# PROCIS

# Product identification, pilot plant design and market potential evaluation for copper indium disulphide (CuInS<sub>2</sub>) on copper tape substrates

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# Abstract

The new, innovative IST-technology for copper indium disulphide ( $CuInS_2$ ) solar cells on copper tapes (CISCuT) is a cost-effective series of consecutive roll-to-roll processes. One major feature of this technology is the multifunctionality of the copper tape (1 cm in width), serving as mechanical carrier, source for in-line CIS-formation and back contact of the solar cell, another is the potential to make flexible cells and modules.

During the PROCIS project, the **CISCuT technology** has been further developed to a baseline for  $CuInS_2$  solar cell fabrication. In this sense, a major project effort has been the **up** scaling from the manually produced 2 mm<sup>2</sup> dot cells at the beginning to large area tape (up to 10 cm in length).

For the definition of the baseline equipment a **comprehensive characterisation and modelling** of CuInS<sub>2</sub> material has been carried out. It was found that with standard processing conditions (a copper band speed of 3-4 cm/s and a temperature of 550 °C for the sulphurisation step) CuInS<sub>2</sub> with an **internal p-n junction** is produced. This material consists of **various Cu-In-S phases** with the result that the photoelectrical properties of "as-grown" CISCuT material differ from conventional CIS layers. Therefore, it requires different charge collecting layers with fortunately no need for the usually applied (toxic) CdS layer. The **Cu/CuInS<sub>2</sub>/CuI/ZnO:Al configuration** was selected as most promising in two aspects: the deposition equipment needed for the involved collecting layers could be integrated in the roll-to-roll technology and, with this cell concept the highest cell efficiency ( $\eta = 5.4$  % on 400 **mm**<sup>2</sup>) is achieved.

In parallel, a simpler Cu/CuInS $_2$ /CuI/metal grid configuration was investigated. In this case, the metal grid replaces the ZnO:Al window layer. However, the up scaling of this cell concept is still in its infancy.

Intensive research has been done to find suitable contacting and interconnection technologies. As a result, **roof-tile integrated modules** with maximum dimensions of (10x20) cm<sup>2</sup> and 10 V output have been produced. The favourable flexibility of the copper tape material could be retained in the module by using specific contacting/lamination methods.

Preliminary **stability and climate tests** have been carried out on CISCuT devices. The results indicate that laminated devices are stable under continuous illumination at room temperature. Humidity in combination with high temperature (85 %, 85 °C) however resulted in delamination and cell corrosion. Therefore, improvement in lamination technology is urgently needed.

A good understanding of device physics could be obtained by extension of standard measurement techniques with Light Beam Induced Current (**LBIC**) Spectroscopy, Secondary Ion Mass Spectroscopy (**SIMS**), Parallel Resistance Analysis by Mapping of Potential (**PRAMP**) and **thermography** measurements.

# **Partnership**



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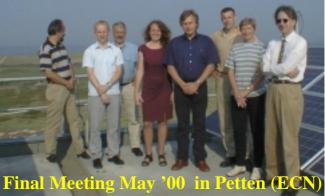


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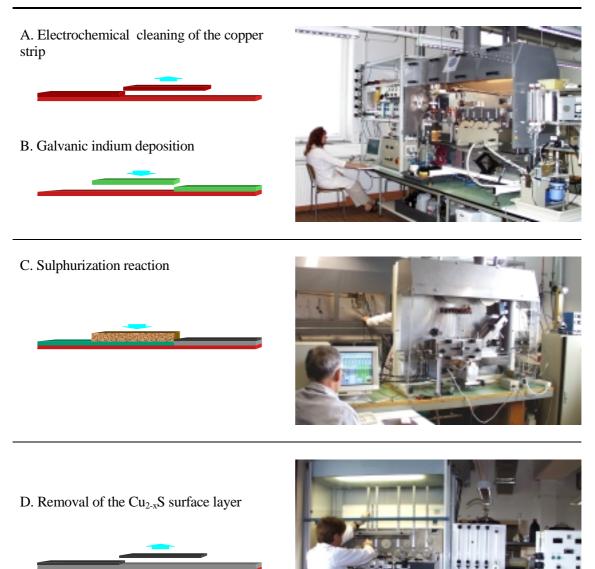


# **CISCuT technology**

The PROCIS project is based on the CISCuT-technology. Basic element of this innovative technology is the one-sided quasi-continuous roll to roll fabrication of a  $1\mu$ m thick CuInS<sub>2</sub> absorber layer on copper tape (see Table 1). This new technology distinguishes itself by the merit that precursor and absorber layer can be formed at atmospheric pressure. Core of the CISCuT technology is the sulphurisation reactor (process C in Table 1) where the copper tape passes the following reaction zones with a tape speed of 4 to 5 cm/s:

- (1) heating, In-melting and formation of the liquid Cu/In precursor (600-750 ms)
- (2) introduction of sulphur loaded nitrogen and solid phase absorber layer generation at a temperature of 590°C (800-1000 ms)
- (3) cooling down (4.6-5.7 s)

# Table 1 Sequential CISCuT absorber preparation



## **CISCuT device physics**

#### 1. Internal p-n junction

The PROCIS project is based on IST results, where photovoltaic behaviour could be established for the first time if the as-grown CuInS<sub>2</sub> was covered with a p-type CuS layer. On  $0.1 \text{ cm}^2$  dot cells a solar cell efficiency of 6 % was measured under 1 sun illumination. However, it was supposed that in the "as-grown" CuInS<sub>2</sub> material itself an internal junction is incorporated. This assumption could be confirmed already in the first project months by different studies at the partners IST, RUG and ECN. A very convincing investigation was provided at partner RUG by measuring of the IV performance on Cu/CuInS<sub>2</sub>/CuS-dots cells (Figure 1). It was found that IV performance decreased if the CuInS<sub>2</sub> area around the CuS dot was masked. This means that the  $CuInS_2$  area outside the dots is also photoactive. This phenomenon can only be explained by the existence of an internal p-n junction in the CuInS<sub>2</sub> layer. At RUG a 2D-simulation programme is developed during the PROCIS project, where not only the light current from underneath the contact dot but also from the area around this dot is calculated. As is obvious from Figure 1 the light current that is generated outside the contact dot experiences the sheet resistance of the upper p-CuInS<sub>2</sub> layer of the junction before it is collected by the contact dot. As is illustrated by the different resistance curves, the current and voltage contribution area increases for a lower sheet resistivity of the p-type CuInS<sub>2</sub> layer. If for a sheet resistivity of 10 k $\Omega$ /square the contributing distance outside the dot is only less than 1 mm, for 10  $\Omega$ /square the CuInS<sub>2</sub> layer collects the current even from a distance of 2 cm outside the dot.

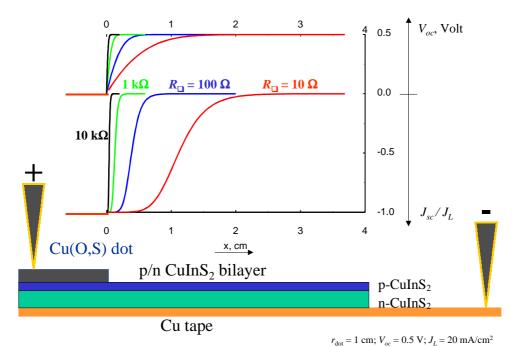
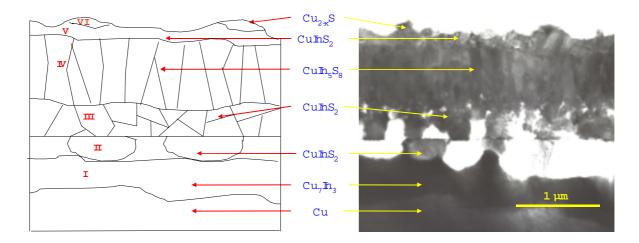


Figure 1: Contribution of p/n CuInS<sub>2</sub> bilayer outside the CuS dot cell to the

photoelectrical properties

# 2. Cu-In-S phases

Parallel to the PROCIS activities IST investigated the solar cell structure in another, nationally co-ordinated project<sup>1</sup>. In the present understanding, the "as-grown" absorber layer is a new kind of solar cell. The photoactive region consists of two types of ternary semiconductors, a  $CuIn_5S_8$  n-type layer and a comparably small  $CuInS_2$  p-type layer (around 100 nm thickness) on top of it. The complete structure of the absorber is even much more complicate (Figure 2). Between the n-type  $CuIn_5S_8$  and the Cu tape two additional  $CuInS_2$ layers are detected. In our present understanding they do not participate in the light conversion process, but the  $CuInS_2$  layer, that is directly grown on the surface of the Cu tape, serves for a good adhesion of the entire absorbing layer.



### Figure 2: TEM cross section micrograph and phase layer estimation of a typical asgrown CISCuT absorber layer

# 3. Band diagram

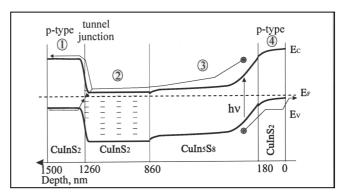
On the basis of the investigation methods Lock in Thermography, Light Induced Voltage Thermography (LIVT), EBIC and Thermopotential measurements of Konovalov et al.<sup>2</sup> we got a presumption of band structure model of the actual "as grown" cells, i.e. cells based on the above-described absorber material with internal pn-junction. Figure 3 gives an idea about the complexity of the "as-grown" layer.

On the x-scale the depth profile is indicated starting with the CuInS<sub>2</sub> top layer:

#### 0-180 nm

region 3 and 4.

p-type CuInS<sub>2</sub> top layer (region 4) 180-860 nm n-type CuIn<sub>5</sub>S<sub>8</sub> layer (region 3) 860-1260 nm n-type CuInS<sub>2</sub> layer (region 2) 1260-1500 nm p-type CuInS<sub>2</sub> layer (region 1)



The photoactive junction lies between Figure 3: Proposal of a band diagram for the as-grown CISCut absorber

<sup>&</sup>lt;sup>1</sup> M. Winkler, O. Tober, J. Penndorf et al., Thin Solid Films, 361-362 (2000) 273

<sup>&</sup>lt;sup>2</sup> I. Konovalov, O. Tober, M. Winkler, PVSEC-11, Sapporo (1999) 23-B-2-4

#### Solar cell structure

The diversity of the during the PROCIS project investigated cell structures is nicely illustrated in the overview scheme given in Figure 4. In all cases the base material is the CISCuT layer produced by the roll-to-roll technology. The as-grown CIS material is etched with 10% KCN before the buffer and window layers are applied.

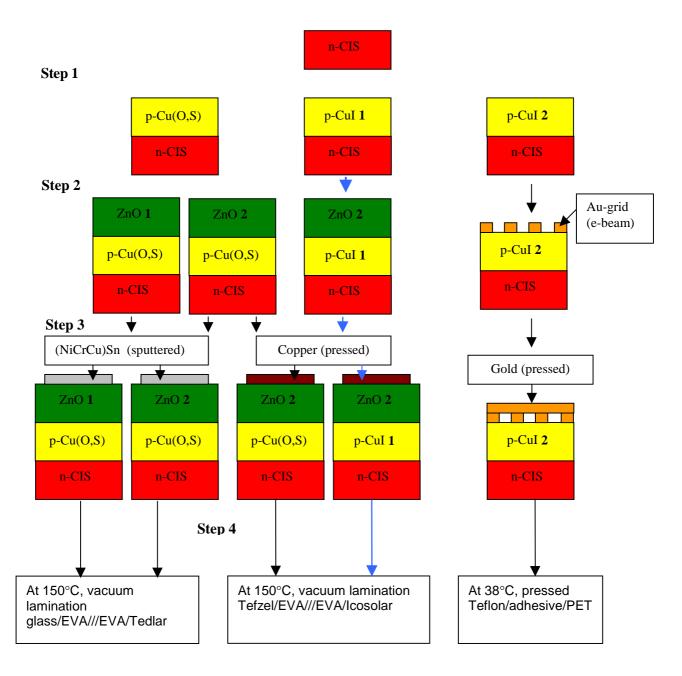


Figure 4: Overview of different solar cell concepts studied in the PROCIS project with main route indicated (blue marked)

#### Step 1: Buffer layer

As is obvious from the scheme, two main buffer layers are tested: copper sulphide (CuS) and copper iodide (CuI). For the CuI buffer layer two different preparation routes are followed, the spraying of non-doped CuI at IST, indicated as p-CuI 1, and the preparation of doped CuI: $I_2$  at ECN, indicated as p-CuI 2.

## Step 2: Window layer/metal grid

As window layer aluminium doped zinc oxide is used (ZnO:Al). The suitability of ZnO:Al layers that are fabricated by different technologies is investigated: the ZnO 1 layer prepared by sputtering at IST and the PECVD layer, ZnO 2, applied by the ECN subcontractor TNO. In Figure 4 all during the project investigated buffer-window layer combinations are listed. Besides, RUG discussed the nature of the additional contact between the p-type buffer layer and the n-type ZnO:Al and the effect on the cell performance. As a consequence, metal grid application has been investigated as potential candidate to replace the window layer.

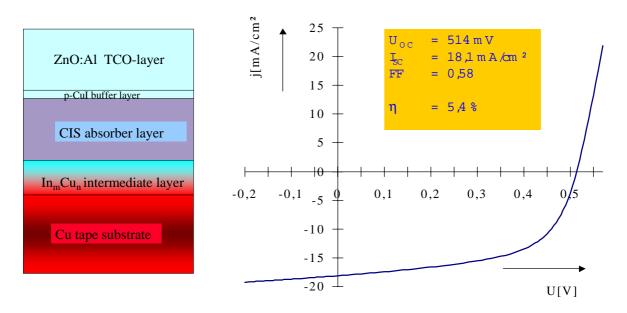
### **Step 3: Contacting /Interconnection**

Proceeding in the scheme, two main contacting routes are selected. At ECN as most favourite material a sputtered (NiCrCu)Sn contact with tin as top layer is chosen. It can easily be interconnected to a tab by the thermode soldering method. At IST a pressed copper wire serves as contact, a very attractive solution for area up-scaling and module fabrication. The strips are interconnected by roof-tile integration. (The also indicated gold contacting is only used for fundamental research.)

### **Step 4: Lamination**

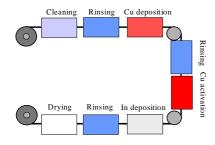
Three lamination routes, developed at either IST or ECN, are given.

After careful investigation, the blue marked route proved to be the most promising cell fabrication way. With a cell efficiency of 5.4 % on 400 mm<sup>2</sup> the Cu/CIS/CuI 1/ZnO1/copper cell configuration (IST) delivered the highest cell performance that is obtained in this project (Figure 5).

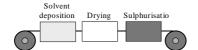


# Figure 5: Scheme of the chosen complete cell structure and IV measurement on the most promising CISCuT solar cell under 1 sun illumination (cell area 4 cm<sup>2</sup>)

Metal foil cleaning, electrolytical Cu and In deposition



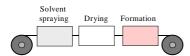
Edge coating and absorber formation by sulphurisation



Removal of the binary Cu 2-x<sup>S</sup> layer by KCN etch



Deposition of CuI buffer layer at the top of the absorber



Deposition of ZnO:Al by a roll-to-roll sputtering process

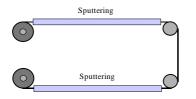


Figure 6: Scheme of the baseline for roll to roll fabrication of complete CISCuT based solar cells on quasi infinite tapes, 1 cm in width, ready for interconnection and lamination to modules. During the 1<sup>st</sup> project year IST and a partner outside this PROCIS project (Odersun Photovoltaics) succeeded to introduce roll-toroll equipment for both the CuS-buffer layer deposition and the zinc oxide formation. Thus, by integration of the last two steps in the rollto-roll technology IST was able to produce complete CISCuT solar cells in several roll to roll processes on a laboratory scale.

In the 2<sup>nd</sup> project year a further break-through is reached by renewing several technology steps:

- Improvement of the Cu tape cleaning procedure and the galvanic indium deposition homogeneity
- Improvement of the absorber homogeneity by improved temperature control and gas management during sulphurisation:

(1) control of constant heat transfer resistance between heater and tape – the main point for reproducible growth temperature,

(2) control of pressure differences and gas flows, and

(3) qualitative on-line control of internal diode characteristics.

• The CuS buffer deposition step is replaced by an automated reproducible CuI buffer layer spray technique and a more or less optimised TCO layer deposition procedure.

In this way, a new module concept has been developed, based on quasi-endless, flexible solar cells, 1 cm in width. The solar cells are fabricated by the CISCuT technology in a sequence of five distinct roll-to-roll batch processes (Figure 6).

## The way from dots to modules

During the project a significant progress was archived concerning the up scaling of the device. The project started with dot solar cell preparation, meaning 0.1cm<sup>2</sup> CuS dots applied on "as-grown" CIS material (see Figure 7).



Figure 7: Starting point: Enlarged part of CISCuT strip with 0.1 cm<sup>2</sup> CuS dots

Meanwhile, the cell device is completed on progressively increasing areas. For first tests (8x8) mm<sup>2</sup> cells are contacted and laminated (Figure 8) and finally up to (100x10) mm<sup>2</sup> devices could be produced (see Figure 10).

Using the most proven roof-tile concept, the solar cell stripes are interconnected in series to strings. Any number of strings are then interconnected in parallel by bus bars (Figure 9). Finally, the absorber is encapsulated in a stack of polymer foils. An assembly line has been developed, which integrates these steps in an automated continuous process in order to realise a base line for module manufacturing.

During the PROCIS project modules with dimensions up to  $(20x10) \text{ cm}^2$  (Voc= 10V) are fabricated (Figure 10).

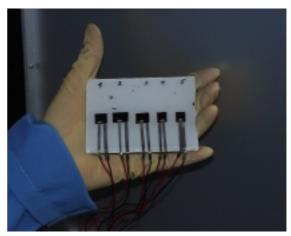


Figure 8: Intermediate state: (8x8) mm<sup>2</sup> contacted and laminated devices

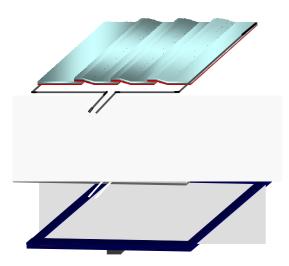


Figure 9: IST-module concept: roof-tile interconnection, flexible foil lamination and edge encapsulation

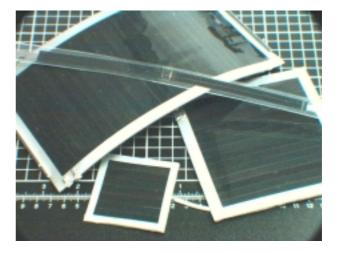


Figure 10: Demonstration modules:

- a) strip module, 1 cm in width
- b) 5x5 cm<sup>2</sup>
- c) 10x10 cm<sup>2</sup> and
- d) 10x20 cm<sup>2</sup> modules, bended to demonstrate the flexibility

# **Exploitation plans and anticipated benefits**

Based on the roll-to-roll technology the CISCuT modules distinguish themselves by their flexibility in dimensions and electrical output. When encapsulated in polymer foils they are even flexible, lightweight and mechanically robust. There is a wide range of applications for mini modules of different power output by varying shape and size. Among others the renewable, decentralised generation of electricity in autonomous systems would be an attractive application for CISCuT modules.

For the baseline a theoretical production output of 100 kWp/yr has been estimated, assuming an efficiency of 5%, a throughput of  $1.8 \text{ m}^2/\text{h}$ , an availability of 85% and a yield of 85%. Currently, the base line is being installed in the labs at the IST and will be completed at the end of the year 2000. The unique feature of this whole technology is that scaling up does not add technological complexity by the very nature of the tape-concept, tape-cell interconnection in variable shapes, sizes, and electrical outputs instead of large area cell production. Collecting grids are in principle not needed in a roof tile module concept. Thus, an improvement in cell performance is immediately translated into in module performance improvement. Another advantage is that investments needed for large-scale production are rather modest, and can be implemented gradually or modular. Therefore, after baseline optimisation a fast transfer to the pilot and series production is planned. Odersun Photovoltaics (ODS) will be the potential producer of the solar cells, first on pilot production scale and later in series production. It has a licence for production, marketing and distribution from the IST. FEI and NEVAG are shareholder in this company to finance the different phases of the whole project as well as to bring there experience for marketing, consultancy and trade into the project.

The economic targets of the CISCuT-technology are: production costs for solar cells below 0,5 Euro/Wp and for PV panels of 1 Euro/Wp. In Table 2 the current cost estimates of this thin film technology are shown for a pilot (1 MWp/yr) and for series production (10 MWp/yr).

Item	Cost value					
	Solar cell production		Module production		Total	
	1	10	1	10	1	10
	MWp/yr	MWp/yr	MWp/yr	MWp/yr	MWp/yr	MWp/yr
	Euro/m <sup>2</sup>	Euro/m <sup>2</sup>	Euro/m <sup>2</sup>	Euro/m <sup>2</sup>	Euro/m <sup>2</sup>	Euro/m <sup>2</sup>
Material	14	14	36	36	50	50
Labour	19	5	15	3	34	8
Depreciation	33	14	33	8	66	22
Overhead	16	15	18	17	34	32
Total	82	48	102	64	184	112
Efficiency	Euro/Wp	Euro/Wp	Euro/Wp	Euro/Wp	Euro/Wp	Euro/Wp
5 %	1.64	0.96	2.04	1.28	3.68	2.24
10%	0.82	0.48	1.01	0.64	1.84	1.12

 Table 2 Cost estimation for 1 MWp/yr and 10 MWp/yr production

There is a large market for autonomous PV systems, especially in the developing countries. World-wide it is estimated that more than two billion people do not have access to the utility grid. Most of these people live in rural areas in the developing countries. In this market sector, the selling prices of the systems will be a key target.