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New Materials for Thin Film Solar Cells

Senthil T.S and Kalaiselvi C.R

Abstract

Thin film technology has a world-wide reputation in the field of thin film deposition process and also it paves a way for innovative techniques in large scale applications. Modern thin film technology has evolved into a sophisticated way to increase the performance and aesthetic value for making new functional devices. One such application is search of new materials for thin film solar cells as it provides the solution for the today’s concern of energy crisis. Depending on the processing technology solar cells are of various types. Among them, silicon wafer solar cells and thin film solar cells are most promising. Thin film technology has made solar cells more feasible to be employed in terms of device design and fabrication. The efficiencies produced by these solar cells still need to be improved. For this many investigations for further improvement from CIGS (copper indium gallium selenide) solar cell to dye sensitized solar cells and perovskite solar cells. Due to toxic nature and environmental impact the use of lead in perovskite solar cells are replaced by tin or some materials which would equalize the achieved efficiency of lead. Hence the developments in search of innovative materials continue its path in thin film solar cells to develop the photovoltaic field by enhancing its efficiency.

Keywords: solar cell, physical vapor deposition, drop casting, interfacial impact, efficiency

1. Introduction

Energy is the key factor for any living creature to exist in the universe. With the advent of industrialization and increase in population led to a surge in the crisis for energy. The reduction of our dependence on fossil fuels (oil, coal and natural gas), as well as the evolution towards a cleaner future requires the large deployment of sustainable renewable energy sources. Among them solar energy is the most abundant and is available throughout the year.
Moreover the solar energy has the greatest potential to fulfill the thirst for energy and the need for innovation of clean and eco-friendly technologies. In this perspective developing solar cells is one of the best approaches to convert solar energy into electrical energy based on photovoltaic effect. Depending on the cell material and the processing techniques solar cells are of two kinds based on wafer and thin film. Thin film solar cells have the key advantage of their dimensionality, having thickness a fraction of other types of solar cells and it is attractive in terms of cost factor with minimum material usage [1]. However thin film solar cells promise to achieve the goal with the low cost and high efficiency from CIGS to dye sensitized solar cells and recently with the advent of perovskite based materials for solar cells.

2. Preparation of thin film solar cells

To prepare solar cell there are variety of methods and materials are used, among them thin film solar cells are unique. In this chapter the historical background and the emergence of new techniques in the growth of thin film solar cells such as CIGS, dye sensitized solar cells and perovskite solar cells are presented.

2.1. CIGS thin film solar cells

Copper indium gallium selenide (CIGS) based solar cells are receiving worldwide attraction for solar power generation. These materials absorb light at a rate of 10–100 times more efficient compared with silicon-based solar cells, thus the thickness of the films obtained in the order of a few microns. The major advantage of this technology is attributed as of low raw material usage with less complex procedure for manufacturing. CIGS solar cells exhibit high radiation resistance, making them suitable for space applications [2].

CIGS is a promising absorber material and received considerable attention due to its direct band gap, high absorption co-efficient and less material wastage. It is an efficient thin film solar cell with the efficiency of 22.8% comparable to crystalline silicon (c-Si) wafer based solar cells [3]. CIGS thin films can be fabricated by various methods among them physical vapor deposition is important.

Thin film deposition by PVD is regarded as a vacuum coating method and is classified into two techniques, evaporation and sputtering. The particles are capable of moving in a straight path as the system is kept in vacuum and the films are coated by physical means that are commonly directional, rather than conformal in nature [4].

2.1.1. Sputtering method

Sputtering deposition is a vacuum based process that is used for CIGS cell fabrication. The fabrication process will involve the following steps:

1. Deposition at room temperature for attaining low temperature process and hence reduced the cost of equipment.
2. Introducing Se vapor at any time during the process to avoid potential damage to the bottom Si cell by invoking unwanted species.

3. Cd free buffer layer also targeting an environmentally friendly process [1].

Deposition of CIGS junction on a soda lime glass substrate covered by Mo layer at 1 μm thick [1]. The best back contact material for CIGS solar cells was found to be molybdenum since it is having high conductivity and relative stability at the high processing temperature. The deposition of Mo layer is by means of DC magnetron sputtering technique. The grown films play a crucial role in the performance of the CIGS device. During the deposition process, parameters such as power, time and pressure should be carefully chosen [5].

The two points to be considered in the CIGS thin films are: (1) the Mo back contact which cannot obviously be used in a tandem cell due to its opacity, (2) the CdS layer deposited by the chemical bath deposition (CBD) technique, which can impact bottom cell properties. The schematic view of the CIGS thin film by sputtering process is shown in Figure 1. The bottom Mo contact uses rather a common bilayer structure, a first adhesion layer is magnetron DC sputtered at high pressure and a second one is deposited at low pressure to increase the conductivity. A standard CdS buffer layer is deposited by chemical bath deposition. Ultimately, it will be replaced by a Zn layer deposited using the sputtering technique at room temperature. The top electrode is composed of an ZnO/aluminum doped zinc oxide (AZO) bi-layer. The absorber layer process is deposited at room temperature using pulsed DC magnetron sputtering and argon plasma [1].

In order to obtain the chemical composition of CIGS absorber, energy dispersive spectroscopy measurements (EDS) were carried out under 10 kV mode and it was shown in Figure 2. Atomic composition of the obtained film was calculated as: Cu—14.8 at%, In—18.35 at%, Ga—2.86 at% and Se—25.95 at%. On the basis of measured values the relative ratios of Cu/(In + Ga) and Ga/(In + Ga) were found to be 0.7 and 0.13, respectively [5].

Figure 1. Preparation of CIGS thin films by sputtering process.
A sputtering technique using low temperature processes and without any hazardous gas diffusion at high temperature can then lead to functional devices. Hence sputtering technique can be successfully used for the fabrication of CIGS thin films solar cells [5]. SEM cross sectional view of CIGS thin film solar cell is shown in Figure 3.

The stoichiometry of CIGS is very complex thereby making uniform and large-area deposition is very difficult. It also indeed of encapsulation which is expensive as it prone to moisture and oxygen easily. Also, their reliance on rare elements of tellurium & indium and recycling of toxic element like cadmium may limit their potential for large-scale production and it would be replaced by some other elements [6].

Figure 2. EDS spectral analysis of the top surface of CIGS absorber layer.

Figure 3. SEM image of CIGS thin film solar cell.
2.2. Dye sensitized solar cell

Dye-sensitized solar cell (DSSC) has been known as a promising photovoltaic device to achieve moderate efficiency at low cost [7]. The principle of DSSC imitates nature's novel effect of photosynthesis. In DSSCs, the photo-sensitizer captured the incident photons that are absorbed on a thin TiO$_2$ layer placed on the anode. DSSCs make use of liquid electrolytes to transfer ions to a counter electrode thus electric current is produced [8]. DSSCs have attained efficiencies of up to 12.3% [9] and attained benefit from their versatile nature and low cost for the manufacturing process. The main component of DSSC is TiO$_2$ thin film that is conventionally prepared by various methods. Among them doctor blade and spin coating methods are simple and low cost techniques [10].

2.2.1. Doctor blade technique

Doctor blade or tape casting is one of the widely used techniques for producing thin films on large area surfaces. In the doctor blading process, a well-mixed slurry consisting of a suspension of ceramic particles along with other additives is placed on a substrate and a constant relative movement is established between the blade and the substrate resulting in the formation of a gel-layer when dried [11]. The diagrammatic view of this technique is shown in (Figure 4).

The existence of an optimized thickness of TiO$_2$ thin film is inherent for the charge storage and transfer to the film so that in DSSC the highest efficiency could be achieved [12]. In this method, TiO$_2$ paste usually employed as a surfactant material to increase the porosity of TiO$_2$ thin film. The improved performance of DSSC could be ascribed to the compact and crack-free TiO$_2$ thin film prepared by the modified doctor blade method [10].

For the modified doctor blade method, a dense TiO$_2$ paste was prepared in a following manner: TiO$_2$ powder was blended in a mixture of polyethylene glycol and de-ionized water in a plastic bag for 10 min under rolling of a steel pipe. After that, by the way of doctor blade method the resulting TiO$_2$ paste was coated on TCO glass [13]. Then the film was dried in air for 30 min. Then the film surface was covered by a drop of lubricating oil and stabilized at 100°C in an oven for reducing cracks. Finally, the film was covered with a flat glass and compressed for 30 s. The derived TiO$_2$ thin film was annealed at 450°C for 2 h [10]. This novel method is also observed to substantially improve the overall conversion efficiency of the resulting DSSC which presents strong potential for DSSC module construction [10].

Figure 4. Doctor blade technique.
Surface morphology of two kinds of TiO$_2$ thin films are shown in Figure 5. Even though they are looking similar, the variation in the thickness is larger for modified doctor blade thin film than the conventional one.

2.2.2. Spin coating method

Spin coating method is one of the most common techniques for the preparation of thin films on substrates. Spin coating method is widely used in micro-fabrication, where it can be used to create thin films with thicknesses below 10 nm [15]. The advantage of spin coating method is its ability to quickly and easily produce uniform films, ranging from a few nanometres to few microns in thickness.

The spin coating procedure includes deposition, spin up, spin off, and evaporation. The substrate being covered by depositing the solution which is rotated at high speeds to coat the substrate using centrifugal force. The volatile solvent easily evaporates and hence the desired film’s thickness is dependent on the concentration of solution, solvent, and spin speeds [16]. The film thickness of the order less than 10 nm is useful in the field of micro fabrication and photolithography [4]. The flow diagram for the spin coating process is shown in the (Figure 6).

Titanium (IV) isopropoxide (TTIP), ethyl alcohol, nitric acid (HNO$_3$) and distilled water were used as received without further purification. The synthesis procedure of nanocrystalline TiO$_2$ thin film can be obtained by mixing titanium isopropoxide with ethanol and the distilled water was added drop by drop by continuous stirring about 1 h. The resulting solution was peptized using nitric acid and refluxed at 80°C. After that TiO$_2$ sol had been prepared and coated on conductive glass substrate with the spin rate of 3000 rpm for 30 s. Then followed by annealing the TiO$_2$ thin films at 450°C [17].

The major challenge of DSSC is that it should withstand its stability under high temperature and its low absorption coefficients due to its interfacial recombination. Moreover the cost of the ruthenium dye used sets its intrinsic drawback limits its scope to small scale applications. Then search for new innovative material pertains to continue its thirst for perovskite related materials by the replacement of liquid electrolyte.
2.3. Perovskite solar cells (PSCs)

2.3.1. Emergence of perovskite

Perovskite solar cells are in focus of the solar cell development research in recent years due to their high efficiency, cost effective fabrication and band gap tuning ability. Perovskite compound was first discovered by Gustav Rose in 1839, named after a Russian mineralogist L.A. Perovski. The specific crystal structure was first found in an inorganic mineral CaTiO$_3$ (ABX$_3$) with a cubic unit cell [18]. The cation A is replaced by a small organic cations such as CH$_3$NH$_3^+$, C$_2$H$_5$NH$_3^+$ and HC(NH$_2$)$_2$+ to create organic-inorganic hybrid materials while the cation B with divalent metal ions such as Pb$^{2+}$, Sn$^{2+}$ or Cu$^{2+}$ and the X anions are halides (Cl$^-$, Br$^-$, I$^-$) [19]. Perovskite are non-excitonic as no external force is needed for the generation of excitons whereas organic photovoltaic and DSSCs are excitonic.

Miyasaka and his co-workers replaced the dye pigment in DSSCs with two hybrid organic-inorganic halide perovskites, CH$_3$NH$_3$PbBr$_3$ and CH$_3$NH$_3$PbI$_3$ and the efficiency of 3.13 and 3.61% obtained was not a considerable one [20]. A major breakthrough happened in 2012 when Gratzel and Park et al. used Spiro-MeOTAD as the hole transport material (HTM) with efficiency of 9.7%. In 2016 the efficiency of perovskite solar cells was improved to be 22.1% [21].

2.3.2. Interfacial impact on the performance

The perovskite solar cells employs a perovskite absorber between an electron transport layer on a conducting glass substrate (FTO) and a hole transporting layer with a metal back contact on top. The working principle of this device was similar to that of DSSCs. Here perovskite material acts as a light absorber and electron transporting layer (TiO$_2$) takes part in charge separation and electron transport whereas the holes are transferred to hole transporting layer. An ideal selective contact does not deteriorate the light absorbing layer and also does not induce degradation of the device. There are also no energy losses when photo-generated
carriers are injected from the light absorbing material into the selective contact, hence no recombination at the interface, and the Fermi level of its corresponding carrier is maintained at the interface without any drop. The contact layer must also be balanced with respect to perovskite layer as otherwise it would lead to charge accumulation at selective contact and leads to interfacial charge recombination [22].

The primary role of a selective contact is to reduce the interfacial recombination between perovskite light absorbing layer and the FTO and Au extracting contacts. It should be as thin as possible in order to reduce the transport resistance but thick enough to avoid pinholes, hindering effective charge recombination. Obviously the goodness of an interfacing material for an efficient electron transport and performance in PSC will lies on the nature and interaction of the chosen selecting contact with the light absorbing perovskite layer. Tan et al. reported that using chlorine-capped TiO$_2$ colloidal nanocrystal film that mitigates interfacial recombination and improves interface binding in low-temperature planar solar cells [23].

Hole transporting material (HTM) also plays a vital role in both extracting and transporting the holes from the perovskite materials to the back electrodes thus minimizing undesired recombination losses at the interfaces. Spiro-OMeTAD is the widely used HTM results in better performance of the device. As of high cost and tedious synthesis inhibits its commercial application looking forward for inorganic semiconductors. Recently CuSCN has been used as HTM in perovskite solar cells and considerable high power conversion efficiency has been achieved [24].

There are numerous techniques employed to deposit different layers of perovskite solar cells like drop casting, spin coating, slot die coating, screen printing, ink-jet printing, etc. Among them drop casting is a simple and low cost method for the deposition of perovskite films [25].

### 2.3.3. Drop casting method

Drop casting is a simple and potentially scalable casting method proposed for the fabrication of micro and nanocrystalline thin films. The impingement of a solution drop onto a substrate in a simple process called drop casting, usually results in spreading of the liquid solution and the formation of a non-uniform thin solid film after solvent evaporation [26]. Drop-casting usually happens by the way of releasing large droplets in a controlled manner that spreads and wet the surface upon impact as far better than spray coating, although its application is limited to small-area films and coatings [27]. Schematic view of perovskite solar cell with different layers is shown in the (Figure 7).

The formation of homogeneous thin perovskite layer is extremely important, and it can be developed by solution process. The process is employed for the most common structure of methyl ammonium lead iodide. The initial components taken in the appropriate ratio is spread over the entire surface of the substrate. Then, the spin-coater is accelerated to the desired rotational speed to evaporate the solvent. If the solvent does not dissolve the perovskite materials and is miscible with DMSO (dimethyl sulfoxide), a toluene or chloroform solution is dripped on the substrate during spinning. At last, all constituents are frozen into a uniform layer on the removal of the residual DMSO and a new complex as an intermediate phase is obtained. Films of different thicknesses were achieved by varying solution concentration [28].
Drop casting is similar to spin coating method but the major difference is no substrate spinning is required and also less material wastage. Film thickness depends on the volume of dispersion used and the particle concentration, both of which can be easily varied. Generally, it is desirable to use solvents that are volatile, wet the substrate, and are not susceptible to thin film instabilities. However, water is not a recommended solvent for depositing some materials because the nanoparticles oxidize as the water evaporates from the sample [29]. In some cases alcohols can replace water, a good choice relies on the use of organic solvents such as hexane or toluene for nanoparticles with hydrophobic capping ligands.

The demerits of drop-casting are that even under ideal conditions, the rate of evaporation differs across the substrate thus leads to variations in film thickness or internal structure. However, it serves as a quick and accessible method to generate thin films even on a small substrates. Figure 8 shows the SEM image of the perovskite thin films prepared with different layers.
3. Recent trends in solar cells

3.1. Flexible perovskite solar cells (F-PSCs)

Now research has been moved towards a flexible PSCs from rigid PSCs and it achieved notable milestones in terms of its efficiency with light weight [30]. Unlike rigid PSCs employ glass substrate for its processing, F-PSCs used flexible substrates like poly ethylene terephthalate (PET) which could not endure at high processing temperature significantly higher than 200°C. Hence various low-temperature techniques have been developed to fabricate electronic selective layers (ESLs) with great progress in attaining high power conversion efficiency (PCE) [31]. The two significant aspects to attain high efficiency in F-PSCs are the low temperature ESLs and the high quality perovskite absorbers that include grain size, trap density, charge transport, carrier lifetime, etc. The F-PSCs give much lower PCE compared with rigid counterparts though they are having similar process used to deposit perovskite absorber film. It requires different deposition methods to achieve desirable power conversion efficiency of perovskite films especially for larger area F-PSCs. The quality of the perovskite film was significantly improved by the inclusion of an additive dimethyl sulfide (DS) thereby enhancing both the grain size and crystallinity. When DS was introduced into the perovskite precursor solution, it chelates with Pb\(^{2+}\) to form an intermediate complex resulting in smaller Gibbs free energy and slower the rate of growth for perovskite to crystallize. Further the trap density of the perovskite film is reduced as the chelation interaction efficiently retards transformation kinetics during the thin film crystallization process, hence PCE of F-PSCs is increased to as high as 18.40%, the highest reported value so far for the F-PSCs. It is also expected that large area F-PSCs may also give improved efficiency as 13.35% [32].

Deployment of flexible PV technology is not only motivated by the quest for high-throughput and low-cost manufacturing but on the view for marketing it would be able to access with its eminent properties as it is being flexible, thin and lightweight, which would make it easy to integrate or apply on any surface or structure (either rigid, curved or flexible) [33] and even have its applications in portable and indoor electronics.

3.2. CIGS perovskite tandem solar cells

The development of high efficiency semi-transparent perovskite solar cells is necessary for the application in integrated photovoltaics and tandem solar cells. Tandem solar cells allow higher efficiencies than single-junction solar cells by better utilizing the energy of short-wavelength photons in the spectrum of sunlight. Top cells comprising a high-bandgap semiconductor to generate photocurrent at high voltage from the short-wavelength part of the solar spectrum. Longer-wavelength light, beyond the bandgap of the top cell, is transmitted to an underlying bottom cell comprising a lower-bandgap semiconductor with broad absorption coefficient. Tandem cells that are unique to inorganic-organic metal-halide-perovskite materials, particularly due to their bandgap-tuneability and luminescence efficiency thus an excellent candidates for applications in building integrated photovoltaics (BIPV) and tandem solar cells. Rapid growth in perovskite solar cells already reached its highest efficiency of 22.1%. However the translation of such high efficiencies to semitransparent perovskite
devices requires the development of suitable transparent conducting electrodes which have high transparency, conductivity and process compatibility with prior device fabrication steps is a major perspective [34].

Deposition of transparent conductive oxides (TCO), such as indium tin oxide (ITO), aluminum doped zinc oxide (AZO), or indium zinc oxide (IZO) acts as an electrode. Halide perovskites are known to have solvent and temperature instabilities hence physical vapor deposition processes are preferred rather than sputtering and spin coating. Thermally evaporated molybdenum oxide (MoOx) and thin Ag are the two existing material systems that have been reported as potential buffer layers for semitransparent devices [35]. PCE of 16.0% can be achieved and an average transparency of 54% in the near infrared region using thin Ag. We can apply the same semi-transparent cells in a 4-terminal (4T) tandem configuration with Cu(In,Ga)Se (CIGS) cell and attained a tandem efficiency of 20.7%. Although a tandem with Si cells would yield higher efficiency, both perovskite and CIGS are thin film technologies which are lightweight and can be deposited on flexible substrate. Further they exhibit radiation hardness but capable to withstand radiation levels several orders higher than crystalline Si, lending them suitable for high altitudes and space applications [36].

3.3. Ultra high band gap solar cells

The recent surge for interest towards the ultra-high band gap absorbers for tandem solar cells from the oldest material selenium with a band gap of 1.95 eV. Moreover, Se devices are air-stable, non-toxic, and extremely simple to fabricate. Se solar cell utilized n-type TiO$_x$ deposited on SnO$_2$ (FTO) coated glass and p-type Se followed by gold contact with its efficiency of 5% lasts same for more than 30 years. This structure is similar to hybrid perovskite solar cells without the advanced hole transporting layer [37]. Now the redesigned Se device for its improvement in terms of its efficiency can be modified in three aspects. First, introducing a reliable inorganic MoOx (molybdenum oxide) with high-work-function as a hole-selective layer between selenium and the gold back contact in order to reduce recombination and improve collection as it is been in both CdTe solar cells as well as other inorganic and organic photovoltaics [38]. Second method by reducing the thickness of the selenium absorber to only 100 nm—20 times less than the previous Se champion cell as well as typical chalcogenide absorbers such as copper indium gallium selenide (CIGS). Finally optimizing the buffer layer to reduce the cliff at interface should significantly improve Voc (open circuit voltage) as well as fill factor. Though Se an attractive alternative candidate for a high-band-gap absorber they are prone to practical applications by simple and inexpensive fabrication process, lack of highly toxic elements such as Cd and Pb, and stability upon prolonged storage and air exposure for these devices. Thus now Se solar cells find its new outlook after three decades with slight modification which suits well for our future energy crisis.

4. International standards for solar panels

IEC Technical Committee TC82 was established in 1981. It is the most important International body regarding photovoltaic related standardization. The main task of TC82 is to prepare
international standards for systems of photovoltaic conversion of solar energy into electrical energy and for all the elements in the entire photovoltaic energy system.

- IEC TC82-IEC Technical Committee 82, solar photovoltaic energy system.
- ISO TC 180-ISO Technical Committee 180, solar energy.
- ASTM E44-ASTM Committee E44 on Solar, geothermal and other alternative energy.
- IEEE SCC21-IEEE SCC21 standards Coordinating Committee on fuel cells, photo-voltaic, dispersed generation and energy storage.

5. Conclusion

Thin film technologies made a remarkable advent in the photovoltaic industry for the manufacturing of solar cells. Thin film solar cells offer a most promising options for reducing the cost of photovoltaic systems. Enormous progress in device performance has been made in dye sensitized to perovskite solar cells. Perovskite solar cells open the door for novel applications in the production of solar cells with increase in stability and reliability. Major concern is about the toxicity of lead and its impact in the environment. Then a major task is finding a material which would replace the lead. Tin can replace lead but the stability issues still pertain and the efficiency achieved was low compared with lead. The device performance suits best in N₂ gas atmosphere to avoid quick degradation of tin. Therefore a thirst for new material without lead such as BiFeO₃, BiFe₂CrO₆ and BiMnO₃. The overall power conversion efficiency is lower than metal halides but they are more stable. Hence it been able to investigate bismuth based photovoltaic materials. Cesium with bismuth, for example, Cs₂BiₓI₉ will give the highest solar cell performance with low toxicity and environment impact. It also proves to be a predominant in the fulfillment of our future energy crisis in terms of its simplicity in manufacturing process and low cost. Moreover there is also an opportunity to develop high-performance tandem cell technology that uses both perovskite and existing technologies and this may allow market introduction as a new premium product.

Author details

Senthil T.S* and Kalaiselvi C.R

*Address all correspondence to: tssenthi@gmail.com

Department of Physics, Erode Sengunthar Engineering College, Perundurai, India

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