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# CISZO

## The potential of CIS solar cells

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## Abstract

This study was performed to identify the possibilities of CIS solar cells. The interest in thin film CIS solar cells is growing rapidly. The potential of CIS mostly stems from its possible high stable efficiency at production costs comparable to other thin films (e.g. a-Si, CdTe). The main drawback of CIS is the limited resources of indium, which limits the total amount of CIS solar cells. However, this is only expected to be a problem on the very long term, so CIS is considered an attractive option to precede a “final” thin-film PV material.



keywords: CIS, thin-film solar cells, technological status
contains: 7 tables, 3 figures, 32 references


## Acknowledgement/Preface


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# CONTENTS

# SUMMARY

Due to the growing international interest in CI(G)S solar cells, this survey has been undertaken to identify its strengths and weaknesses. In the SWOT table below the results of this survey are summarised.

| **SWOT analysis of CIS** | |
|---|---|
| Strengths | ❖ CIS has a high record efficiency of 18.8 % on 1.1 $cm^2$; high efficiencies can be maintained on large areas (e.g. 12.1 % on 3738 $cm^2$ by Siemens)<br>❖ CIS modules have entered the market at relatively high efficiencies (> 9%)<br>❖ a (modified) CISCuT process is a fast, atmospheric pressure, roll-to-roll deposition process<br>❖ the complicated phase diagram of $Cu(In,Ga)(S,Se)_2$ allows bandgap engineering |
| Weaknesses | ❖ time consuming (expensive) batch wise deposition techniques are used today, partly forced by the complex phase diagram of $Cu(In,Ga)(S,Se)_2$<br>❖ indium resources are limited which may result in a cost increase (although the indium material contributes only 2.5% to the production costs today)<br>❖ CdS is the best window layer known thus far, but Cd has a bad perception (Cd free window layers are possible) |
| Opportunities | ❖ the PV market is expected to continue growing<br>❖ thin films are generally believed to be the route to low cost PV |
| Threats | ❖ a-Si (and CdTe) modules are on the market at an acceptable price<br>❖ based on cost estimates no winners or losers can be identified<br>❖ f-Si has a "big brother" in R&D activities (both mc-Si and electronics)<br>❖ f-Si may profit from the good reputation of wafer Si modules |

# 1. INTRODUCTION

For the purpose of this report the Dutch title of the project "CIS Zonnecellen" has been translated into "The potential of CIS solar cells". CISZO is used as an acronym of the Dutch title. The project was performed under Novem contract nr. 146.120-017.1 and ECN project nr. 7.4450.

## 1.1 background for this investigation

Crystalline silicon is currently the work-horse of the PV industry. It is generally believed that crystalline silicon will keep that position for several years. It is also believed that the costs of crystalline silicon solar cells will be further reduced. However, it is anticipated that this cost reduction will eventually not lead to a competitive price level compared to fossil fuel electricity generation. It is also a general feeling that thin film solar cells will surpass crystalline silicon in low cost manufacturing and be able to compete with fossil fuels in the future. Because of the complexity and multidimensionality of market introduction and cost price development for solar photovoltaics, still a number of thin film solar cell technologies are considered as promising. There are five groups of thin film solar cells which may compete with crystalline silicon in the mid- or long-term:

1. amorphous silicon and related alloys (a-Si)
2. thin film crystalline silicon (f-Si)
3. organic solar cells, dye sensitized or other (DSC)
4. cadmium telluride (CdTe)
5. copper indium diselenide and related alloys (CIS)

Three to four years ago, based on a strategic orientation into thin film solar cells [1], it was recognised that no winners or losers could yet be identified. Among the five technologies no decisive factors could be identified within the limits of uncertainty. At that time it was decided for The Netherlands to concentrate on silicon (multi-crystalline, amorphous and thin film crystalline silicon) and organic solar cells. Within the margins of uncertainty two factors were given a somewhat heavier weight, resulting in the decision not to invest in the so-called polycrystalline semiconductors (CdTe and CIS) in The Netherlands:

- the uncertainty in the perception of the public related of the environmental aspects (of mainly cadmium)
- a major lack of scientific background and infrastructure in The Netherlands

Meanwhile, however, a number of things has changed, although still no winners or losers can be identified.

- the environmental aspects must not be overemphasised (e.g. the Cd content of CdTe and CIS solar cells is much lower than that of accepted products like NiCd batteries [2] and BP Solar will start CdTe module production)
- the industrial interest in (thin film) solar cells has increased, also in The Netherlands
- new CIS deposition techniques have narrowed the gap in scientific background and infrastructure

The international interest in CIS is growing. This is influenced by the good prospects CIS has compared to the other thin films. Compared to a-Si the expected efficiencies of CIS are higher, and CIS lacks the well known degradation effect of a-Si. In the laboratory, cell efficiencies of about 18% are demonstrated, which is very high for a thin film, whereas for a-Si a maximum of 15% initial efficiency has been reported. The large scale introduction of f-Si will take more time than expected a few years ago, while CIS is on the market (Siemens). In Western Europe CdTe seems to be hindered by the perception around Cd, even though one of the best ways to immobilise Cd is by bonding it to CdTe. Although organic solar cells have a high potential to result in low cost PV, the development is in an early stage however and if or when organic solar cells will make their promise come true is still uncertain.

On the other hand, CIS also has its drawbacks compared to some of the other thin films.

- a-Si modules are already available at an acceptable price.
- CdTe is on the market too (although mainly for indoor, low power applications), and compared to CIS the deposition process is far less complicated.
- f-Si has the advantage of a "big brother" in R&D activities (not only mc-Si PV, but also semiconductor industry).

## 1.2 method

In this study, three main sources have been used. Starting with scanning the scientific literature, the status of CIS and the main research topics have been identified. The patent literature is scanned to identify the companies that are most active in CIS. Finally, informal discussions with people from industry were held to get the most recent information.

## 1.3 boundaries

This report mainly focuses on CIS. CIS, however, should be considered as a member of the family of polycrystalline semiconductors. This family consists of CIS in all its varieties (including Ga, S, etc.), CdTe, $FeS_2$, $FeSi_2$, $SnSe_2$, other chalcopyrites and lots of other materials. However, CIS is probably the most important member of the polycrystalline semiconductors for mid-long term developments.

Discussions on CIS comprise the main part of this report. When appropriate, CIS is compared with other thin film materials. Chapters 2 to 4 are a status report on CIS, both scientific and industrial. In Chapter 5 some conclusions are drawn on the strength, weakness, opportunities and threads (SWOT) for CIS solar cells.

# 2. SCIENTIFIC REVIEW

## 2.1 CIS module

The general fabrication method of a CIS module comprises 9 process steps, see Table 1 [3]. Figure 1 shows the structure of such a (sub-)module.

Table 1 *generic CIS module fabrication sequence*

| Process step | Standard method | alternatives |
|---|---|---|
| 1. glass cutting and cleaning | scribe & break; wash, rinse, dry | plasma clean |
| 2. Mo back contact deposition | DC microwave sputtering | e-beam evaporation |
| 3. Patterning (#1) | laser scribing | etching, lift-off, photolithography |
| 4. CIS absorber formation | Cu/In/Ga precursor deposition + selenization | co-evaporation |
| 5. CdS buffer layer deposition | chemical bath deposition | evaporation, CVD, sputtering |
| 6. Patterning (#2) | mechanical scribing | laser scribing |
| 7. ZnO transparent conductor | DC microwave sputtering | RF microwave sputtering, CVD, ALE |
| 8. Patterning (#3) | mechanical scribing | laser scribing |
| 9. contacting & encapsulation | vacuum lamination with EVA | UV-cured acrylic, Tefzel |

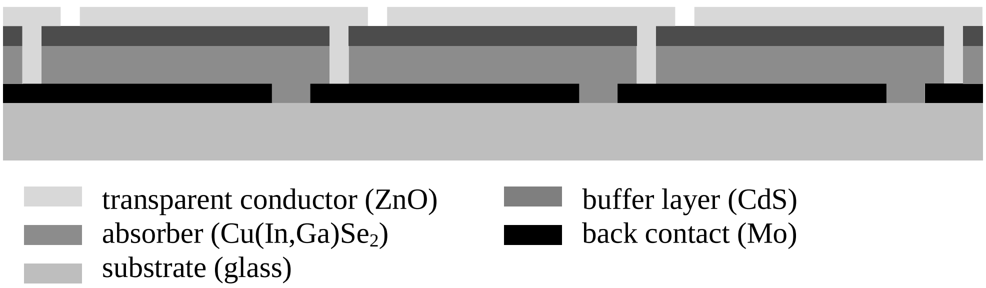


Figure 1 *CIS module*

## 2.2 active research in CIS photovoltaic thin films

An overview of the current research activities in the CIS field is given in Table 2. These activities have been categorised here into seven units, i.e.

(i) solar cell manufacturing and processing;

primary investigations concern the gallium incorporation to reduce the dark current, improve the open circuit voltage (e.g. see Figure 2, [4]) and improve the adhesion of the absorber layers to the molybdenum back contact. In addition, the yearly electricity output may be higher. Thus far, the optimum gallium content in the absorber layer for best device performance is about 27 % (Ga/Ga+In). Devices with total area efficiency of 15.5% have been fabricated by the University of Delaware, Institute of Energy Conversion using a gallium content up to 40% in the absorber layer, which corresponds to a band gap of about 1.3 eV. The gallium is either distributed uniformly in the absorber layer or is tailored from back to front of the absorber layer, depending on the deposition conditions of the CIGS film grown by physical vapour deposition. Efforts to increase the gallium beyond 40% in the absorber layer have not been successful yet.

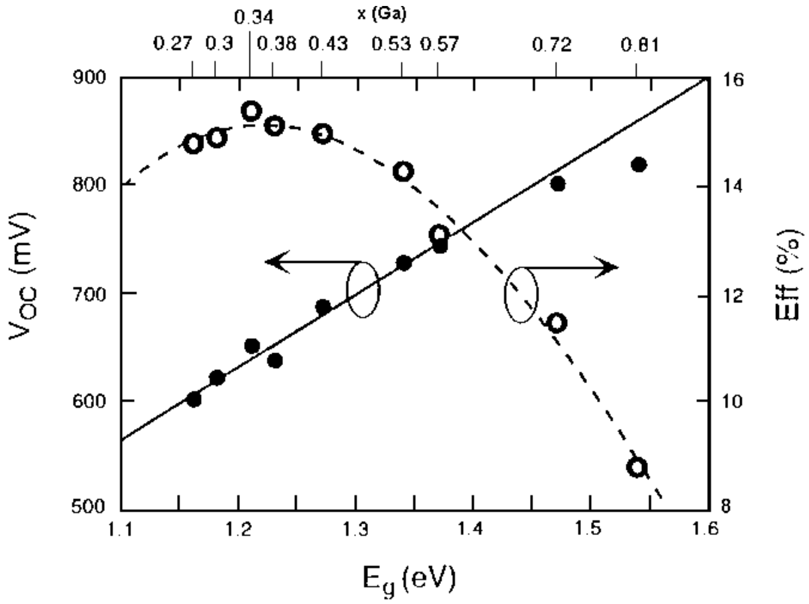


Figure 2 *influence of Ga content on $V_{oc}$ and efficciency*

Another active topic is the CdS buffer layer. Efforts are under way to replace this layer by a non-cadmium containing alternate buffer layer. Alternatives are indium compounds (e.g. $In_xSe_y$) or zinc compounds, deposited by a wide variety of deposition methods (Physical Vapour Deposition PVD or Chemical Bath Deposition CBD). The Showa Shell company is quite successful in this, as can be seen from Table 3.

(ii) contacts

Here the zinc oxide ZnO as alternative for transparent conducting tin oxide $SnO_2$ is aggressively pursued because of its superior optical and electrical properties at the required low deposition temperature. ZnO can be sputtered or deposited using MOCVD. A problem, however, is that ZnO-containing CIGS cells may be more sensitive to humidity, in particular when synthetic material is used for encapsulation. For the past few years, a critical issue that has received much attention has been the diffusion of sodium from the soda-lime glass through the grain boundaries of the molybdenum back contact into the CIGS absorber layer. The following observations have been reported by various groups: grain growth and improvements in the morphology of the film, increase in hole density from CV measurements, improvements in fill factor and open circuit voltage, which consequently improve solar cell performance. Extrinsic doping is also being investigated by using $Na_2S$ or $Na_2Se$. Another observation is that the presence of sodium in the absorber layer allows more flexibility in the stoichiometry of the CIGS films. In addition, recently some activities have been started to investigate interconnection possibilities, probably induced by Siemens Solar, developing mini-modules consisting of 2-4 long interconnected strips.

(iii) materials science

Materials science is primarily performed on universities and technological institutes. Research is directed toward crystal structure and composition and toward electronic properties. Development of in-situ analysis instruments is strongly pushed, since this is of crucial importance for CIGS (pilot) production. Noticeable is the enormous increase in the number of research institutes active in this field in the past few years.

(iv) modelling

Remarkably, there are few reports on modelling, predominantly results of device simulators. Some work is done on thermodynamic phase modelling.

(v) pilot production

Several companies have a preliminary form of (in-line) production. They are located in the United States, Germany (Siemens, IST, ZSW), Sweden and Japan. No or little CIGS has been shipped commercially in 1996 or 1997, possibly with the exception of space applications. Siemens Solar Industries shipped some CIGS 5 & 10 Watt modules in 1998. Furthermore, Showa Shell announced to start CIS production in 2003.

(vi) system applications

Little work is presented on system performance or long-term module stability. It is known that CIGS may suffer from humidity problems. However, at NREL Siemens CIS modules have been tested outdoor for several years without degradation of the system indicating that the problem can be solved [5].

(vii) device analysis

This implies the standard characterisation techniques such as current-voltage and spectral response measurements.

In Table 2 an overview is given of the research topics and the institutes working on them [6].

Table 2 *research on CIS*

| **topics** | **Institutes** |
|---|---|
| 1. Cell processing<br>- Ga alloying (delamination absorber layers to Mo contact, higher Voc )<br>- non-vacuum deposition and low T processing (< $500^oC$)<br>- elimination CdS layer (buffer layers as $In_xSe_y$ or Zn compounds, prevent absorption in CdS)<br>- humidity (moisture)<br>- post-deposition treatments (annealing in air or $H_2$, selenization, chemical oxides, light-soaking)<br>- tandem cells (with a-Si:H or CdTe)<br>- other compounds (e.g. $Cu_2ZnSn_4$ or $CuGaSe_{2)}$ | Institute of Energy Conversion IEC (Delaware), National Renewable Energy Laboratory NREL, Tokyo Institute of Technology TIT, International Solar Electric Technology ISET (Inglewood, CA), Washington State University WSU, Aoyama Gakuin University, Institut fur Physikalische Elektronik IPE (Stuttgart), University of Florida UF, University of South Florida USF, Florida Solar Energy Center FSEC, Departamento de Ingeneria Electrica (Mexico), Matsushita Electric Ind. (Kyoto), Universitat Regensburg, Rand Afrikaans University (Johannesburg, SA), Korea Advanced Institute of Science and Technology, Ecole Nationale Superieure de Chimie de Paris CNRS, Yazaki Corporation (Susono-city, Japan), Dipartimento di Fisica (Parma, Italy), Universitat Gottingen (Germany), Universitat Konstanz, Korea Institute of Energy Research, Korea Advanced Institute of Science and Technology, Academy of Sciences of Belarus (Minsk) |
| 2. Contacts<br>- TCO development ($ZnO$,$Cd_2SnO_4$,$CdIn_2O_4$,$Zn_2SnO_4$) (transparency, electronic, humidity, deposition rate, Ga or Al doping, preparation method, annealing in air)<br>- Mo back contact by sputtering (adhesion, stress, electric properties, deposition rate)<br>- sodium leakage from glass or Mo back contact<br>- interconnection, grid (Ni,A or Ni or Ni/Cu/Nil) and laser scribing<br>- flexible substrates (or alternatives as stainless steel) | Solarex (Newtown, PA), IPE (Stuttgart), Microchemistry Ltd. (Espoo, Finland), Hahn-Meitner Institut (Berlin), NREL, Siemens Solar Ind. (Amarillo, CA), University of Toledo (OH), Iowa Thin Film Technologies ITT |
| 3. Materials science<br>- composition and crystal structure (X-ray photoelectron spectroscopy XPS, UPS, SIMS, Atomic Force Microscopy AFM, X-ray diffraction XRD, Auger Electron Spectroscopy AES, Differential Scanning Calorimetry DSC, ellipsometry, electron probe microanalysis EPMA, SEM&TEM, Rutherford Back Scattering RBS)<br>- electronic (life-time measurements, current-voltage CV,DLTS, photo- and electroluminescence, photoelectron spectroscopy, ion implantation)<br>- in situ analysis (e.g. surface photovoltage spectroscopy) | University of Illinois (Urbana, IL),University of Gent, University of Florida UF, Colorado School of Mines (Golden, CO), Institut fur Angewandte Photophysik (Dresden), Universitat Wurzburg, IPE (Stuttgart), Universitat Bayreuth, Uppsala University (Uppsala, Sweden), NREL,IEC, Universitat Erlangen-Nurnberg, Hahn-Meitner Institut, Science university of Tokio, University of Salford (UK), Warsaw University (Poland), Departamento de Energias Renovables CIEMAT (Madrid), CNRS Universite Montpellier, Tel-Aviv University (Israel), Swiss Federal Institute of Technology (Zurich), Royal Institute of Technology (Kista, Sweden), McGill University (Quebec Canada), Pacific Northwest Laboratory (PNL (Richland, WA) |
| 4. Modelling<br>- devices (AMPS, SPICE, SCAPS 1-D,SCS)<br>- thermodynamic (phase diagrams, CALPHAD) | Princeton (NJ), Purdue University, University of Gent, Pennsylvania State University PSU Colorado School of Mines (Golden, CO), University of Ljubljana (Slovenia), University of Gent (België) |
| 5. Pilot production (terrestrial & space)<br>- upscaling (throughput and large area deposition)<br>- alternatives for encapsulation materials<br>- production cost modelling<br>- removal local defects (or shunts)<br>- concentrator cells | Showa Shell (Atsugi City, Japan), Siemens Solar Ind. (Amarillo ,CA), Solarex (Newtown, PA), Energy Photovoltaics EPV (Princeton, NJ), ITN Energy Systems (Wheat Ridge, CO), Global Solar Energy (Wheat Ridge ,CO), Zentrum fur Sonnenenergie und Wasserstoff Forschung ZSW (Stuttgart), Boeing Defense & Space Group (Seattle, WA), Lockheed Martin LM (Denver, CO), Nordic Solar Energy (Kista ,Sweden), Phototronics Solartechnik (Putzbrunn), Materials Research Group MRG (Golden, CO), Daystar Technologies (Denver, CO), International Solar Electric Technology (Inglewood, CA), Matsushita Electric (Japan), Optical Coating Lab (USA) |
| 6. Systems<br>- module characterisation and system performance (e.g. temperature coefficients)<br>- stability (accelerated life-time testing) | NREL, Colorado State University (Fort Collins, CO), University of Toledo (OH), ISPRA, Phototronics Solartechnik (Putzbrunn) |
| 7. Device analysis<br>- IV, SR, EBIC, LBIC, photoreflectance | NREL, IEC, University of Gent, Universitat Bayreuth, IPE, Tokyo University of Science and Technology, Siemens Solar (Munich), Universitat Oldenburg , Rand Afrikaans University (Johannesburg, SA), Hahn-Meitner Institut, Matsushita Electric Ind., Loughborough University (UK), Cochin University (India) |

## 2.3 realised efficiencies

In Table 3 an overview of realised efficiencies is given. The record CIS efficiency shows the potential of CIS, but the results of Showa Shell (>14% on 50 $cm^2$), Siemens (>12% on 3738 $cm^2$) and IPE (~14% on 90 $cm^2$) show that high efficiencies can be maintained on larger areas. These module efficiencies are significantly higher compared to the record a-Si module efficiency of 10 % reported by United Solar Systems Corporation and the 7.5 % stabilised production efficiency of this triple junction device. The first CIGS product of Siemens Solar entered the market at efficiencies exceeding 9 %.

Table 3 *highest efficiencies* [7]

| **efficiency records** (%) | **institute / company** | **method** | **area** ($cm^2$) | **comments** |
|---|---|---|---|---|
| **18.8** (NREL,1999) | NREL | | 1.1 | [8]; record thin film |
| **16.4** (NREL,1994 | NREL | sequential deposition of Cu and InSe/GaSe and selenization in Se vapour | 1.025 | |
| **14.2** (JQA,1996) | Showa Shell | | 51.7 | Cd free buffer layer |
| **11.8** (NREL,1998) | Siemens Solar Industries | deposition of metal precursors and reaction in Se vapor or $H_2$ Se | 3651 | |
| **noticeable:** | | | | |
| **17.7** (NREL,1996) | NREL | sequential deposition of Cu and InSe/GaSe and selenization in Se vapour | 0.413 | |
| **12.1** | Siemens Solar Industries | | 3738 | [9] |
| **11.4** (NREL) | Siemens Solar Industries | | | 1.2 kW 30 module array [10] |
| **12.4** (NREL) | ISET | metal precursors and non-vacuum selenization | 0.47 | non-vacuum deposition, no Ga |
| **14.1** (NREL) | NREL | electrodeposition | 0.40 | CIGS [11] |
| **13.1** (NREL) | IEC | | 0.40 | high Ga content (high Voc) |
| **15.5** (NREL) | Solarex | | 0.41 | |
| **15.4** (FhG-ISE, 1996) | IPE | coevaporation | 0.45 | |
| **13.9** (FhG-ISE, 1996) | IPE | coevaporation | 90 | 15 interconnected cells |

# 3. INDUSTRIAL STATUS

## 3.1 important industrial players

A disadvantage of the patent literature is that it is not easily accessible; patents are normally written to give as little information as possible. However, it does give information on the companies who are doing research on CIS and on the area of their research. To identify the major players in CIS, the recent patent literature has been searched. Most results have been obtained using the on-line IBM patent search. Although this source has the disadvantage that only the US patents are found, the US is such an important market, that it is believed that this is not a serious problem.

Table 4 *US patents on CIS*

| company | period | topics | ref |
|---|---|---|---|
| Atlantic Richfield Company, Los Angeles, CA | 1984 – 1991 | co-deposition by magnetron sputtering, window layer, multi-junction cells | [12] |
| Matsushita Electric Industrial Co., Ltd., Kadoma, Japan | 1990 – 1998 | precursor deposition, deposition equipment, window layer, co-evaporation, precursor pastes, module sealing | [13] |
| Siemens Solar and other Siemens companies | 1992 – 1997 | sequential deposition; sodium control, module design, window layers, TCO, multi junction | [14] |
| The Boeing Company, Seattle, WA | 1982 – 1993 | window layer, multi junction, module design, deposition, interconnection, light weight | [15] |
| Yazaki Corporation, Tokyo, Japan | 1998 | deposition system, electrodeposition | [16] |

From Table 4 it is concluded that the Atlantic Richfield Company (PV activities are taken over by Siemens) and the Boeing Company are no longer active in (developing) CIS. From the patents of Boeing it is obvious that they were active in the field of space applications. Matsushita, Siemens and Yazaki on the other hand are still active in CIS. Based on the patent information, Matsushita and Siemens work on evaporation, while Yazaki works on electro-deposition.

Apart from the above mentioned companies, also ZSW (Stuttgart, vapour deposition) [17] and EPV (Princeton, vapour deposition) [18] have R&D programmes on CIS. All the companies mentioned use vacuum deposition techniques and a glass substrate. ISET (precursor paste deposition) [19] developed a non vacuum technique on glass. IST developed a different approach. In their so called CISCuT technology [20] they start with a copper tape which serves as a back contact, the substrate and the copper source for the active layer. The deposition technique (electro-plating) is also a non-vacuum technique. Besides, due to the use of the flexible copper substrate, the process can be transformed into a continuous roll-to-roll process.
From Siemens, ISET and ZSW it is known that they plan to have a pilot production line operational before the end of the century. In Vienna (July 1998) Siemens announced to start shipping CIGS modules from August 1998 (5 and 10 Wp modules). According to [9] Siemens produced some 250 kW CIS modules in 1998. In March 1999 they extended their CIS line with 20 Wp and 38 Wp modules [9]. Elsewhere it was announced to start a 3 MW CIS plant. ZSW is

in negotiation with private companies to commercialise their module technology [21]. Showa Shell announced to start CIS production in 2003.

## 3.2 industrial techniques

In Table 1 a generic production scheme is given. In general terms the production scheme of CI(G)S is comparable to that of a-Si. The main difference in the production of CIS solar cells is the formation of the active layer. Due to the complicated phase diagram (see Figure 3, [22]) the forming of the active layer is a complicated competition between kinetics and thermodynamics. Besides, additional special effects are necessary to activate the layer (e.g. sodium diffusion from the sodalime glass). Therefore only three deposition techniques are believed to be of practical importance in production: 1) co-evaporation of Cu, In (and Ga) followed by phase formation and selenization; 2) sequential deposition of Cu, In (and Ga) (or InSe/GaSe) followed by phase formation and selenization; and 3) deposition of non-metallic Cu, In (and Ga) precursors followed by decomposition of the precursors, phase formation and selenization.

The third deposition technique has the advantage that the composition is controlled in a separate step, and a high materials utilisation is achievable. Besides, 1) and 2) are vacuum techniques which makes them in principle more expensive and less suitable for a high throughput production process.

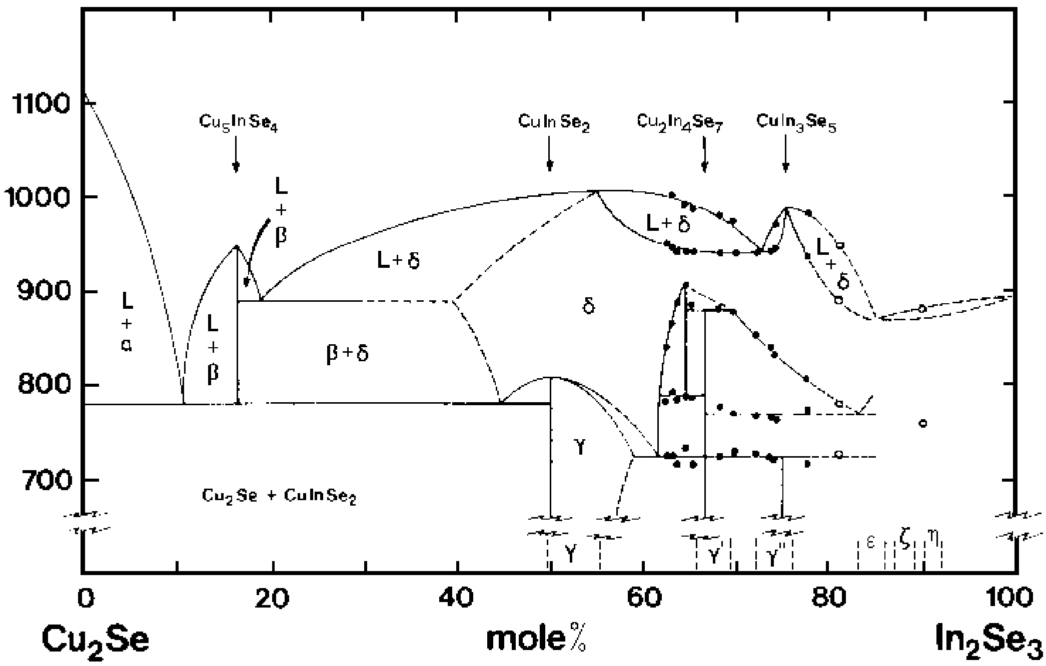


Figure 3 *$Cu_2Se$ – $In_2Se_3$ pseudobinary phase diagram*

## 3.3 costs prospects of CIS

Only a limited number of cost estimates for CIS modules can be found in the literature. Mostly only general statements are given saying “CIS modules will cost well below USD 1.00 or USD 0.50 per Wp”. ISET and EPV gave the most comprehensive calculation, so their results are presented here in Table 5. For comparison, also cost estimates for f-Si, a-Si and CdTe are given in this table.

Siemens CIS modules are on the market since summer last year at a selling price of about USD 13 per Wp for a single 10 Wp module [23].

Table 5 *production cost estimate for thin film modules*

| Source | | ISET | ISET | EPV | ECN | Maycock | musicFM |
|---|---|---|---|---|---|---|---|
| ref. | | [19] | [19] | [18] | | [24] | [25] |
| active layer | | CIS | CIGS | CIGS | f-Si | a-Si | CdTe |
| efficiency | (%) | 11 | 15 | 12 | 16 | 8 | 12 |
| yield | (%) | 85 | > 85 | 92 | 90 | 95 | 88 |
| utilisation | (%) | 85 | > 85 | 50 | 95 | | |
| volume | (MW/yr) | 16 | 50 | 10 | 10 | 10 | 60 |
| materials | ($/Wp) | 0.54 | | 0.27 | 0.44 | 0.32 | 0.53 |
| labour | ($/Wp) | 0.21 | | 0.11 | 0.08 | 0.11 | 0.11 |
| depreciation | ($/Wp) | 0.15 | | 0.12 | 0.12 | 0.40 | 0.03 |
| overhead | ($/Wp) | 0.06 | | 0.06 | 0.14 | 0.11 | 0.02 |
| manufacturing costs | ($/Wp) | 0.96 | 0.6-0.75 | 0.56 | 0.78 | 0.94 | 0.69 |

From Table 5 it is obvious that, on a $/Wp production cost basis, CIS is competitive with the other thin film materials. However, CIS has some advantages over the other thin films:

- + compared to f-Si, CIS is much nearer to market introduction (Siemens has started shipment of CIS last year)
- + compared to a-Si, CIS is expected to give higher stable efficiencies, hence the area-related BOS-costs will be lower on a $/Wp basis. From the Siemens product leaflets on their 5 and 10 Wp CIS modules [26] a total area efficiency (assuming a framing width of 1.25 cm) of over 9 % is estimated
- + compared to CdTe, CIS does not necessarily contain Cd, which can give it a more environmentally benign perception
- + although the deposition process of CIS is much more complicated, this complexity allows bandgap engineering, increasing the efficiency of the system

Some disadvantages of CIS over the other thin films are:

- compared to CdTe, the deposition process of CIS is much more complicated
- CdTe and a-Si are already on the market; although CdTe is currently only used for consumer electronics
- the limited availability of indium

Although it is difficult to present a reliable market forecast for the various thin film solar cells, some considerations can be made:

- based on our experience with f-Si and evaluation of international progress we think that it will take another 5 to 10 years before f-Si will be on the market as a major technology (Astropower may be on the market sooner)
- whether organic solar cells will ever reach the high power market is uncertain, but it will take at least 10 to 20 years
- at the moment CdTe is probably a good choice for a new player on the market; it is an easily produced material. However, because of its simplicity, the room for increase of its efficiency is limited.
- despite the fact that a-Si is already on the market for several years, stable efficiencies of commercial modules are still limited to about 7.5 % for triple junction cells. The first commercially available CIS modules have already higher efficiencies
- mc-Si is still the work-horse of the PV industry. It has proven to be a reliable technique and it has the highest industrial terrestrial efficiency. New mc-Si plants are still being planned and built. Therefore, we expect mc-Si to be a major PV material for a substantial period of time.

# 4. ENVIRONMENTAL ASPECTS

For the evaluation of the environmental aspects of CIS modules, three distinct periods can be identified: 1) the production of the modules; 2) the use of the modules for electricity production; and 3) the waste management and disposal after discharge of the modules.

## 4.1 natural resources

The natural resources of In are limited. When the CIS production would grow to 100 MWp/yr (about the total yearly PV production nowadays), then CIS would consume about 2 % of the total annual In production. However, when the total known reserves of In would be used to produce CIS modules, only 100 to 200 GWp [27] (compared to a worldwide installed electrical capacity of about 2700 GW [28]) could be produced using today's processing schemes and module designs.

## 4.2 production of modules

The environmental aspects of CIS during the production are highly dependent on the actual deposition method of the active CIS layer and the window layer.

The state of the art nowadays is a CdS window layer applied by chemical bath deposition. Using this technique, the main contamination will occur during accidents and spoiling of the chemicals. Good precautions, work procedures and industrial practise will limit this to an acceptable level.

For CIS several deposition methods are in use. From an environmental (and economical) point of view, the deposition method with the highest materials utilisation is the best method. This means that in principle the precursor paste method in which a predefined paste is used to apply the CIS precursors, should be preferred. However, with the other deposition methods environmental pollution can be controlled using proper waste management, possibly forced by legislation conditions [29].

## 4.3 operation period

A solar array is a passive instrument without moving parts, and the modules have to be well-sealed to ensure a long lifetime. Therefore, leaching of the constituents of the module should not take place during normal operation. Only in case of glass breakage the constituents of the module may be released to the environment.

Steinberger [30] has experimentally determined the leaching of the constituents of CIS modules, after breakage into small (10 mm) pieces, both by rainwater and in the soil. Even after breakage into such small particles, the concentration of the constituents of the module in rain water stays 1 to 2 orders below the limit concentrations of the German drinking water regulation when about 0.5% of the roof-mounted modules are broken. By leaching in the soil (assuming the broken module falls on the ground) the concentration of the constituents in the soil stay also below the threshold values of the Kloke list [31], indicating no environmental problems.
In practice a module will not be crushed into such small pieces. The more common incident, breakage due to impact or mechanical stress, will usually result in a much less extensive destruction of the module, and thus in lower leaching.

## 4.4 end-of-life modules

Even though CIS PV modules can be handled as non-hazardous waste under the US environmental regulations [32], recycling of CIS modules is important due to the limited indium resources. Besides, from § 4.3 it can be concluded that the drain water of a landfill may contain unacceptable concentrations of the module constituents. However, due to the (expected) long lifetime of PV modules, large quantities of end-of-life CIS modules will come to the market only over several decades. Therefore, at the moment the interest in CIS recycling is limited. In contrast, on their CIS module product leaflet Siemens says: "Siemens modules are recyclable" [26]. However, it is not clear which part of the modules will be recycled.

The materials make up about 35 to 45 % of the costs of the CIS module. The glass and cover material account for about one third of this amount. Indium is the most scarce and expensive material in a CIS module, but it accounts for only 2.5-5 % of the total module costs [27, 32] and is thus not expected to be a driving factor in recycling.

At the moment there is no commercial driving force for recycling CIS modules. When in the future legislation and environmental laws are more strict, recycling may become an issue. Possible recycling technologies, as given by Eberspacher et al [32] are given in Table 6. The costs of recycling are estimated by them from break-even in the best case (assuming a credit of about $ 0.05 / W for avoiding future environmental liability) to $ 0.11 / W in case of generator-based recycling via direct transport to smelter.

Table 6 *PV module recycling technology*

| process | options |
|---|---|
| disassembly | - if framed, frame removed for separate recycling<br>- if going to smelter, then likely remove junction box, if any<br>- if double-pane construction without pottant, then likely remove back sheet |
| pre-processing | - if non-hazardous and if going to smelter, then likely shred or grind |
| materials separation | - if glass/PV/plastic film construction, then perhaps thermal decomposition, or solvent or acid dissolution of plastic, pottant, and, perhaps, PV layers<br>- if unencapsulated substrate/PV plate, then mechanical, thermal or chemical removal of PV layers<br>- if glass/PV/glass construction, then likely to remain as mixed material waste, i.e. no materials separation. Perhaps possible to separate materials using mechanical, thermal or chemical means. |
| recycling | - if materials are separated, then recycle as appropriate for different materials<br>- if materials not separated, then likely use mixed waste processing, e.g. smelting, pyrolysis, incinneration, molten metal baths, etc. |

# 5. DISCUSSION AND CONCLUSIONS

Up to now, internationally, two main type of CIS deposition processes were under consideration, both to obtain high efficiency laboratory cells and production modules, co-evaporation and sequential layer deposition. However, although both techniques are under development for commercial production (Siemens probably uses sequential layer deposition, ZSW uses co-evaporation), both technologies feature several difficulties, problems and drawbacks. The problem with co-evaporation is that it is complicated and difficult to scale up. The problem with sequential layer deposition is the phase-diagram that has to be crossed upon CIS formation, with the occurrence of all sorts of compounds, phases, including liquid, etc. This gives rise to a kinetically controlled process, which may be sensitive to small variations in the process parameters. In addition, both processes are vacuum processes. Although this is not necessarily a problem (many industrial processes are vacuum processes) it does not seem to be necessary.

Based on Chapters 2 to 4, four factors should be considered when selecting an attractive CIS deposition process:

- Simple/easy processing. Preferably, a deposition process is chosen that does not suffer from the phase diagram problem or the complex nature of the co-evaporation process. In addition, the CIS formation process is preferably fast. For sequential layer deposition formation times of 30 minutes are normal! Furthermore atmospheric pressure processes are preferred, such as electrodeposition and screen printing.
- The use of flexible substrates. Although this is not a prerequisite, there seems to be a good basis for it in The Netherlands. The use of flexible substrates is generally considered to be beneficial for the producibility. For CIS, polyimide, copper, stainless steel and titanium have been used.
- Environmentally friendly. Se, although a trace element necessary to human life, is rather toxic in relatively small amounts, especially in the form of $H_2Se$. Processes that make use of toxic materials, also including the use of Cd in CdS in the case of CIS, are always considered to be undesirable although manageable. In the case of Se in CIS, at present, there is a significant efficiency benefit if Se is used. Nevertheless, it is attractive to prevent the use of Se and Cd in the production process. If it turns out that Se is absolutely necessary to obtain acceptable efficiencies it can always be introduced. Since it is possible to use Cd-free buffer layers, they may be used with preference.
- High materials utilisation. An important issue in CIS is the deposition method to be used. Because of the limited indium resources, and of environmental aspects, a deposition technique with a high materials utilisation is preferred over other deposition techniques. Also from an economical point of view a high materials utilisation is desirable.

In this chapter only considerations concerning the CIS formation process are reported, since this is the most critical issue. In a further elaboration a number of other factors needs to be included as well, like device design, characterisation, etc.

The results of this report are concluded in the short SWOT diagram given below:

Table 7 *SWOT analysis of CIS*

| | |
|---|---|
| Strengths | ❖ CIS has a high record efficiency of 18.8 % on 1.1 $cm^2$; high efficiencies can be maintained on large areas (e.g. 12.1 % on 3738 $cm^2$ by Siemens)<br>❖ CIS modules have entered the market at relatively high efficiencies (> 9%)<br>❖ a (modified) CISCuT process is a fast, atmospheric pressure, roll-to-roll deposition process<br>❖ the complicated phase diagram of $Cu(In,Ga)(S,Se)_2$ allows bandgap engineering |
| Weaknesses | ❖ time consuming (expensive) batch wise deposition techniques are used today, partly forced by the complex phase diagram of $Cu(In,Ga)(S,Se)_2$<br>❖ indium resources are limited which may result in a cost increase (although the indium material contributes only 2.5% to the production costs today)<br>❖ CdS is the best window layer known thus far, but Cd has a bad perception (Cd free window layers are possible) |
| Opportunities | ❖ the PV market is expected to continue growing<br>❖ thin films are generally believed to be the route to low cost PV |
| Threats | ❖ a-Si (and CdTe) modules are on the market at an acceptable price<br>❖ based on cost estimates no winners or losers can be identified<br>❖ f-Si has a "big brother" in R&D activities (both mc-Si and electronics)<br>❖ f-Si may profit from the good reputation of wafer Si modules |

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**Abstract**

This study was performed to identify the possibilities of CIS solar cells. The interest in thin film CIS solar cells is growing rapidly. The potential of CIS mostly stems from its possible high stable efficiency at production costs comparable to other thin films (e.g. a-Si, CdTe). The main drawback of CIS is the limited resources of indium, which limits the total amount of CIS solar cells. However, this is only expected to be a problem on the very long term, so CIS is considered an attractive option to precede a “final” thin-film PV material.

**Key words**

CIS, thin-film solar cells, technological status

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