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# Flexible CIGS, CdTe and a-Si:H based thin film solar cells: A review

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ABSTRACT

Flexible thin film solar cells such as CIGS, CdTe, and a-Si:H have received worldwide attention. Until now, Si solar cells dominate the photovoltaic market. Its production cost is a major concern since Si substrates account for the major cost. One way to reduce the module production cost is to use the low-cost flexible substrates. It reduces the installation and transportation charges also, thereby reducing the system price. Apart from metallic foils, plastic films and flexible glass, paper substrates such as cellulose papers, bank notes, security papers and plain white copying papers are also used as substrates for flexible solar cells. In this review, recent developments in flexible CIGS, CdTe and a-Si:H solar cells are reported. Progress on various flexible foils, fabrication and stability issues, current challenges and solutions to those challenges of using flexible foils, and industrial scenario are reviewed in detail. Encapsulation issues and solutions related to water vapor transmission rate are discussed.

## 1. Introduction

Silicon (Si) solar cells dominate the PV market (92%) followed by cadmium telluride (CdTe, 5%), copper indium gallium selenide ($CuInGaSe_2$ or CIGS, 2%) and amorphous silicon (a-Si:H, ~1%). Si wafer with thickness around 180 µm is the traditional material being used for module manufacturing and it has attained significant level of maturity at the industrial level. Its production cost is a major concern for energy applications. About 50% of the cost of Si solar cells production is due to Si substrate, and device processing and module processing accounts for 20% and 30% respectively [1].

An alternate to Si solar cells is the thin film solar cells fabricated on glass substrates. The main demerits of using glass substrates are fragile nature of modules, cost of glass wafer having thickness of 300–400 µm, and low specific power (kW/kg) etc. Specific power is an important factor when solar cells are used in space applications. A high specific power exceeding 2 kW/kg can be achieved [2] by flexible solar cells on polymer films which is useful for terrestrial as well as space applications. Production cost can be lowered by using flexible substrates and roll-to-roll production (R2R) technique. Apart from light weight, flexibility and less cost of installation, flexible cell processing involves low thermal budget with low material consumption. Other than solar cell applications, smaller specialized applications are beginning to become more viable independent markets, including applications for mobile power and

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building or product integration, which can benefit greatly from flexible thin film options. Flexible cells on buildings (known as building integrated photovoltaics or BIPV) can minimize the cost of support, shipments etc., and installations can be handled easily. However, flexible solar cell technology is less mature when compared to the cells fabricated on rigid substrate counterpart.

Due to four main requirements - high efficiency, low-cost production, high throughput and high specific power, a major research and development focus has been shifted towards flexible solar cells. It can offer a unique way to reach terawatt scale installation by using high throughput R2R fabrication technique. Most commonly used substrates are polyimide, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), and metal foils such as stainless steel (SS) and titanium (Ti). During fabrication, impurity (such as iron (Fe) and chromium (Cr)) diffusion from metal foils into the device/active layer is a major concern. Polymer foils are preferable due to no metallic impurities. It can be used for both substrate and superstrate configurations, whereas in the case of metallic foils, substrate structure is the only option. Also, due to insulating properties, polymer foils are suitable for monolithic integration (i.e. cell to cell interconnection). Most frequently used polymer foils are polyimide. Its maximum processing temperature is limited to 450 °C which is a barrier for high efficiency solar cells, for example CIGS cells. Polyimide foils are more cost competitive than metal foils. The main concern with superstrate structure by using polymer foil is the transparency and its stability during high temperature processing conditions.

During the deposition of films, to avoid stress related issues (i.e. delamination, cracking and poor adhesion) in the film stack, thermal expansion co-efficient of flexible substrate should be in the range of the deposited films. If the thermal expansion co-efficient of the substrate is too high, cracking occurs in the film. Also, to circumvent pinholes and shunting, substrate roughness should be small. Average roughness of 12.5 μm thick polyimide and polished stainless steel are 1.3 nm and 2 nm respectively [3].

Solar cells on flexible glass have also been reported [4]. As compared to metal foils, flexible glass benefits from low contamination and roughness. As compared to polymer foils, flexible glass is compatible with high temperature processing and possesses high optical transparency which enable more photons to reach the absorber.

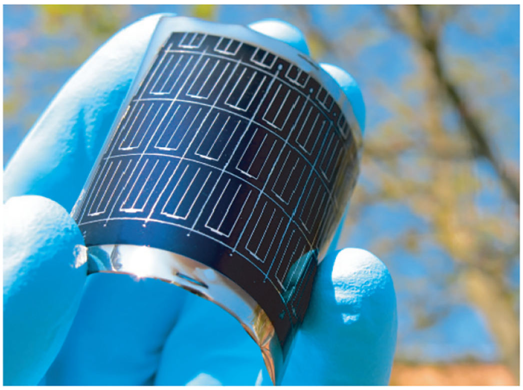
CIGS cell efficiency and stability are comparable to Si solar cells. Recently, Tiwari group (EMPA Switzerland) reported a record efficiency of 20.4% on flexible polymer foil (23% in glass), independently confirmed by Fraunhofer Institute for Solar Energy Systems Freiburg [5,6]. Recently, the same group reported an efficiency of 20.8% using low temperature processing of 450 °C [7]. Similar to CIGS absorber, CdTe is also an excellent absorber material for thin film solar cells due to its ideal bandgap of ~1.5 eV. Close-spaced sublimation (CSS) technique is used to deposit CdTe films to obtain large grains and high growth rate. On polymer and steel foils, CdTe cell efficiency is reported to be 13.8% and 10.9% respectively [8]. On flexible willow glass substrate, 16.4% efficiency (22.1% on rigid glass by First Solar) has been reported [9]. Unlike CIGS and CdTe, a-Si:H is a disordered material, however, its absorption co-efficient ($10^5$/cm) in the visible region of the solar spectrum is similar to CIGS and CdTe. This is due to disorder in the a-Si:H film and relaxation rule in the momentum conservation [10]. Flexible a-Si:H solar cells are fabricated either by direct deposition onto plastic substrates or by a transfer method (i.e. high temperature deposition on a template and then transfer to a plastic substrate) using Helianthos concept. To obtain a dense and homogeneous film by plasma enhanced chemical vapor deposition (PECVD, RF 13.56 MHz) [10], a low deposition rate of 0.1–0.5 nm/sec is used. Hot wire chemical vapor deposition (HWCVD) is used for high deposition rate and device quality films. For a-Si:H solar cells, stabilized efficiency of 7.1% [11] and above 10% have been reported on flexible glass and rigid substrates.

The aim of this paper is to review recent developments in flexible CIGS, CdTe and a-Si:H solar cells due to their increasing importance. Existing issues to be solved are discussed and methods to further improve the cell performance are suggested. Future prospects of these flexible solar cells are outlined. In this review, merits of flexible solar cells are presented in Section 2.0. Flexible CIGS solar cells are reviewed in Section 3, while CdTe and a-Si:H solar cells are reviewed in Section 4 and Section 5 respectively. These three types are compared and its applications are presented in Section 6. Summary and conclusions are given in Section 7.

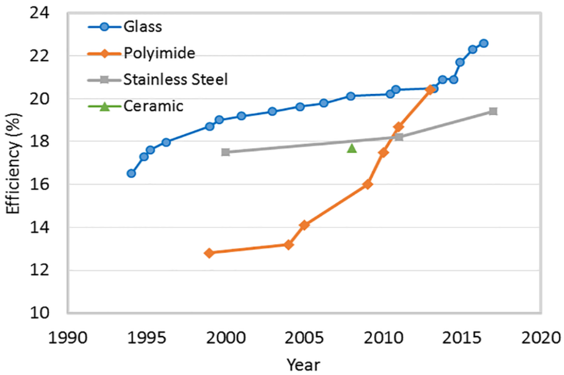
## 2. Merits of flexible solar cells

The performance of flexible solar cells is comparable to rigid substrates. Flexible substrates are more advantageous than standard soda-lime glass (SLG) substrates. As mentioned below, there are several merits of using flexible substrates:

- Flexible modules are best suited for curved surfaces and used in BIPV. Since modules are produced from thin film materials it is suitable for mass production.
- An important benefit is that it has potential to reduce the production cost. R2R deposition is beneficial in terms of production cost than that of rigid substrates. Glass cover is an added expense when rigid substrates are used.
- Materials required to produce CIGS, CdTe and a-Si:H flexible modules are much cheaper than conventional Si wafer, glass cover, frames used in Si modules.
- For roof top application, flexible modules are ideal due to light weight. Using lightweight support, it can be installed over the roof top where glass covered conventional heavy and bulky Si modules are not suitable when roof test fails due to an added weight and structural issues. Flexible modules can also be installed over the roof of the vehicle, uneven surfaces of building.
- Installation/labor cost is much lower for flexible modules due to less installation time since racking assembly, glass cover etc. are not required.
- Low power output flexible modules for example a-Si:H require large number of modules to get desired output which can be installed easily above the roof top.
- Glass covered rigid modules are fragile. Flexible modules are not fragile it can be rolled up, transported and handled easily.



(a)




(b)

**Fig. 1.** (a) Photograph showing flexibility of a CIGS device on polyimide with scribed individual cells. Typical structure consists of substrate/Mo/CIGS/CdS/i-ZnO/Al-ZnO/$MgF_2$, where the notations have their usual meanings. $MgF_2$ is used to minimize reflection losses. (b) Timeline of record efficiency of CIGS for various substrate types. CIGS on glass substrates (blue circles) have led the efficiency records with a brief exception in 2013. CIGS on polyimide made significant gains between 2005 and 2013. The scarcity of SS and ceramic records reflects less research. Fig. 1(a) reproduced with permission from [12]. Permission granted (No. 4243861044867). Copyright © 2017 Macmillan Publishers Limited. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 3. Flexible CIGS solar cells

The future of solar cells has often been envisioned to be cost effective R2R manufacturing of flexible thin film solar cells such as CIGS. To date, however, the vast majority of thin film manufacturing has taken place with glass-glass encapsulation as a drop in replacement for Si modules. While the last decade has witnessed extremely rapid growth and progress in the solar industry, the quickly changing environment and rapidly dropping Si module prices created an extremely challenging environment for smaller PV companies and less mature PV technologies which resulted in numerous bankruptcies of thin film aspirants. Nevertheless, CIGS technology and flexible-production know-how has been continuing to progress with reasonable optimism for future growth. The dramatic reduction in CIGS module production costs has increased the importance of balance of systems (BOS) such as module racking, and soft costs such as engineering and installation time which are key areas where light weight flexible CIGS solar cells offer advantages. With the growing size of the photovoltaic market, smaller specialized applications are beginning to become more viable independent markets, including applications for mobile power and building or product integration, which can benefit greatly from flexible thin film options. A photograph of CIGS cell on polyimide is shown in Fig. 1(a) while the efficiency trends for various substrates are shown in Fig. 1(b).

Miasole pivoted from rigid glass-glass to flexible SS based modules in 2016 and flexible thin film tool manufacturers seem to have new momentum in 2017. Despite most CIGS volume comes from rigid glass-glass panels manufactured by Solar Frontier, a handful of companies have been offering increasingly efficient flexible CIGS products. CIGS review is split into six sub-sections, viz. overview of CIGS fabrication and substrates, progress on different substrates, challenges of flexible substrates, commercial status, fabrication issues and stability, and future outlook.

### 3.1. Overview of CIGS fabrication and substrates

CIGS, unlike organic and perovskite solar cells, requires processing at high temperatures (~550 °C) in reactive chalcogen

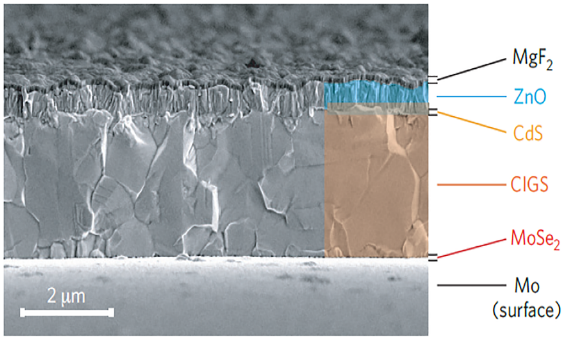



**Fig. 2.** Typical CIGS structure (SLG/Mo/CIGS/CdS/i-ZnO/Al-ZnO/MgF) shown in scanning electron micrograph obtained from a complete CIGS device on polyimide with efficiency greater than 18%. Here, Mo, CdS, ZnO (i-ZnO, Al-ZnO) and MgF stands for molybdenum, cadmium sulfide, intrinsic zinc oxide, aluminum doped ZnO and magnesium fluoride. Reproduced with permission from Ref. [12], Adrian Chirila et al., Highly efficient $Cu(In,Ga)Se_2$ solar cells grown on flexible polymer films, Nature Materials 10 (2011) 857–861. Permission granted (No. 4243861044867). Copyright © 2017 Macmillan Publishers Limited.

environments to form a high quality absorber layer. SLG is one of a limited list of low-cost materials that can tolerate such a high temperature and reactive processing, and it has been a standard substrate for the typical CIGS structure (Fig. 2). The most common material stack consists of SLG/Mo/CIGS/CdS/i-ZnO/Al-ZnO/MgF followed by a nickel (Ni)/Al grid. The film is predominantly deposited from the back contact to front (substrate type) due to the high temperature required for CIGS formation which can destroy the p-n junction interface if the fabrication order is reversed.

The CIGS layer can be either crystallized in a single step during growth with sufficient chalcogen vapor pressure (co-evaporation), or formed by depositing a precursor film (typically a metal stack), which is then reacted by annealing in a sulfur/selenium environment. The numerous vacuum (evaporation, sputtering, etc.) or non-vacuum (solution, nanoparticle) methods are discussed in detail elsewhere [13–15]. Traditionally, the highest efficiency devices have been formed by co-evaporation due to the increased freedom to tailor the film composition and particularly [Ga]/[group III] ratio throughout the film depth. This allows for controlled bandgap grading, which has been found to be critical for high efficiency cells. In recent years, however, Solar Frontier has challenged this orthodoxy and demonstrated a number of record cells (including 22.8% uncertified) [16] using a sputtering and selenization based method. For these record cells, the bandgap grading profile is achieved through multi-step selenization with a final stage using sulfur.

Incorporation of alkali elements, such as sodium, potassium and cesium, is performed to passivate the CIGS layer (among other effects), and has become increasingly common as a post-deposition treatment after the CIGS layer is formed. Sodium incorporation has long been known to be beneficial to CIGS performance [17,18], however, in recent years it has become clear that potassium and heavier alkali elements (cesium and rubidium) are essential to improve the performance beyond 20%. Since potassium was first applied to the record 20.4% cell from EMPA, multiple subsequent efficiency records have been achieved by implementing and optimizing potassium post-deposition treatments. The most recent 22.9% record was enabled by optimizing post-deposition treatments with heavier alkali elements [19]. For flexible cells, the treatments are essential because no Na is provided by the base substrate as is the case with SLG (although it is worth noting that most high efficiency cells on glass, as well as industry, rely on controlled NaF additions and often block diffusion from SLG).

The traditional n-type buffer layer in high-performance research cells is CdS typically deposited by chemical bath deposition, but industry often employs vacuum deposition of Zn(O,S,OH) and or (Zn,Mg)O. This not only reduces the environmental hazards associated with Cd usage but also allows higher current due to more transmission in the range 350–500 nm. Non-CdS buffer layers have been employed with most success by Solar Frontier who has achieved an uncertified efficiency of 22.8% using a Zn-based buffer layer [16,20]. The final layers including an intrinsic ZnO layer and a transparent conductive oxide (TCO, viz. ZnO:Al) are often deposited by sputtering which are followed with Ni/Al grids which can be either screen printed or deposited through vacuum techniques. The intrinsic ZnO is used to prevent shunting paths caused by the diffusion of Al from ZnO:Al into the absorber, and conductive ZnO (i.e. ZnO:Al) is used for the lateral collection of charge carriers into the top current collecting grids [6]. The high temperature annealing or growth step still dictates many of the requirements of the fabrication sequence including substrate choice which are discussed below.

### *3.2. Progress on different substrates*

Cell efficiency and other parameters for recent champion cells for various substrate types are listed in Table 1. The champion cells are fabricated on polyimide and SS substrates [23–25]. On polyimide, high efficiency has been reported to be 20.4% with $V_{oc}$ of 736 mV, $J_{sc}$ of 35.1 mA/cm$^2$ and FF of 78.9%. On SS, the corresponding values are 19.4%, 760 mV, 32.6 mA/cm$^2$ and 79%. For about last two decades, flexible substrates have lagged the efficiency records of CIGS on glass as shown in Fig. 1(b). CIGS on polyimide has historically been only 2/3 the efficiency of glass champion cells, however, in recent years significant progress has been made, and in 2013, flexible polyimide was for a time, more efficient than glass counterparts. The relative frequency of CIGS records on glass and the more spaced timing between polyimide and stainless steel records also reflect the relative research volumes for each substrate.

**Table 1**
Recent record CIGS devices for various substrate types (* uncertified efficiency). Efficiency in glass substrates are given for comparison.

| Substrate | Eff. (%) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | Year | Company/institution | Alkali metals/buffer layer | Ref. |
|---|---|---|---|---|---|---|---|---|
| Glass | 22.9 | 746 | 38.5 | 79.7 | 2018 | Solar Frontier | Cesium | [19] |
| | 22.6 | 741 | 37.8 | 80.6 | 2016 | ZSW | KF + RbF | [21] |
| | 22.8* | 711 | 41.4 | 77.5 | 2016 | Solar Frontier | KF, with (Zn,Mg)O/ Zn(O,S, OH) buffer | [16] |
| | 20.8 | 757 | 35.8 | 79.1 | 2014 | ZSW | KF | [22] |
| Polyimide | 20.4 | 736 | 35.1 | 78.9 | 2013 | EMPA | KF | [23] |
| SS (50 mil) | 19.4* | 760 | 32.6 | 79 | | | | |
| | 19.1 | 750 | 33 | 77 | 2017 | Miasole | KF | [23] |
| SS (25 mil) | 18.7* | 720 | 35 | 74.4 | 2017 | Global Solar | KF | [25] |

CIGS records depicted in Fig. 1(b) have been set by 5 institutions over the last 5 years, while record polyimide devices have been set 7 times by a single institution (EMPA) [23,26]. Similarly, few institutions (EMPA, Miasole and Global Solar) have been intensively optimizing SS substrates and fewer still have been optimizing on flexible ceramics (AIST) or other metal foils which is reflected in the scarcity of record data points. Despite this, back in 2008, Ti foil and flexible ceramics based on Zirconium Oxide ($ZrO_2$) achieved 17.4% and 17.9% respectively suggesting strong efficiency potential for these substrates [27].

As noted by the rapid progress in polyimide in the years between 2005 and 2013, the current state of records does not necessarily reflect technological limitation of each substrate – but rather the current state of optimization. The technical barriers for flexible substrates are not unsolvable. It is likely that today's efficiency gap between flexible substrates (20.8%) and the record 22.9% [7,19] cell can be narrowed significantly by applying recent lessons pioneered on glass such as optimizing heavy alkali earth elements and improving buffer layers. Therefore, the future progress of flexible CIGS is bright.

### *3.3. Challenges of flexible substrates*

As mentioned above, flexible substrate choice include metal foils (most commonly SS), polyimide sheets, and thin flexible ceramics. The default fabrication recipes, optimized around SLG properties, require tweaking for application to flexible substrates.

Flexible CIGS cells allow monolithic integration and offer high output voltage and low production cost. Three requirements of photovoltaic modules are low production cost of cells, high efficiency and easy installation. To fulfill these requirements, flexible substrates should have high thermal stability, thermal expansion co-efficient matching with CIGS for good adhesion, excellent dielectric properties, and no impurity diffusion from substrates. Flexible substrates do not satisfy all these requirements together. For example, Al is an excellent low cost material for thermal stability, however its thermal expansion co-efficient does not match with that of CIGS film [28]. Ceramic foil such as $ZrO_2$ can meet the above requirements, nevertheless due to its high cost and brittle nature it is not suitable for R2R production.

Polyimide substrates, which are attractive due to their light weight, and highly flexible nature, suffer primarily from poor high temperature stability which limits fabrication temperature to around 450 °C. Low temperature fabrication recipes have been attempted for many years but efficiencies have lagged and remained below 15% until 2000 and still below 16% since 2010 [12,29]. The efficiency record for polyimide is 20.4%, obtained by using low temperature three-stage deposition process followed by a sodium fluoride (NaF) and potassium fluoride (KF) post-deposition treatment [23]. In 2019, an improved efficiency of 20.8% has been reported [7]. The co-evaporation process is amenable to low temperature due to minimized elemental diffusion distances which require time and temperature as well as the ability to directly tailor the bandgap and elemental grading through the film depth.

Due to the lack of a Na source inherent in flexible substrates, alkali (NaF, KF, and Rubidium fluoride RbF at $<$ 400 °C) addition – before, during or after the CIGS growth process have been found to be critical to device efficiency [21,30,31].

Unlike polyimide, SS can withstand the high temperatures used for SLG, however, diffusion of impurities (Fe, Ni, Cr) from the steel substrate, particularly Fe, forms deep states in the CIGS absorber and therefore can limit the efficiency [32]. Diffusion barriers have been often used to combat this challenge including the use of Al-oxide ($Al_2O_3$), $Si_3N_4$, Ti-nitride (TiN), nickel phosphorus (NiP) [33], or enameled steel which adds an extra cost, however, tailoring the Mo back contact and reducing fabrication temperature have also been shown to be successful methods to mitigate this problem.

Thermal expansion co-efficient of SS match with that of CIGS film [34]. In 2011, EMPA demonstrated a 17.7% CIGS cell on stainless steel without a diffusion barrier by increasing Mo density and thickness and transferring the low temperature co-evaporation processes used for polyimide [35].

The conductivity of SS or other metallic substrates creates an additional challenge for monolithic integration of multiple cells on a single substrate. For monolithic integration, flexible substrates should have insulating property or an insulating layer must be added between the substrate and Mo back contact in order to allow isolation between cells. This layer often serves dual purpose as the diffusion barrier for impurities. Low cost technique is not available for insulating layer deposition with good insulating properties. As an alternative to monolithic integration, cells can be cut and tabbed or wired, as it is done for Si solar cells. This strategy, while less elegant, provides the advantage that cells can be binned with common efficiency to minimize cell bottlenecks that could be present in a full module.

A final concern for flexible substrates is flexible encapsulation in order to provide a strong environmental barrier for the 20 years

**Table 2**
A list of flexible CIGS companies, past and present.

| Company | CIGS deposition on flexible substrates | Status | Notable results |
|---|---|---|---|
| Miasole (Hanergy) | Sputterig, Stainless steel substrate | Purchased by Hanergy in 2013 | 19.4% cell, ~17% module |
| Global Solar (Hanergy) | Co-evaporation, Stainless steel | Purchased by Hanergy in 2013 | 18.7% cell |
| Flisom | Co-evaporation, Polyimide | Equipment manufacturing partners with EMPA with 20.4% record polyimide | 16.6% small sub-module |
| Midsummer | Sputtering, Stainless steel substrate | Equipment manufacturer with multiple order in 2017 | 18.8% aperture area 6" cell (16.4% total area) |
| Ascent | Sputtering, Polyimide | Purchased by TFG Radiant in 2011, shifted to solar charging market. Currently restructuring loans to continue operations | – |
| Nuvosun (Dow) | Sputtering, Stainless steel substrate | Purchased by Dow – CIGS BIPV roof tile but no longer being manufactured – now licensing silicon based shingle to RGS | – |
| Solarion | Polyimide substrate | Purchased in 2015 – now selling Si modules | – |
| Nanosolar | Nanoparticle ink, Al substrate | Bankrupt 2013 | 17.1% cell |
| Odersun | Sputtering, Cu substrate | Bankrupt 2012 | – |
| Solopower | Electrodeposition, Stainless steel substrate | Bankrupt 2013, minimal operation under name SoloPower Systems | – |

life-span expected for solar cells. More details of flexible CIGS and encapsulation are reviewed in Ref. [26].

### 3.4. Commercial status

CIGS has a long history of research and commercialization. A thorough history and retrospective look at CIGS was recently published [36]. Industrial work on flexible CIGS dates back to ISET in 1992 [26]. However, as previously mentioned, glass substrates have provided a more mature production process, and today the vast majority of CIGS product manufactured has a rigid glass-glass encapsulated structure, a large fraction of which is produced by Solar Frontier (~1GW in 2016) [37].

Average selling price for CIGS PV modules which had been stable at approximately $4/Watt in the years leading up to 2007, plummeted to less than $1/Watt 5 years later, and have continued to decline to less than $0.5/Watt by the end of 2016. Multiple leading manufacturers in the first quarter of 2017 claim production costs [37] of less than $0.40/Watt (excluding BOS and installation charges). Production cost can be lowered further by using flexible substrates.

Today, more than a dozen companies continue to make progress in the CIGS technology, and a number of notable examples are demonstrating the potential of flexible CIGS. An incomplete list of current companies producing flexible solar cells is shown in Table 2. The table also includes notable CIGS companies that have shut down in the last few years. A more complete list and details of industrial CIGS players can be found elsewhere [13,26].

A number of notable flexible CIGS results are worth highlighting. Miasole, which pivoted recently to all stainless steel modules in 2016 reported a record efficiency of 19.4% for a small cell and module aperture area efficiency of ~17% [24]. Global Solar uses a slightly thinner (1 mil) SS substrate has also made significant progress by demonstrating a champion cell of 17.7% in 2016 [38], and 18.7% in 2017 [25]. Finally, Flisom is commercializing equipment to manufacture CIGS on flexible polyimide in collaboration with EMPA.

Although sales volume is a small fraction of Si, with production lines measured in tens of MW, flexible CIGS product maturity and sales volume appear to be growing in recent years. Flexible CIGS tool manufacturers such as Midsummer also showed momentum in selling their R2R CIGS on SS with multiple product orders in 2017. Even Solar Frontier, the leading CIGS manufacturer by volume, demonstrated SS based flexible CIGS panels in 2015.

### 3.5. Fabrication issues and stability

Despite the promises, flexible CIGS creates a number of fabrication issues for manufacturers. Processing conditions established for an acceptable compositional grading profile for CIGS is not easy to maintain during production. When SLG substrates are used, during CIGS deposition, sodium is supplied by the substrate. For flexible substrates, sodium containing film is required prior to back contact (Mo) deposition. Sodium doping in CIGS (~$10^{19}/cm^3$) [39] provides passivation and improves electrical performance and yields high $V_{oc}$ and fill factor. When sodium free substrates (i.e. flexible substrates) are used, accurate level of Na doping in CIGS from sodium containing film is an issue. As a side note, doping level depends on the thickness of sodium containing layer.

When flexible substrates are used, Ga grading in CIGS is steeper than that of rigid (SLG) substrate for similar processing steps. This is due to the variation in indium and Ga diffusion rates [28]. Steeper Ga grading results in narrow band gap CIGS that results in lower $V_{oc}$ and higher $J_{sc}$. Another issue is laser patterning when flexible substrates are used. When the substrates are thin, process integration is critical since laser beam focusing is difficult [39] which increases leakage current in the device. Processing conditions used for thick and SLG substrates cannot be used for flexible substrates.

Beyond the typical issues of producing CIGS at scale, the flexible substrates must withstand the high temperatures and reactive chalcogenide environments used for CIGS fabrication. For polyimide substrates, this places an upper limit on the fabrication temperatures which traditionally have been used to achieve high efficiency. Some metal foils, such as SS can withstand the high temperatures but can be limited by impurity diffusion of elements such as Fe from the substrate into the CIGS layer. A metal foil or conductive substrates in general, are also less advantages to monolithic integration, requiring either an extra insulating layer or an alternative interconnection scheme. Other substrates such as flexible ceramics or flexible glass without such problems have also been explored, however, there remain open questions about substrate cost, and the vast majority of research as well as the history of champion CIGS efficiencies has continued to be on traditional SLG. Due to these issues, the concept of a 20% efficient flexible CIGS module had seemed out of reach until recently. In 2013, EMPA (Switzerland) demonstrated a record efficient CIGS cell on polyimide, surpassing even the glass-based CIGS of the time [23]. This demonstrates that despite processing challenges, bridging the efficiency gap between rigid and flexible cells is feasible.

Mechanical robustness of flexible CIGS cells is affected by stress in the film (internal stress) and stress induced by bending the module. The latter depends on the film thickness, Young's modulus of the substrate and film. Strain in the CIGS film induced by bending (radius 50 mm) test is higher in ultra-thin (100 µm) flexible glass substrates than that of 25 µm thick polyimide substrates. Bending induced degradation of solar cells is irreversible and deterioration is permanent when reset into initial state [40]. More deterioration was noticed in the most bent region, mainly due to a slight increase in series resistance which decreases fill factor, $V_{oc}$, $J_{sc}$. Degradation can be lowered by using substrates having low thickness and Young's modulus.

Metal foil is used for high mechanical and thermal stability ($>$ 600 °C) [41]. However, it requires diffusion barrier as mentioned as above. Commercial metal sheet contain deep grooves, spikes and cavities over the surface since foils are rolled up during manufacturing, and undergo bending. To improve mechanical robustness of the device, foils are polished or a layer is coated to level the foil. A good mechanical stability has been reported for flexible CIGS cells [12].

Bending induces stress in the module leads to cracks or delamination. A strong adhesion between back contact (Mo) and CIGS is required to avoid stress [29]. During high temperature ($>$ 450 °C) deposition of CIGS film, thermal expansion co-efficient (heat expansion) of flexible glass should be close to that of CIGS film. Otherwise adhesion issues and cracks can occur. For ultra-thin glass, Mo and CIGS, TEC is around 5-12 $\times$ $10^{-6}$/K [29,40].

In flexible cell, unbearable external loads during the operation can produce internal stress leading to cracks and interface layers split apart [42]. For flexible CIGS cell, a tolerable limit for compressive stress without cracks is around 70 MPa [43].

Long term environmental stability is one of the main factors for commercialization. CIGS films are tolerant against high energy radiation. Unlike other technologies like perovskite solar cells, CIGS stability is not an issue. However, one of the main concerns is the protection from environment and flexible encapsulation with a life-span of 20 years.

### 3.6. Future outlook

CIGS solar cells offer the highest efficiency and mature flexible solar cells for mainstream applications. The efficiency outmatches alternatives such as dye-sensitized solar cells and organic solar cells, and unlike perovskites, stability is not an obstacle, and toxicity concerns are minor or surmountable. In fact, flexible CIGS modules shipping today now rival the efficiency of multi-crystalline Si solar cells. It is not yet clear whether the future of flexible CIGS will stay positioned in niches where flexibility is integral to the product, or it will vie for larger portion of the solar market. The past decade, which has been competitive for solar cell manufacturers have left a stronger group of pioneers that may give flexible CIGS a tough chance.

## 4. Flexible CdTe solar cells

Among thin films, CdTe has demonstrated the highest scalability and reproducibility so far, as reported by the successful industrial production within the last 10 years. The high absorption coefficient allows producing high efficient devices also with ultra-thin absorbers, values exceeding 10% have been obtained with thickness below 1 µm [44,45] and around 10% for only 0.5 µm [46]. The CdTe thickness reduction could be a crucial point for increasing efficiency and stability of flexible devices. Both rigid and flexible CdTe solar cells perform best when made in superstrate configuration, and this happens mainly for two reasons:

(i) The special process required with the so-called "activation treatment" where typically a Cd chloride ($CdCl_2$) thin layer is deposited on top of the CdTe and then the stack is annealed in air [47,48]. The activation treatment acts as a step for increasing the electrical properties of the absorber and for improving the junction between CdS and CdTe [49]. So if it is made after CdTe deposition on CdS, the performance is higher.
(ii) The back contact generally requires an addition of Cu for high performance. In substrate configuration Cu is deposited on the back of the solar cell, and during CdTe deposition (with high substrate temperature) Cu reacts with CdTe film, which causes degradation in the film [50–52].

Recent studies at EMPA have shown that in substrate configuration it is possible to reduce these limitations by depositing a Cu-

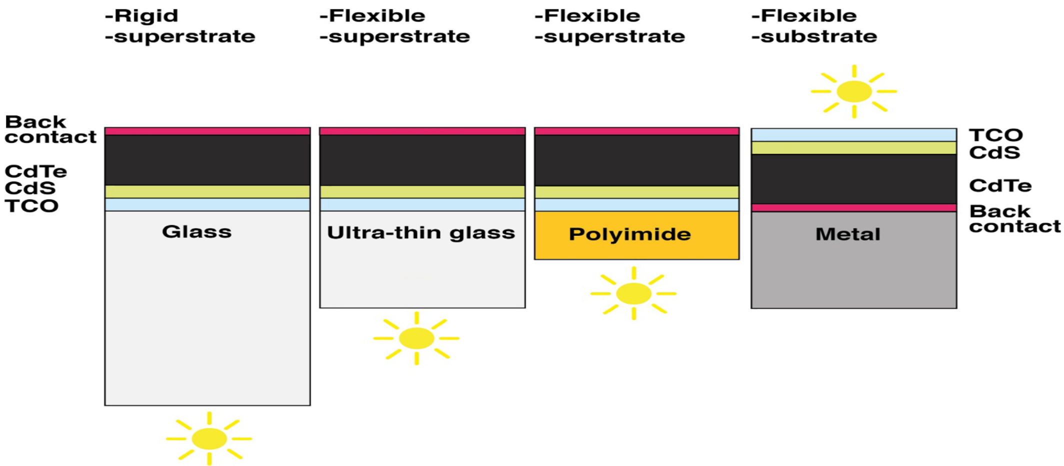



**Fig. 3.** Schematic of superstrate and substrate CdTe devices (the substrates' width is not proportional but indicative of the differences between the devices). Both in substrate and superstrate configurations, light enters through wide bandgap window material (CdS). In the substrate structure, opaque substrates are used, CdS need not undergo high temperature processing.

free back contact, namely $MoO_x$, followed by CdTe and an ultra-thin Cu layer on CdTe; moreover, $CdCl_2$ is applied before and after CdS deposition. Cu diffusion into CdTe is performed at around 400 °C. A record efficiency for CdTe substrate cells of 13.6% has been obtained [53]. In this way, the temperature and time of annealing strictly control Cu diffusion. On the other hand, if Cu is deposited prior to CdTe deposition, this diffusion will depend on external parameters since the time at which the Cu is kept at high temperature is depending on the CdTe deposition rate.

The $CdCl_2$ treatment promotes recrystallization of the CdTe and enhances grains growth. It also improves the CdTe/CdS junction properties by enhancing inter-diffusion of sulphur into the CdTe and reducing the lattice mismatch between the two layers. So the treatment has a double purpose, which makes it necessary to be used after the CdTe deposition. When CdTe is deposited in substrate configuration, $CdCl_2$ has to be applied two times, a first time before and a second time after CdS deposition [53,54].

CdTe solar cells in superstrate configuration have reached the superior efficiency of 22.1%, reported by First Solar Inc. So superstrate configuration is still preferable also for flexible devices. On the other hand, this requires special substrates that have to fulfill transparency and flexibility requirements at the same time. Various configurations of CdTe solar cells are shown in Fig. 3.

It is also very important to mention two additional improvements that have been done recently to increase efficiency that are the CdS substitution with a more transparent buffer layer, (i) magnesium zinc oxide is a very good solution [55] and (ii) $CdSe_xTe_{1-x}$ intermediate layer for band gap grading [56–58].

### *4.1. State of the art: Fabrication methods and issues*

The paths for fabricating efficient CdTe solar cells have been divided into two main cases: (i) To optimize a fabrication process for substrate configuration CdTe solar cells by using a non-transparent substrate such as metal-based or polymer-based layers, and (ii) To fabricate and optimize a flexible CdTe cells on transparent substrate capable of withstanding high process temperatures. In Fig. 4, CdTe cells on rigid glass, flexible cells on ultra-thin glass (such as willow glass) and polyimide substrate are shown.

#### *4.1.1. Substrate configuration cells*

In the case (i) mentioned above, the most commonly used substrates are Mo or thick polyimide (for example Kapton®). In any case

**Fig. 4.** From left to right: CdTe cells on glass, ultra-thin glass and polyimide made at the laboratory for photovoltaic and solid state physics, University of Verona. The cells on polyimide are more flexible than the cells deposited on ultra-thin glass. However, polymer results in a reduced transparency compared to ultra-thin glass, as it is clearly visible in the picture.

best working devices have been fabricated using Mo as back contact, either deposited on a Kapton® or a Mo sheet.

Mo allows a superior stability on the subsequent depositions, and at the same time, it is a good conductive metal for electrical contact. However, it does not have high enough work function for providing a good Ohmic contact. On the contrary, a small energy barrier is formed if pure Mo is contacted with CdTe. This has been proved by Williams et al. [54], where a barrier height of 0.51 eV has been reported. In order to overcome or at least limit this barrier issue, the following two steps can be introduced:

- Deposition of an interfacial layer with high work function between Mo and CdTe.
- Increase CdTe doping on the backside (close to back contact) of the CdTe layer.

Dhere et al. have studied different interfacial layer for CdTe substrate configuration devices, where CdTe is deposited by CSS at high substrate temperatures [59]. A $Cu_xTe$ layer is deposited on top of Mo prior to the CdTe deposition, this might not only improve the back contact performance but also enhances CdTe doping by forming a $p^+$ zone near the back contact. In Ref. [60], it has been shown that $MoO_x$ deposited by RF sputtering from a compound semiconductor target allows a good performing device with suitable back contact. However two more steps are crucial for a good substrate type solar cell:

- Double $CdCl_2$ annealing (on the CdTe and CdS/CdTe junction)
- CdTe doping

Kranz et al. have brilliantly solved these issues by applying $CdCl_2$ treatment after CdTe deposition and after CdS deposition, moreover CdTe have been doped by depositing a monolayer of Cu on the CdTe/$MoO_x$/Mo stack and annealing [53]. In this way, a record efficiency for substrate cells of 12.6% on glass substrate [53] has been obtained.

#### *4.1.2. Superstrate configuration cells on flexible and transparent substrates*

In the case (ii), the main possibility for producing flexible CdTe-based devices is to maintain the most productive superstrate configuration and study an innovative highly temperature resistant substrate, which is at the same time transparent enough to allow UV/visible radiation to be absorbed by the CdTe layer. In order to fabricate a superstrate solar cell, the substrate has to be stable under the different processes that are applied for the device fabrication. The substrate has to withstand in the process sequence: TCO deposition, CdS and CdTe deposition, $CdCl_2$ activation treatment, back contact deposition and annealing. In particular for high efficiency cells, CdTe is deposited by high substrate temperature processes such as CSS or vapor transport deposition. For above 500 °C, it is extremely difficult to find a suitable substrate. For this reason, historically, using low temperature CdTe process [2], the first superstrate type CdTe solar cells have been made on a soft polyimide foil.

Different polymers can be used for cell fabrication but the best ones are Upilex-S by UBE and CPI (Crystal Clear) Kapton® by Du Pont [61,62]. The latter performs a remarkable transparency also at the low wavelength region allowing higher photocurrents. However, the processing temperature cannot go over 450 °C, so the most used technique is thermal evaporation. The best efficiency of 13.8% has been reached so far by thermal evaporation of CdS and CdTe on a ZnO:Al/ZnO stack [62].

More recently, a new type of substrate has been available, which overcomes the limitations of polymers - a flexible glass, with a thickness of 100 µm. In this case, an alkali free glass with a thickness of 100 µm becomes perfectly flexible, but at the same time remains stable under high temperatures and chemical treatments.

Solar cells based on flexible glass can be typically prepared with high substrate temperature processes. The first introduction of ultra-thin flexible Corning glass for CdTe devices has been made by Rance et al. [64]. The devices were made by CSS at temperatures above 600 °C, after $CdCl_2$ vapor treatment and deposition of ZnTe:Cu back contact, a record efficiency of 14.05% was obtained. This value has been overcome by researchers from the same group, by the application of a sputtered CdS:O instead of the prior chemical bath deposited CdS, gaining in transparency which resulted in a higher response in the blue light region with a higher efficiency of 16.4% [9]. A summary of the best efficiencies for CdTe flexible solar cells is presented in Table 3.

### *4.2. Issues in flexible CdTe solar cells*

Solar modules require long-term stability (~20 years). This is even a more important issue when it comes to flexible devices where there must be no change in efficiency as the module is being flexed. Stability and fabrication issues are discussed below.

#### *4.2.1. Stability issues*

CdTe solar cells, whether built in superstrate or in substrate configuration, have to perform long-term stability. Generally CdTe is

**Table 3**
Best efficiencies of flexible CdTe solar cells.

| Structure | Substrate | Lab | Substrate T (°C) | Eff. (%) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm$^2$) | FF (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| Superstrate | Flex glass | NREL | > 550 | 16.4% | 831 | 25.5 | 77.4 | [9] |
| | PI film | EMPA | < 450 | 13.6% | 846 | 22.3 | 73.4 | [63] |
| Substrate | Mo foil | EMPA | < 450 | 11.5% | 821 | 21.8 | 63.9 | [53] |

a very robust and stable material and no particular problems have been addressed for stability when suitable encapsulation against moisture is applied. In earlier times an age-old issue of performance stability was due to copper diffusion. However this has been practically solved by strongly reducing the copper amount, and by adding a copper barrier at the back contact, such as ZnTe that acts as a barrier to Cu [65] as also previously mentioned. Other solutions to this problem also have been introduced such as a barrier or $As_2Te_3$ [66] or the incorporation of copper in the form of a chlorine salt [67], which allows introducing an extremely low amount of copper by combining it with the CdTe back surface. However now CdTe based solar cells on glass have demonstrated an optimal stability for long time performance as also demonstrated by the large module production.

For flexible solar cells, new issues have to be considered in terms of stability. The bending and stretching of the module should not affect the performance of the device. Only few reports are available for the stability of flexible devices. Rance et al. show a study of the effects of tensile and compressive stresses for flexible cells on ultra-thin glass [64]. The cells were fastened with PVC tubes in order to be able to bend them. Different curvatures were experimented and tested and the resulting efficiencies were measured. Analogous data for cells on polymers were not reported, however, the change in efficiencies (in some cases efficiency increases when cells are bended) are not attributed to the type of substrate but to the stress in the CdTe itself, so similar results would be expected for the cells on polymer substrates [64].

Tensile and compressive stresses have been measured by applying Raman spectroscopy on CdTe devices deposited on both polyimides (CPI and Upilex-S) and ultra-thin glass (Schott) based substrates [68]. The data obtained are coherent with the results reported by Rance et al. [64], and the conclusions are that polyimide substrates give a higher distortion to the CdTe layer compared to ultra-thin flexible glass. Rigid glass and ultra-thin glass have very similar thermal expansion coefficients.

Moreover, in the case of cells having polyimide substrates, a very important issue is the stability of the substrate to ultra-violet (UV) radiation. In this case, an anti-UV coating has to be deposited on the other side of the substrate.

#### *4.2.2. Module structure fabrication challenges*

Polyimide based cells require an optimization of laser scribing technique to avoid substrate damage. A specific analysis for interconnection of polyimide based CdTe mini-modules has been presented in Ref. [62], where they demonstrated the possibility of using a conventional laser scribing technique for the fabrication of a mini-module with 9.4% efficiency on 31.9 $cm^2$ active area (i.e. area not covered by the grid lines), confirming the feasibility of flexible CdTe module production even with polymer substrates.

In terms of ultra-thin glass no issues on the laser scribing process occur, and a very similar approach to the rigid substrate can be used. So with a smart management of the in-line production on thin glass (breaking of the substrate has to be avoided), especially in terms of avoiding temperature shocks by designing proper temperature ramps, fabrication of flexible modules on ultra-thin glass would just use the same technology which is already widely applied in mass production.

On the other hand, for both polyimide and thin glass based cells, a crucial point in terms of scalability is the possibility of a R2R production that would allow high feasibility for large scale fabrication. For this reason, again it is important that bending of the stack should not affect the performance of the cells. We have already demonstrated in the above section that no particular problems occur for ultra-thin glass, while for polymers some larger tensile stresses might affect the initial efficiency.

Moreover, while ultra-thin glass allows the same transparency as a solid device, for polymers the absorption at low wavelength regions is not negligible. Most of the polymers (such as Kapton® and UBE-Upilex S) require an extremely reduced thickness, typically 7.5 µm [62,68]. On the other hand, improved Kapton® polymers such as CPI show a superior transparency and are rather independent from the thickness [63].

### *4.3. Future developments*

Contrarily to other thin film materials, CdTe solar cells have come to large mass production, for the moment concentrated mainly on one company. The simple stoichiometry and high reproducibility reduce problems with inhomogeneity, which are more frequent for other high efficiency thin film solar cells. However, the large mass production of Si wafers has put production costs of thin film modules just at the same level of Si modules.

Actually thin films have a higher potential for cost reduction if we can take the advantage of their ability to adapt to different shapes. This will allow integrating and substituting conventional roofs with energy producing roofs.

Application of CdTe to new substrates must be studied since CdTe is an extremely simple material to be grown and it is not affected by the different substrates, has reduced issues in inhomogeneity for large scale, it has a large potential of mass production in flexible configuration.

Superstrate devices are the easiest to be fabricated, they would be optimal for windows and flexible glass while substrate devices would be preferred on tiles and ceramic substrates. Improvements for flexible CdTe photovoltaic devices in substrate configuration should include:

- Development of innovative substrates that can be combined with materials for buildings.
- Introduction of new buffer layers to protect devices from impurity diffusion from the substrate.
- Application of new back contacts in order to have efficiency improvement and stability to the subsequent deposition processes.
- Implementation of improved doping techniques in order to enhance electrical properties.

Improvements for flexible CdTe photovoltaic devices in superstrate configuration should include:

- Development of low-cost ultra-thin glass and polymer substrates.
- Application of UV protection layer for polymer films.

In both configurations a thorough study of degradation and stability during bending of the cells would be required.

## 5. Flexible a-Si:H solar cells

The success of a-Si:H thin film materials is based on the high throughput and large area deposition processes for solar cells and display technology applications. Though several types of inorganic thin films (GaAs, CIGS, CdTe, etc.) have been reported [69], a-Si:H type of cells has shown the widest range of products among inorganic thin films, e.g., a-Si:H solar modules on glass substrate of 5.7 $m^2$ size or long rollable flexible substrates. This is possible due to the CVD deposition processes, especially the very high frequency (VHF) PECVD that allows an easy scaling up or movable substrate of large dimensions and long depositions without down time. The deposition on flexible substrates is especially notable, ranging from metals (SS, Al) to high temperature plastics (polyimide or Kapton®) to low temperature or temperature sensitive plastics such as polycarbonate (PC), polyethersulfone (PES), PET, PEN and papers (cellulose papers, bank notes and security papers). Depending on the transparency of the substrate, substrate type (n-i-p) and superstrate type (p-i-n) cells are made. Direct fabrication with n-i-p configuration is made on metal foils, high temperature plastics (polyimide or Kapton®), or any opaque materials like tiles, paper etc., whereas low temperature plastics (PC, PET, PEN) and even thin flexible glass mostly use p-i-n configuration. A lift-off technique (transfer type) however can be used on any type of substrates. The status of flexible a-Si:H solar cells, and their long term potential as energy source are reviewed below.

### 5.1. Flexible substrates: Metal foils, plastics, papers and flexible glass

As mentioned above, flexible cells are mainly categorized into two types based on the type of substrate: (i) metal foils and (ii) plastics and papers. A third category, based on thin glass is also worth noting. A review on them is presented below.

#### 5.1.1. Metal foils

Both SS and Al foils have been used for a-Si:H solar cells. The former is well established commercially, especially by United Solar Ovonic (ECD) known as Uni-Solar. One of the main disadvantages of these types of cells is the difficulty in making monolithic integration that is hampered by an opaque, in addition, a conducting substrate. Substrate type single junction a-Si:H, double junction a-Si:H/a-SiGe:H and triple junctions a-Si:H/a-SiGe:H/a-SiGe:H, a-Si:H/a-SiGe:H/nc-Si:H and a-Si:H/nc-Si:H/nc-Si:H solar cells with PECVD deposition of semiconductor layers have been reported. The SS foil needs a planarization step to mitigate the effect of spikes or protruding features. One of the ways is to use UV lacquer that serves two additional purposes: (i) the electrically insulating layer on steel foil enables monolithic series interconnection [70], (ii) nanoimprint lithography can be done to enhance light scattering effect [71]. Anodization and nanoprint lithography have emerged as two main techniques for fabricating textured surfaces. Al substrate allows texturization by anodization [72] and nanopatterned plasmonic textures can be made [73]. R2R anodized electrodeposited Ni-Fe foil based a-Si:H cells are also used for water splitting [74]. Nanodent texture by anodization of Ti foil is another option [75].

#### 5.1.2. Plastics and papers

There are basically two types of substrates: expensive plastic substrates for high temperature processing and low-cost temperature sensitive substrates for flexible a-Si:H solar cells. These two types are mainly distinguished by their glass transition temperature ($T_g$). Fabrication on these substrates are reviewed and presented below.

**(a) High temperature resistance substrates**: These expensive plastics whose $T_g$ is higher than that of the thin film Si materials allow the semiconductor layers to be deposited at their optimum temperature condition (~200 °C). These plastics also show tolerance to other layers depositions (silver, TCO, etc.). Polyimide (Kapton® from DuPont) has been extensively used, though commercially is not very attractive due to high cost. Powerfilm (Iowa thin film) and Fuji Electric make such modules. For these opaque substrates, the monolithic series integration by R2R processed "series connection through apertures formed on film" (SCAF) structure was used by Fuji electric. An efficiency of ~12% for a-Si:H/nc-Si:H solar cell in n-i-p configuration has been achieved.

**(b) Low-cost substrates**: In these temperature sensitive substrates, their $T_g$ is well below the $T_g$ of the Si layers. PEN, PET, PC, PES and various types of "papers" are in this category. These substrates have received lots of interest, as they not only have the potential to reduce the cost, but also some of them allow to fabricate the device in superstrate configuration, which has definite advantages as far as monolith integration for module manufacturing is concerned. This type of substrates poses challange to fabricate the semiconducting (Si intrinsic and doped) layers and the textured front TCO on them for superstrate type cells or textured back reflector in substrate type cells, which are made optimally at temperatures much higher than the substrate deformation. Laser scribing also poses difficulties, as the temperature can shoot up locally. Moreover, the post fabrication annealing and lamination are serious issues. Hence, two methods are followed to address these issues. The first is the fabrication of complete cell on a temperature resistant temporary (sacrificial) substrate, thus, the layers are deposited at their optimum growth temperature, and then transferred to a permanent substrate, and the second is to find deposition parameter space to grow layers at temperatures below 150 °C. These two cases are discussed below.

**(i) Transfer type (lift-off) process**: There are various transfer methods developed for all sorts of inorganic type flexible solar cells [76]. Helianthos concept is the best example of this type for a-Si:H cells. An a-Si:H cell is made on a metal (kitchen Al) foil with the following sequence: deposition of textured TCO (Fluorine-doped tin oxide, FTO) at 400–500 °C by atmospheric pressure chemical vapor deposition (APCVD) using tin tetrachloride as precursor, a-Si:H p-i-n layers at 150–200 °C by PECVD, TCO (ZnO:Al) by PVD (magnetron sputtering), Ag metal contact by PVD (evaporation or sputtering), laser scribing, and then attach it to a permanent substrate (PET), followed by removal of Al foil by sodium hydroxide, lamination of the front side and the backside with low water vapor transmission rate (WVTR) polymer encapsulant. The whole process is done in R2R production of PVD and PECVD machines. This method of p-i-n processing is extended to a-Si:H/nc-Si:H tandem cell. Akzo-Nobel along with Utrecht University invented this cell processing, for which subsequently TUD, TUE, ECN and TNO from Netherlands and FZ Juelich from Germany contributed significantly to develop to module stage. In the standard PECVD process, 35 cm width foil is used by the industry for the pilot module production and for commercialization further development is needed. As the belt size in R2R process depends on deposition rate, a high rate deposition process is desirable, especially for the tandem cell manufacturing that needs a thick nc-Si:H (~1500 nm) bottom cell. VHF PECVD was explored to this end and an efficiency of 7.9% for single junction and 8.1% for a-Si:H/nc-Si:H tandem cell were reported, very similar efficiencies as compared to the standard RF PECVD. The whole tandem cell in a batch process is completed within 30 min, including the time consuming deposiotion of doped layers. Once applied to R2R, the tandem cell fabrication with a reasonable belt size can be accomplished using VHF PECVD. The second development has to be the width of the foil that needs an upgradation of the R2R machine design. Tests have been made on 140 cm width foils. Module production with large width foils by Hyet Solar by this technique is expected in the near future that would increase the power per module. Other lift-off or peel-and-stick methods for a-Si:H solar cells use glass as temporary substrate [77], colloidal transfer-printing method [78] and water-assisted transfer printing [76]. The latter method showed an efficiency of ~7% for a-Si:H single junction.

**(ii) Low temperature process**: There are two areas where adaptation to the conventional fabrication process of a-Si:H solar cell is done. The first is the textured front (superstrate cell) or back (substrate cell) surfaces. Normally these textured surfaces are made at high temperatures. In the substrate type cell, natural texture in Ag is achieved with depositions at > 300 °C. Whereas in the superstrate cell, natural texturing is achieved in TCO (Fluorine doped tin oxide $SnO_2$:F) with depositions at > 400 °C. There are two solutions to avoid high temperature processing: (i) Textured substrate - hot-embossing is a very effective technique, though nanolithography and holographic gratings are also used, especially useful for paper substrate. The latter two are also explored for high temperature resistant substrates, not necessarily only for low temperature plastics. The highest efficiency of a-Si:H cell on PEN type substrates was achieved by nanolithography at EPFL; (ii) Textured TCO – post-deposition texturization is performed on TCO. For example, Al (also boron, Ga) doped TCO (ZnO) is texture-etched to create inverse pyramidal crater type surface using diluted (~1%) HCl etching. This type of textured TCO is also used routinely on glass and other high temperature substrates. Here, the ZnO is deposited at room temperature by magnetron sputtering (due to particle bombardment, actual substrate temperature reaches 100 °C during the deposition period). In a typical substrate type cell, 1000 nm ZnO is deposited by sputtering, followed by texture-etching using HCl, then deposition of ~100 nm Ag, ~100 nm ZnO:Al, followed by the n-i-p a-Si:H cell and top contact (Fig. 5). For a superstrate cell, the fabrication is more simple, deposition of 1000 nm of ZnO:Al, followed by texture-etching, then the p-i-n cell and back contact. An issue with employing a thick TCO layer is that it adds high stress (typically compressive) that forces the foil to curl and it creates cracks in TCO and cell. Symmetric deposition of thick layers on both sides of substrate, followed by texture etching on one side for cell fabrication is one of the solutions. Additional precautions to protect the moisture sensitive ZnO, such as barrier layer between plastic and ZnO (e.g. $ZnSnO_x$) [79], or H/Ar treatment on ZnO [80] are essential.

**(c) Paper substrate**: It is a very attractive proposition for low power niche application. Among papers, cellulose type papers are best suited for a-Si:H solar cell fabrication, as the paper material degrades at temperatures only above 250 °C. For one type of cellulose paper (FS-2 paper substrates made by Felix Schoeller Group), it has been shown that planarization by a hydrophilic mesoporous material that mitigates the macro rough fibrous surface and enhances the wetting property and sticking of back metal contact is very useful and an efficiency of 3.4% is obtained for a-Si:H cell with n-i-p configuration [81]. Adding textured back reflector on FS-2 paper through UV nanoimprint lithography, the efficiency of a-Si:H cell was enhanced to 5.5% [82]. An interesting result is solar cell on plain white copying paper (80 g/$m^2$) used in office copying machines. The commodity paper was first planarized

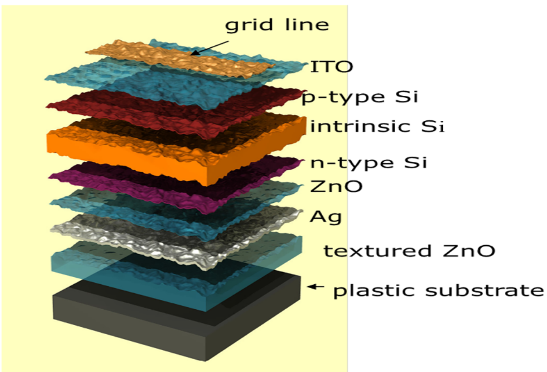



**Fig. 5.** Structure of a typical a-Si:H substrate type cell on plastic foil. For PET, PEN, PC type substrates all the processing is done below 130 °C. Symmetric ZnO:Al layers on both sides of the plastic foil is applied to minimize curling/stress. The p-type layer is a protocrystalline material made from high hydrogen dilution of silane gas. The n-type layer is a double layer of phosphous doped a-Si:H/nc-Si:H. Ag is used for grid lines. The intrinsic layer is a-Si:H made from hydrogen diluted silane. All silicon layers are made by VHF PECVD in a multi-chamber.

**Table 4**
Efficiency of some prominent a-Si:H based cells on flexible foil (T transfer method, *stabilized, # measured under AM0 light condition for space application).

| Cell type | Substrate | Source | Eff. (%) |
|---|---|---|---|
| p-i-n (a-Si:H) T | Polyester | Univ. Utrecht/Nuon, Netherlands | 7.7 [84] |
| p-i-n (a-Si:H) | PC 130 °C | University Utrecht | 7.4 [85] |
| p-i-n (a-Si:H) | PS | Aarhus University, Denmark | 9.5 [86] |
| n-i-p (a-Si:H) | PEN 150 °C | IMT, (EPFL) Switzerland | 8.7 [87] |
| n-i-p (a-Si:H) | E/TD 150 °C | AIST, Japan | 6 [88] |
| n-i-p (a-Si:H) | PET 100 °C | Univ. Utrecht, Netherlands | 5.9 [89] |
| n-i-p (nc-Si:H) | LCP 150 °C | AIST, Japan | 8.1 [90] |
| p-i-n (a-Si:H/nc-Si:H) T | Polyester | Helianthos (Hyet Solar) | 9.4* [91] |
| n-i-p (a-Si:H/nc-Si:H) | PEN | IMT, (EPFL) Switzerland | 11.2 (9.8*) [92] |
| n-i-p (a-Si:H/a-SiGe:H) | Kapton® | Fuji Electric, Japan | 10.1 (9*) [93] |
| n-i-p (a-Si:H/a-SiGe:H/nc-Si:H) | SS | Uni-Solar, USA | 16.3 [94] |
| n-i-p (a-Si:H/a-SiGe:H/a-SiGe:H) | SS | Uni-Solar, USA | 13* [95] |
| n-i-p (a-Si:H/a-SiGe:H/a-SiGe:H) | Polymer | Uni-Solar, US | 9* [96] |

by UV curable acrylate lacquer (MO18), followed by another layer of the same lacquer that was imprinted with a periodic nano-texture. An n-i-p a-Si:H cell made by HWCVD (at 200 °C!) on this substrate delivered 6.7% efficiency, almost the same efficiency as on SS [83].

**(d) Flexible Glass**: An extremely thin (~100 µm) glass acts as a flexible foil. The advantage of this type of substrate is the excellent encapsulation property with ultra-low WVTR, which is impossible to achieve with any of the previous two types (metal foils and plastics) of substrates. Moreover, possibility of superstrate type cell fabrication, easier monolithic integration, optimal temperature processing, high light transmission of the substrate, and light weight etc. are the definite plus points. The main drawback is that these substrates, though bendable, are not rollable and restricted in the extent of bending. Substrate handling without breakage is also an issue and this poses questions on the up- scaling of the device. Nevertheless, initial results on small area devices on FTO coated 100 µm thin glass show an encouraging efficiency (6.95% for a-Si:H and 9.3% for a-Si:H/µc-Si:H cell) [11]. The efficiency of a-Si:H solar cells on various flexible substrates are given in Table 4.

### 5.2. Encapsulation

One of the biggest issues facing plastic substrate based solar cells is the high WVTR and gas permeation (~1 $g/m^2$/day), which is not the case with solar cells on glass substrates where the cell is protected on both sides by a very low WVTR of around $10^{-12}$ $g/m^2$/day. The flexible cells based on SS have this advantage only on the back side (metal), whereas the top side still needs to be encapsulated with transparent layer with low WVTR. Moreover, they have to protect the plastic from UV and in addition to being themselves UV resistant. Normally polymer encapsulation, such as DuPont™ Tedlar® polyvinyl fluoride films as back sheet and DuPont™ Teflon® ETFE or Teflon® FEP films (fluoropolymer Tefzel) front sheet, along with DuPont "Elvax" EVA resin encapsulant, is used, which makes the module very expensive. On the other hand, stability of the module on plastic substrates cannot be promised for a long warranty period (> 10 year), making the levelized cost of electricity (LCOE) price too high. Organic/inorganic multilayer structure can be used to address this issue.

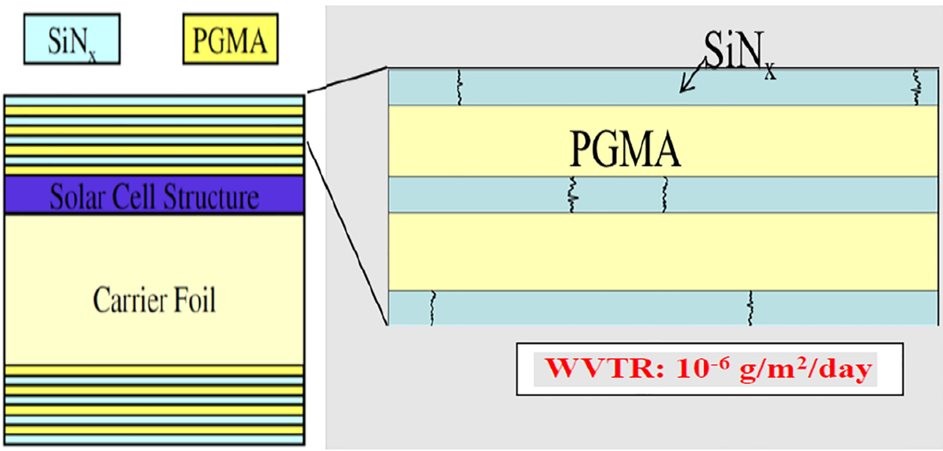



**Fig. 6.** Moisture impermeable encapsulation scheme for a-Si:H solar cells on foils. Amorphous $SiN_x$ is made by HWCVD, PGMA is made by i-CVD (a variant of HWCVD). All depositions of the mult-ilayer are done below 110 °C substrate temperature.

A WVTR of $5x10^{-6}$ g/m$^2$/day has been reported by a three layer (Fig. 6) organic/inorganic structure of a-$SiN_x$/PGMA/a-$SiN_x$ (PGMA stands for poly(glycidyl methacrylate)) made by HWCVD for the inorganic layer and i-CVD (initiated chemical vapor deposition) for the organic layer [97]. Simulations and modeling can be used to explain the permeation dynamics of such multilayers and for optimizations of the layer stack [98]. Meyer Burger is supplying an integrated tool consisting FLEx LT PECVD tool mainly for depositing an inorganic barrier coating and the PiXDRO JETx inkjet printer for an organic planarization step and claims a WVTR of $10^{-6}$ g/m$^2$/day. Single layer $Al_2O_3$ by R2R atomspheric atomic layer deposition [99], $SiO_x$ by R2R magnetron sputtering [100], silica-like bilayer by R2R atmospheric pressure-PECVD [101], $SiO_xC_zH_w$ (organic)/$SiO_x$ (inorganic)/$SiO_xC_zH_w$ (organic) layer stack by PECVD [102] are some of the other options.

### 5.3. Degradation

**Terrestrial modules**: Cells on polymer foil have shown excellent environment stability [103]. The degradation due to damp heat for 1000 hrs, humidity freeze for 90 cycles, and UV exposure for 1000 hrs is only $< 2\%$, $< 3\%$ and $< 5\%$ respectively. The polymer encapsulated cells of Hyet Solar and their Powerfoil® products have passed the IEC 61646 and EN 61730 tests (accelerated lifetime testing, hailstones, cut susceptibility, fire testing) [104], whereas the cells on SS (Unisolar) are operating in the field for more than 20 years. The light induced degradation (LID) with AM 1.5 light is now $< 4\%$ for triple junction [105,106] and double junction [91] and it is comparable to the LID of such cells on glass substrate [107] and both giving comparable stabilized efficiencies (~13.6%). However, it should be noted that the stabilized record efficiency (13.6% on SS foil) [105] is not obtained from the champion initial efficiency (16.3%), which only emphasizes that it is the absolute value of stabilized efficiency that is important and should be compared with other type of modules, and not the amount or rate of degradation.

**Other applications**: The LID with AM0 light for 1000 hrs shows only 6.1% loss for a-Si:H/nc-Si:H/nc-Si:H and 7.3% for a-Si:H/a-SiGe:H/a-SiGe:H Uni-Solar triple junctions on SS foils [96]. The degradation studies with proton and electron beam show that the radiation tolerance of a-Si:H solar cells is far superior than that of c-Si solar cells for space use, however, advantages compared with other types of thin PV cells are still not conclusive. The proton induced degradation is considerably smaller for a-Si:H and nc-Si:H cells compared with c-Si cells [108] which is attributed mainly to the thickness of the absorber layer [109].

### 5.4. Industrial scenario

A-Si:H solar module fabrication is in fact one of the most successful case of flexible solar cell product. Uni-Solar made high efficiency multi-junctions solar cells on SS foil (6 lines of 2.5 km foil in one run) and ran a very successful business. In the first decade of this millennium, the R2R production technology became a hot topic [110] and many companies and R&D facilities, inspired by the success of Uni-Solar, ventured into R2R manufacturing, though for practical purposes mostly can be categorized as pilot level. PowerFilm and Fuji electric had commercial production of cells at a smaller scale ($< 25$ MW) using Kapton® as substrates. Akzo-Nobel/Nuon/Hyet Solar (Netherlands), Flexcell (VHF electronics, Switzerland) had interesting products on polyester foils, but could not start commercial production, most probably due to economic consideration. As far as equipment tools are concerned, there is a very few possibility to get an off-the-shelf system. The solar cell manufacturing (R&D) companies have developed their own systems. However, Applied Material (US) has reported R2R PECVD deposition equipments for solar cell fabrication [111], whereas Meyer Burger has for the encapsulation, as mentioned earlier.

### 5.5. Flexible a-Si:H applications and outlook

There are several applications - space application (robustness to radiation damage and light weight less than 1200 W/Kg) [96], medical application (radiation detector), agriculture (micro-V textured PC green house), wall paper, food industry (package label), textiles (mobile charger), outdoor utility (tent), security (features in bank notes, credit cards, passport, art objects), metal-air batteries etc. The space application is particularly a high investment application which does not suffer from WVTR problem, however, the radiation damage to the efficiency still is an issue [112]. Other than the niche market, the success will predominantly depends on (i) the cost of encapsulation compared to cell fabrication and life time warranty, and (ii) the stabilized efficiency value which is limited to the temperature and stress effect. The latter issue demands that only multi-junctions will be successful. In that case high deposition rate at low temperature deposition will remain a challenge. At present the transfer method looks more promising, as the temperature effect can be avoided. Uni-Solar stopped production and the other flexible solar cell companies (Fuji, VHF electronics, PowerFilm, Hyet solar, etc.) either became inactive or restricted to only R&D activity. This is due to the traction in business confronting the low-cost c-Si based modules. However, the flexible a-Si:H cell technology is robust. The Uni-Solar modules are still in operation after long years ($> 20$ years) in field. The robustness of the modules is best demonstrated in the module rolls (Fig. 7) where they remain intact even with friction from rolling over. The amorphous nature of the material protects its flexibility that is unique to this type of cell. Uninterrupted kilometer wise solar foils fabrication has been demonstrated by Uni-Solar and Hyet Solar. Hence throughput and large area applications are certainly an advantage. One particular area where a successful demonstration of large area light weight a-Si:H modules (Building Applied Photovoltaics systems, BAPV) is the large IKEA roof tops (Hyet Solar in Netherlands IKEA) on which c-Si types of solar modules would lead to collapse of roof.

Among the thin film PV technologies, Si thin film has an advantage when very large ($> 10$ m$^2$) modules are employed, due to the lowest efficiency loss with up scaling [114] and easy monolithic integration compared to other type of cells. Hyet solar can produce $> 24$ m long foil single modules and they claim a 30% reduction in BOS with extreme light weight (600 gr/m$^2$) and ultra-thin

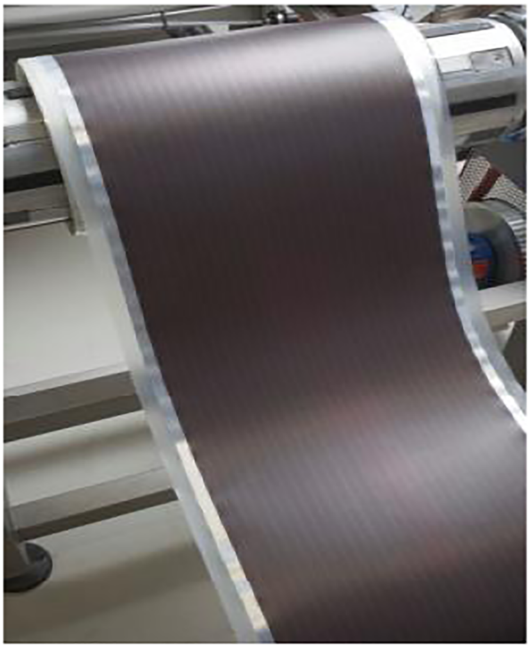


**Fig. 7.** R2R Helianthos a-Si:H flexible solar cells [113]. Single junction superstrate type of a-S:H cell by PECVD is deposited by R2R process at standard temperature (as on glass) on 35 cm Al foil roll as temporary substrate and transferred to a polyester foil roll by a lift-off process.

(0.5 mm) modules resulting from almost zero cost of transportation, low cost mechanical installation ($<$ \$0.05/Wp) and electrical installation ($<$ \$0.05/Wp) for BIPV foils, and a 35% reduction in LCOE (a low \$0.025/kWh) with their 8% conversion efficiency foils compared to glass panels (c-Si) with 15% efficiency.

## 6. Comparison between flexible CIGS, CdTe and a-Si:H cells and applications

In terms of stoichiomety, producing CdTe and a-Si:H solar cells is easier than CIGS solar cells. Stability of CIGS and CdTe based cells is higher than that of a-Si:H cells. For high efficiency, CIGS and CdTe are suitable candidates however at present on flexible foils CIGS cells have shown higher efficiency than CdTe cells, due to the fact that CIGS is built-in substrate configuration, which is the best structure for flexible photovoltaics. Up scaling has been already demonstrated for CIGS cells, with some limitation on the type of substrates to be used. CdTe solar cells have the simplest stoichiometry that helps to improve industrial scalability; on the other hand the best configuration for this technology is superstrate configuration (about 22% vs 13.6% in substrate configuration). This needs the application of a flexible substrate that has to be also extremely transparent, leaving very small choice for a suitable substrate (the best is the ultra thin glass solution). The a-Si:H type is good at low cost, easily scalable, long single module can be used to wrap across a complete big roof. The biggest advantage is that a large number of substrates can be used. Hence there are unlimited types of applications as mentioned below.

Flexible modules can be fixed by glue on the metal roof and automobile roof and mounting racks are not required for installation A 60 W flexible module is used to power camping equipments such as headlamps, tent etc. Flexible modules are also used in GPS systems, recharging field communication radios, mobile phone, laptop computers, sensors and night vision goggles. Flexible cells are integrated into dress and backpacks to generate power (~1W) that can be used to energize portable devices, for example mobile phone. Flexible panel installed over the vehicle roof is used to charge batteries.

## 7. Summary and conclusions

Flexible CIGS, CdTe and a-Si:H thin film solar cells are reviewed. Thin film solar cells have acquired a competitive photovoltaic market in the past years against the formidable Si photovoltaics which has a dominant market share of around 90%. The reason for the sustaining existence of thin film cells even in a non-favorable eco system is due to specialty such as less material wastage and low thermal budget processing etc. Thin films are an ideal type to fabricate on flexible substrates due to their ability to adapt to the shape of the substrate, to their robustness and their high absorption coefficient. The potential of flexible thin film PV is beyond the limited market, it has the potential, with well-established technology to large production volumes, combining high throughput and large area devices.

For polymer foils, absorption in the low wavelength region is not negligible. One of the biggest issues with polymer foils is the high WVTR and gas permeation of about 1 $g/m^2$/day. This is not the case with glass substrates where the cell is protected on both sides by a very low WVTR of $\sim 10^{-12}$ $g/m^2$/day. The ultra-thin (~100 μm) glass solves these issues; its transparency is the same as the rigid glass. It has an excellent encapsulation property with ultra-low WVTR which is not possible to achieve with metal and plastic foils. However, the cost of ultra-thin flexible glass is high. Though flexible glass substrates are bendable, they are not rollable and they are restricted in the extent of bending.

In terms of efficiency and stability, CIGS solar cells are comparable to Si solar cells. However, the main issues are lower yield, lower manufacturing capacity and higher module production cost. High temperature processing of CIGS solar cells is an issue for plastic foils, whereas for metal foils, impurity diffusion from foils to the device is an issue. To avoid this, diffusion barriers such as $Al_2O_3$, $Si_3N_4$ etc., are used in flexible CIGS cells. High efficiency CIGS devices are fabricated by co-evaporation to tailor the film composition for controlled bandgap grading. Using three stage deposition followed by post-deposition (NaF and KF) treatment at < 400 °C, highest efficiency of 20.4% has been reported on polyimide. One of the main concerns is the protection from environment and flexible encapsulation with life-span of 20 years is required.

CdTe solar cell performs better in superstrate configuration. For polyimide foils in superstrate configuration, its stability against UV radiation is an issue; an anti-UV coating on the other side of the substrate is required. For monolithic integration, plastic foils are preferred over metallic foils due to an extra insulating layer for metal foils. Flexible glass and flexible ceramics do not have such issues; however, the cost is the problem. For substrate devices, tiles and ceramics can be used. For both superstrate and substrate type cells, stability during bending is required. Simple stoichiometry and high reproducibility of CdTe solar cells reduce the problems with inhomogeneity which are more frequent in CIGS solar cells.

For a-Si:H solar cells, apart from standard foils and flexible glass, other notable substrates are papers such as cellulose papers, bank notes and security papers. Paper substrate is very attractive for low power application. Among papers, cellulose papers are suitable since the material degrades > 250 °C. Planarization by a hydrophilic material reduces the rough surface of the paper and improves the wetting property useful for back contact metal. About 6.7% efficiency is obtained for single junction on plain white copying paper which is almost equal to the efficiency on SS foils. High efficiency multi-junction solar cells on a long SS foil has been reported by Uni-Solar (6 lines of 2.5 km foil in one run). In standard PECVD process (RF 13.56 MHz), 36 cm width foil is used by the industry in pilot module production and further development is required. Since the belt size in R2R fabrication depends on the deposition rate, a high deposition rate is required particularly for the tandem cell that requires a thick (1500 nm) nc-Si:H bottom cell. VHF PECVD was explored for high deposition rate and similar efficiencies have been reported as compared to the standard PECVD. The success of flexible a-Si:H cells strongly depends on the cost of encapsulation and stabilized efficiency. For encapsulation, a three layer hybrid structure (a-$SiN_x$/PGMA/a-$SiN_x$) can be used due to its very low WVTR of $5 \times 10^{-6}$ g/m$^2$/day. Since polymer foils are moisture sensitive, Si containing moisture barriers such as $SiO_x$, $SiN_x$ and $SiO_xN_y$ are used. Plasma treatment improves the adhesion between polymer foil and moisture barrier. Flexible a-Si:H cell technology is robust. Uni-Solar modules are still in operation for more than 20 years in the field. The robustness is best demonstrated in the module rolls even with friction from rolling over. The amorphous nature of the material protects its flexibility that is unique to this type of cell.

An emerging solar cell technology is flexible perovskite solar cells based on hybrid organic-inorganic perovskite thin film and it offers low cost power production. Perovskite absorber materials can be deposited by inexpensive techniques such as spin-coating, spray-coating etc. Its suitable band gap of 1.52 eV, high absorption co-efficient ($10^5$/cm), bending stability and maintaining efficiency even after bending tests makes it suitable for roll-to-roll production line. The main issue of perovskite solar cell is moisture absorption leading to degradation of perovskite absorber layer and poor long-term stability. If the moisture induced degradation issues are solved, apart from flexible CIGS, CdTe and a-Si:H modules, flexible perovskite modules can also be used successfully in BIPV, roof-top, automobile and wearable electronics (for example health monitor) applications.

In conclusion, as compared to conventional Si solar cells, efficiency of flexible CIGS cell is comparable and stability is not a concern. Less energy input is required to deposit CIGS film than that of Si. The other technology flexible CdTe cell has demonstrated successful industrial production due to simple stoichimetry, high reproducibility, high efficiency and fabrication in both superstrate and substrate configuration. In the case of flexible a-Si:H, since PECVD is the standard technique used for fabrication with processing temperature around 200 °C, temperature sensitive plastic foils can be used. The success of flexible a-Si:H cell is due to high throughput, large area, and long time PECVD deposition without down time. Therefore, future progress is bright for flexible CIGS, CdTe and a-Si:H solar cells. Bridging the efficiency gap between rigid and flexible cells is feasible and the gap can be narrowed by applying the knowledge pioneered on glass.

## Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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