

# Manufacturing of CSS CdTe solar cells

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## Abstract

Due to its basic physical and chemical properties CdTe has become a favoured base material for thin film solar cells, using robust, high-throughput manufacturing procedures. The technology shows significant potential for attaining cost levels of  $< 0.5$  Euro/W<sub>p</sub>. Close-spaced sublimation (CSS) is the fastest and simplest deposition process for both semiconductors used, CdTe and CdS, permitting in-line production at a high linear speed of about 1 m/min. The individual manufacturing steps for integrated modules are explained in view of their incorporation into the production line. ANTEC solar GmbH is engaged to enter the production of CdTe thin film modules on a scale of 10 MW<sub>p</sub> (100 000 m<sup>2</sup>) per annum, using CSS as the deposition procedure for the semiconductor films, and high-rate in-line sputtering for transparent and opaque contacts. Standard module size will be 60 × 120 cm<sup>2</sup>. The production line is presently under construction. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** CdTe; Thin film solar cells; Close-spaced sublimation

## 1. Introduction

After more than 30 years of research and development, the CdTe thin film solar cell is entering the production phase. The study began in 1968 [1], as interest in new thin film solar cells was expressed by representatives of space agencies for communication satellites. With the fast maturation of silicon solar cells this interest has faded, only to be resumed due to the impact of the energy crisis in the early 1970's. Today, 'renewable' energy sources have found strong general acceptance for the reduction of CO<sub>2</sub>-emission and saving of fossil fuels. The CdTe modules, to be discussed here, will avoid about 16 000 kg of CO<sub>2</sub>/m<sup>2</sup> (net) over a lifetime of 30 years. Many institutions of higher learning (Professor Richard Bube and his students of Stanford University being the first to dedicate years of effort [2]) have accumulated significant know-how and technology for this material. In 1972 the 'magic' value of 10% efficiency was reached for the first time in an industrial laboratory. Renewed impetus has been created by the work of Professor Ting Chu and his scholars at the Southern Methodist University in the USA [3], which finally led to the still valid maximum efficiency of 15.8%. While this was being accomplished, some industrial companies again entered the field and invested significant means to develop deposition techniques and procedures suited to production.

In 1991, the work presented here was started by the author of this paper. In 1997, a financing consortium was assembled and a new industrial entity founded, dedicated to

introduce the production of CdTe thin film modules to Germany at a production rate of 100 000 m<sup>2</sup>/year. This meant that the technology for CdTe thin film modules had to be adapted, re-engineered and upscaled to suit in-line production processes. The manufacturing steps for the CdTe thin film modules are a set of physical and chemical procedures, which in some cases have been found accidentally and optimized empirically, and are only now becoming understood in more detail by ongoing research at institutions of higher learning in Europe and the USA. Here, we will describe these procedures and indicate their transformation into production processes, giving an outline of the manufacturing line under construction.

## 2. Manufacturing steps for CdTe thin film modules: process adjustment for in-line production

### 2.1. Basic aspects

High volume manufacture of CdTe thin film modules requires the transformation of batch processes into in-line procedures, allowing motion of the substrate from start to finish. Several processes developed in the laboratory for demonstration of the modules potential had to be completely re-engineered. Equipment had to be designed, eg. equipment which allows glass plates to be heated up to several hundred degrees and cooled down to room temperature while moving through vacuum tunnels. These require-

ments lead to an in-line vacuum plant of significant length ( $>100$  m).

## 2.2. The film sequence

The film sequence is of the ‘superstrate’ arrangement, in so far as the sun is positioned ‘above’ the substrate and light enters the structure through the substrate glass, carrying a transparent conductive oxide (TCO), which is based on the indium–tin–oxide compound system. A thin CdS-film represents the n-conductor, transmitting a large part of active sunlight onto the CdTe p-conductor film, which can be very thin because of its strong light-absorption. For practical reasons a thickness of about  $3\text{--}7\text{ }\mu\text{m}$  is preferred. The sequence of the cell-stack is concluded by a metallic back-contact. Fig. 1 shows the typical film sequence of the cell.

## 2.3. The substrate

The cheapest possible substrate for thin film solar cells is commercial float glass. Consequently substrate temperatures are limited to approximately  $500^\circ\text{C}$  by the softening point of such glass. This glass has an extremely flat surface. It can be bought from distributors cut to size and ready to use.

## 2.4. The TCO-film

This film should have optoelectronic properties which represent a compromise between the highest possible conduction and the highest possible transmission for light of wavelengths effective in CdTe, coupled with easy manufacture. ITO-films of  $<10\text{ }\Omega/\square$  of area and  $>80\%$  optical transmission, between 500 and 850 nm, can be produced today in standard sputtering equipment. It will evidently influence the growth morphology of the following CdS-film, and also shields it from impurities emanating from the glass, due to its high chemical and mechanical stability. Such films have high hardness, an important feature for the mechanical structuring of the films. State-of-the-art commercial equipment can be build for the in-line deposition of such films, including the heat-up and cool-down stages.

## 2.5. The CdS-film

CdS as a photoconductor has been known for a long time. It has an energy gap of 2.5 eV, and thus, is not suited for

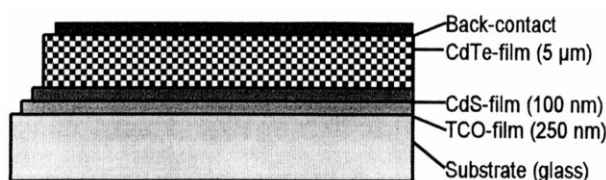


Fig. 1. The film-sequence of the CdTe thin film solar cell.

solar energy conversion by itself. It has been prepared in film form for use in light meters using powder slurries, which have been deposited onto substrates and recrystallized under the influence of  $\text{CdCl}_2$ . This has led to highly photoconductive films. As an n-partner for CdTe it was used for the first time in 1970 in the first CdTe thin film solar cell [1]. In this case, n-type conductivity was required, which occurs natively by means of S-vacancies in a moderate measure. Doping with In, which is a very effective donor, has proven to be less suited for solar cells because In can enter the following p-CdTe, dope it n-type and produce a buried junction in this material. CdS can easily be deposited as thin film by sublimation from the solid material. It can also be deposited by electrodeposition, and by chemical deposition from an aqueous solution. All of these methods can lead to good solar cells. The CdS film acts as a transparent window, similar to  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  in GaAs solar cells, and shows no photoelectric activity, probably due to low minority carrier lifetime and insufficient field for drift.

## 2.6. The CdTe film

CdTe has an energy gap of 1.45 eV, and is therefore very well suited to efficient conversion of solar light into electricity. Furthermore, the energy gap is ‘direct’, resulting in an absorption coefficient for visible light of  $>10^5\text{ cm}^{-1}$ , so that the absorber layer need only be a few  $\mu\text{m}$  thick to absorb  $>90\%$  of photons at energies above 1.45 eV. Current densities of up to  $27\text{ mA/cm}^2$  and open-circuit voltages of 880 mV, leading to AM 1.5 efficiencies of 18.5%, can be expected for cells made from CdTe [4]. CdTe has an extremely simple phase-diagram, which indicates that only the compound CdTe is stable at temperatures of  $500^\circ\text{C}$  or more. It also sublimes congruently, which allows it to be vaporized from open crucibles filled with CdTe granulate and condense onto closely spaced substrates by CSS. At temperatures above  $500^\circ\text{C}$ , CdTe, under such conditions, grows p-doped to  $\geq 10^{14}\text{ cm}^{-3}$ . Such a doping-level, although somewhat low, can be tolerated in thin film solar cells. The advantage in avoiding complex doping processes is worth the small deficiency. The CSS process, as indicated in Fig. 2, can be successively applied for in-line deposition of both semiconductors CdS and CdTe. In view of the

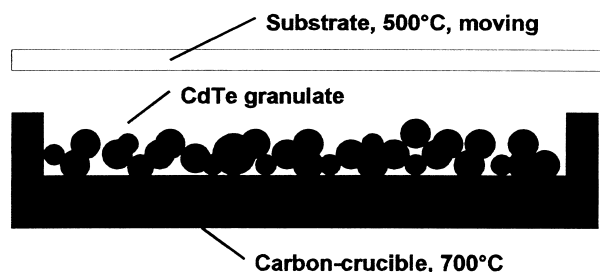


Fig. 2. Schematic illustration of close-spaced sublimation.

required low vacuum conditions (mbar-region), exceptionally low-cost equipment can be built.

### 2.7. Activation

As light-generated electrons (minority carriers in p-CdTe) have to traverse the CdTe-CdS junction, conventional wisdom would expect significant recombination at the abrupt interface, which surely should have abundant recombination centres. CdS and CdTe in thermal equilibrium, can form mixed compounds  $\text{CdS}_x\text{Te}_{1-x}$  only for limited ranges of  $x$  ( $0 < x < 1$ ), leaving a miscibility gap, eg. between  $x = 0.16$  and  $x = 0.86$  at  $650^\circ\text{C}$  [5]. It has been definitely shown that even when the deposition abruptly switches from CdS to CdTe, mixed  $\text{CdS}_x\text{Te}_{1-x}$  phases are formed at the interface between CdTe and CdS [6,7]. Surprisingly, in the first experiments on this type of junction, complete current loss did not occur at the junction as happens, eg. at a GaAs/GaP junction. Later, it turned out that certain (empirical) treatments can improve the junction.  $\text{CdCl}_2$ , the well-known recrystallization mediator for CdS photoconductors, if present on the CdTe film or in the gas phase adjacent to the film at elevated temperatures, ‘activates’ the junction. The activation process is not yet completely understood, but it has become obvious that morphological and electronic changes occur [8]. In as-deposited cells, large parts of the junction are inactive, but activated cells do show high homogeneous sensitivity, independent of bias. More detailed studies on the activation process have shown that the density of interface states at the physical boundary is markedly reduced, decreasing the voltage-limiting reverse saturation current in the diode. Unfortunately, an increase of defect-centres in the space charge region occurs, limiting the improvement [9]. Recently, direct evidence has been produced, showing that the grain boundaries in the CdTe films are well passivated by  $p$ -type accumulation regions, driving the photo-generated electrons into the grains and away from the grain boundaries [7]. In the case of very small grained CdS-films, the activation step also leads to an intermixing and recrystallization at the interface. In films made by CSS, which are quite large grained ( $>1\ \mu\text{m}$ ), the morphology of the material does not change markedly upon activation, but more importantly, minority carrier lifetime still increases remarkably [10].

With the requirement of processes suitable for technical upscaling, different methods for activation have been studied. An alternative process uses gaseous chloride-containing species, such as HCl [11,12], or vaporized  $\text{CdCl}_2$  [13,12], during a heat treatment. In view of in-line production, the activation process is actually the most intricate process in manufacturing. Fortunately, the vapour pressure of  $\text{CdCl}_2$  is virtually zero at standard conditions, allowing easy handling of the activation agent in production. After activation,  $\text{CdCl}_2$ -residues can be completely removed from the module surface by short-time annealing.

### 2.8. Back-contact deposition

It is well-known from semiconductor technology that it is not easy to contact a low-doped  $p$ -type semiconductor. Generally this problem is solved by either using a metal of high work-function, or generation of a highly doped  $p^+$ -layer at the surface of the semiconductor, generating a very thin Schottky barrier to any metal deposited at the surface which can be crossed by charge carriers via tunneling. The problems for CdTe are evident for both cases: low-cost metals of work function  $> 4.5\ \text{eV}$  are not available and  $p$ -doping in CdTe suffers from a strong tendency for self-compensation of acceptors. Furthermore, acceptors cannot be introduced by diffusion-doping from the surface, as dopants generally diffuse preferentially along grain boundaries, leading to shunting of the cell before sufficient doping levels are achieved. In many cases, copper (an acceptor in CdTe) has been added, eg. in graphite contacts still used for experimental contacting, which, upon annealing, can diffuse into the CdTe film. Reduced stability can be a negative consequence, as Cu is a fast-diffusing species in most semiconductors [13,14], and may propagate into the semiconductor even at operating temperatures of the cells ( $\geq 60^\circ\text{C}$ ), and degrade the cell. Efforts in the past have been directed primarily towards three semiconductors: HgTe, ZnTe:Cu, Te and  $\text{Cu}_2\text{Te}$  [15–17]. All of them have led to unstable contacts.

Recently, a new intermediate step in contacting has become known. Upon etching a CdTe surface with a nitric/phosphoric acid mixture (‘N-P-etch’), a very thin Te-layer is generated, which, being a degenerate  $p$ -type semimetal, eases the problems of contacting. It has furthermore been shown that etching reaches down into the film proper along grain boundaries, de facto depositing a Te ‘cap’ onto the individual grains and enlarging the contact area [18]. Evidently, shunting is achieved by extended etching. This effect has been spectacularly visualized by SIMS measurements at NREL in the USA [18].

Presently, contacting generally consists of a triple procedure: (a) etching; (b) deposition of a  $p$ -type semiconductor; and (c) deposition of a metal film for low resistance current collection and cell interconnection in module production. It should be taken into account that practical modules, under power-generating conditions, will operate at an elevated temperature, which will slightly improve rectifying contacts by thermal excitation of majority charge carriers. In view of production, evidently, etching is also a complex step, but equipment for etching substrates in-line can be built by chemical engineering equipment manufacturers. The remaining films required for contacting can easily be deposited by in-line sputtering equipment.

### 2.9. Modularization

Thin-film solar cell technology readily lends itself to making integrated modules. A typical module has around

100 individual cells/metre of module length, connected in series by applying three sets of separation cuts to the growing film stack during production by laser ablation and/or mechanical machining. Narrow individual cells running parallel to one edge of the substrate are defined and sequentially connected: the top electrode of cell one contacts the bottom electrode of cell two, while being separated from the top electrode of cell two. The top electrode of cell two connects to the bottom electrode of cell three, and so on. The TCO films can be structured by ablation with Nd:YAG lasers. For production, a system has to be designed which will allow cutting at a speed which is compatible with the overall transport speed of the modules. If required, more than one laser can be operated in parallel, increasing the speed.

In conventional (amorphous silicon) thin film solar cell technology, usually all three cuts have to be made by laser-scribing. For CdTe thin film solar cells, another technique can be used: the CdS/CdTe double film adheres quite well to the TCO film, which is very flat and rather hard. CdTe, being very brittle, allows the second and third cuts to be made using mechanical tools, which cut the brittle CdTe and slide on the TCO film without cutting it. The third cut can also be performed with a mechanical scribing tool. Speed can be increased by parallel scribing of more than one line. Evidently, no tool can be used indefinitely without wear. ANTEC has developed a system, which allows the service and change of tool only once a week in the production line. Although the substrates have to be immobile for structuring, a stop-and-go process has been devised, allowing a quasi-continuous movement for all these processes.

After the modules are finished, they have to be 'packed', ie. contacted and laminated between two glass sheets, one sheet being the substrate on which the film sequence has been deposited and treated. This is done in the customary way.

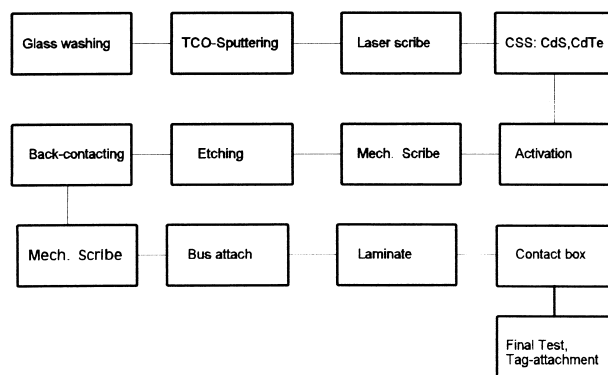


Fig. 3. Flow plan of the production line.

### 3. Assessment of manufacturing steps for production

The procedures described above contain (a) state-of-the-art procedures; (b) new, but simple procedures; and (c) new developed procedures.

Standard procedures are sputter-deposition of ITO, SnO<sub>2</sub>, metals. Dedicated equipment can be easily constructed. In some cases, multiple sputtering targets are needed in order to achieve the required film thickness at the given transport-speed of the substrates (around 1 m/min). The final steps, of contacting and lamination, also use state-of-the-art- techniques. Equipment can be bought custom-made on the market.

Simple, but new processes are essentially the core processes for the active semiconductors, namely CSS-deposition of CdS, CdTe, and if required, back contact semiconductors. It has been shown that CdTe can be deposited onto stationary substrates at rates of 10 μm/min and more. For production, two or three crucibles containing a week's supply of starting material may be used. As mentioned, the vacuum requirements are very low, so that no high-vacuum equipment is needed (for CdTe oxygen-incorporation to



Fig. 4. View on the CSS-stage of the production line including heat-up and cool-down stages.



Fig. 5. View of one of two sputter units including heat-up and cool-down stages.

some extent is indeed considered advantageous by some researchers). Laser-scribing of the TCO film does not require basic new technologies. Equipment can be bought on the market and processing data have to be developed and adjusted.

More involved new processes are etching and activation. Etching requires the immersion of the substrates carrying the activated CdS/CdTe film stacks into acid water solutions, rinsing and drying. Although essentially simple, procedures and equipment have to be developed to incorporate these processes into the production line under tightly controlled parameters. Activation requires exposition of the substrates carrying the TCO-CdS-CdTe film-stack to e.g.  $\text{CdCl}_2$ , at elevated temperatures. Fortunately, traces of oxygen do not play a detrimental role (the activation step in the laboratory can even be executed in air). Furthermore,

$\text{CdCl}_2$  at room temperature has an extremely low vapour pressure. Some special chemical engineering skills have been needed to conceive an in-line activation stage which fits into the production line. Mechanical scribing has turned out to be more involved, due to the requirement that the production line should have only one service interval per week. Scribing tools have to survive one week under tough tolerances. This task has been solved at ANTEC.

#### 4. The production-line

The manufacturing plant is defined as a single in-line thin film processing unit. The core of the deposition line will be fully automated with minimal human interference. Only in the module-making part (lamination, contacting) will



Fig. 6. Look into the module assembly hall.



Fig. 7. View of the input stage for cover glass (washer).

components be manually handled. Comprehensive data processing and recording will allow each module to be traced through the line, see Fig. 3.

At Rudisleben, located close to Erfurt in the State of Thüringen, two existing production halls, each of 3000 m<sup>2</sup> floor space, have been rented. They are presently being remodelled for the production line. The line at a total length of 180 m will be folded once, and cut at the end of the semiconductor manufacturing steps in hall A, and continue in hall B which is connected to hall A by a corridor. Clean conditions are required for the plant, but not a 'clean-room' environment. The substrate will be protected by laminar flow boxes in the first process-steps only. Delivery of raw glass and dispatch of modules (approximately 2000 T/year) by truck, will be eased by a new freeway under construction. Fig. 4 shows a photograph of the CSS-semiconductor deposition stage, which includes heat-up and cool-down stages, with the actual CSS deposition unit approximately in the middle of this segment of the line. Fig. 5 shows one of two sputtering units for sputtering of the TCO film and the back-contact, including heat-up and cool-down stages in the manufacturer's assembly hall. Fig. 6 shows a view of hall B in which the modules will be finally assembled and tested. Fig. 7 shows the input stage of the cleaning unit for the cover glass to be introduced into the assembly unit.

## 5. Conclusions

The production line for thin film CdTe modules is under construction. Envisaged costing is in accordance with a recent international study [19].

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