INTRODUCTION

CHAPTER I

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1.1 INTRODUCTION

A thin-film solar cell (TFSC), also called a thin-film photovoltaic cell (TFPV), is a solar cell that is made by depositing one or more thin layers (thin film) of photovoltaic material on a substrate. The thickness range of such a layer is wide and varies from a few nanometers to tens of micrometers.Many different photovoltaic materials are deposited with various deposition methods on a variety of substrates. [1].

Thin Film Photovoltaic cells use a much smaller amount of semiconductor material just 1.2 microns thick versus hundred of microns of crystalline silicon. And they use direct band gap semiconductor absorption bands, enabling them to achieve similar efficiencies of c-Si PV that have 24% cell or 12-18% module efficiencies. Moreover, TFPV may be less costly to manufacture because it lends itself to automated processing and better scalability. TFPV cells typically consist of three layers deposited on a large glass or metal substrate: a transparent conductive oxide (ITO or SnO_2) layer, a middle semiconductor photovoltaic layer, and a thin metal layer (Al, Au, Cu or Mo). Typical semiconductor materials for thin-film solar cells include cadmium telluride (CdTe), copper indium gallium diselenide (CIGS), and amorphous silicon (a-Si) layer. The best laboratory CdTe cells have achieved efficiencies of more than 15%, and CIGS, almost 20%. However, when produced in high volumes and fully packaged, actual module efficiencies are much lower than published cell efficiencies [2]. Photovoltaic offers any advantages over other methods of converting solar energy into electrical energy these include,

- Simplicity
- Profitability
- Environmental compatibility in addition it produces no gaseous or thermal pollution during operation.

The classical inorganic PN-junction solar cell, always demand the use of extremely pure starting materials and somewhat sophisticated production procedure. A very promising alternative to classical, inorganic PN junction solar cell is the concept of nanoporous, dye sensitized photo electrochemical solar cell, introduced by O'Regan and Gratzel in 1991 [3].

1.2 IMPORTANCE OF DYE SENSITIZED SOLAR CELL

A dye-sensitised solar cell (DSSC) is a device to change light into electrical energy by light sensitization established on wide energy–band semiconductor. Because of lower manufacturing cost, DSSCs are of great interest. With their simple and easy manufacturing process, DSSCs can be assembled in general environments at room temperature, and their cost is only around one-third of the traditional silicon–based solar cells. In future, if the cost can be further reduced, when DSSCs are compared with silicon based solar cell having the same efficiency, the total cost of DSSCs can be only one-tenth that of silicon-based solar cells [4]. The solar cell consists of a dye covered semiconductor electrode and a counter electrode arranged in a sandwich type configuration. The most investigated wide band gap semiconductor for DSSC is the titanium dioxide. It is an inert, non-toxic and inexpensive material with adequate spectroelectrochemical properties for solar cell application [5].

1.2.1 ADVANTAGES OF DSSC [6,7]

- Low Generation cost
- Environment-Friendly
- Flexibility
- Possibility of engineering into flexible sheets
- DSSCs work even in diffused-light conditions
- Low cost of sensitisation material production
- Ease of fabrication

- Possible to realize various colour
- Low process temperature.

1.3 CHALLENGES FOR ARTIFICIAL DYE SENSITIZED SOLAR CELL

The efficiency of DSSC is determined mainly by the sensitizer used. The marketed dyes for commercial use are mostly chemical synthetics, such as N719 and N3 dyes, both of which have satisfactory photoelectric conversion efficiency. However, these dyes always use some heavy metals, which are both expensive and produce environmental pollution. Generally, transition metal coordination compounds (ruthenium transition metal polypyridyl complexes) are used as effective sensitizers. This is because over the entire spectrum of visible light, there is intense charge-transfer absorption and metal to ligand charge transfer. However, ruthenium polypyridyl complexes contain heavy metals, which make this kind of DSSC is unpopular from environmental aspects. Moreover, the synthesis process of this complex is very complicated and expensive. In order to replace the rare and expensive ruthenium compounds, many kinds of natural dyes have been actively studied and tested as low cost materials. [4].

1.4 IMPORTANCE OF NATURAL DYES SENSITIZATION

The use of natural pigments as sensitizer for the conversion of solar energy in electricity is interesting because, on one hand it enhances the economical aspects and on the other it has significant benefits from the environmental point of view [8]. Natural dyes serve as cheap and eco friendly alternatives to artificial sensitizer for DSSC. Naturally, some fruits, flowers, leaves, show various colours and contain several pigments that can be easily extracted and then employed in DSSCs [9]. Therefore, unlike artificial dyes, the natural dyes are,

- Easily available
- Easy to prepare
- Low in cost
- Non-toxic
- Environmentally friendly and

- Fully biodegradable [10].

In most cases, the photo activity of natural dyes is attributed to the presence of anthocyanin. The word anthocyanin is derived from two Greek words meaning plant and blue. Anthocyanins are natural compounds that give colour to fruits, vegetables and plants and are also largely responsible for the purple–red colour of anthum leaves and for the red colour buds and young shoots. Chlorophyll is the pigment that effectiveness as a photosensitizer in the process of photosynthesis of green plants, which have a maximum absorption at a wavelength of 670nm.The natural dye, adsorbed onto the semiconductor surface, absorbs visible light and promotes electron transfer across the dye/semiconductor interface. The use of a natural product as the semiconductor sensitizer enables a faster and simpler production of cheaper and environmentally friendly solar cells [11].

1.5 SIGNIFICANCE OF *EUGENIA JAMBOLANA* AS DYE SENSITIZER

A fairly fast growing species, it can reach heights of up to 30 m and can live more than 100 years. Its dense foliage provides shade and is grown just for its ornamental value. The wood is strong and is water resistant. Jambul trees start flowering from March to April. The flowers of jambul are fragrant and small, about 5 mm in diameter. The fruits develop by May or June and resemble large berries. The fruit is oblong, ovoid, starts green and turns pink to shining crimson black as it matures. The fruit has a combination of sweet, mildly sour and astringent flavour [12].

Eugenia Jambolana is known as black plum, a sweet fruit, rich in potassium, magnesium and phosphorus, that is also known for its many medicinal uses, some of them as important as the anti-cancer and its benefits that its extracts have exerted in some clinical trials and studies. The anthocyanins, one of the active constituents found in black plum, is the pigment responsible for the colour. Some of these anthocyanins include pelargonidin, delphinidin, cyanidin, petunidin, peonidin, and malvidin. [13].

Fig 1.1 Eugenia Jambolana

1.6 TITANIUM DIOXIDE (TiO_2)

Titanium dioxide, also known as titanium(IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. TiO_2 thin films are the most widely used coatings because of their desirable properties, such as good transmission in the visible and near infrared regions, good adhesion, and high stability against mechanical abrasion, chemical attack, and high temperatures [14]. The characteristics of TiO_2 films are strongly dependent on the preparation methods and the deposition parameters. TiO_2 films are extensively studied because of their interesting chemical, electrical and optical properties. TiO_2 is a high band gap semiconductor that is transparent to visible light and has excellent optical transmittance. TiO_2 has high refractive index and good insulating properties, and as a result it is widely used as protective layer for very large-scale integrated (VLSI) circuits and for manufacture of optical elements.

TiO_2 films have potential uses for a number of electronic device applications such as dye-sensitized photovoltaic cells as well as antireflective (AR) coatings, gas sensors, electro chromic displays, and planar wave-guides. The high dielectric constant of TiO_2 makes it an alternative to silicon dioxide for ultra thin gate oxide dielectrics used in memory and logic devices. Several methods have been used to prepare titanium di-oxide films, and these include chemical vapour deposition (CVD), pulsed laser deposition, reactive sputtering and sol-gel deposition, and chemical bath deposition method, modified chemical bath deposition (SILAR) [15, 16].

1.6.1 PROPERTIES OF TITANIUM DIOXIDE

- Titanium dioxide is a semiconductor, which is optically transparent in the visible region.
- Low cost material, chemically inert, non-toxic, biocompatible [17].

1.6.2 APPLICATIONS OF TITANIUM DIOXIDE

1. It can be employed for solar energy conversion based on dye, polymer, or quantum dot sensitized nanocrystalline TiO_2 solar cells using conjugated polymers as solid electrolyte
2. Titanium dioxide is also used as a material in the memristor, a new electronic circuit element. [18].
3. Titanium dioxide is being explored as a means of increasing the efficiency of solar energy conversion. Specifically, a solar cell enhanced with titanium dioxide would provide an emission-free way to produce hydrogen for use in fuel cells [19].
4. Synthetic single crystals and films of TiO_2 are used as a semiconductor, and also in Bragg-stack style dielectric mirrors due to the high refractive index of Titanium di-oxide [20].
5. The titanium dioxide is used in self–cleaning glass.

1.7 THIN FILM DEPOSITION TECHNIQUE

"Thin" is a relative term, but most deposition techniques control layer thickness within a few tens of nanometres. Thin film can be prepared from a variety of materials such as Metals, semiconductors, insulators or dielectrics etc, and for this purpose various preparation techniques have been employed [21,22]. The deposition techniques and its associated process parameters have a characteristic effect on the nucleation and growth-dominated microstructure of a thin film and thereby on it physical properties [23].

A thin film deposition process involves three steps,

1. Creation of atomic/molecular/ionic species
2. Transport of these species through a medium
3. Condensation of the species on a substrate

Depending on whether the vapour species have been carried by physical, chemical and electro chemical process, the deposition process can be broadly classified into two main groups, namely physical method and chemical method.

1.7.1 PHYSICAL DEPOSITION

Physical deposition uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. Physical vapor deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the desired film material onto various surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation with subsequent condensation,plasma sputter bombardment,electron beam method,thermal evaporation and pulsed laser deposition [24].

A **thermal evaporator** uses an electric resistance heater to melt the material and raise its vapor pressure to a useful range. This is done in a high vacuum, both to allow the vapor to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Obviously, only materials with a much higher vapor pressure than the heating element can be deposited without contamination of the film. Molecular beam epitaxy is a particularly sophisticated form of thermal evaporation.

An **electron beam evaporator** fires a high-energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapor pressure materials can be deposited. The beam is usually bent through an angle of 270° in order to ensure that the gun filament is not directly exposed to the evaporant flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nanometres per second.

Sputtering relies on a plasma (usually a noble gas, such as argon) to knock material from a "target" a few atoms at a time. The target can be kept at a relatively low temperature, since the process is not one of evaporation, making this one of the most flexible deposition techniques. It is especially useful for compounds or mixtures, where different components would otherwise tend to evaporate at different rates. Note, sputtering's step coverage is more or less conformal.It is also widely used in the optical media.

Pulsed laser deposition systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.

Cathodic arc deposition (arc-PVD) which is a kind of ion beam deposition where an electrical arc is created that literally blasts ions from the cathode. The arc has an extremely high power density resulting in a high level of ionization (30–100%), multiply charged ions, neutral particles, clusters and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionization and excitation can occur during interaction with the ion flux and a compound film will be deposited.

Electrohydrodynamic deposition (Electrospray deposition) is a relatively new process of thin film deposition. The liquid to be deposited, either in the form of nano-particle solution or simply a solution, is fed to a small capillary nozzle (usually metallic) which is connected to a high power source. The substrate on which the film has to be deposited is connected to the ground terminal of the power source. Through the influence of electric field, the liquid coming out of the nozzle takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets under the influence of Rayleigh charge limt. The droplets keep getting smaller and smaller and ultimately get deposited on the substrate as a uniform thin layer. [25, 26]

1.7.2 CHEMICAL METHOD

Chemical methods are commonly preferred for obtaining large area thin films. This method depends on the deposition of films from aqueous solutions either by passing a current or by chemical reactions under appropriate conditions and is generally used for the deposition of thick metallic or alloy films. By the very nature of their preparative conditions these films are not generally of high purity. The chemical methods are divided into several types.

- Chemical vapour deposition
- Electro-less deposition
- Anodic oxidation
- Cathodic deposition
- Spray pyrolysis
- Chemical bath deposition
- Modified chemical bath deposition

When a volatile compound of the substance to be deposited is vaporized and the vapour isothermally decomposed or reacted with other gaseous vapour or liquids at the substrate to yield non–volatile reactive reaction product, which deposit automatically on the substrate, this process is called as **chemical vapour deposition** [23].

Electro-less deposition is similar to cathodic deposition expect that it takes place in the absence of an applied external field. It is commonly used for the deposition of nickel films. Both this and the cathodic deposition method suffer from the disadvantage that their use is limited mainly to the deposition of metallic films on to substrates that are electronically conducting (i.e.) metals [27].

Oxide films are formed by **Anodic oxidation**. Oxide films of limited thickness are formed by a large number of metals when exposed to oxygen. Anodic polarization result in productive high-resistance oxide films. This process involves the migration of ion or oxygen or both. Ultra thin and thick films, capacitor and protective layers can be produced by this method [23].

Cathodic deposition is a standard method of electro plating. Two metal electrodes are dipped into an electrolyte solution and on application of an external field access the electrodes; metals ions from the solution are deposited on the cathode as a thin film. In order to maintain charge balance, the anodic metals gradually dissolves in the electrolyte [27]. The deposition rate is proportional to the electrolysis time and current density. The deposition rates can be influenced by the geometry of the cathodes, the temperature and the agitation of the electrolyte.

Spray pyrolysis is essentially a thermally stimulated reaction between clusters of liquid/vapors atoms of different chemical species. The spray pyrolysis soluble salts of the constituent atoms of the desired compound on a substrate maintained at elevated temperature. The sprayed droplet on reaching the hot substrate undergoes pyrolytic decomposition and forms a single crystal or clusters of crystallites of the product, the other by product and excess solvent escape in the vapour phase. The thermal energy for decomposition and subsequent recombination of the species and sintering and recrystallization of the crystallites is provided by hot substrates [23].

Chemical bath deposition an inexpensive and convenient method for large area preparation of thin films. Chemical bath deposition is also known as chemical solution deposition. It was first described in 1869 and it has been used since to deposit films of many different semiconductors. Chemical solution is based on the precipitation or electro less process in solution. While the application of chemical solution deposition for the growth of electronic materials has been known for a long time and deposition of numerous chaleogenide semiconductors has been demonstrated its development has remained very limited until recently [17]. The Chemical bath deposition (CBD) method is one of the cheapest methods to deposit thin films and nanomaterials, as it does not depend on expensive equipment and is a scalable technique that can be employed for large area batch processing or continuous deposition [28].

Successive ionic layer adsorption and reaction (SILAR) method has emerged as one of the solution methods to deposit a variety of compound materials in thin film form. The SILAR method is inexpensive, simple and convenient for large area deposition. A variety of substrates such as insulators, semiconductors, metals and temperature sensitive substrates (like polyester) can be used since the deposition is carried out at or near to room temperature. The prime requisite for obtaining good quality thin film is the optimization of preparative condition, concentration of the precursors, nature of complexing agent, pH of the precursor solutions and adsorption, reaction and rinsing time durations etc.

1.8 OBJECTIVES OF THE STUDY

In the present work,

i) To deposit TiO_2 film by SILAR method.

ii) To study the structural, optical and morphological characteristics of deposited thin film.

iii) To sensitize the deposited thin film using natural dye.

iv) To study the effect of dye sensitization on the characteristics TiO_2 thin film.