



Schweizerische Eidgenossenschaft
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Eidgenössisches Departement für
Umwelt, Verkehr, Energie und Kommunikation UVEK
Bundesamt für Energie BFE

Rapport final 30 Juin 2015

THIN LAYERS FOR HIGH-EFFICIENCY SILI- CON SOLAR CELLS THROUGH IDEAL COU- PLING OF INDIVIDUAL COMPONENTS

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Numéro du contrat et du projet de l'OFEN: SI/500750-01

Les auteurs de ce rapport portent seuls la responsabilité de son contenu et de ses conclusions

Abstract

The global goal of this project, which started in March 2012 and ended in February 2015, was to further increase the conversion efficiency of thin film silicon photovoltaic devices, with parallel application of the new processes to high efficiency crystalline Si cells. For this purpose, six axes were defined that ranged from a better understanding of the key fabrication parameters to an improved reliability and characterization of the developed devices. All device efficiencies could be significantly improved during the project, both at laboratory and industry levels.

In particular, much progress has been made towards a better understanding of amorphous and microcrystalline silicon material properties, partly thanks to dedicated characterization and development of new deposition regimes. In particular, the impact of excitation frequency on microcrystalline silicon material quality was demonstrated through a careful comparison between cells deposited with VHF (40.68 MHz) and RF (13.56 MHz). While both frequencies allow for the growth of very good bulk material quality, the efficiency of the cells prepared at VHF is, in the range considered here, typically lower. Electron microscopy measurements evidenced the fact that, for similar microcrystalline silicon grains quality, the absorber layer deposited at RF is denser than when deposited at VHF. However, in turn, VHF sustains better material quality at larger growth rate on rough morphology such as on rough front electrode or, in the case of a tandem, after the amorphous silicon top cell.

Additionally, developments were undertaken with fluorinated precursors leading to a new type of absorber layer microstructure, with larger grains and enhanced absorption in the near infrared, resulting in very high short-circuit current densities. For amorphous silicon, a detailed screening of various deposition processes and corresponding material properties was carried out. This resulted in cells with particularly low gap and consequently high current density, but also in a high bandgap solar cell dedicated to the use as top cell in multi-junction devices leading to triple-junction voltages up to 1.93 V.

A lot of work was also pursued to further improve light management and opto-electrical coupling, as required for such thin (of the order of 3 μm) devices. In particular, a novel approach to model the basic mechanism governing light trapping was developed, underlining the important role of parasitic absorption in the non-active layers. More transparent, silicon oxide based, doped and buffer layers are hence now routinely implemented in thin-film silicon solar cells, which further present the advantage of improving the electrical performance on rough morphologies, thanks to a “shunt-quenching” effect. In addition, work has been pursued in further optimizing the front and back electrodes with e.g. the development of metallic back reflectors.

The reliability of solar cells and modules, and more particularly its link to various external stresses such as oxygen or water was also under scrutiny. In particular, simulations of the water penetration with time in PV modules could successfully be simulated, as a function of encapsulant material, module configuration and climatic location. Since water ingress is a common source of possible failure for most photovoltaic (PV) technologies (thin-film silicon, crystalline silicon, CIGS,...), these simulations provide crucial inputs to better predict long-term outdoor performance of PV modules.

Thanks to all these developments, significant progress was made in terms of conversion efficiency, with a certified world record of 10.7% for a microcrystalline single-junction solar cell (achieved in 2013), followed by a certified micromorph tandem efficiency of 12.6% in 2014, right below the 12.7% official world record achieved right after by the National Institute of Advanced Industrial Science and Technology (AIST). Ultimately, an initial efficiency over 14% was reached in tandem (collaboration with Delft University) and triple-junction configuration (without germanium), while first tests of quadruple junctions provided insights on the roadmap to follow to reach stabilized efficiencies above 14% with already available building blocks. On the industrial level, an outstanding stabilized module efficiency of 12.3% on 1.43 m^2 was demonstrated by TEL Solar.

Finally, several of the layers developed in this project, including transparent conductive (TC) layers to be used as electrodes, were applied and tested in crystalline silicon heterojunction solar cells. Efficiencies as high as 22.4% were achieved with the standard design, while an efficiency of 22% could be reached with a back-contacted solar cell design. Development of new TC layers based on

Indium Zinc Oxide (IZO) led to very promising results with very high opto-electronic properties together with a high thermal stability.

The results of this project hence open further perspectives for the use of the developed processes and layers in higher efficiency c-Si solar cells.

Résumé

Le présent projet, qui s'est déroulé de mars 2012 à fin février 2015, avait pour but principal d'améliorer l'efficacité des cellules solaires en couches minces de silicium. En parallèle, les développements ont également été transférés sur des cellules haute efficacité à base de silicium cristallin. Pour atteindre le but général, 6 axes de recherche principaux ont été définis, allant d'une meilleure compréhension des paramètres de dépôt (en particulier du plasma utilisé pour dissocier les molécules de gaz) à une fiabilité à long terme et une caractérisation plus approfondie des dispositifs développés. Pendant les 3 ans du projet, l'efficacité des dispositifs photovoltaïques a été améliorée aussi bien au niveau de la recherche en laboratoire que dans l'industrie.

En particulier, une meilleure compréhension des propriétés des matériaux amorphe et microcristallin a été acquise, entre autre grâce à une meilleure caractérisation des couches et le développement de nouveaux régimes de dépôt. En particulier, nous avons démontré l'impact de la fréquence d'excitation du plasma sur la qualité du silicium microcristallin à travers une comparaison entre des couches et cellules déposées à très haute fréquence VHF (40.68 MHz) ou à fréquence radio RF (13.56 MHz). Bien que les deux fréquences permettent la croissance d'un matériau de très bonne qualité, l'efficacité des cellules préparées à VHF est, dans le cadre de notre étude, généralement inférieure. Des mesures de microscopie électronique mettent en évidence le fait que, pour une qualité de matériau similaire, la couche photo-active déposée à RF est plus dense. Par contre, la très haute fréquence permet d'obtenir de meilleures cellules à haut taux de dépôt sur une morphologie rugueuse, que celle-ci soit directement donnée par l'électrode avant ou, comme dans le cas d'une cellule tandem, qu'elle soit liée à la croissance non conforme de la cellule amorphe.

De plus, l'utilisation de précurseurs fluorés a conduit au développement d'un nouveau type de matériau microcristallin pour la couche photo-active, avec des grains plus gros et une meilleure absorption dans le proche infrarouge, permettant de générer une densité de courant très élevée. Pour le silicium amorphe, un examen des divers procédés de dépôt et une étude approfondie des propriétés des matériaux correspondants ont été réalisés, qui ont permis l'obtention de cellules présentant soit un très haut courant soit une haute tension de circuit ouvert, permettant d'obtenir des valeurs allant jusqu'à 1.93V en jonction triple.

Beaucoup de travail a également été poursuivi pour améliorer la gestion de la lumière et le couplage opto-électrique, tels que requis dans des dispositifs aussi fins (de l'ordre de 3 μm). En particulier, une nouvelle approche analytique permettant de modéliser les mécanismes de base régissant piégeage de la lumière a été élaborée, qui démontre l'importance de l'absorption parasite dans les couches non-actives. Des couches dopées à base d'oxyde de silicium, plus transparentes, sont donc désormais systématiquement utilisées dans les cellules solaires en couches minces de silicium. Ces couches présentent en outre l'avantage d'améliorer les performances électriques des cellules déposées sur des morphologies rugueuses, en limitant l'impact des "shunts" électriques. En outre, le travail d'optimisation des couches électrodes avant et arrière a été poursuivi, avec par exemple le développement de réflecteurs arrière métalliques.

La fiabilité des cellules et modules solaires, et plus particulièrement les possibles défaillances liées aux sources de stress externes telles que l'oxygène ou l'eau, a également été considérée dans ce projet. En particulier, des simulations ont été réalisées montrant à quelle vitesse l'eau pénètre dans des modules photovoltaïques, en fonction du type de matériau encapsulant choisi, de la configuration du module (avec un verre ou un polymère à l'arrière) et sa localisation géographique. Etant donné que la pénétration d'eau est une source fréquente de défaillance pour la plupart des technologies photovoltaïques (PV) (couches minces de silicium, cristallin, CIGS, ..), ces simulations représentent des informations essentielles pour pouvoir mieux prédire le rendement à long terme des modules PV.

Grâce à tous les développements entrepris dans le cadre de ce projet, des progrès significatifs ont été obtenus en terme d'efficacité, avec un record du monde certifié de 10.7% pour une cellule solaire microcristalline à jonction simple (réalisé en 2013), suivie d'une cellule tandem micromorphe d'une efficacité certifiée de 12,6 % en 2014, juste en dessous du record du monde officiel de 12.7% obtenu peu après par l'Institut National des Sciences et de la Technologie (AIST) au Japon. De plus, une efficacité initiale supérieure à 14% a été atteinte en configuration tandem (collabora-

tion avec l'Université de Delft) et triple (sans germanium), tandis que les premiers tests de jonctions quadruples ont donné des indications supplémentaires sur la route à suivre pour atteindre une efficacité stable supérieure à 14% au moyen des matériaux déjà disponibles. Sur le plan industriel, une remarquable efficacité stable de 12.3% a été démontrée par TEL Solar pour un module d'une surface totale de 1.43 m².

Finalement, plusieurs des couches développés dans ce projet, y compris de nouveaux types de couches transparente conductrices utilisé comme électrodes, ont été testées et transférées dans des cellules cristallines à hétérojonction, permettant d'atteindre des rendements aussi élevés que 22.4% en hétérojonction simple et 22% en configuration avec contacts arrière. Le développement de nouvelles couches conductrices basées sur de l'oxyde de zinc et indium (IZO) a conduit à des résultats très prometteurs avec des propriétés optoélectroniques et une stabilité thermique très élevées.

Les résultats de ce projet démontrent clairement les possibilités d'implantation des couches et procédés développés dans des cellules cristallines à haute efficacité.

Zusammenfassung

Das vorliegende Projekt, das von März 2012 bis Februar 2015 lief, hatte zum Ziel, die Effizienz von Dünnschichtsolarzellen zu verbessern und gleichzeitig auch Anwendungen der neu entwickelten Prozesse im Bereich der kristallinen Solarzellen zu zeigen. Dafür wurden sechs Achsen definiert, die von einem tieferen Verständnis der Herstellungsprozesse über verbesserte Charakterisierung bis hin zu Untersuchungen der Zuverlässigkeit von kompletten Bauteilen reicht. Während der 3 Jahre des Projektes ist die Wirksamkeit der Solarzellen verbessert gewesen, ebenso auf dem Niveau der Forschung wie in der Industrie.

Im Lauf der letzten drei Jahre wurde ein besseres Verständnis von amorphem und mikrokristallinem Silizium erzielt, indem neue Regimes der Depositionsparameter untersucht wurden. Der Einfluss der Anregungsfrequenz auf die Materialqualität konnte anhand von Solarzellen aufgezeigt werden, die mit hoher Frequenz (VHF, 40.68 MHz) bzw. Standardfrequenz (13.65 MHz) deponiert wurden. Während in beiden Fällen gute Materialqualität in Referenzschichten erzielt wird, zeigten Solarzellen aus VHF-Abscheidung meist niedrigere Wirkungsgrade. Per Elektronenmikroskopie konnte nachgewiesen werden, dass die Schichten aus der Abscheidung mit Standardfrequenz dichter sind. Nichtsdestotrotz, Abscheidung mit hoher Frequenz ergibt bessere Qualität, wenn mit hohen Depositionsraten oder auf stark texturierten Oberflächen gearbeitet wird, so zum Beispiel in Zellen mit stark streuenden Frontkontakten oder aber auf einer amorphen Topzelle im Fall von Tandemzellen. Ausserdem führte die Verwendung von fluorinierten Precursorgasen zu einer neuartigen Form von mikrokristallinem Silizium, das durch grössere Körner und eine stärkere Absorption im Infraroten gekennzeichnet ist. Letzteres spiegelt sich in Solarzellen mit aussergewöhnlich hohen Stromdichten wieder. Im Bereich des amorphen Siliziums wurde eine systematische Studie der Depositionsprozesse ausgeführt, bei der Regimes für besonders niedrige und besonders hohe Bandlücken gefunden wurden. Ersteres ergibt hohe Stromdichten, letzteres hohe Leerlaufspannungen die in Tripelsolarzellen zu Werten von bis 1.93 V geführt haben.

Ein weiterer Schwerpunkt war die weitere Verbesserung der effizienten Lichteinkopplung, wie sie für dünne Zellen Solarzellen benötigt wird. Hierfür wurde eine statistische Beschreibung dahin gehend verbessert, dass auch parasitäre Absorption in den inaktiven Schichten beschrieben wird. Die Ergebnisse bestätigten die Notwendigkeit, dotierte Schichten und Pufferschichten aus transparenterem Siliziumoxid zu machen. Dies birgt den zusätzlichen Vorteil, dass dotierte Schichten aus diesem Material Leckströme unterdrücken und dadurch die elektrischen Eigenschaften von Zellen auf stark texturierten Substraten verbessern. Die Front- und Rückelektroden selbst wurden ebenfalls weiterentwickelt, zum Beispiel durch die Einführung von metallischen Rückreflektoren, die für bestimmte Zellkonfigurationen von Vorteil sein können.

Schliesslich wurde auch die Zuverlässigkeit untersucht, insbesondere im Zusammenhang mit externen Belastungen wie Sauerstoff oder Feuchtigkeit. Das Eindringen von Wasserdampf konnte in Abhängigkeit von Verkapselungsmaterial, Modulkonfiguration und klimatischer Umgebung simuliert werden. Da dies einen der wichtigsten Alterungsmechanismen in der Photovoltaik darstellt, unabhängig von der verwendeten Technologie, lassen sich die gewonnen Erkenntnisse allgemein verwenden, um das Langzeitverhalten von Ausseninstallationen vorherzusagen.

Alle Verbesserungen zusammengekommen führten zu einem bedeutenden Fortschritt des Wirkungsgrades für verschieden Zelltypen: Das PV-Lab konnte 2013 einen zertifizierten Weltrekord von 10.7% für eine mikrokristalline Zelle zeigen, 2014 gefolgt von einem zertifizierten Weltrekord von 12.6% für eine Tandemzelle (mittlerweile mit 12.7% vom AIST überboten). Ausserdem wurde ein anfänglicher Wirkungsgrad von mehr als 14% für eine Tandemzelle (in Zusammenarbeit mit Delft University) und eine Germanium-freie Tripelzelle erzielt. Ausserdem zeigen erste Tests mit Quadrupelzellen den Weg zu stabilen Wirkungsgraden von 14% auf der Basis von existierenden Prozessschritten auf. Im Bereich Industrialisierung konnte TEL Solar einen herausragenden Wirkungsgrad von 12.3% auf einer Modulfläche von 1.43 m² zeigen.

Als Anwendung, die über Dünnschichtsolarzellen hinausgeht, wurden mikrokristalline Kontaktschichten und leitfähige Oxide aus diesem Projekt ferner für die Anwendung in kristallinen Siliziumsolarzellen mit Heteroübergang verwendet. Dadurch wurden Wirkungsgrade von bis zu

22.4% erzielt, einer Konfiguration mit allen Kontakten auf der Rückseite erreichte 22%. Transparente Kontaktschichten auf der Basis von Indium-Zink-Oxid (IZO) führten ebenfalls zu vielversprechenden Ergebnissen hoher Temperaturstabilität.

Die Resultate dieses Projektes öffnen weitere Perspektiven für den Gebrauch der entwickelten Prozesse und Schichten in c-Si Solarzellen höherer Effizienz.

Introduction and Background

Photovoltaic (PV) has kept following a remarkable growth rate the last years with over 170 gigawatt-peak of worldwide installed capacity end of 2014 [1]. The market share of crystalline silicon (c-Si) has further risen to 90%, while thin-film technologies (based on cadmium-telluride (CdTe), copper-indium-gallium-selenide (CIGS) and silicon) more or less maintained their 10% share. Time has been particularly difficult for thin film silicon because of the very harsh competition and low prices of c-Si based modules. Many companies thus went bankrupt or stopped their thin-film silicon activities, including Flexcell and TEL Solar in Switzerland.

While the potential of thin-film silicon as low cost technology was convincingly demonstrated by production costs as low as 0.35 €/W_p, the major limitation remains the conversion efficiency (8-10% at module level, versus 16-20% for crystalline silicon). Still, a huge industrial effort has been made these last years to upscale thin-film silicon technologies which results in a difference in conversion efficiency between cells and modules the lowest of all PV technologies [2]. Furthermore, and despite this very difficult context, thin-film silicon remains a serious candidate for the building integrated PV (BIPV) sector where its advantages in terms of color, flexibility in size and substrate type (either rigid or flexible) are obvious [3, 4]. Furthermore, we should note that the developments achieved in this project find direct application to the field of PV for high efficiency c-Si solar cells as well and also to research fields such as direct fuel production from photo-electrochemistry [5, 6].

Project goals and methodology

The global goal of the project was to improve the efficiency of thin-film silicon PV device by addressing the main challenges of this technology. Indeed, a combination of improvements in material deposition techniques, in layers – but also interface – properties, and in light trapping was definitely necessary to bring thin-film silicon devices one step further. However, this was not sufficient and a dedicated work on improving the coupling of the sub-cells in a multi-junction device was also mandatory. Finally, a detailed study on the impact of external stresses, such as humidity, both on cells and modules completed this project. A second goal was to apply the newly developed layers to silicon heterojunction solar cells, which offer promises of high efficiency at moderate production costs.

Short project description (2012-2015)

In order to enhance the efficiency of thin-film silicon multi-junction solar cells, six research axes (or work packages) were defined, as depicted in Figure 1.

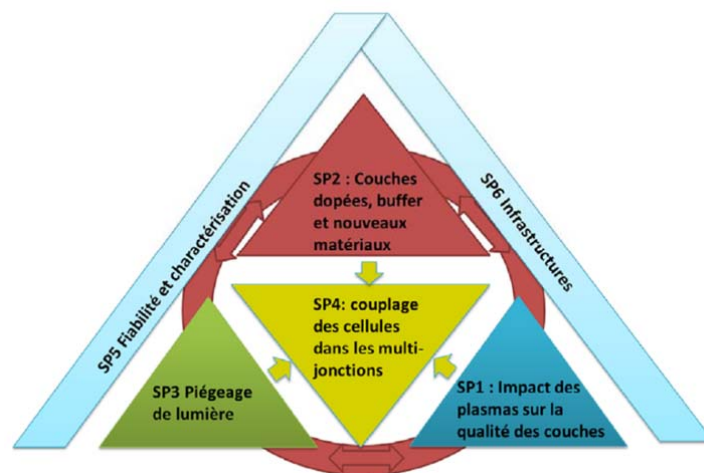


Figure 1: Summary of workpackages of SFOE-EPFL PV-Lab project 2012-2015

Work package 4 represents the core of the project which integrates the results of the work packages 1 to 3. These packages focus on the impact of plasma properties on layers quality, the impact of doped layers, buffers and new materials and the definition of an optimum light management in such thin devices. To help achieving these tasks, two other axes complete the view. The first one concerns reliability and characterization, which are the key bases of scientific progress, and the second one is the infrastructure which needs to be regularly updated to maintain an adequate technology park for future developments.

Work performed and results achieved

While the first 2 years of the project mainly focused on getting a better general understanding on e.g. the link between the plasma processes and the material quality or on ways to improve light harvesting and light management in multi-junction devices, the third year mainly dealt with combining all developments together, which led to two certified world records: one with a single-junction microcrystalline silicon ($\mu\text{c-Si:H}$) solar cell at 10.7% (2013) [7] and one with a micromorph tandem at 12.6% (2014) [8]. Recently, a close collaboration with Delft University led to the development of a tandem solar cell with a 14.8% stabilized efficiency [9]. Further developments also focused on triple-junction devices where initial efficiencies of over 14% could be reached as well (the corresponding cells are currently under light-soaking procedure). This result was achieved thanks to the development of a high bandgap amorphous silicon top cell that allowed reaching initial open-circuit voltage values as high as 1.93 V.

The first section of this report will hence summarize the developments of dedicated absorber layers for use in multi-junction thin film silicon solar cells, be it for the top cell or for the bottom cell, e.g. with the use of fluorinated microcrystalline silicon. Then, section 2 will briefly describe the development of improved buffer layers and how the use of an a-Si:H buffer layer permitted to reach a remarkable V_{oc} value of 608 V in a very thin single-junction $\mu\text{c-Si:H}$ solar cell.

Section 3 will detail the work performed to improve light harvesting and light trapping in multi-junction devices, e.g. by means of improved transparent conductive oxide layers or by the use of a metallic back reflector. Furthermore, we will show that new insights could be gained into the light-trapping capacity of state-of-the-art devices and we could, in particular, demonstrate that the main cause of light loss between ideal and present state-of-the-art light management schemes comes from parasitic absorption rather than sub-optimal light scattering [10]. Moreover, a collaboration with Stanford university showed that carefully designed periodic structures can well compete with state-of-the-art random structures as optimum superstrate for high-efficiency amorphous silicon solar cells [11].

Then the 4th section is dedicated to multi-junction results, with the combination of all recent advances in terms of process and device architecture with the application of a geometric anti-reflective coating at the air/glass interface as well as the incorporation of silicon oxide (SiO_x) material as doped, buffer, and intermediate reflecting layer (IRL). All these efforts led to the certified efficiency of 12.6% achieved in 2014, only very recently overtaken by the National Institute of Advanced Industrial Science and Technology (AIST) with a certified tandem efficiency of 12.7% [12].

The most promising developments performed in this project were also transferred to crystalline silicon based solar cells with e.g. the application of improved transparent conductive oxide (TCO) layers. In particular, tests were performed where a thin indium tin oxide (ITO) layer was added at the interface between an IO:H layer and the silver front electrode grid. Such IO:H/ITO bilayers have a low contact resistance, sheet resistance, and free-carrier absorption, and outperform IO:H-only or ITO-only layers in solar cells. With this, a certified efficiency of 22.1% was achieved for a 4- cm^2 screen-printed silicon heterojunction solar cell employing an IO:H/ITO bilayer as front transparent conductive oxide [13]. Furthermore, rear reflectors were also developed based on low-refractive-index magnesium fluoride (MgF_2) and were introduced in place of the usual transparent conductive oxide/metal reflector. Implementation of an MgF_2 /Al reflector hence enabled to reach an efficiency of 21.3% in heterojunction solar cells with a short-circuit current density of nearly 38 mA/cm^2 .

Finally, a conversion efficiency as high as 22.4% could be achieved on p-type wafer [14] while back-contacted silicon heterojunction solar cells with conversion efficiencies up to 21.5% were reported with a high short-circuit current density close to 40 mA/cm² and an open-circuit voltage exceeding 720 mV [15].

The report then concludes with the major achievements obtained in terms of reliability and characterization together with a summary of the infrastructure upgrade throughout the 3 years of the project. It was in particular demonstrated that water ingress is a major issue both at cell and module level. Simulations were performed with Finite Element Method to evaluate the evolution of water with time for two modules configurations, at different locations and with various encapsulant materials. Concerning characterization, novel set-ups were developed within the frame of this project allowing for open-circuit voltage (V_{oc}) separation, fill factor (FF) analysis and complete current-voltage (I-V) separation, as well as rapid light-soaking with 3 suns intensity.

More details on the scientific results summarized hereafter can be found in the individual annual reports and all the developments and results achieved in the frame of this project have given birth to more than 40 technical and scientific papers, as listed at the end of this report.

1. Dedicated absorber layers for silicon thin film solar cells

1.1 Development of new a-Si:H materials for use in multi-junction devices

Various deposition regimes to fabricate more stable a-Si:H absorber layers have been extensively studied over the three years of the project, see e.g. [16-18]. Next to the development of high-efficiency single-junction devices, specific devices aiming at (i) the highest possible current density, and (ii) the highest possible open-circuit voltage, have also been developed. This has led to the fabrication of (i) a device that gives a current density > 20 mA/cm² at a negative bias voltage of -1 V, as presented in our last annual report, and (ii) a device with an open-circuit voltage > 1 V [16, 18]. This latter device was achieved using a high H₂/SiH₄ dilution in the gas phase during deposition, at a high process pressure of 9 mbar and at relatively low substrate temperatures. To get a better stability, and to make the top cell deposition temperature compatible with middle and bottom cell deposition, the deposition temperature for the high gap top cell was fixed at 200°C for all silicon-based layers in the device.

We thus managed to fabricate excellent high-gap top cells with a limited degradation rate. Table 1 summarizes the most relevant device parameters obtained, both in initial state and after ~300 h of light-induced degradation. The a-Si:H top cells have such a thickness that they give the desired current density when applied in triple-junction devices and were deposited on the same superstrate type as most triple-junction devices. In Figure 2, the External Quantum Efficiency (EQE) curves before and after light-soaking are shown for a 170 nm-thick solar cell with a high-gap absorber layer. The figure shows a slightly reduced EQE after light-soaking on over basically the entire relevant wavelength range, suggesting a slight degradation of the bulk absorber layer.

Such a high-gap solar cell was then successfully implemented as top cell in triple-junction devices, as later shown in Section 4.

Table 1: Main device parameters of newly developed high gap a-Si:H top cell in initial state and after ~300 h of light soaking

	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	Eff (%)
Initial	13.62	965	73.0	9.6
After light-soaking (~300 h)	13.11	937	66.1	8.1

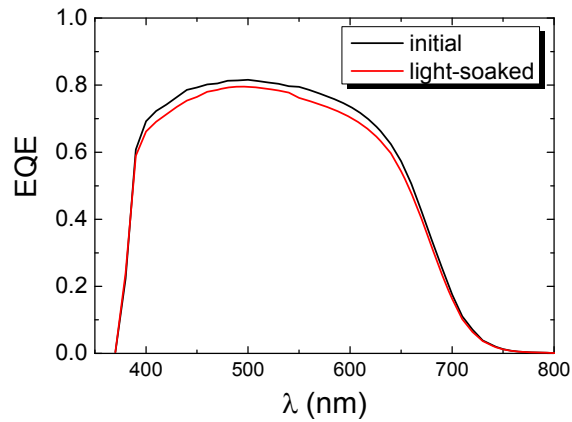


Figure 2: External Quantum Efficiency (EQE) curves of the newly developed high-gap top cell before and after light-soaking, for an absorber layer thickness of 170 nm

1.2 Realization of $\mu\text{c-Si:H}$ layers with very high near infrared absorption

Following the promising results achieved by J.-C. Dornstetter et al. [19], we decided to test the use of a fluorinated precursor during microcrystalline silicon deposition, to obtain microcrystalline silicon layers with a high crystallinity ($> 90\%$) and large grains. A similar deposition process to the one reported in [20] was hence developed in one of our reactors. Electron microscopy measurements of fluorinated microcrystalline silicon ($\mu\text{c-Si:H:F}$) layers well showed the presence of large grains (of ~ 100 nm of width) however accompanied by structural defects, such as porous zones and stacking faults within the grains, see details in [20].

Even though the electrical performance, and in particular the open-circuit voltage, of the single-junction solar cells incorporating fluorinated microcrystalline silicon as absorber layer remained lower than expected, probably because of these defects, very high short-circuit current densities could be achieved thanks to the outstanding response in the near infrared. This way, up to a total short-circuit current density (J_{sc}) of 31.9 mA/cm^2 was reached in a tandem incorporating $\mu\text{c-Si:F:H}$ for a total silicon thickness of less than $3.5 \mu\text{m}$ [21].

1.3 Optimized processes and certified single-junction record efficiency

The role of plasma excitation frequency on $\mu\text{c-Si:H}$ material quality was studied by comparing VHF (40.68 MHz) and RF (13.56 MHz). We demonstrated that this latter provides better solar cells for moderate growth rates of around 5 Å/s or less [22]. While both frequencies allow for the growth of very good bulk material quality, electron microscopy measurements however highlighted that the absorber layer deposited at 13.56 MHz is denser than when deposited at 40.68 MHz. However, at larger growth rate on rough morphology, VHF leads to better material quality and higher solar cell efficiency.

Combining all advances, a champion device was obtained in 2013 (Figure 3). This efficiency of 10.7% (as certified by Fraunhofer ISE) is significantly higher than the previous value of 10.1% held by Kaneka corporation, but in the meantime the world record was claimed by the National Institute of Advanced Industrial Science and Technology (AIST, Japan) with an outstanding value of 11.8% [23].

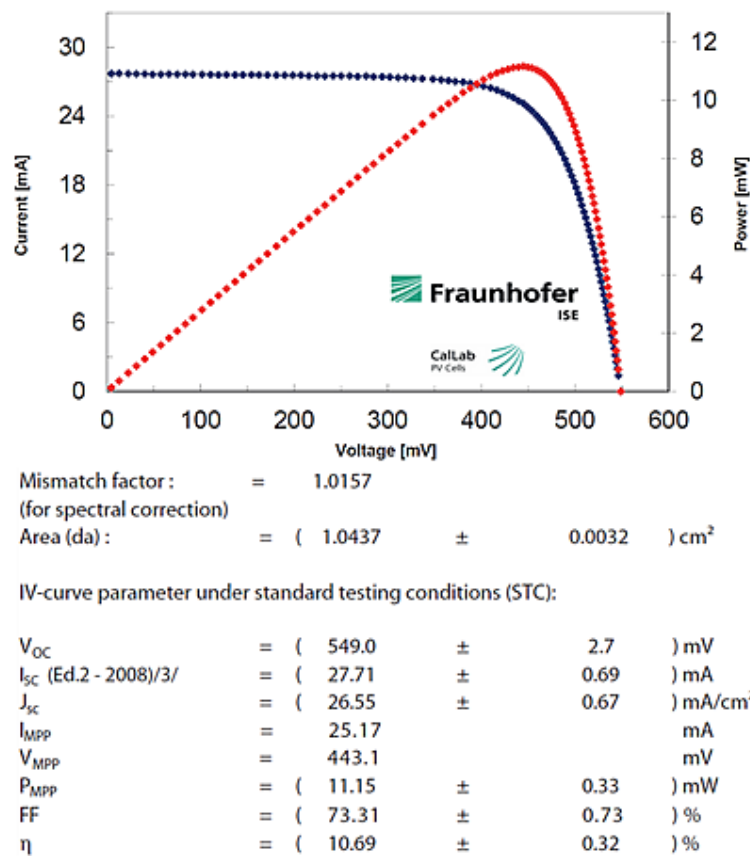


Figure 3: IV curve and electrical parameters of the certified record microcrystalline silicon single junction device achieved in 2013. The present world record – 11.8% - is held by the National Institute of Advanced Industrial Science and Technology (Japan) [23].

2. Novel buffer layers for silicon thin film solar cells

2.1 Buffer layers based on novel alloys (SiGe/C/N/O)

Silicon oxide (SiO_x) buffer layers were successfully incorporated in both amorphous silicon [16, 24] and microcrystalline silicon solar cells [24, 25], and are currently used in state-of-the-art devices by all groups active in the field. Comparison of cells with and without SiO_x buffer suggest that enhanced electrical performances arises from (i) an anti-reflecting effect (in combination with a p-doped SiO_x layer), (ii) an improvement of the collection efficiency, (iii) a shunt-quenching effect and (iv) a possible reduction of boron contamination in the absorber layer linked to deposition conditions.

Furthermore, carbide (a-SiC:H) buffer layers were also applied in amorphous silicon solar cells incorporating a wide-bandgap absorber layer [16].

2.2 Passivating layers for high- V_{oc} microcrystalline silicon solar cells

Similarly as in the heterojunction technology, a passivating silicon interlayer was introduced at the i-n interface in p-i-n single-junction microcrystalline silicon solar cells. For thin devices ($\sim 500\text{nm}$), that are particularly sensitive to interface quality, V_{oc} values above 600mV could hence be reached by implementing such interlayer in state-of-the-art devices (Fig. 4). Furthermore, such a high open-circuit voltage value could be, for the first time, maintained for crystallinity values up to 70%, with all silicon layers deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD). A remarkable V_{oc} value of 1.53V could hence be demonstrated in a micromorph tandem cell by

combining this microcrystalline cell with a high-gap amorphous silicon top cell. Improving the inter-interfaces is thus one of the keys towards higher V_{oc} s in microcrystalline silicon devices.

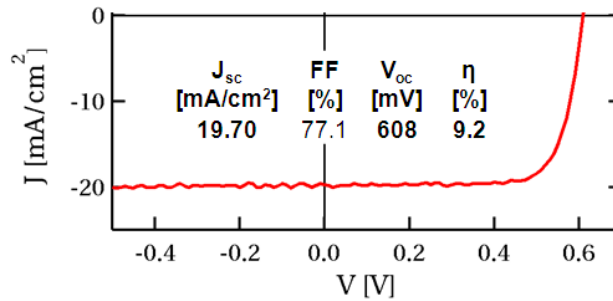


Figure 4: IV characteristic of a thin high- V_{oc} microcrystalline cell implementing a passivating interlayer

3. Light trapping

3.1 Fundamentals of light trapping (analytical model)

A statistical model was refined towards a better description of parasitic absorption in the supporting layers and an improved description of the light scattering process [11]. Applied to microcrystalline solar cells on two types of substrate texture, it became clear that these do not provide a Lambertian light scattering into the silicon layers upon the first scattering event at the front interface. Based on scaling laws that underlie the model, we would expect that features with a higher inclination angle are preferable for ideal light scattering [12]. The model is also helpful to identify the origin of losses in present devices, suggesting that parasitic absorption is dominant with respect to sub-optimal light scattering. The light absorbed with present light trapping schemes in 1- μ m-thick microcrystalline cells is able to provide current densities up to 33 mA/cm². The difference to measured current densities of 25 mA/cm² in such devices is explained by an equivalent of ca 1 mA/cm² due to insufficient scattering and ca. 6 mA/cm² due to parasitic absorption. This finding is a strong motivation to further improve the transparency of the doped layers and the transparent contacts.

3.2 Improved electrical properties of transparent conductive oxide (TCO) layers

A hydrogen plasma post-deposition treatment was developed for Low Pressure Vapor Deposited (LPCVD) Zinc Oxide (ZnO) layers: an improvement of mobility was observed for all standard electrodes, which surpasses the improvement observed when a simple annealing step is performed. The largest increase was observed for the non-intentionally-doped sample (+70%), with mobility values up to 60 cm²/V/s for 2- μ m-thick layers [26]. Furthermore, this plasma treatment can advantageously be performed on the back electrode of complete solar cells and leads, in this case, to an improvement of both the TCO layer but also the solar cell [27].

3.3 Front and rear electrodes optimized with respect to the developed silicon layers

3.3.1 Development of metallic back reflectors for single-junction devices

A systematic study was made regarding the impact of the back reflector with respect to the front-electrode morphology. In particular, we proposed a novel type of back reflector consisting of a thin layer of LPCVD ZnO:B (in the order of 100 nm) combined with silver; this back reflector was introduced as an alternative to our traditional dielectric back reflector, made of a 5- μ m-thick LPCVD ZnO:B rear electrode in conjunction with a dielectric quasi-Lambertian white sheet. In contrast to conventional metallic back reflectors, where the ZnO buffer layer is deposited by rf-

sputtering, we privileged the LPCVD deposition method for ZnO deposition in order to prevent degradation of the silicon layers that might result from mechanical or sputter-induced damaging (as reported in [28]). Prior to the deposition of the metal back reflector, a short Ar-plasma surface treatment (typically of a few minutes) was made to smoothen out the nanorough surface texture at the ZnO:B/Ag interface; this treatment was introduced as an efficient way of drastically reducing the nanoroughness-induced plasmonic absorption in Ag.

For single-junction $\mu\text{c-Si:H}$ cells deposited on state-of-the-art Z5 45' LPCVD ZnO:B front electrodes – where 45 refers to the duration of the Ar plasma treatment – the implementation of a metallic back reflector led to a noticeable improvement of the light trapping in the red and near infrared wavelength range. Applying a very rough front-TCO texture (Z5 20'), no real gain was measured with the metallic back reflector as compared to the dielectric back reflector; in contrast, for cells deposited on a smooth front electrode (denoted as Z5 80'), the gain in photocurrent (see Fig. 5) with the metallic back reflector became even more pronounced than on Z5 45'. The detailed results of this study can be found in [29].

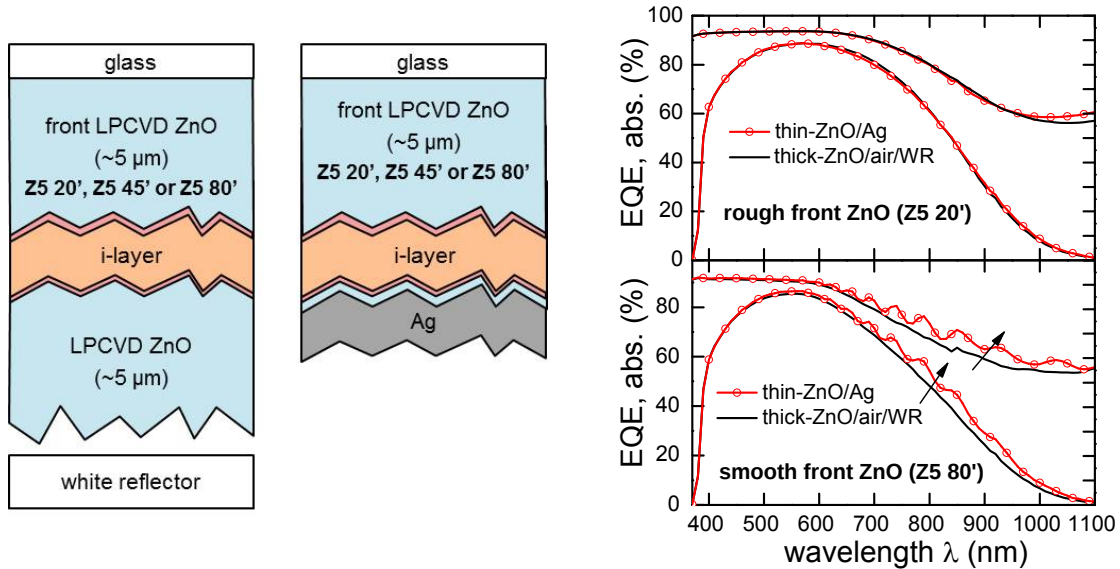


Figure 5: Sketch of solar cells applying the two types of back reflector, namely the white sheet (left) and the metallic back reflector (right). EQEs of solar cells applying the two types of back reflector grown on a rough (Z5 20') and a smooth (Z5 80') front electrode.

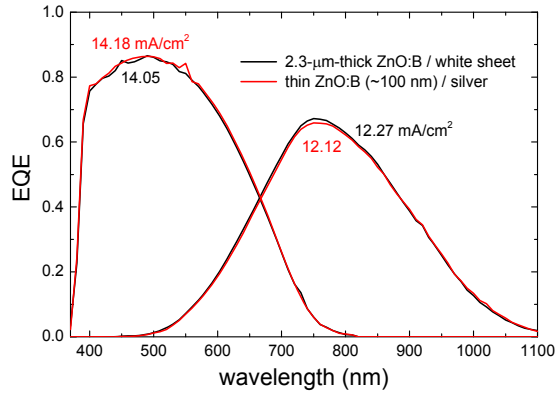
In addition to the optical gain that results from the incorporation of the metallic back reflector, the FF also benefits from the higher lateral conductivity of the metal as compared to LPCVD ZnO:B. Overall, an increase in conversion efficiency from 9.1% to 10.2% (with no antireflective coating) could be achieved in 2.2-μm-thick $\mu\text{c-Si:H}$ solar cells (1 cm²) using the newly optimized combination of smooth front electrode (Z5 80') and silver back reflector. Furthermore, efficiencies up to 10.6%, among the highest in our laboratory (and worldwide), could be obtained in an industrial KAI reactor with an antireflective coating at the air/glass interface.

3.3.2 Extension to the case of multi-junction devices

We broadened the study to the case of multi-junction devices, first, to the case of micromorph tandem solar cells – here deposited on a 2.3-μm-thick state-of-the-art front electrode (referred to as Z2.3). We established that, in this case, both types of back reflector provide similar optical cell performance, which translates into almost identical current densities in the component cells. This is illustrated in Fig. 6, where nearly similar EQEs are obtained for co-deposited micromorph cells applying (i) a thin layer of ZnO:B (~ 100 nm) combined with silver and (ii) a 2.3-μm-thick ZnO:B rear electrode in conjunction with a white sheet. Still, we demonstrated a gain in FF with the metallic back reflector, ascribed to the higher conductivity of silver as compared to the thick ZnO:B

rear electrode (see Fig. 6, right). The improved fill factor (FF) translates into an absolute efficiency gain of 0.3% (11.9% to 12.2%).

However, we observed that the gain in FF becomes less pronounced as the number of junctions in the device increases (i.e. from a micromorph to a triple-junctions configuration) because of the lower current density.



Back refl.	J_{sc} (mA/cm ²)	Voc (mV)	FF (%)	Eff (%)
white refl.	11.8	1380	73.9	11.9
silver	11.9	1380	74.5	12.2

Figure 6: (left) EQEs of co-deposited micromorph tandem cells applying the two types of back reflector, i.e. the standard 2.3- μ m-thick ZnO:B layer combined with a white-sheet, and a thin ZnO:B layer (~ 100 nm) in conjunction with silver; (right) Corresponding cell parameters derived from the I-V measurements under AM 1.5g.

4. Coupling in multi-junctions

4.1 Micromorph record device in superstrate configuration

Starting from the internal record efficiency of 11.8% in the stabilized state and 13.7% in the initial state in micromorph tandem configuration, the conversion efficiency was further improved over the subsequent years by combining all recent advances in terms of process and device architecture. In particular, the application of a geometric anti-reflective coating at the air/glass interface, produced by nano-imprinting [30] and up-scalable [31, 32], as well as the incorporation of SiO_x material as (i) doped [33], (ii) buffer [16, 24] and (iii) improved IRLs led to an efficiency of 12.3% in 2013 and a certified efficiency of 12.6% in 2014 [8], among the highest reported for thin film silicon technology.

This record was only very recently overtaken by the National Institute of Advanced Industrial Science and Technology (AIST) with a certified tandem efficiency of 12.7% [12]. TEL Solar also reported a certified efficiency of 12.34% at the module size (gen-5) equivalent to 13.2% at the cell size [34]. Finally, Delft University was able to reach an outstanding micromorph initial efficiency of 14.8% [9] following a close collaboration with PV-Lab.

4.1.1 Sets of doped and buffer layers for the fabrication of record tandem devices on rough substrates

The same doped and buffer layers already implemented in single-junction devices have been used in tandem micromorph devices. But, additionally, a new process has been developed in the PECVD octopus system to obtain low-index n-doped SiO_x layers, in particular for implementation as IRL. As the top cell suffers from light-induced degradation, it is crucial to keep the absorber layer as thin as possible while still achieving a high current density; this can be obtained by promoting reflection of the light back to the top cell, by reducing the refractive index of the IRL. With a relatively high pressure (4 mbars compared to typically < 1 mbar), we were able to fabricate SiO_x layers with an excellent quality.

By varying the CO₂ to silane flow ratio over a wide range (extending to 6:1), very low refractive indices could be obtained, as low as 1.75 at 600 nm (see Fig. 7, left) with no additional series re-

sistance in the device. When used as an IRL in a micromorph tandem, this low refractive index resulted in a very large top-cell photocurrent boost; Fig. 7 (on the right) shows the EQE achieved for tandem cells incorporating these layers, plus a reference without any intermediate reflector. The tandem device fabricated with the highest CO₂ flow in these series had a stabilized, independently confirmed, conversion efficiency of 12.63% ($V_{OC} = 1.38$ V; $J_{SC} = 12.83$ mA/cm²; $FF = 71.3\%$) [8].

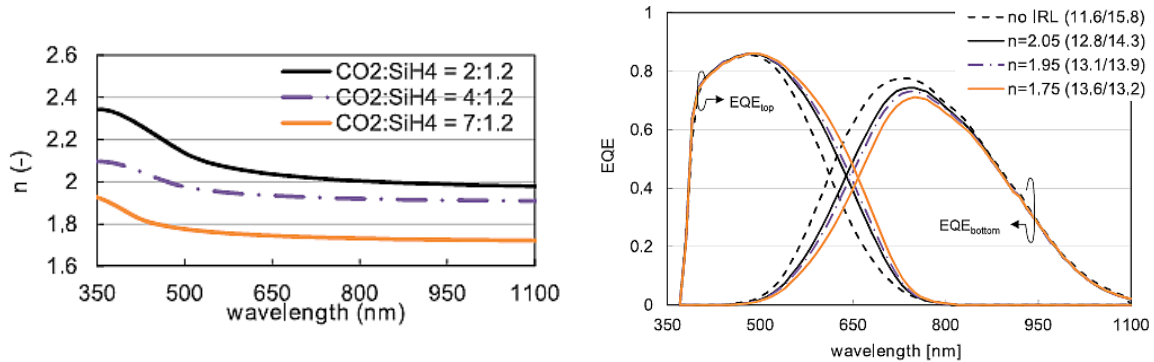


Figure 7: (left) Wavelength-dependent refractive index for three different 70-nm-thick layers with varying CO₂ flow. (right) EQE curves (initial) of tandem cells employing these intermediate reflector layers [6].

4.1.2 Record module by Tokyo Electron (TEL Solar)

A very close collaboration with industry took place during the 3 years of the project, more particularly with TEL Solar, which was able to reach an impressive stabilized module efficiency of 12.34% (independently confirmed) [34]. This efficiency was obtained on a Gen 5-size (1.1 x 1.3 m²) and demonstrates an efficiency increase of as much as 1.5% absolute compared to the previous best value. This result was achieved by joint efforts of TEL Solar Trübbach, TEL Solar-Lab Neuchâtel and TEL Technology Center Tsukuba in Japan.

This record module features several characteristics and properties that have been recently disclosed [35]: (i) a dedicated narrow gap reactor was used, which led to the fabrication of improved μ c-Si:H absorber layers due to reduced defect densities, (ii) a H₂ plasma was applied which led to a mobility increase of the ZnO-based electrodes, and (iii) a Gen 5 anti-reflective coating was added to the front glass of the modules. Furthermore, a report was recently published that covers most of TEL Solar developments [36].

4.2 Triple-junctions record devices in superstrate configuration

Two types of triple-junctions solar cells were investigated within the last three years, the first based on the a-Si:H/ μ c-Si:H/ μ c-Si:H p-i-n configuration [37] and the second with the a-Si:H/a-SiGe:H/ μ c-Si:H p-i-n configuration [38]. Simple architecture and sub-cell combinations were used here, keeping the same building blocks as available for single-junction or tandem devices.

For the first configuration, no specific IRL was applied between top and middle cell. For the best cells, the top cell thickness was kept very thin (~ 140 nm), which led to a low light-induced degradation (5%-7% relative loss in efficiency); the thickness of the middle and bottom cell μ c-Si:H absorber layers was 1.5 μ m and 2.6 μ m, respectively. With this configuration, triple-junctions solar cells with an initial efficiency of 13.7% and a stable efficiency of 12.8% were fabricated on > 1 cm² with a total Si thickness below 4.3 μ m. I-V characteristics of the corresponding cell under AM1.5g are shown in Fig. 8.

In other devices, summed current densities over 30 mA/cm² could be demonstrated, for only ~ 4.2 μ m of μ c-Si:H, by using IOH (In₂O₃:H) on replicated nanotextured front structures instead of the conventional LPCVD ZnO:B front electrode.

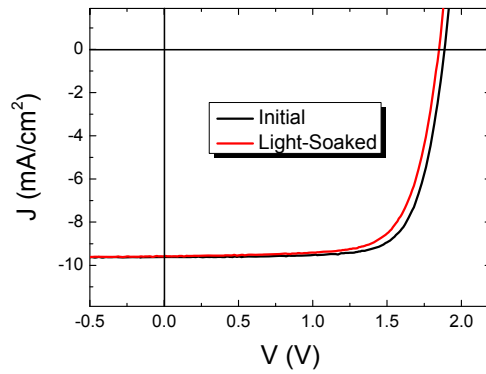


Figure 8: *I-V characteristics under AM1.5g of our best triple-junctions solar cell in the initial (13.7%) and light-soaked state (12.8% after 1000 h) demonstrating a very low light-induced degradation*

In a-Si:H/a-SiGe:H/ μ c-Si:H triple-junction cells, an IRL is introduced between the middle and the bottom cell since the a-SiGe:H middle cell absorber suffers from severe light-induced degradation. Moreover, incorporating an IRL allows not only the use of a thinner middle cell absorber but also the use of a lower Ge-content, leading to higher V_{OC} and FFs. Our best Ge-based triple-junctions cell was achieved using thicknesses of 130 nm, 220 nm and 2.6 μ m for the top, middle and bottom cells, respectively. We obtained an initial efficiency of 13.6% and an efficiency of 11.3% after light-soaking [38].

4.3 Incorporation of best superstrates to realize stabilized efficiencies above 13.5% in tandem or triple-junctions configuration

As already mentioned, we were able to fabricate tandem devices with initial and stabilized efficiencies as high as 14.1% [39] and 12.6% [8], respectively, and triple-junctions devices with an initial efficiency of 13.7% and a stabilized efficiency of 12.8% (same cell) [37].

To overcome these efficiencies, several approaches were followed, among which the use of multi-scale textured front electrodes probably represents the most promising one. In this approach, a “U”-shape texture embossed in glass – showing either random or periodic features of several microns – is combined with a sub-micrometric texture made of LPCVD ZnO:B (with a thickness $\leq 1 \mu$ m). This approach was motivated by, first, the recent world records obtained on the so-called “honeycomb” periodic textures [40] and, second, the excellent results achieved on double-texture front electrodes [41, 42].

4.3.1 Optimized superstrates for micromorph tandem solar cells

For micromorph tandem solar cells, we showed that properly chosen single 2-D grating, i.e. with no additional submicron ZnO:B texture, can provide cell efficiencies as high as those obtained with our state-of-the-art 2.3- μ m-thick ZnO:B. We also highlighted the complementary roles of 2-D gratings and ZnO:B in double textures: similar results as those achieved with our state-of-the-art front electrode were obtained for significantly reduced ZnO layer thickness [42].

Finally, by combining sub-micrometer ZnO layers with an optimized “U”-shaped modulated textured glass superstrate provided by the Delft University of Technology (TU Delft), we were able to surpass the initial efficiency provided by our standard front electrode. The beneficial effect of this novel texture is ascribed to its smooth, growth-friendly surface morphology – granting excellent electrical properties – and also to its outstanding light-trapping ability (as revealed by the EQEs presented in Fig. 9). The beneficial impact of multi-texture can also be seen in Fig. 10, where cross sections through tandem cells on different types of front electrodes morphology are shown. The left and middle pictures show tandem cells on “standard” 1 and 2.5 μ m thick ZnO electrodes: in the first case, the small texture is not sufficient for adequate scattering of the near infra-red spectrum

whereas the rougher morphology of the thicker ZnO layer can be problematic because of defective zones forming above V-shaped valleys of the texture (illustrated by arrows). The third picture shows the combination of a 1 μm thick zinc oxide layer with a texture etched into the underlying glass substrate [43].

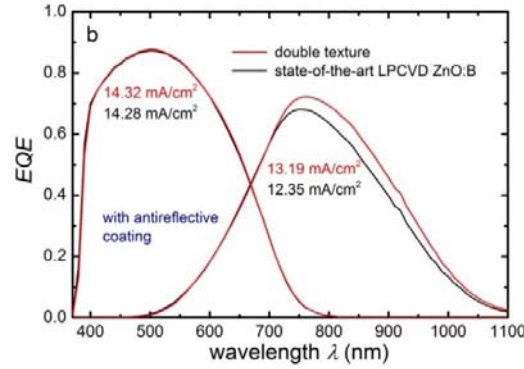


Figure 9: EQE of micromorph tandem cells deposited on the double-textured front electrode (red) and on our state-of-the-art 2.3- μm -thick ZnO front electrode (black).

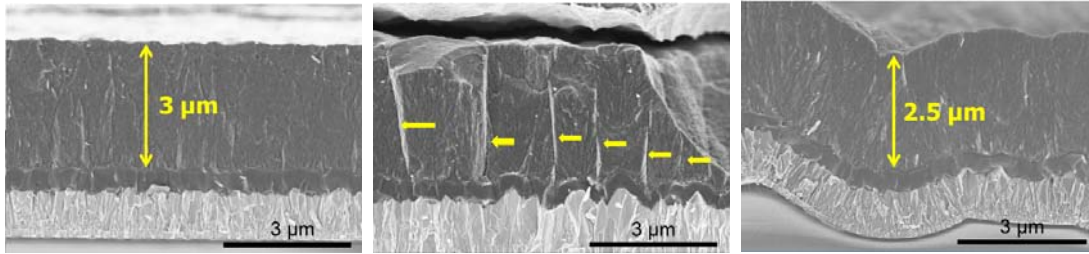


Figure 10: Cross-sections through tandem cells deposited on front Zinc Oxide with small (left) and medium texture (middle), and on Zinc Oxide with small texture but applied on textured glass (right)

The performance of the best tandem solar cell deposited on such double-textured front electrode with a 300 nm thick top cell, 100 nm thick intermediate reflector and 2.7 μm thick bottom cell is shown in Fig. 11: with an anti-reflection coating at the front, the device shows an excellent initial efficiency of 14.8% [9].

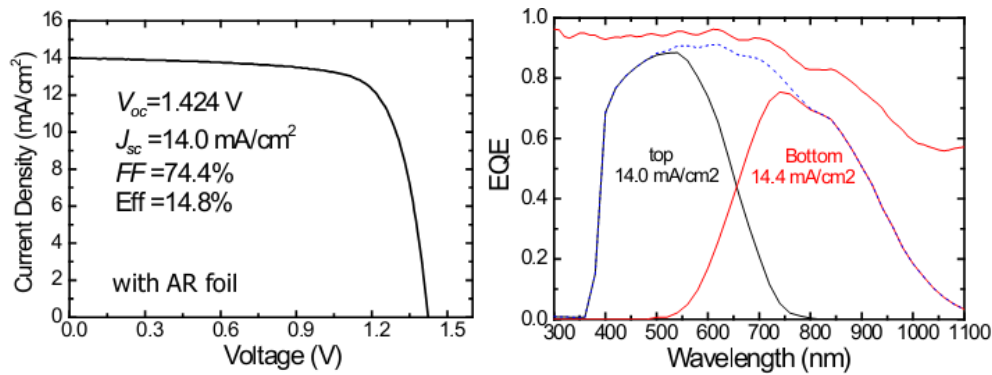


Figure 11: Initial current-voltage characteristics (left) and external quantum efficiency (right) of a micromorph tandem cell deposited at TU Delft on the modulated texture [9, 43].

4.3.2 Optimized superstrates for triple-junctions solar cells

Following the same approach, we demonstrated a significant increase ($> 1.5 \text{ mA/cm}^2$) in the bottom-cell current density of triple-junctions devices deposited on multi-scale textured front electrode,

as compared to cells grown on standard single-texture ZnO:B front electrode (see Fig. 12). The first double-texture front electrode consists of the superposition of a honeycomb texture with a period of 3.5 μm embossed in glass and a 1- μm -thick LPCVD-ZnO:B layer (see Fig. 12, on the right). The other double-texture substrate uses chemically etched glass as underlying texture. Both types of multi-scale textures provide a smooth and growth-friendly surface morphology, which results in excellent electrical properties. Overall, an initial efficiency of 14.1% was obtained on the multi-scale texture based on honeycombs, which is the highest initial efficiency measured so far in-house for triple-junctions devices with standard absorber-layer thicknesses (see Table 2).

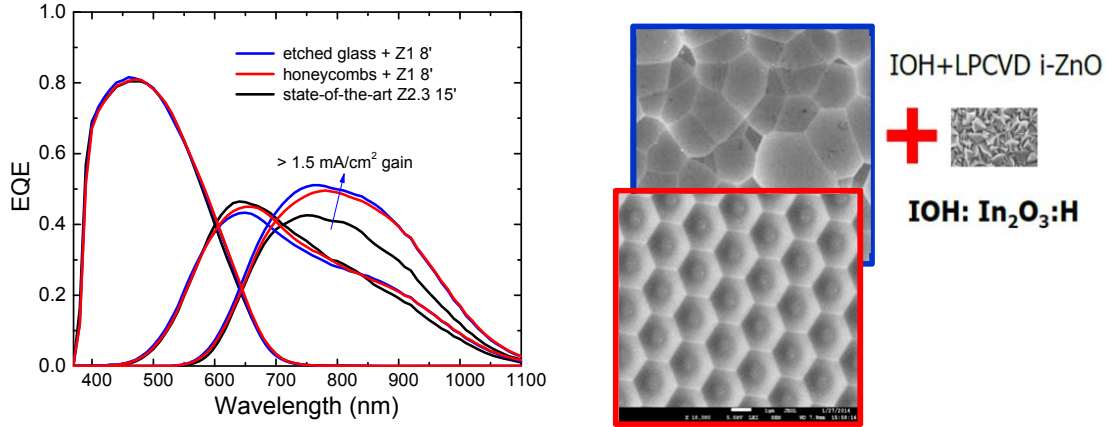


Figure 12: (left) EQEs of top, middle and bottom cells of a triple-junctions solar cell deposited on state-of-the-art single-texture LPCVD ZnO:B superstrate (Z2.3 treated for 15 minutes), and on double textured front electrodes. (right) Scanning Electron Microscopy (SEM) micrographs of randomly- and periodically-textured glass superstrates. To complete the double-texture electrode, a highly transparent and conductive indium oxide (IOH) layer as well as a thin layer of LPCVD ZnO:B are added.

Table 2: Cell parameters of as-deposited triple-junctions cells deposited on state-of-the-art and double-texture front electrodes.

Substrate	V_{oc} (V)	FF (%)	limiting J_{sc} (mA/cm^2)	Eff (%)
Z2.3 15'	1.931	77.4	8.0	11.9
Honeycombs + Z1	1.931	75.7	9.6	14.1

4.4 Quadruple cells in p-i-n configuration

A promising approach to further increase the efficiency of thin-film Si cells is the use of quadruple-junction devices. Several device configurations, including a-Si/a-SiGe/ μc -Si/ μc -SiGe [44], a-Si/a-Si/ μc -Si/ μc -Si [45] and a-Si/a-SiGe/ μc -Si/ μc -Si have been tested. For the latter configuration, a V_{oc} as high as 2.6 V was achieved [38] but the efficiency was limited to 10.1% due to the non-optimized current matching and relatively low total current. This quadruple junction device consists of a 110 nm thick a-Si:H standard gap top cell, a low Ge-content a-SiGe:H second cell (~220 nm) plus SiO_x :H intermediate reflector, a 1.7 μm thick μc -Si:H third cell, and a 2.5 μm thick μc -Si:H bottom cell. We think that stabilized efficiencies above 14% are definitely within reach with building blocks already present in the laboratory (see next section 4.5). The J-V and EQE curves of the aforementioned quadruple-junction cell are shown in Figures 13 and 14.

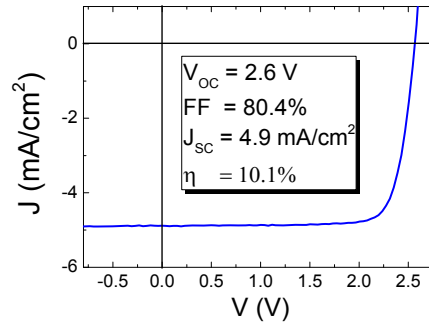


Figure 13: I-V curve of the first quadruple junction thin-film solar cell fabricated in our laboratory. The low current density and the high FF reflect the mismatch in the cell.

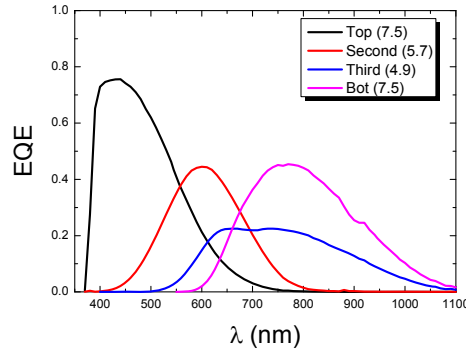


Figure 14: EQE curves of the different sub-cells of our first quadruple-junction cell.

4.5 Final integration with 15.5% initial and 13.8% stable efficiency and demonstration of the potential to reach 15% stable with multi-junctions devices

Tandem cells do not seem to have the potential to reach the desired stabilized efficiencies, so going to a larger number of junctions is crucial. Recently, AIST reported a stabilized efficiency of 13.7% for triple-junction devices [46], almost matching the desired value. Furthermore, we recently discussed a roadmap for quadruple-junction cells to obtain stabilized efficiencies above 14% with building blocks currently available in the lab [38, 47]. With these building blocks, and further improvements such as the substrates presented in section 5.3.2, stabilized efficiencies of 15% seem very ambitious, but within reach if the degradation rate of thick (~250-300 nm) a-Si:H devices can be further limited. For this purpose, the usefulness of our novel intermediate reflector layers (see section 5.1.1) has already been demonstrated but further exchanges with other laboratories remain necessary.

5. Application to high efficiency crystalline silicon solar cells

Many developments that were undertaken in this project could successfully be transferred to silicon heterojunction solar cells that consist in mono-crystalline silicon wafers passivated with thin a-Si:H layers. Such devices allow for conversion efficiencies above 21 %, also at industrial-production level.

5.1 Surface passivation properties of amorphous silicon films

It was previously established that atomically sharp interfaces between the a-Si:H layers and the wafer are crucial to obtain well passivating films [48]. Another critical early finding was that post deposition annealing at moderate temperatures can significantly improve the a-Si:H/c-Si interface passivation properties [49]. More recently, we established that such important gains are mainly driven by annealing induced changes in the microstructure of the thin a-Si:H films [50]. On a more fundamental level, we could establish that the electronic properties of a-Si:H films deposited on

crystalline silicon surfaces actually show great similarities with the properties known for bulk amorphous silicon. Briefly, for this, we investigated low-temperature annealing of a-Si:H and found an identical energy barrier for the reduction of deep defects in the bulk of a-Si:H films and at the interface that such layers form with c-Si surfaces. This finding gives direct physical evidence that the defects determining a-Si:H/c-Si interface recombination are silicon dangling bonds [51].

Importantly, the presence of an atomically sharp interface between a-Si:H film and c-Si wafer, combined with post deposition annealing to improve the surface passivation are not yet sufficient to achieve high-efficiency silicon heterojunction solar cells. We established that the passivation quality of the buffer layers should already have an outstanding level in the *as-deposited* state. This finding triggered intense research into the link between plasma deposition conditions and film properties. For this, we used a variety of tools, including quantum cascade laser spectroscopy, to verify the so-called silane depletion fraction in our plasmas [52]. We assessed that the best passivation films are deposited under highly depleted plasmas, meaning that a large fraction of the injected silane molecules are dissociated into radicals during film growth [53]. However, such conditions can easily lead to the earlier mentioned undesired epitaxial growth [28]. We resolved this issue by the introduction of a layer-by-layer deposition sequence of the thin buffer layers, where short hydrogen plasmas are inserted during the deposition sequence [54, 55]. Using such optimized buffer layers, we achieved aperture-area certified efficiencies on 4 cm² cells of 22.14% ($V_{oc} = 727$ mV, FF = 78.4%) and 21.38% ($V_{oc} = 722$ mV, FF = 77.1%) on n- and p-type FZ wafers, respectively, proving that heterojunction schemes can perform almost as well on high-quality p-type as on n-type wafers. To our knowledge, this is the highest efficiency ever reported for a full silicon heterojunction solar cell on a p-type wafer, and the highest V_{oc} on any p-type crystalline silicon device with reasonable FF [56]. Fig. 15 presents an example of heterojunction solar cell as developed at PV-Lab.

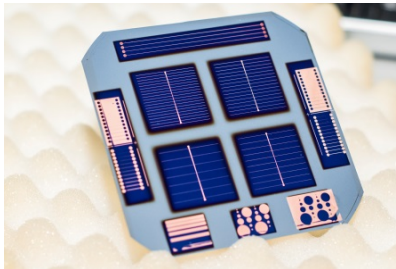


Fig. 15: Example of c-Si based heterojunction solar cell as developed at PVLAB.

5.2 Improvements in optical design

Following the establishment of well performing passivating contacts, based on thin a-Si:H films, yielding proven high voltages, our attention was focused on how to improve the current generated by our devices. A first evident loss is caused by the frontside metallization. For this, usually low-temperature silver pastes are used. Narrower and taller lines can be obtained by stencil printing. More important gains can be obtained by copper plating. In our work, we plated fingers as thin as 10 micron, with a 1:1 aspect ratio, yielding important gains in short-circuit current density. Obviously, replacing silver by copper also has attractive cost advantages. Thanks to the fact pure metals are deposited, the line conductivity of such fingers is also much better than that of metal pastes. Interestingly, copper metallization appears to be also well compatible with silicon heterojunction technology, as the used transparent conductive oxides, such as ITO, are good barriers against copper in-diffusion [57].

Important gains can also be obtained by addressing potential losses in both short and long wavelengths. Accurate photon ‘accountancy’ can be done by simply comparing the external quantum efficiency of a solar cell with its 1 – reflectance curve. The discrepancy between both curves represents absorbed photons that did not contribute to collected current. In our devices, we find that at the front the collection efficiency of carriers generated in the ITO and doped a-Si:H layers is zero, and only 30% of light absorbed in the intrinsic a-Si:H layer contributes to the short-circuit current

[58]. Some of these optical losses can be mitigated by replacing the amorphous silicon films by wider bandgap amorphous silicon oxide layers. In our work, we tested stacks of intrinsic amorphous silicon and amorphous silicon oxide as front intrinsic buffer layers and showed that this increases the short-circuit current density by up to 0.43 mA/cm^2 due to less reflection and a higher transparency at short wavelengths [59].

However, we found that the gain in current is more than offset by losses in fill factor. Aided by device simulations, we linked these losses to impeded carrier collection, fundamentally caused by the increased valence band offset at the amorphous/crystalline interface. We show this in Fig. 16 where temperature dependent IV characteristics are presented. From the evolution of the shape of these curves, one can infer that the cells with a silicon oxide layer on the hole collecting side do impede hole collection. From this, we conclude that it may be preferable to collect electrons at the a-SiO_x:H buffer layer side, as the larger VB offset should not impede electrons. In that case, the cell architecture should be redesigned towards a rear-emitter cell (when using n-type wafers).

Next, the front transparent conductive oxide layer is another source of significant optical and electrical losses in silicon heterojunction solar cells, mainly because of the trade-off between free-carrier absorption and sheet resistance. As its thickness and carrier density are constrained by anti-reflection and lateral conduction requirements, the front TCO can be improved only by increasing its electron mobility. Motivated by this, we demonstrated that hydrogen-doped indium oxide (IO:H), which has an electron mobility of over $100 \text{ cm}^2/\text{Vs}$, reduces these losses compared to traditional, low-mobility transparent conductive oxides. Unfortunately, this layer suffers from high contact resistance at the interface of the IO:H layer and the silver front electrode grid. This problem was avoided by inserting a thin indium tin oxide (ITO) layer at the IO:H/silver interface. Such IO:H/ITO bilayers have low contact resistance, sheet resistance, and free-carrier absorption, and outperform IO:H-only or ITO-only layers in solar cells. With this, we obtained a certified efficiency of 22.1% for a 4-cm^2 screen-printed silicon heterojunction solar cell employing an IO:H/ITO bilayer as the front transparent conductive oxide [14]. Figure 17 presents the illuminated IV characteristic of this device.

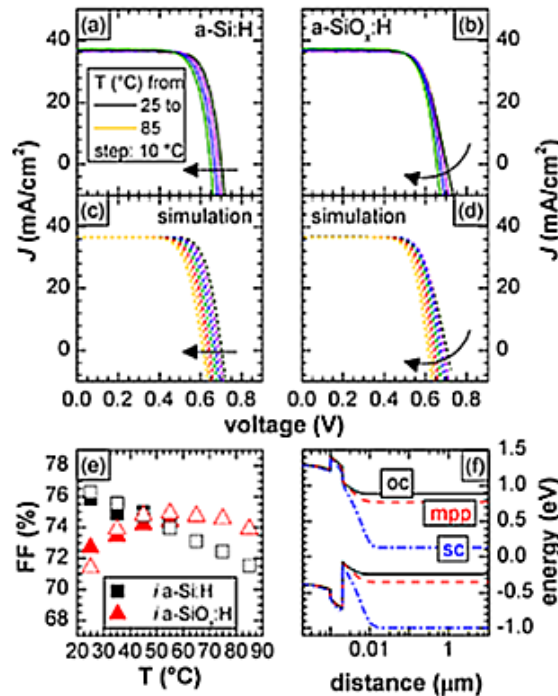


Figure 16: (a), (b) J-V measurements (temperature: 25–55 degr. C in steps of 10 degr. C) and (c), (d) simulations (25–85 degr. C, in steps of 10 degr. C) for devices with an i a-Si:H or i a-SiO_x:H front passivation layer. The arrows indicate the increasing temperature and illustrate the different behaviors. (e) FF evolution with temperature (filled symbols: J-V measurements, open symbols: simulation) for both cells. (f) PC1D simulation of the energy bands close to the a-SiO_x:H/c-Si interface in short-circuit (sc), at maximum power point (mpp) and in open-circuit (oc) conditions.

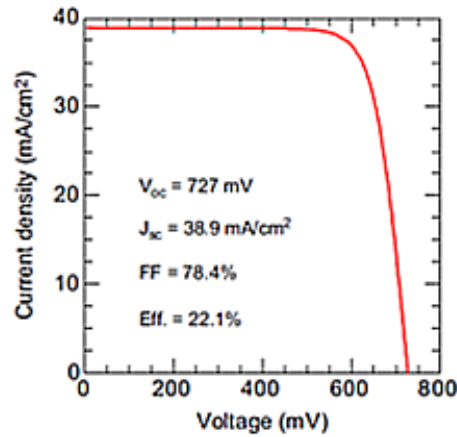


Figure 17: Current density–voltage characteristic of a record 4-cm² SHJ solar cell employing an optimized IO:H/ITO front bilayer. Certified by Fraunhofer ISE CalLab.

Transparent conductive oxides also play an important role at the rear of our devices. For this, we made an extensive experimental investigation of the TCO layers, indicating that the rear layer serves as a crucial electrical contact between amorphous silicon and the metal reflector [60]. If very transparent and at least 150 nm thick, the rear TCO layer also maximizes infrared response. An optical model that combines a ray-tracing algorithm and a thin-film simulator revealed us why: parallel-polarized light arriving at the rear surface at oblique incidence excites surface plasmons in the metal reflector, and this parasitic absorption in the metal can exceed the absorption in the TCO layer itself. Thick TCO layers—or dielectric layers, in rear-passivated diffused-junction silicon solar cells—reduce the penetration of the evanescent waves to the metal, thereby increasing internal reflectance at the rear surface. Importantly, with an optimized rear TCO layer, the front TCO dominates the infrared losses in heterojunction solar cells.

The optical design of a solar cell can be further improved by inserting a dielectric between its absorber and rear metal electrode, as this increases the rear internal reflectance by both limiting the transmission cone and suppressing the plasmonic absorption of light arriving outside of the cone [61]. Following this philosophy, we fabricated rear reflectors with low-refractive-index magnesium fluoride (MgF₂) as the dielectric, and with local electrical contacts through the MgF₂ layer [62]. These MgF₂/metal reflectors are introduced into amorphous silicon/crystalline silicon heterojunction solar cells in place of the usual transparent conductive oxide/metal reflector. An MgF₂/Ag reflector yields an average rear internal reflectance of greater than 99.5% and an infrared internal quantum efficiency that exceeds that of the world-record UNSW PERL cell. An MgF₂/Al reflector performs nearly as well, enabling an efficiency of 21.3% and a short-circuit current density of nearly 38 mA/cm² in a silicon heterojunction solar cell without silver or indium tin oxide at the rear.

Ultimate design freedom at the front can be obtained by adapting the back contacted structure to silicon heterojunction solar cells. In that case, the only requirements for the layers present at the front are good surface passivation, high transparency, and anti-reflective properties. In our work, we fabricated back-contacted silicon heterojunction solar cells with conversion efficiencies above 21%. Our process technology relies solely on simple and size-scalable patterning methods, with no high-temperature steps. Using in situ shadow masks, doped hydrogenated amorphous silicon layers are patterned into two interdigitated combs [63]. Transparent conductive oxide and metal layers, forming the back electrodes, are patterned by hotmelt inkjet printing. With this process, we obtain high short circuit current densities close to 40 mA/cm² and open-circuit voltages exceeding 720 mV, leading to a conversion efficiency of 21.5%. However, moderate fill factor values limit our current device efficiencies. Unhindered carrier transport through both heterocontact layer stacks, as well as higher passivation quality over the minority carrier-injection range relevant for solar cell operation, are identified as key factors for improved fill factor values and device performance. These are topics of intense further investigation in our lab.

6. Reliability and Characterization

6.1 Reliability

6.1.1 Damp-heat tests in microcrystalline cells

Dark degradation of $\mu\text{c-Si:H}$ material represents one of the major issues for the long-term stability of $\mu\text{c-Si:H}$ -based thin film silicon devices. Although this degradation - metastable and linked to water vapor ingress – was demonstrated to be reversible after annealing (similarly to light-induced degradation), its effect needed to be further investigated to be able to predict solar cell performances in stabilized state. In order to accelerate the degradation process and gain further insights, degradation tests were performed in climatic chambers in damp heat conditions at 100% humidity and 50°C.

Microcrystalline silicon solar cells showed a similar degradation after only 2 days in the DH chamber compared to 2 months in ambient air storage, underlying the relevance of this method for a faster probing of the stability of $\mu\text{c-Si:H}$ -based devices. Further accelerated degradation tests of micromorph tandem solar cells (this time in DH conditions similar to those for modules certification (85°C, 85%)) revealed that the metastability of multi-junction devices is clearly linked to the density of the $\mu\text{c-Si:H}$ absorber layers. In particular, no significant degradation was observed for devices containing $\mu\text{c-Si:H}$ material with a high density, deposited at rf-frequency and low deposition rate [22]. Noteworthy, degradation arising from the IRL was also identified as a possible source of metastability [8].

6.1.2 Water ingress in crystalline silicon PV module

The impact of moisture ingress on long-term PV module performance is key point for many technologies (thin-film silicon, but also crystalline silicon (c-Si), CIGS,...). For c-Si based modules, different parameters contribute to the possible failure of modules with humidity: the type and formulation of the encapsulant material, the module design (e.g. either glass/glass or glass/backsheet) and the climate corresponding to the location where the module is installed. We could in particular simulate, with 2-D finite element method (FEM) the water penetration as a function of module configuration and time, in a cool and humid climate such as Neuchâtel.

These results were part of those presented at the last NREL reliability Workshop in February 2015, where Eleonora Annigoni got the “Best Poster Award”, and additional results can also be found in the 2014 annual report on this project. Fig. 18 presents the expected water concentration as a function of time, for a glass/glass (G/G) and a glass/backsheet (G/BS) module configuration for three positions within the module: at the edge (E) and at the back (B1, back of first cell from the edge, B2 back of the second cell) and/or front (F1, front of the first cell).

The simulations confirm that the water penetration is much faster in the G/BS configuration because of the permeability of the backsheet material. Indeed, Fig 18 shows that the moisture content at the back of the cells is already larger in G/BS after 1 year than at similar place in G/G after 20 years (red curves). Furthermore, in G/BS configuration, seasonal variations are clearly visible with an increase in water concentration during cold and humid winter.

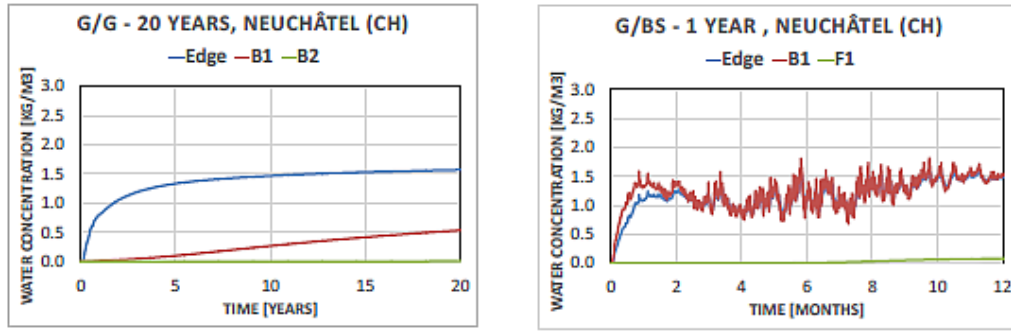


Figure 18: 2-D FEM simulations of the water concentration as a function of time and module configuration (glass/glass (G/G) and glass/backsheet (G/BS)), for three positions within the module: at the edge (E) and at the back (B1, back of first cell from the edge, B2 back of the second cell) and/or front (F1, front of the first cell). These simulations correspond to c-Si modules located in Neuchâtel. Note that the time scale is in years for the G/G configuration and in months for the G/BS, where a much faster water ingress is observed because of the backsheet permeability

6.2 Characterization

6.2.1 V_{oc} and FF separation in micromorph devices

To probe the quality of each sub-cell composing micromorph tandem devices, setups aiming at V_{oc} separation, FF analysis and complete I - V separation [64] were developed. The latter was shown to enable a more precise characterization of micromorph tandem solar cells and corresponding sub-cells than other existing techniques; the suitability of the developed technique is illustrated in Fig. 19, left [65]. Furthermore, the development of micromorph cells also benefited from the use of single-junction μ c-Si:H solar cells deposited on an amorphous n-layer (fake a-Si) to reproduce both the morphology and the optical filtering of the a-Si top cell in tandem devices (Fig. 19, on the right).

Results regarding the dependency of the photocurrent mismatch on FF and efficiency values of micromorph devices were presented in an extended presentation at the IEEE conference in Tampa Bay, and published in a journal paper [66]. By comparing simulated and experimental data, it was shown that the deposition rate of the bottom cell can impact the degradation of the top cell in tandem devices.

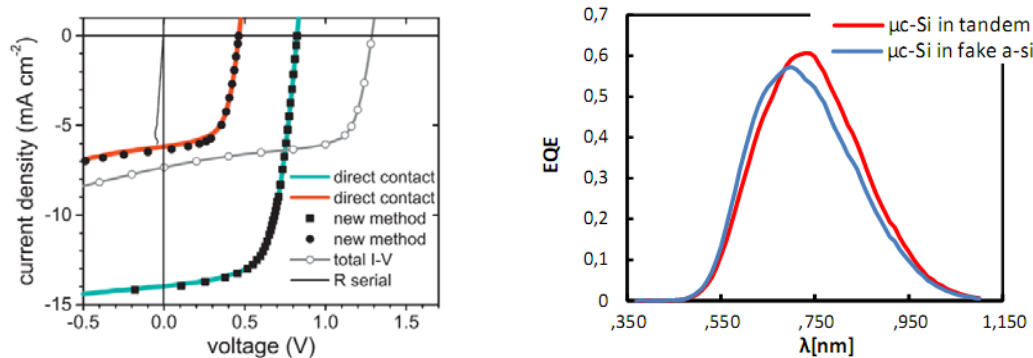


Figure 19: (left) Illustration of the I - V separation method, showing the I - V curves of a micromorph device including a conductive interlayer, the curves obtained with the I - V separation method for both sub-cells, and the I - V curves measured for both sub-cells in direct contact with the conductive interlayer; (right) Illustration of the optical filtering provided with the "fake a-Si" method, which corresponds well to the filtering of a top cell in micromorph conditions.

6.2.2 Accelerated degradation with 3-sun illumination system

A 3-sun illumination system based on LEDs was designed and fabricated for accelerated light-induced degradation testing of a-Si:H-based solar cells. Characterization of the spectrum indicated that the quality is better than class A. Temporal stability was measured to be well below $\pm 2\%$ for a 6 h period (class AAA). The spatial homogeneity of the light intensity was measured to be 2% on the full illumination area ($16 \times 16 \text{ cm}^2$). In contrast to standard degradation setups, typically working at 1 sun illumination, the advantage of this setup is obviously its higher intensity; in addition, the use of different types of LED offers a great spectral flexibility over the spectrum range 400-750 nm. To finish, the simulator is completed with an I - V measurement setup and a temperature controlled sample stage that allows for standard characterization but also for performance tracking during light soaking. Further details on this setup can be found in [67]. In the meantime, several academic institutions approached PV-Lab for permission to rebuild or copy this design.

7. Brief infrastructure overview

Various new equipments were purchased and set in operation during the 3 years of the project, including PECVD systems dedicated to thin film silicon and heterojunction solar cells developments and two new LPCVD systems (a large-area tool and a high-temperature tool) for TCO developments. Furthermore new gas sources were also implemented such as SiF_4 , Ge and TMGa and the characterization park was completed with set-ups developed within this project and described in paragraph 6. End of 2013, PV-Lab moved to a new building (Microcity) but all the characterization and deposition equipments were gradually set back in service in the second half of 2014.

National and international collaborations

Regular academic contact/scientific and sample exchanges were maintained both with national and international entities (ETH Zürich, Zürich University of Applied Sciences, CSEM Neuchâtel, EMPA, Forschungszentrum Jülich, Helmholtz Zentrum Berlin, Academy of Science Prague, University of Delft, Energy Research Center Netherlands, Berkeley University and National Laboratories, Caltech, National University of Singapore, AIST Japan. Strong exchanges now also take place with the CSEM PV-center, for TCO and crystalline silicon based solar cells developments, as well as regarding module reliability, where the fundamental aspects are studied at PV-Lab.

PV-Lab has been - until very recently - or is still involved in several European projects (Fast Track, Flex-o-Fab, Pliant, Hercules, CHEETAH, Next Buildings) as well as national projects (CCEM Connect-PV, Nanoterra, SNF projects). Furthermore, two NRP project just started end of 2014: the first one, PV 2050, addresses the topic of multi-junctions solar cells based on various combination of thin films (chalcogenides, perovskites, novel dye sensitized devices) or including a bottom crystalline cells with the potential to reach conversion efficiencies close to 30%. The second one, Active Interfaces, tackles the main obstacles that have so far limited the full deployment of PV integrated in the built environment.

A strong synergy existed between most of these projects and this SFOE project. In addition, collaborations with industrial partners have been ongoing, either in the frame of CTI projects or through direct mandates, e.g. with TEL Solar, Roth & Rau Research AG, Meyer Burger, Indeotec, Air Liquid, Pasan.

Perspectives

The layers and processes developed in the frame of this project have allowed reaching remarkable lab efficiencies. Industry has also demonstrated significant progress on large scale that result in virtually the same efficiency on 1.43 m^2 as on record 1 cm^2 cells. The levels reached today are remarkable, but in the mean-time the crystalline Si market could reach a volume size and production costs which were not expected 4 years ago. Consequently, due to their lower conversion effi-

ciency, thin film silicon modules were not able to make their way to the mass PV market. Even though many companies stopped their activities, several manufacturers remain on the market, with still possible improvements, and thin film silicon modules remain one of the most attractive choices for BIPV solution, in black, orange or semi-transparent form. In partnership with various module makers, results of this project might hence still be implemented in the manufacturing of more efficient products.

On the other hand, the knowledge developed throughout the thin film silicon activity has allowed the achievement of highly efficient crystalline silicon solar cells based on the heterojunction structure. Promisingly, internal calculations showed that modules based on such technology, made out of thin wafers, have a chance to reach attractive costs (0.35-0.49 €/W_p) at the 500 to 1000 MW level for a 20% conversion efficiency [68]. All the layers and processes developed in this project will thus be implemented in next generation high-efficiency crystalline silicon solar cells and modules, with prospects for further improved solar electricity generation costs.

Acknowledgements

All the PV-Lab collaborators, who contributed to the results presented in this report, are warmly acknowledged, as well as exchange scientists including H. Tan from Delft, bachelor and master students and civil service participants. We also thank A. Hessler, M. Dadras and M. Leboeuf for assistance and support in electron and scanning probe microscopy, as well as the PV-center team.

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