

Photovoltaic (PV) technology is used to convert sunlight into electricity directly without any interface for conversion. Solar radiation distribution and its intensity are two key factors which determine efficiency of solar PV industry. Such two parameters are highly variable over the countries. It has clearly been indicated in Fig. 1. Asian countries have highest potential to receive solar radiation compared to other temperate countries as sunshine duration in such countries is high in a year

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| Figure 1 Maps of global horizontal irradiation (GHI) |

## Photovoltaic technology

The major benefit of solar energy over other conventional power generators is that the sunlight can be directly converted into solar energy with the use of smallest photovoltaic (PV) solar cells. In other words, we say that this is a technology used to convert sunlight into electricity directly without any interface for conversion. There has been a large amount of research activities to combine the Sun’s energy process by developing solar cells/panels/module with high converting form. the most advantages of solar energy are that it is free reachable to common people and available in large quantities of supply compared to that of the price of various fossil fuels. solar energy requires considerably lower manpower expenses over conventional energy production technology.

## Types of PV cells

Solar cells are typically named after the semiconducting material they are made of. These materials must have certain characteristics in order to absorb sunlight. Some cells are designed to handle sunlight that reaches the Earth's surface, while others are optimized for use in space. Solar cells can be made of only one single layer of light-absorbing material (single-junction) or use multiple physical configurations (multi-junctions) to take advantage of various absorption and charge separation mechanisms.

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| Figure 2 Types of solar cell |

Solar cells can be classified into first, second and third generation cells. The first-generation cells also called conventional, traditional or wafer-based cells are made of crystalline silicon, the commercially predominant PV technology, that includes materials such as polysilicon and monocrystalline silicon. Second generation cells are thin film solar cells, that include amorphous silicon, CdTe and CIGS cells and are commercially significant in utility-scale photovoltaic power stations, building integrated photovoltaics or in small standalone power system. The third generation and fourth generation of solar cells includes a number of thin-film .Many use organic materials, often organometallic compounds as well as inorganic substances. [10]

The following are the different types of solar cells.

## Perovskite solar cell

In 1839, Edmund Becquerel was the first to convert sunlight into electricity. In 1873, Willoughby Smith discovered photoconductivity (PC) in selenium. In 1883, Charles Fritts proposed the first design of PV cell, which was based on the Selenium wafers. The theory of photo-electric effect proposed by Albert Einstein in 1905 explained how light knocks out the electron from the metal surface. Later for this work, he was awarded with the Nobel Prize. In 1918, Jan Czochralski laid the foundation of Silicon (Si) based solar cells by developing a technique to grow single-crystal silicon (Si). In 1954, the birth of PV occurred, when the crystalline silicon-based solar cell was developed in Bell lab, USA that had power conversion efficiency (PCE) of 4.5%. Since then, researchers have been actively searching for a low-cost device structure and some new materials exhibiting the PV effect. As a result, second-generation solar cells came into existence. These cells were basically based upon III-V device existence. These, and CIGs solar cells were introduced in the field of solar photovoltaics. The early 1990s came up with the third generation of solar cells with Dye-sensitized structure. In 2000s Organic Photovoltaic cells (OPV) were introduced. Currently, crystalline silicon solar cells dominate the market, but the factors, such as the requirement of the expensive manufacturing process and costly raw materials are urging researchers to come up with a new PV technology that has the combination of both high efficiency and low-cost manufacturing.[11]

## Perovskite material

The perovskite materials are gaining huge interest among the researchers because of their brilliant PV performance, low-cost raw material, and requirement of easy processing conditions. The PSCs do not require any sophisticated processing conditions; instead, they can be synthesized in laboratories using wet chemistry with the help of simple low-cost techniques, such as spin coating, dip coating, screen printing, dual source evaporation techniques, etc. The perovskite materials can also be grown on a flexible substrate. Despite all the merits, poor device stability and short lifetime are creating hindrances in the path of commercialization of PSCs. The enormous capability of PSCs is evident from the abrupt increment in the power conversion efficiency (PCE) from 3% to 25.2% (28% in tandem architecture) over the past 10 years. while other technologies took nearly 30 years to witness this milestone. Perovskites material incorporated in a solar cell can serve as both, an absorber layer and an efficient charge transport layer. The performance comparison of PSC and Silicon solar cell is illustrated in [Figure 3](#_bookmark2).

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| Figure 3. Comparison of performance of PSC and Silicon solar cell (a) comparison of cost (b) comparison of lifetime (c) comparison of efficiency of silicon, PSC and Si/P tandem cell. |

## Perovskite material properties

The perovskite materials are considered as one of the eminent materials for new generation PV technology because of their unique properties, such as high electron mobility (800 cm2/Vs), high carrier diffusion length (exceeding 1 µm), an bipolar charge transport behavior, high absorption coefficient (greater than 105 cm−1) due to s-p antibonding coupling, low exciton binding energy (less than 10 meV), high photo luminesce (PL) quantum efficiency (as high as 70%), high carrier lifetime (exceeding 300 ns), optimum bandgap, low surface recombination velocity, tunable bandgap, great structural defect tolerance, and amiable grain boundary effect. The main difference between inorganic and organic absorbers is in the exciton type. The organic absorber layer has basically Frenkel type exciton while the inorganic layer has Wannier type. The perovskite material used in solar cells has Wannier type exciton. Therefore, the generated charge carriers behave in the same manner as they do in inorganic material. The properties of perovskite materials are summarized in the

Table **1** and the PCE of various cells to date is shown in Table 2 The properties indeed are adjustable by controlling the shape and size of the constituent particles during fabrication.

**Table 1 Properties of perovskite materials**

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| --- | --- |
| **Properties** | **Value Range** |
| Bandgap | 1.5–2.5 eV |
| Absorption coefficient | 105 cm−1 |
| Exciton binding energy | Less than 10 meV |
| Crystallization energy barrier | 56.6–97.3 kJ mol−1 |
| PL quantum efficiency | 70% |
| Charge carrier lifetime | Greater than 300 nm |
| Relative permittivity | 3 |
| Carrier mobility | 800 cm /Vs |
| Trap-state density | 1010 cm3 (single crystals), 1015–1017 cm3 (polycrystal |

**Table 2 The PCE of various PV cells to date**

|  |  |  |  |
| --- | --- | --- | --- |
| **Solar cell** | **Types** | **Efficiency**[12] | **Developer name** |
| Silicon | Single crystal | 26.1 | ISFH (Institute for Solar Energy Research Hamelin) |
|  | Poly-cry | 22.3 | FhG-ISE (Fraunhofer Institute for Solar Energy Systems) |
|  | Thin film | 21.2 | Solexel |
|  | a-Si:H | 14 | AIST (National Institute of Advanced Industrial Science and Technology) |
|  | Silicon hetero structure | 26.7 | Kaneka (Kaneka Solar Energy) |
| GaAs | Single crystal | 27.8 | LG (LG Electronics) |
|  | Thin-film | 29.1 | Alta device |
| CIGS |  | 23.4 | SolarFron (Solar Frontier) |
| CdTe |  | 22.1 | FirstSolar (First Solar Inc) |
| Quantum dot |  | 16.6 | Univ. Of Queensland |
| Dye-sensitized |  | 11.9 | Sharp (Sharp Solar) |
| Organic |  | 16.5 | SCUT-CSU (South China University of Technology - Central South University) |
| Perovskite |  | 25.2 | KRICT/MIT (Korea Research Institute of Chemical Technology/ Massachusetts Institute of Technology) |

## Historical background of PSCs

The perovskite is basically Calcium titanium oxide (CaTiO3). It is a mineral found by Gustav Rose in the Ural Mountains of Russia in 1939. Count Lev Alekseevich Perovski (1972–1856), a Russian mineralogist further carried the research and thus, the material was named after him as ‘Perovskite’ [13]. In the 1990 s, Mitzi and co-workers investigated the optoelectronic properties of the organic–inorganic perovskites. They reported that the material exhibited strong exciton features, and further suggested that it could be used in the field of LEDs, transistors and solar cells [14]. The phenomenon of PV generation was first seen in this material by Kojima and coworkers. In 2009, they were first to use perovskite material in solar cells by utilizing it as a liquid sensitizer in DSSC configuration. The MAPbI3 and MAPbBr3 (where MA stands for CH3NH3) were used as liquid sensitizers, and the device attained an efficiency of 3.81% and 3.2%, respectively. However, the device was highly unstable and lasted only for a few seconds due to the presence of liquid electrolyte [15]. Park et al. used quantum dots of nanocrystalline material and utilized similar dye-sensitized concepts. They raised the cell efficiency from 3.8% to 6.54%, but the device collapsed after 10 min of successful operation due to the dissolution of MAPbI3 quantum dots into the redox electrolyte solution [16]. Because of the instability raised due to the presence of liquid electrolytes, this configuration did not gain much attention. In 2012, Kim et al. overcame the problem arising due to the presence of liquid electrolytes by fabricating an all-solid-state PSC. The Spiro-OMeTAD was used as a hole transport layer and the device attained an efficiency of 9.7%. This made a remarkable change in the history of the perovskite sensitized solar cells as it not only raised the efficiency but also made a considerable enhancement in the lifetime by withstanding exsitu long term stability test for about 500 h without any encapsulation [17].In 2013, Burschka et al. obtained an efficiency of 15% by using the 2-step sequential deposition technique, and fabricated the cell in planar architecture. They adopted the sequential deposition technique where they first deposited PbI2 layer followed by deposition of CH3NH3I in- stead of processing both of them together. This structure gave a high Jsc (20 mA/cm2) due to the creation of a dense and uniform perovskite layer [18]. In 2014, Im et al, fabricated MAPbI3 based solar cells using two-step solution processing. They attained a high performance by controlling the size of MAPbI3 cuboid, which enabled proper light-harvesting and enhanced charge transportation. They re- ported that the cuboid size depended on the concentration of MAI solution and also upon the exposure time of PbI2 to MAI before spin coating. This group of researchers obtained an improved PSC with an efficiency of 17.01% [19]. Giordano et al. in 2015, improved the electronic properties of mesoporous titania layer (m-TiO2) by the addition of Lithium (Li) in it and attained superior device performance with PCE of 19.3%. The Li doped mesoporous titania layer (m-TiO2) gave better electronic properties and faster electronic trans- portation due to the reduction in electronic trap states. This device exhibited negligible hysteresis loss (less than 0.3%) [20]. In 2015, Yang et al. demonstrated a technique to deposit improved quality FAPbI3 film with (1 1 1) crystallographic orientation, uniform, dense and large microstructures. They used FAPbI3 instead of MAPbI3 and attained power conversion efficiency (PCE) of 20.2% [21].In 2016, Li et al. fabricated a perovskite film with uniform morphology and crystalline behavior by using the vacuum flash solution processing method (VASP). They used FA0.81MA0.15PbI2.51Br0.45 as an absorber layer and attained PCE of 20.5% [22]. In 2016, Bi et al. introduced a new approach for perovskite film fabrication and attained improved electronic property by using a polymer. They improved the growth and nucleation processes by using poly (methyl methacrylate) (PMMA) and attained PCE of 21.6% [23]. Recently, Yang et al. used multiple cations (comprising FA) and mixed halide anion as an absorber layer. They succeeded in reducing the concentration of deep-level defect states by the addition of iodide solution into the organic cation solution. This defect engineering enabled the scientists to achieve an efficiency of 22.1% for small scale and 19.7% in 1 cm2 cell [24].Then came the breakthrough in 2018 when researchers from Chinese Academy of Sciences attained the highest efficiency of 23.3%. Further, in December last year, the maximum efficiency of single-junction silicon solar cell was defeated by Perovskite in tandem architecture along with Silicon by attaining PCE of 28%. The efficiency of single-junction PSC was raised to 23.7% and high Voc closer to the bandgap was attained by tailoring a high quality perovskite layer offering minimum recombination loss [25]. Currently, the highest efficiency of single-junction PSC has reached 25.2% by KRICT (South Korea). They used a highly efficient hole conductor layer, Nickel oxide (Nix), which is deposited over a large area. NiOx is an inexpensive material and it has ability to withstand high temperatures up to 70 °C. The layers were deposited by rotatory coating method [26]. The advancement in the progress of PSCs in past years is shown in Fig. 2.

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| Figure 4 Recorded Power Conversion Efficiency of the PSC in progressive years. |

It is seen that, as compared to silicon solar cells the PSCs exhibit rapid development. The details of PSCs are enclosed in Table 3. It is important to note that all the leading perovskite solar cells (PSCs) have the incorporation of Formamidinium (FA) as cation which is also believed to be more stable than Methylammonium (MA) and also has an optimal red-shifted bandgap. However, the size of FA is very large, which produces lattice distortion [27].Now the power conversion efficiency (PCE) of perovskite-based solar cells is expected to reach up to 30% by 2020. Apart from the extensive research going in efficiency hike, work is also being done to increase the stability and lifetime of perovskite solar cells (PSC). Gracini et al. engineered an ultra-stable 3D/2D CH3NH3PbI3 perovskite junction that had PCE of 13% and was stable for one year [28]. Hwang et al. used a layer of Polytetrafluoroethylene, a hydrophobic polymer over the top of the PSC and noticed a minimal degradation for over 30-days in ambient air condition [19]. From all these works, it is concluded that it is one of the most rapidly growing PV cells with advancements taking place to date.

**Table 3 Increment in efficiency in a progressive year**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **PCE (%)** | **Voc(v)** | **Jsc** | **FF** | **Device configuration** | **Year** |
| 3.8 | 0.61 | 11 | 0.57 | Pt-FTO/Electrolyte solution/CH3NH3PbI3/TiO2 | 2009 |
| 6.54 | 0.706 | 15.82 | 0.586 | Pt/Liquid Electrolyte/CH3NH3PbI3 (QD) / TiO2/FTO | 2011 |
| 9.7 | 0.888 | 17 | 0.62 | Au/spiroOMeTAD/CH3NH3PbI3/mTiO2/FTO | 2012 |
| 15 | 0.993 | 20 | 0.73 | Au/spiroMeOTAD/TiO2/CH3NH3PbI3/Glass | 2013 |
| 17.01 | 1.056 | 21.64 | 0.741 | Au/spiro-MeOTAD/Cuboid MAPbI3/ MAPbI3/m-TiO2/c-TiO2/FTO | 2014 |
| 19.3 | 1.114 | 23 | .74 | Au/Spiro-OMeTAD/Perovskite/m-LiTiO2/ Perovskite/ FTO | 2014 |
| 20.2 | 1.06 | 24.7 | 0.775 | Au/PTAA/Perovskite/(bl/m-TiO2)/FTO | 2015 |
| 20.5 | 1.1143 | 23.24 | 0.759 | Au/Spiro-OMeTAD/Perovskite/m-TiO2/ bl-TiO2/ FTO | 2016 |
| 21.6 | 1.14 | 23.7 | .78 | Au/Spiro-OMeTAD/Perovskite/m-iO2/ Perovskite/bl-TiO2/ FTO | 2016 |
| 22.1 | 1.11 | 25 | 0.817 | FTO/TiO2/m TiO2/perovskite composite layer/perovskite upper layer/PTAA/Au | 2018 |
| 22.7 | 1.14 | 24.92 | 0.792 | FTO/d-TiO2/mp-TiO2/NBH/P3HT/Au | 2019 |

## Structural properties of hybrid organic-inorganic perovskite materials

The Perovskite materials comprise the crystal structure similar to Calcium Titanate (CaTiO3) and it follows the general formula of ABX3 (where X is generally Oxygen, Nitrogen, Carbon or Halogen). Halide perovskites are of two types (i) Alkali halide-based perovskite (ii) Organic-inorganic halide-based perovskite. The Alkali halide-based perovskite comprises of monovalent alkali cation (A) as Cs+, Rb+, K+, Na+ and Li+, divalent cation (B) as (Pb2+, Sn2+, Ge2+) and halogen anions (X) as Cl−, Br−, I−, F−. Organic-inorganic halide based perovskite has organic monovalent cation (A) as CH3NH3+, CH3CH2NH3+, NH2CHNH2+ [29]. Where ‘A’ ion having coordinate (0.0, 0.0, 0.0) in the crystal coordinate system and ‘B’ having coordinate (0.5, 0.5, 0.5) both represent cationic radii, with the size of A usually greater than B, and ‘X’ represents anionic site with coordinate (0.5, 0.5, 0) The cations ‘A’ and ‘B’ coordinates with 12 and 6 ‘X’ anions creating cuboctahedra and octahedral geometries respectively. This halide based perovskite has attractive electrical, optical and magnetic properties that enable users to apply them in the field of solar cells [30]. Ideal perovskite structure has the highest symmetry possessing cubic structure as shown in, Figure the BX6 octahedral network occupies the corner of the structure while A occupies the interstices. This BX6 octahedral network plays a vital role in the determination of phase transition, bandgap and transport properties. The perovskite formation tendency can be depicted by using Goldschmidt tolerance factor (t) which is given by

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|  |  | (1) |
|  |  | (2) |

where RA, RB, and Rx represent ionic radii of A, B cation and X anion respectively. The value of the tolerance factor lies between 0.88 and 1.1 for a stable crystal structure of perovskite. It is usually expected that perovskite is stable if ‘t’ lies within the specified range, but it is also seen that perovskite is not stable even if ‘t’ is in the range of 0.8–0.9 [31] . An additional consideration for perovskite formation is taken into account, with the octahedral factor (μ), which is given by Eq. (2). It is used to determine the distortion and stability of the perovskite structure. The perovskite is stabilized for an octahedral factor ranging from 0.45 to 0.89 [32]. The most common absorber material used for PSC is methylammonium lead trihalide (MAPbI3 where X is the halide which can be Cl, Br or I). The unit cell parameters increase from 5.68 to 5.92 to 6.27Ȃ as the size of the halide atom increase from Cl to Br to I. However, the aspherical shape and larger size of Methylammonium (MA) leads to the distortion in the network leading to phase transition with a decrease in the temperature, For T < 160 K, the orthorhombic structure, for 162.2 K < T < 327.4 K tetragonal structure, and for T > 327.4 K cubic structure is observed. The bandgap of methylammonium lead halide usually lies within the range of 1.5–2.3 eV, where MAPbI3 is a direct bandgap material with a bandgap of 1.55 eV approximately, whereas MAPbBr3 has a comparatively wider bandgap of 2.3 eV for 800 nm absorption onset. FAPbI3 (where FA is Formamidinium) shows comparatively narrower bandgap of 1.48 eV, signifying larger current extraction when employed as the absorber layer, but this material has shown lower stability. The structural properties of methylammonium lead halide also show variation depending upon the type of halogen atom used. On using smaller sized Br− instead of I− reduces the lattice constant thereby transiting into a more stable cubic phase. This fact is also evident by examining the crystal structure of MAPbI3 and MAPbBr3 which crystallize in the tetragonal form and cubic form respectively.

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| Figure 5 ABX3 perovskite structure showing (left) BX6 octahedral and (right) AX12 cuboctahedra geometry. |

## Device architecture

Since the advent of the first PSC in dye-sensitized architecture, numerous works have been carried out in order to enhance the device stability and efficiency. The advancements in device architecture were one of the performance deciding factors in the evolution of the PSCs. In 2009, the perovskite was first used as a liquid electrolyte in dye-sensitized solar cell (DSSC) configuration; however, this configuration was not further used due to the low efficiency (3.8%) and unstable nature of the device due to the presence of the liquid electrolyte. Then this liquid electrolyte was replaced by Im et al. and the first solid-state PSC came into limelight, the implementation of the solid hole transport layer (Spiro-OMeTAD) was done, which not only improved the device efficiency (10%) but exhibited successful operation for 500 h also. The PSCs basically has five components: (i) a metal-based cathode, (ii) Hole transport layer (HTL) (iii) absorber layer (iv) Electron transport layer (ETL) (v) Transparent Conductive Oxide (TCO). The transport layer plays a vital role in deciding the performance of a PSC. The function of HTL is to collect holes from the absorber layer and transport it towards the cathode and block electrons. For any material to function as a hole transport material (HTM), it must have its highest occupied molecular orbital (HOMO) slightly higher than that of the perovskite absorber layer. Various HTMs used are: Spiro-OmeTAD, NiO, CuO, CuI, Cu2O, PTAA, etc. The function of ETL is to collect electrons from the absorber layer and transport it towards anode and block holes. For a material to be used as an electron transport material (ETM), it must have its HOMO and LUMO (Lowest unoccupied molecular orbital) levels higher than that of the perovskite absorber layer. The ETMs must possess high transmittance in UV–Vis region so that all the photons pass through it, and are maximum absorbed by the absorber layer. Various ETMs used are: TiO2, SnO2, SiO2, ZnO, etc. Transport layers must exhibit the properties, such as good thermal stability, non-toxicity and must be resistive towards external degrading factors. Currently, the efficiency of the PSC is raised up to 25.2% due to the enormous work carried to improve the device performance. This evolution in device performance. The various architectures like mesoporous, super- mesoporous, regular and planar came into existence. A brief discussion on the evolution of device architecture along with its performance details is discussed in the following section.

### Dye-sensitized structure

In 2009, the first PSC was fabricated by Kojima and coworkers. They used DSSC architecture. The perovskite sensitizer was used over TiO2, which acted like a liquid electrolyte. They used fluorine-doped SnO2 transparent conductive glass (FTO) as a substrate, transparent conductive oxide as a hole blocking layer, a counter electrode, a compact thin TiO2 (c-TiO2 and a micron thick mesoporous TiO2 (m-TiO2), which was sensitized over MAPbI3 and MAPbBr3 perovskite formed by spin coating the precursor solution created by using the equimolar concentration of methylammonium and lead halide. MAPbI3 sensitized PSC exhibited the best performance in terms of efficiency, PCE = 3.81%, Voc = 0.61v, FF = 57%, Jsc = 11 mA/cm2 and the solar cell using MAPbBr3 sensitizer attained comparatively higher photo- voltage with Voc = 0.91v, PCE = 3.13%, FF = 59%, Jsc = 5.57 mA/ cm2. Figure 6(a) compares the spectra of IPCE PV cell of MAPbI3/TiO2 and MAPbBr3/TiO2 and (b) represents the I-V characteristic of MAPbI3 and MAPbBr3 PV cells under the exposure of 1.5AM irradiation.

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| Figure 6 (a) IPCE action spectra for photoelectrochemical cells using CH3NH3PbBr3/TiO2 (solid line) and CH3NH3P bI3/TiO2 (dashed line). |

The current density in MAPbI3 is higher because it has a comparatively lower bandgap (1.5 eV) than MAPbBr3 (2.3 eV). This work clearly indicated the potential of hybrid organic–inorganic perovskite materials (HIOPs) towards the PV application. However, this device was not further used because of poor device stability and low efficiency due to the presence of liquid electrolyte [15]. In 2011, Im et al., used perovskite sensitized cell in DSSC configuration using 2–3 nm of MAPbI3quantum dots in order to coat the 3.6 µm thick m-TiO2 layer. This device exhibited almost double the PCE obtained earlier with PCE = 6.54%, VOC = 0.706v, FF = 58.6% and Jsc = 15.82 mA/cm2. This work indicated the high absorption coefficient of the perovskite (MAPbI3) materials which is one of the most desirable features of materials to be used for PV application. However, the device performance was reduced by 80% as perovskite quantum dots dissolved in the liquid electrolyte after 10 min in continuous illumination.

### Solid state mesoscopic structure

The instability raised due to the usage of liquid electrolyte was overcome by Hui-Seon Kim and co-workers in 2012. They reported the first solid-state mesoscopic structure heterojunction solar cell and attained a PCE of 9.7%. The view of the device cross-section is shown in [Figure 7](#_bookmark10). This group used nanoparticles of MAPbI3 as a light harvester, and deposited microns thick m-TiO2 that filled the pores with the hole transport material, (spiro-MeOTAD). This created a direct contact between the hole transport layer and the sensitizer, whereas the rest of the HTL served as a capping layer over m-TiO2, shown in [Figure 7](#_bookmark10)(c). This capping layer further prevented shunting between ETMs and back contact. Under the illumination of AM-1.5, the device exhibited higher efficiency and better stability with PCE = 9.7%, Voc = 0.88v, FF = 62%, Jsc = 17 mA/cm2. The usage of the solid-state hole conductor dramatically improved the efficiency and stability by operating successfully for 500hr of continuous illumination. High-performance PSCs can be fabricated by reducing the thickness of the mesoporous layer which is beneficial for better pore filling [33].Mahmood et al. reported a PSC with a mesoporous ZnO film (440 nm thick). They adopted electro spraying process to fabricate and the device attained PCE = 10.8%, Voc = 1.01v, FF = 67%, Jsc = 16 mA/cm2 [34]

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| Figure 7 (a) Real device picture (b) Cross-sectional view of the device (c) SEM image of the cross-section (d) Active layer-underlayer-FTO interfacial junction structure. |

### Meso-superstructure structure

Based upon the previous work, Henry J. Snaith proposed a modified structure of the device where the m-TiO2 was replaced by an insulating layer of m-Al2O3. They demonstrated that Al2O3 does not inject a photoexcited electron but acts as a scaffold layer. The primary intention of this work was to study the behaviour of electron transports through the perovskite layer and to examine the importance of m-TiO2 in the functioning of PSC. The result came out to be surprising as not only the charge transport occurred at a faster rate but also the photocurrent was increased by the replacement. Their work revealed the fact that the phenomenon of charge collection was ten times faster with this modification. The open-circuit voltage arose from 200 to 300 mv, thereby increasing the PCE up to 10.9%, Voc = 0.98v, FF = 63%, Jsc = 17.8 mA/cm2. James M. Ball and co-workers in 2013, fabricated a PSC using mixed halide, MAPbI3-xClx absorber and lowered the processing temperature from 500 to 150 °C for the first time and attained the PCE = 12.3%, Voc = 1.02v, FF = 67%, Jsc = 18 mA/cm2. As earlier works suggested that the porous electron transport layer requires high-temperature sintering, so here researchers investigated its necessity by processing the absorber layer at a lower temperature. This led to the possibility of fabrication of PSCs upon a flexible substrate and multifunctional device architecture. It was seen that even processing at low temperature, all the primary functions of solar cells were fulfilled: absorption, carrier generation and collection along with minimum recombination loss. Therefore, this work suggested that the metal oxide scaffold which was fabricated over the perovskite layer could be processed in low temperature which further implied the compatibility of PSCs over a flexible substrate and also in multijunction architecture

### Regular structure

The favorable results obtained by mesosuperstructured configuration (MSSC) influenced the researchers to work more on this domain to acquire better results. After the properties like low trap density and longer diffusion lengths in HIOPs were revealed, it was indicated that thicker perovskite film could be used by replacing ETL in PSCs. Then the thickness of the absorption layer was increased expecting that it will improve the absorption at longer wavelength photon and will avoid the shunting of the electrodes also. Thus, a device was created based upon the MSSC structure but it had a comparatively wider perovskite layer. This structure grabbed the attention of researchers across the world and was termed as a ‘Regular Structure’ because of the gained popularity. Heo et al. in 2013, proposed this configuration which had pillared perovskite structure, where the pores of the m-TiO2 were completely filled with MAPbI3 thereby, forming MAPbI3 pillars. These pillars were further coated with thin polytriarylamine (PTAA) as a hole transport material (HTM) using Au as an electrode. The device achieved the PCE = 12% Voc = 0.997v, FF = 72.7%,Jsc = 16.5 mA/cm2[35].However, the device performance was limited due to the poor surface morphology. Then further modification was done in this structure by Burschka et al. by the implementing thicker perovskite film over thinner m-TiO2 layer, a thin (50 nm) perovskite capping layer was also used over the top of m-TiO2 (300 nm) layer using the two-step deposition method. They attained PCE = 15%, Voc = 0.993v, FF =, Jsc = 20 mA/cm2 The same fabrication technique was later adopted by Im et al. who used 100 nm m-TiO2 layer and raised the width of the capping layer to 150 nm and obtained comparatively better results with PCE = 17%, Voc = 1.056v, FF = 74%, Jsc = 21.64 mA/cm2 .A modification was further suggested by Giordano et al. when they doped the TiO2 layer with Lithium and a thicker capping layer with thickness of 300 nm and attained PCE = 19.3%, Voc = 1.114v, FF = 74%, Jsc = 23 mA/cm2. Zhang et al. modified the film fabrication technique by using external- electric-field (EEF) supported the annealing process instead of using conventional annealing technique to enhance the performance of the PSC. Under the optimized condition, in electric field (E) of 2.5 v/μm, PCE of regular PSC improved from 16.77% to 19.18% and that of in- verted PSC from 15.33% to 17.26%. This modification caused the better carrier extraction and superior film quality [36]

### Planar n-i-p heterojunction structure

This architecture was analogues to the thin film inorganic solar cells. The device structure had TCO cathode, an n-type ETL, intrinsic perovskite layer, p-type HTL, and a metal anode. This configuration eliminated the mesoporous layer from the regular structure. In 2012, Snaith et al. proposed the planar heterojunction PSC with mixed halide MAPbI3-XClx absorber layer, but unfortunately due to incomplete film coverage, shunting occurred and the device attained low PCE of 1.8%. Further to improve the film quality, Snaith et al. in 2013 came up with a dual-source co-evaporation of PbCl2 and MAI and deposited the MAPbI3-XClx layer over c-TiO2 layer and attained PCE = 15%, Voc = 1.07v F = 67%, Jsc = 21.5 mA/cm2.The maximum efficiency in this architecture to date was given in 2018 by Dong Yang co-worker. They proposed a high efficiency planar n-i-p structure using EDTA complex tin oxide (SnO2) as ETL, FAPbI3 as the absorber layer with a slight amount of Cs doping for improvement of phase stability, Spiro-OMeTAD as hole transport layer (HTL) and attained PCE = 21.6%, Voc = 1.11v, FF = 79.2%, Jsc = 24.55 mA/cm2 Mustafa Haider et al. in 2018 used a new HTL in this configuration whose schematic is shown in [Figure 9](#_bookmark12). They used nickel phthalocyanine (NiPc) as a HTL and claimed it to be stable and cost-effective in comparison to spiro-OMeTAD. The device attained PCE = 12.1%, Voc = 0.94v, FF = 73%, Jsc = 17.64 mA/cm2. The device exhibited better stability by retaining 80% of the efficiency in the atmosphere upto 38 days. The comparison of the stability of the device with NiPc and Spiro-OMeTAD is shown in Figure 8. It is well reported that PSCs with organic HTMs although attain quite high initial PCE but undergoes rapid degradation. The PSCs with inorganic HTMs not only attain good PCE but also show comparatively better device stability. The most stable behavior is exhibited by carbon based HTMs Xingyue et al. demonstrated carbon-based planar n-i-p PSC with ETL as Ni-doped rutile TiO2 and HTL as copper phthalocyanine (CuPc). They noticed that the Fermi level of ETL shifted upwards upon doping with Ni.

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| Figure 8**.** Normalized efficiency decay curves of devices based on NiPc and commercial spiro-OMeTAD in air. |

It also increased the carrier mobility and conductivity with enhanced film morphology, thereby enhancing the charge transportation and extraction. This device displayed PCE of 17.46% which is claimed to exhibit the best performance among all the carbon-based PSCs, other parameters being Jsc = 22.41 mA/cm2, FF = 0.726 and Voc = 1.073v. The device retained its 97% of the initial efficiency for 1200 h [37].

### Inverted planar structure

Along with the planar n-i-p structure and regular structure, the researchers from the PV community adopted a configuration from the field of organic solar cells, the planar p-i-n heterojunction structure. This configuration is usually termed as an inverted structure as it has a revere sequence of ETLs and HTLs from the regular structure. This structure has an anode (TCO), a p-type HTL, perovskite intrinsic layer, an n-type ETL and a metal cathode. In 2013, Jeng et al. fabricated planar p-i-n PSC by using MAPbI3 as an active layer, BCP and Polypolystyrene sulfonate (PEDOT: PSS) as electron transport and hole Transport material respectively with the device structure ITO/PEDOT: PSS/MAPbI3/C60/bathocuproine (BCP)/Al. The device exhibited PCE of 1.6% which was further raised to 3.9% upon the re- placement of C60 with phenyl-C61-butyric acid. Later Snaith et al.

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| Figure 9**.** (a) Schematic of n-i-p planar structure using NiPc as HTL (b) Normalized efficiency decay curves of devices based on NiPc and commercial Spiro-OMeTAD in air. |
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| Figure 10**.** Device architecture cross section: (a) DSSC (b) Mesoporous (b) Supermesostructure (c) Regular (d) Planar nip (e) Planar pin (inverted planar) structure. |

acquired PCE of 9.8% with the incorporation of mixed halide and re- placing the HTL by PC61BM with the structure of FTO/PEDOT:PSS/ MAPbI3-XClx /PC61BM /TiO2/Al [38].In 2018, Jie Tang et al. formed a high performance inverted planar structure using a new HTL and obtained better results by achieving better transparency and low loss of photon flux. They used NiO nano- crystals prepared by the solvothermal method as HTL, PCBM/BCP as ETL, MAPbI3 as an absorber layer and Au as an anode. They varied the thickness of the NiO HTLs to 30 nm, 55 nm, 70 nm, 100 nm, and 170 nm and obtained the best performance in the structure with NiO layer thickness of 55 nm. The device attained PCE = 15.47%, Voc = 1.06v, FF = 75.02% and Jsc = 19.41 mA/cm2. They also compared two HTLs PEDOT: PSS and NiO nanocrystal and claimed NiO nanocrystal to exhibit superior performance [39].Schematic illustration of the above-mentioned architectures is shown in [Figure 10](#_bookmark13).

# Solar Cell Physics

Solar cells and photodetectors are devices that convert an optical input into current. A solar cell is an example of a photovoltaic device, i.e., a device that generates voltage when exposed to light. The photovoltaic effect was discovered by Alexander-Edmond Becquerel in 1839, in a junction formed between an electrode (platinum) and an electrolyte (silver chloride). The first photovoltaic device was built, using a Si pn junction, by Russell Ohl in 1939. The functioning of a solar cell is similar to the photodiode (photodetector). It is a photodiode that is unbiased and connected to a load (impedance). There are three qualitative differences between a solar cell and photodetector

1. A photodiode works on a narrow range of wavelength while solar cells need to work over a broad spectral range (solar spectrum).
2. Solar cells are typically wide area devices to maximize exposure.
3. In photodiodes the metric is quantum efficiency, which defines the signal to noise ratio, while for solar cells, it is the power conversion efficiency, which is the power delivered per incident solar energy. Usually, solar cells and the external load they are connected to are designed to maximize the delivered power.

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| Figure 11 : Typical solar spectrum at the top of the atmosphere and at sea level. The difference is the radiation absorbed/scattered by the atmosphere. The spectrum of a black body at 5250°C is also superimposed and used for modelling. Modified from <http://en.wikipedia.org/wiki/Sunlight> |

## Solar Spectrum

The solar spectrum typically extends from the IR to the UV region, wavelength range from 3 m to 0.2m. But the intensity is not uniform. A typical solar spectrum, as a plot of spectral irradiance vs. wavelength, is shown in Figure 11.The area under the curve gives the total areal intensity and this is approximately 1.35 kW m-2. The solar spectrum can be approximated by a black body radiation curve at temperature of approximately 5250°C. There is also a difference in the spectra measured at the top of the atmosphere and at the surface, due to atmospheric scattering and absorption. The path length of the light in the atmosphere depends on the angle, which will vary with the time of day. This is given by the air mass number (AM), which is the secant of the angle between the sun and the zenith (sec ). AM0 represents the solar spectrum outside the earth's atmosphere. AM1 is when the angle is zero, i.e. sun is at the zenith and it has an intensity of 0.925 kW m-2. AM2 is when sun is at angle of 60° and its intensity is 0.691 kW m-2. The different spectra are plotted in Figure 12.

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| Figure 12. Typical solar spectrum for different air mass conditions. The plot shows AM0 (spectrum outside the atmosphere), AM1 (at the zenith), and AM2 (at an angle of 60◦). This again can be modelled by black body spectrum, at various temperatures. Adapted from Physics of semiconductor devices - S.M. Sze. |

The data can also be plotted as a photon flux density i.e., number of photons per unit energy per unit area per unit time. This is shown in Figure 13.

## Solar cell working principle

A simple solar cell is a pn junction diode. The schematic of the device is shown in Figure 14 The n region is heavily doped and thin so that the light can penetrate through it easily. The p region is lightly doped so that most of the depletion region lies in the p side. The penetration depends on the wave- length and the absorption coefficient increases as the wavelength decreases. Electron hole pairs (EHPs) are mainly created in the depletion region and due to the built-in potential and electric field, electrons move to the n region and the holes to the p region. When an external load is applied, the excess electrons travel through the load to recombine with the excess holes. Electrons and holes are also generated with the p and n regions, as seen from Figure 14 The shorter wavelengths (higher absorption coefficient) are absorbed in the n region and the longer wavelengths are absorbed in the bulk of the p region. Some of the EHPs generated in these regions can also contribute to the current. Typically, these are EHPs that are generated within the minority

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| Figure 13.: Solar spectrum plotted as photon flux density vs. energy for AM0 and AM1.5. The difference in the spectra is due to the absorption/scattering by the atmosphere. Adapted from Physics of semiconductor devices - S.M. Sze. |

carrier diffusion length, Le for electrons in the p side and Lh for holes in the n side. Carriers produced in this region can also diffuse into the depletion region and contribute to the current. Thus, the total width of the region that contributes to the solar cell current is wd+Le+Lh, where wd is the depletion width. This is shown in Figure 15 The carriers are extracted by metal electrodes on either side. A finger electrode is used on the top to make the electrical contact, so that there is sufficient surface for the light to penetrate. The arrangement of the top electrode is shown in Figure 16

Consider a solar cell made of Si. The band gap, Eg, is 1.1 eV so that wavelength above 1.1 µm is not absorbed since the energy is lower than the band gap. Thus, any λ greater than 1.1 µm has negligible absorption. For λ much smaller than 1.1 µm the absorption coefficient is very high and the EHPs are generated near the surface and can get trapped near the surface defects. So, there is an optimum range of wavelengths where EHPs can contribute to photocurrent, shown in Figure 15

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| Figure 14 : Principle of operation of a pn junction solar cell. Radiation is absorbed in the depletion region and produces electrons and holes. These are separated by the built-in potential. Depending on the wavelength and the thickness different parts of the device can absorb different regions of the solar spectrum. Adapted from Principles of Electronic Materials - S.O. Kasap |
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| Figure 15 : Photogenerated carriers in a solar cell due to absorption of light. w is the width of the depletion region, while Lh and Le are minority carrier diffusion lengths in the n and p regions. The amount of absorption reduces with depth and hence the depletion region must be close to the surface to maximize absorption. This is achieved by having a thin n region. Adapted from Principles of Electronic Materials - S.O. Kasap |

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| Figure 16 : Finger electrodes on a pn junction solar cell. The design consists of a single bus electrode for carrying current and finger electrodes that are thin enough so that sufficient light can be absorbed by the solar cell. Adapted from Principles of Electronic Materials - S.O. Kasap |
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| Figure 17 : (a) pn junction solar cell under illumination with an external load. The equivalent circuit (b) without and (c) with an external load. The illumination causes a photocurrent to flow through the external circuit. When an external load is applied the potential drop across it creates a forward bias current, that opposes the photocurrent. Adapted from Principles of Electronic Materials - S.O. Kasap |

## Solar cell I-V characteristics

It possible to calculate the I-V characteristics of the solar cell by considering its equivalent circuit. The I-V characteristics depend on the intensity of the incident radiation and also the operating point (external load) of the cell. Consider a pn junction solar cell under illumination, as shown in Figure 17 If the external circuit is a short circuit (external load resistance is zero) then the only current is due to the generated EHPs by the incident light. This is called the photocurrent, denoted by Iph. Another name for this is the short circuit current, Isc. By definition of current, this is opposite to the photo current and is related to the intensity of the incident radiation, Iop, by

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|  |  | (3) |

where k is a constant and depends on the particular device. k is equivalent to an efficiency metric that measures the conversion of light into EHPs.

Consider the case when there is an external load R, as shown in Figure 17. The equivalent circuit for this case is shown in Figure 18 There is a voltage across the external load, given by V=IR. This voltage opposes the built in potential and reduces the barrier for carrier injection across the junction. This is similar to a pn junction in forward bias, where the external bias causes injection of minority carriers and increased current. This forward bias current opposes the photo current generated within the device due to the solar radiation. This is because Iph is generated due to electrons going to the n side and holes to the p side due to the electric field within the device,

i.e. drift current while the forward bias current is due to diffusion current

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| Figure 18 : (a) A solar cell connected to an external load (b) Equivalent circuit, with a constant current source, a forward biased pn junction and the external load. The current from the forward biased pn junction opposes the constant current source. |

caused by the injection of minority carriers. Thus, the net current can be written as

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|  |  | (4) |
|  |  | (5) |
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where Id is the forward bias current and can be written in terms of the reverse saturation current, Is0 and external voltage, V. The overall I-V characteristics is plotted in Figure 19In the absence of light, the dark characteristics is similar to a pn junction I-V curve. The presence of light (Iph) has the effect of shifting the I-V curve down. From Figure 19it is possible to define a photo current Iph, which is the current when the external voltage is zero and an open circuit voltage, Voc, which is the voltage when the net current in the circuit is zero. Using equation [(4),](#_bookmark13) Voc can be calculated as

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|  |  | (6) |
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Higher the photon flux, higher is the value of Iph (by equation (3)) and higher the value of Voc. Similarly, lower Is0 can also cause higher Voc. Since Is0 is the reverse saturation current for the pn junction it is given by

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|  |  | (7) | |
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| Figure 19 : I - V characteristics of Si pn junction solar cell under dark conditions and under illumination with light of increasing intensity. Short circuit current and open circuit voltage both increase with increasing illumination. Adapted from Principles of Electronic Materials - S.O. Kasap | | |

The reverse saturation current can be lowered by choosing a material with a higher band gap, Eg, which will cause ni to be lower. But this will also reduce the range of wavelengths that can be absorbed by the material, which will have the effect of lowering Iph. The total power in the solar cell circuit is given by

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|  |  | (8) |

For maximum power, its derivative with respect to voltage should be zero. This gives a recursive relation in current and voltage.

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|  |  | (9) |
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This can be seen from Figure 20. The area under the curve, corresponding to Im and Vm, gives the maximum power. From equation (9) it can be seen that the maximum power is directly proportional to Voc and can be increased by decreasing Is0. This means that smaller ni and a larger Eg are favourable but the trade-off is that less radiation is absorbed.

## Solar cell materials and efficiency

Conventional solar cells are made of Si single crystal and have an efficiency of around 22-24%, while polycrystalline Si cells have an efficiency of 18%. A schematic representation of such a cell is shown in Figure 16. The efficiency of the solar cell depends on the band gap of the material and this is shown in Figure 21. Polycrystalline solar cells are cheaper to manufacture but have a lower efficiency since the microstructure introduces defects in the material that can trap carriers. Amorphous solar cells have an even lower efficiency but can be grown directly on glass substrates by techniques like sputtering so that the overall cost of manufacturing is lowered. There are also design improvements in the solar cell that can enhance the efficiency. PERL (passivated emitter rear locally diffused) cells, shown in figure 12, have an efficiency of 24% due to the inverted pyramid structure etched on the surface that enhances absorption.

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| Figure 20 : I-V curve for a solar cell with maximum power indicated by the shaded area. The corresponding voltage and current are Vm and Im. The value depends on the external load applied. Adapted from Physics of semiconductor devices - S.M. Sze. |
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| Figure 21 : Solar cell efficiency as a function of band gap of the semiconductor material. There is a particular band gap range where the efficiency is maximum. Adapted from Physics of semiconductor devices - S.M. Sze. |
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| Figure 22 : Si solar cell with an inverted pyramid structure to enhance absorption of the incoming radiation. These are called PERL cells. The inverted pyramid structure causes multiple reflections at the surface, which help in absorption of the incoming radiation. Adapted from Principles of Electronic Materials - S.O. Kasap |

Typical solar cells are made of the same material so that the pn junction is a homojunction. Some solar cell materials and their efficiencies are summarized in table 1. A comprehensive state of current research in different solar cell technologies and their efficiency is available in Figure 23. Heterojunction solar cells are also possible and they have the advantage of minimizing absorption in regions other than the depletion region, but overall cost increases because of the use of different materials and the tight processing conditions needed to produce defect free interfaces. A schematic of such a cell based on GaAs/AlGaAs is shown in Figure 24. The shorter wavelengths are absorbed by the AlGaAs layers while the longer wavelengths, with higher penetration depths, are absorbed by the GaAs layer. This leads to an overall efficiency of around 25%, see table 1. It is also possible to have a homojunction solar cell but with a passivating layer of another material at the surface to reduce defects. This is shown in Figure 25. The surface passivating layer removes the dangling bonds and minimizes carrier trapping. The passivation layer is a thin layer of a higher band gap material to minimize absorption. Similarly, amorphous semiconductor materials like Si and Ge also have a passivating layer of H, a-Si:H or a-Ge:H, to reduce dangling bonds. Another way of improving solar cell efficiency is to have more than one cell in tandem. These are called tandem solar cells and a schematic is shown in Figure 26. These consist of two pn junction solar cells, with the first one having a higher band gap than the second. Thus, the shorter wavelengths can be absorbed in cell 1, see Figure 26, while the longer wavelengths are absorbed in cell 2. The advantage is that a larger portion of the solar radiation is used so that tandem cells have high efficiency, see table1, but it also adds a layer of complexity in growth and increases cost. Tandem cells can also be made using amorphous Si:H and Ge: H. These are cheaper to make and more efficient than individual amorphous solar cell devices.[40]

**Table 4 : Some common solar cell materials and their characteristics. Adapted from Principles of Electronic Materials - S.O. Kasap**

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| **Semiconductor** | **Eg (eV )** | **Voc (V )** | **Jsc(mA cm-2)** | **η (%)** | **Comments** | |
| Si, single crystal | 1.1 | 0.55-0.7 | 42 | 16-24 | Single crystal, PERL | |
| Si, polycrystaline | 1.1 | 0.5-0.65 | 38 | 12-19 |  | |
| Amorphous Si:Ge:H film |  |  |  | 8-13 | Amorphous films with tandem structure, large-area fabrication | |
| GaAs,Single crystal | 1.42 | 1.02 | 28 | 24-25 |  | |
| GaAIAs/GaAs,tandem |  | 1.03 | 27.9 | 25 | Different band gap materials\ in tandem increases absorption efficiency | |
| GaInP/GaAs,tandem |  | 2.5 | 14 | 25-30 | Different band gap materials in tandem increases absorption efficiency | |
| CdTe,Thin film | 1.5 | 0.84 | 26 | 15-16 |  | |
| InP, single crystal | 1.34 | 0.87 | 29 | 21-22 |  | |
| CuInSe2 | 1.0 |  |  | 12-13 |  | |
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| Figure 23 : Efficiency of various research solar cells. The latest diagram is available at <http://www.nrel.gov/ncpv/> | | | | | |
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| Figure 24 : (a) GaAs/AlGaAs based heterojunction solar cell. (b) Energy band alignment across the junction. AlGaAs has the higher band gap and can absorb higher energy radiation while GaAs can absorb the lower energy portion of the solar spectrum. Adapted from Principles of Electronic Materials - S.O. Kasap | | | | | |
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| Figure 25 : Schematic of a GaAs based homojunction solar cell with a sur- face passivating layer to minimize surface recombination. This layer should be thin and have a high band gap to minimize absorption. Adapted from Principles of Electronic Materials - S.O. Kasap | | | | | |
|  | | | | | |
| Figure 26 : Tandem solar cells. The higher band gap cell is closer to the illuminating surface to absorb the short wavelengths and the smaller band gap cell is at the interior to absorb the longer wavelengths. Adapted from Principles of Electronic Materials - S.O. Kasap[40] | | | | | |

# Materials and Methodology

## Introducing SCAPS

SCAPS is a one-dimensional solar cell simulation program developed at the department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium. Several researchers have contributed to its development: Alex Niemeyer’s, Marc Burgelman, Koen Decock, Johan Verschraegen, Stefaan Degrave. SCAPS is originally developed for cell structures of the CuInSe2 and the CdTe family. Several extensions however have improved its capabilities so that it is also applicable to crystalline solar cells (Si and GaAs family) and amorphous cells (a-Si and micromorphous Si). An overview of its main features is given belowup to 7 semiconductor layers

* almost all parameters can be graded (i.e., dependent on the local composition or on the depth in the cell):
* Eg, χ, ε, NC, NV, vthn, vthp, µn, µp, NA, ND, all traps (defects) Nt
* recombination mechanisms: band-to-band (direct), Auger, SRH-type
* defect levels: in bulk or at interface; their charge state and recombination is accounted for
* defect levels, charge type: no charge (idealisation), monovalent (single donor, acceptor), divalent (double donor, double acceptor, amphoteric), multivalent (user defined)
* defect levels, energetic distributions: single level, uniform, Gauss, tail, or combinations
* defect levels, optical property: direct excitation with light possible (impurity photovoltaic effect, IPV)
* defect levels, metastable transitions between defects
* contacts: work function or flat-band; optical property (reflection of transmission filter) filter
* tunnelling: intra-band tunnelling (within a conduction band or within a valence band); tunnelling to and from interface states
* generation: either from internal calculation or from user supplied g(x) file
* illumination: a variety of standard and other spectra included (AM0, AM1.5D, AM1.5G, AM1.5Gedition2, monochromatic, white,)
* illumination: from either the p-side or the n-side; spectrum cut-off and attenuation
* working point for calculations: voltage, frequency, temperature
* the program calculates energy bands, concentrations and currents at a given working point, J-V characteristics, ac characteristics (C and G as function of V and/or f ), spectral response (also with bias light or voltage)
* batch calculations possible; presentation of results and settings as a function of batch parameters
* loading and saving of all settings; start-up of SCAPS in a personalised configuration; a script language including a free user function
* very intuitive user interface
* a script language facility to run SCAPS from a ‘script file’; all internal variables can be accessed and plotted via the script.
* a built-in curve fitting facility
* a panel for the interpretation of admittance measurements

## The Basics

SCAPS is a Windows-oriented program, developed with Lab Windows/CVI of National Instruments. We use here the LW/CVI terminology of a ‘Panel’ (names used in other softwares are: a window, a page, a pop-up.). SCAPS opens with ‘Action Panel’.[41]

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| --- |
| 3.  4.  2.  5.  6. |
| Figure 27The SCAPS start-up panel: the Action panel or main panel. The meaning of the blocks numbered 1 to 6 is explained in the text. |

There are dedicated panels for the basic actions:

1. Run SCAPS.
2. Define the problem, thus the geometry, the materials, all properties of your solar cell
3. Indicate the circumstances in which you want to do the simulation, i.e., specify the working point
4. Indicate what you will calculate, i.e., which measurement you will simulate.
5. Start the calculation(s)
6. Display the simulated curves

|  |  |
| --- | --- |
| Run SCAPS: |  |

Click the above pictogram on the Desktop, or double-click the file scaps3200.exe in the file manager (or any other SCAPS version). SCAPS opens with the Action Panel.

|  |  |
| --- | --- |
| Define the problem: |  |

|  |  |
| --- | --- |
| Click the button set problem in the action panel, and chose load in the lower right corner of the panel that opens. Select and open the problem file. or you can set a new problem by clicking on new option. |  |

## Define Working Point

The working point specifies the parameters which are not varied in a measurement simulation, and which are relevant to that measurement. Thus:

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|  |

* the temperature T: relevant for all measurements. Note:
* in SCAPS, only NC(T), NV(T), the thermal velocities, the thermal voltage KT and all their derivatives are the only variables which have an explicit temperature dependence; you must input for each T the corresponding materials parameters yourself.
* the voltage V: is discarded in I-V and C-V simulation. It is the dc-bias voltage in C-f simulation and in QE simulation. SCAPS always starts at 0 V, and proceeds at the working point voltage in a number of steps that you also should specify. The frequency f: is discarded in I-V, QE and C-f simulation. It is the frequency at which the C-V measurement is simulated.
* the illumination: is used for all measurements. For the QE measurement, it determines the bias light conditions. The basis settings are: dark or light, choice of the illuminated side, choice of the spectrum. A one sun ( = 1000 W/m2) illumination with the ‘air mass 1.5, global’ spectrum is the default, but you have a large choice of monochromatic light and spectra for your specialized simulations. If you have an optical simulator at your disposal, you can immediately load a generation profile as well instead of using a spectrum.

### Shunt conductance and series resistance

It is possible to introduce an external shunt conductance and series resistance to the structure on the action panel, see Figure 28

|  |
| --- |
| shuntseries |
| Figure 28 Introducing external shunt conductance and series resistance. |

## Select the measurement(s) to simulate

In the action-part of the Action Panel, you can select one or more of the following measurements to simulate: I-V, C-V, C-f and QE. Adjust, if necessary, the start and end values of the argument, and the number of steps.

|  |  |
| --- | --- |
| Start the calculation(s): |  |

Click the button calculate: single shot in the action panel. The Energy Bands Panel opens, and the calculations start. At the bottom of the Panel, you see a status line, e.g. “iv from 0.000 to 0.800 Volt: V = 0.550 Volt”, showing you how the simulation proceeds. Meanwhile, SCAPS stands you a free movie how the conduction and valence bands, the Fermi levels and the whole caboodle are evolving.

### Display the simulated curves

|  |
| --- |
| Go to other panels  Save Results |

After the calculation(s), SCAPS switches to the Energy band panel (or the AC-band panel). You can now look at your ease to the band diagrams, carrier densities, current densities, at the last bias point calculated (stop your calculations earlier, or use the pause button on the Action Panel if you want to look at an intermediate state at ease). You can output the results (buttons print, save graphs, show (then the numbers are shown on screen; cut & paste to e.g., Excel is possible), or save (then the numbers are saved to a file). You can switch to one of the specialized output Panels (if you have already simulated at least one corresponding measurement). We only show the example of the IV Panel.

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## Batch calculations

When you want to explore the influence of one or a few parameters to the solar cell characteristics, you can take profit of the batch option. When you click Batch set-up, a panel opens where you can choose which parameter to vary, over which range, and in which mode (Lin, Log or custom). You can also define more than one parameter, and vary all of them (in a nested way or ‘simultaneous’), but be modest to start. A batch calculation is launched when calculate: batch is clicked. After a batch simulation all parameters on the panels are reset as they were before the calculation.

### The batch set-up panel

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| --- |
| Batchsetup |

The batch set-up panel allows you to vary up to nine different parameters, when you want to vary more you can also vary entire definition files.

### Varying entire definition files

SCAPS offers the opportunity to vary entire definition-files in a batch calculation. This option is activated by checking the ‘vary definition files’-checkbox. A list of files can then be set by clicking the ‘edit/load list of definition files’-button. This list of files is treated in a similar way as any other parameter which has a file- nature rather than a numeric-nature. When definition files are varied in a batch, only those parameters which are present in ALL of these definition files can be varied further as a batch parameter.

### Varying parameters of the initial state work point

There are two ways to vary the initial work point variables in the batch set-up: all together, by specifying a list of .wp2 files (Figure 29 Selecting all parameters of the initial state work point as a batch parameters; al list of .wp2 files has to be specified, where each .wp2 file was made by saving the initial state work point in a file.(Figure 29) or each parameter separately (Figure 30)

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| --- | --- |
|  |  |
| Figure 29 Selecting all parameters of the initial state workprint as a batch parameter; al list of. wp2 files has to be specified, where each. wp2 file was made by saving the initial state workprint in a file. | |
|  | |
|  | |
| Figure 30 Selecting a single parameter of the initial working point as a batch parameter. | |

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## Recorder calculations

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In a regular single shot or batch calculation, the detailed panels are only available for the last measurement point. To be able to see them as a function of the batch parameters you can launch a record calculation. You should first select the properties which you want to keep track of by clicking Record set-up. With the Recorder facility, you can do a batch calculation and register or record selected cell properties as a function of the batch parameter(s). The list of properties to be recorded is made in the Record Set-up, see [Figure 8.1](#_bookmark163). With the help of the five choice-menus (type-property-layer-defect-level) the user can chose a property and add it to the list on the left side of the panel using an Insert or Replace button. There are eight types of properties to be recorded: I-V characteristics, General properties, Cell definition, Interfaces, Energy band panel, Generation panel, Occupations and AC panel.

|  |
| --- |
| recordsetup |
| Figure 31 Setting up a recorder |

Clicking the ‘Calculate: recorder’-button leads to a batch recording, which is only available when a batch is set. In this case the action list as it is set on the action panel will be ignored. SCAPS will determine which calculations need to be done in order to record the asked properties.

## Solar cell definition

The recommended way to introduce your solar cell structure into SCAPS is to use the graphical user interface. This way you can interactively set all parameters.

### Editing a solar cell structure

When clicking the ‘Set Problem’-button on the action panel, the ‘Solar cell definition’-panel is displayed. This panel allows to create/edit solar cell structures and to save those to or load from definition files. These definition files are standard ASCII-files with extension ‘\*.def’. Layer-, contact-, and interface properties can be edited by clicking on the appropriate box as shown in [Figure 32.](#_bookmark16) In a similar way, layers can be added by clicking ‘add layer’

|  |
| --- |
| celdef |
| Figure 32 Defining a solar cell structure |

### Reference conventions for voltage and current

The user can input own reference conventions for the applied voltage V and the current J in the external contacts. When setting a new problem, or editing an existing problem that does not contain any reference data (e.g. an older .def file), the new options in the solar cell definition panel ([Figure 33](#_bookmark18) right) are invisible, and the default reference conventions are set. Upon checking the option in the More Numerical Settings Panel ([Figure 33](#_bookmark18) left), these options are visible and can be operated right away. When a newer problem is loaded that contains reference information, the checkbox ‘allow change of” is set automatically, and the three options of  [Figure 33](#_bookmark18) right are enabled. (As of 2-1-2014, this More Numerical Settings Panel is not yet available to the user; the option “allow change of references” is always enabled).

|  |  |
| --- | --- |
|  |  |
|  |  |
| Figure 33 Setting user reference conventions for voltage and current. Left: checkbox in the More Numerical Settings Panel. Right: new facilities in the Solar Cell Definition Panel. | |

The three new facilities are:

#### ‘Apply voltage V to’: when ‘left’ is set, then the right contact is the reference contact, and the voltage V is applied to the left contact; this is the default, and the only possible option in SCAPS<3.2.0. When ‘right’ is set, the left contact is the reference contact, and the voltage V is applied to the right contact; in an JV curve, this correspond to a reversal of voltage axis compared to the traditional JV curves in SCAPS.

1. ‘Current reference as a’: when ‘consumer’ is set, then the current reference arrow is set such that P = JV is the power consumed by the cell, and thus - JV the power generated by the cell. When ‘generator’ is set, then the current reference arrow is set such that P = JV is the power generated by the cell, and thus - JV the power consumed by the cell. Setting of the current reference arrow thus depends both on the selected voltage reference and on the consumer/generator selection.

#### ‘Invert the structure’: the solar cell structure is mirrored along the x axis: the leftmost layer becomes the rightmost layer, and so on. This inversion of structure also swaps the interfaces, and all grading information in the layers and the defects. Clicking two times the inversion button brings the original cell back. This inversion only concerns the structure: the illumination side, the voltage and current reference settings all remain unchanged.

With these 3 settings, one can define 8 different problems, resulting in 4 different aspects of the JV curves. We illustrate this in [Figure 28](#_bookmark19)  to make the user more familiar with the concepts of voltage, current and power references.

|  |  |  |
| --- | --- | --- |
|  | Pn V left contact referred as consumer | C:\Marc\scaps\SCAPS Manuals\Basic SCAPS Manual\pn left consumer.png |
|  | Pn V to right contact referred as consumer | C:\Marc\scaps\SCAPS Manuals\Basic SCAPS Manual\np left consumer.png |
|  | Pn V to right contact referred as generator |  |
|  | pond to left contact referred as generator |  |
| Figure 34 Possible references of V and J for pn structures. The calculations are for the problem file simple pn.def and the illumination is always from the right | | |

Internally in SCAPS, only the default reference is used (voltage applied at the left contact, current reference arrow from left to right, resulting in a reference as a consumer. In all output (graphs, show/save tables), the result is shown consistent with the user’s choice of reference. Note that the electric field in the SCAPS output is not subject to the user-set V and J references: it is always referred to the positive x-axis, thus from left to right.

## Navigating to the analysis

The analysis-panels can easily be accessed from the action panel or any other analysis panel,

|  |  |
| --- | --- |
| ResultsonActionPanel | ResultsonOtherpanel |
| Figure 35 : Navigating to the results from the action panel (left) or any other panel (right) | |

Several options are available on every panel: saving data, showing data, saving graphs and plotting the panel (sending to a printer). There are options available for scaling and zooming of graphs and to show more info about the plotted curves. Other options are panel specific. At the bottom of every panel there are two comment windows. The left window is auto-generated and gives the definition file used with its last saving and the when the simulation was performed. The right window can be used to write personal comments several processes can be show by checking the appropriate checkboxes such as, energy band, iv-panel, ac-panel, cv-panel, QE-panel

# Results and Discussions

## SCAPS-1D Numerical Simulation.

Understanding the fundamentals of solar cells is made simpler through numerical modelling, which also provides valuable insights into determining the key factors that control the device’s performance. One-dimensional equations governing the semiconductor material characteristics under steady-state circumstances can be numerically solved using Solar Cell Capacitance Simulator One Dimension (SCAPS-1D) software.Poisson’s equation (10) describes the correlation between the electric field (E) and the space charge density (ρ) of a p−n junction as given below

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| --- | --- | --- |
|  |  | (10) |

where n(p) refers to the electron (hole) density, Ndef stands for the potential defect (donor or acceptor) density, and N+ (N−) stands for the ionized donor (acceptor) density, q denotes the elementary electronic charge, ψ stands for the electrostatic potential, and εs stands for the static relative permittivity of the medium.[42]

D

A

[Equations (11)](#_bookmark0) and [(12)](#_bookmark0) represent the electron and hole continuity in a steady state

|  |  |  |
| --- | --- | --- |
|  | G – Un(n, p) = 0 | (11) |
|  | + GP – UP(n, p) = 0 | (12) |

Here, jn/jP stands for the electron/hole current density; G stands for the electron−hole generation rate, and Un,p stands for the rate of net recombination. The density of the electron and hole current is written using eqs (13) and (14)

|  |  |  |  |
| --- | --- | --- | --- |
|  | |  | (13) |
|  |  | | (14) |

where the electron/hole mobility is denoted by μ n/, and the diffusion is denoted by D

**Table 5 TCO, ETLs, CBTS HTL, and Cs2BiAgI6 Absorber Layer’s Initial Input Parameters**[43][44]

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Parameters | ITO | TiO2 | **CBTS** | **Cs2BiAgI6** |
| Thickness (nm) | 500 | 30 | 100 | 800a |
| Band gap, Eg (eV) | 3.5 | 3.2 | 1.9 | 1.6 |
| Electron affinity, X (eV) | 4 | 4 | 3.6 | 3.90 |
| Dielectric permittivity (relative), εr | 9 | 9 | 5.4 | 6.5 |
| CB effective density of states,Nc (1/cm3) | 2.2 × 1018 | 2 × 1018 | 2.2 × 1018 | 1 × 1019 |
| VB effective density of states,  NV (1/cm3) | 1.8 × 1019 | 1.8 × 1019 | 1.8 × 1019 | 1 × 1019 |
| Electron mobility, μn (cm2/Vs) | 20 | 20 | 30 | 2 |
| Hole mobility, μh (cm2/Vs) | 1 × 1021 | 10 | 10 | 2 |
| Shallow uniform acceptor , NA (1/cm3) | 0 | 0 | 1 × 1018 | 1 × 1015a |
| Shallow uniform donor density, ND (1/cm3) | 1 × 1021 | 9 × 1016 | 0 | 0 |
| Defect density, Nt (1/cm3) | 1 × 1015a | 1 × 1015 | 1 × 1015a | 1 × 1015a |

aTo obtain the optimal HTL, ETL, and back contact metal combination in this study, these variables are kept constant during the first optimization

## Cs2BiAgI6 Perovskite Solar Cell Structure.

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| Figure 36: (a) Crystal structure of the absorber (b) device structure (c) band diagram and (d) energy band alignment of an optimized solar cell structure | |

In this study, the simulation was performed on SCs with an n-i-p planar heterojunction structure comprising the ETL, Cs2BiAgI6 absorber Figure (10)a, HTL, transparent conduction oxide (TCO), represent the p-region, i-region, and n-region, respectively. The absorber layer (Cs2BiAgI6) of the solar cell creates excitons when it is exposed to light. The exciton is a restricted state made up of an electron and a hole. The exciton can penetrate the n(p) area based on the length of the diffusion. The exciton separates at the n-to-i-layer interface, and the e− and remaining holes are sent toward the direction of the n-layer and p-layer, successively. Similarly, the exciton separates at the i-to-p-layer interface, and the holes and remaining e− are sent in opposite directions, toward the p-layer and the n-layer. The electrical field that exists between these layers allows the separation of excitons and also the movement of e− and holes. As a TCO, indium tin oxide (ITO) is employed, with a work function of 4.4 eV. Assumed to be 500 nm in thickness is the TCO

**Table 6. Interface Defect Layers’ Input Parameters**[43]

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Interface** | **Defect type** | **Capture cross section: electrons/holes(cm2)** | **Energetic distribution** | **Reference for defect energy level** | **Total density (cm-3) (integrated over all energies)** |
| ETL/Cs2BiAgI6 | neutral | 1.0 × 10−17  1.0 × 10−18 | single | above the VB maximum | 1.0 × 1010 |
| Cs2BiAgI6/HTL | neutral | 1.0 × 10−17  1.0 × 10−18 | single | above the VB maximum | 1.0 × 1010 |

layer. The thickness of the ETL, HTL, and absorber layers is changed over a wide range to optimize device performance. In this proposed device configuration, The ETLs named TiO2, PCBM, ZnO, IGZO, SnO2, and WS2 are used as ETLs, and CBTS is used as an HTL. In addition, the absorber layer Cs2BiAgI6 is sandwiched between the ETL and the HTL in every device structure and serves as the light- absorbing layer. Figure 36b demonstrates the structure of the optimized Cs2BiAgI6- based PSCs. Figure 36c represents the band diagram of the Cs2BiAgI6- based PSC device configuration where TiO2 is used as the ETL along with the CBTS HTL, and the corresponding energy band alignment is shown in Figure 36d. Each ETL with an absorbing layer and CBTS as the HTL are utilized by the energy band diagram to influence the valence band offset. The difference between the absorber layer and HTL represents the valence band. The effectiveness and performance of the PSCs are significantly impacted by the alignment of the energy levels. In the PSCs, holes are simultaneously transferred to CBTS as the HTL while e− are injected into the corresponding ETL conduction band. After that, holes and e− are collected at the respective Au (back contact metals) and ITO. However, the electron affinity of each studied ETL should be higher than that of Cs2BiAgI6 to extract the electron at the ETL/Cs2BiAgI6 interface, and the HTL ionization energy should be lower than that of Cs2BiAgI6 to extract the holes at the Cs2BiAgI6/CBTS HTL interface. In addition, the solar cell’s performance is significantly impacted by the energy band mismatch at the ETL/Cs2BiAgI6 and the Cs2BiAgI6/CBTS as the HTL. The performance and effectiveness of the optimized six ETL-based double perovskite solar structures are investigated with the help of the input parameters of interface defect layers. In all cases of simulation, a frequency of 1 MHz, AM 1.5 G spectrum of sunlight was used by maintaining the surrounding temperature of 300 K

## Effect of Absorber, ETL and HTL Layers Thicknesses on PV Performance

### Absorber Layer Thickness

The absorber layer thickness plays an important role in affecting the PSC performance through the enhancement in photon absorption and device efficiency. The Cs2BiAgI6 absorber layer thickness is varied from 0.1 to 1.5 μm to optimize the device performance. The variation of VOC, JSC, FF, and PCE is demonstrated for the ten sets of device configurations while increasing the thickness of the Cs2BiAgI6 absorber layer, as shown in Figure 37. VOC decreases with the increasing absorber layer thickness due to the rise in the value of JSC as governed by the equation

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| --- | --- | --- |
|  | .[45] | (15) |

JSC initially increased rapidly and then saturated due to the saturation in the number of photons available for absorption. The FF decreased monotonically with an increase in the absorber thickness due to the improved series resistance. The decline in the FF might be due to the dominance of carrier recombination and parasitic resistance losses. As the change in voltage has relatively little impact on the PCE curve, this rise in JSC also explains an increase in PCE. Due to the increase in the recombination rate with the absorber layer thickness, VOC gradually decreases. The PCE initially improved with the absorber thickness and showed peaks at 1000, for TiO2 ETLs, which ultimately determined the optimum absorber thickness. The initial rise of PCE is due to an increase in the generation of electron - hole pairs as the absorber layer thickness increases. However, the increased radiative recombination and charge route resistance causes a decrease in PCE for thicker absorbers.[43]

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| Figure 37 : Effect of the variation in the PV parameters PCE, FF, JSC, and VOC due to the variation in the thickness of the absorber, | |

### ETL(TiO2) Thickness

The properties of the charge transport layers should be carefully tuned to design highly efficient PSCs. A suitable ETL aids in increasing transmittance and lowering recombination in PSCs. The thicknesses of the TiO2 as ETLs were varied from 30 to 500 nm while keeping other parameters constant to determine the performance of double PSC. Figure 38 shows that the thickness of the ETL has less impact on the PV performance parameters of Cs2BiAgI6-based PSCs. The partial absorption of a thicker ETL slows down the charge generation and collection pace and may cause a slight decline in JSC and PCE. Equn (16) shows the relation between the ETL layer thickness and transmittance.[46]

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| --- | --- | --- |
|  |  | (16) |

where de stands for the film thickness, Te stands for the transmittance, and αe denotes the absorption coefficient. However, it is observed from Figure 38 that on increasing TiO2, VOC remains constant. The JSC value for increasing thicknesses TiO2, remains constant there is a decline in the value of JSC. The FF and PCE layers remained constant, as shown in Figure 38 After trial and error, the optimized thickness of TiO2, is found to be 30nm. The optimum thickness of ETLs helps to achieve the maximum PCE value for the device configurations.

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|  |  |
| Figure 38: Effect of the variation in the PV parameters PCE, FF, JSC, and VOC due to the variation in the thickness of ETL | |

### HTL Thickness

The impact of changing the thickness of the CBTS HTL on PV parameters in Cs2BiAgI6- based PSCs using TiO2 as ETLs are shown in Figure 39. HTL thickness modification is crucial to maximize performance and minimize direct contact between the perovskite and cathode. This layer also serves as a capping layer. We examine only CBTS as the HTL in thickness optimizations because only CBTS exhibited a maximum PCE Figure 39 shows that the values of VOC, JSC, FF, and PCE remained constant for all ETLs with increasing thickness of CBTS as the HTL. The VOC value decreases around 1.10 V for TiO2 for the increased thickness of CBTS. The FF and PCE values of TiO2 at around 83.3 and 21.68%, respectively, are the highest among the ETL. It has been observed in the previous study that the PCE value increased with increasing HTL thickness.[47].Typically, a p-type layer must be thicker than an n-type layer to reduce the recombination rate because it aids in the efficient prompt transportation of equivalent charge carriers to the respective terminals.[48] But during the variation of HTL thickness, 100 nm is observed to be the best thickness for a higher PCE, and hence 100 nm is chosen as the optimized HTL thickness for further calculations.

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|  |  |
| Figure 39 : Effect of the variation in the PV parameters PCE, FF, JSC, and VOC due to the variation in the thickness of HTL TiO2 as ETL. | |

## Effect of Absorber Layer Properties.

### Absorber Layer Acceptor Density.

Electron−hole pairs are produced as a result of the incoming radiation’s photons being absorbed by the perovskite absorber layer. To enhance the performance of SCs, a little amount of n-type or p-type dopants may be added to the perovskite absorber layer.[49] Here, in this section, the NA of the absorber is changed from 1010 to 1017 cm−3 to see its impact on the PV parameters. Figure 40 shows that the VOC for the optimized ETL is constant for NA values up to 1014 cm−3, and thereafter VOC increases with the NA. When NA rises, the Fermi energy level of the holes decreases, which increased the VOC level. As the absorber layer NA rises, the built-in potential also increases; this may contribute to the rise in VOC brought on by the increased charge separation. The PCE value decreases when the NA value exceeds 1017 cm−3 of optimized SC structures. In addition, the PCE also decreases when the defect states rise with the increase in NA. All of the PV parameters VOC, JSC, FF, and PCE remained constant till 1017 cm−3; hence, the ideal NA for better performance can be between 109 and 1017 cm−3.60 As the absorber NA increases, an electric field is generated at the interface layers of the PSC. However, the creation of the electric field also makes the possibility of charge carrier recombination conceivable. Therefore, the ideal acceptor doping density should be selected to produce higher performance. Finally, the optimized NA of the absorber layer for TiO2 ETL is set at 1015 cm−3.

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|  |  |
| Figure 40 : Effect of the variation in the PV parameters PCE, FF, JSC, and VOC due to the variation in the thickness of HTLs TiO2 as ETLs. | |

The absorber layer defect density

Nt is a critical factor in determining the effectiveness and performance of PSCs. The properties of the light-absorbing layer and its form significantly influence the PCE of PSCs. When light is incident on the perovskite absorber layer, photocarriers are produced. However, a poor morphology of the ETL could lead to insufficient perovskite layer coverage. A lower-quality film has higher Nt, which raises the recombination rate.[50]. Nt of the ETL was changed from 109 to 1018 cm−3 for Cs2BiAgI6- based structures. Figure 41 shows that the VOC, JSC, FF, and PCE values are constant till 1014 cm−3 of Nt. Beyond the Nt value of 1014 cm−3, the PV parameters are reduced for TiO2, ETL. According to the earlier literature, this declination in PV parameters with an increase in Nt happened due to the nonradiative Shockley− Read−Hall (SRH) recombination, which is also the main reason for carrier recombination, lifespan reduction, and a decline in the PSC performance.42 Figure 11b shows that the PCE for Cs2BiAgI6-based PSCs is about 22%, and for Nt of 1018 cm−3, the PCE is reduced to about 1%. The existence of several kinds of recombination mechanisms, such as trap-aided SRH recombination and interface recombination in PSCs, is primarily responsible for this significant degradation in the PCE. The SRH recombination rate is defined using eqs (17)and (18)

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(17) (18)where σ stands for the capture cross section of electrons and holes, Et stands for the defect energy level, Ei stands for the intrinsic energy level, ni is the intrinsic carrier concentration, n/p is the concentration of electrons/holes, τ stands for the lifetime of holes and electrons, Vth stands for the thermal velocity of charge carriers, and Nt stands for the total defect density of the absorber layer of the PSC. The optimized Nt for TiO2 is fixed, to 1012 cm−3, for the maximum PCE using the trial-and-error method.

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| Figure 41 : Effect of the variation of the defect density of the absorber layer for ETL | |

## Effect of ETL properties.

### **ETL Donor** Density.

The changes of PV parameters, such as VOC, JSC, FF, and PCE, versus doping concentration (ND) of TiO2 as ETL, are shown in Figure 42 ND of ETL was changed from 1010 to 1019 cm−3 Figure 42 The VOC value remained constant with ND for ETL. On increasing ND, TiO2 showed a VOC value of around 1.12 V. JSC values for TiO2 remained constant with ND. The FF of ZnO decreases with an increasing value of ND of the ETL. The remaining ETL maintains a constant FF value with the change of ND. TiO2 exhibit a constant PCE profile with increasing ND. However, ETL show a small rise in FF and PCE with increasing ND because a higher value of the ND of the ETL makes charge extraction and transmission at the ETL/ Cs2BiAgI6 contact more feasible. Due to the large series resistance at the lower ND of the ETL, the performance of the PSC degrades.[51][52] The optimum ND of TiO2 is set at 9 × 1017 cm−3 for further optimization.

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| Figure 42 : Effect of the variation of the donor density of ETL | |

### Effect of ETL Defect Density.

VOC, JSC, FF, and PCE values are computed for different ETLs by increasing ETL Nt from 1010 to 1017 cm−3. Figure 43 showed that almost all performance parameters VOC, JSC, FF, and PCE exhibited constant values for ETL layers on increasing Nt of the ETL. ETL showed a VOC value of around 1.09 V. ETL layer showed a JSC value of around 24 mA/cm2. The FF value of the ETL layer remained constant which showed a slight decrease after 1016 cm−3. the PCE of 23.5% is achieved with TiO2. From the simulated data, the optimized Nt of the ETL is 1015 cm−3 PSC structures.

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| Figure 43 :. Effect of the variation of the defect density of the ETL. | |

## Effect of HTL properties.

### HTL Acceptor Density

Figure 44 shows the change of photo-voltaic parameters with increasing HTL NA (acceptor concentration) for TiO2 ETL. NA is varied from 1015 to 1021 cm−3 for SC structures. From Figure 44 it is evident that PCE values with ETL showed comparatively low values with NA < 1016 cm−3 due to the small electric field, which reduces carrier extraction. In addition, on increasing NA beyond 1016 cm−3, a constant PCE value is obtained for device configurations. A similar pattern has been seen for the FF value for all presented PSCs, where FF increases as NA from 1015 to 1016 cm−3. The JSC value for ETL associated with PSCs exhibited a constant value with an increasing NA. The constancy indicates that the NA variation of the HTL has an insignificant impact on JSC. The JSC is observed for TiO2 associated SC structures is around 24 mA/cm2. The ETL showed a constant VOC value with NA variations. Optimum NA was found to be 1018 cm−3 for ETL and we fixed the value of NA for further optimization.

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| Figure 44 : Effect of the variation of the donor density of the HTLs | |

### HTL Defect Density.

Nt of the HTL in this section varies from 1011 to 1018 cm−3, as shown in Figure 45. The PCE value of different ETLs remained constant with increasing Nt of the HTL until 1017 cm−3. The PCE value decreased sharply after 1017 cm−3. Therefore, with increasing Nt, the PCE value has an insignificant impact of Cs2BiAgI6-based PSC. The VOC and JSC values remained constant for ETL device configurations on increasing Nt of CBTS as the HTL. Therefore, increasing Nt of CBTS has an insignificant impact on device configurations. The optimized value of Nt is set to 1015 cm−3 for device structures for further optimization.

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| Figure 45 :. Effect of the variation of the defect density of the HTLs. | |

## Effect of Interface Properties.

### Defect Density at the Interface of HTL and the Cs2BiAgI6 Absorber Layer.

Several defect states frequently coexist at the interface between perovskite and transport material. The performance of the SC depends significantly on the interface quality. According to the earlier study, the interface defect density (Nt) on the irradiation side will affect solar cell performance more than the interface defect states at the rear interface.[53] The performance parameters VOC, JSC, FF, and PCE have been investigated for the change of Nt of the CBTS HTL/Cs2BiAgI6 interface from 1010 to 1022 cm−3 for all of the ETLs, as shown in Figure 46. The PCE and FF values exhibited the same declining pattern on increasing the defect density (Nt) of the CBTS HTL/Cs2BiAgI6 interface. The maximum values of PCE and FF are exhibited at Nt in the range 1010−1014 cm−3, and after Nt, of more than 1016 cm−3, the PCE and FF values start decreasing. In contrast, ETL with Cs2BiAgI6 perovskite exhibited a PCE of more than 22.9% at 1010 cm−3. The JSC value with changing Nt remained almost constant. From the simulation data, it is observed that on increasing the defect density, the recombination rate increased, and the PCE value decreased. Increased trap and recombination centres are produced due to higher defect concentrations at the interfaces, which reduces SC performance. The simulation results showed that an ideal Nt for device simulation is 1010 cm −3.Therefore, the optimum Nt is set at 1010 cm−3 for device configurations for further optimization.

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| Figure 46 : Effect of the defect density variation of the HTL/Cs2BiAgI6 interfaces on PV parameters PCE, FF, JSC, and VOC | |

### **Defect Density at the Interface of the Cs2BiAgI6 Absorber Layer and ETL**.

The effects of the Cs2BiAgI6-ETL interface defect density (Nt) on the effectiveness of gradient doping PSCs are examined in this section. Nt was varied from 1010 to 1018 cm−3. From Figure 47it is observed that the value of VOC, JSC, FF, and PCE decreases on increasing the Nt. The PV value remained constant till 1014 cm−3 and then start decreasing with Nt variations. TiO2 as ETLs for the Cs2BiAgI6 SC structure showed the highest PCE, The FF value of TiO2 after exceeding 1015 cm−3, the FF value decreased rapidly. The lowest JSC of 24 mA/cm2 is exhibited for TiO2. VOC is much more sensitive to the changes in Nt as compared to JSC. The formula in eq 10 may be used to describe the interface recombination-imposed VOC limit.[54]

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where St is the rate of interface recombination, n is the ideality factor, and is the height of the effective barrier. This formula reveals that a high St will be produced by a high interface defect density, which will reduce VOC. However, the optimum Nt value is found to be 1010 cm−3, which is similar to that obtained in the case of HTL/ Cs2BiAgI6.

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| Figure 47 : Effect of the defect density variation of the Cs2BiAgI6/ETL interfaces on PV parameters PCE, FF, JSC, and VOC. | |

## Effect of Temperature, Shunt, and Series Resistances

### Series Resistance

RS stands for internal resistance, which is made up of the device’s active layer resistance and its ohmic contact resistance. According to Figure 48 the effect of the variation of the series resistance from 0 to 8 Ω cm2, keeping the shunt resistance constant at 105 Ω cm2 for optimized TiO2 ETL-associated structures, are investigated. It was observed that increasing RS had no discernible impact on JSC and VOC. The FF and PCE for the structures have, however, significantly decreased as a result of the increase in RS. This was found to be consistent with the findings for both inorganic and organic solar cells. [55][56] Practically speaking, the value of RS for solar cells often decreases as a result of aging related effects that cause inconsistent photovoltaic performance. Accordingly, to improve the FF and get the highest performance feasible, RS must be kept to a minimum value throughout the device’s fabrication. One could consider lowering the active layer of a device’s thickness during manufacture to lower RS. Nevertheless, reducing the thickness is rarely a good strategy, particularly for perovskite solar cells, since this results in a noncomplementary absorption when the thickness is maintained under 200 nm. Other experimental methods to lower RS include decreasing the contact resistance between the active layer and electrodes[57] or creating donor−acceptor interfaces that interact well. From Figure 48 the lowest JSC is observed in the case of the TiO2-based ETL.

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| Figure 48 :. Effect of the variation of PV parameters as a function of series resistance for the ETL | |

### Shunt Resistance

The shunt (RSh) of the devices, which accounts for the leakage of current at the donor−acceptor and active layer-electrode borders, is an additional internal electrical characteristic that affects the performance of solar cells. In a forward bias connection, the greater recombination rate equates to a higher RSh value. The value of RSh is often connected to the charge recombination process (whether it be geminate or nongeminate). In other words, a reduced carrier recombination rate under light illumination, i.e., without biasing, shows that the device has a high RSh value. The J−V characteristic of a solar cell behaves normally under ideal one-sun illumination conditions, according to the Shockley equations, which can be written as eqs (20)and (21)[58]

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|  |  | (20) |
|  |  | (21) |

where JPH is the photocurrent density. The effects of the variation of RSh are depicted in Figure 49. Effect of the variation of PV parameters as a function of shunt resistance for the ETL RSh is varied from 101 to 107 Ω cm2 keeping Rs constant for of the optimized solar cell structures to observe its effect on VOC, JSC, FF, and PCE. It can be observed that for RSh values greater than 100 Ω, VOC, JSC, FF, and PCE attain constant values after increasing linearly from very low values. A detailed examination of the figure revealed that compared to JSC, the increment rates for both VOC and FF were greater. To be connected with the VOC and FF responses, the change in RSh caused by charge transfer, the emission process, and their recombination behavior may be more remarkable.

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| Figure 49 :. Effect of the variation of PV parameters as a function of shunt resistance for the ETL | |

### Temperature

The majority of solar cell performance demonstrates instability due to deformation between layers occurring at high temperatures. To study the relationship between temperature and solar cell efficiency, the temperature range of the simulation models was changed from 250 to 500 K. In Figure 50. Effect of the variation of PV parameters as a function of temperature for the ETL., the performance of the optimized solar cell structures is observed. It can be seen that the PCE, FF, and VOC values decrease with increasing temperature, although the JSC values remain constant. VOC values decrease at high temperatures due to the increase in the reverse saturation current density (J0) at higher temperatures, as is evident from the inverse relationship between VOC and J0 explained using eq (22)

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where denotes the thermal voltage. Furthermore, the flaws worsen when the temperature rises and VOC gets smaller. So, there is a serious degradation in the SC performance as temperature increases.

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| Figure 50 :. Effect of the variation of PV parameters as a function of temperature for the ETL. | |

## Effect of Capacitance and Mott−Schottky.

Mott− Schottky (M−S) is a well-known and reliable tool used to evaluate the built-in potential (Vbi), which shows the distinction between an electrode’s operational functions and its amount of doping. M−S theory is mainly focused on the properties of p−n junctions, but it is also applicable to organic devices.[59] In the M−S plot, the Vbi of organic semiconductor devices is commonly represented by the x-axis intercept, and the concentration of occupied trapping centers is indicated by the slope of 1/C2 (V). Here, in this study, the variation of capacitance and M−S with respect to the applied voltage is conducted in the case of optimized solar cell structures, where CBTS is taken as the HTL and TiO2 are the ETL and Cs2BiAgI6 is the absorber. According to Figure 16a, the capacitance increases nonlinearly with the applied voltage. M− S decreases with the voltage, which can be observed in Figure 51. Variation of Mott−Schottky (1/C2) plot, with the applied voltage for the studied PSC

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| Figure 51 :. Variation of Mott−Schottky (1/C2) plot, with the applied voltage for the studied PSC | |

## Effect of Generation and Recombination Rate.

It is possible to determine the generated electron−hole pair at any point within the solar cell, for any light wavelength, or the complete standard solar spectrum. The surface of the SC structure, where the bulk of the light is absorbed, shows the highest generation rate. The generation rate of an SC is a function of both the position and wavelength and indicates how many electron−hole pairs are produced at each location of the device due to photon absorption at a particular wavelength. The generation rate is crucial for achieving the best efficiency out of SCs. PS shows the generation rate of optimized solar devices. Recombination is the opposite of generation, which involves coupling and annihilating the conduction band electrons and holes. The recombination rate is affected by the density of charge carriers and lifetime. Additionally, each defect state in the different PSC layers has an impact on the electron−hole recombination. The maximum recombination rate was observed in the range of 0.7−1.0 μm for the best solar cells as similar to the generation rate (Figure 52 Variation of capacitance (C) plot, with the applied voltage for the studied PSCThe position from 0.7 to 1.0 μm showed a higher recombination rate because more conduction band electrons crossed the energy barrier and entered the valence band to become more stabilized and take up the position of the valence band hole. The resulting energy levels affect the recombination rate of the electron−hole within the solar device, and imperfection and grain boundaries allow the recombination rate distribution in the solar structure to be nonuniform.

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| Figure 52 : Variation of capacitance (C) plot, with the applied voltage for the studied PSC | |

## J−V and QE Characteristics.

Figure 53 Quantum efficiency curve and J-V characteristics curve shows the final optimization of the J−V characteristic curve of SCs under consideration. In contrast, at the final optimization, TiO2 ETL-associated structures showed optimum J−V characteristics Figure 53: Quantum efficiency curve and J-V characteristics curve represents the variation of quantum efficiency (QE) as a function of the wavelength of double PSC structures during and final optimization. The light wavelength affects the QE. It is the proportion of charge carriers generated by a solar cell to photons that strike the and J more photons can be absorbed by a thicker absorber, the QE typically improves with increasing absorber thickness.61 It is observed QE is almost constant in the wavelength range from 350−700 nm and decreases thereafter under final optimized conditions Figure 53 : Quantum efficiency curve and J-V characteristics curve According to Figure 53 : Quantum efficiency curve and J-V characteristics curve, QE is almost 100% for TiO2 at a ∼350 nm wavelength under initial optimization conditions,

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| Figure 53 : Quantum efficiency curve and J-V characteristics curve | |

## Results of SCAPS-1D Compared to Earlier Research.

The earlier study proposed optimized solar cell structures among ninety-six solar structures using SCAPS-1D software.In this study, the performance parameters of the SCs with the architectures ITO/TiO2/Cs2BiAgI6/CBTS/Au, are optimized, and the results of the optimization study are listed in Table 7 for a fair comparison The experimental works reported very low PCE values of less than 3% and low JSC in comparison to the theoretical reports. Additionally, VOC, JSC, and FF values of the presented work are also higher than the previously published works on the Cs2BiAgI6 absorber-based SC structure.

# Conclusions

We used SCAPS-1D simulations to comprehensively optimize the photovoltaic characteristics of lead-free double Cs2BiAgI6 perovskite solar cells, and the key findings are outlined below:

The simultaneous variation of the absorber layer thickness with the acceptor density revealed that the best PCEs can be achieved with the ETLs for absorber thickness in the range of 0.5 to 1.2 μm and the NA in the range of 1 × 109 to 7 × 1017 cm−3 . The organic ETL (PCBM) showed that the lower PCE . For the absorber layer thickness >0.5 μm and absorber defect density less than 5 × 1017 cm−3 , oxide-based ETL TiO2 exhibit the highest PCE of around 23.7%.

The PV characteristics are greatly impacted by the absorber layer and ETL thicknesses, but the HTL thickness has a negligible effect.

Although the dopant density of the absorber layer, ETL, and HTL significantly affects the PV performance of the analyzed devices, the defect density of the charge transport layers has a negligible effect on the PV parameters. The amount of dopant density present in the charge transport layers influences the SC performance.

The PV parameters get much worse when the number of defects at the HTL/Cs2BiAgI6 and ETL/Cs2BiAgI6 interfaces goes up. The optimum value of the defect density for both of these interfaces was found to be 1010 cm−3 for the best SC performance.

The optimized ITO/TiO2/Cs2BiAgI6/CBTS/Au device structure delivers the best PCE of 23.71%, which is almost 20.9% higher than the experimentally fabricated Cs2BiAgI6 PSC and 8.5% higher than the theoretical device..

Table 7. Optimization Parameters, Namely, Thickness, Shallow Uniform Acceptor Density, NA (1/cm3), Shallow Uniform Donor Density, ND (1/cm3), and Defect Density, Nt (1/cm3) of the HTL (CBTS), the Absorber Layer Cs2BiAgI6, and ETL (TiO2) set layers thickness (nm) shallow uniform acceptor density, NA (1/cm3) shallow uniform donor density, ND (1/cm3) defect density, Nt (1/cm3)

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| Layers | Thickness | Shallow Uniform Acceptor Density, NA (1/cm3) | Shallow Uniform Donor Density, ND (1/cm3) | Defect Density, Nt (1/cm3) |
| TiO2 | 30 | - | 9 × 1017 | 1 × 1015 |
| CBTS | 100 | 1 × 1018 | - | 1 × 1015 |
| Cs2BiAgI6 | 1000 | 1 × 1015 | - | 1 × 1012 |

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# Acknowledgments

We are thankful to Dr. Burgelman and his team, the Department of Electronics and Information Systems University of Gent Belgium for developing SCAPS -1D tool.

I express my deep gratitude, regard to my supervisor, Dr. Swapan Kumar Mandal, for his constant encouragement and valuable suggestions. I would have made no progress without his help and support.

I would like to convey my heartfelt gratitude to Paramesh Chandra (Ph.D. Scholar, Visva-Bharati), my mentor, and Toton Sarkar (Ph.D. Scholar, Visva-Bharati), for their invaluable advice and assistance in completing my project.

I thank my classmate Rahul Pal for his assistance in different ways.

I am really grateful to my family for their constant support and encouragement.

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