Openbaar eindrapport TKI Urban Energy project PERCSpective

Uitgangspunten en doelstellingen van project en partners

With silicon module prices steeply decreasing, enhancement in efficiency is a key element towards further reduction in the levelized cost of electricity (LCOE). In this perspective, 2-terminal (2T) monolithic Si-perovskite tandem technology, which has demonstrated a staggering increase in efficiency up to 32.5%, has triggered a strong industrial interest. In terms of commercialization, the use of PERC bottom cells appears to be most appealing: The installed PERC capacity eclipses that of SHJ, which has mostly been used so far for 2T tandems. Being able to upgrade existing PERC lines for tandems thus has a huge market potential. Moreover, it does not require an overhaul to SHJ by the conservative and low-margin PV industry. These considerations, in addition to optional bifaciality and being a low-cost technology, make PERC a highly suited candidate for tandem applications. However, heterojunction Si cells interface quite readily with perovskites due to their full-area conductive front side passivating layer and transparent conductive oxide (TCO) front contact layer. Standard PERC cells lack these two important aspects for monolithic integration, calling for front side innovation, as addressed in this project.

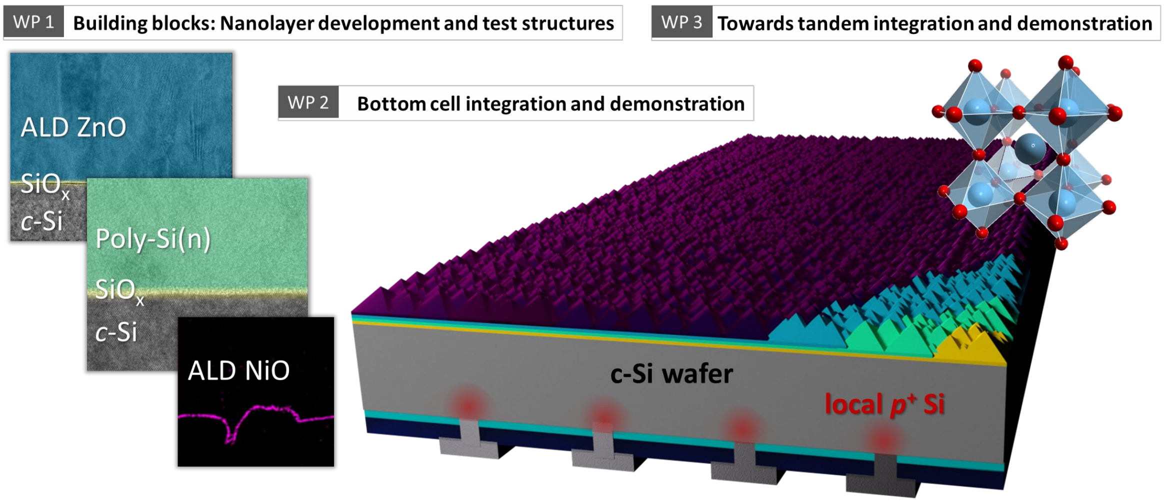

Figure 1 Overview of the joint activities by the partners within the context of this project, illustrating the building blocks being developed on the silicon PERC bottom cell.

The project was inspired by the recent invention at the TU/e that ALD Al-doped ZnO can yield very good surface passivation on n-type crystalline silicon as well as on poly-Si passivating contacts. This sparked the idea to apply this ALD ZnO:Al layer as a passivating and interconnecting TCO between the PERC bottom cell and the perovskite top cell. Since the field of Si-perovskite tandems is rapidly evolving with various contending architectures, the project strategically addressed multiple architecture options, mainly being:

- **Si bottom cell front contact:** either traditional n^+-diffused emitter or poly-Si(n)

- **Texture:** Choice of a planar (+wet-processed perovskite) or textured (+dry-processed perovskite) bottom cell

The project focused on various building blocks (ALD ZnO:Al, ALD NiO and LPCVD poly-Si) to make the interconnection possible and on developing accompanying process flows. These building blocks were first tested on dedicated test structures such as lifetime samples and contact resistivity structures. Once optimized, their performance was to be validated in tandem demonstrator devices.

Behaalde resultaten

1.1 ZnO:Al contacts

TU/e devised routes to fabricate ZnO:Al-based contacts to n^+-diffused emitters and poly-Si contacts, which are highly passivating, conductive and transparent. Specifically, a high passivation level of 700 mV and 735 mV implied V_{oc} was achieved on 130 Ω/sq n^+-diffused emitters and poly-Si(n) contacts, respectively. Contact resistivity values down to 14 mΩcm^2 were achieved, while optical simulations indicated that this contact stack should enable active-area short-circuit current density values in the range of 40 mA/cm^2. Altogether, these values indicate the ZnO:Al should serve as excellent contacts in the tandem and the results mostly exceeded the targets originally set in the project planning.

Importantly, a few key steps and insights were needed to arrive at these good contact properties. These findings have all been published in three peer-reviewed scientific publications that are available open-access (one, two, three). Briefly summarized, these steps and insights are as follows. For achieving surface passivation with ALD ZnO:Al, it is imperative to intentionally grow a tunnel SiO_2 (~1-2 nm thick) on the HF-dipped Si wafer. Various preparation methods for the SiO_2 layer were shown to work (UV/O_3, RCA clean, NAOS). Also, an Al_2O_3 capping layer has to be deposited on the ZnO:Al, followed by a thermal anneal step around 400-500 °C. During this anneal step, hydrogen inside the ALD layers can hydrogenate/passivate defects at the SiO_2 interface, resulting in excellent passivation. The Al_2O_3 capping layer prevents effusion of hydrogen during this anneal step.

This approach of Al_2O_3 capping and annealing was also shown to improve both the electrical conductivity and the optical transparency of the ZnO:Al considerably. This enables the ZnO:Al to reach conductivity and transparency levels typically only attainable by indium-based TCOs. The improvement is thought to originate from a combination of passivation of (grain boundary) defects by hydrogen, improved dispersion and activation of the Al-dopants and grain coarsening.

For obtaining a good contact resistivity, doping of the ZnO (by Al) as well as *n*-type doping of the contacted silicon proved vital. Specifically, no proper contacts could be made by either intrinsic ZnO and undiffused Si (nominal 3 Ωcm *n*-type wafers), while very low contact resistivities can be obtained with ZnO:Al on both n^+-diffused emitters as well as poly-Si contacts.

Spatial ALD equipment supplier SALD was able to transfer these encouraging results with ZnO:Al obtained by lab-scale temporal ALD by TU/e also to their spatial ALD platform: hardware improvements were implemented that enabled deposition of these doped ZnO:Al layers with a high quality and uniformity similar to temporal ALD, with the added benefits that spatial ALD bring such as a high throughput. When tested on PERC half-fabricate devices, the passivation level enabled by the spatial ALD layers often even outperformed that of the temporal ALD counterpart.

1.2 ALD NiO hole-selective contact

While TU/e had already demonstrated good results with plasma ALD NiO and perovskites prior to PERCspective, it was of a great interest to develop a thermal ALD process. The selection of a thermal ALD process opens up opportunities for scaling up the NiO process by batch ALD or spatial ALD. TU/e developed an ALD process based on $Ni(^{t}Bu\text{-}MeAMD)_2$ as precursor and H_2O as co-reactant. These findings are to be included in a manuscript (to be submitted) and were also presented in an oral contribution at the AVS 2022 conference.

The ALD NiO was shown to be very beneficial for tandem applications, not per se in increasing the maximum attainable efficiency, but more so in improving the reproducibility and yield of the cells. Specifically, nowadays self-assembled monolayers are used to form state-of-the-art hole-selective contacts to the perovskite. While these yield champion devices, typically there is a significant spread in efficiency in the batch. By combining the SAM (in our case a form of 2PACz) with ALD NiO, a narrow efficiency distribution is obtained without impairing the average cell efficiency. This insight shows that such use of NiO is likely a key step when moving from lab-scale demonstrator devices towards a stable baseline in mass production. <TODO REFER TO PAPER IN PREPARATION>

The ALD NiO and $ZnO:Al/Al_2O_3$ building blocks were also shown to be able to improve the passivation of the poly-Si(n) passivating contact significantly by providing hydrogen to the stack during thermal annealing. While such hydrogenation is routinely done from conventional dielectrics in PV such as SiN_x and Al_2O_3, being able to do this also from NiO and ZnO:Al is of interest since these are p-type and n-type conductors, respectively, and already form a building block in the tandem. These findings have been published in detailed in this peer-reviewed publication which is available open-access: link.

1.3 LPCVD poly-Si(n) tailored for tandem cells

TNO and Tempress developed an approach to make poly-Si contacts by LPCVD with properties tailored to the tandem application. Specifically, “conventional” poly-Si contacts are made rather thick and highly doped, since this is compatible with the firing metallization approach that is commonplace in industry. For tandem application, the cell current would suffer from significant parasitic absorption of light in the poly-Si layers, mostly in the infrared due to free-carrier absorption. Thus, TNO and Tempress developed processes to make a thinner (65 nm instead of 140 nm) and more lowly-doped ($1x10^{20}$ vs. $1.8x10^{20}$ cm^{-3}) poly-Si layers based on in-situ doped LPCVD of *a*-Si:H and post-deposition crystallization. Promisingly, optical modelling indicates the parasitic light absorption should be minimal for these novel layers, on the same order as in a conventional diffused emitter. Additionally, these two poly-Si types (conventional and novel) were also used to benchmark the hydrogenation performance in the aforementioned study (see publication link).

1.4 Process flows for integration in PERC-type bottom cells

An important aspect of the project was to explore how to best implement the building blocks in PERC-type bottom cells. This includes questions on processing order (front first or rear first?), wafer finish (type of polish or texture), surface cleanliness and gettering, handling, as well as dealing with potential wrap-around of the ALD layers and cell area definition.

One of the key challenges was selective removal of the Al_2O_3 capping layer used on top of the ZnO:Al: Since the Al_2O_3 capping layer is electrically insulating, it has to be removed selectively from the ZnO:Al after the anneal, in order to be able to make an electrical contact to the ZnO:Al TCO. Within this project, a new wet-etching solution was developed that is highly selective to etching Al_2O_3. The solution consists of 0.1M Na_2CO_3, pH-controlled to 11.6 by KOH dripping and heated to 60 °C. Details can be found in one of the aforementioned publications (link).

In the end, the consortium found compatible process routes that should lead to good integration of the building blocks with the PERC bottom cells. For the ZnO:Al, it was established that a low contact resistivity could be achieved on both n^+-diffused surfaces as well as poly-Si(n) contacts (see section 1.1). The poly-Si(n) contacts were found to yield good passivation on both planar and textured bottom cells. The ZnO:Al stack could also yield excellent passivation in PERC cells with a front n^+-diffused emitter on planar surfaces, as witnessed by an iV_{oc} of 700 mV. Surprisingly, on textured surfaces the passivation level was strongly impaired. The reason for this remains unknown, as previously on undiffused textured surfaces a very high passivation level was found (see aforementioned paper link) Hence, it was decided to explore different top-cell routes for the perovskite formation. For n^+-diffused emitters, the focus was on planar (chemically-polished) bottom cells with perovskite formed by wet processing. For poly-Si(n) contacts, the focus was on textured bottom cells, where the top cell perovskite was formed by dry processing (thermal evaporation).

Throughout the project, the various building blocks were integrated in different stages in the tandem cells. One of the highlights was the achievement of a 23.7% efficiency, which at the time of discovery set the efficiency record for PERC-perovskite solar cells. This was achieved still with conventional ITO instead of developed ZnO:Al, but did utilize the ALD NiO. Additionally, a PERC-like tandem cell was fabricated, which featured a heterojunction rear side for the bottom cell. This cell achieved an efficiency of 24.7%.

At the end of the project, tandem cells were fabricated that include all the developed building blocks. For the n^+-diffused route, the cells unfortunately suffered from a relatively low performance on the order of 20%. Whether this relates to a processing issue or a more fundamental issue would require further research. At the time of writing, the final tandem cells with a textured front surface (and dry-processed perovskite) are being finalized.

Perspectief voor toepassing en spin-off

Currently there is a strong push for initiating silicon-perovskite tandem (pilot) production in Europe, with various recently-started EU projects for example. This includes also specifically the use of PERC-perovskite tandems, e.g. through the PEPPERONI project. As such, the initiation of the PERCspective project appears very timely as it laid some of the groundwork, and its focus on the building blocks seems to have been very strategic.

The developed building blocks directly find their application in the tandem application, be it combined or stand-alone. Therefore, it is expected that the insights gained and processes developed within PERCspective will contribute to these EU ambitions. Moreover, PERCspective has contributed strongly to the visibility of the Dutch knowledge institutes and equipment manufacturers within the field. Regarding the latter, the fact that most building block processes were developed on or translated to the industrial tools of the equipment manufacturers present within the consortium, will contribute to their presence and competitiveness in this emerging market.

Bijdrage van het project aan de doelstellingen van de TKI Urban Energy

The targets of the TKI Urban Energy are a sustainable infrastructure and a reinforcement of the knowledge position. The PERCSpective project has contributed towards reaching this goal through the generation of Dutch knowledge on essential building blocks for the Si-perovskite tandem solar cells, and importantly also by developing their fabrication processes on industrial tools of the Dutch equipment manufacturers. Currently there is a strong momentum to bring solar cell manufacturing back to Europe, with an emphasis on Si-perovskite tandem technology. The PERCSpective project has strengthened the knowledge position of the consortium within this upcoming field and has also led to exposure. As such, this will most likely lead to a more prominent role for both the academic partners and companies within the PERCSpective project in realizing this envisioned goal of European mass-production of silicon-perovskite tandem technology.

Overzicht van openbaar verkrijgbare publicaties van PERCSpective resultaten

1. **ALD Zinc Oxide as a Passivating Conductive Contacting Layer for *n*$^+$-doped Surfaces in Si Solar Cells**
   B. Macco, B.W.H. van de Loo, M. Dielen, B.B. van Pelt, N. Phung, J. Melskens, W.M.M. Kessels
   Solar Energy Materials & Solar Cells 233, 111386 (2021), *https://doi.org/10.1016/j.solmat.2021.111386*
2. **Carrier-selective contacts using metal compounds for crystalline silicon solar cells**
   J. Ibará-Michel, J. Dréon, M. Boccard, J. Bullock, B. Macco
   ***Invited review** for Progress in Photovoltaics: Research and Applications*, *January*, 1–34 (2022). https://doi.org/10.1002/pip.3552
3. **Temporal and Spatial Atomic Layer Deposition of Al-Doped Zinc Oxide as a Passivating Conductive Contact for Silicon Solar Cells**
   B. Macco, M. L. van de Poll, B.W.H. van de Loo, T. M.P. Broekema, S.B. Basuvalingam, C.A.A. van Helvoirt, W.J.H. Berghuis, R. J. Theeuwes, N. Phung, W.M.M. Kessels
   Solar Energy Materials & Solar Cells 245, 111869 *(2022), DOI: 10.1016/j.solmat.2022.111869*
4. **Effective hydrogenation of poly-Si passivating contacts by atomic-layer-deposited nickel oxide**
   N. Phung, C.A.A. van Helvoirt, W. Beyer, J. Anker, R. Naber, M. Renes, W.M.M. Kessels, B. Geerligs, M. Creatore, B. Macco
   IEEE J. Photovoltaics, PP, 1–9 (2022). https://doi.org/10.1109/JPHOTOV.2022.3206895
5. **Atomic Layer Deposition of Conductive and Semiconductive Oxides – A review**
   B. Macco and W.M.M. Kessels

Invited review *for Applied Physics Reviews, 9 (4), 041313 (2022), https://aip.scitation.org/doi/10.1063/5.0116732*

6. **Efficient Continuous Light-Driven Electrochemical Water Splitting Enabled by Monolithic Perovskite-Silicon Tandem Photovoltaics**
   Datta, K., Branco, B., Zhao, Y., Zardetto, V., Phung, N., Bracesco, A., Mazzarella, L., Wienk, M. M., Creatore, M., Isabella, O. & Janssen, R. A. J., 10 Nov 2022, (E-pub ahead of print) In: Advanced Materials Technologies. XX, X, 2201131.