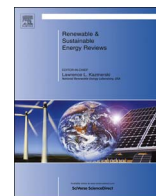




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A review of thin film solar cell technologies and challenges

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ABSTRACT

Thin film solar cells are favorable because of their minimum material usage and rising efficiencies. The three major thin film solar cell technologies include amorphous silicon (α -Si), copper indium gallium selenide (CIGS), and cadmium telluride (CdTe). In this paper, the evolution of each technology is discussed in both laboratory and commercial settings, and market share and reliability are equally explored. The module efficiencies of CIGS and CdTe technologies almost rival that of crystalline solar cells, which currently possess greater than 55% of the market share. α -Si is plagued with low efficiency and light-induced degradation, so it is almost extinct in terrestrial applications. CIGS and CdTe hold the greatest promise for the future of thin film. Longevity, reliability, consumer confidence and greater investments must be established before thin film solar cells are explored on building integrated photovoltaic systems.

1. Introduction

Harnessing the sun's energy to produce electricity has proven to be one of the most promising solutions to the world's energy crisis. However, the device to convert sunlight to electricity, a solar cell, must be reliable and cost effective in order to compete with conventional sources. Several solar technologies including wafer, thin film and organic, have been researched to achieve reliability, cost-effectiveness and high efficiency with huge success. For instance, crystalline silicon has been very successful from laboratory to commercial integration, and makes up to 90% of the global PV market [1]. Cost effectiveness can be seen in the use of less material as well as increasing energy conversion efficiency. While wafer technology is capable of meeting the high efficiency goal, thin film can satisfy minimum material usage as well. Both goals need to be met simultaneously to enable the production of electricity at a low cost and allow high market penetration of solar electricity.

α -Si, CdTe and CIGS are the three most widely commercialized thin film solar cells. Common among the three materials is their direct band gap (Table 1), which enables the use of very thin material [3]. They also have a very low temperature coefficient; however, in contrast, wafer technologies and their performance are not impeded by low light intensity. Additionally, all the three technologies can be incorporated into building integrated photovoltaics (BIPV). The amorphous silicon solar cell finds its use mainly in consumer electronics such as calculators, watches, etc. [2,6].

The absorption coefficient of thin film materials is much lower than

that of its crystalline counterparts. When compared to CdTe and CIGS, α -Si not only requires a lower amount of silicon, but is also less toxic. CdTe's usage of cadmium proves to be harmful to both the producer and the consumer, slightly limiting its commercial applications [3]. Throughout history, α -Si has had the longest time in the commercial arena, starting with its introduction as a reliable power source of watches, clocks, and calculators in the late 1980s [2,6]. However, CIGS and CdTe are relatively new technologies, and are more promising in terms of energy conversion efficiency than α -Si. Despite this advantage, CIGS and CdTe technologies still lag behind crystalline silicon solar cell counterparts in efficiency and reliability.

In this work, we review thin film solar cell technologies including α -Si, CIGS and CdTe, starting with the evolution of each technology in Section 2, followed by a discussion of thin film solar cells in commercial applications in Section 3. Section 4 explains the market share of three technologies in comparison to crystalline silicon technologies, followed by Section 5, which discusses the reliability, more specifically a comparison between fill factor and temperature coefficients, and the materials availability of thin film technologies. Section 6 highlights emerging next generation thin film technologies such as Perovskite materials, Copper zinc tin sulfide (CZTS), and quantum dots (QD). In Section 7 we draw conclusions and highlight major accomplishments and developments based on the review.

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Table 1
Physical properties for three different thin film materials.

	a-Si	CdTe	CIGS
Absorption coefficient	$1.7442 \times 10^6 \text{ cm}^{-1}$	$1.1148 \times 10^6 \text{ cm}^{-1}$	$> 1 \times 10^5 \text{ cm}^{-1}$
Band gap	Direct 1.75 eV	Direct 1.44 eV	Direct 1.0 eV–1.6 eV
Sufficient thickness	1 μm	3–5 μm	1–2 μm
Temperature coefficient	–0.3%/°C	–0.25%/°C	–0.26%/°C
Toxicity	None	Cadmium	None

2. Evolution of thin film solar cell

2.1. α -Si solar cell

One of the attractive features of α -Si is that it is a direct band gap material, which allows a significant fraction of sunlight to be absorbed within a thin layer of a few micrometers [1]. However, short orders in amorphous material and the dangling bonds result in short minority carrier diffusion lengths and abnormal electrical behavior. Hydrogen passivation, also designated as α -Si:H, can reduce dangling bond densities by several orders of magnitude, thus helping to improve the minority carrier length. However, this hydrogenation is responsible for the Staebler-Wronski light degradation effect.

The optical absorption spectrum of hydrogenated α -Si:H is transparent up to 1.7 eV and is highly absorptive starting at 2 eV. These initial properties have led to a wide spread interest in α -Si in solar industry and research institutes. Additional benefits of α -Si:H include low manufacturing cost, and a shorter energy payback time.

Fig. 1 shows the first α -Si:H solar cell with an energy conversion efficiency of 2.4% fabricated by Carlson and Wronski in 1976 at RCA Laboratory [4]. This is a p-i-n α -Si:H structure deposited at 250–400°C onto a glass substrate coated with indium tin oxide (ITO). Fig. 1 shows a relatively thick intrinsic layer between thinner p-type and n-type layers which allows for large diffusion lengths for both minority and majority carriers. The i-layer, which is typically between 250 and 500 nm in thickness, often contains small amounts of boron (0.1–1 ppm) to ensure nearly intrinsic behavior under illumination. The absorber intrinsic layer possesses a generated electric field, creating the electric charge separation and enabling collection [5]. Additionally, the p- and n-type doped regions are very thin. The p-layer is usually a hydrogenated amorphous-silicon carbon alloy doped with boron, and the n-layer is either phosphorus doped α -Si:H or phosphorus doped microcrystalline α -Si:H and is about 20–30 nm thick. The rear contact is evaporated or sputtered aluminum.

Fig. 2 shows the evolution of laboratory α -Si solar cells, which began in 1976 when Carlson and Wronski [4] fabricated their first p-i-n α -Si solar cell with efficiency of 2.4%. Based on this structure, they estimated the theoretical maximum efficiency of α -Si solar cell to be ~14–15%. In 1977, they were able to improve the efficiency to 4% [5].

In 1978, Wilson [6] used the MIS or Schottky diode structure (Fig. 3) instead of the p-i-n, which led to 4.8% efficiency. The Schottky barrier α -Si solar cell is constructed with a metal-to-N junction rather than a p-n semiconductor junction [6]. Schottky barrier α -Si solar cells

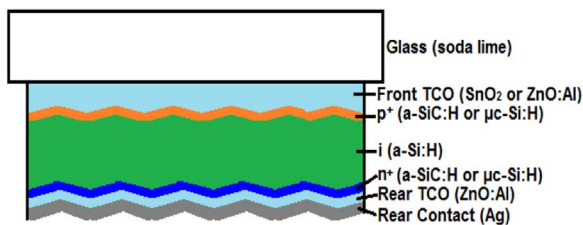


Fig. 1. The structure of p-i-n α -Si:H solar cell on a glass superstrate.

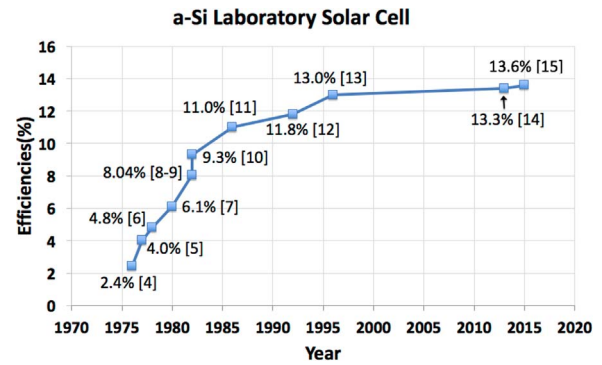


Fig. 2. A graph of the improvements in efficiency of laboratory α -Si solar cell.

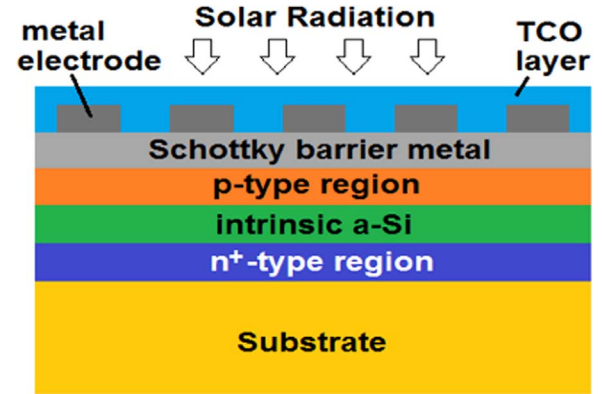


Fig. 3. Layout of the Schottky barrier α -Si solar cell. An illustration of a Schottky barrier α -Si solar cell with a highly doped p-type region adjacent to the Schottky barrier high work function metal.

incorporate a thin, yet highly doped, p-type α -Si, between a Schottky barrier height work function metal and the intrinsic region of α -Si. This increases the V_{oc} and J_{sc} of the Schottky barrier α -Si solar cell [6]. In 1980 Carlson [7] reported efficiency of 6% on the p-i-n structure and 6.1% efficiency for the Schottky counterpart.

The introduction and discovery of hydrogenated α -Si:H in 1982 by Tawada et al. [8,9] gave an initial starting point for the growth of α -Si, which led to the achievement of 8.04% efficiency. In 1986, Yamazaki et al. [10] reported 9.3% efficiency after introducing light trapping features developed by Yablonovitch and Cody in 1982 [16] and hydrogenated α -Si:H. In the early 1990s, research efforts were placed on the development of multi-junction cells and modules (Figs. 4 and 5), which have multiple bandgaps to allow response at multiple wavelengths. The solar spectrum encompasses a variety of photon energies, and photons with energies less than the semiconductor bandgap are

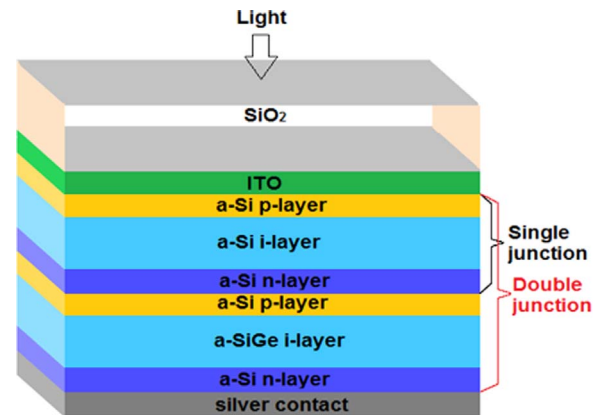


Fig. 4. A layout of a double junction α -Si:H/a-SiGe:H solar cell.

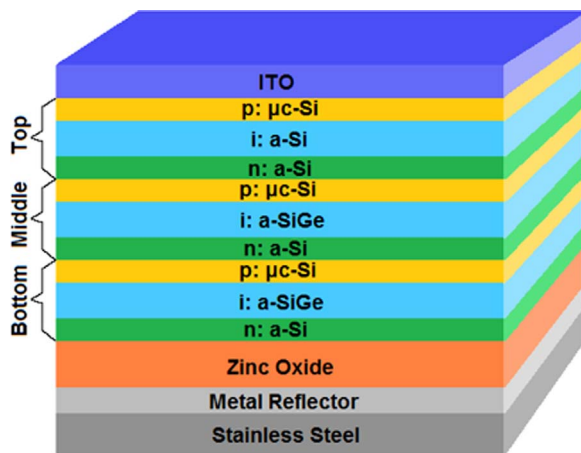


Fig. 5. A layout of a triple junction α -Si:H/ α -SiGe/ α -SiGe solar cell.

often not absorbed. In multijunction technologies, bandgaps can be readily adjusted via varied alloying, but it is required that the top junction has a higher bandgap than the bottom junction. Some of the energy that would normally be lost in single junction solar cells can be captured and converted [11]. Additionally, multijunction technologies exhibit less light-induced degradation, yet it has also been shown that wiring two mechanically different α -Si cells optically in series may yield higher performances as well [17]. With the multi-junction concept, Guha et al. [11] demonstrated $\sim 11.0\%$ α -Si: H solar cell.

Yang et al. from United Solar Systems Corporation achieved stabilized conversion efficiencies of 11.8% in 1996 [12] and 13% [13] using a “spectrum splitting, triple-junction structure”. This improvement in the laboratory α -Si solar cell was constructed and accomplished through a dual junction and low band-gap α -Si: H/ α -Si: Ge alloyed cell (Fig. 4). In addition, a more efficient TCO, also known as the top conducting oxide, was created along with a p-n tunnel junction between the component cell, allowing for a better transfer of current and electric generation within the cell [12,13].

In 2013, Kim et al. [14] demonstrated a 13.4% stabilized efficiency α -Si: H solar cell using α -Si: H in the top cell, α -SiGe: H in the middle cell, and hydrogenated microcrystalline silicon (μ c-Si: H) in the bottom cell. Similar triple junction technologies were explored by Sai et al. [15] with an α -Si: H/ μ c-Si: H/ μ c-Si: H cell, and a stabilized efficiency of 13.6% was achieved. The improvement in PCE was attributed to the introduction of textured substrates with a hexagonal dimple array (also known as “honeycomb-textured substrates”) into multi-junction technologies that achieved better light trapping [15]. These advances further show how the improvements of α -Si: H technologies are and will be emphasized on the growth and discovery of triple junction technology, and how triple junction technologies will be exploited in the future, especially because μ c-Si: H possesses a higher tolerance to light soaking than pure amorphous materials [18]. The usage of multiple semiconducting materials has allowed for a broader absorption of wavelengths, thus improving the cell's power conversion efficiency.

2.2. CIGS solar cell

Fig. 6 shows the evolution of the CIGS solar cell technology efficiency. Kazmerski et al. [19], in 1976, created the first thin film CIGS solar cell having a conversion efficiency of 4.5%. The structure of the CIGS is given in Fig. 7, with soda lime glass as the substrate. On top of the glass is the molybdenum, which contacts the p-type Cu(InGa)Se₂. The p-type Cu(InGa)Se₂ forms the main junction with n-type CdS, which serves as the buffer layer. An intrinsic zinc oxide layer lies on top of the CdS and finally, the n-type ZnO:Al layer functions as the front contact. Altogether, the semiconductor used in this solar cell is 1.2–

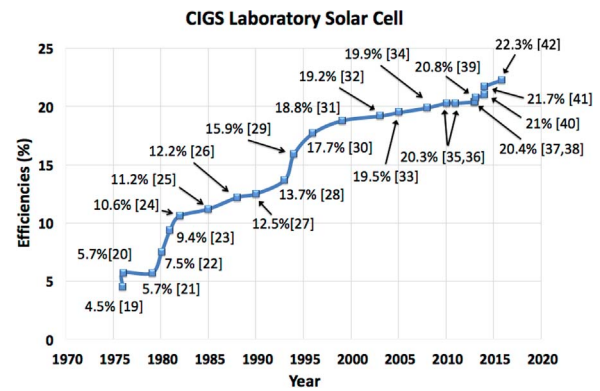


Fig. 6. Best laboratory efficiencies for CIGS solar cell.

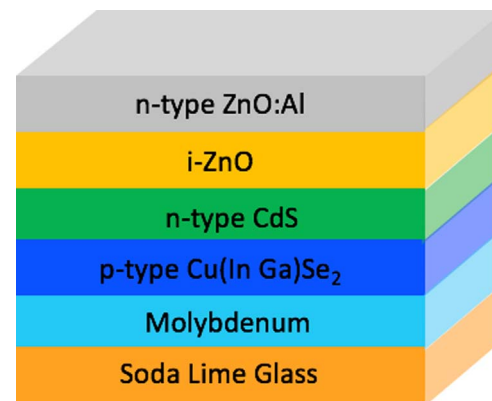


Fig. 7. The structure of CIGS solar cell.

4.04 μ m, which is very thin compared to the crystalline silicon at 170–200 μ m.

Further work by Kazmerski et al. [20] included using an In fingered contact as a top electrode, which allowed passage of $\sim 75\%$ of the incident radiation and improved the efficiency to 5.7%. This improvement was attributed to better absorption of carriers through the CdS window and improved junction characteristics. Additionally, the lattice parameters of InP and CuInSe₂ proved to match with CdS, further minimizing interfacial states. However, the low efficiency of below 10% was due to high series resistance and ideality factor, and the low J_{SC} was attributed to the grain-boundary recombination. In 1980, Mickelsen and Chen [21] fabricated a CdS/CuInSe₂ heterojunction solar cell with 5.7% efficiency using a simultaneous elemental evaporation technique to deposit CuInSe₂ film. This cell showed a remarkably high short circuit current density (J_{SC}) of ~ 31 mA/cm² for a 1-cm² cell, even without an antireflection coating (ARC). The high J_{SC} was attributed to combination of Fermi position and band bending in the high-resistivity CuInSe₂, further lowering open circuit voltage (V_{OC}).

By using n-type and p-type CuInSe₂ in conjunction with CdS, Chen and Mickelsen [22] improved efficiencies to 7.5%. Peculiar to this structure were the adjustments of the two selenide layers and addition of 10% CdSe in the CdS layer. Based on this result, they proposed a 10% efficiency cell through optimization of selenide resistivity and minimization of photon losses. In 1981, Mickelsen and Chen [23] demonstrated a 9.4% efficient thin-film CuInSe₂/CdS solar cell. The efficiency improvement was due to the difference in the method of evaporating the two selenide layers. The films were deposited with fixed In and Se deposition rates, and the Cu rate was adjusted to achieve the desired composition and resistivity. The transport property of the heterojunction is dominated by interface state recombination, and the low V_{OC} was primarily blamed on high resistivity of Se. To understand the limitations of the cell performance, the cells were annealed in a combination of H₂/Ar and then subsequently annealed in pure oxygen.

The J_{SC} improved in all the cases due to thermal effect independent of ambient but V_{OC} and fill factor (FF) only improved in an oxygen-containing environment. Thus, a significant improvement in the cell efficiency can be achieved by subjecting the cells to a post deposition bake at 200 °C in air or an oxygen containing environment. In 1982, Mickelsen and Chen [24] used a mixed $Zn_xCd_{1-x}S$ to improve the V_{OC} and J_{SC} and thus resulted in a record efficiency of 10.6%. The excellent crystallinity features between the selenide/sulfide interfaces in the columns without unwanted planar grain boundaries was responsible for the high J_{SC} . The addition of Zn to the sulfide layer increased the V_{OC} because of the improved match in electron affinity between the sulfide and selenide layers.

Potter et al. in 1985 [25] introduced ZnO in conjunction with p-type $CuInSe_2$ and thin undoped (Cu, Zn)S or CdS to achieve an efficiency of 11.2%. A thin film of CdS allowed the efficient capture of photons with < 520 nm wavelength, while the ZnO antireflection coating improved J_{SC} by 25%. In 1988, Mitchell and Liu [26] further improved the efficiency by an additional 1%, resulting in a 12.2% efficiency using the same structure as Potter. By texturing the ZnO layer, optical reflection was significantly reduced to ~6%. A combination of the direct band gap of ~1.0 eV, which enhanced the photocurrent, and annealing, which reduced the resistivity of the CIS film, led to a 1% absolute improvement in efficiency. In 1990, Devany et al. [27] replaced the ternary $CuInSe_2$ with quaternary $CuInGaSe_2$, whose band gap can be adjusted by the percentage of In incorporation. By exploiting the higher bandgap of the quaternary $CuInGaSe_2$ layer, the V_{OC} was increased, and the infrared absorption losses in ZnO were minimized, thus achieving a 12.5% efficiency.

In 1993, Chen et al. [28] reported 13.7% efficiency with the quaternary (CIGS) layer as the p-type absorber, $CdZnS$ mixed alloys as the n-type layer and an n-type overlayer of ZnO transparent conducting oxide for majority carrier collection. The efficiency improvement was due to an improved CIGS grain structure resulting from an increase in the substrate temperature (> 500 °C). Therefore, by reducing the reflection loss, decreasing the ZnO absorption losses, and increasing the Ga content in the selenide, a total efficiency of 13.7% was reached. Gabor et al. [29] in 1994 reported a 15.9% efficient $CuIn_xGa_{(1-x)}Se_2$ solar cell made from $(In_x, Ga_{1-x})_2Se_3$ precursor films. In 1996, Tuttle and others [30] used Mo back contact as a conduit for impurity migration from the glass to absorber and sputtered ZnO emitter along with MgF_2 antireflection coating, which led to efficiency of 17.7%. The enhanced V_{OC} can be attributed to a slight shift in the absorber band edge to higher energies, which resulted from the reduced recombination in the conduction band of CdS and the reduced thickness of the CdS layer.

By optimizing the ZnO window layer, improving the interface between CIGS absorber and CdS buffer layer, enhancing diffusion length of the minority carriers and reducing recombination in the space-charge region, Contreras et al. [31] reported an efficiency of 18.8% in 1999. Ramanathan et al. [32] in 2003 used bandgap grading of different concentrations of Ga and In to increase V_{OC} , which led to efficiency of 19.2% $ZnO/CdS/CuInGaSe_2$ thin film cells. In 2005, Contreras et al. [33] reported a 19.5% efficient CIGS solar cell. The improvement in their cell resulted from the engineered bandgap of the absorber to ~1.14 eV, low values of the diode saturation current density (J_{02}) of $\sim 3 \times 10^{-8}$ mA/cm², and an ideality factor (n -factor) of $1.30 < n < 1.35$ which led to reduced space-charge region recombination. Repins et al. in 2008 [34] reported an efficiency of 19.9% as a result of decreased recombination from lowering the bandgap in a portion of the space charge region. Thus, the V_{OC} stayed the same as reported by Contreras [33] but the FF soared to 81.2% with ideality factor of 1.14 and J_{SC} value of 2.1×10^{-9} mA/cm².

The major goals of manufacturers and researchers worldwide are low-cost and high efficiency solar energy production. Researchers from companies, research institutions, national laboratories and universities are investigating to improve the efficiency by any means while making

the device low-cost compatible. The Center for Solar Energy and Hydrogen Research, ZSW [35,36], in Germany in 2010 reported a record 20.3% efficient CIGS cell with a total thickness of 4 μ m including the metal contacts. In 2013, the Swiss Federal Laboratories for Materials Science and Technology (EMPA) [37] engineered a thin film CIGS solar cell on a flexible polymer substrate with an efficiency of 20.4%. The thin CIGS layer is mounted onto a polymer substrate, permitting roll-to-roll continuous production of the cells. Powalla et al. [38] also reported a 20.4% efficient cell using a static co-evaporation process. Peculiar to their cell was the use of $Zn(O,S)$ buffer layer instead of the conventional CdS between the light absorbing CIGS layer and the transparent ZnO front electrode. The heart of their technology lies in the high-vacuum cluster deposition system that allows the static co-evaporation of the CIGS absorber's constituent elements and the sputter deposition of i-ZnO and $ZnO:Al$ as window materials. Powalla et al. [39] with continued investigation reported an improved efficiency of 20.8%, which resulted from intentional potassium doping of the $Cu(In, Ga)Se_2$ layer. The new doping process allowed a shift in the CIGS absorber composition towards higher gallium content while maintaining the efficiency. The novel deposition procedure also enabled partial overcoming of the saturation of V_{oc} and allowed a shift in CIGS absorber composition at higher gallium content. The saturation of V_{oc} for higher Ga content previously had prevented the progression for higher-band gap CIGS cells. In 2014, Herrmann et al. [40] reported a 21% efficient CIGS cell. The improvement in efficiency was attributed to increased CIGS deposition rates. Additionally, a 21.7% efficiency in 2014 was reported by Jackson et al. [41]. The improved efficiency stems from the optimization of the alkali post deposition treatment of the cell [43]. Finally, an efficiency of 22.3% was achieved by Solar Frontier through improvements to the CIS absorber layer and junction formation process [42].

2.3. CdTe solar cell

CdTe serves as a prime candidate for all thin film solar cells. It is a direct band gap material like CIGS with a large absorption coefficient, and it is a stable compound which can be produced from a wide variety of methods. A thin film of CdTe is adequate for producing high efficiency cells if both bulk and surface recombination are curbed.

The first significant laboratory CdTe cell was reported in 1972 by Bonnet and Rabnehorst (Fig. 8) who developed a thin film graded gap CdTe-CdS p-n heterojunction solar cell with 6% efficiency. This cell (Fig. 9) was created in a three-step process involving high temperature vapor phase deposition of CdTe and high vacuum evaporation of CdS [44]. One of the features of this includes a graded gap junction to improve the transport of the photogenerated carriers to enhance the J_{sc} . Bonnet and Rabnehorst encountered several problems involving the back contact between Mo and CdTe, because using pure Mo as a substrate lead to considerably high series resistances and.

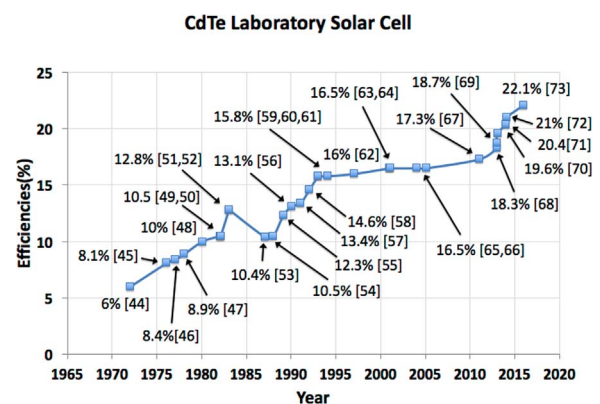


Fig. 8. Best laboratory efficiencies for CdTe solar cell.

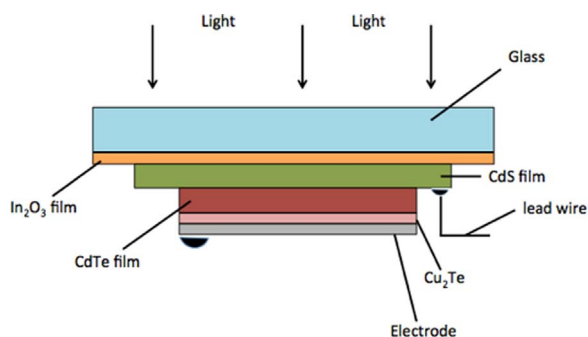


Fig. 9. Schematic cross section of a ceramic thin film CdTe solar cell.

low FF. Solutions to making a good non-rectifying contact to wide band gap p-type semiconductors include using a high work function metal, and generating a heavily-doped layer in the semiconductor adjacent to the contact metal. This creates a resulting depletion layer so thin that charge carriers can efficiently tunnel through.

Rapid interest in the CdTe field resulted in a variety of different fabrication methods. Previous work by Bonnet involved vapor growth and vacuum deposition, but in 1976, Nakayama et al. [45] explored screen-printing methods in CdTe solar cells. The In_2O_3 film and the CdS ceramic film were coated on top of a glass substrate. The CdS ceramic layer served as an ohmic contact transparent electrode to the CdTe layer, reducing both the series resistance and the surface recombination at the n-CdTe layer. This resulted in an 8.1% efficient CdTe solar cell [40]. Bube and others [46] further explored CdS/CdTe heterojunction solar cell with 8.4% efficiency. In this structure, interdiffusion of donors from the n-CdS into p-CdTe during junction formation were believed to have created n-CdS/n-CdTe/p-CdTe junctions, in which the CdS film served as a contact to the CdTe homojunction. It is noted that increasing the effective acceptor doping concentration in the CdTe to 10^{17} cm^{-3} would be significant in minimizing the effects of the interface recombination velocity.

CdS/CdTe solar cells have a distinct cost advantage over single-crystal silicon solar cells. Efforts to establish techniques for the fabrication of cells with improved conversion efficiencies are shown through the inventions of Eastman Kodak Company [47,48], where polycrystalline CdS and polycrystalline CdTe in contiguous layers resulted in a conversion efficiency of 8.9%. Depositing and sublimating semiconductive layers in an oxygen-containing atmosphere allowed for the incorporation of oxygen atoms into the semiconductor layer, resulting in a more efficient device. The same technique of introducing oxygen to the semiconductor layers achieved an efficiency of 10.5% later. The oxygen enhances the p-type character of the CdTe film and ensures the shallow-junction behavior of the device. Tyan and others [49] in 1982 at Eastman Kodak Company, reported a 10% efficiency by integrating a layer comprising tellurium between the metal contact and the layer of p-type CdTe. The surface portion of the CdTe in contact with the tellurium layer is cadmium deficient and the CdTe layer has intact grain boundaries.

Increasing experience and previous work from literature showed junction preparation technique often controlled the final cell properties. Vacuum evaporation of CdS results in heterojunctions, whereas chemical vapor deposition techniques of CdS produce buried homojunctions. In 1983, Werthen and others [50] demonstrated that using low-doped CdTe greatly improved V_{OC} . Although low-doped CdTe resulted in depletion region recombination but significantly reduced the recombination at the interface. Werthen and others concluded that an additional heat treatment of the semiconductor layers may have been important in improving efficiencies, and recognized low-doped CdTe to be a viable approach for all CdTe solar cells.

Kuribayashi and others [51,52] with the introduction of carbon electrode and oxygen during deposition of the CdS and CdTe layer to

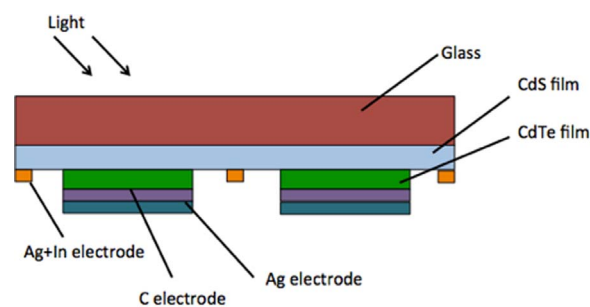


Fig. 10. Cross section of the CdS/CdTe solar cell.

enhance the p-type character of the CdTe film and ensure the shallow-junction behavior of the device, improved the efficiency to 12.8% in 1984. Appropriate amounts of Cu (50–100 ppm) in the carbon paste during the diffusion of the carbon into the CdTe layer during heat treatment helped make the CdTe layer p⁺ type and additionally contributed to further reduce the contact resistance between the CdTe and carbon electrode as shown in Fig. 10.

1987 revolutionized the CdTe solar cell industry. Previous efforts mentioned in this review focused on the optimization of processes such as electrodeposition, screen printing, and close-space sublimation. Closed space sublimation offers the advantages of simple deposition apparatus and high transport efficiency done with low vacuum conditions at moderate temperatures. Works of previous researchers involved the creation of p-CdTe based heterojunctions, however, these heterojunctions led to problems with making low resistivity contacts and low minority-carrier lifetimes.

Meyers and others at Ametek [53] introduced a novel n-i-p design (Fig. 11) that possesses many advantages over the state-of-the-art CdTe heterojunction devices, designed to accommodate its innate properties. High efficiency cells were often constructed of high resistivity CdTe, which were generally better quality than low resistivity films. Additionally, rectification rather than low resistance contacts was utilized, and the field in the i-layer assisted in the collection of charge carriers. CdS and ZnTe are naturally n-type and p-type materials as well. The minimal discontinuity in the valence band edge at the CdTe/ZnTe interface permits the free flow of holes from the CdTe into the ZnTe. Such rapid improvements led to an efficiency of 10.4% [54]. Creating a successful ohmic contact to CdTe is generally very hard because of CdTe's large work function. Thus, a buffer layer of high conductivity p-type semiconductor such as p-ZnTe was used.

With these rapidly increasing efficiencies, cost became a major factor in the commercialization of the CdTe solar cells. The goals of many researchers involved achieving high efficiency CdTe solar cells using low-cost simple high throughput processing. Unlike previous attempts of developing a CdS/CdTe junction, Bottenberg and others at Arco Solar [54] focused on the creation of a three-layer device without CdS that utilized a front conductive layer (a wide band-gap transparent

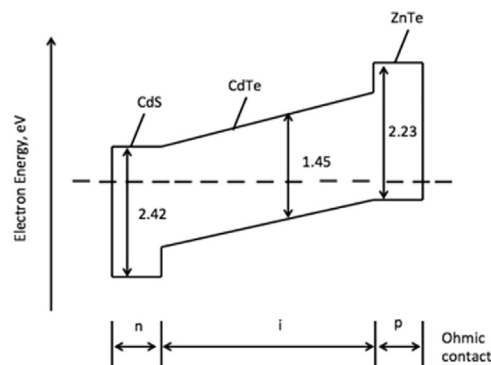


Fig. 11. Idealized energy band diagram of the CdS/CdTe/ZnTe n-i-p solar cell.

conductor to eliminate the need for a CdS layer). Their work achieved an efficiency of 10.5%.

In 1989, 12.3% efficiency was achieved by Chamberlin and others at Photon Energy [55]. Suitable doping applied to the CdTe made the material more conductive with hole concentrations as high as $2.8 \times 10^{16} \text{ cm}^{-3}$. Additionally, the use of various chemical rinses and etches on the CdTe surface helped to reduce contact resistance, leading to higher device efficiencies. Totszser et al. [56] further improved the material band gap at the CdS/CdTe interface and reported efficiencies of 13.1%. Their findings were promising- a reduced electric field at the junction caused an increased trapping of the light generated electrons by midgap recombination centers.

However, the difficulty of producing low-resistivity p-CdTe films, along with forming stable low resistance contacts to the p-CdTe films became a challenge, which generated a lot of research interest. Chu et al. pushed efficiencies to 13.4% [57]. Peculiar to their method was the preparation of CdS films from an ammonical solution of Cd-salt, ammonium salt, and thiourea. Previous efforts in the deposition of CdS formed discontinuity, but Chu's methods showed highly adherent, smooth, reflective CdS surfaces. Chu continued this rapid improvement through the development of a device measuring 14.6% efficiency [58]. The high efficiency was attributed to the interface reaction between CdS and CdTe during the deposition of CdTe at high temperatures. It was observed that $\text{CdS}_x\text{Te}_{1-x}$ formed at the interface, shifting the electrical junction from the metallurgical interface into CdTe, improving photovoltaic characteristics of the junction. Thus, the control of CdS/CdTe interfacial chemistry became extremely important to achieving high solar conversion efficiencies. In 1993 and 1994, Britt and others [59–61] at the University of South Florida improved upon Chu's work, reporting efficiencies of 15.8%. Fig. 12 shows their structure.

The high temperature used during the deposition of CdTe by close spaced sublimation (CSS) was hypothesized to have caused the formation of an interdiffused region between CdS and CdTe. $\text{Cd}_x\text{S}_{1-x}\text{Te}$ region shifted the electrical junction away from the metallurgical junction. Additionally, the use of graphite paste containing mercury proved to serve as an adequate electrical contact in this work. Britt et al. [59–61] found further discoveries by annealing CdS layers in H_2 prior to deposition, resulting in improved photovoltaic characteristics, including an increase in bandgap energy of 0.12 eV, reduction in interface states, and increase in grain size. Annealing has also left the surface of the films Cd-rich, and also resulted in thinner CdS films to sufficiently reduce and avoid the formation of shunting paths as shown in Fig. 13. Thinner films also resulted in the enhancement of the blue response of CdTe/CdS solar cells.

1997 marked a year of a new world record efficiency of 16% set by researchers at the Matsushita PV Research and Development Center

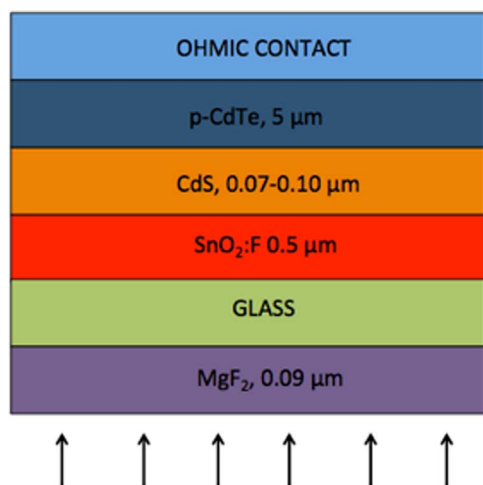


Fig. 12. Configuration of a thin-film CdTe solar cell.

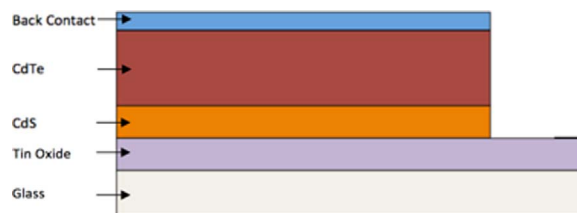


Fig. 13. The structure of CdTe/CdS thin film solar cells [60].

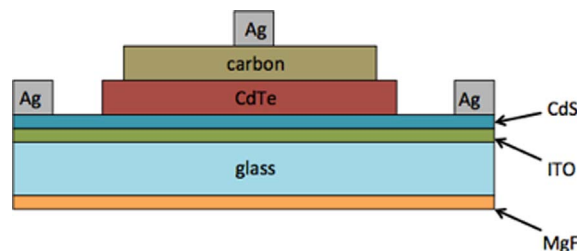


Fig. 14. The cross-sectional scheme of a CdTe/CdS solar cell [61].

[62]. The cell was prepared from a CdS layer that was deposited by metal organic chemical vapor deposition, a low-temperature and low-cost technique, and from a CdTe layer deposited by CSS. The increase in the conversion efficiency is due to the decrease of high-quality CdTe thickness, which is closely related to the series resistance of solar cells. The fill factor approached 73% as well. Fig. 14 shows the structure of their cell.

Wu et al. at NREL [63,64] took a unique approach by modifying the conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ device structure. A new device using a modified CTO/ZTO/CdS/CdTe device structure was developed. Four approaches were taken: firstly, a novel process was developed to prepare high-quality cadmium stannate (Cd_2SnO_4 , CTO) transparent conductive oxide (CTO films, which have two to six times lower resistivity, higher transmittance and smoother surfaces than conventional SnO_2 TCO films. By replacing the SnO_2 transparent conductive oxide with Cd_2SnO_4 , J_{sc} and FF of CdTe cells was improved. The low resistivity of CTO films allows for the increase in the width of the sub-cell in modules, thereby increasing total-area module efficiency. Additionally, a Zn_2SnO_4 (ZTO) novel buffer layer was used in these devices, along with a modified CdS film with a higher optical bandgap, resulting in 16.5% efficiency.

Focus in research had now shifted to the improvement of the transparent conductive oxide layer. Because CdTe cells operate best in a superstrate configuration in which light enters the active junction through the glass, the transparent front contact is deposited first and must survive all subsequent deposition steps. Three characteristics are necessary for a TCO to be used as a front contact: high transparency of better than 85% in the wavelength of interest, low resistivity of $2 \times 10^{-4} \Omega \text{ cm}^{-1}$, and good stability at a range of temperatures. No diffusion from the TCO into layers deposited is allowed.

Wu et al. at NREL continued their work [65] and reported efficiencies of 16.5%. The same Cd_2SnO_4 (CTO) replaced the SnO_2 TCO, and similar technologies of the high resistivity ZnSnO_x (ZTO) buffer layer were placed between the TCO and the CdS film as shown in Fig. 15. However, this time, in order to improve the FF and the efficiency, Wu et al. [65] developed an oxygenated nano-crystalline CdS:O window layer with a higher optical bandgap (2.5–3.1 eV) than the poly-CdS film. The bandgap increased with an increase in oxygen content and a decrease in grain size. The oxygen present in the nano-crystalline CdS:O films suppressed the Te inter-diffusion from the CdTe to the CdS film and the formation of a $\text{CdS}_{1-y}\text{Te}_y$ alloy, resulting in higher quantum efficiency. Controlling the Te inter-diffusion is important because small changes in the Te contact in the CdS can result in a decrease in bandgap. This led to the achievement of 75.51% FF.

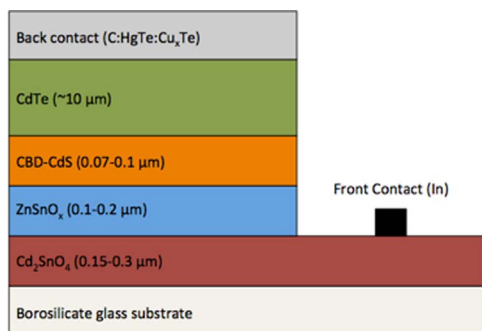


Fig. 15. Modified CTO/ZTO/CdS/CdTe device structure.

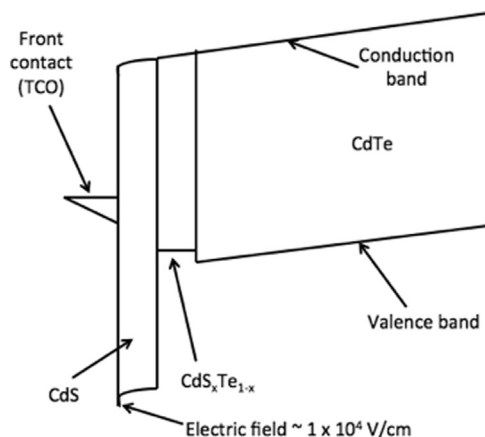


Fig. 16. Ideal band diagram at the CdS/CdTe interface.

16.5% efficiency was additionally achieved by Acevedo in 2005 [66]. Their results let to the speculation that there is a presence of a CdS_{Te} alloy film due to the diffusion of sulfide into CdTe and Te into CdS. This interlayer helps to improve the efficiency of the solar cell by reducing the interface carrier recombination, further shown in Fig. 16. Additionally, the thermal annealing after the deposition of the CdCl₂ on top of the CdTe layer resulted in a better organized CdTe matrix.

First Solar Research and Development has dominated the past decade, with reported efficiencies of 18.7%, 19.6%, 20.4%, and 21% [67–73] with a heavier focus on commercialization. First Solar utilizes a continuous manufacturing process, creating a complete solar module shown in Fig. 17 in less than 2.5 h.

It is reported that the window layer, CdS, is deposited by VTD (vapor transport deposition), and then an absorber layer (CdTe) is deposited. First Solar continues to create record-setting research cells that demonstrate the highest single junction thin film on record. (Figs. 18 and 19).

3. Commercial thin film technologies

In Table 2, thin film commercial module efficiencies are compared

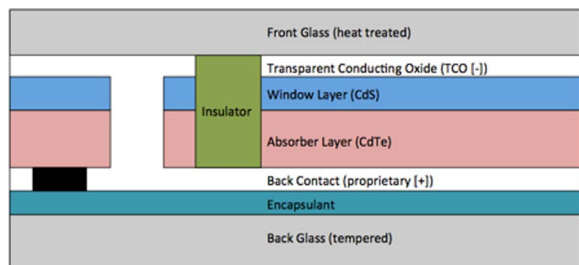


Fig. 17. A traditional First Solar CdTe solar cell.

2011 GLOBAL PV SHIPMENTS- 23.6 GWp

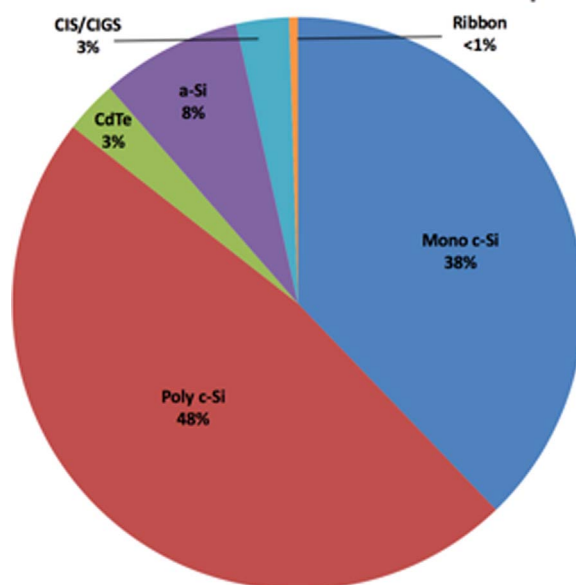


Fig. 18. Global PV shipments in 2011.

2014 GLOBAL PV SHIPMENTS- 39.3 GWp

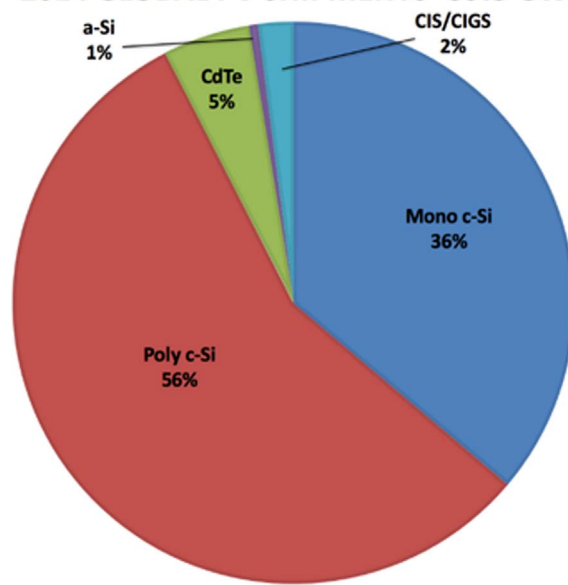


Fig. 19. Global PV shipments in 2014.

with crystalline silicon commercial module efficiencies. Thin film commercial module efficiencies are climbing and prominent. In fact, it was First Solar's CdTe thin film solar panels that broke the \$1/Watt milestone in early 2009 [93]. The CdTe industry is mainly dominated by First Solar, who has also recently demonstrated a record module of 18.6% efficiency [91], higher than that of the best commercial application multi-crystalline module ever previously recorded. CdTe has proven to be a thin film material that can rival crystalline silicon in the near future. Yet, issues regarding the proper disposal of toxic cadmium remain.

The future of large-scale amorphous silicon solar panels is not promising. Roadblocks for α -Si include low module efficiencies, mainly attributed to the Staebler-Wronski effect, which leads to degradation under illumination. Many α -Si companies have gone out of business in the past decade such as Xunlight, Masdar PV, OptiSolar, Signet Solar, and Sunfilm due to low demand, and the efficiency of α -Si commercial

Table 2

Chart of commercial a-Si, CdTe, CIGS, and crystalline silicon module efficiencies as reported by manufacturers.

<i>a-Si</i>	Champion Research Module	12.24% [83]
	MICROMORPH™ G5 - TEL Solar	
	NA-V135H1 (2010) Sharp Thin Film Module a-Si/micro-Si	9.5% [90]
<i>CdTe</i>	Champion Research Module First Solar	18.6% [91]
	FS-4112 First Solar Series 4™ PV module	14.04% [87]
	CX3-85 - Calyxo	8.51% [88]
<i>CIGS</i>	Champion Research Module TSMC Solar	16.5% [92]
	SL2 CIGS Thin-Film Module - Solibro	13.3% [76]
	SF170-S CIS Module - Solar Frontier	13.8% [80]
	FLEX-02N - Miasole	16% [81]
	M-GE101E092 - Manz	16% [82,83]
	SP3S-250 - SoloPower	12.7% [84]
	Powerflex BIPV 100 W Global Solar/Hanergy	12.7% [85]
	TS-165-C2- TSMC Solar	15.2% [86]
	Monocrystalline X-Series Residential Solar Module - SunPower	21.5% [79]
	Heterojunction with intrinsic Thin-layer HIT- Panasonic	19.0% [74]
<i>Crystalline Silicon</i>	Trina Solar 60-cell ALLMAX M PLUS	17.7% [75]
	Poly 156 - CSG PV Tech Co.	16.0% [77]
	Q.Pro-G4 - QCells	16.2% [78]
	Mono125 - CSG PV Tech Co.	14.9% [77]

modules have remained stagnant as a result [94, 95]. The demand for α -Si solar technology will still remain in the small device industry (i.e. pocket calculators, watches, etc.). However, alternative α -Si/micro-Si tandem solar cells are emerging from manufacturers such as Kaneka and Sharp.

CIGS is a growing technology behind CdTe that may see more market share than CdTe in the near future. Hanergy's acquisition of Miasole and Solibro and Solar Frontier's emergence in the CIGS industry has established a strong position in the thin film market. There are obvious areas of improvement in the CdTe/CIGS industries, such as increasing window transparency by replacing CdS with a wider bandgap material, and potential reduction of CIGSS absorber thickness to less than 1 μm [90].

For all thin films, improved efficiency is essential for competition with wafer-based technologies, such as crystalline silicon, which boasts efficiencies of up to 21.5%. Stacked or tandem cells offer alternate routes as well. Other important factors include cost of materials and assembly, and price per watt measurements.

4. Market share

PV industry shipments have grown 15% in the last year, from 34.0-GWp in 2013 to 34.0-GWp in 2014 [100]. Within the PV industry, the growth of thin film companies has catapulted, with more than 100 companies entering the market between 2001 and 2009 and production increasing from 14 MW to 2141 MW [98]. It is expected that in the long term, thin film PV technology will surpass crystalline technologies, if the efficiency and reliability are bankable.

However, contrary to these predictions, investors are concerned about the declining status of the thin film industry due to low-cost manufacturing and rising efficiencies of crystalline silicon technologies as well. The decreasing prices of crystalline silicon modules have led to a declining demand for thin film technologies in the past two years. Thin film producers face a PV market where falling module prices have eroded their competitive advantage and global demand has decreased.

In 2008, thin film technologies had a 14% share, which further increased in 2009 to 17%. The market share of thin film photovoltaics is progressively decreasing, with only a 7–8% market share in 2014 [98–101]. Thin film, contrary to popular belief, has been on the wane

since 2009 because it is more expensive, less efficient, and less bankable than low-cost crystalline silicon technologies made in foreign countries, such as China, Philippines, and Thailand etc. where manufacturing costs are low [96].

α -Si, the first thin film solar cell technology, has become almost obsolete from commercial arena. At its entry in 1982, α -Si grew at an annual rate of 30% [101], but now it has less than 1% of the global PV market share. Possible re-entries and growth in the market include space applications, which α -Si technology has advantage over the crystalline material due to low mass and low radiation damage. The consequences of the Staebler Wronski effect would not be a major setback as opposed to terrestrial operation [102]. Additionally, the future of α -Si is looking towards the integration of microcrystalline and amorphous composition mixes and multiple junctions, which have shown promising results [103].

CIGS has the greatest influence and prominence in the thin film industry, next to CdTe. Investments of up to 2 billion USD have been made into commercial CIGS companies, and more investment inflow should help CIGS companies such as Wurth Solar compete against CdTe giants such as First Solar and Hanergy.

Yet, with the decreasing market share of thin film, it must be realized that if thin film does not ultimately replace commercial crystalline silicon technologies, it has a large advantage in many sunbelt countries with very diffuse light conditions and hot temperatures. Thin film technologies with better temperature coefficients and ideal power conversion efficiencies in adverse environments do have advantages over crystalline silicon.

5. Reliability and materials availability

The reliability of thin film is questionable in comparison with the emergence and production of competitive and low-cost crystalline silicon solar panels. In terms of technology performance, due to the different temperature coefficients, it is realized that the loss of power due to higher operating temperature will vary heavily depending on the type of thin film. For example, light induced defects may be more prevalent in α -Si thin film technologies due to material degradation as part of the Staebler-Wronski effect [104]. The strength of the effect is related to device structure, as devices with thinner intrinsic layers exhibit less performance loss because of a decreased recombination of photocarriers [105].

Fig. 20 refers to the effects of temperature on the fill factor of CIGS, CdTe, TF-Si, α -Si, and α -Si/micro-Si. With the exception of α -Si, all other module technologies exhibit a linear behavior with increasing temperature. The anomaly of α -Si is due to the Staebler-Wronski effect, in which a regenerative and beneficial effect occurs due to the annealing of the cell. The study of temperature coefficients is important because they often determine PV system design and sizing [107]. Many

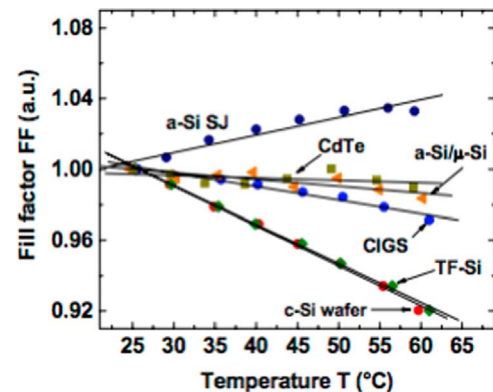


Fig. 20. Experimentally determined comparison of the fill factor of different module technologies as a function of temperature [106].

current manufacturers, notably First Solar, collaborate with National Renewable Energy Laboratory (NREL) to learn more about the reliability of their commercial modules [108].

With regards to materials availability, thin film PV technologies utilize a variety of chemical elements ranging in abundance and production. The material constrained growth of installed capacity in the year 2020 is estimated at about 20 GWp/year for CdTe, 70 GWp/year for CIGS, and 200 GWp/year for a-Si: Ge [109]. The usage of toxic, regulated elements (Cd) and reliance on rare elements (Te, In) constrain the potential for large-scale thin film deployment; however, the development of thinner films could ultimately reduce metal inputs by a factor of 10 and result in decreased materials requirements [111].

With the CdTe material, a method for extracting tellurium more efficiently and cost-effectively from copper ores could significantly improve prospects for large-scale deployment. Regardless, further development poses the following dilemma: in order to supply 100% of 2050 global electricity demand with CdTe PV, around 737,000 metric tons of Cadmium and 786,000 metric tons of tellurium are required [110]. However, the current annual production of cadmium exceeds telluride production by nearly double the magnitude, thus meaning that even deploying 25 TW_p of CdTe PV would require the equivalent of 34 years of global cadmium production and about 1500 years of global tellurium production at current rates [110]. On the other hand, CIGS materials are facing replacement, as gallium could eventually substitute for indium because of materials scarcity. Zweibel [111] assumes that a 75% substitution is likely and that near 100% substitution may happen, allowing for the usage of more abundant elements for CIGS production.

Materials scaling considerations may be deciding factors in determining which technologies fulfill the majority of PV demand in the future. Despite its numerous benefits over silicon technologies, complete reliance on CdTe or CIGS would require over 75 times more tellurium or gallium for PV than has ever been produced for all other uses combined. Additionally, it is clear that silicon based technologies are advantageous in material availability, as silicon is 20,000 times as abundant as gallium and 300,000,000 times more abundant as tellurium [110]. However, major approaches in thin films such as using more robust materials and cell architectures to improve reliability, and decreasing dependence on rare elements by creating new materials may allow for further market growth of thin film technologies.

This shortage and toxicity of materials used in a-Si, CIGS, and CdTe technologies have sparked an increase in exploration of emerging next-generation thin film technologies, highlighted in the next section. However, it is important to note that emerging thin films have not reached the scale to precisely quantify materials utilization and manufacturing yield in high-volume module production, yet they may be more desirable thin film alternatives given increased performance and commercialization.

6. Emerging next generation thin film technologies

With intense R&D efforts in materials science, several new thin-film PV technologies have emerged that have high potential, including perovskite solar cells, Copper zinc tin sulfide (Cu₂ZnSnS₄, CZTS) solar cells, and quantum dot (QD) solar cells.

6.1. Perovskite materials

In less than three years of development, hybrid organic-inorganic perovskite solar cells have achieved efficiencies of over 20% [112,113]. Perovskite materials have the formula ABX₃, where A represents an organic cation, B is an inorganic cation, and X is a halide. The bandgap can be continuously tuned from ~1.6 eV (pure I) to 3.2 eV (pure Cl), with smaller band gap materials providing better solar cell efficiencies [114]. Perovskite salts form polycrystalline films with a perovskite structure at or near room temperature by precipitation from a variety

of polar solvents. Advantages include long carrier diffusion lengths [115,116], low recombination losses [117], low materials cost, and bandgap tunability.

Despite a sharp onset in the absorption spectrum of perovskites, the photocurrent loss due to parasitic absorption in the hole-conducting layer and the back reflector is very substantial. In addition to this, the fill factor in perovskite solar cells is fairly low (FF=0.73), due to a combination of non-uniformity in the absorber (e.g. pinholes), and carrier-selective contacts that lead to carrier shunting, along with resistive losses associated with non-ideal carrier-selective contacts. Additional challenges include high sensitivity to moisture, cell instability, and the use of toxic lead [112,113]. However, a possible entry point into the market lies with large-band gap perovskites serving as a top-cell in Si/perovskite tandem cells.

6.2. Copper zinc tin sulfide (CZTS)

Cu(Zn, Sn)(S, Se)₂ (CZTS) is a solar cell material similar to CIGS, but the scarce element In is replaced by Zn and Ga is replaced by Sn [120], allowing for CZTS to be an earth-abundant alternative with similar processing strategies and challenges as CIGS [121,122]. The kesterite crystal structure of CZTS is used for PV applications, and like CIGS, the band gap of CZTS can be tuned over a range from 1.0 to 1.6 eV.

The record CZTS cell has an efficiency of 12.6% [118,119], yet suffers from large voltage loss due to recombination at defects in the bulk material and at the charge extraction interfaces. This best result was achieved through a Cu-poor, Zn-rich stoichiometry with the band gap being controlled by the S/Se ratio. Major breakthroughs in the development of CZTS solar cells depends on finding an alternative back contact with lower optical loss (higher reflectivity) that can withstand the full device processing and maintain low series resistance [120].

6.3. Quantum dots (QD)

Quantum dot photovoltaics use solution processed nanocrystals, also known as quantum dots (QDs) to absorb light [123–125]. The best QD solar cells have been made using PbS or PbSe QDs as the active layer [126]. Changing the size of quantum dots tunes the band-gap of colloidal metal chalcogenide nanocrystals, allowing for the creation of multi-junction solar cells and the efficient harvesting of near-infrared photons. The benefits of quantum dot photovoltaics lie in simple room-temperature fabrication and air-stable operation [127]. Current challenges in this field include further understanding of QD surface chemistry [128–130], and improving mid-gap states/inherent disorder in quantum dot films that limit open-circuit voltages.

These emerging technologies range from R&D to early commercialization but have not yet been deployed at scale. However, they offer unique device properties and reliance on earth-abundant materials and simple processing methods, potentially opening doors to novel applications for solar PV [110]. Assuming improvements in stability, efficiency, and manufacturability, these emerging thin-film technologies may overcome many of the limitations of today's deployed technologies at a lower cost.

7. Conclusion

This paper has reviewed the three thin film technologies: α-Si, CIGS and CdTe. CIGS and CdTe are more promising to compete with the mainstream crystalline Si technology in efficiency. With the rising module efficiency of these two thin film technologies, their market share will grow in the future, provided the cost of production continues to be lower than the crystalline Si counterpart. The reliability of these technologies is a concern with regard to temperature, and additionally, materials availability may be a deciding factor in determining which technologies capture the majority of the PV demand in the future. CdTe

remains the prime candidate of all thin film technologies, and as a direct band gap material, it requires only a 1–2 μm thickness for high efficiencies. The past decade has been dominated by First Solar, which holds the world record in thin film efficiencies and has broken the \$1/Watt milestone in 2009. Despite this, the proper disposal of cadmium remains an issue with this thin film technology.

α -Si solar cell will continue to dominate the consumer electronics industry, which has been its niche since its inception in the early 80 s. However, because of the very low efficiency and instability, terrestrial applications with α -Si solar cell are not economical. More so, the systems cost (inverter, power electronics, wiring, land, racking etc.) will be much higher than the cost of purchasing the solar cells. Due to the high balance of systems cost, the cost of electricity from α -Si solar cell will be much higher than the other two thin film technologies and even crystalline Si. This is the major reason the commercial activities of the α -Si technology are almost extinct. However, CIGS technologies show potential if issues regarding materials availability are absolved, and recombination losses are reduced. Major milestones may be accomplished with (1) increased efficiencies, (2) reduced materials usage, and (3) reduced manufacturing complexity and cost.

Thin film technologies hold promise, but currently, the low cost manufacturing of competitive crystalline silicon technologies is causing a decline in the status of the thin film industry. CdTe possesses the largest market share, followed by CIGS and an almost non-existent market share for α -Si. The future of α -Si lies in μ -Si mixes and multi-junction technology. Additionally, emerging thin film technologies such as CZTS and Perovskites that use earth-abundant materials and simple processing may open doors for novel applications of PV, given increased stability and reliability. More so, Quantum dot photovoltaics are very promising in creating high efficiency multi-junction solar cells in addition to simple room-temperature fabrication and air-stable operation. However, understanding of QD surface chemistry and improving mid-gap states/inherent disorder still remains. On the whole, despite the decreasing market share, more applications in adverse environment, diffuse light conditions, and hot temperatures will allow thin film solar cells to thrive in upcoming decades.

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