

HipoCIGS: enamelled steel as substrate for “thin film” solar cells

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Introduction

Even during the difficult economic situation over previous years, the global photovoltaic market has been growing significantly. The big potential for solar photovoltaic and its advantages for the society are more obvious than ever. Continuously increasing production capacities, enhanced performance of the solar modules, and a reduction of costs are for a big part explaining the technological success of the conventional photovoltaic technology based on crystalline-Si wafer technology [1].

The thin-film PV technologies are less developed, but through their already existing and future possible advantages propose a high market potential.

Depending on the material used there are four types of thin film solar cells:

- amorphous silicon (a-Si) and thin-film silicon (TF-Si)
- cadmium telluride (CdTe)
- copper indium gallium diselenide (CIS or CIGS)
- TiO₂ dye-sensitized solar cell (DSC)

The thin-film solar cells are less expensive than the older c-Si wafer cells. They can be grown on flexible substrates as metal foils or polyimide films. They are also less fragile than c-Si cells and easier to handle. These advantages enable the production of the monolithically connected flexible modules with high speed roll-to-roll manufacturing systems. The main disadvantage of the thin-film solar cells are their lower efficiency and relatively more complex structure. For the efficiency comparison of some PV technologies see Fig. 1:

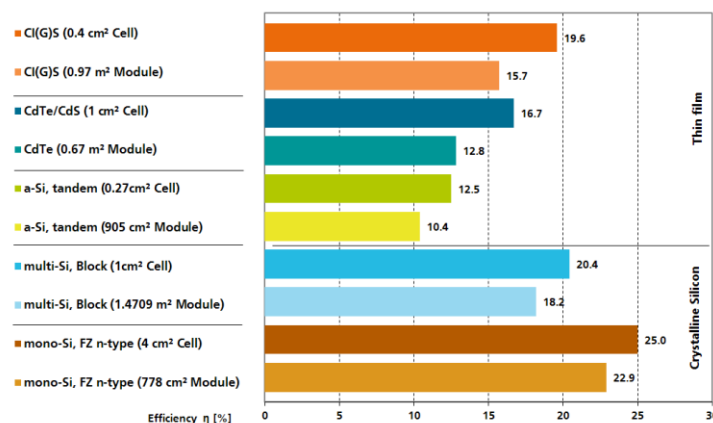


Figure 1: Efficiency Comparison of Technologies: Best Lab Cells vs. Best Lab Modules [2]

The highest efficiencies achieved with CIGS absorbers are above the efficiencies achieved with CdTe or a-Si-based multi-junction thin film solar cells and modules. Consequently the CIGS technology is a promising candidate for a new high efficient and low cost generation of solar cells, particular using flexible substrates.

The schematic structure of a CIGS solar cell on a soda lime glass substrate is shown in Fig. 2. The substrate is 2-4 mm thick rigid glass. The p-type semiconductor - vacuum evaporated CIGS absorber is sandwiched between a metallic electrical contact (sputtered Mo) at the back side and a n-type semiconductor (Chemical Bath Deposited CdS-buffer layer) as well as TCO - transparent electrical contact (sputtered ZnO:Al/ZnO) at the front side.

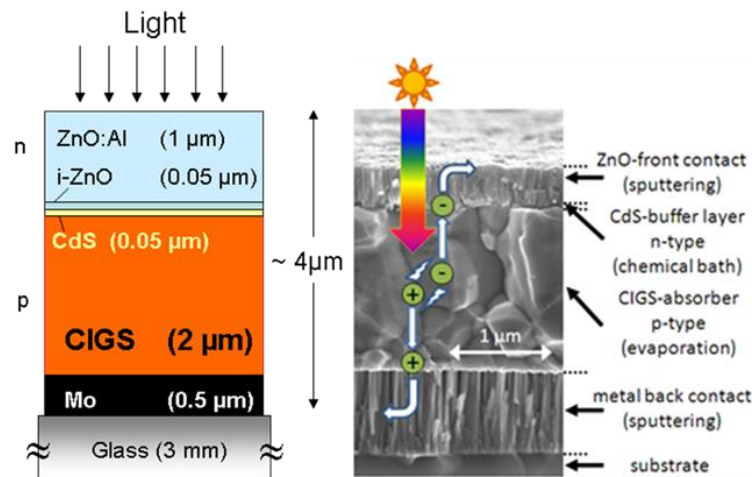


Figure 2: Schematic cross-section of a standard CIGS solar cell

The transfer of the knowledge and efficiencies from CIGS on a glass substrate, to CIGS on flexible foils is a big challenge, due to:

- high temperature during the formation of the CIGS absorbers
- contamination of the absorbers by diffusion of undesired elements out of the substrate (metal foils)
- the need for additional Na doping [1]

On the other hand, enamelled steel foils are a promising material as a substrate for the flexible CIGS solar cells, due to their multiple functions. For example: back side corrosion protection, electrical insulation, high-temperature stability, surface smoothening, surface hardening, alkali source for the CIGS layer, diffusion barrier, etc. Enamelled steel combines the advantages of a glass surface with the stability and flexibility of a metal sheet. Therefore the development of the solar modules is challenging compared to glass based substrates.

The HipoCIGS project to advance the Cu(In,Ga)Se₂ technology on flexible substrate is funded by the European Commission under the FP contract No.241384. Eight different companies and institutes took part in this project: ZSW (D), Flisom (CH), EMPA (CH), MCT GmbH(D), WUT(PL), TATA Steel Europe (D), TNO (NL) and PEMCO (B). Main goal was to develop innovative flexible substrate materials and deposition processes enabling the inline and/or roll-to-roll production of highly efficient flexible solar modules.

The goal of PEMCO's part in the project was to identify and to develop the best suited and best high-temperature stable enamel, to be used as substrate for the fabrication of CIGS solar cells and high efficient flexible CIGS solar modules.

Methods and Results

The schematic cross section of the new approach of a CIGS solar cell on flexible substrate is presented in Fig. 3.

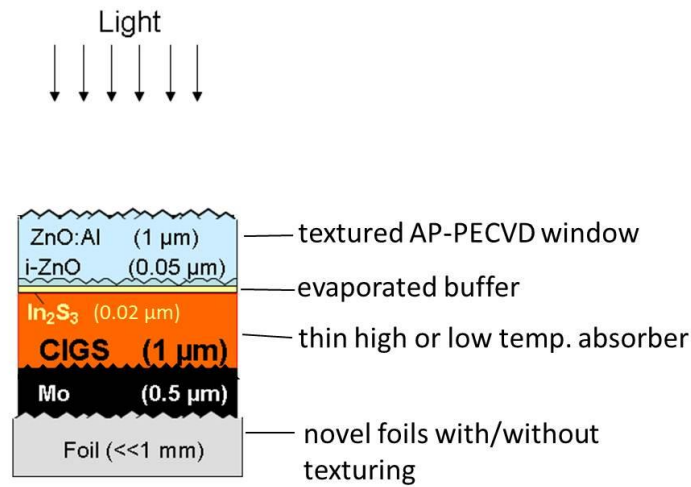


Fig. 3 Schematic cross section of the new approach of a CIGS solar cell on flexible substrate

The rigid soda lime glass substrate has to be changed to a flexible substrate, in our case enamelled low carbon steel. The thickness of the absorber has to be reduced. Advanced R2R – compatible process technologies should be developed. Simultaneously, the efficiency value of the solar cell must be improved or at least become comparable to a glass substrate.

CIGS is grown at substrate temperatures approximately between 450°C and 650°C. Desired and undesired diffusion of different elements plays an important role during the formation of the absorber. High deposition temperatures of the CIGS layer are favourable to achieve high semiconductor quality and efficiencies. The enamelled substrates can allow application up to 650°C. The critical point at such high temperature process is thermal expansion mismatch of layers and substrates which lead to delamination and the appearance of cracks. The quality of the substrate is therefore one of the most important issues for obtaining high performance solar cells [1].

The requirements of a flexible substrate are:

- sufficient layer adhesion onto the substrate
- adjusted thermal expansion coefficient
- low degassing of the substrate
- no bubble formation in a vacuum at 650°C nor selenium vapour
- high thermal and chemical stability
- flexibility to enable roll-to-roll processing

The optimum substrates should additionally be cost effective, allow easy handling and have high environmental stability.

The low carbon steel ED quality with thickness 0.7 - 1.0mm (mainly for development of enamel compositions and producing mini-modules) and thinner, more flexible steel 0.5mm (for producing of large size module) was defined as best.

In order to avoid surface defects and bubble structure growth in the enamel layer and to guarantee enamel adhesion to the substrate, definition of the best suitable pre-treatment is desirable.

The steel-enamel bond is the result of complex chemical reactions at the phase boundary which involve both enamel and steel surface. The adherence behaviour of the dielectric enamels is similar to white enamels. There are two different ways to achieve good adherence:

- 1st system: use of ground coat (cobalt and nickel bearing enamel): degreased steel - ground coat - dielectric coat
- 2nd system: use of direct-on enamels: pre-pickled/nickled steel - dielectric coat

As the T_g temperature (transformation of a glass-forming liquid into a glass) of the ground coat emails is lower compared to the direct-on dielectric enamel, the 1st system (steel - ground coat - dielectric coat) is less stable at temperatures up to 650°C in vacuum and under Se atmosphere without bubble formation and degradation. Nickel layer, 2nd system, on the other hand limits the gas reactions. Therefore the 2nd system (pre-pickled/nickled steel - dielectric coat) is more suitable for CIGS processing.

The well-known pre-treatment (pickle/nickel) procedure for direct on enamelling was adjusted to meet requirements.

To survive a high temperature CIGS-process (650°C) without change of surface morphology and without chipping off, specific dielectric enamel compositions with higher T_g (min. 620°C), minimal bubble formation and adjusted thermal expansion coefficient were developed. To test enamelled substrates as alkali source in a high temperature inline multi-stage CIGS process, enamel compositions with different ratio and concentration of Na and K were defined.

The produced enamelled sheet steel samples with different sizes were provided to ZSW (D) and EMPA (CH) for application and characterisation of the solar cells and the modules.

The Mo back contact was deposited by DC sputtering. CIGS absorber layers were grown by co-evaporation of the constituent elements in a multi-stage inline process at a substrate temperature of about 600°C. Solar cells were prepared from the absorber layers by subsequent chemical bath deposition of a CdS buffer layer, RF sputtering of ZnO layer, DC sputtering of a ZnO:Al front contact layer, and electron beam evaporation of Ni/Al contact grids. A thin MgF_2 layer was finally deposited on some samples as an anti-reflective coating (ARC) [3]. The mini-module and PV parameters of the resulting solar cells on enamelled steel are shown in Fig. 4.

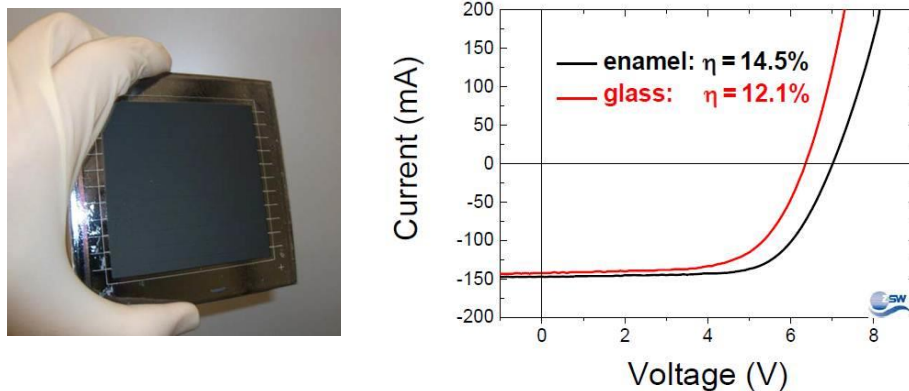


Fig. 4 Mini – Module: 14.5% efficiency on enamelled steel substrate, inline 10 cells, $A=48\text{cm}^2$ (left); IV-curves of cells on enamelled substrate and on reference glass substrate (right).

The efficiency of the cells on enamelled steel was higher compared to cells on glass reference substrates. Based on SIMS measurements (ZSW) it was found that alkali diffused out of the enamel layer into CIGS layer and the enamel layer blocks the diffusion of Fe. Potassium (K) hinders the inter diffusion of CIGS elements during growth, leading to a stronger Ga and Cu gradient correlated with a higher In content in the CIGS layer on the enamelled substrate. The composition of the enamel layer plays the role of a diffusion barrier and as a precursor layer during the high temperature CIGS processing [1, 3].

Unfortunately, if the substrate temperature of the CIGS process is too high (higher than the T_g temperature of the enamel composition) and heating and cooling ramps are too fast, shrivelling (see Fig. 5) of the enamel layer appears and hinders cell and module production [1].

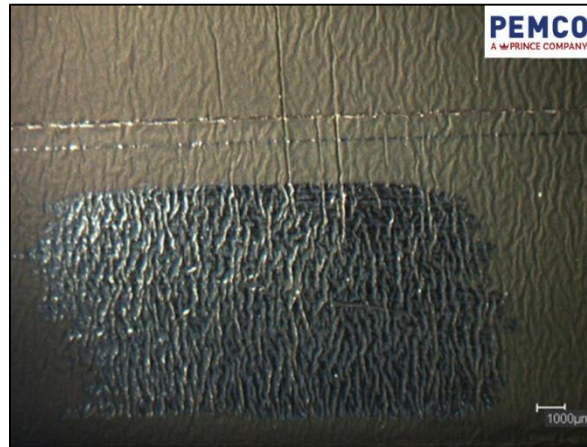


Fig. 5 Shrivelling of the enamel layer due to too high substrate temperature of the CIGS process

Thanks to the special enamel layer composition (adjusted alkali doping) and with an optimized grid, the record-breaking cell efficiency of 18.6% was reached (see Fig. 6).

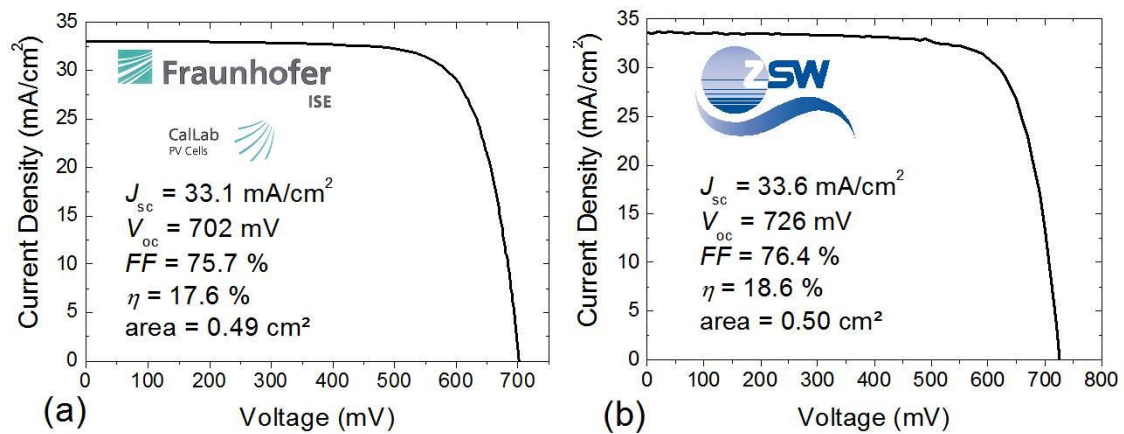


Fig. 6 JV- curves of record cells on enamelled substrate: as confirmed by ISE (left); as measured at ZSW (right)[1].

To produce higher voltage solar modules, single cells have to be connected in series. Large area enamelled low carbon steel substrates and a high temperature multi-stage inline CIGS process were used for the development of CIGS modules (Fig. 7). For module processing the Mo layer was structured with ns-laser (P1), the second (P2) and the third (P3) trenches were scribed mechanically with a stylus. An efficiency of 12.9% was achieved on a large area enamelled substrate. In contrary the efficiency of the glass reference substrate was only 11.6% [1, 3].

This demonstrates the high potential of enamelled steel as an alternative to rigid glass substrate for thin-film solar cells.

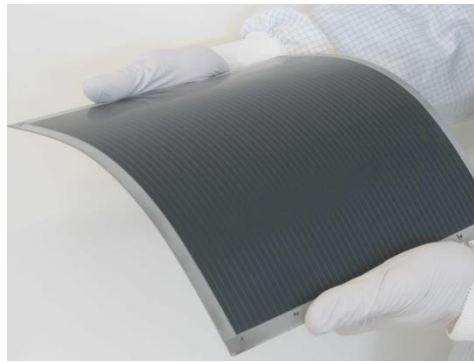


Fig. 7 Solar module on enamelled steel 23 X 30 cm².

Conclusions

The use of enamelled steel as substrates for CIGS solar cells shows many advantages.

The enamel compositions allow effective doping of the CIGS absorber without need of any external Na supply. The CIGS alkali doping on the enamel can be precisely adjusted. The enamel layer is a diffusion barrier and effectively blocks Fe diffusion into the CIGS absorber.

The use of enamelled substrates allows higher efficiency than the reference soda lime glass substrate. The back side of the enamel acts as insulation layer for monolithic interconnection of the cells on the conducting metal substrate.

The flexibility of the thin, enamelled sheet allows the roll-2-roll module production. The active layers can be sputtered by standard laser and mechanical scribing (structuring).

The main disadvantages of the enamelled sheet substrates at this time are the expensive pre-treatment procedure (pickling and nickeling) of the steel sheet and the shrivelling of the enamel layer in case of too high a temperature during CIGS processing, or too fast heating and cooling ramps.

The advantages by further optimizing of the enamel can be considerably improved. In view of the market interest it is highly probable that CIGS-technology on enamelled substrates will become a real opportunity for the enamel field.

Acknowledgements and References

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