DURSOL
Exploring and Improving Durability of Thin Film Solar Cells

Final report

The project objectives are focused towards the understanding of fundamental degradation phenomena in thin film solar cells and enhancement of lifetime. Degradation is due to complex mechanisms related to inherent material stability or interdiffusion phenomena across junctions. Device lifetime is also affected by external influences such as ambient atmosphere and solar light, and depends on the type of semiconductors being used in the devices and how the solar cells are encapsulated. The way degradation processes are identified relies on the observation of the temporal evolution of device performance and its relationship to microscopic changes in device materials and morphology. The goal of this project is to use the competences of the partners in micromorph silicon, compound semiconductors, dye sensitized and organic thin film solar cells, solar cell testing as well as modeling to scrutinize durability of thin film photovoltaic devices. An additional goal of the project is to provide a research platform for students and scientists in the field of photovoltaics (PV) offering workshops and conferences where world renowned experts can be met personally. Major funding of the project is provided by the CCEM and swisselectric research.

Status of project

The project started on January 1st 2011 and is now reaching the end of its third and last year. Since the DURSOL project incorporates research and development objectives in several technological directions, a topical structure including four principal modules was defined as follows:

- Module 1: Chemical alteration of the PV device components by external influence
- Module 2: Improving morphological stability of the PV device layers
- Module 3: Mechanical effects of stress on device lifetime
- Module 4: Barrier properties of encapsulation materials

Periodical meetings were held and focused alternatively on the different module topics. These meetings also included a steering committee meeting as well as a laboratory tour at the host institution. All partners have hosted one of the meetings at their institution including PVlab (EPFL, Neuchâtel), ISAAC (SUPSI, Canobbio), CSEM (Muttenz), LPI (EPFL, Lausanne), Empa (Functional Polymers and Thin Films and PV, Dübendorf).

In course of the project, the planned tasks have been successfully carried out. Also, the majority of the planned milestones have been reached. One milestone dedicated to mini module testing was not tackled due to the lack of encapsulated modules for this purpose. Instead a calibrated solar simulator for smaller cells was built up and is used by the consortium to perform calibrated device performance measurements.

A lot of bilateral exchange of know-how, processes and devices has taken place between the partners and the collaboration has given rise to new project initiatives, among which a large research proposal to the Swiss NFP70 program. The project has given rise to numerous conference contributions and prestigious publications, one being a Nature communication. Industrial contributions are greatly acknowledged. Amcor Flexibles AG provided encapsulation pouches for some of the project partners. BASF provided organic semiconductors for polymer solar cells. Solaronix SA participated in a dye sensitized solar cell demonstrator that was exhibited at the 2012 energy exhibition at the Swiss Museum of Transports. Fluxim AG made their numerical codes available to model various transient current experiments within the DURSOL consortium. Unfortunately, one of our industrial partners Pramac Swiss SA shut down in June 2012.

Finally, there have been three DURSOL conferences and workshops. The first took place on April 4th 2012 at Empa and focused on Durability of Thin Film Solar Cells. The second took place on October 22nd 2013 at Empa addressing Environmental and Economic Impact of PV Energy Production. Each of the conferences attracted more than 70 participants. A third workshop took place at ZHAW in Winterthur on February 5th–6th 2014 related to Time and Length Scales of Degradation in Next Generation Solar Cells.

Co-financed by CCEM and swisselectric research

List of abbreviations

CELIV	Charge Extraction by Linearly Increasing Voltage
C-V	Capacitance-Voltage
DSSC	Dye Sensitized Solar Cells
LIT	Lock-in Thermography
NIR	Near-Infrared
OPV	Organic Photovoltaics
PV	Photovoltaic

Major partners

- Empa – Laboratory for Functional Polymers (FP)
- Empa – Laboratory for Thin Films and Photovoltaics (TFPV)
- EPFL – Laboratory of Photonics and Interfaces (LPI)
- EPFL – Photovoltaics-Laboratory (PV-Lab)
- CSEM – Polymer Optoelectronics
- SUPSI – Swiss Photovoltaic Module Test Centre
- ZHAW – Institute of Computational Physics (ICP)

Main Investigator

Frank Nüesch, Empa

Project Partners

Empa

EPFL

CSEM

SUPSI

ZHAW

Time frame of Project

2010–2013

Project Website

dursol.ch

DURSOL
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Main scientific results of workgroups

CdTe thin film solar cells (Empa – TFPV)

In the course of this project the efficiency of CdTe solar cells in substrate configuration was raised from 8.6 % to 13.5 %. This was achieved by the use of new back contact materials, of which MoO_x was found to be the most suitable. It was found that thermally evaporated MoO_x performs better in terms of cell efficiency and lifetime. Other buffer layers based on Sb performed poorer. Also the mechanism of how Cu dopes CdTe could be elaborated allowing a deeper understanding of the functionality of CdTe solar cells in general. Stressing tests revealed a fast drop of the open circuit voltage for all buffer layers within 100 h. A similar degradation kinetics was observed for the fill factor when Sb based buffer layers were used. The origin of the fast efficiency drop during the first 100 hours of stressing is assumed to lie in the instability of formed Cu acceptors. This assumption is supported by acceptor density profiles calculated from capacitance-voltage (C-V) measurements showing a drop of acceptor density accompanied by an enlargement of the space charge region upon stressing (figure 1). The stability of CdTe solar cells in substrate configuration was assessed by periodic performance measurements under stressing conditions in our self-built stress testing chamber. A very promising result with the least degradation of less than 20 % loss in efficiency upon a 1000 hour stress test at 80 °C and one sun illumination has been achieved.

Thin film silicon solar cells (EPFL – PV-LAB)

The degree of crystallinity in microcrystalline silicon solar cells and its effect on stability have been thoroughly investigated and understood. Different kinds of substrate electrode morphologies have been tested to better clarify the influence of the electrode's roughness on μc-Si:H growth quality and, more particularly, density of defective zones. A smoothening ZnO capping on a standard rough front-electrode was introduced to further reduce the crack density in the Si absorber layer. A H_2 plasma posttreatment of the completed device lead to an increase in stability and to a record efficiency of 10.7 %.

Regarding growth and stability of thin film solar cells based on amorphous Si, various deposition regimes have been explored. Efficient layers could be achieved at both high and low silane pressures.

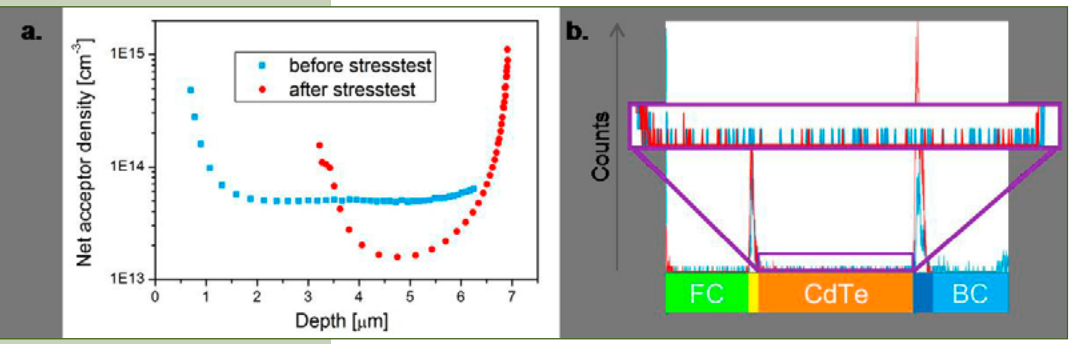
Important testing equipment has also been set up. A new solar simulator, fully based on LEDs and allowing for up to 5 sun light intensity with tunable spectrum, was developed to study accelerated light induced degradation of amorphous silicon solar cells. For measuring adhesion in a reliable and reproducible way a compressive shear test was introduced to characterize adhesion of standard PV encapsulant materials (PVB, EVA, Silicones, TPU) to various rigid substrates (glass, PMMA, PC) before and after degradation in damp-heat conditions (300 h). Finally, an embedded miniaturized capacity sensor for in situ monitoring of moisture ingress in a photovoltaic module has been implemented.

Organic solar cells (EMPA – FP)

Within the DURSOL project, solution-processed, stable and high-performance organic solar cells based on cyanine dye molecules were developed. The research work has been mainly carried out in the topics of modules 1 and 2. For device optimizations and lifetime studies, more than 1500 solar cells were fabricated in this study. Optimized devices based on trimethine dyes with efficiency of 3.7 % can now be achieved using regular and inverted device architecture. Accelerated lifetime testing of regular devices at 80 °C for 17 days unraveled a burn-in period of ~3 days after which

Figure 1:
a) Depth (W) profile of net acceptor density N(W) calculated from C-V measurements performed at 30 °C with a frequency of 300 kHz, an amplitude of 50 mV, and bias voltages between -1.5 and 0.5 V. Calculations are based on the formulas:
$N(W) = C^3 (q \varepsilon \, dC/dV)^{-1}$
and $W(V) = \varepsilon/(C(V))$
(cf. Hegedus et al. Prog. Photovolt: Res. Appl. 2004; 12:155–176).

b) Secondary ion mass spectroscopy (SIMS) measurement of the depth dependent Cu distribution for a cell before (blue) and after (red) stressing. The sputtering started at the front contact (FC, green) then crossed the CdS (yellow) and CdTe (orange) and finally the back contact (BC, blue). The inset shows the magnification of the Cu counts inside the absorber; a reduction of Cu counts upon stressing is clearly visible.



DURSOL
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performance stabilized at 15 % of the initial efficiency. In the inverted architecture, cyanine cells were stable when stored in the glove box for several months, and no sign of degradation was observed under illumination in nitrogen (for 24 h) or ambient atmosphere (for 6 h), proving the inherent stability of these materials in solar cell applications.

An extended study of cyanine dye counterions showed their importance for thin film morphology and interface formation phenomena. For near-infrared (NIR) absorbing cyanine dyes, performance could be increased to 2.2 % upon choosing large counterions as compared to perchlorate anions. To inhibit diffusion of counterions out of the cyanine layer and to render the films insoluble, a universal crosslinking strategy for cyanine counterions was developed. This also allows to solution deposit further layers onto the cyanine film without dissolving the latter.

Device degradation in organic solar cells using phase separated blends of organic semiconductors often is due to reconstruction of the morphology with aging eventually leading to catastrophic failure. We therefore synthesized a fullerene functionalized with a single alkyl chain bearing a diacetylene moiety. In a thin film, the molecule self-assembles into lamellar arrays. The stabilization proceeds through solid-state polymerization of the diacetylene moieties (figure 2). By blending the fullerene derivative with a cyanine dye, various nanostructure fullerene morphologies are obtained that can be stabilized by thermal polymerization. In ongoing work, we study the application of these stabilized blend morphologies in organic solar cells

Polymer solar cells (CSEM, Polymer Optoelectronics)

The role of PEDOT:PSS anode buffer layer in uptake of water from the ambient atmosphere and subsequent degradation of polymer solar cells has been investigated. Other buffer layers consisting of MoO_3 and V_2O_5, respectively, were benchmarked against commonly used conducting polymer anode layers such as polythiophene derivative PEDOT:PSS. Laser beam induced current mapping was applied to investigate degradation of polymer solar cells using different hole transporting layers. Aging studies under the influence of water were completed with transient electrical measurements and the calcium test.

Dye sensitized solar cells (EPFL – LPI)

For realizing flexible dye sensitized solar cells, ionic liquids provide an attractive solution to the problem of solvent penetration through plastic foils. One of the main goals of the project is to understand the variations in the photovoltaic parameters of the dye-sensitized solar cells (DSSCs) during long-term stability tests of DSSC devices. The selected DSSC devices were fabricated with C106 dye in conjunction with various new ionic liquid electrolytes containing sulfolane as a plasticizer, Pt as a counter electrode. After 300 h aging under full sunlight intensity at 60 °C the device performance dropped mainly due to the decrease in the fill factor. The reason for this kind of device behavior is due to the poisoning of counter electrodes.

To confirm this observation, counterelectrodes made of a conducting polymer were used

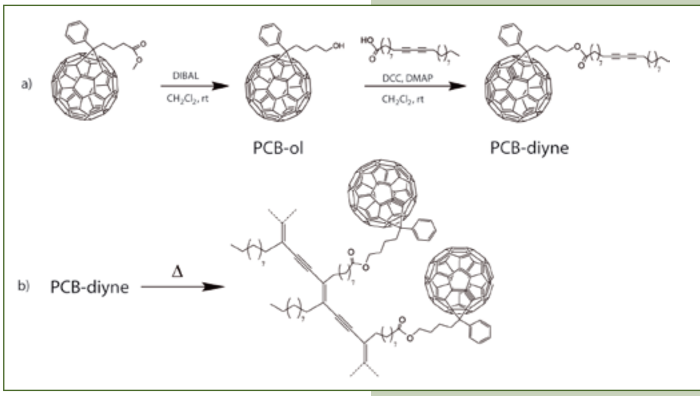

Figure 2:
a) Synthetic route for a diyne-functionalized fullerene.
b) Crosslinking and stabilizing at elevated temperature.

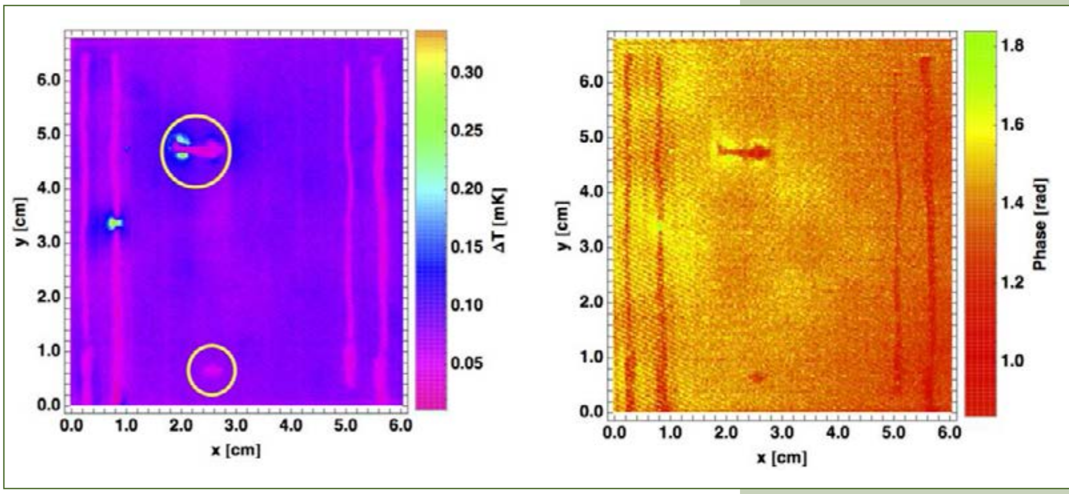

Figure 3:
Lock-in thermography (LIT) of an amorphous silicon solar module with two artificially introduced shunts (resistors soldered on PV-module between anode and cathode, highlighted with yellow circles on the left image). The defects are observable in the LIT measurement, both in the demodulated amplitude (left) and in the demodulated phase image (right). A bias voltage of -4V, AC frequency 1Hz and modulation amplitude 8V were used.

DURSOL
Exploring and Improving Durability of Thin Film Solar Cells

and the device performance was tested as a function of aging time. Electrochemical impedance spectroscopy allowed to understand the impact of fundamental processes in such solar cells. Device lifetime using conducting polymer electrodes were stable for 1000 h at 60 °C, while those using Pt counterelectrodes failed in about 200 h.

Physical simulation of solar cells (ZHAW, ICP)

Numerical models of the various solar cell techniques being investigated within the DURSOL project have been implemented for: DSSCs, OPVs and thin film silicon solar cells. The progress was achieved within collaborations with experimental groups (EMPA-FP, EMPA-TF, EPFL-LPI, CSEM and EPFL-PVLab). Among these various techniques, CELIV, impedance spectroscopy and electroabsorption were successfully set up. These techniques allow to better extract material parameters and to confirm results from electrical device simulation. A numerical model of the charge and heat transport in monolithically interconnected thin-film solar cells was developed and experimentally validated using lock-in thermography (LIT) measurements of amorphous silicon mini solar modules where artificial shunts were introduced in the otherwise defect free module (figure 3). A scalar light scattering model was extended for coherent layers and experimentally validated for microcrystalline/a-Si solar cells. The optical model for thin-film solar cells has been extended including bidirectional scattering distribution functions.

Main achievements

- Interface layers for increased stability of thin film PV technologies:
  - Thermal evaporation of MoO_x back contact as well as doping the active layer with copper increased CdTe efficiency from 8.6 % to a champion efficiency of 13.5 % and lead to longer lifetime. Under harsh aging tests (1000 h at 80°C and 1 sun) 20 % of the initial efficiency was retained (Empa, TFPV).
  - Hydrogen plasma treatment of the back electrode was further optimized and lead to a record efficiency of 10.7 % for microcrystalline silicon solar cells. Smoothening ZnO layers on top of the back electrode were found to avoid the formation of porous zones within the Si absorber layer and ensure good stability upon ambient storage (EPFL, PVlab).
  - Annealing and hydrogen plasma treatments of fresh amorphous silicon devices considerably enhanced device stability as revealed by 40 days of ambient storage in the dark (EPFL, PVlab).
  - Transparent NIR active solar cells based on heptamethine cyanine dyes, with average visible transmission >60 % and efficiency of 1.5 % were achieved. To achieve this, silver electrodes coated with a thin organic optical film were developed (Empa, FP).
- Long term stability of DSSC using ionic liquid electrolytes containing sulfolane as plasticizer is affected by poisoning of the counterelectrode and is substantially improved by replacing Pt with PEDOT:PSS (EPFL, LPI).
- Functionalized fullerene derivatives and cyanine dye salts were synthesized and thin films thereof could be successfully stabilized by crosslinking (Empa, FP).
- New equipment has been installed and used by the DURSOL partners:
  - A new solar simulator, fully based on LEDs and allowing for up to 5 sun light intensity with tunable spectrum, was developed to study accelerated light induced degradation of amorphous silicon solar cells (EPFL, PVlab).
  - Compressive Shear Test was used to characterize adhesion of standard PV encapsulant materials (PVB, EVA, Silicones, TPU) to various rigid substrates (glass, PMMA, PC) before and after 300 h degradation in damp-heat (DH) conditions (EPFL, PVlab).
  - Embedded miniaturized capacity sensors for in situ monitoring of moisture ingress in a photovoltaic module have been implemented (EPFL, PVlab). This measurement was combined with the Ca test method developed at CSEM.
  - Climate chamber for accelerated solar cell and mini-module testing (Empa, TFPV).
  - Encapsulation of selected samples employing novel AMCOR substrates with barrier layers were achieved (CSEM).
  - In collaboration with Fluxim AG, know-how and hardware were built up for: charge-extraction by linearly increasing voltage (CELIV), electrical impedance spectroscopy (EIS), light pulse current response and others (ZHAW, ICP).
  - A calibrated spectral response measurement set up was implemented to the existing steady state sun simulator (ISAAC, SUPSI).
- Results were communicated in form of publications (among which a Nature Communication) and conference contributions.
- 3 workshops with world renowned speakers were organized within the DURSOL project.

Collaborations between project partners

- LPI-EPFL collaborated with ZHAW-ICP on the simulation and modeling of small amplitude transient and impedance spectra in DSSCs.
- LPI-EPFL has been working with CSEM to increase device performance using expertise in light management.
- SUPSI offered calibration of reference cells used by the partners.
- CSEM performed Ca tests on encapsuled test devices.
- CSEM encapsulated Empa-FP solar cells used for light-soaking studies at elevated temperatures.
- ZHAW-ICP has performed transient current experiments on various solar cell devices (Empa-FP, Empa TFPV, CSEM).
- Empa FP and SUPSI collaborated on the detection of hot spots in organic solar cells using thermography mapping.