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CdTe Thin Films: Deposition Techniques and Applications

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Abstract

The II-IV semiconductor compound, CdTe, has suitable electrical and optical properties as photovoltaic and high-energy radiation sensor material. As an absorber material for thin-film-based solar cells, CdTe holds the potentiality to fabricate high-efficiency solar cells by means of low-cost technologies. This chapter presents a comprehensive review on the CdTe thin-film deposition techniques as well as on the several configurations for the solar cell structures that have led the best efficiency conversion. Current CdTe thin-film deposition techniques include sputtering, close spaced vapor transport (CSVT), chemical spray pyrolysis, and electrodeposition. These techniques have easily been adapted to deposit polycrystalline CdTe films on various flexible and rigid substrates. In regard to the device structure configuration, a variety of partner materials (transparent contact, optical window, buffer layer) were tested, and CdTe film thickness was varied to develop opaque and semitransparent devices by some techniques mentioned above. In this chapter, we will discuss about each technique used for CdTe thin-film deposition as well as its advantages and disadvantages.

Keywords: CdTe, thin films, deposit techniques, solar cell, semiconductor

1. Introduction

Nowadays, the electrical power generation by photovoltaic conversion of solar light continuously increases. This can be attributed to the development of new photovoltaic materials and

inexpensive production technologies, which have led to the price reduction of the watt-hour generated by photovoltaic means. An interesting approach to the solar cells cost reduction consists of using polycrystalline semiconductor thin films.

A thin-film solar cell comprises different semiconductor layers as will be described below, including the so-called absorber or active material. Among these, cadmium tellurium (CdTe), silicon (Si), gallium arsenide (GaAs), CZTS, CIGS, and perovskites are currently used to fabricate high-efficiency solar cells at industrial level [1].

The cadmium telluride (CdTe) semiconductor belonging to II-VI family has been studied for many years. The oldest studies on CdTe synthesis and applications date 1890–1920 decades. In the last 10 years, CdTe has been mainly studied as a polycrystalline thin film and as a quantum dot. As a thin film, it has been prepared by close space vapor transport (CSVT) [2], laser ablation [3], electrodeposition [4] and spray pyrolysis [5], and sputtering [6], and it has been mostly used as the absorber material of thin-film solar cells. More recent deposition techniques of CdTe are based on taking CdTe nanocrystals dispersed in water or organic solvents [5] and transform them into CdTe thin films by using very simple and cheap deposition techniques such as dip-coating or spin-coating and an annealing process [7].

1.1. Solar cell operation: a brief

As stated above, thin-film solar cells consist of various semiconductor materials, each one having an important function in the solar cell functioning and performance [8]. **Figure 1** sketches the different semiconductor layers that compose typical thin-film solar cells. The absorber semiconductor or optically active material has an optical bandgap in 1.0–1.45 eV range, an absorber coefficient in the order of 10^4 cm^{-1} , and a p-type conductivity. **Table 1** lists the band structure parameters and melting point of more important absorber semiconductors.

The generation of electric current, called photocurrent, occurs in two steps: first, photons are absorbed from sunlight, which generates electron-hole pairs. Second, these pairs have to move inside the depletion zone of solar cell to be separated, generating photocurrent. In solar cells based on CdTe, this separation occurs in the p-n junction. As the solar cell generates electricity, it is characterized by the Shockley equation:

$$I = I_{ph} - I_0 \left(e^{\frac{qV}{k_B T}} - 1 \right) \quad (1)$$

where k_B is the Boltzmann constant, q is the electron charge, T is the temperature, and V is the voltage between terminals of the solar cells.

The solar cell is a semiconductor device; as mentioned earlier, the most used semiconductors for this application are cadmium tellurium (CdTe), amorphous silicon, gallium arsenide, CZTS, CIGS, and perovskites. **Table 1** shows the most relevant properties for these semiconductor materials.

An important II-VI semiconductor is CdTe, which has been well studied and applied to solar cell devices. CdTe has excellent electrical and optical properties for its application to solar cells.

Semiconductor	E_g (eV)	Electron affinity (eV)	Melting point (°C)
CdTe	1.45	4.28	1092
a-Si	1.12	4.05	1414
GaAs	1.424	4.07	1230
CZTS	1.45	4.5	
CIGS	0.97–1.43	4.07	1400

Table 1. Properties of the principal semiconductor material with application in solar cells.

It has a bandgap of 1.42 eV (optimal for the solar spectrum), and it is a semiconductor of direct band transitions that allows thin film applications. Other property is its absorption coefficient of 10^4 cm^{-1} , which allows 90% absorption with a 1 μm thickness of the thin films. Other advantage is the possibility of obtaining p- and n-type conductivity in the films, enabling formation of homojunctions. However, the material has some “disadvantages” when applied to solar cells; for example, it is highly resistive that it does not allow excellent carrier collection. Additionally, CdTe has a high work function of 5.7 eV, which affects the semiconductor-metal junction. To improve this junction, it is necessary to find a metal with a work function greater than that of the CdTe. Finally, the CdTe homojunction has a high surface recombination speed that does not allow the manufacture of devices with homojunctions [2]. As a result, CdTe solar cell devices have been commonly processed considering CdS/CdTe heterojunctions. The properties of each part of the solar cell will be explained later, and the deposit techniques for CdTe films too.

For all of the reasons mentioned above, it is necessary to have a better understanding of all components of the solar cells, which would allow improvements in CdTe solar cell efficiency. In addition, since efficiency/cost ratio is an important figure of merit to be considered, it is mandatory to revise most commonly used processing routes for each component of CdTe solar cells for reducing processing cost. In this chapter, we present a review on CdTe solar cells where particular emphasis will be given to techniques used for depositing each component of the solar cell. A comparison between the different deposition techniques is presented.

1.1.1. Configuration of solar cells based on CdTe

The most known configuration of CdTe solar cells is the p-n junction. Some people have stated that the MIS-type configuration improves solar cell efficiency [9]; however, for any of the configurations, the structure of the solar cells is similar. CdTe solar cells are often fabricated considering the superstrate structure, which is presented below:

Glass/substrate/TCO/CdS/CdTe/Black contact

Figure 1 shows the configuration of CdTe solar cells where each one of the components will be explained below.

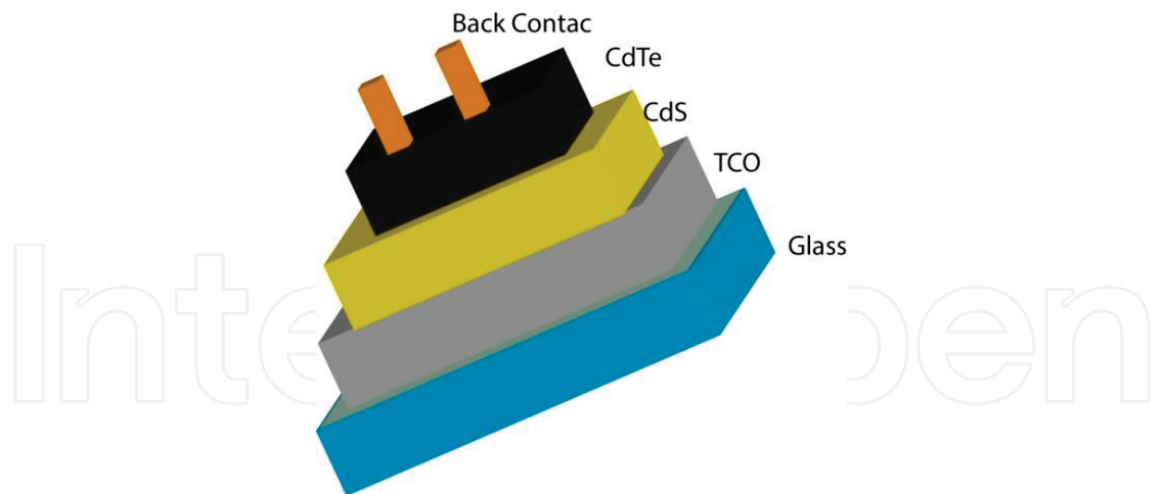


Figure 1. Configuration of the solar cell based on CdTe.

1.2. Glass—substrate

This component is important because all films will be deposited on the substrate. For this reason, the substrate has to endure the different deposition processes. The commonly used substrate is soda lime with 3 mm of thickness that endures high temperature (deposition of CdTe films) and presents chemical stability (deposition of CdS films). Other advantage of this substrate is its cost that is 5 USD/m².

1.3. Transparent conducting oxide (TCO)

The two most used TCOs are SnO₂:F [10] and ITO [11]. Like glass substrate, TCO thin film has to endure high temperature and present chemical stability because of configuration. Additionally, the TCO must comply with:

- high bandgap ($E_g > 4$ eV)
- transmittance between 80% and 90%
- laminar resistance $\approx 5 \Omega/\square$

The most commonly used TCOs in solar cells based on CdTe are SnO₂:F, ITO, Cd₂SnO₄, and ZnO:Al. Comparatively, ITO combines optical and electrical properties needed for good TCO very well; however, the abundance of indium in the upper continental crust is low (about 0.05 ppm). Due to its stronger mechanical and chemical stability at high temperature, together with the relative abundance of Sn, it makes SnO₂:F one of the most used TCOs [12].

Properties that an adequate TCO must have are as follows:

- High transparence
- Low sheet resistance
- High surface quality (low density of pinholes and low roughness)

Of course, the laminar resistance and transparency are parameters that depend on the opposite of the thickness of the TCO, so the way to optimize a TCO as a function of its thickness is to use the well-known figure of merit of Haccke [13]:

$$\text{F.M.} = \frac{(T_{ave})^{10}}{R_{sh}} \quad (2)$$

where T_{ave} is the average transmittance and R_{sh} is the sheet resistance.

High resistance and transparent buffer layer between the TCO and the CdS is usually used in the CdTe solar cell technology.

Properties that an adequate buffer layer must have are as follows:

- To decrease possible diffusion of atoms from the TCO to the rest of the films in the device
- To improve the surface morphology of TCO with respect to the roughness and pin-holes
- To ensure the deposition of CdS films with thicknesses lower than 100 nm with good surface coating of the films

1.4. Cadmium sulfide (CdS)

Since the CdTe homojunction did not work, it was required to replace the n-type CdTe. For this purpose, the material has to be transparent so that CdTe absorbs the greatest amount of light. The cadmium sulfide is the right one.

For the CdTe films, the material should be transparent and should have two properties: transmittance at least of 70% and the bandgap greater than that of the CdTe. The CdS has these two properties: its band gap is $E_g = 2.45$ eV and its transmittance is controlled by its thickness. The minimum thickness to guarantee the transmittance and an adequate morphology is around 100 nm; however, the best thickness of the CdS is 120 nm with the efficiency of 21% [14]. This material has thermal and chemical stability to CdTe thin-film deposition.

At present, CdS thin films are deposited by chemical bath [15]. The more recent works present a variant to the chemical bath known as shallow where with this deposition technique the cost is reduced [16]. On the other hand, some works show an improvement of the efficiency of the solar cells when the CdS becomes intrinsic [17]; for this reason, the solar cells of CdTe are sometimes considered as MIS configuration where the CdS is the intrinsic part.

1.5. Cadmium telluride (CdTe)

The most important material of the solar cells is the active or absorbent material and the p part of the heterojunction. The properties of the CdTe are as follows:

- Its bandgap is the optimum for the absorption of the solar spectrum, i.e., it is $E_g = 1.45$ eV. Additionally, its bandgap presents direct transitions that allow fabrication of thin films.

- CdTe has an absorption coefficient around $\alpha_{CdTe} \approx 10^4 \text{ cm}^{-1}$ whereby 90% of the photons are absorbed in 1 μm of the film.
- On the other hand, one property that is a disadvantage is its high resistivity and high work function that affects the semiconductor-metal union in the back contact.

Currently, CdTe thin film is deposited by physical techniques such as CSVT, sputtering, electrodeposition, and spray pyrolysis. It is known that the CdTe films need a thermal treatment of CdCl_2 to improve the morphology and to reduce the recombination centers [18]. Other treatment is with fluorine [19].

1.6. Back contact

The ideal back contact meets two conditions: it has a p-type conductivity and it has a work function greater than that of the CdTe; these conditions are most important because they guarantee an ideal union in the band of the metal and the CdTe (see **Figure 2**). This part of the solar cell is deposited by coevaporation.

The most used back contact is Cu-Au [20] alloy, but this back contact is not ideal for the following reasons: first, these back contacts are, in general, Schottky barriers, and the other reason is diffusion of the copper atoms inside the solar cell, which degrades the device. This degradation occurs because the copper atoms create threads that connect the back contact with frontal contact, short-circuiting the solar cell; additionally, the solar cell is exposed to solar radiation whereby this problem increases [21]. Finally, the copper oxidizes with the environment; this problem is solved by depositing gold films on the copper, but the use of gold in industrial scale can be expensive. Other metal alternatives as back contact are molybdenum [22], nickel [20], etc. However, these metals are also expensive.

Another way to obtain a good back contact is by using compounds such as Cu_xTe [23–25] and Bi_2Te_3 [26] for creating a p⁺ region.

With points mentioned above, it is important to know the technology used in the deposition of each component of the solar cell. For example, the window materials are deposited by chemical techniques because these techniques are of lower cost and the properties of the films

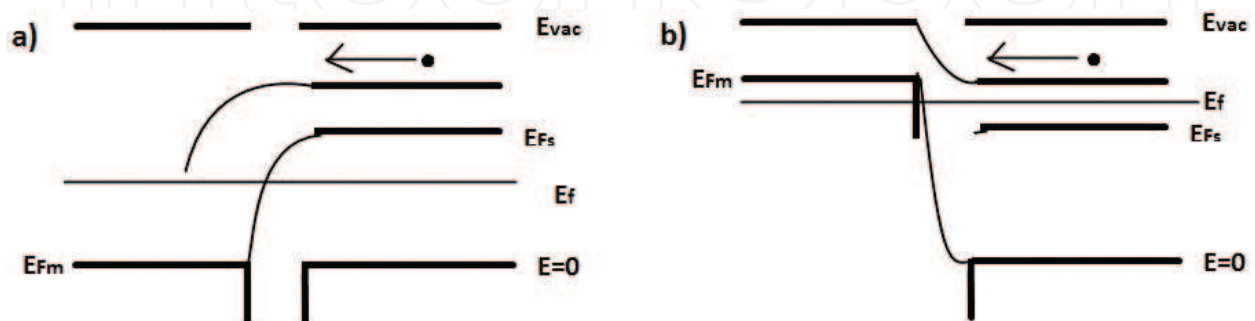


Figure 2. Bending of bands in the metal-semiconductor junction: (a) the metal work function is greater than that of the semiconductor, and (b) the work function of the metal is less than that of the semiconductor.

obtained by these techniques are suitable for the operation of the solar cell, while for the CdTe films the best result was obtained when the film was deposited with physical technique.

The next section discusses the different techniques used to deposit CdTe film.

2. CdTe thin-film deposition

The first part about thin-film deposition is the classification of the deposition techniques as *physical and chemical techniques*. The first technique starts with solid material which is sublimated to transport this gas and deposited on the substrate. This technique requires high vacuum, and in some cases ultrahigh vacuum. The second technique starts the deposition with reagents that by chemical reactions generate the material to deposit. The principal difference between these techniques is the use of the vacuum during the deposition of the film. For this reason, it is considered that the first technique is more expensive than the second one. Another difference is the control of the deposition speed, which is more precise with the physical technique. The consideration of the technique to be used is determined by the application of the deposited film because the properties of the film depend on the technique used.

In the case of CdTe, at present, this film has been deposited by diverse techniques, for example, CSVT, sputtering, laser ablation, spray pyrolysis, and electrodeposition, each with different properties, and they are explained below.

2.1. Close spaced vapor transport (CSVT)

The CSVT is a physical technique that consists of sublimating the material to transport the gas to deposit it on the substrate. One of the advantages is the close space, where the space to transport the gas is close whereby the control of the growth rate improves. With this technique, it is possible to obtain the films with thickness of 500 nm [2].

The deposition system consists of two blocks, which can be made of graphite or metal. These blocks must be heated by halogen lamp or electrical resistance; for this reason, each block has temperature control. The block below is known as source and the block above is named as substrate. Between the blocks, a graphite boat is placed. The CdTe to deposit is placed inside it. In this case, some people used powder or tablet of CdTe, and finally the substrate is placed on the graphite boat. All system is in the vacuum chamber. **Figure 3** shows a simple CSVT system. The mechanics of growth consist of creating a temperature grading between the block, where the source temperature is higher, in the case of the CdTe; the source temperature is around 500°C. When the CdTe is sublimated, this is transported to the substrate that has a lower temperature causing the material to be deposited on the substrate. For this thin-film deposition, high vacuum around 10^{-6} Torr is necessary.

One advantage of this technique is the morphology because authors have reported grain size around 5 μm [5]. Another advantage is that films are uniform in small area (1 inch^2), but larger areas are more complicated because a uniform heating in the substrate block is necessary.

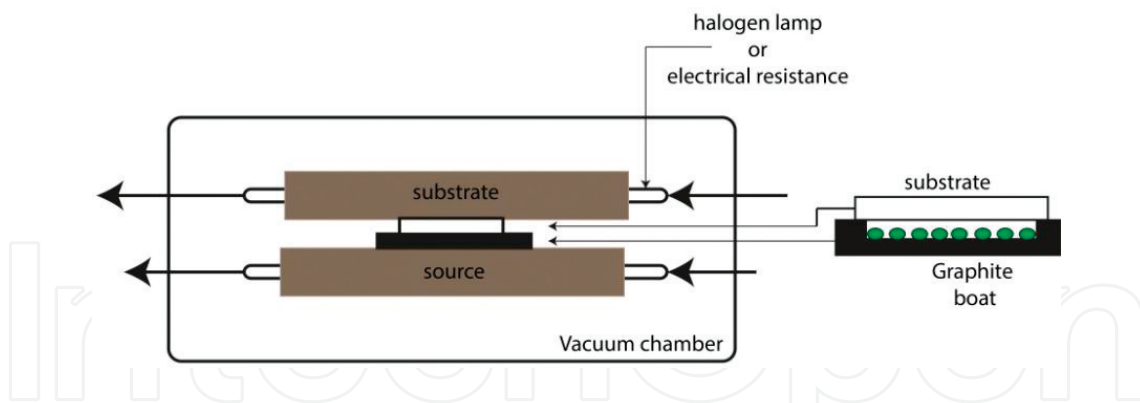


Figure 3. A simple CSVT system. This system generates a temperature gradient between the substrate and source where the temperature of the source is higher. For this temperature difference, the material is deposited on the substrate; the variable is substrate and source temperature.

Another disadvantage is the manipulation of the sample because the vacuum is broken between each deposition; for this reason, this technique cannot be industrialized.

This technique is excellent in small laboratory and could be harnessed if uniform heating in the blocks is guaranteed; for this, the halogen lamp is better than electrical resistance.

2.2. Sputtering

Sputtering technique is a physical technique which sublimates the material of the target; for this, the target is bombarded by energetic ions. The ions are obtained from plasma that is generated inside the system; this system has a vacuum chamber. When the ions strike on the target, these change momentum with the atom of the target. When the ions strike with energy greater than the binding energy, the atoms of the target are ejected; this process is named sputtering. The variables to consider in this process are energy of ions, incident angle, mass of ions, and mass of the atom in the target. Commonly, these ions are obtained from an ionized gas, which can be argon. **Figure 4** shows a simple sputtering system.

The advantage is the control of the growth speed; as same as CSVT, in this case, it is possible to obtain *ultrathin films*. Arhlesh Gupta reported films with thickness of 600 nm and efficiency of 9.4% [6]. In this case, the grain size reported is around 2 μm [27]. At present, the efficiency is 14% [28].

In general, with this technique, it is possible to obtain “ultrathin films” or transparent CdTe films that are the current trend, semitransparent technology. An advantage is the industrialization of the technique. Other advantage is the possibility to use flexible substrate in this process.

2.3. Laser ablation

Laser ablation is also a physical technique. It is similar to CSVT because the process of deposition is done by sublimation of the material. The difference is the process of the sublimation because in this case the material is sublimated with a laser beam. To get this, the laser

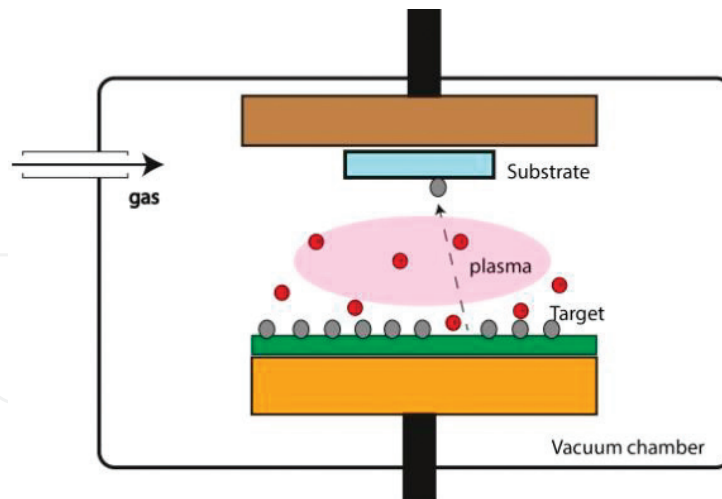


Figure 4. A simple sputtering system. The plasma is generated by electric shock with the used gas. The target is bombed to release ions from it; these ions are deposited on the substrate. The variable is the electric current and the kind of gas.

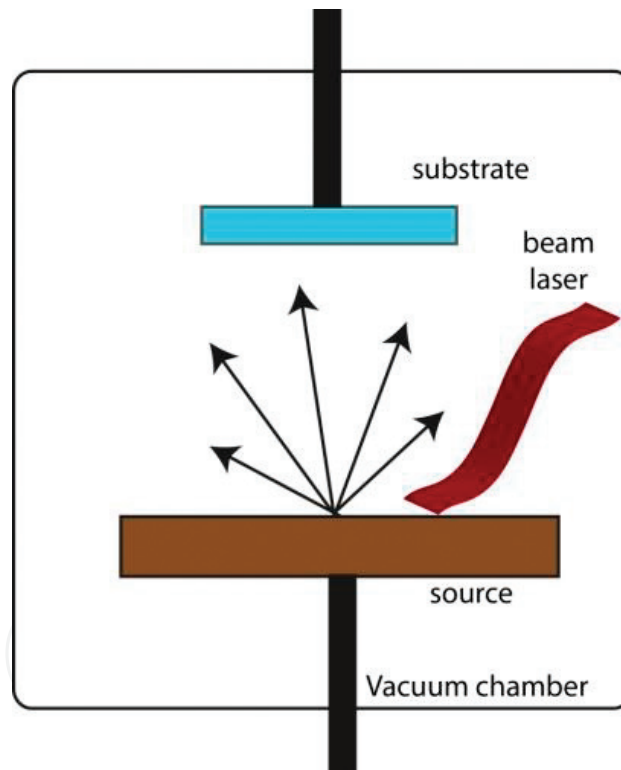


Figure 5. Simple ablation laser system. The beam laser impacts in the target that absorbs the energy to sublimate; this gas is deposited in the substrate. The variable is intensity of the laser beam.

beam energy needs to be “small” so that the incident photons are absorbed by the material, and this can be sublimated. This deposit process is controlled with the pulse and intensity of the laser beam. Additionally, this technique is important because it can be used in the industry. **Figure 5** shows a simple laser ablation system. One advantage of this technique is that the substrate maintains a low temperature being possible to use flexible substrate.

Since 1994, there has been a report about this technique used to grow CdTe films, where solar cells have 3% of solar cell efficiency [3]. At present, films with a thickness between 1.8 and 3 μm and an average grain size of 300 nm have been reported [29].

2.4. Spray pyrolysis

The spray pyrolysis is a chemical technique used mainly to deposit TCO film; this is a simple technique where the material, that is in the solution, is pulverized by the pressure of a gas (argon, air, nitrogen, etc.). For this process, it is important to control the flow of the solution and the pressure of the gas. The pulverized solution is sprayed on the hot substrate to obtain the film. At present, spray pyrolysis has two different systems, which are differentiated by the kind of pulverization. The one described previously is named pneumatic and is shown in **Figure 6**, and the other system is named ultrasonic as it uses an ultrasonic system to pulverize; this system is not shown because there is no report on CdTe film deposited by this method.

One previous step to use this system is synthesis of the solution, because it is important to prevent oxidation on the surface. For this, the use of ammonium is excellent as it supports the protection of the ions. In this case, some authors use colloidal system of CdTe with reports on nanoparticle around 20 and 60 nm, and with this solution, they can deposit films with 500 nm thickness; the authors reported photovoltaic effect, but they did not manufacture solar cell.

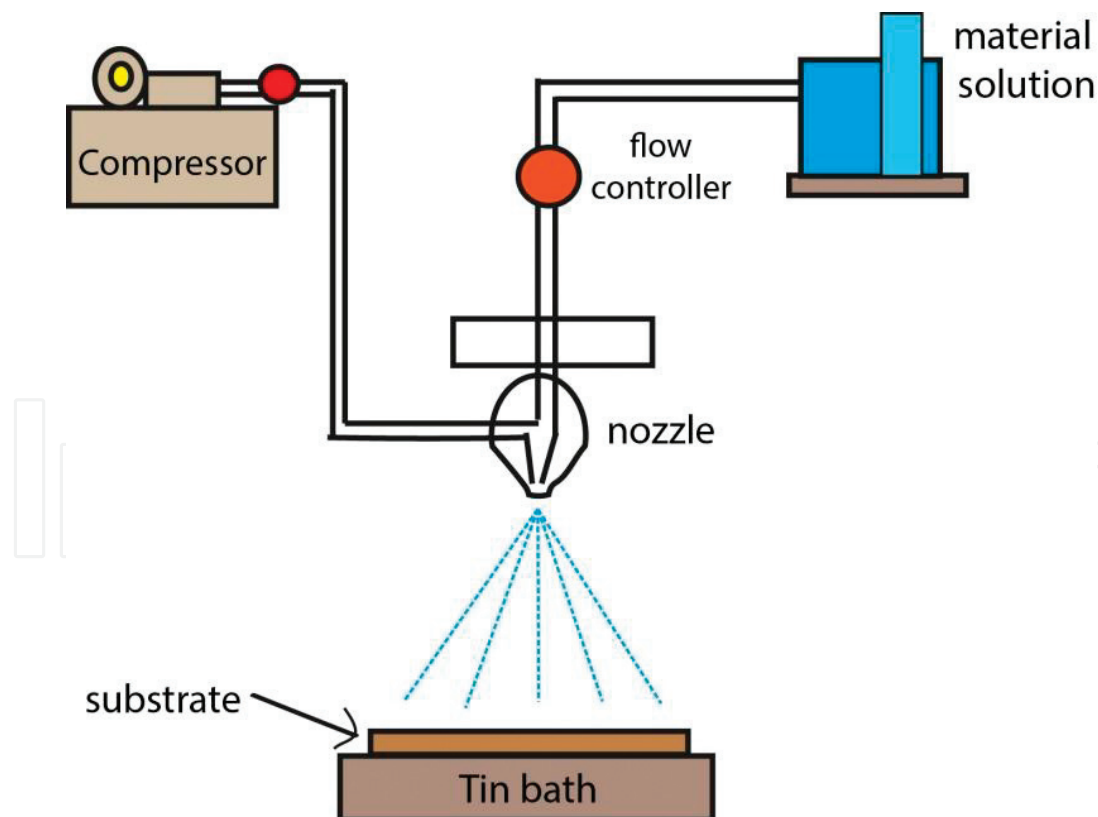


Figure 6. Spray pyrolysis system. The solution moves through the tubes to meet the air in the nozzle to produce the spray, which arrives on the substrate that is heated to deposit the material. The variables are concentration solution, pressure, and the substrate temperature.

Another effect reported is the change in the bandgap of the CdTe because it is formed by colloidal particles [5].

For this technique, CdTe solution is necessary; usually, this solution is a colloidal system. For this colloidal system, the stabilizing agent or surfactant is important because it stabilizes the CdTe molecule; for this reason, one surfactant is necessary, which, in addition to the above, is easy to remove in the deposition process. The most used surfactant is TGA [30] and oleic acid [31].

The TGA surfactant offers excellent protection to CdTe molecule and it is easy to remove, but the problem with this stabilization agent is when it is removed, the CdTe molecule gets broken and then this solution cannot be used for material deposition. The second surfactant, oleic acid, protects CdTe molecule too, but it is difficult to remove it, this involves a chemical process with ferrozine and an additional process [32]. Ammonium hydroxide can be an excellent surfactant because it protects the CdTe molecule, supports with the pH solution, and is easily removed. The authors did not report efficiency, but they obtained photovoltaic effect [5, 32].

Drop-casting is a chemical technique, which is reported as a spray pyrolysis, but the problem with this technique is the formation of cracks [33].

On the other hand, it was possible to manufacture solar cells under the following configuration:



The CdS was omitted for this device but it has 8.8% of efficiency [28]. With this technique, it is possible to obtain large deposit areas and this technique can be industrialized.

2.5. Electrodeposition

Electrodeposition is a chemical technique in which an electric current is used in an electrolytic solution with the objective that there is an ion movement toward the cathode. When the ions arrive on the cathode then the material is deposited. The simple deposition system is shown in **Figure 7**. We can observe that the deposition system is really simple.

With this technique, Mathew et al. manufactured solar cells. They reported efficiencies between 8.6 and 11% [4]. Another thing they reported is the morphology; they obtained film with 500 nm of size grain. This morphology is not appropriate for the electrical application such as solar cells. This report is important because it is a disadvantage of the chemical techniques; the morphology obtained by these techniques is not the best to make solar cells but the reported efficiencies are acceptable. This topic is important and will be discussed later.

This technique has several advantages; for example, with this technique, it is possible to use flexible substrates. Another advantage is that the substrate is not heated [4], and finally, this technique can deposit larger areas and, therefore, can be industrialized.

All of the above are a short summary about the work around CdTe. It is important to know about the advantages and disadvantages of these techniques. Generally, these techniques have two differences: the cost and the properties obtained.

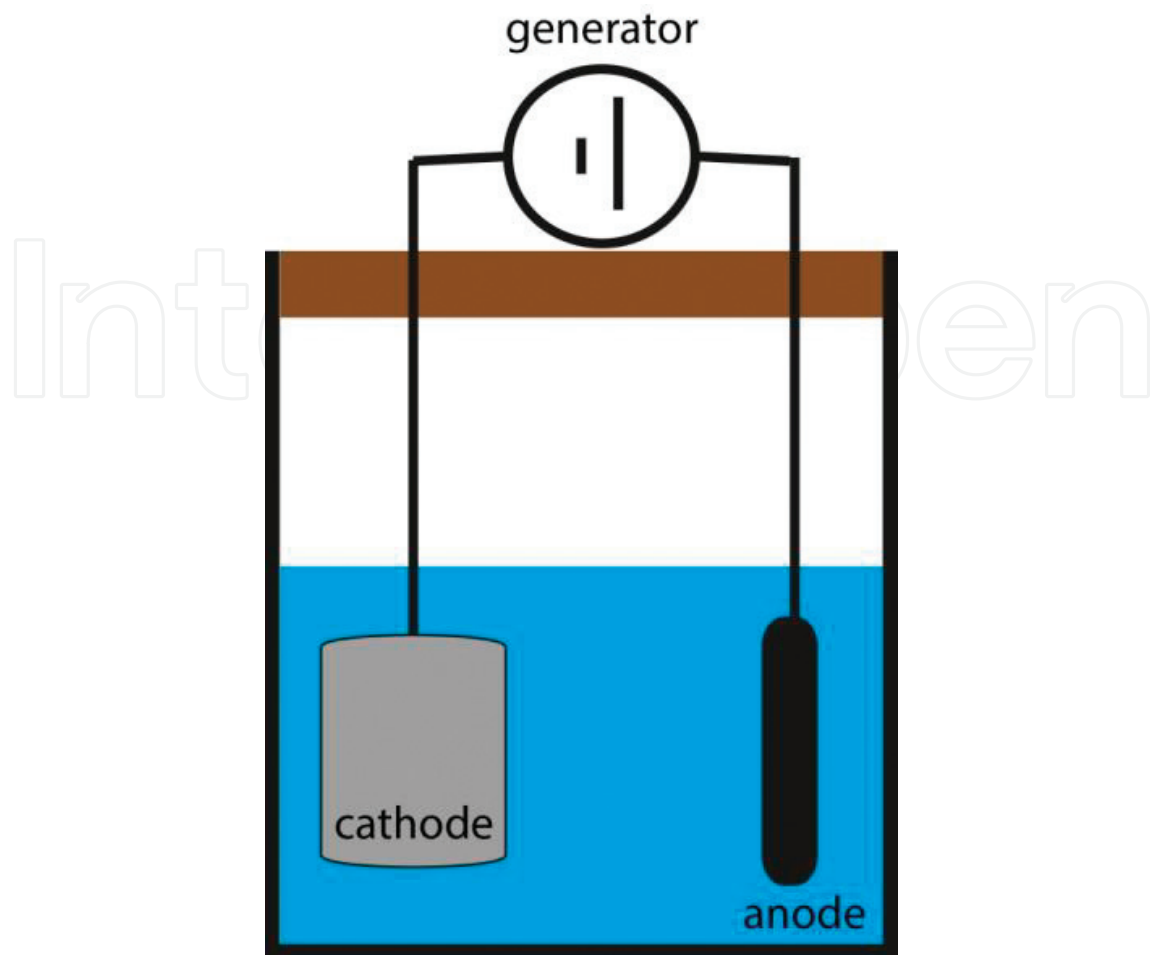


Figure 7. Simple deposition system of electrodeposition technique, the solution is an electrolyte that is deposited by electric current and moved from the anode to the cathode where the material is deposited; the variables are electrolyte concentration and amperage.

3. Comparison of techniques

As mentioned in the beginning, the CdTe is an important material because it is applied to solar cells or renewable energy. The thought around CdTe has changed over time. The first idea about solar cell was “with CdTe solar cells the world will be saved,” after that the idea was “the best efficiency,” and at present, the idea is “the best efficiency and cost ratio,” which are the most important because of the presence of technological limitations; for example, in the CdTe case, the efficiency stops for a few years around 16% because of technological limitations.

On the other hand, manufacturing of CdTe solar cells consists of several processes; if the cost is reduced for these processes, then the cost of the solar cells would be reduced. The best way to do it is to implement chemical techniques; in the case of TCO and CdS, this is possible. But in the CdTe case, this is more complicated because this film was deposited by physical technique. The main reason is the relationship of efficiency with the morphology of the films. The best morphology is obtained by physical technique; the disadvantage is the difficulty of scaling to

Technique	Type	Vacuum (Torr)	Substrate temperature (°C)	T _{max} (c)	Process time (h)	Thickness (μm)	Grain size (nm)	Efficiency (%)	Scaling
CSVT	Physical	10 ⁻⁶	>400	600	3	5	5000	12	No (system)
Sputtering	Physical	10 ⁻⁶	No	600	2	2	2000	14	Yes
Laser ablation	Physical	10 ⁻⁶	No	600	2	3	300	3	No (efficiency)
Spray pyrolysis	Chemical	P ₀	<350	350	1.5	0.5	500	8	Yes
Electrodeposition	Chemical	P ₀	No	100	1	2	500	11	Yes

P₀: atmospheric pressure.

Table 2. Differences between all the techniques used to deposit CdTe films.

large area because all of them need vacuum chamber and heating to the substrate in some cases. Sputtering is the best technique in this case because this is feasible, but this technique has long deposition time. For the CSVT, the difficulty is in escalation to large areas. Another disadvantage of this technique is the time expenses due to the vacuum that the process requires. The chemical technique eliminates this steep, but the efficiency of the solar cells is reduced.

All techniques have advantages and disadvantages; in summary, the physical techniques are of high cost, and the manufacturing process is not continuing because of vacuum chamber, while chemical techniques are of lower cost, but the efficiency is lower. For this, it is necessary to establish an efficiency/cost ratio, which should be high. The difference in efficiency between physical and chemical techniques; the physical technique guarantees grain size greater than that obtained through the chemical technique, which affects the electrical properties of the material. When the grain size increases, the intergranular barrier potential decreases, allowing better diffusion of the charged carriers toward the p-n union and enhancing thereby the contribution of these photogenerated carriers to current density.

Table 2 shows the comparison of all the techniques used to deposit CdTe films. In this table, the kind of technique, the pressure used, the temperature used in the process, the process time, the grain size and thickness obtained, the efficiency, and finally if the technique is scaling to large area or industrialization are given. And also, if the technique is not scaled, the reason is written.

4. Conclusion

The objective of this chapter is to summarize the different techniques used for depositing thin films of CdTe. All the techniques mentioned above are innovative because it is possible to obtain thin films with different properties by these techniques; for example, physical techniques are used to manufacture conventional solar cells, while chemical techniques can be

used to manufacture transparent technology because their deposition time is low. In other words, the technique used depends on the applications of the thin films.

At present, three different technologies are used in solar cells based on CdTe: rigid (conventional), semitransparent, and flexible. The technology determines the technique to be used. Additionally, the configuration of the solar cell changes when the technology changes; in conventional and semitransparent technology, the configuration is superstrate, while in flexible technology, the configuration is substrate. This change on the substrate is due to application; in the case of the first two technologies, the substrate used is soda lime that resists high temperature, and in the last case, the substrate used is a polymer that can resist the temperatures used to deposit CdTe films, which can be done by sputtering, electrodeposition, or laser ablation. Besides, CdTe films could be deposited by spray pyrolysis, but it is necessary to adjust deposit parameters. In the case of the semitransparent technology, it is necessary to have a low growth speed; the most suitable techniques are sputtering, laser ablation, and spray pyrolysis. In the case of the CSVT, it is necessary to adjust the deposition gradient. The conventional technology and technique can be used, but the deposit time has to be considered; that is, it is not reasonable to take a day to deposit a film.

The advantage of each technique depends on the technology used; that is, advantage and disadvantage cannot be stated if the technology is not mentioned. In the conventional technology, the low growth speed is a disadvantage, while this is an advantage in the semitransparent technology.

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