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NEW PROCESSES AND DEVICE STRUCTURES FOR THE FABRICATION OF HIGH EFFICIENCY THIN FILM SILICON PHOTOVOLTAIC MODULES

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Abstract

The project objective was to contribute to the field of thin film silicon technology based on amorphous and microcrystalline silicon photoactive layers by findings that can lead to increased thin film silicon module efficiencies while ensuring lower costs and long-term stability. This project had four axes which focused on layers with new or better properties (e.g. new materials to be incorporated into devices), on improved processes (e.g. new plasma regimes leading to higher quality layers), on improved devices (integration of all layers into state-of-the-art devices), and on enhanced cell and module reliability.

The project focused on the use of advanced materials and optical structures to increase device efficiency. Mixed-phase p and n doped silicon oxide layers are now implemented in most devices and we were able to reveal their nanoscale filamentary structure responsible for their unique properties. In particular, it could be shown that these layers reduce the parasitic absorption (increase in current) and improve the performance of devices deposited on substrate with high roughness. These layers are now routinely used for most amorphous and microcrystalline cells. A new understanding of the impact of plasmas on the growth on rough substrates was acquired, allowing disentangling effects linked to bulk material issue from effects linked to porous zones appearing on rough substrates. Strong accent was also on improving cell stability by minimizing light induced degradation and gaining better control over the morphology evolution which is important for the growth of high quality silicon layers. Much effort went into the development of new concepts for the transparent front electrode to improve transparency and conductivity, including the introduction of non-intentionally doped zinc oxide, zinc oxide bilayers and hydrogenated indium oxide. But also new concepts to overcome the trade-off between light trapping and electrical cell performance were introduced including nanoimprinting, nanomoulding and multi-scale electrode architectures.

Combining many individual novel concepts and improvements, a micromorph cell with an excellent initial efficiency of 14.1% was demonstrated within the project, a 1.5% absolute improvement with respect to the final results of the preceding 2005-2007 OFEN project. Stabilized efficiencies increased moderately from 11.1% to 11.5% for solar cells on glass. Noteworthy the trend toward thinner bottom cells (from 3 um to 1.2 um), allows identical stabilized efficiencies but opens the perspective for higher throughput in industry. Microcrystalline silicon solar cell efficiency improved from 9.9% to 10.9% compared to the preceding project period. Based on the project findings, we expect now to be able to bring the stabilized efficiencies to significantly higher level.

Globally, the findings of the project should contribute to lower the cost of thin film silicon modules, while continuing increasing efficiencies. Production costs of 0.35 to 0.44 €/W_p should soon be possible for modules containing only 1-1.5 micron of silicon and two zinc oxide layers, making it further one of the most attractive technology for a world with a significant solar electricity share.

Zusammenfassung

Das vorliegende Projekt begann im Dezember 2007 und endete im Dezember 2011. Hauptziel war es, Solarzellen und –module auf der Basis von Dünnschichtsilizium weiterzuentwickeln. Die Forschungsarbeiten dienten dem Ziel, einerseits die Wirkungsgrade zu steigern, andererseits die Produktionskosten zu senken, letztlich aber auch die Zuverlässigkeit der Produkte zu verbessern. Das Projekt startete in einer weltweiten Phase der Euphorie da fast 20 neue Produktionslinien anliefen oder angekündigt waren (2007-2010), wovon fast 10 in direktem Bezug mit der Schweizer Industrie standen. Der starke wirtschaftliche Druck Ende 2011 führte zu einer gespannten Lage und zwang alle Dünnschicht Technologien, schnelle Fortschritte in Richtung kostengünstiger Industrialisierung zu erzielen.

Das Projekt basierte auf vier Hauptachsen:

1) **Realisierung von dünnen Schichten mit neuen oder verbesserten Eigenschaften**, welche eine Integration in die Solarzellen erlaubt (aktive Silizium Schichten aber auch nicht aktive Schichten, wie transparente leitfähige Elektroden),

2) **Entwicklung verbesserter Abscheidungsprozesse** (schnelle Plasmaprozesse, die dennoch hohe Schichtqualität erlauben),

3) **Implementierung neuer Schichten und Abscheidungsprozesse in Zellen** mit höherem Wirkungsgrad und potentiell tieferen Fabrikationskosten,

4) **Untersuchung von Faktoren, die die Langzeit Zuverlässigkeit der Schichten beeinträchtigen,** um eine Lebensdauer von mindestens 25 Jahren garantieren zu können.

Diese vier Hauptachsen wurden durch zwei Transversalachsen vervollständigt:

a) Anpassung der Einrichtungen und Anlagen, um eine leistungsstärkere Forschung zu ermöglichen und die Industrie zu unterstützen,

b) Strategische Überlegungen, um zur Kostenreduktion unter 1€/Wp beizutragen.

Die Hauptresultate dieses Projektes verbinden jeweils mehrere dieser Achsen und sind im folgenden zusammengefasst:

- Eine neue Art von dotierten Siliziumoxid Schichten ist entwickelt worden. Durch das Beimischen von Sauerstoff werden diese Schichten transparenter als traditionelle dotierte Schichten, und sie weisen einen tieferen Brechungsindex auf. Es konnte gezeigt werden, dass die Schichten je nach Prozessführung eine phasengetrennte nanometrische Filamentstruktur ausbilden, durch die sich Einbussen in der Leitfähigkeit verhindern lassen. Ausserdem erlauben diese Schichten eine wesentliche Verbesserung nicht nur der optischen Eigenschaften, sondern auch gleichzeitig des Wachstums von Zellen auf raueren Substraten. Siliziumoxid Schichten werden inzwischen in den meisten Zellen, die in unserem Labor hergestellt werden, verwendet und finden bereits Anwendung auf industrieller Ebene.
- Eine besseres Verständnis des Einflusses von Plasmaprozessen auf die Qualität der mikrokristallinen Schichten konnte erreicht werden. Es hat sich herausgestellt, dass die Plasmaeigenschaften die porösen Zonen, die sich auf rauen Substraten bilden, kritisch beeinflussen, jedoch für die intrinsische Materialqualität viel weniger von Bedeutung sind. Die phasengetrennten Siliumoxidschichten erlauben den negativen Einfluss poröser Zonen teilweise zu kompensieren, aber die Wahl geeigneter Plasmabedingungen für raue Substrate erweist sich als essentiell, um Zellen mit hohen Wirkungsgraden zu erzielen.
- Die Entwicklung neuer Elektroden, die sowohl starkes Light Trapping als auch günstige Wachstumsbedingungen bieten, wurde wesentlich vorangetrieben. Fortschritte wurden bei der Realiserung von transparenteren Elektroden erzielt (z.B. mit Zinkoxid Doppelschichten, nicht-dotierten Zinkoxid Schichten oder Wasserstoff dotierten Indium Oxid Schichten) aber auch bei der Realisierung von Elektroden mit speziell geeigneten Oberflächenstrukturen, die via Nanoimprinting und Nanomoulding hergestellt wurden. Dadurch lassen sich Rauhigkeiten auf zwei unterschiedlichen Längenskalen vereinen indem man zunächst grosse Strukturen in ein transparentes, UV-härtbares Polymer stempelt und dann mit den natürlichen Oberflächenstrukturen von Zinkoxid überwächst. Eine solche Doppelstrukturarchitektur führte dank hoher Stromdichte und gleichzeitig guten elektrischen Eigenschaften zu einer mikromorphen Zelle mit neuem Rekordwirkungsgrad.

- Zahlreiche innovative Strukturen basierend auf Nanodrähten und plasmonischen Nanopartikeln sind untersucht worden. Aufgrund von theoretischen Überlegungen sollten diese Konzepte prinzipiell zu einer Verbesserung der Zellleistung beitragen, in der Realität konnten sie etablierte Konzepte aber noch nicht übertreffen.
- Im Vergleich zum vorhergehenden Projekt wurde der Anfangswirkungsgrad um 10 bis 15% (relativ) verbessert. Mikromorphe und mikrokristalline Zellen erreichten einen Wirkungsgrade von bis zu 14.1% und 10.9% respektive. Alle Zellen haben von den Material- und Prozessverbesserungen profitiert. Der stabilisierte Wirkungsgrad von mikromorphen Zellen konnte leicht auf 11.5% gesteigert werden. Hinter diesen vordergründig moderaten Verbesserungen der Wirkungsgrade stecken jedoch spektakuläre Reduktionen in der Prozessdauer und damit in den Produktionskosten. So konnte im Vergleich zum vorherigen Projekt die Dicke der mikrokristallinen Siliziumschichten um einen Faktor von 2 bis 2.5 von vormals 3 auf nun 1.2 µm verringert werden. Der Wirkungsgrad der letzten Zellserie, die im Rahmen dieses Projektes realisiert wurde, sollte diesen Wert nach Stabilisierung noch um einige Relativprozente überbieten können (erwartet sind 11.8%).

Die zahlreichen wissenschaftlichen Resultate dieses Projektes wurden in über 30 technischen und wissenschaftlichen Publikation und Patenten kommuniziert. Dabei wurden zahlreiche Faktoren identifiziert, mit denen sich die Leistung von Tandemzellen aus Dünnschichtsilizium weiter steigern lässt. So sollten sich durch gezielte Verbesserung der beiden Einzelzellen Wirkungsgrade von ca 13-14% erreichen lassen. Für Dreifachzellen liegen diese Werte nochmals 1-2% höher. Auf Modulebene eröffnet sich dadurch eine Perspektive mit Wirkungsgraden jenseits der 12% Marke.

Dank dieses Projektes sind Materialien mit neuen Eigenschaften verfügbar und schnellere Produktionsverfahren wurden etabliert. Dank einer besseren Lichteinkopplung benötigen die Solarzellen ausserdem weniger Rohmaterial. Diese drei Punkte sind unumgänglich, um die Herstellungskosten von Dünnschichtsiliziummodulen weiter zu senken, da die relativ lange Abscheidungszeit der mikrokristallines Schichten wesentlich zu den Kosten beiträgt. Durch die Verwendung von mikrokristallinen Schichten mit Dicken von weniger als einem Mikrometer konnte Oerlikon Solar in ihren neuen Produktionslinien « Thin Fab II » Module mit einem Wirkungsgrad von über 10% für Produktionskosten von 0.35 bis 0.44€/W demonstrieren. Die ausgezeichnete Ökobilanz einer Technologie die auf unbedenklichen und reichlich verfügbaren Materialien beruht, wird durch die Verwendung von solch dünneren Schichten nochmals wesentlich verbessert. Dünnschichtsilizium ist gerüstet für eine Zukunft in der steigende Energiebedürfnisse durch Solarstrom gedeckt werden.

Résumé

Le présent projet s'est déroulé de décembre 2007 à décembre 2011. Son objectif principal était de contribuer au développement des technologies en couches minces de silicium pour les applications photovoltaïques. Au travers d'une recherche avancée, il s'agissait d'identifier et de comprendre les facteurs permettant soit une amélioration du rendement des cellules solaires, soit une diminution des coûts de production, soit une meilleure fiabilité. Le projet a démarré dans un contexte mondial euphorique par rapport à la thématique puisque près de 20 nouvelles lignes de production ont été démarrées ou annoncées à cette période (2007-2010), dont près d'une dizaine en lien avec des industries Suisse. Le contexte était plus tendu, dans un environnement compétitif fort à fin 2011, et a forcé les couches minces à faire des progrès rapides pour démontrer le potentiel d'une industrialisation à très bas coût.

Le projet avait quatre axes principaux qui incluaient :

1) **la réalisation de couches minces avec des propriétés nouvelles** ou améliorées et qui puissent être intégrées dans les cellules solaires, que cela soit des couches actives (i.e. en silicium) ou des couches non actives, tels les électrodes transparentes conductrices,

2) **la mise au point de procédés de fabrication** améliorés (par exemple des procédés plasma plus rapide ou donnant des couches meilleures),

3) la combinaison de ces couches et procédés de fabrication pour **obtenir des dispositifs plus performants**, que cela soit au travers d'un meilleur rendement, ou, par exemple, au travers d'une réduction potentielle du coût de fabrication,

4) une partie du projet s'est attachée à considérer les **problèmes de fiabilité des couches utilisées**, afin de garantir une durée de vie d'au moins 25 ans des matériaux utilisés.

Ces quatre axes principaux étaient complétés par deux axes transverses:

a) l'adaptation des structures de recherches et des équipements pour une recherche plus performante, y compris dans le soutien aux industries,

b) des considérations stratégiques pour contribuer à l'abaissement des coûts de production bien en dessous du 1€/Wp.

Les résultats majeurs du projet lient toujours plusieurs des points mentionnés ci-dessus et peuvent être résumés de la manière suivante :

- Des couches d'oxydes dopés conducteurs d'un nouveau type ont été développées. Ces couches sont conductrices, mais plus transparentes que les couches dopées standard, avec un indice de réfraction plus faible. Il a été possible de déterminer que ces couches sont biphasées avec une structure filamentaire (d'une épaisseur de quelques nanomètres seulement) responsable de leurs propriétés uniques. En particulier, ces couches améliorent fortement non seulement les propriétés optiques (moins d'absorption parasite) des cellules solaires, mais permettent également la croissance des cellules solaires sur des supports ou substrats plus rugueux. Ces couches sont maintenant largement utilisées dans la majorité des cellules fabriquées dans notre laboratoire et commencent déjà à être employées par certains industriels.
- le rôle des procédés plasma sur la qualité des couches microcristalline a pu être bien mieux compris. En particulier, il apparait que les propriétés du plasma sont très critiques pour les zones poreuses qui apparaissent lorsque la couche croît sur un substrat très rugueux. Elles le sont moins pour la qualité du matériau principal, tel que déposé par exemple sur un substrat plat. Les couches d'oxydes du point précédent permettent de compenser en partie les problèmes liés au plasma sur les substrats rugueux, mais le choix de conditions plasma appropriées sur substrats rugueux est un point qui devient désormais central pour la réalisation de cellules à hauts rendements.
- Un effort conséquent a été consenti pour le développement et le test d'un ensemble de nouvelles électrodes qui doivent permettre à la fois un bon piégeage de lumière et une croissance des couches actives favorables. Des progrès ont été réalisés dans la réalisation d'électrodes moins absorbantes (par exemple avec des couches de ZnO en bi-couches ou non-dopées, ou encore des couches d'oxydes d'indium hydrogénés) ou d'électrode à surface « désignée » telle qu'obtenue en nano-réplication ou nano-moulage. La réalisation d'architectures « multi-échelles » a été démontrée

grâce à la nano-réplication d'une surface texturée dans un polymère transparent, suivi de la croissance d'une couche rugueuse d'oxyde transparent conducteur apportant la deuxième texture. Cette architecture d'électrode novatrice a permis de garder un courant élevé dans les dispositifs tout en améliorant les autres paramètres électriques, permettant les rendements record en cellule micromorphe mentionnés plus loin.

- De nombreuses structures innovatrices basées par exemple sur des nano-fils ou des nanoparticules plasmoniques ont également été étudiées, avec des démonstrations de principes de fonctionnement mais des résultats pour l'instant en deçà de ceux obtenus avec des structures plus traditionnelles.
- Par rapport au projet précédent les rendements initiaux ont pu augmenter de 10 à 15% relatif. Des cellules micromorphes à 14.1% de rendement initial ont été réalisées, ainsi que des cellules microcristallines à 10.9% de rendement. Toutes ces cellules ont bénéficiés des améliorations de procédés et matériaux décrits précédemment. Les rendements stabilisé des cellules micromorphes ont légèrement gagnés à 11.5% stable, mais, de manière spectaculaire des rendements identiques au projet précédent sont maintenant obtenus avec des couches de silicium microcristallin 2 à 2.5 fois plus faible (i.e. 1.2 µm vs 3 µm). Les dernières séries préparées dans le cadre de ce projet devraient dépasser de plusieurs pourcents relatifs ces derniers résultats (rendement escomptés à 11.8%).

Les nombreux résultats scientifiques issus de ce projet ont été consignés dans plus de 30 publications techniques et scientifiques, ainsi qu'au travers de brevets. De manière générale, la plupart des facteurs qui limitent la performance des dispositifs multi-jonction en couche minces ont été identifiés et des solutions trouvées. La prochaine étape importante sera d'être capable de mieux découpler les performances des sous-cellules qui composent par exemple la micromorphe, afin d'atteindre le potentiel de rendement qui se trouve à 13-14% pour des jonctions doubles et 1 à 2% plus haut pour des jonctions triple. Cela ouvre des perspectives pour des modules avec des rendements au-delà de 12%.

Grâce à ce projet, de nouveaux matériaux ont été développés, une meilleure compréhension des procédés a permis la mise en place de procédés plus adaptés, et des dispositifs utilisant moins de matières ont pu être développés, notamment grâce à de grandes améliorations optiques (électrodes et couches dopées moins absorbantes). Ce dernier point est crucial car il permet de réduire un des principaux coûts dans la fabrication des panneaux en couches minces de silicium, à savoir le dépôt de la couche de silicium microcristallin. En utilisant des couches microcristallines de moins d'un micron d'épaisseur, Oerlikon Solar montre que les lignes de fabrication de nouvelle génération « Thin Fab II » devraient permettre la production de modules à un coût de 0.35 à 0.44€/W avec des rendements supérieurs à 10%. Cela reste accessible en utilisant uniquement des matériaux abondants et non toxiques, et avec un bilan environnemental encore amélioré grâce à l'affinement des couches. Cela devrait contribuer à faire grandir l'impact de la technologie du silicium en couche mince dans une société (mondiale) qui se prépare à avoir largement recours à l'électricité solaire.

Introduction and background

These last four years have seen extreme changes in the field of photovoltaics (PV), and in particular in the field of thin film silicon technology. 2008-2009 will likely be remembered as the golden years, with several equipment makers selling multiple thin film silicon production lines worldwide to new entrants (e.g. 15 production lines sold by Oerlikon Solar), as well as massive investments in technology (e.g new lines at Flexcell, Yverdon). These massive industrial investments have allowed or forced the resolution of many problems linked to upscaling (e.g. homogeneity of layer deposition on large area) and product reliability.

Several tens of companies are now producing routinely amorphous and micromorph modules with efficiencies of up to 10% using mass production tools. The best modules even reach 10.8% stable efficiency at the pilot line level, e.g. at Oerlikon Solar, Sanyo or AMAT.

However, the strong price pressure on PV products, originating from the massive investments and production capacity increase in Asia, has become a concern for many companies worldwide active in module manufacturing. In this context, the economic situation for thin film silicon companies is also delicate, as most of them are still operating at relatively low production volumes but with high initial investments. The cost of thin film silicon has, hence, to be reduced further through gains in efficiency and through faster and/or cheaper processes.

Table 1: Example cost structure for a 120-140 MW production line amortized over 7 years with a residual value of 20% for a Thin Fab line in Chine, ordered in 2012-2013. Data provided by R. Benz, Oerlikon Solar

Contribution	Amount (€/W_p)	Type of cost
Capital investment	0.08-0.12	fixed
Labour	0.01	fixed
Materials	0.12-0.15	variable
Gas	0.07-0.08	variable
Utilities	0.03	variable
Maintenance	0.04	variable
Yield loss	0.01	variable
Total module manufacturing cost	0.35-0.44	

The positive aspect of the recent price pressure was to initiate processes for targeting dramatic cost reductions in the manufacturing. In the case of thin film silicon, incorporating the latest findings in research and piloting experiments should lead to module production costs well below 1 €/Wp. Indeed, incorporating several elements developed at IMT in the frame of this project, or developed currently e.g. in the frame of the EU-FP7 Pepper project, Oerlikon Solar was recently able to propose an aggressive cost reduction roadmap. This is illustrated in Table 1, which shows that even at a modest production volume of 120-140 MW, thin film silicon should prove highly competitive in terms of production costs. The next generation line should be able to deliver modules at 0.35-0.44 €/Wp (see Table 1), allowing systems costs in the range of 0.9-1.2 €/Wp for large plants, allowing solar electricity cost in the range of 5 €cts/kWh in sunny countries (assuming 1 €/Wp investments, levelized cost of electricity (LCOE) with 5% cost of capital, 2000 kWh/kWp, 0.5% annual yield decrease, 25 years lifetime and 2% maintenance costs). The cost reductions are a mixture of increased throughput (e.g. using thinner silicon layers, faster transparent conductive oxide (TCO) deposition, …), efficiency gain through better cell design (e.g. more transparent TCO, use of doped oxide layers, improved absorber materials, better laser scribing) and of a strong effort to reduce the costs of various elements in the module (reflecting polymers instead of white paste + polymer, junction boxes, …), all that while improving the product reliability.

These new module production plants should be available with capital expenditure (CAPEX) a factor of three inferior to the first lines, which is not only important in achieving cost reduction but also reduces the risk for the investors. Also, it has to be noted that only five years ago, module target manufacturing costs were in the range of 1 to 1.5 €/Wp. The last 4 years have hence seen a fast improvement in the technology, to which the past SFOE projects and this project have partly contributed.

Fig.1a. Application examples of modules manufactured e.g. by Oerlikon Solar customer (left and middle) and micromorph modules from Inventux (right).

Figure 1b. Application exemples of thin film silicon modules: amorphous flexible silicon modules from Flexcell (left) b) micromorph façade, synthesis image (middle) c) amorphous façade with modules from Schüco (right)

Figure.1c. Customized semi-transparent trapezoidal modules from Schüco/Malibu for high-end building architecture (left and middle) and a large area thin film silicon power plant (right).

Globally the perspectives for thin film silicon continue to be interesting:

1) As components of large power plants in sunny areas, thin film silicon remains one of the very attractive options with the most moderate impact on environment (no toxic materials), with no problem in the supply chain and with good life cycle assessments [see e.g. "Life cycle assessment of a micromorph photovoltaic system" Bravi M. et al., Energy 36, 4297-4306 (2011)]. For the upcoming terrawatt solar society thin film silicon is currently likely the only reliable thin film technology with no constraint in material supply. The promising low manufacturing costs need, however, to be considered in conjunction with the area related costs, which are higher for lower efficiency modules. Efforts both on module efficiency increase and lowering of area related BOS are hence key challenges for thin film silicon.

1) As esthetic building elements: the huge potential for eco-friendly and esthetic roofing or façade has remained a niche market so far. Thin film silicon modules have the potential to play a role in this market because of their pleasant natural colors as well as possible adaptation thereof (see also annual report on Archinsolar), or adaptable shape (see. e.g. customized size modules by Schüco/Malibu).

Project goals and methodology

In the general economic context, the project remained fully relevant, as its global objective was to allow for a lowering of the cost of solar electricity based on thin film silicon. In particular, this project aimed at developing materials, processes and device structures for the future generation of thin film silicon modules, based on amorphous silicon or silicon-germanium alloys, and microcrystalline silicon. The objective of this "technology push" project was, hence to make the necessary breakthroughs that would allow in the medium to long term, to further reduce module production costs at elevated efficiencies, while ensuring perfect module reliability.

Short project description (2008-2011)

The project had four major research axes, and two transversal domains, sketched in Figure 1. The project's goals were, hence, to be achieved by introducing innovation and optimisation in four major areas:

- Layers with new or better properties (e.g. new materials with higher transparency)
- Improved processes (more stable, faster processes, yielding higher quality layers)
- Increased device and module efficiency
- Enhanced cell and module reliability

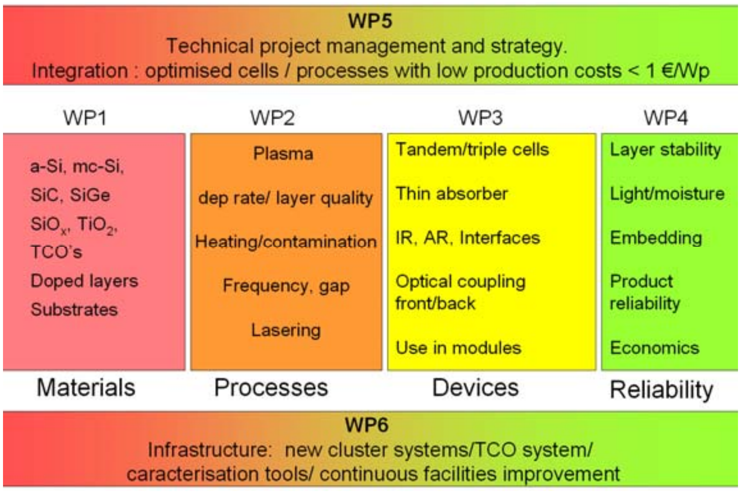


Figure 2: Summary of work packages of SFOE-EPFL PV-Lab project 2008-2011.

Work performed and results achieved 2008-2011

In what follows we summarize results achieved during this 2008-2011 SFOE project "New processes and device structures for the fabrication of high-efficiency thin-film silicon photovoltaic modules". Due to the strategic importance of the micromorph technology on glass substrates for the future of thin-film silicon photovoltaics, we retrace in section 1 roughly the timeline of micromorph cell development at EPFL's PV-Lab starting from the main achievements of the preceding 2005-2007 SFOE project "Thin-Film Silicon Solar Cells: Advanced Processing and Characterization". This report therefore does not precisely respect the division of the project into the work packages defined above. While the introduction of nanocrystalline silicon oxide layers (section 1.1) and advances in the design of the transparent electrodes (section 1.2 and 1.3) have led to significant step-wise improvements in micromorph cell efficiency, we emphasize that the continuous improvements in deposition of the silicon layers (section 1.4) were instrumental in achieving new record efficiencies. These evolutionary improvements were only possible through the continuous effort and commitment of the people involved. Recent achievements for solar cells in the substrate configuration are summarized in section 2. A status report of the module design group is given in section 3. More details on the scientific results are reported in the individual annual reports and in the publications listed in the references at the end of the report, which the reader is invited to consider. Noticeably, over 40 technical and scientific papers are directly linked to this project.

1. Micromorph cell development in superstrate configuration

1.1 Nanocrystalline silicon oxide layers

Nanocrystalline silicon oxide layers have been instrumental to the many achievements of PV-Lab during this project. This exciting new class of materials allows precise independent fine tuning of the optical and electrical properties and finds multiple applications inside thin-film silicon solar cells which allowed several new lab record efficiencies in all device configurations. Significant performance improvements over the last years underline the importance of combining the evolution of our understanding of these layers at the device level with new insights on the atomic scale structure of these materials gained by benefitting from next-generation analytic techniques.

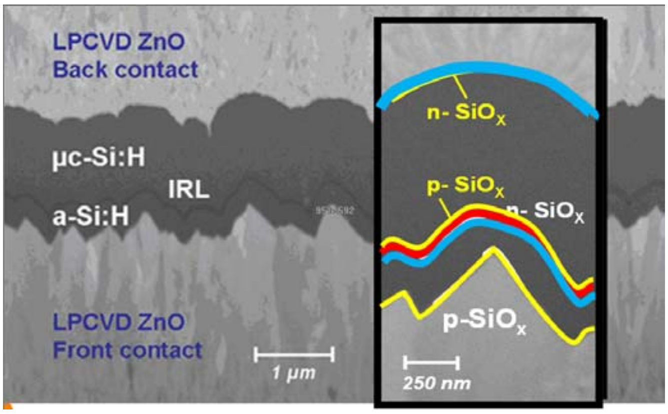


Figure 3: Scanning electron microscopy cross-section of micromorph cell illustrating the locations where the new layers can be implemented in the device.

1.1.1 Starting point: Zinc oxide (ZnO) based intermediate reflectors

The first nanocrystalline silicon oxide layers where synthesized in the context of the 2005-2007 SFOE project “Thin-Film Silicon Solar Cells: Advanced Processing and Characterization”. The initial motivation for the development of silicon oxide layers was their promising use as intermediate reflector layers between the amorphous top cell and the microcrystalline bottom cell of a micromorph tandem cell. Already in 1996, Fischer et al. [1] had introduced a sputtered ZnO intermediate reflector (ZIR) to tune the current matching in micromorph cells. In 2006, Dominé et al. [2] were able to demonstrate a maximum 2.8 mA/cm2 current gain in the top cell with a ZIR of thickness 110 nm. Using a top and bottom cell with thicknesses of 290 nm and a 3.0 um and ZIR with thickness 50 nm, a micromorph cell with Jsc=12.8 mA/cm2, Voc=1315 mV and FF=70.2% resulting in an initial efficiency of 11.8% was achieved. For an update on the topic see Ref. [3].

1.1.2 Silicon oxide based intermediate reflectors

In 2007, Buehlmann et al. [4] published a first paper on n-type silicon oxide intermediate reflectors (SOIR) deposited in the same reactor and with the same process gases as used for thin-film silicon solar cells. By varying input gas ratios, SOIR layers with a wide range of optical and electrical properties were obtained. In this paper, a micromorph cell with a top cell thickness of 270 nm, 95 nm SOIR and 1.8 um bottom cell resulting in Jsc=12.1 mA/cm2, Voc=1400 V, FF=71.9% and an initial cell efficiency of 12.2% was reported. An improved initial efficiency was reported shortly afterwards by Dominé et al. [5] using a top cell thickness of 300 nm, SOIR of 150 nm and a bottom cell with 3 um, resulting in Jsc=12.7 mA/cm2, Voc=1380 mV, FF=72.2% and an initial efficiency of 12.6 %. At the of 2008, at the EUPVSEC in Valencia, Dominé et al. [6] presented an even better cell with 340 nm top cell, 150 nm SOIR and 3.5 um bottom cell yielding Jsc=13.8 mA/cm2, Voc=1360 mV, FF=70.8 and an initial efficiency of 13.3%. The paper also reported a high stabilized efficiency of 11.1% with Jsc=12.5 mA/cm2, Voc=1320 mV, FF=67.2%.

1.1.3 Shunt quenching with silicon oxide layers

A second important application for nanocrystalline silicon oxide layers was reported by Despeisse et al. [7] in 2010 who integrated resistive silicon oxide interlayers between the active area and the back contact of the cell. They observed a massive relative increase of up to 7.5% in fill factor and of 6.8% in conversion efficiency for amorphous silicon cells deposited on highly textured substrates, together with improved yield and low-illumination performance. The observed performance gain is higher for rougher substrates, suggesting that the silicon oxide interlayer mitigates the negative effects of growth-induced areas of porous, low-density material on the electrical cell performance by quenching the resulting undesired local current drains.

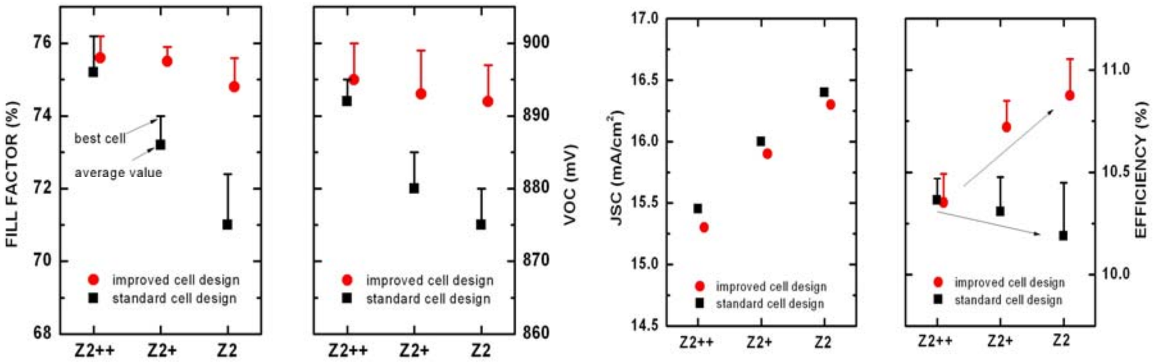


Figure 4: Initial performance of 250 nm thick amorphous silicon cell deposited on as-grown (Z2), lightly (Z2+) and heavily (Z2++) treated zinc oxide electrodes for a standard cell without and an optimized cell design with shunt-quenching nanocrystalline silicon oxide layer.

1.1.4 Silicon oxide window layers

Also in 2010, Cuony (ex Buehlmann) et al. [8] presented first results on p-type nanocrystalline silicon oxide. As for the n-type layers, p-type silicon oxide layers also help in reducing the detrimental effects of the roughness on the electrical cell characteristics. In addition, as this layers does not only create the electric field for carrier extraction, but also acts as a window layer, parasitic absorption could be reduced significantly resulting in a much improved blue response in the external quantum efficiency. On relatively flat substrates, a reduction of the reflection losses could further be observed, as the refractive index of silicon oxide is intermediate between the refractive index of the zinc oxide front electrode and the silicon absorber layer. The impact of this effect is reduced on rough substrates, as the roughness zone exhibits also an effective medium with intermediate refractive index.

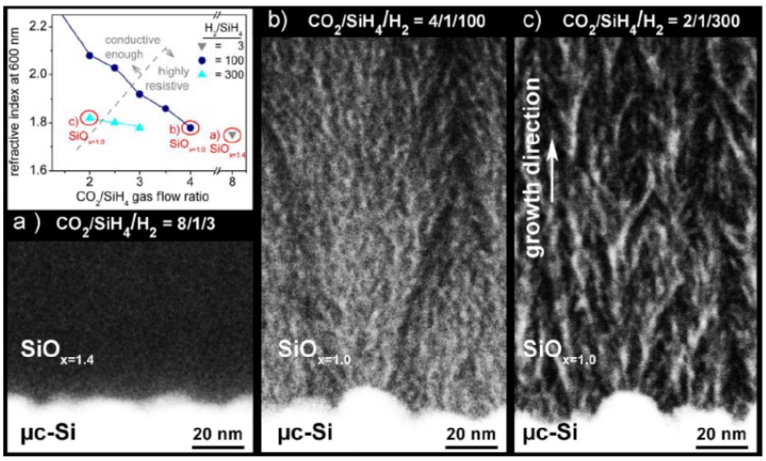


Figure 5: Transmission electron microscopy cross-section of three silicon oxide layers encircled in the inset graph, with the same refractive index of 1.8, but different nanostructure due to different input gas ratios used for deposition. The layers are grown onto a microcrystalline silicon layer to ensure a good electrical contact for transverse conductivity measurements.

1.1.5 Nanoscale phase separation in silicon oxide layers

This paper also reports first experimental evidence for the phase separation in nanocrystalline silicon oxide layers into a conducting silicon-rich region and an insulating oxide-rich region. In 2012 an indepth study on the structural properties of nanocrystalline silicon oxide layers based on advanced energy filtered transmission electron microscopy was published by Cuony et al. [9] performed in collaboration with EPFL's Center for Interdisciplinary Electron Microscopy. This study revealed for the first time the filamentary silicon structures embedded in the silicon oxide matrix and gives a clear visual explanation for the anisotropic transport properties of these layers, which are at the origin of the shunt quenching properties. Furthermore the study demonstrated that the photoluminescence wavelength of these layers can be tuned via quantum confinement by adjusting the filament size.

1.2 Front electrode transparency vs conductivity

The transparent front electrode is crucial for the micromorph cell performance. As it is the first layer of the device crossed by the incoming light, its transparency is fundamental. At the same time, it has to be sufficiently conductive to extract carriers without significant resistive losses. As conductivity is improved, transparency tends to decrease requiring a trade-off to be found. Advances at PV-Lab in improving this trade-off are discussed in the following.

1.2.1 Non-intentionally doped zinc oxide

Integration of both n- and p-type nanocrystalline silicon oxide layers together with optimized processes for the deposition of intrinsic silicon layers lead to a micromorph cell with 240 nm top cell, 70 nm SOIR and 2.8 um bottom cell with Jsc=13.8 mA/cm2, Voc=1380 mV, FF=72% resulting in an initial efficiency of 13.7%. Presented in 2010 by Boccard et al. [10] a crucial ingredient for this result was the use of non-intentionally doped ZnO electrodes, which minimizes parasitic free carrier absorption, while providing excellent light scattering. The importance of reducing parasitic absorption was investigated already earlier by Boccard et al. [11], who used identical non-intentionally doped ZnO layers deposited on top of flat indium tin oxide layers with varying thicknesses to study free carrier absorption independently from light scattering.

1.2.2 Nanoimprinting and hydrogenated indium oxide

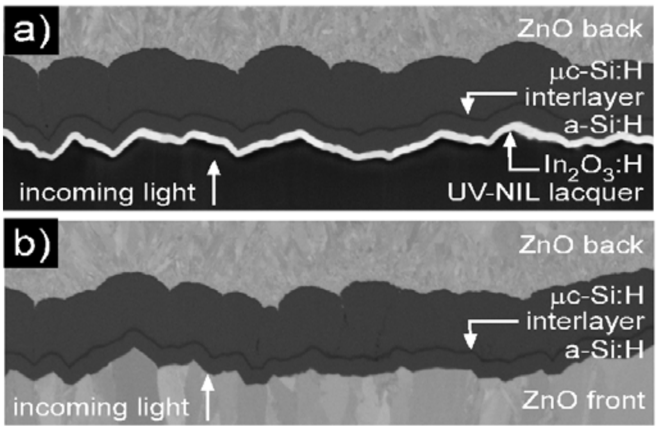


Figure 6: Scanning electron microscopy cross-section of micromorph solar cells on a replicated transparent superstrate with hydrogenated indium oxide front electrode (a) and the the standard zinc oxide front electrode (b), which served as a master for the replication process. Both cells achieved an initial efficiency of 12.0% without antireflection coating on the air-glass interface.

A similar conclusion was derived by Battaglia et al [12], who compared ZnO, indium tin oxide, hydrogenated indium oxide and non-absorbing insulating silicon nitride electrodes. This study further revealed the contribution of the doped silicon layers to the parasitic absorption and presented a method allowing one to directly relate the optical reflectance to the external quantum efficiency [13]. This method provides a useful experimental tool to evaluate the light trapping potential of novel photonic nanostructures by a simple optical reflectance measurement, avoiding complications with electrical cell performance. To obtain equivalent light scattering for all four electrodes, the morphology of ZnO was transferred onto glass using a high-fidelity nanoimprinting technique developed originally for plastic substrates by Escarré et al [14] and Söderström et al [15]. Indium tin oxide or hydrogenated indium oxide were subsequently deposited on top of the replicated morphology by sputtering to obtain a functional electrode. By demonstrating micromorph cell efficiencies as high as for state-of-the-art zinc oxide electrodes, a subsequent study validated nanoimprinting as an experimental platform to integrate arbitrary surface morphologies into high-efficiency thin-film silicon solar cells [16].

1.2.3 Thick vs thin zinc oxide electrodes

In a subsequent study, Boccard et al [17] compared a thin doped ZnO electrode with a thick non-intentionally doped ZnO electrode with identical sheet resistance and identical scattering properties but reduced free carrier absorption. Such an electrode was fabricated by polishing a thick non-intentionally doped ZnO layer followed by the deposition of a thin non-intentionally doped ZnO layer separated from the thick layer by a thin epitaxial stopping layer. Results indicated once more the importance of minimizing free carrier absorption in the electrodes to achieve high currents. This investigation further concludes that already a relatively small ZnO roughness provides sufficient light trapping in the bottom cell and allows high top cell currents thanks to excellent light incoupling and optimal interplay with the SOIR. This study presents a micromorph cell with 280 nm top cell, 70 nm SOIR, 2.8 um bottom cell exhibiting Jsc=13.8 mA/cm2, Voc=1390 mV, FF=70% and an efficiency of 13.5%. This cell design lead to the lab's highest stabilized efficiency of 11.5% with Jsc=13.5 mA/cm2, Voc=1350 mV, FF=63.8%.

1.2.4 Thinner bottom cells

At the same time, focus shifted towards thinner bottom cells compensated by a more aggressive light trapping made possible by the nanocrystalline silicon oxides. With a top cell of 260 nm, a bottom cell with only 1.1 um, Despeisse et al [18] presented a micromorph cell with 12.5 mA/cm2, Voc=1360 mV and FF=74.5% resulting in an initial efficiency of 12.7%. Although 1% lower in initial efficiency compared to the thick cell reported by Boccard et al [17], stabilized efficiencies turned out to be very close with 11.3% for this thin cell. Battaglia et al demonstrated a thin micromorph cell with 250 nm top cell, 1.1 um bottom cell and a hydrogenated indium oxide front electrode which achieved a matched current of 12.9 mA/cm2 without antireflection coating on the air-glass interface [16]. The trend to thinner bottom cell was confirmed by Oerlikon Solar with the introduction of the first generation ThinFab on September 7 2010. In the same press release Oerlikon Solar also announced their new certified world-record micromorph cell with a stabilized efficiency of 11.9% [20] obtained in collaboration with Corning Incorporated.

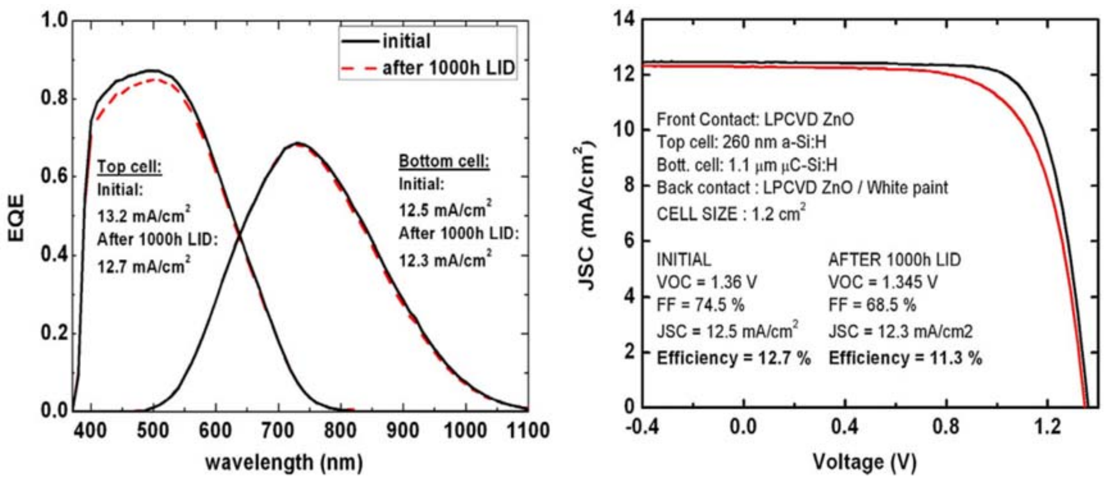


Figure 7: a) External quantum efficiency and b) IV characteristics of a thin micromorph cell before and after light soaking with a only 1.1 micron thick bottom cell achieving a stable efficiency of 11.3%.

1.2.5 Zinc oxide bilayers

Ding et al introduced ZnO bilayers consisting of a highly boron-doped nucleation layer followed by a non-intentionally doped bulk ZnO layer. This approach enables the growth of larger pyramids at equivalent thickness resulting in enhanced light scattering and improved carrier mobility at reduced carrier densities for equivalent sheet resistances. Bilayers were also observed to be more resilient to damp heat degradation compared to non-intentionally doped films with equivalent sheet resistance, which represents an additional important advantage for the integration in industrial modules. In the frame of the EU-FP7 project Pepper, ZnO bilayer processes were transferred to Oerlikon Solar were they replace the standard ZnO layers in the ThinFab production lines.

1.3 Silicon layer quality vs light trapping

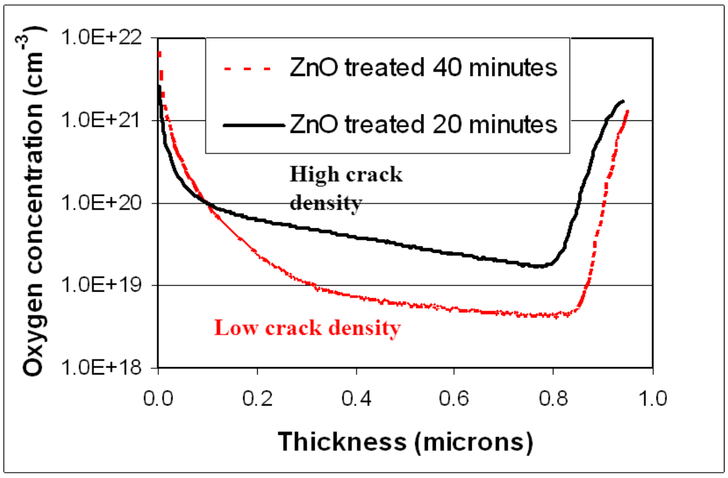
In addition to providing maximum transparency at a high conductivity level, the front electrode is further in charge of coupling and trapping light efficiently in the absorber layers. As it also serves as substrate for cell deposition, its morphology must be suitable for high-quality absorber material growth. This represents the second trade-off between optical and electrical cell performance addressed in this section.

1.3.1 Argon plasma treatment

Developments at PV-Lab during the previous SFOE project period had introduced thick ZnO layers for maximizing light scattering in the bottom cell. Increasing the ZnO thickness was also a mean of reducing the parasitic free carrier absorption as it enabled a reduction of the boron doping while maintaining sufficient conductivity. These modifications results in the desired increase in current but also lead to a significant reduction in the electrical cell performance characterized by Voc and FF. In 2006, Bailat et al [22] introduced an argon plasma treatment to adapt the morphology of thick ZnO layers for optimum silicon layer growth which enabled a microcrystalline silicon single junction cell with a remarkable efficiency of 9.9% with Jsc=24.7 mA/cm2, Voc=545 mV, FF=74.1%. Although not mentioned explicitly before, this argon plasma treatment was applied to all the front electrodes discussed above and has been instrumental to the improvement of the micromorph cell efficiencies. While thick ZnO layers require a long treatment time of up to 60 min, new generation thin ZnO electrodes usually receive a 4 min plasma treatment.

1.3.2 The detrimental role of cracks

Python et al [23] carried out a detailed investigation of the effect of substrate morphology on the growth and electrical properties of microcrystalline silicon solar cells. They showed that cell performance improved when going from the genuine V-shape of as-grown ZnO electrodes to the optimized U-shape of plasma-treated ZnO electrodes and showed that this effect is universal, i.e. independent of the substrate and feature size. U-shaped substrates prevent the formation of areas of porous, low-density material (often called ‘cracks’ due to their appearance in scanning and transmission electron microscopy images) in the active absorber which are detrimental for electrical device performance. Numerical simulation of the growth process reproduced satisfactorily these experimental findings. Also it was demonstrated that this porous phase is prone to oxidation as seen in Fig. 8. The role of the plasma processes in influencing the properties of these cracks is now much better understood (see part 1.4.1).



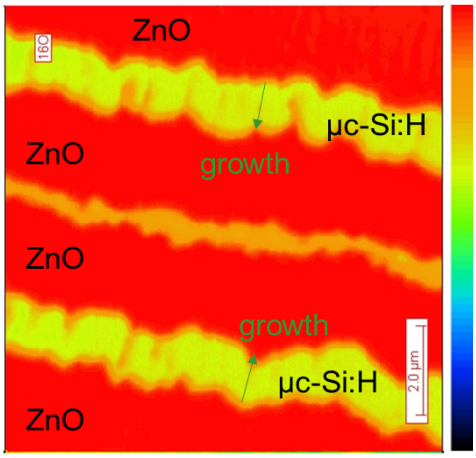


Figure 8: Oxygen penetration into a microcrystalline silicon layer grown on a rough substrate as measured by nano secondary ion mass spectrometry. In the image to the right, red areas are oxygen rich, yellow areas are silicon rich. Besides the high oxygen concentration in the ZnO and doped silicon oxide layers, one can also clearly distinguish oxygen penetration into the cracks of microcrystalline silicon.

1.3.3 Titanium oxide antireflection layers

Although the electrical performance could be improved, the argon plasma treatment also causes a slight, but important, reduction of current due to increased reflection of light out of the cell. Primary reflection at the interface between ZnO and silicon is also a problem for sputtered ZnO electrodes which are subsequently etched in hydrochloric acid to obtain a rough morphology with U-shaped craters. However, this morphology is very well adapted for the growth of high quality microcrystalline silicon layers enabling high Voc and FF values. During the previous SFOE project, Buehlmann et al [24] had studied the use of TiO2 antireflection layers between the ZnO and silicon layers and showed that important gains in current can be achieved on relatively flat, for example strongly treated, ZnO electrodes, but that the gain reduced with increasing roughness, as the roughness zone acts as an effective medium with intermediate refractive index, which also reduces reflection.

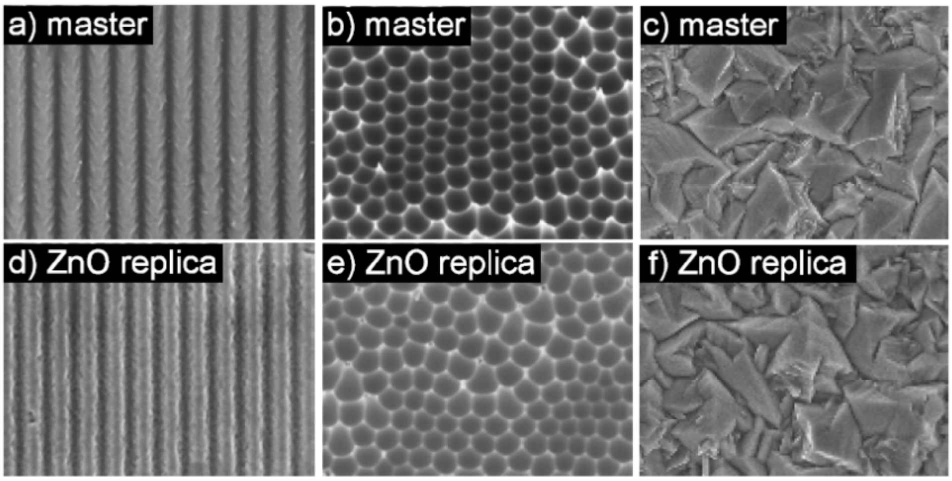


Figure 9: Scanning electron microscopy images of master test structures and their corresponding nanomoulded ZnO replicas: a) A one-dimensional periodic grating fabricated by interference lithography, b) a nanotextured aluminum surface with a quasi-periodic hexagonal dimple pattern prepared by anodic oxidation of aluminum, c) random pyramid network of ZnO grown by low-pressure chemical vapor deposition, d-f) images of the corresponding nanomoulded ZnO replica. Image size 6 μm x 4 μm.

1.3.4 Zinc oxide nanomoulding

To free ZnO electrodes from morphological constraints, Battaglia et al [25] developed an elegant nanomolding process, which allows the fabrication of ZnO layer with arbitrary surface morphology. In this method, ZnO is deposited on a textured mould. The ZnO film carrying the structure of the mould is then transferred onto a glass substrate using a UV curable resin for anchoring. Amorphous silicon single junction as well as micromorph tandem junction solar cells on nanomoulded ZnOs, with efficiencies as high as on state-of-the-art ZnO substrates were demonstrated. In addition, a honeycomb texture, based on anodically textured aluminum, was transferred onto ZnO via nanomoulding and successfully integrated into amorphous silicon solar cells.

Nanomoulding of ZnO can also be used to decouple interlinked ZnO growth parameters. For example, doping reduces the average pyramid size. By means of nanomoulding, Escarré et al fabricated ZnO films with the same thickness and pyramid size, but with varying doping and studied the influence of free carrier absorption on micromorph solar cells, without interference from varying light scattering properties.

1.3.5 Zinc oxide with new crystallographic growth orientation

A fundamental work was undertaken to understand better the growth of ZnO. By controlling the deposition parameters of low-pressure chemical vapor deposition, Nicolay et al [27] succeeded in switching the crystallographic orientation of ZnO layers resulting in new surface morphologies achieving respectable current densities of 14.4 mA/cm2 in the top cell and 12.7 mA/cm2 in the bottom cell without antireflection coating. However, electrical performance of this cell with 250 nm top cell, 100 nm SOIR and 2 um bottom cell must yet be optimized.

1.3.6 Multi-scale zinc oxide electrode

A first implementation of this concept was introduced by Dominé at IMT and in parallel by Asahi Glass Company. It was further explored by Boccard et al. [29] who used a very thick ZnO layer which provided large U-shaped featured after prolonged plasma treatment. The addition of a thin ZnO layer after the deposition of an epitaxial stopping layer provided small, sharp features. The two-step tuning of the morphology is beneficial for tailor light scattering for the top and bottom cell individually. While large smooth features provide good light trapping in the bottom cell, the addition of small features can efficiently improve the top cell current, while allowing for high-quality silicon layer growth enabling high Voc and FF. The typical multi-scale ZnO electrodes are shown in Fig. 10.

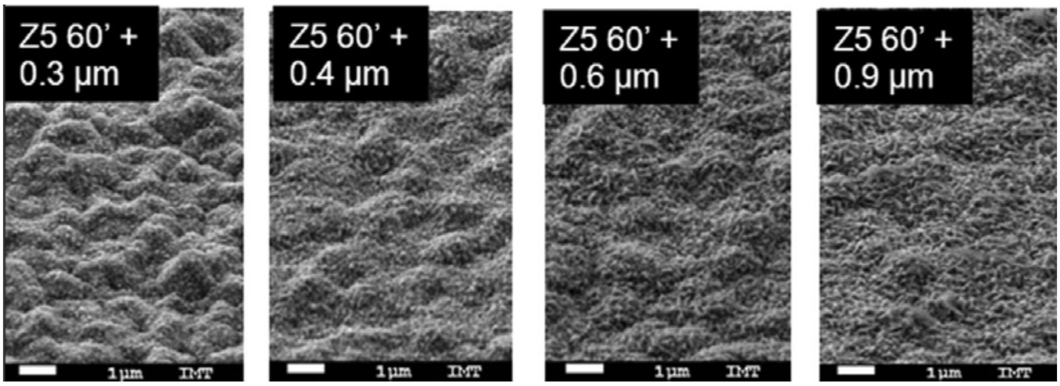


Figure 10: Scanning electron microscopy images illustrating the influence of the thickness of the second ZnO layer deposited for creating multi-scale ZnO electrodes: smoothening of the large features accompanied by an increase in the size of the small features.

1.3.7 Multi-scale hybrid electrode

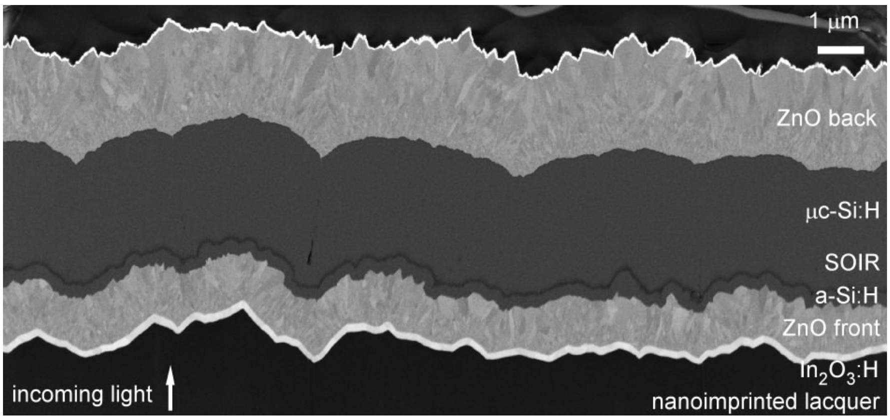


Figure 11: Scanning electron microscopy image of micromorph record cell on novel multi-scale electrode architecture consisting of a nanoimprinted structure with large smooth features, a hydrogenated indium oxide layer which provides conductivity with minimum parasitic absorption and the thin non-intentionally doped zinc oxide for optimum light incoupling and good electrical cell performance.

In a second implementation of this multi-scale concept, Boccard et al [29] replaced the thick ZnO layer by a transparent replica fabricated by nanoimprinting and the addition of a thin hydrogenated indium oxide layer which allows the use of a very thin non-intentionally doped ZnO with relatively small, sharp features. While the hydrogenated indium oxide and the non-intentionally doped ZnO guarantee minimum parasitic free carrier absorption, they provide sufficient conductivity to avoid resistive losses. In addition the combination of the small, sharp features of the ZnO with the large smooth features of the replica, guarantee optimum light incoupling and an efficient interplay with the SOIR, while providing a sufficiently smooth substrate of the growth of high-quality silicon layers enabling high Voc and FF. This innovative multi-scale concept led to a new initial lab record efficiency of 14.1%, for the first time reaching above the 14% benchmark. The cell further demonstrated an impressive current sum of 28.3 mA/cm2, with 14.3 mA/cm2 in the top cell and 14.0 mA/cm2 in the bottom cell. Despite these high current densities, an excellent electrical cell performance of Voc=1411 mV and a FF=71.5% was maintained. However, with a yet clearly suboptimal morphology of the replica, which is not able to fully eliminate all cracks in the bottom cell, there is an immediate potential for further efficiency improvements, which will be addressed in the next SFOE project. A similar approach of hybrid texturation was followed for new stabilized world-record micromorph cell efficiency of 11.9% reported by Bailat et al [20] in 2010 on textured glass substrates. This record was brought to 12.3% in 2012 (current world record, after further process optimization). The IMT results lay currently at 0.8% below the certified world record but likely for thinner devices. How to break the barriers for going well above 13% will be discussed in the part “perspectives”. Finally we note that in the very last month of the project new sets of micromorph devices with even thinner layers (250 nm top cell, and 1.3 μm bottom cell), could reach 13.8% and displayed after 220 hours light soaking still 12.1% efficiency.

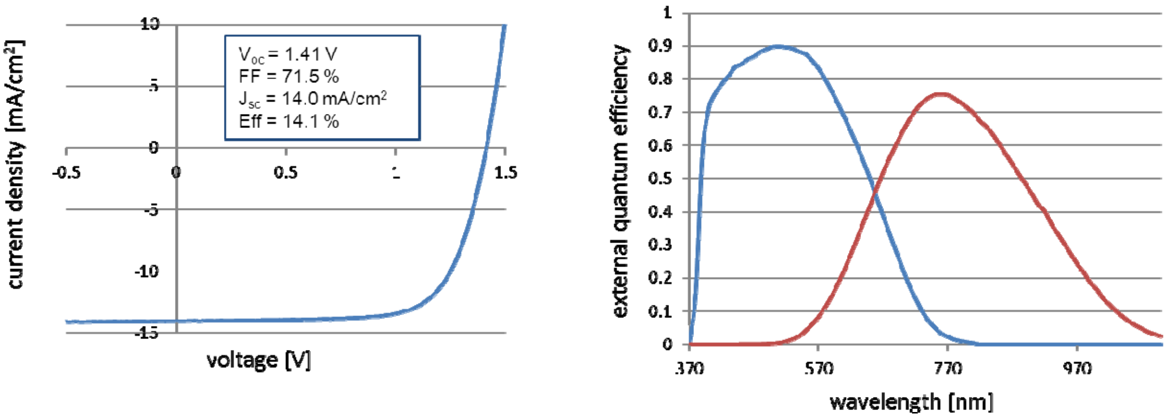


Figure 12: Current density-voltage characteristics and external quantum efficiency of micromorph record cell with an initial efficiency of 14.1%.

1.3.8 Antireflection coating

In the new record cell, a novel antireflection concept on the air-glass interface is implemented, consisting of a nanoimprinted array of pyramids [31]. The master for these pyramids was obtained by alkaline etching of a Si(100) wafer, resulting in well-oriented pyramids with Si(111) facets, which differ from the randomly-oriented pyramid structure of ZnO grown by chemical vapor deposition. The structure is well known in the crystalline silicon community, where it is the industrial standard to reduce reflection losses. A careful analysis for their transparent counterpart applied to our thin-film silicon solar cells revealed that such pyramids reduce reflection thanks to a double-rebound. In addition the pyramidal structure is beneficial as it provides an anti-escape effect based on total internal reflection.

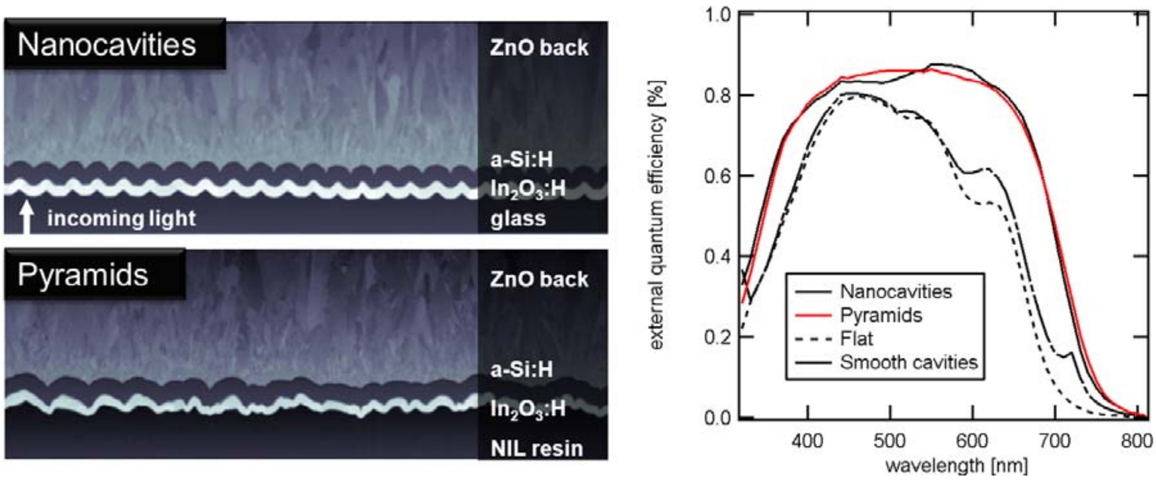


Figure 13: Left) Scanning electron microscopy views of cross-section of amorphous cells on periodic (top left) and random substrate (bottom left). Corresponding external quantum efficiency curves (right) showing that the periodic structures can perform as well as the usual random pyramid structure of ZnO.

1.3.9 Periodic vs random textures

In a recent study performed by Battaglia et al [32] in collaboration with Stanford University, periodic vs random structures are compared. Guided by insights from waveguide theory, tailored periodic arrays of nanocavities on glass were fabricated using nanosphere lithography. To allow direct experimental comparison between the periodic nanocavity morphology and the random pyramidal morphology of zinc oxide, it is important to isolate the influence of the electrode material properties, for example, the band gap, carrier density, and mobility, which affect the transparency of the material. To deconvolute the effect of morphology on light trapping from the material properties, nanoimprinting was used to transfer the random pyramidal morphology of zinc oxide onto a transparent lacquer, which behaves optically like glass. The study showed that both periodic and random texture provide excellent light trapping and allow to achieve Voc’s values as high as on flat substrates. This is illustrated in Fig.13 which shows a cross section of random and periodic structures and the related external quantum efficiencies.

1.4 Silicon layer quality and stability

As mentioned already several times, silicon layer quality is crucial for achieving high efficiencies. Of course, silicon layer quality not only depends on the front surface morphology, but can be influenced decisively with the plasma process parameters.

1.4.1 Intrinsic vs extrinsic defects in microcrystalline silicon

Bugnon et al [33] conducted an extensive study to improve our understanding of the fundamental mechanism involved in the growth of microcrystalline silicon layers on highly textured substrates. The impact of intrinsic and extrinsic defects must be carefully distinguished. While traditional analytic methods such as Fourier transform infrared spectroscopy and Fourier transform photocurrent spectroscopy are sensitive to the intrinsic material properties, they do not detect the influence of extrinsic effects such as localized porous regions (“cracks”, M2 in Fig. 15), appearing on rough substrates, and which we have shown earlier to be detrimental to the electrical device performance. By fabricating microcrystalline solar cells with the same intrinsic bulk material quality (M1 in Fig. 15), but with increasing extrinsic defect densities, which negatively affect efficiencies, it was shown that the impact of extrinsic effects on the electrical cell performance can be reduced by adapting surface morphology (U-shaped valleys rather than V-shaped ones) and/or implementing nanocrystalline silicon oxide layers (shunt quenching), or as shown in the context of this work by lowering the hydrogen flow during deposition. In particular it is now proven that the porous zone, are much more sensitive to the plasma process than the bulk zone, which explains the high combined sensitivity or variability of many plasma process conditions when depositing on rough substrate.

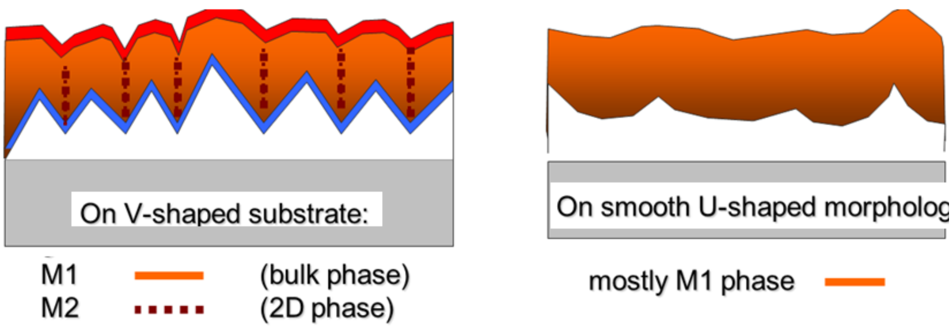


Figure. 15: Illustration of the growth on a rough substrate. The phase M2 is highly sensitive to the plasma parameters and appears essentially on V-shaped substrates. On flatter substrates, the M2 phase hardly appears and Voc and FF are usually improved. In this case however, the current is lower. The quality of the M1 phase depends also on the plasma process but in a much less critical way [32].

1.4.2 New microcrystalline record cell

New lab record efficiencies above 10% were achieved for microcrystalline single junction solar cells by Hänni et al. [34] in the small area reactor and by Bugnon et al [33] in the large area reactor. In both systems, the p-type silicon oxide layers were optimized. In addition, the introduction of a higher resolution in the control of the silane gradient during intrinsic layer deposition led to improved performance. An efficiency of 10.6% was achieved at a deposition rate of 0.3 nm/s for an absorber layer thickness of 2 um. With the newly developed antireflective coating, an efficiency of 10.9% was measured for the same cell with a cell size of 5x5 mm^2 (current extracted from EQE data). This record microcrystalline cell was also instrumental for achieving the 14.1% record micromorph cell.

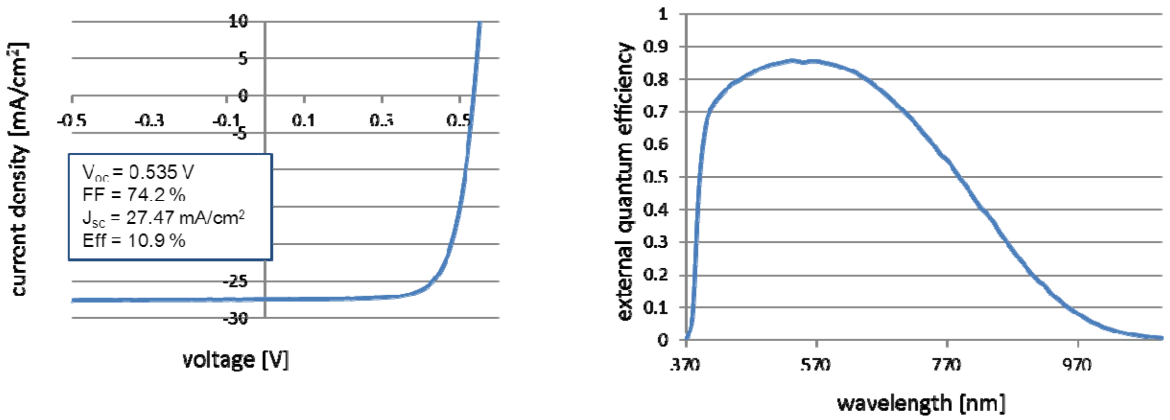


Figure 16: Current density-voltage characteristics and external quantum efficiency of microcrystalline silicon record cell with an efficiency of 10.9%. The cell area is 5x5 mm^2.

1.4.3 Top cell stability

Optimization of the p-layer in the amorphous silicon top cell lead to improved cell stabilities with respect to light induced degradation. In the small plasma-enhanced chemical vapor deposition (PECVD) systems, an improved stabilized fill factor of 68% was achieved in a single junction cell with an intrinsic layer of 220 nm by reducing the boron doping and the thickness of the p-type silicon carbide layer [35]. In the KAI system, we tried to improve the fill factor by reducing the deposition rate of the p-type silicon carbide layer. With this approach, we were not able to achieve fill factors above 66%. Subsequently, the p-type silicon carbide layer was replaced by a p-type silicon oxide layer [36]. To achieve open-circuit voltages comparable to the standard carbide layer, a relatively high boron doping had to be applied, resulting in amorphization of the carbide layer. Stabilized fill factors of 65% and 66% were achieved with this approach for absorber thicknesses of 250 nm and 180 nm respectively. An even higher fill factor of 67% was obtained for a cell with a 180 nm absorber by further replacing the intrinsic carbide buffer layer with an intrinsic oxide.

Cell stability was also investigated with respect to the absorber thickness. Fill factor stability is clearly improved at reduced intrinsic layer thickness. Deposition at higher temperatures is an alternative route to improve fill factor stability, but also leads to a lower open-circuit voltage. Strong accent was therefore put on improving the product of open-circuit voltage and fill factor. Initial open-circuit voltages above 1 V were achieved, resulting in maximum open-circuit voltage-fill factor products of up to 0.73 V [35]. Further work will concentrate on further improving these values, also in the stabilized state.

1.4.4 Measurement accuracy, reproducibility and uniformity

Measurement accuracy has improved significantly over the years. Not only the spectral match and stability of the solar simulator was significantly improved with the acquisition of a new state-of-the-art solar simulator and daily monitoring, but also new metrological developments such as the current matching machine and the Voc separator [37] have contributed to more accurate and reproducible measurements in particular of micromorph solar cells. This is an important point to note as these improvements in metrology led to an apparent attenuation of the efficiency improvements. Although not discussed explicitly above, the reproducibility of the results has also been improved significantly with the establishment of quasi-weakly deposition runs of standardized top and bottom cells, which allow for a good monitoring and compensation of system drift. Also uniformity was much improved giving access to precise comparative studies from which especially the front electrode developments benefitted massively.

1.5 Other topics

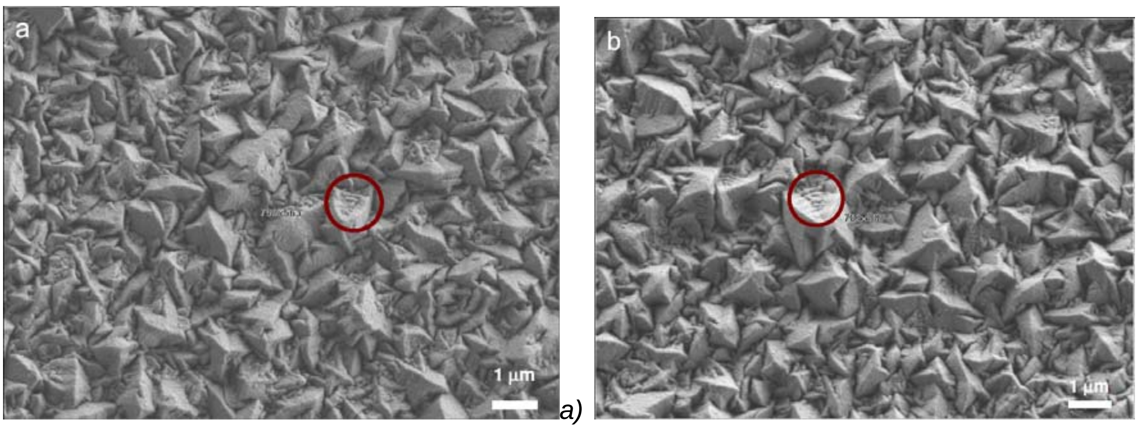
In the above summary, we concentrated on providing a coherent status report of the developments of the micromorph tandem cell on glass superstrates in our lab due to its important strategic role for the future of thin-film silicon solar cells. For other important topics such as the development of triple junction cells, and laser scribing, which will continue to be of strategic importance to the upcoming SFOE project, the reader is referred to the annual reports.

Figure 17: Amorphous mini-modules obtained by laser patterning and monolithic integration (left). Test coating on a the new Indeotec cluster system (right)

2. Cell development in the substrate configuration

2.1 Nanoimprinting

Nanoimprinting, already discussed above in the context of solar cells on glass, was originally developed at PV-Lab as a means of fabricating light trapping structures for flexible solar cells as bridle zinc oxide grown by chemical vapour deposition does not exhibit sufficient adhesion and peels of easily. The nanoimprinting setup designed and fabricated in-house consists of two chambers separated by a membrane, which allows stamping and illumination in vacuum. Arbitrary surface textures can be replicated. The process has been refined continuously over the project period to a point where a morphological fidelity analysis using local height and the even more sensitive angle histograms extracted from atomic force microscopy images yield practically indistinguishable results [38][39][40]. This is illustrated in Fig.18 which shows a ZnO master sample and a replicate of it in polymer. This system has also been instrumental to the development of the nanomoulding process [25] and the multiscale electrode design which lead to the new lab record micromorph cell [29].



b)

Figure 18: Scanning electron microscopy plane-views of a ZnO master surface (a) and of a replicated surface using the techniques described e.g. in [37]

2.2 Metal backreflectors

2.2.1 Rough substrates

Replicating the pyramidal structure of zinc oxide onto a plastic substrate via nanoimprinting, Söderström et al demonstrated a tandem solar cell with an amorphous top and bottom cell yielding an initial efficiency of 9.5% which stabilized at 8.1% [41]. Improvements in the reflectivity of the silver layer on the nanoimprinted plastic substrate further enabled an amorphous silicon single junction cell on plastic with an efficiency of 9.9% [42]. As deposited silver films exhibit strong parasitic plasmonic absorption leading to massive current losses. A simple annealing step leads to a subtle but important modification of the silver layer morphology and a substantial increase in the silver grain size. Both aspects do not only result in a substantial increase in the reflectivity, whose effect is directly observable as an increase in the external quantum efficiency, but also to improved electrical cell performance.

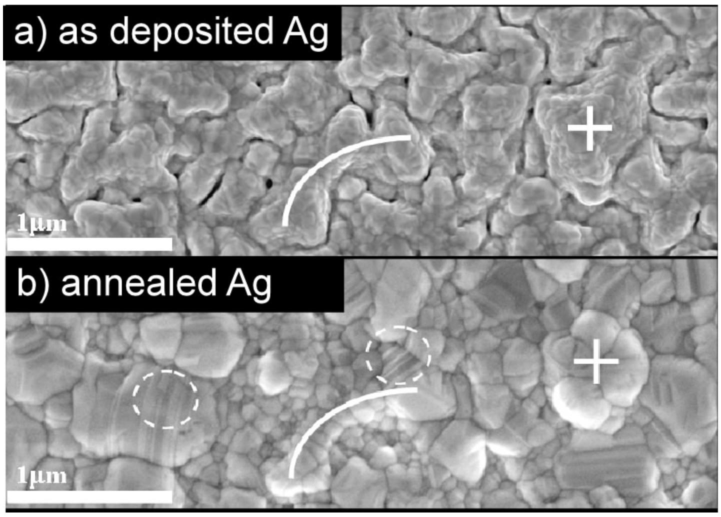


Figure 19: Morphological modification of thermally roughened silver back reflector upon annealing resulting in improved reflectivity. Scanning electron microscopy plane-view.

2.2.2 Nanocone backreflector

In collaboration with Stanford University, the influence of periodic back reflectors with archetypical morphologies on the performance of hydrogenated amorphous silicon thin-film solar cells in substrate configuration was investigated. Arrays of vertical nanopillars and convex nanodomes were shown to be detrimental to the electrical cell performance, whereas concave nanocones enable excellent electrical properties and provide powerful light trapping. On an optimized nanocone back reflector design a solar cell with an initial efficiency of 9.7% could be demonstrated [43].

2.2.3 Plasmonics

Silver nanoparticles embedded in a dielectric material have strong scattering properties under light illumination, due to localized surface plasmons. This effect is a potential way to achieve light trapping in thin film solar cells. Pahud (ex Eminian) et al [43] studied light scattering properties of nanoparticles on glass and ZnO, and on silver coated with ZnO. Large nanoparticles embedded in the dielectric at the back contact of amorphous silicon solar cells (Fig. 20) are found to lead to a remarkable increase in short circuit current of 20% compared to co-deposited cells without nanoparticles. This increase is strongly correlated with the enhanced cell absorption in the long wavelengths and is attributed to localized surface plasmons. While a clear current enhancement due to light scattering was observed, this approach could not rival the standard texturing methods. It is well know that a tight particle size distribution is absolutely mandatory for optimum performance as too small particles lead to strong parasitic absorption, while too large particles exhibit a very low scattering cross section. To improve the particle size distribution and gain control over the particle shape, first tests with silver nanoparticle arrays fabricated via nanostencil lithography in collaboration with Prof. Jürgen Brugger's group are underway.

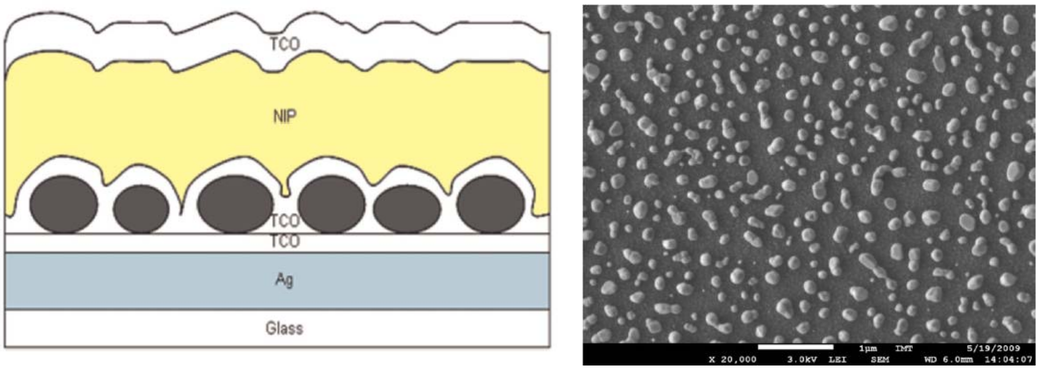


Figure 20: Thin film amorphous silicon solar cell in n-i-p configuration with plasmonic back reflector. A current gain of 20% could be demonstrated when compared to a flat reflector [43]

3. Reliability and encapsulation

This part on reliability served three purposes: 1) confirm that the materials used are stable providing the right encapsulant are used, 2) protect small devices from external influence, 3) generate a basic knowledge for failure mode of large area modules.

Figure 21 illustrates a typical effect that can occur for a solar cell stored in darkness. Water ingress can take place from the edge of the cell, likely following the path created by the porous regions created at the bottom of the V-shaped pyramids.

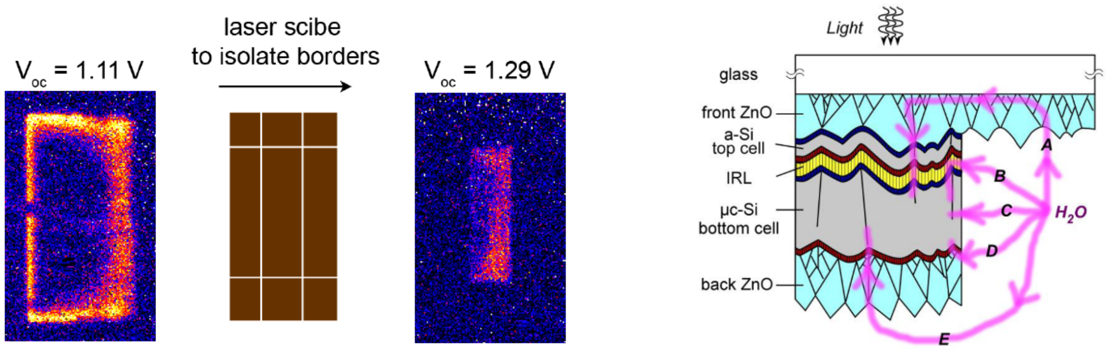


Fig.21: (right)) Infra-red lock-in thermography imaging showing the leakeage current occuring at the edges of the cell after long-time unencapsulated storage in air. The Voc dropped from from 1.3 to 1.1 V after storage. By lasering the degraded part, the initial Voc is recovered. (left) Various possible paths for moisture/oxygen penetration in the cell

3.1 Encapsulation and lamination processes

3.1.1 Small size in-house cells

We developed lamination processes and contacting solutions adapted to small size cells deposited on thin glass. Small substrates (4cm x 4cm x 0.5mm) were encapsulated (glass/glass and glass/backsheet) in our in-house built small-laminator. When compared to our large area industrial 3S laminator, it allows precisely placement of the substrates in the chamber, does not need a pre-heating step, is able to apply more than 3 bars of membrane pressure (1 bar for the 3S laminator) and has a fast cooling system. After careful adjustment of the temperature and pressure profile steps, it is possible to laminate glass/glass substrates without breakage. Different types of processes and wires have been tested for in house cells contacting (Cu-Sn ribbons with acrylic conducting glue, silver filled epoxy glues, ultra-sonic soldering, direct contact through the polymer, etc). Ultra-sonic soldering of thin Cu wires stands out as the more reliable process so far and allows, after contacting and encapsulation, to end up with constant values of series and shunt resistances.

3.1.2 Full size modules

A series of large size thin-film silicon modules were laminated with various polymers in a glass/glass and glass/foil configuration. For each encapsulant used, the process parameters had to be defined in order to obtained laminates without any defects (like bubbles formation) while ensuring maximal adhesion between the polymers and the glass substrate. Base-line lamination processes have been set up for each polymers.

3.2 Adhesion of polymers on glass

It is known that a good adhesion between the encapsulant and the different substrates of a PV module is needed to ensure long-term reliability. Several testing procedures exist (peeling, lap-shear, compressive tests) that use a metric derived from the force at interface failure to characterize the adhesion. It has however not been demonstrated that those metrics relate directly to the real interfacial adhesion and the obtained results usually relate to an apparent adhesion strength. In this work, we describe a new design for compressive-shear testing of polymer layers bonded to rigid substrates. We use it to characterize adhesion of ethylene-co-vinyl acetate (EVA) and polyvinyl-butyral (PVB) to a glass substrate before and after degradation in damp-heat conditions. Our results show that a peak-force based metric is unable to capture the evolution of adhesion through degradation and a new metric based on the elastic strain energy of the encapsulant is proposed. Moreover, we show that PVB adhesion to glass is much more affected by damp-heat exposure where polymer saturation takes place, in comparison to the adhesion of EVA to glass. The presented characterization protocol is a powerful tool that can help in assessing the reliability of an encapsulant facing specific degradation conditions.

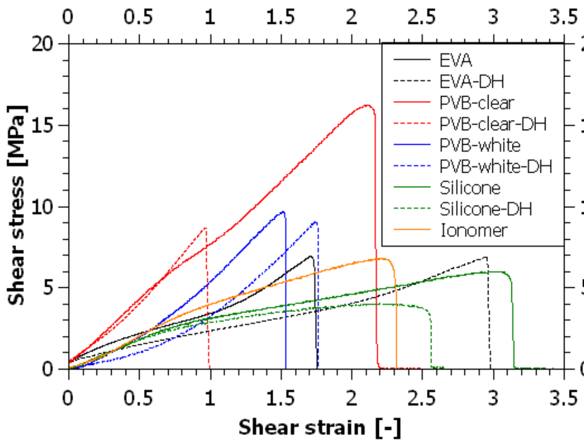


Figure 22. Compressive shear test results, showing the shear stress as a function of the shear strain for various polymers.

3.3. Diffusion of water vapor: ZnO layers as a humidity sensor

Water vapor diffusion in PV modules can drastically affects several constituents, such as front and back contacts and the adhesion of the polymers. We studied the correlation between the moisture content in the polymer and the degradation of the resistivity of the transparent conductive oxide (TCO) using it as a humidity sensor. The moisture affects the resistivity of the TCO due to the water vapor absorption at the grain boundaries which reduces the inter-grain mobility of the free carriers.
A lot of efforts were made to understand and monitor ZnO degradation in damp heat depending on the polymer used as encapsulant. We developed measurement systems allowing a continuous monitoring of the resistance value in the damp heat (contactless and four-wires probes methods). We used as a typical sample configuration: a sheet of polymer between a coated TCO glass and a back glass, laminated together. We measured the evolution of the sheet resistivity during damp-heat exposure in damp-heat chamber according to the norm IEC 61646 (85°C and 85% relative humidity). The inductive method is contactless and permits to avoid any preferential pathway of water vapor along contact wires. The four-probe measurement shows highly reliable and reproducible results.

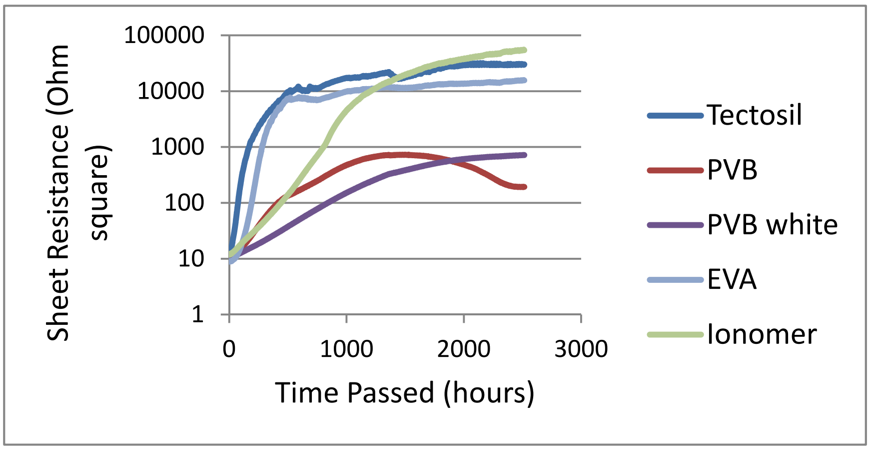


Figure 23: TCO resistivity as a function of time in damp heat (85°C / 85% relative humidity) for various polymers

These results give important information on the barrier effect of the polymers against the water vapor ingress, which is known to cause thin film silicon modules to fail. Experiments were made to understand more deeply the interaction and compatibility of ZnO layers with the encapsulants as well as to further improve the module reliability in general by defining the most appropriate encapsulation design (edge sealant, frame, polymers, glass, foil).

In addition we also monitored the evolution of the optical transmission in the near-infrared domain. Fourier transform infrared spectroscopy measurements have been fitted to a Fickian diffusion model which gave good results. Indeed, the water molecule has several absorption peaks in the infrared region. The ratio of a water absorption peak (transmission dips) and a water independent peak, combined with Karl Fisher measurements (water titration) permits to quantify the water content inside the polymer bulk.

3.4 Mechanical tests on full size modules

Mechanical load, breakage and hail tests

Fully operational systems allowing performing mechanical tests (breakage, load and hail) were built. These mechanical tests are used to understand deeper the impact of a given polymer or other material on the stability of the module. We also studied the effect of glass thickness (2mm instead of 3mm) on the mechanical stability of the PV module. These are useful tools to highlight the role of the polymers, in terms of adhesion but also considering their specific material characteristic (young modulus) in the crucial role that they play in the module stability. Using the compressive shear test described below, a simple analytical model was developed, to estimate what will be the deflection of a module in a given configuration, before breaking during a load test.

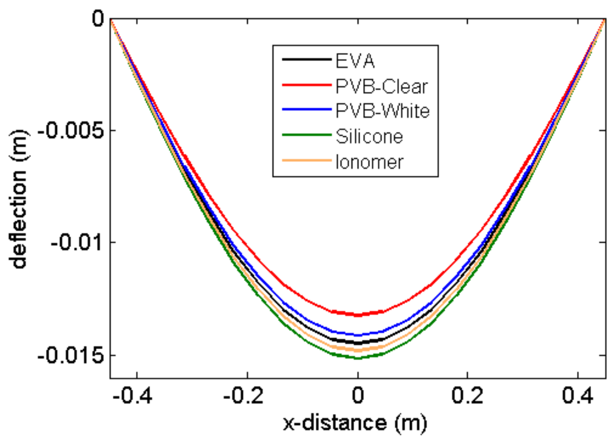


Figure 24: (left) Home-built mechanical load test. (right) Simple analytical model based on the CST measurements showing the deflection induced on the modules with various encapsulant under a load of 2400P.

3.5. Perspectives on reliability and packaging.

The part of the project has allowed us to identify possible failures losses at the cell level (e.g. moisture issue in the absorber layer or in the TCO), and to identify through the development of the required test techniques possible issues linked to the choice of polymers. So far we did not systematically apply packaging to the record devices, as we targeted high efficiencies without protection. In the next steps, fully encapsulated optimized cell stacks will be built allowing for a partial compensation of issues linked to cracks and porous regions, and/or TCO conductivity losses. The macroscopic tests allow us on one side to identify issues at the interfaces (microscopic phenomena) and also to directly test some possible module structure. However the test can help to prepare an official certification as performed in certified centers such as SUPSI.

4. Infrastructure

For the detailed infrastructure improvements during the project period, the reader is referred to the annual reports. The project has targeted at a general improvement of the infrastructure with the acquisition and ramping up of new deposition and characterization systems as well as at automation of several old systems. Several pieces of equipment were co-developed with industrial partners. In principle it is now possible to process samples on large are (40x50 cm^2) both for LPCVD and PECVD, laser scribing and lamination. Key equipment installed in the last four years is summarized below:

1. An automated Indeotec SA cluster system, upgraded to five deposition chambers, with load-lock for 10 samples (12.5x12.5 cm^2 samples size)

2. A dual chamber large area PECVD system was upgrade with several plasma diagnostic tools

3. An automated large area (40x50 cm^2) in-house LPCVD system with load-lock

4. Acquisition of new reactive ion etcher (RIE) from Oxford for surface treatment (6” substrates)

5. Acquisition and operation of sputtering tool for 30x30 cm^2 sample (refurbished MRC, 3 targets)

6. A laser scribing system was developed (in partnership with Schneeberger/Solneva) allowing scribing on size >40x50 cm^2. Three wavelengths are available (with 2 laser sources). The sample or the laser/beam can be moved.

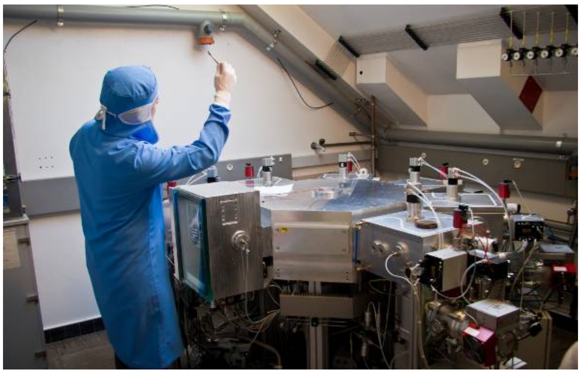
7. A new mid-size area (22x22 cm^2) multiple-lamps high-end solar simulator from Wacom was acquired. New tools to achieve proper current matching under operating conditions in micromorph cells were developed

8. A new large size area (100x100 cm^2) solar simulator (issued from a CTI project with Pasan) was built. It allows measurement of both high capacitance c-Si cells, but also of tandem modules (possibility to adapt the spectrum)

9. Spectroscopic ellipsometry was installed (Jobin-Yvon) and is now commonly used for layer characterization

10. The photothermal deflection spectroscopy (PDS) set-up was fully rebuilt

These changes were accompanied by several changes to software and automation of most system in the laboratory. In the next 3 years several new pieces of equipment’s will be installed, including, among others, a new PECVD large area cluster, a PVD cluster tool, and a high temperature (500°C) MOCVD tool.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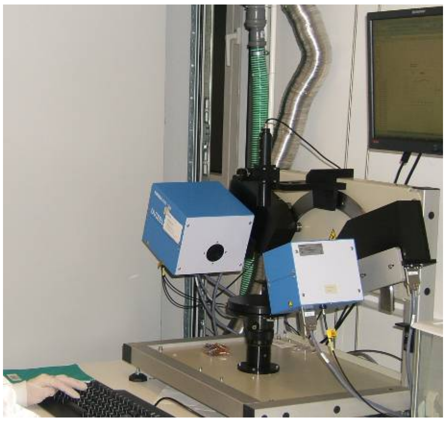
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Figure 25: Exemples of equipements ramped-up or installed and/or used during the project. The numbers refers to the list given in the text.

National and international collaborations

Regular academic contact/scientific and sample exchanges were maintained throughout the project both with national and international entities (ETH Zürich, Zürich University of Applied Sciences [45], CSEM Neuchâtel, Forschungszentrum Jülich, Friedrich-Schiller Universität Jena [46], Helmoltz Zentrum Berlin, Academy of Science Prague, University of Delft [47], Energy Research Center Netherlands, University of Utrecht, Trinity College Dublin, Stanford University [32], Caltech, National University of Singapore [48][49][50], AIST Japan …)

PV-Lab was and is involved in several European projects (N2P, Silicon Light, Pepper, Hetsi and 20 plus, FastTrack) as well as national projects (Dursol, Axpo, Archinsolar, Velux in collaboration with CSEM) and benefited from the support of the National Science Foundation. A strong synergy could be realized between all these projects and this SFOE project.

Collaboration with Industry

National and industrial collaborations with industrial partners were also ongoing or reinforced, either in the frame of CTI projects, direct mandates or equipment development, e.g. with Oerlikon Solar [20][21], VHF Technologies, Solneva, Essemtech, Indeotec SA, Dupont, Bosch Solar [3], Pramac, Schott Solar, IBM, Air Liquid, Gadir, Centro Ceramico, Photosolar. Projects more related to crystalline silicon included also Roth & Rau Switzerland, 3S Photovoltaics, Metalor, Pasan. The PV-Lab also had meetings with several leading companies in electronics and PV visiting Neuchâtel and discussing possible collaboration.

Globally, the “Technology platform” program set-up during the preceding projects could be used successfully in the frame of a support to various industries linked to PV.

Also PV-Lab offered 2 to 3 PV-Schools annually to companies such as Oerlikon, Flexcell, Sontor, Air Liquid. These schools are based on an intense teaching program with hands-on exercises, and address typically industry groups of 10 to 15 people.

Evaluation of 2008-2011 and perspectives beyond 2012

The period of 2008 to 2011 was particularly fertile in terms of technologic and scientific output and of key findings related to the micromorph technology. Technologically all fields improved, and this on a sound “understanding” basis. Several patents were also directly issued from the project. In partnership with industries several other patents were also applied for. Scientifically, a strong publication output has characterized this period, and detailed scientific aspects can be found directly in the relevant literature.

Some of the key findings can be summarized as follow:

- The improvements of the optical structures (advanced TCO, and optical schemes) allowed gain in current, but it was mostly found that a reduction in free carrier absorption was the reason for the increase in current, rather than improved geometries. Hence structures allowing at the same time a reasonable growth of tandem cells and a stronger intrinsic light trapping still need to be developed. Based on the new replication and nanomoulding tools realized in this project, on the better growth control of the LPCVD ZnO layers, and on the more aggressive light trapping features made possible by the other material and process improvements, a direct potential for further current gains is accessible. So far we note that none of the structures based on nanowires or plasmonic effects could surpass the more traditional approaches (e.g. with natively textured ZnO).
- The now ubiquitous use of doped silicon oxide layers has allowed optical gain and a better resilience on rough substrate, or even in the case of cells on opaque substrates a barrier effects that allows an increase in Voc. These layers open the possibilities to increase the number of junction (less parasitic optical losses) and to work on “difficult” substrates (shunt quenching effects). Hence their use, or variation thereof, will be of prime importance for the next research steps.
- The clear understanding of the role of plasma process and roughness on the growth of the films provides a correct picture of the challenges but also of the routes to push the technology further In particular it is necessary to work with processes that allow a simultaneous achievement of high quality for both deposited phases. The requirement becomes more and more stringent when the substrate tends to favor the creation of porous regions.

Eventually this project has allowed record microcrystalline cells and high stable FF amorphous cells. This translated so far into among the highest reported initial efficiencies for micromorph devices, which, however still suffered a too strong light-induced degradation. The improvement of the initial efficiency (up to at least 15.5%) and stable efficiencies (targeting 14%) requires now four major ingredients:

1) So far the best individual single junction cells could not yet be optimally coupled in tandem or triple junctions. This is linked to the change of morphology induced by the first cell which creates unfavorable growth conditions for the second device. Hence much more effort need to be done to create a better substrate morphology after the growth of the first cell (e.g. by a suitable planarization process)

2) The use of all optimal materials, optical structures and plasma processes achieved in this project should now be systematically applied for various types of substrates and multiple junction configurations.

3) The optimization of the single cells Voc and FF taking into accounts 1 and 2 should be revisited and the potential for µc-Si cell with Voc close to 0.6 V and a-Si:H with Voc at 1 V should be fully exploited.

4) A joint optimization of all layers/substrates and the use of suitable buffer layers should be carefully performed.

A first step towards such improved devices was realized in the last month of the project with thin-high current micromorph cells (250nm/1300 nm absorber thicknesses) reaching 13.8 initial efficiencies and with still over 12.1% efficiencies after 220 hours of light soaking. These cells represented a first step of integration, but still without an improved surface morphology after the top cell deposition.

Indeed, we think that, providing the best of elements 1 to 4 can be brought together with sufficient energy and coordination, thin film silicon technology should be able to move to stable efficiency close to 14% or higher, which should translate into low cost modules with at least 12% efficiency and even more at a later stage. Based on the immense industrialization effort of the last 8 years, we know that many results can be transferred now quite effectively from the laboratory to the production lines. In particular, one of the uniqueness of thin-film silicon is the possibility to introduce novel layers simply by varying the plasma composition. This opens further opportunities for new material synthesis, advanced buffer and doped layers leading to further efficiency increase, without sacrificing on the potential very low production costs. Thin-film silicon technology should capitalize on that to exploit its full potential which remains exemplary, for the reasons discussed in the introduction.

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