



Design of CZTS-Perovskite thin-film Hetero-Junction Solar Cell

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Abstract—The Thin film technology is one of the fastest growing technologies because of the increase in energy demands and scarcity of energy materials. In thin film solar PVs PSC & CZTS are two of the most promising, abundant and efficient thin film solar PVs. They offer tunable band-gaps that can be adjusted for maximum PCE. Perovskite is one of the efficient solar PV material with a band-gap ranges between 1.55 to 2.3 eV which is too much close to the optimum photovoltaic conversion material. But it is less stable and vulnerable to environment while CZTS is more stable but have less band-gap as compared to perovskite. So, we make a tandem of perovskite & CZTS to utilize their efficiencies and durability. We simulate different thickness of layers and band-gaps of this tandem using SCAPS-1D, which is one of the best utilities for efficiency calculations of thin film solar PVs. We performed different simulations for that tandem while changing the allowable thickness of absorber layers & their band-gaps to obtain an optimum solution. During multiple simulations I obtained a better efficiency of 22.61% which was the greater efficiency during my simulations. I have used SCAPS-1D for modeling and simulations of thin film Perovskite and CZTS solar cells, calculated their I-V curve QE (quantum efficiency) for different thickness whose ranges are 200-500 nm for perovskite and 200nm to 1.2um for CZTS with step-length thickness of 25nm. I selected the best configuration for my simulations for better performance, on which I performed further simulations and chose model with efficiency of 22.61%. Which shows that a handsome amount of conversion efficiency is achievable for tandem solar cells consist of Perovskite and CZTS.

Keywords—

PSC Perovskite Solar Cell
CZTS Copper Zinc Tin Sulfide
QE Quantum efficiency
PCE Power conversion efficiency

I. INTRODUCTION

This We know a basic law of energy which govern all the natural phenomena and is valid till date. which is known as “law of energy’s conservation”, which states - “energy can neither be generated nor destroyed but can be converted from one form to another and total quantity of energy does not change”.

There exist different forms of energy with definite formulae. These forms are energy due to motion known as kinetic energy, due to position-potential energy, other types of energies are heat, solar, electrical, chemical, nuclear, elastic. If we sum up the formulae for each of these contributed energies, then there is no difference except transfer of energy – going in or out of the system.

Energy is the basic need for the nature performance and sustainability. Every material object needs energy in one or the other form. Human itself work due to availability of energy. Human body maintain itself at constant temperature of 37 °C. So it contains energy. It is fact that body of the human body is regularly cooled by the surrounding-environment, so thermal energy is dissipated to the outside. More-over blood is pumped into the vessels of the blood. As this blood travels through the blood vessels, its kinetic energy is reduced due to friction with the walls of the vessels this kinetic energy which is lost is basically transformed into heat energy. So to keep this blood circulation in the vessels the heart provides the required energy which further need energy which is supplied by food we eat in the form of chemical energy and that chemical energy is obtained from potential energy of the food. Which is basically conversion of different energy forms for specific purpose. Furthermore, human require energy for movement and brain consume a lot of energy. The calculated adult human consumes about 10,000 kJ or 2500 kcal every day[1]. Electricity is predicted to be lied between 8TW and 25 TW with growth of nearly 3.75-17.81% within 10 to 20 years[1]. Fossil-fuel i.e; natural-gas, oil and coal is dominating source worldwide which is 85% in 2008. But increase emissions of green-house gases are between factor of 5 and 35 is forecasted[1]. So transfer from fuel to renewable energy sources like wind, biomass, solar, hydropower and tidal is must and must be matured to face the future energy crises. Among other renewable energy sources sun energy is regarded as the most sustainable source due to its availability and cleanliness[1]. Besides this solar photovoltaics technology has emerged as the faster growing technology compared to other due to great amount of cost declination between 2008 and 2012, 60% reduction has been recorded in the price of PV modules per MW[1].

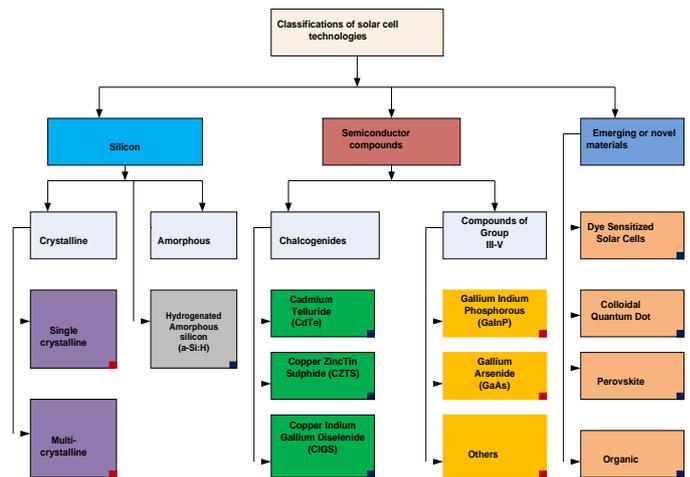
Sunlight is the most abundant and sustainable source of energy, but it is not divided evenly on the earth surface. Surfaces

with low latitude that is semi-arid and arid areas, in the range of 35LN to 35LS, collect the most normal direct irradiance (DNI). For example, the Desert named Mojave (latitude: 35LN) situated in the United States, and the Negev-Desert (latitude: 30.5LN) which is located in the southern Palestine receive 1921 kW-h-m⁻²/year and power of 2007 kW-h/m²/year, respectively a report by NASA Solar Insolation, 2008[1]. All other deserts of the globe, are situated between these two latitudes and are able to obtain the require energy all over the globe with solar power generation technologies.

The name of the solar photo-voltaic is derived from a Greek word “Phos” which means light and word “voltaic” which means electricity and is given the name due to large contribution of an Italian scientist Alessandro Volta in this field. Photo-Voltaic effect which is the basis of photovoltaics is the conversion of light into electricity. A device that converts optical energy from sun to electrical energy using photo-voltaic by effect of semiconductors solar cell. This phenomenon is basically the optical and electrical characteristics of semiconductor. When a photon, having higher energy to band-gap energy of the semi-conductor material then this photon is absorbed so that it energizes electron to shift it from valence band (V_v) to conduction band (V_c) so electron&hole pair is formed which form electric field across the p-n junction. Due to inherent properties of semiconductor solar cell efficiency is limited to 15-20% [2]. Depending upon the design of the module, installation and environment, each PV panel have different performance level. A well-researched study by scientists and engineers it is deduced that the mean between fossil-fuels consumption and emission of carbon dioxide, it can now be estimated that for international community’s target accomplishment of limitation of Carbon di Oxide emission and to control or lessen the harmful effects of climate change due to consumption of fossil fuel and production of CO₂, about 25,000 GW of clean energy is needed by 2050 [3]. By the virtue of decrease in system installation and increases in industrial experience, PV shall become a better economical source of electricity production. Other findings show that the predicted PV installation is 200GW in 2020 and 2TW in 2050 globally [4]. These statistics show that there will be a great reliance on PV technologies, in term of resources and production. In predicted power thin film solar-PV has 10% more share which is expected to be increased in the next 10-12 years [4]. This is evident from the fact that due to advancement in PV technology and concentrated solar power (CSP), these technologies have been periodically dominated the (IEA) projected targets made for different periods of time. For example, the 2006 International Energy Agency’s (IEA) projection cumulative solar capacity in 2020 and 2011 IEA’s projection for 2030 have been surpassed in year 2012 and 2014 separately [3, 5]. It is evident that solar PV has emerged the resultant energy producers due to its high contribution in today’s energy especially in the off-grid areas [6] and is considered one of the prominent RE for the future [7, 8]. That statistics of solar PV indicates the option that PV technology can supply handsome chunk of future energy- mix and make it an important technology for future energy’s demand and sustainability and for better environment [9, 10]. It is therefore, evident that main focus of national and international energy policies is PV technology.

The journey of photo-voltaic starts from the 19th century discovery of Becquerel in which he discovered photo-voltage by the action of light on electrode immersed in electrolytic solution in the year 1839 A.D [11]. Table 1.1 shows the remarkable contribution after this discovery.

Despite the above contributions and improvements, electricity from a solar cell is still hard to afford by a common man. In this situation thin film solar cells make the choice based on cost-effective novel, ecofriendly and abundant material which shall make remarkable contributions. Hence improvement in this technology is need of the day. Major two types of thin film PV technology based on construction type. Which are categorized in the following table.



key: ■ Represents thin-film PV ■ Represents wafer-based PV

Fig.1 Division of PV based on key active material

The (1). Commercial thin film solar cell technology. It includes (CdTe), (a-Si:H), copper-indium-gallium deselenide (CIGS).

(2). Emerging or novel thin film -PV technology. Here we shall focus on evolving or novel technology of thin film- PV. It includes colloidal quantum dots PV (QDPV), Dye sensitized solar cells (DSSCs), Organic photovoltaic (OPV), Perovskite and (CZTS).

Developing or novel thin-film technology is under research stage and offer better properties which include visible transparency, high definite power in terms of watt/grams and novel form-factor [12]. In this chapter we shall discuss perovskite and CZTS under this emerging thin film technology. The origin of “Perovskite” from the calcium titanate crystal structure which was revealed by a German scientist named “Gustav-Rose” and this structure was given name by a Russian researcher named “Lev-Perovski”. Which was modified to Perovskite with passage of time. Since that time the term “Perovskite” was raised to all such type of compounds which have similar crystal assembly of calcium-titanate. General formula deduced for perovskite light absorption layer is AB-X₃, where A is cation-organic (i.e; CH₃NH₃⁺), B- is divalent cation-mate (i.e; Pb⁺², Sn⁺²) and X which shows halide anion (i.e; Cl⁻, Br⁻, I⁻). Organic inorganic halide-perovskite CH₃NH₃I, photovoltaic turned great amount of attention of scientists and

engineers towards itself due to its steady and great amount of efficiency enhancement from 3.8 to 22.1 % since 2009 [13, 14], for applications in optoelectronic devices, highly efficient electroluminescence from visible range to near infrared range (NIR) light detector applications and lasers [15, 16]. Perovskite is regarded as one of the potential replacements of thin film silicon PV devices which prevail solar PV market with remarkable efficiency of 26% [17]. This small gap of efficiency between PSC and Silicon solar PV of scientists and engineers especially those who have experience in organic PV or (DSSCs) because its materials are used in engineering of PSC. Origin of (PSC) starts from the device structure of DSSCs [11].

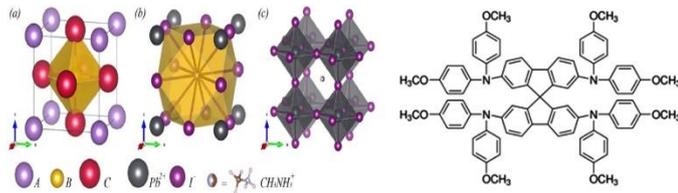


Fig. 2 Perovskite ABX₃ Construction (left) & SPIRO-OMeTAD Concluded from research ref [18] by © Copyright 2015 permission

Two of the important properties of perovskite is its largely tunable bandgap (i.e; PSC has a band-gap from 1.5 to 2.3 eV)[19]& high light captivation co-efficient which is larger than 10⁴ cm⁻¹[20, 21] that is comparable to other thin film PV constituent ingredients. i.e; materials of CZTS and CdTe[22, 23]. Its suitable and low-cost fabrication techniques also play an important role as compared to Si-based fabrication that is costly and complex high vacuum deposition method. Although it has great amount of efficiency but have two major problems causing hurdle for its improvements which need attention, i.e; (i) device instability [24] and (ii) Hysteresis of J-V [25].



Fig. 3 A basic perovskite crystal of the form ABX₃ [26]

For this purpose, we use CZTS-more stable, abundant, non-toxic light absorbing material with perovskite to make our thin film solar cell stable and efficient. For a long-term future development of PV technology, it is necessary to use such materials which are abundant, non-toxic and stable material just like silicon. For that purpose, CZTS (Kesterite -- quaternary compound) semiconductor has been developed as an owing postulant for such type of next-generation solar cell technology. It captivated attention of researchers owing to its three important properties, i.e; high efficiency, non-toxicity and low cost-earth

abundant material [27,28]. Kesterite (CZTS) come-from chalcogenite family having diamond like structure and it is regarded as exact derivative of commercialized CIGSe (CuInG_{1-x}Se₂) and CdTe PV technology, which are known for complimentary electronic and optical properties which have demonstrated an efficiency of more than 22%[17]. The bandgap of CZTS is 1.5eV which is so close to optimum band-gap of a single junction PV. Furthermore, bandgap of it can be adjusted between (1.5 to 1.6 eV) during the process of fusing with other elements i.e; Ag,Ge, creating it an appropriate contender for uppermost cell bandgap goal for Si based tandem solar cell stacks[29]. Photovoltaic devices fabricated by CZTS absorber layer are one of most efficient, non-toxic and abundant thin-film PV cells under research by scientists and engineers at present time. Despite its useful properties its reported conversion efficiency so far is hardly 9% for number of years of research and development [30] which is far lower as compared to suggested efficiency limit of 33% [31], due to high deficiency in Vo (Eg/q-Vo; here Eg is bandgap, q is charge on electron[32]. Many types of preparation techniques have been implemented and employed for CZTS thin film solar cell preparation in different scientific literature [33]. In which highest solar conversion efficiency of CZTS based on solution process have been reported which is 10.1% [34]. For vacuum process based prepared pure CZTS PV cell, PCE of 8.4% have attained to date[29] while lab based fabricated solar cell have attained an attractive efficiency of 12.6% [35, 36]. In CZTS the major challenge is the management of disorder of cation defects, a phenomenon in which zinc and copper cations are internally substituted, which result into point defects and this point defect is the major cause in decrease of Voc[36].

II. METHODOLOGY

Model structure of hybrid CZTS Perovskite thin film solar cell

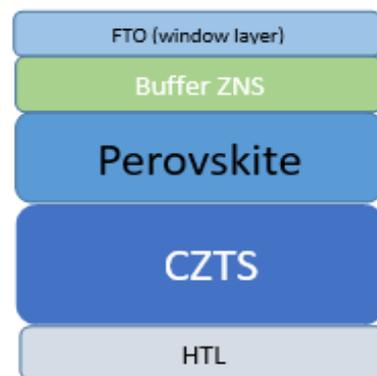


Fig. 4 proposed hybrid structure of Perovskite-CZTS solar cell

Fig. 4 displays the proposed hybrid structure of thin-film CZTS and Perovskite PV which consist of five layers. The top layer which can also be called as window layer I have used ITO (Indium Tin Oxide) that is primarily used as anti-reflection coating in opto-electronics such as liquid crystal displays (LCDs) and different kinds of electroluminescence, along this it has been used in thin film solar PVs[1,2] due to its two major qualities i.e.; high transmission efficiency of more than 85% and

low specific electrical resistivity of $1 \times 10^{-4} \Omega\text{-cm}$ [3,4,5]. These properties make it one of the most suitable window layers for maximum light transmission. The second layer we installed in the structure is buffer layer made of zinc-sulfide which has a wider band-gap than subsequent layers of that model. This buffer layer along with absorption of highly energetic photons also improve conductivity of window layer, drop in its resistivity up to 50% in the window layer as well as make it crystalline. Next layer is copper zinc tin oxide (CZTS). It is known as kesterite also and chemical formula is $\text{Cu}_2\text{ZnSnS}_4$, it has attracted attention for manufacturing thin film solar PVs due to its abundance, huge efficiency, low price and non-toxicity[6,7]. After that we have PSC material which is organic inorganic lead halide perovskite, ABX_3 where A is organic monovalent cation, B is lead or tin Sn(II) & X is the anion species like I⁻, Br⁻, Cl⁻[8]. Benefits of this type of semiconductor materials contain low material cost, low recombination-losses, large charge-carrier-diffusion length and probability of anion and cation swap for band gap[9]. The main disadvantages of perovskite include control of properties of material and film morphology, high vulnerability to moisture, instability of cell and the use of toxic material i.e; lead.

All simulations have been performed by SCAPS-1D which is frequently used for solar cells simulations it is free tool to measure important terms like V_o , short circuit current I_s , fill factor FF and efficiency- η of PVs. Its simulations are based upon three important semiconductor equations for the study of the solar-cell routine parameters: Poisson's equation, continuity equation of holes and continuity equation of electrons. SCAPS-1D software solves these three partial differential equations in a numerical way for electrostatic potential of holes and electrons concentrations as a function of positions X.

Poisson's equation can be formulated as follows:

$$\frac{\partial}{\partial x} \left(\epsilon \frac{\partial \psi}{\partial x} \right) = \frac{-q}{\epsilon_0} \left[p - n + N_D^+ - N_A^- + \frac{\rho_{def}(n,p)}{q} \right] \quad (1)$$

Where ϵ is the dielectric constant, ψ is the electrostatic potential while q is charge on electron or electronic charge, p and n are the free charge-carriers/volume while N_D^+ and N_A^- are ionized-donor and acceptor type dopants, i.e; localized states & ρ_{def} is the defect of charge density. Now continuity equation for conservation of free holes and free electrons in a device are expressed as;

$$\frac{\partial p}{\partial x} = -\frac{\partial J_p}{\partial x} + G - U_p(np) \quad (2)$$

$$\frac{\partial n}{\partial t} = \frac{-J_n}{\partial x} + G - U_n(np) \quad (3)$$

Where n and p are free carrier conc, N_D and N_A are charged dopants, $\rho_{def}(n,p)$ distribution of defects, J_p , J_n are the

holes and electrons current densities, U_p , U_n are the recombination rates and generation rate is represented by G .

During simulations we changed some parameters while keeping other key parameters constant; i.e; absorber layer thickness was changed while keeping doping concentrations etc kept constant. In second step we changed doping concentration in the absorber layer and checked for their output key parameters. We performed simulations in the room temperature or ambient temperature (25°C or 300K). At the final step we concluded the optimum thickness and doping concentration of absorber layer after several simulations results by observing J_{sc} , V_{oc} , FF% and conversion efficiency percentage, performed by SCAPS-1D.

III. RESULTS AND DISCUSSION

We observed different parameter values for different thickness of each layer as well as defects in respective layers. These parameters include voltage, current, fill-factor, efficiency. Which are described in the following manner:

Window layer:

We start with the top window layer whose thickness has been varied and observed the key parameters, where in our simulations optimum thickness value is 160nm where maximum open circuit voltage, short circuit current density, percentage fill-factor and conversion efficiency obtained with values of 0.8706 V, 24.55044 mA/cm², 75.02% and 15.71% respectively as shown in fig.5.

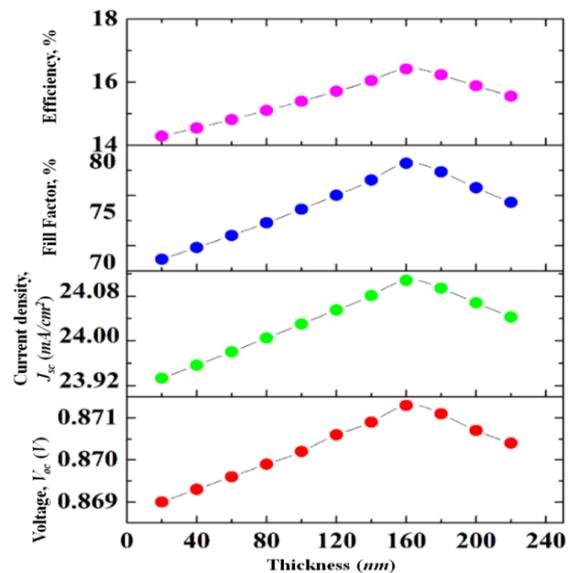


Fig. 5

Then we changed the doping concentration in the window layer and observed different values of performance parameters for different value of defect or doping values. During which we obtained an optimum value at 22 doping concentration/cm³ where performance parameters in term of V_{oc} , J_{sc} , percentage fill-factor FF, and efficiency of the value of 0.8720 V, 23.081452 mA/cm³, 78.18% and 17.14% respectively as shown in fig.6.

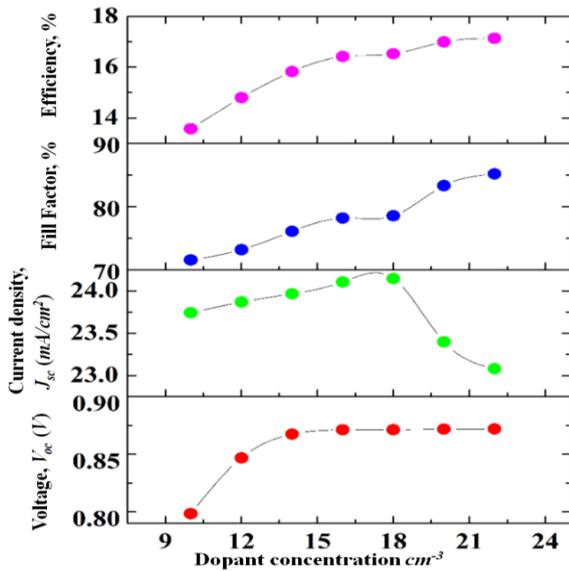


Fig. 6

Buffer layer:

The main function of the buffer layer in heterojunction thin film solar cell is to form such a junction layer which admit maximum number of light rays to absorber layer and junction layer [1]. Here we observed buffer layer by changing its width and doping concentration and observed different performance parameters of the thin film solar cell and we obtained the following result during the process. During simulations of buffer layers for different width, we obtained optimum solution at 220nm where we obtained, Voc, Jsc, fill-factor FF and efficiency ,ef of 0.8737 volt, 24.106716 mA/cm2, 85.37 % and 17.97% respectively as sown in fig. 7.

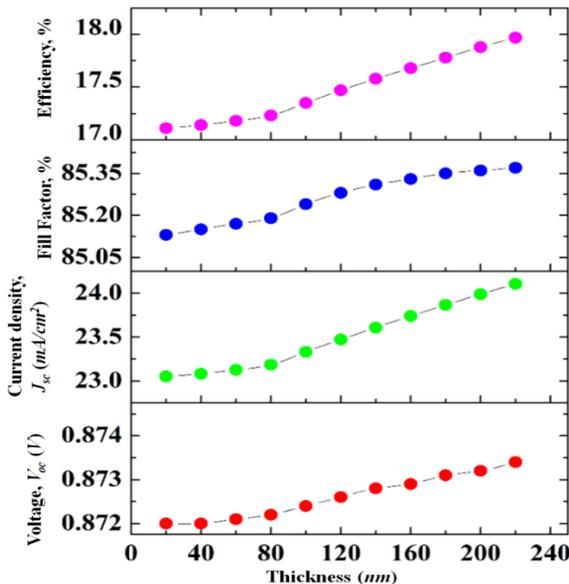


Fig. 7

Now by changing the doping concentration of the buffer layer we performed different simulations during which we obtained an optimum solution at defect value of 20/cm3 of

buffer layer where we obtained maximum values of Voc, Jsc, fill-factor percentage and efficiency percentage of 0.8735 volt, 24.213276 Amp/cm2, 85.35% and 18.05 % respectively as sown in fig. 8.

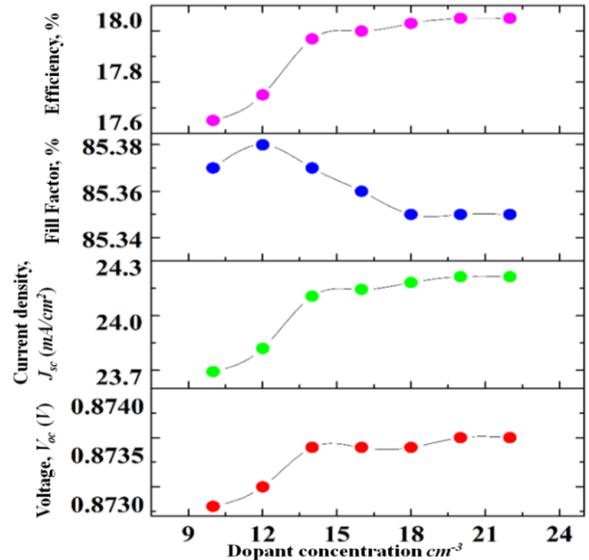


Fig. 8

Absorber layer1 (Abs1) or Perovskite layer:

Graph of Abs 1:

From the simulation graph it's is obvious that the optimum thickness is 400nm for which optimized cell performance parameters occur. Beyond this thickness, although there is increase in other parameters except fill-factor which decreases which largely effect cell performance as sown in fig. 9.

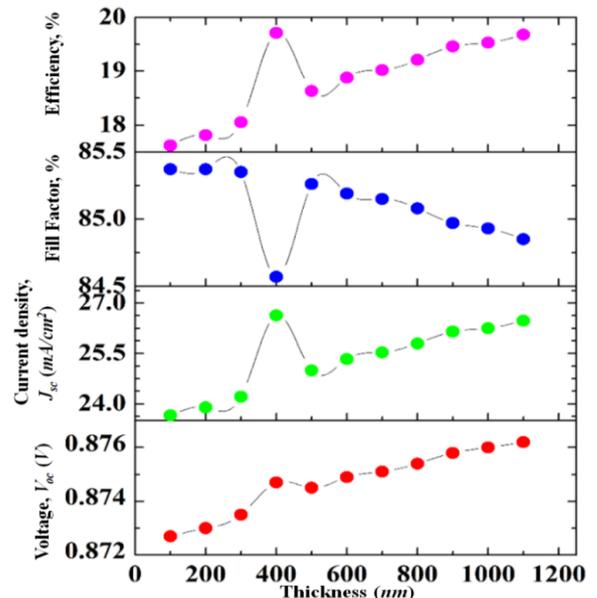


Fig. 9

Absorber layer 2 (Abs 2) or CZTS layer:

Then we observed absorber layer-2 or copper zinc tin sulphide (CZTS). Whose simulations are stated in the following table which shows key performance parameters for different thickness of CZTS layer. During our simulations we obtained an optimum solution at thickness of 1000nm where we obtained Voc, short Jsc , fill-factor% and efficiency% of 0.8926 volt, 28.860649 A/cm2, 82.93% and 21.36% respectively as sown in fig. 10.

Furthermore, during simulations keeping I obtained efficiency of 22.6% for tandem Perovskite-CZTS solar cell by changing the band-gaps of perovskite and CZTS to 1.9 eV and 1.6 eV respectively as sown in fig. 11. For that formation I obtained an efficiency of 22.60%. This high efficiency is as a result of making high bandgap absorbing material where recombination losses are low. I took the sample of already made structure where efficiency was 22.57% [37].

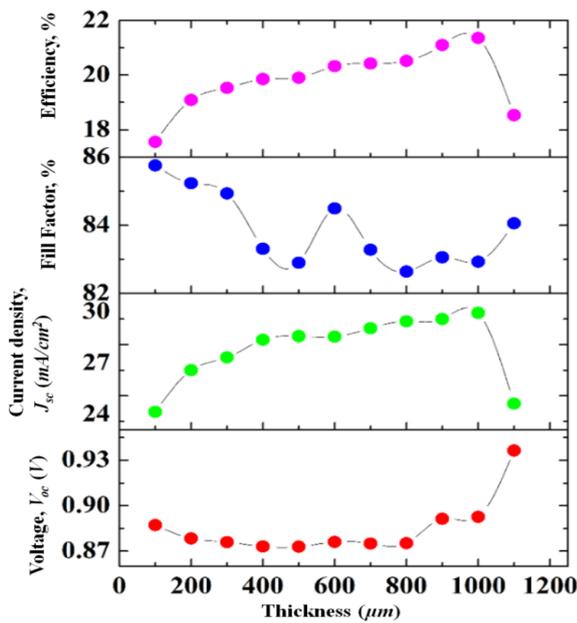


Fig. 10

BSF:

It is the last layer of the stack known as back surface field or hole transport layer- HTL in thin film solar cells. It's basically a p-type which serves as p-type dopant in the back surface. This layer controls recombination losses as well as keeping series resistance at low level by providing ease to mobile carriers to be collected at the back electrode, thus enhancing fell-factor. We had performed simulations on its thickness as well as defects and picked-up optimized solution of this layer through SCAPS-1D. Following are the tables showing optimum width and defect of back surface field. It shows that the optimum width of this layer is 440nm for which we have 0.9157 V-Voc, 29.142192 A/cm2 - Jsc , 82.99% fill-factor percentage and 22.15% conversion efficiency percentage. The following simulation diagram shows the performance parameters dependence on the thickness of the HTL material which about linearly increases by increasing its thickness up to 440nm and beyond this thickness series resistance increases which decreases fill-factor. Which can be easily seen from the following simulations diagram

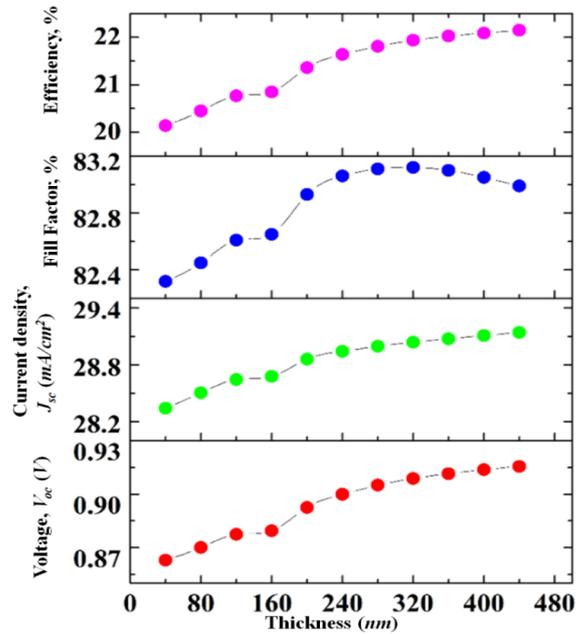


Fig. 11

The following figure shows the simulated program result of defect/ doping concentration which effects the performance parameters of thin film solar cell in which 21 mass/cm3 concentration which shows maximum EF% of 23.22%, FF of 83.87% , Jsc of 29.139922 A/cm2 and Voc of 0.9750. After this, fill-factor declines due to due to increase in series resistance so optimum solution is that as sown in fig. 12.

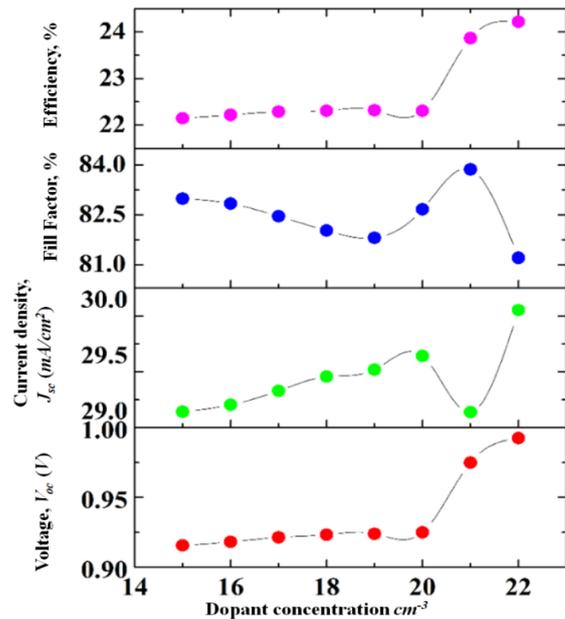


Fig. 12

CONCUSLION

I worked on the perovskite solar cell due to its organic inorganic properties and high conversion efficiency and abundancy. As its efficiency is high but its life time is so short and is vulnerable to environment so the need of tandem is felt for which CZTS an abundant, stable and non-toxic is the best material to make tandem with Perovskite cell to make it durable and efficient. As their bandgaps can be tuned to obtain high quantum efficiency. As Perovskite have high bandgap of 1.55 to 2.3 electron volts and CZTS have 1.45 to 1.6 electron volts. So for high energy photon i.e UV light we place Perovskite absorber layer and for low energy photons i.e; infrared we place CZTS as it has smaller bandgap.

From simulations keeping the bandgap and thickness of the absorber layers we obtain a best efficiency of the tandem which was 22.60%. For future works I shall recommend different fusions of absorber layers buffer layers and using tunnel junction between the perovskite-CZTS layers as well as keep changing bad-gap and thickness of the absorber layers we can obtain higher efficiencies.

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