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Next – generation interdigitated back-contacted silicon heterojunction solar cells and modules by design and process innovations

NextBase - Deliverable report
D4.2 – IBC devices with transition metal oxide (TMO) based contact stacks with $V_{oc}>740\ mV$ and $FF>82\%$
D4.2 – IBC devices with TMO based contact stacks with $V_{oc}>740$ mV and $FF>82\%$.

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Contents

1 Introduction ......................................................................................................................................... 5
2 IBC cells with carrier-selective metal oxide contacts ........................................................................ 6
3 Electron contact layers ......................................................................................................................... 7
   3.1 Zinc oxide (ZnO) ............................................................................................................................ 7
   3.2 Tin oxide (SnO₂) ............................................................................................................................ 8
   3.3 Magnesium oxide (MgO₃) .............................................................................................................. 11
4 Hole contact layers ............................................................................................................................... 14
   4.1 Tungsten Oxide (WOₓ) .................................................................................................................. 14
       Sputtered tungsten oxide (WOₓ) ...................................................................................................... 14
       PEALD-deposited Tungsten Oxide .................................................................................................. 17
   4.2 Indium Tungsten Oxide (IWOₓ) ................................................................................................... 18
5 Summary of experimental results ........................................................................................................ 23
6 Risks and interconnections .................................................................................................................. 25
   6.1 Risks/problems encountered ......................................................................................................... 25
   6.2 Interconnections with other deliverables ..................................................................................... 25
7 Conclusions .......................................................................................................................................... 26
8 References ............................................................................................................................................ 27
List of acronyms, abbreviations and definitions

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Si:H</td>
<td>Hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>ARC</td>
<td>Anti-reflection coating</td>
</tr>
<tr>
<td>μc-Si</td>
<td>Microcrystalline silicon</td>
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<tr>
<td>μc-SiC</td>
<td>Microcrystalline silicon carbide</td>
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<td>Cat-doping</td>
<td>Catalytic doping</td>
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<td>CSC</td>
<td>Carrier-selective contact</td>
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<tr>
<td>dsp</td>
<td>Double-side polished</td>
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<tr>
<td>dst</td>
<td>Double-side textured</td>
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<tr>
<td>EQE(λ)</td>
<td>Wavelength-dependent external quantum efficiency</td>
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<tr>
<td>FF</td>
<td>Fill factor</td>
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<tr>
<td>FSF</td>
<td>Front surface field</td>
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<td>HWCVD</td>
<td>Hot wire chemical vapor deposition</td>
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<td>IQE</td>
<td>Internal quantum efficiency</td>
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<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>IBC</td>
<td>Interdigitated back contact</td>
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<tr>
<td>iVoc</td>
<td>Implied open circuit voltage</td>
</tr>
<tr>
<td>IWox</td>
<td>Indium tungsten oxide</td>
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<tr>
<td>λ</td>
<td>Wavelength</td>
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<tr>
<td>Jsc</td>
<td>Short circuit current</td>
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<tr>
<td>jsc</td>
<td>Short circuit current density</td>
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<td>Magnesium oxide</td>
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<tr>
<td>MoOx</td>
<td>Molybdenum oxide</td>
</tr>
<tr>
<td>MST</td>
<td>Modulated surface texture</td>
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<tr>
<td>PEALD</td>
<td>Plasma-enhanced atomic layer deposition</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced chemical vapour deposition</td>
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<td>Reflectance</td>
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<td>Silicon nitride</td>
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<tr>
<td>SiO₂</td>
<td>Silicon oxide</td>
</tr>
<tr>
<td>SHJ</td>
<td>Silicon heterojunction</td>
</tr>
<tr>
<td>T</td>
<td>Transmittance</td>
</tr>
<tr>
<td>TMO</td>
<td>Transition metal oxide</td>
</tr>
<tr>
<td>V&lt;sub&gt;oc&lt;/sub&gt;</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>WOx</td>
<td>Tungsten oxide</td>
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<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
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1 Introduction

The deliverable “D4.2 – IBC devices with transition metal oxide (TMO) based contact stacks with $V_{oc}>740$ mV and $FF>82\%$” is part of NextBase’s WP4 “Novel layer stacks and contacting materials”. It is connected to T4.2 “Development and optimization of novel TMOs for selective contacts”, which aims at exploring a wide range of potential contact materials. The goal of the deliverable is to demonstrate the implementation of these alternative charge selective junctions in highly efficient IBC silicon heterojunction solar cells, in order to improve cell performance by reducing transport losses. Furthermore, such TMOs can be deposited by sputtering, thermal evaporation or ALD, which might provide cost advantages over conventional PECVD-deposited a-Si:H contacts.

Chapter 2 reports on the fabrication of the currently best IBC cells with non-silicon carrier-selective contacts manufactured in the NextBase consortium, which show an efficiency of 22.2%. They were realized with molybdenum oxide, MoO$_x$, for the hole- and magnesium fluoride, MgF$_x$, for the electron-selective contact. These materials have also been used previously in double-side contacted CSC based silicon solar cells [1]. Unfortunately, despite the encouraging initial performance, stability of this device was unsatisfactory, as also acknowledged by previous authors.

Motivated by these findings, both project partners involved in T4.2 / D4.2, EPFL and HZB, have devoted considerable effort to exploring various alternative potential contact materials. Based on an initial literature review, the most promising candidate materials were selected from a wide range of available materials, e.g. for the electron contacts: TiO$_x$, ZnO$_x$, SnO$_x$, LiF$_x$, CsF$_x$, KF$_x$, CsO$_x$; for the hole contacts: MoO$_x$, CuO$_x$, WO$_x$, NiO$_x$. Chapters 3 and 4 provide details on the properties of the most promising electron and hole contact materials investigated within the project including proof-of-concept implementations of such films in both side contacted heterojunction cells. Chapter 5 summarizes the reported results.

<table>
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<th>Type</th>
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<td>IBC devices with TMO based contact stacks with $V_{oc}&gt;740$ mV and $FF&gt;82%$</td>
<td>HZB</td>
<td>DEM</td>
<td>PU</td>
<td>M36</td>
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</table>
2 IBC cells with carrier-selective metal oxide contacts

The following figure presents the currently best IBC cell demonstrated to date with non-silicon carrier-selective contacts. It was manufactured within NextBase with a shadow mask process for IBC structuring, a full area (i) a-Si:H passivation, MoOx/Ag stack for the hole- and MgF₂/Mg/Al/Ag stack for the electron-selective contact. It has the following device parameters, measured at STC: $V_{oc}$ 709 mV, $j_{sc}$ 41.5 mA/cm², FF 75.6%, power conversion efficiency 22.2% [2].

![Diagram of IBC cell with TMO contacts](image)

**Figure 1.** Left: IBC-SHJ cell with TMO contacts for both holes and electrons. Left: Device structure. Right: Illuminated I-V curves for the best cell, initially and after 30 & 100 hours in air.

This remarkable result surpasses the best previously published silicon cell with non-silicon contacts in literature, which is also a both-side contacted device, i.e. a simpler structure: Bullock’s DASH cell [3] uses MoOx and TiOx/LiF as contact materials and achieves $V_{oc}$ 706 mV, $j_{sc}$ 38.4 mA/cm², FF 76%, PCE 20.7%. A relatively fast degradation however occurred upon waiting in air, which can come from the uncapped (i)a-Si:H layer in the gap between n and p contacts or to detrimental material interaction in the electron stack [3]. Also, the moderate contact selectivity, relatively high contact resistance and strong infrared-light parasitic absorption at the rear fundamentally limit the efficiency of this device. This indicates that optimization of the current design can lead to only marginal improvements, and alternative material stacks are required to reach 26% efficiency.

Our efforts towards identifying such candidate materials are summarized in the following chapters.
3 Electron contact layers

3.1 Zinc oxide (ZnO)

We investigated the possible use of Al-doped ZnO (AZO) cosputtered with SiO$_2$ as an electron contact layer, in view of its relatively low work function yet good conductivity. This combination presumably enables the use of relatively thick (>10 nm) films in TMO-based electron-selective contact stacks. AZO:SiO$_2$ is also expected to be less reactive with the surrounding Si or metal layers than nanometer-thin fluoride compounds. Layers of various thicknesses and with several compositions of AZO:SiO$_2$ were fabricated and investigated with various capping metals as electron-selective contacts in 2-side-contacted solar cells, as sketched in Figure 2. Main results are that optimal thickness and efficiency is roughly independent of the composition, and the capping metal has a strong influence on the selectivity of the contact. This highlights that AZO:SiO$_2$ cannot be a high-performance electron-selective contact, and that further material research is required to evidence one that could be.

![Figure 2](image1.png)

*Figure 2 Sketch of the devices used to probe the ZnO:SiO$_2$ contact, and $V_{oc}$ and $FF$ of the resulting solar cells as a function of the thickness of the layer.*

In further developments, tuning of the ZnO film and following the insertion of a suitable interface layer, we could manage to thicken the film up to a thickness of 100 nm while preserving a high $V_{oc}$. As shown in Figure 3. This enables a better optical performance, making such stack promising for high-performance electron-selective contacts (work submitted for publication).

![Figure 3](image2.png)

*Figure 3 $V_{oc}$ and $J_{sc}$ of 2-side contacted solar cells using a ZnO contact with improved properties as a function of the thickness of the ZnO film.*
3.2 Tin oxide (SnO$_x$)

Another interesting option for electron contacts / transport layers is tin oxide, SnO$_x$. As a contact material in silicon thin film materials, it has proven its process compatibility and long term stability in such devices.

**Figure 4** GPC and resistivity of SnO$_2$ layer as a function of a) oxygen plasma step duration, b) RPS power.

Within NextBase, we have explored the deposition of SnO$_x$ thin films via plasma-enhanced atomic layer deposition (PEALD). Each PEALD sequence consisted of a TDMASn pulse (1.5s)-N$_2$ purge (5s)-Oxygen plasma (varied duration)-N$_2$ purge (5s). TDMASn and N$_2$ pulses were optimized to yield saturation of the film growth per cycle (GPC). However, for the PEALD process the saturation point for the plasma step cannot be adjusted in the same way as for thermal ALD by the step saturation method, mostly due to plasma kinetics. If the reaction kinetic is slow and plasma species are distributed isotropically [4], [5], it is possible to obtain better quality layers before the saturation point. Therefore, the parameters of the oxidation step (pulse time, plasma power) were optimized with regard to conductivity of the SnO$_2$ layer and not by step saturation. Thus, both saturation point of GPC and resistivity of the layers were investigated simultaneously. Figure 4(a) shows the GPC of SnO$_2$ layers upon variation of the oxygen plasma step duration. With the short pulses below 4 seconds the growth is reduced, which indicates that such pulse duration is too short for the saturated ALD process. With the increase of the oxygen pulse up to 8-10 seconds, the changes in the GPC are minor, and it can be considered as a saturated process. However, Figure 4(a) shows that the minimal resistivity of the layer can be achieved at 6 seconds of oxygen plasma pulse. Similar optimizations were carried out for the oxygen plasma power, Figure 4(b), for an addition of argon to the precursor gas and for the deposition.
temperature (not shown), which allow to further improve the opto-electronic properties of the SnO$_2$ layers.

Using our EMIL facility at the Berlin synchrotron BESSY II, we have used X-ray and UV photoelectron spectroscopy (XPS, UPS) to investigate the stoichiometry and valence band of our SnO$_x$ films grown on (n)a-Si:H/c-Si substrates, i.e. the relevant structure for silicon heterojunction devices incorporating SnO$_x$. XPS of the Sn3d core level shows that during the first 10 ALD cycles an intermediate state of tin is present, as evidenced by the appearance of Sn$^{2+}$. During the subsequent formation of the bulk of the film, no Sn$^{2+}$, or metallic Sn$^0$ are present in the film, indicating a well-defined SnO$_2$ film growth.

**Figure 5** UPS spectra of SnO$_2$ layers deposited on top of n-doped amorphous silicon and measured after different numbers of ALD cycles. a) secondary cut-off with bias Voltage of 10 V, b) valence band region of the UPS spectra with normalized signal intensity, c) work function of SnO$_2$ layers on n-aSi:H, d) valence band edge energies relative to $E_F$ as a function of ALD cycles.

Additionally, it was possible to quantify the work function and the valence band edge position of the SnO$_2$ layers after different growth steps from the UPS measurements. The cut-off region of the UPS spectra and extracted work function values of the layers with increasing number of ALD cycles are shown in Fig. 8, respectively. In both graphs a drastic shift of the work function for the first cycles is apparent, which presumably reflects the oxidation of the silicon surface [6]. During the first 5-10 cycles, the intermediate tin oxide layer is grown, which features a lower work function than the thick SnO$_2$. However, after 15 cycles the work function stabilizes, which indicates that at this stage the incubation of SnO$_2$ on the silicon/silicon oxide surface has been completed and the growth has entered a stable
regime. This corresponds to our observations of Sn 3d core level. The work function for the final SnO$_2$ layer after 80 cycles was measured to be 4.82 eV. That is in the range of literature values, which are between 4.4 and 5.7 eV, depending on the surface state of material [6]. However, this value is higher than reported for other n-type semiconductors, such as ZnO (4.4 eV) [7] or TiO$_2$ (4.2 eV) [8]. Such high work function can be an issue for using SnO$_2$ layers as electron contacts in silicon heterojunction solar cells, due to its negative impact on the fill factor, as it was shown in simulations of silicon heterojunction solar cells [9], [10].

Using the method proposed by Kraut et al. [11], we were able to estimate the valence band offset at the SnO$_2$/a-Si:H interface as $\Delta E_v = E_b(SnO_2) - E_b(Si) + \Delta E_{CL}$, where $E_b(SnO_2)$ is the difference between the core level position of Sn$^{4+}$ 3d$_{3/2}$ and the valence band edge, $E_b(Si)$ is the difference in core level positions of Si 2p$_{3/2}$ and the valence band edge for bare n-aSi:H substrate and $\Delta E_{CL}$ is the difference in core level positions between Sn$^{4+}$ 3d$_{3/2}$ and Si 2p$_{3/2}$ in the intermediate state. We find a valence band offset of ~1.8 eV. With the band gaps of a-Si:H and our SnO$_2$ as determined from spectral ellipsometry, we calculate a substantial conduction band offset of ~0.8-1.0 eV, i.e. a substantial barrier which would indeed hinder charge carrier transport of electrons across the SnO$_2$/a-Si:H interface.

![Figure 6](image)

*Figure 6* Output of solar cells with c-Si/i-aSi:H/n-aSi:H/SnO$_2$/ITO rear contact stack, with varied SnO$_2$ layer thickness at the rear side.

Finally, the optimized layers were applied in silicon solar cells, as part of the electron transport contact, i.e. the layer stack SnO$_2$/{n,i}a-Si:H implemented as the rear contact of both side contacted cells. As shown in Figure 6, with increased thickness of the SnO$_2$ layer, both $V_{oc}$ and FF decrease, which confirms the presence of a potential barrier in this stack. Note, that also the reference cells (“0 ALD cycles”) are limited in fill factor due to an optimized top contact & metallization; the low $j_{sc}$ is due to the absence of light trapping since polished wafers were used. Nevertheless, it is clear from both the experimentally determined high conduction band offset and the concomitant poor cell performance, that the
application of SnO$_2$ in the present configuration is unfortunately not suitable as a non-silicon CSC on crystalline silicon.

### 3.3 Magnesium oxide (MgO$_x$)

Another candidate material for electron CSCs in silicon solar cells is magnesium oxide, MgO$_x$. A water based ALD process using Bis(ethylcyclopentadienyl)magnesium (Mg(CpEt)$_2$) was investigated to fabricate MgO$_x$ films. This precursor was shown to be a suitable precursor for the growth of high quality MgO layers in the deposition range of 125-200°C, and it can be used in ALD using water as oxidizing agent [12]. In order to see if MgO layers are suitable for the implementation in SHJ solar cells, passivation properties and contact resistance of MgO layers were investigated.

![Figure 7](image-url) **Figure 7** Effective excess minority carrier lifetime at $10^{15}$ cm$^{-3}$ injection level after MgO layer deposition at 150 °C (a) for the HF-treated c-Si wafer, (c) for i-aSi:H/MgO layer stacks on c-Si as a function of the annealing temperature. (b) Carrier lifetime at $10^{15}$ cm$^{-3}$ injection level, modelled defect densities and effective charge for i-aSi:H/MgO layer stacks on c-Si substrate, as a function of the number of ALD deposition cycles.

Samples with symmetrical layer stacks on both sides of the wafer were produced in order to investigate changes of the passivation quality in terms of minority carrier lifetime upon deposition of MgO layers. With the direct deposition of a thin MgO layer on c-Si substrates, no passivation was achieved, neither in the as-deposited state, nor after annealing. However, for a thicker MgO layer, i.e. after 75 ALD cycles ($d_{\text{MgO}} \approx 9.8$ nm), changes in the passivation quality were observed. Figure 7(a) shows the minority carrier lifetime for such an MgO layer deposited on a c-Si wafer. For the as-deposited stack no passivation is observed. However, after an annealing step of 5 minutes at 200-250 °C, a slight
passivation effect, yielding a lifetime of around $150 \mu s$, is observed. A similar experiment was done with MgO deposited on i-aSi:H coated c-Si substrates. In this case, it was possible to observe significant changes in the effective lifetime with varying MgO thickness. In Figure 7b, the effective minority charge carrier lifetime in c-Si wafers coated with such layer stacks is shown as a function of the number of ALD cycles. After the direct deposition of MgO layer on top of i-aSi:H, there is a noticeable degradation of the lifetime for all MgO layer thicknesses. Using fits of semi-analytical simulation model for minority carrier lifetime [13], [14], we find that this corresponds to the drastic increase in defect density (middle panel in Figure 7b). However, similar to the MgO/c-Si layer stack, the passivation recovery and improvement is observed after an annealing step at 200 °C, with the maximum increase for the sample after 45 MgO ALD cycles, which corresponds to the point with the lowest defect density. At the same time, the total effective charge is slightly increasing with the number of deposition cycles. Therefore, it is possible to conclude that the main c-Si interface passivation mechanism is chemical passivation by the i-a-Si:H film, which degrades upon MgO deposition, then recovers during the annealing step. Additionally, the fixed charge reverses its sign: While it is rather small and negative, $\sim -1 \times 10^{11} / \text{cm}^2$ after i-a-Si:H deposition, it increases to $> +5 \times 10^{11} / \text{cm}^2$ after MgO deposition and anneal, for all MgO thicknesses except the thinnest (15 cycles). This indicates, that MgO/i-aSi:H stacks are indeed suitable as electron contact layers, since the positive fixed charge will lead to a downwards band bending and attract electrons at this contact.

Figure 8: Illuminated one-sun J(V) characteristics for solar cell devices with A) MgO/c-Si layer stack as electron contact on the rear side, B) MgO/i-aSi:H/c-Si stack. The MgO layer thickness was varied. Colors of the curves for both graphs represent the same number of deposition cycles. Schematic representations of the devices are shown as insets.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>MgO cycles</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF (%)</th>
<th>Efficiency (%)</th>
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<tr>
<td>MgO/c-Si</td>
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<td>33.4</td>
<td>0.664</td>
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<td>MgO/i-aSi:H</td>
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<td>Reference</td>
<td>0</td>
<td>33.3</td>
<td>0.698</td>
<td>73.4</td>
<td>17.0</td>
</tr>
</tbody>
</table>

Table 2: Solar cell parameters for the best devices fabricated on planar Si wafer incorporating the ALD-grown MgO layers and Al rear contact. *: Ti/Ag instead of Al rear contact.

As a next step, solar cells with MgO/c-Si and MgO/i-aSi:H/c-Si layer stacks as rear contacts on flat (n)c-Si wafers were fabricated in order to check the possibility of implementing our ALD layers in the...
devices. The MgO layer thickness was varied in the range of 20-50 ALD cycles to see the influence of the layer thickness on the final solar cell performance. In Figure 8 the J(V) characteristics for such devices are shown. Additionally, Table 2 shows the results for the best cell for each type of stack. Due to the flat surfaces of the c-Si wafers used for these cells, the short circuit current is strongly limited. For cells with the MgO/c-Si stack, an efficiency of 16.4 % is achievable with a thin MgO (20 ALD cycles, d_{MgO} ≈ 2.5 nm). For comparison, a reference cell with (n,i)a-Si:H contact shows an efficiency of 17%. With a further increase in layer thickness, we observe that a transport barrier is formed, which is reflected in the S-shape of J(V) curves and a decrease of V_{oc} and FF. This degradation is in line with the an increasing contact resistance that was determined on test samples with circular contact pads using the Cox & Strack method. For the MgO/i-aSi:H/c-Si stack, it is obvious that the additional thin i-aSi:H layer helped to keep the passivation on a level that allows V_{oc}s above 680 mV for devices. This shows that the i-aSi:H layer makes it possible to sustain the passivation, and that a thin layer of MgO is sufficient to function as a proper electron transport layer. The slight degradation of the V_{oc} and FF for such stacks as compared to the reference can be attributed to the possible diffusion of aluminum through the MgO stack during the evaporation of the aluminum contact. Indeed, with an alternative metallization consisting of a Ti/Ag stack, an improved efficiency of 17.3% could be demonstrated, outperforming (albeit on this moderate overall level) the reference cell with (n)a-Si as electron contact. Therefore, we conclude that MgO is a potentially interesting electron-selective contact material for silicon solar cells. However, further device optimizations will be necessary to evaluate its ultimate potential.
4 Hole contact layers

4.1 Tungsten Oxide (WOx)

HZB’s work within NextBase on WOx as a potential hole-selective contact material started from the encouraging results obtained in a previous EU-funded project, HERCULES (EU FP7). Briefly, the results in that project were obtained on WOx films that were thermally evaporated in UHV MBE system, where direct photoelectron analysis (XPS, UPS) could be carried out. We could demonstrate, that WOx with stoichiometries close to WO$_3$, yielded work functions close to 6 eV. These were high enough for a hole contact layer, for which we had established a minimal required work function of ~5.5 eV. Furthermore, we could show band bendings of up to 600 meV and solar cell fill factors of up to 60% with WOx/(i)aSi/cSi contact stacks, which could be improved to ~700 eV and 70% with an additional (p)a-Si:H interlayer (Figure 9 and [10]). However, it had also become clear that the density of oxygen vacancies was a critical parameter: High O vacancy densities reduce work function, band bending and, finally, solar cell fill factor. Thus, that thermal evaporation was not well suited to this task. Therefore, cell efficiencies remained below those of the (p,i)aSi/(n)cSi reference cells.

![Figure 9. Background – final result of HERCULES (FP7): WOx/SHJ cells with reactively sputtered WOx films [10].](image)

**Sputtered tungsten oxide (WOx)**

Therefore, in NextBase, sputtering of WOx films was explored as an alternative deposition technique. Here, the stoichiometry can be easily tuned by adding oxygen to the sputter gas; furthermore, sputtering would be a more viable industrial technique.

We find that varying the oxygen gas flow during sputtering enables variation of the WOx conductivity from 0.01 (Ωcm$^{-1}$) to 1000 (Ωcm$^{-1}$) (see Figure 10, left), while the band bending in the interface is changed by 70 meV and iFF of solar cells by 1.5 %. WOx shows higher resistivity, by about a factor of 10, and higher absorption in the visible range than ITO (Figure 11). Therefore stacks of a thin WOx film acting as high work function electron-CSC and ITO providing lateral carrier transport antireflection...
Properties are used in solar cells. It was found that at least 20nm of WOx are required to stabilize the WOx/silicon interface induced band bending, solar cell implied and real FF against the influence of the lower ITO work function.

Figure 10: (a) Resistivity of sputtered WO3 layers plotted versus the oxygen fraction in the sputtering gas. It is possible to vary the conductivity by 3 orders of magnitude depending on the sputtering conditions. (b) j(V) curves of silicon heterojunction solar cells with tungsten oxide hole contacts sputtered using different partial oxygen flows. The high resistivity of layers sputtered at high partial oxygen flows limits the solar cells transport properties.

WOx hole contacts of different thicknesses and conductivity were applied in solar cells (see Figure 10, right) and it was found that the highest FF is achieved with about 20nm thick interlayers of WOx with the highest possible conductivity, meaning the lowest partial oxygen flow during sputtering. It was found that sputtering enables a drastic improvement of WOx/silicon solar cells compared to thermal evaporation, due to the precise control of the WOx conductivity. Unfortunately the resistivity of sputtered WOx is still limiting the FF of these devices.

Figure 11. Optical properties of reactively sputtered WOx films on glass, with varying oxygen concentration during sputtering [15].

Therefore, further experiments were conducted where a precise control of ITO and WOx film thickness was maintained. These experiments were carried out on planar wafers to enable direct control of the deposited thicknesses. The thickness of the overlying ITO was adjusted to maintain a total metal oxide thickness of 80–85 nm. Samples with WOx thicknesses from 0 to 40 nm were prepared using a partial oxygen flow of 8.75%. The results are summarized in Figure 12: In panel (a) it can be seen that 20 nm
of WOx yields the maximum FF. For higher WOx thicknesses the FF is decreasing because of the high series resistance of the WOx layers. For thicknesses below 20 nm, the FF is lower, because the low ITO work function is projected through the WOx and onto the interface to (p)a-Si:H, as evidenced by c-Si band bending extracted from surface photovoltage measurements on reference samples. Unfortunately, the WOx solar cells show lower FFs than the reference solar cells without WOx, which reveals that the high resistivity of WOx is still limiting these solar cells.

**Figure 12.** Dependence of solar cell parameters on tungsten oxide thickness for SHJ cells with WOx/(i)a-Si:H front contact. The cells were fabricated on planar (100) wafers and have the structure ITO/WOx/(p,i)a-Si:H/(n)c-Si/(i,n)a-Si:H/ITO. Black squares with ranges mark average values with the standard deviation of the 12 cells on each respective wafer. Red circles mark the maximum value of each wafer and green circles mark the implied FF and implied $V_{oc}$ from photoconductance decay measurements performed after ITO deposition [15].

The decreasing trend in cell efficiency vs. WOx thickness, Figure 12 (d), is dominated by the decreasing $J_{sc}$ (panel (c)). This is mostly because WOx sputtered at 8.75% partial oxygen flow has a higher parasitic absorption than ITO. Indeed, the highest efficiency of 16.7% is obtained for the thinnest (11 nm) WOx.

To sum up our findings, the conductivity of these sputtered and not intentionally doped WOx films is about one order of magnitude below that of typical transparent conductive oxides, while the parasitic absorption is higher than in, e.g., ITO. Therefore, WOx was applied in stacks with ITO in this study. It was found that about 16–18 nm of WOx is necessary to benefit from the high WOx work function and prevent a detrimental influence of the lower ITO work function on the interface between WOx and silicon. The best solar cell using WOx as the hole contact and thus not having any p-doped layer showed 16.6% efficiency. The WOx in this solar cell was prepared using 7.5% oxygen in the sputter gas and had
a resistivity of about 0.01 Ω/cm. Additionally, using WOx as an interlayer between p-type amorphous silicon and ITO lead only to efficiencies comparable to but below the reference solar cells. All solar cells showed higher implied FFs than the corresponding cells without WOx. However, it was not possible to transfer this high implied FF into a device. The main reason for this is the high series resistance of WOx and an overall lower band bending for WOx layers with higher conductivity. Thus, it was shown that sputtering of WOx enables decent control of its conductivity and stoichiometry, but the overall conductivity of these layers is still too low to enable highly efficient hole contacts on silicon. These results were published in IEEE J. Photovoltaics [15].

**PEALD-deposited Tungsten Oxide**

Similar to the PEALD deposition of SnOx reported above, we also investigated an alternative tungsten oxide deposition process using plasma-assisted processes. WOx was grown from a W(CO)6 precursor. The deposited layers showed no traces of carbon contamination, and exhibit work functions of ≈ 5.5-5.75 eV. However, due to the non-uniform distribution of oxygen plasma in the chamber, the thickness distribution is highly inhomogeneous on the different positions of the substrate.

![Figure 13](image)

**Figure 13** Relative area ratio W 4f/O 1s core level (black), Relative area of oxygen vacancies in W 4f core level (blue) as function of a distance from the plasma source

Additionally, with XPS measurements it was possible to monitor that not only the thickness, but also the stoichiometry of the layer varies slightly. The change of the stoichiometry with changing distance from the plasma source is presented in Figure 13. We find, that only W6+ species are present in the W 4f core level; the change of stoichiometry is caused by the increase of oxygen vacancies with an increase of the distance from the plasma source. Thus, further process optimization is required in order to obtain fully stoichiometric films irrespective of sample position in a proper ALD process. PEALD deposited WOx layers are implemented as a front emitter for the SHJ solar cells, with a front stacking sequence of ITO/WOx/(i)aSi/(n)cSi and varying WOx thickness. As seen from Figure 14, S-shapes are observed in illuminated I-V curves. Accordingly, as listed in Table 3, low VocS with low fill factors (FF) for all WOx layer thicknesses (varying number of ALD cycles) are observed. On the other hand, the passivation of the structure remained on a high level, and is comparable with the reference structures, as observed from TRPCD and PL measurements. However, the final Voc of the device shows a drastic drop from expected measured i-Voc (>710 mV). Therefore, further investigation is needed in
order to estimate possible effects of barriers at the interfaces and/or low film conductivities and loss of charge carrier selectivity.

![Graph](image)

**Figure 14** IV Solar cell performance with WOx layer, as a hole-selective layer for different ALD cycles

**Table 3** Solar cell performance with WOx as a hole-selective layer for increasing no. of ALD cycles

<table>
<thead>
<tr>
<th>WOx ALD cycles</th>
<th>Average Jsc, mA</th>
<th>Average Voc, mV</th>
<th>Average FF, %</th>
<th>Average Eff,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-34,8</td>
<td>514</td>
<td>51,0</td>
<td>9,1</td>
</tr>
<tr>
<td>500</td>
<td>-34,6</td>
<td>492</td>
<td>48,9</td>
<td>8,3</td>
</tr>
<tr>
<td>600</td>
<td>-34,5</td>
<td>503</td>
<td>46,0</td>
<td>8,0</td>
</tr>
<tr>
<td>800</td>
<td>-33,7</td>
<td>510</td>
<td>46,8</td>
<td>8,1</td>
</tr>
</tbody>
</table>

### 4.2 Indium Tungsten Oxide (IWOx)

In a next step, we investigated novel mixtures of tungsten oxide (high WF, low conductivity) and indium oxide (low WF, high conductivity) in order to find a trade-off between high work function and high conductivity. If the conductivity of the layers is good enough, even a carrier selective TCO might be possible. We investigated the full range from pure tungsten oxide to pure indium oxide. We used thermal evaporation as deposition method with various temperatures for the tungsten oxide and indium oxide sources. The relative amount of indium and tungsten oxide was measured using X-ray photoelectron spectroscopy (cf. Figure 15).
Figure 15. Electron core levels of tungsten (W 4f) and Indium (In 3d) for samples with various amounts of indium oxide and tungsten oxide in the mixture. The respective binding energy and intensity of the core level components are shown in panels c and d. [16]

Additionally the work function of all these mixtures were investigated using He-UPS. The measured work functions ranged from 6.25 eV (tungsten oxide) to about 4.25 eV (indium oxide). We found that tungsten oxide features the highest work functions and induces the strongest band bending into crystalline silicon. Both values decrease continuously with increasing indium content. However, the measured band bending is much lower than the Anderson Model [17] predicts for such a large difference in work function. The pinning factor of non-passivated Silicon is known to be close to S=0.1 [18], which we observe here as well. Additionally we investigated the band gaps of these layers by means of optical spectroscopy and found a slight decrease of the band gap with increasing indium oxide content, which is concomitant with a shift of the valence band towards the Fermi level, $E_F$, which again was measured by means of He-UPS.

Figure 16 shows the mentioned data in combination as the band alignment vs. varying InOx content, plotted relative to the Fermi level ($E_F$). The work function is the most prominent change in the band alignment. The band gap and the valence band edge decrease only slightly about 0.4 eV by following the same trend. Hence, the energetic position of the conduction band stays constant about +0.3 eV above the Fermi level, whereas the valence band approaches the Fermi level from -3.5 eV for pure WOx to -3.18 eV for pure InOx.
D4.2 – IBC devices with TMO based contact stacks with $V_{oc}>740$ mV and $FF>82\%$.

For further evaluation we discuss the heterojunction of the metal oxide mixtures with crystalline silicon ($E_G=1.12$ eV, electron affinity = 4 eV, work function $WF = 4.3$ eV, for present dopant concentration) shown in Figure 17. The conduction of carriers in these high-work-function metal oxides is facilitated by defect states close to $E_F$ and the offset between the Fermi-level in WOx and the valence band of c-Si is only 210 meV, which can be overcome by thermionic emission. Therefore, although strong Fermi level pinning is observed, the tungsten-oxide-rich mixtures should be suitable as hole-selective contact for crystalline silicon.

The indium-oxide-rich mixtures show a significantly lower band bending, which leads to a larger offset to the Fermi level in the metal oxide and additionally to a less pronounced carrier selectivity, since the rejecting barrier for the electrons in the conduction band of the c-Si is smaller. Comparing the offset
in the vacuum energy levels at the InOx/c-Si and WOx/c-Si interface, an inversion of the surface dipole charge is observed.

First experiments of thermally evaporated (I)WOx applied as hole selective contact in silicon heterojunction (SHJ) solar cells showed moderate results with mainly difficulties in charge carrier extraction, leading to strong S-shapes in the IV-curves as seen in Figure 18 for a thickness variation of pure tungsten oxide as hole selective contact.

![Figure 18. IV-Measurement of Heterojunction solar cells with different thicknesses of thermal evaporated tungsten oxide as p-contact](image)

A second series aimed for a well suited trade-off between the high-work function WOx and the highly conductive InOx, where a layer with C_{In}=16% InOx-content in the mixture showed the most promising results. Hence, a thickness variation with C_{In}=15% InOx-content in the mixture was conducted, but showed the same problems with extraction barriers. The layer stack is the same as shown in Figure 18 with IWOx instead of pure WOx. The obtained AM1.5-illuminated I-V parameters of both thickness variations are shown in Figure 19 for different thicknesses of the applied metal oxide contact. The cells with pure tungsten oxide showed a slightly higher fill factor, which might be due to better selectivity,
because of the higher band bending as seen above. Still, best FF values are of the order of 50% only. Furthermore, the passivation quality is not good enough to reach reasonable open circuit voltages.

![Graph](image)

**Figure 19.** IV-Parameters of two cell-series: One with pure tungsten oxide as hole selective contact and the other one with 15% indium oxide in the mixture. The thickness of the (i)WOx was varied for each series.

To conclude this section, we find that despite an encouraging tunability of the IWOx work function by changing the indium content in the film, it was not possible to obtain decent solar cell results using IWOx/(i)a-Si:H/c-Si hole contacts. The reasons are probably twofold: a) Femi level pinning at the IWOx/Si interface causing low band bending and a barrier to hole transport at the heterointerface, and b) degradation of the aSi/cSi interface upon IWOx deposition, as evidenced by the low $V_{oc}$. 

D4.2 – IBC devices with TMO based contact stacks with $V_{oc}>740$ mV and $FF>82%$. 22 / 28
5 Summary of experimental results

The results presented in the preceding chapters on the development of different electron- and hole-selective contacts are summarized in Table 4 together with some relevant material parameters, and with solar cell efficiencies where applicable.

Table 4. Summary of the most important electronic properties of the metal oxides investigated by NextBase consortium partners, and efficiencies of solar cells processed with these layers.

<table>
<thead>
<tr>
<th>Material</th>
<th>Use as</th>
<th>Work function [eV]</th>
<th>Band bending* [meV]</th>
<th>Conductivity [S/cm]</th>
<th>Best cell efficiency [%]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_x$</td>
<td>n-CSC, TCO</td>
<td>4.82 (150 °C PEALD) 4.3 (120 °C water)</td>
<td>72</td>
<td>5.6*10$^{-3}$ PEALD 10$^{-3}$ (80°C water)</td>
<td>14.2</td>
<td>17.3 with (i)a-Si:H - Ti/Ag metallization; 16.4 without (i)a-Si:H ALD [23]</td>
</tr>
<tr>
<td>MgO$_x$</td>
<td>n-CSC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ALD</td>
</tr>
<tr>
<td>WO$_x$</td>
<td>p-CSC</td>
<td>6.4</td>
<td>625</td>
<td>&lt; 10$^{-6}$</td>
<td>16.6</td>
<td>sputtered [15]</td>
</tr>
<tr>
<td>WO$_x$</td>
<td>p-CSC</td>
<td>5.5-5.75</td>
<td>500</td>
<td>1.5*10$^{-5}$</td>
<td>9.1</td>
<td>PEALD</td>
</tr>
<tr>
<td>IWO$_x$</td>
<td>p-CSC</td>
<td>6.4-4.3</td>
<td>600-400</td>
<td>InOx: 1; WOx: 10$^{-4}$; IWOx: ~10$^{-5}$</td>
<td>14.2 (@ 16%InOx)</td>
<td>Thermal co-evap. of InOx and WOx [16]</td>
</tr>
<tr>
<td>NiO$_x$</td>
<td>p-CSC</td>
<td></td>
<td></td>
<td>&lt;~10$^{-3}$</td>
<td></td>
<td>Ni e-beam in O$_2$</td>
</tr>
<tr>
<td>AZO</td>
<td>n-CSC</td>
<td>3.9</td>
<td>28 – 65</td>
<td>19.5</td>
<td></td>
<td>Magnetron sputtered ~2-nm-thick, in combination with passivating (i)a-Si:H and Al [24]</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>n-CSC</td>
<td>3.5</td>
<td></td>
<td>&lt; 10$^{-6}$</td>
<td>20.5</td>
<td>Evaporated ~1.6-nm-thick, in combination with passivating (i)a-Si:H and Al</td>
</tr>
</tbody>
</table>

As can be seen from the table, although the work functions of the investigated materials are suitably high (for hole contact materials) or low (for electron contact materials), they mostly do not translate into high band bendings on (n)c-Si wafers. Furthermore, the conductivities are rather moderate, therefore the films would not be suitable as a front side TCO in both-side contacted cells. However, the conductivity is sufficient for application in IBC cells, where good lateral conductivity is provided by the metallization. Furthermore, it was found that the TMOs do not passivate c-Si wafers sufficiently to...
allow for high $V_{oc}$, with the possible exception of MgOx (minority carrier lifetime $\sim 150 \mu s$ demonstrated for MgOx/(n)c-Si samples after anneal in a not fully optimized process). Thus, a PECVD-deposited intrinsic amorphous silicon layer, (i)aSi:H, is necessary in all cases, which further increases contact resistance. Therefore, the cell results are limited to fill factors well below 80% and $V_{oc} < 720$ mV. The currently best IBC-SHJ cell with non-silicon CSCs processed within NextBase uses a full area (i)a-Si:H passivation processed at 200 °C, followed by a sequence of two shadow-masked evaporation steps at room-temperature: MoO$_x$/Ag for the hole- and MgF$_x$/Mg/Al/Ag for the electron-selective contact as presented in chapter 2. It exhibits the following device parameters, measured at STC: $V_{oc}$ 709 mV, $J_{sc}$ 41.5 mA/cm$^2$, FF 75.6%, and a power conversion efficiency of 22.2% [2]. This world-record efficiency for non-silicon-contacted device is remarkable—yet way underperforming compared to silicon-based contacting approaches.
6 Risks and interconnections

6.1 Risks/problems encountered

When setting up the NextBase project, the work in WP4 – particularly the exploratory work of TMOs in T4.2 – were planned as a potentially high benefit study to improve cell performance. T4.2 was seen as a risk mitigation strategy regarding contact resistance issues in IBCs that were expected to become more severe when the contacts for both charge polarities have to share the rear side of the wafer. However, the work on PECVD-a-Si:H and nc-Si:H-based contacts for IBC-SHJ has made very good progress (cf. progress and deliverable reports for WPs 5 & 6). Indeed, these materials have proven to be suitable for Voc's well above 700mV and a FF potential beyond 80% (D4.1, M24), and have therefore been selected as contact materials for WP 5 & 6 (MS 2, at M24). Thus, progress in the “conventional” silicon-based contact strategies make the use of alternative contact layers a lower priority. Deliverables D4.1 and D4.2 could thus have been linked at the proposal stage as being two options for the same objective, as fulfilling one is enough for project success. Also, it turned out that although the objectives of this deliverable (Voc and FF) make sense for the final device objective, since this deliverable reflects work on layer properties, a metric based on layer properties (typically targeting the passivation and contact resistivity required to enable the Voc and FF metrics that were chosen here) would have been preferable. Such insights are very valuable for future project writing. Overall, these difficulties and the failure in demonstrating excellent solar cell properties with TMO-based contacts are not precluding the main goals of the NextBase project to be reached, in particular the 26%-efficiency at the cell level and 22%-efficiency at the module level.

6.2 Interconnections with other deliverables

This deliverable is related to the following deliverables/milestones/tasks:

- Deliverable D4.1: “IBC devices employing a-Si:H and c-Si:H based contact stacks with Voc>740 mV and FF>82%” [M24].
- Milestone 2: “Selection of most suitable front stack and back contact system” [M24].
- Task 4.2: “Development and optimization of novel TMOs for selective contacts”.
7 Conclusions

The goal of this deliverable was to demonstrate the implementation of alternative charge selective junctions using transition metal oxides (TMOs) in highly efficient IBC silicon heterojunction solar cells, in order to improve cell performance by reducing transport losses. Furthermore, we were aiming at exploring different deposition techniques such as sputtering, thermal evaporation or ALD, which might provide cost advantages over conventional PECVD-deposited a-Si:H contacts.

During the project, considerable effort was devoted to both understanding the basic materials properties and implementing optimized films into solar cells, and new insights into the physics of these materials were generated. However, the best cell results for all-TMO IBC SHJ cells fall short by 31 mV and 6.4%, respectively, of the \( V_{oc} \) of 740 mV and FF of 82% envisaged for the deliverable. This is mainly due to the limitations of TMO materials properties, while the developed processes — e.g. the shadow mask process mentioned above for the current best cell, or photolithography for e.g. ALD-based films — are in principle well suited to process highly efficient cells. Note that these findings are in line with results reported by other groups in literature; notably, to our knowledge, fill factors above 80% have not been demonstrated with all-TMO-based SHJ cells. The studies summarized above have still yielded a wealth of useful information on the properties of these materials and their interfaces to Si and the metal contacts, as also demonstrated by the peer-reviewed publications referenced in Table 4.

Furthermore, it has become very clear that such TMO films are not only interesting for SHJ cells, but also as contact materials for perovskite solar cells and as cell interconnect in the emerging perovskite/silicon tandem cells and other potential next-generation photovoltaic devices. Thus, these studies are expected to have an impact beyond the NextBase project and to pave the way for future developments.
8 References

[16] D. Menzel, M. Mews, B. Rech, and L. Korte, “Electronic structure of indium-tungsten-oxide alloys and their energy band alignment at the heterojunction to crystalline...
D4.2 – IBC devices with TMO based contact stacks with $V_{oc}>740$ mV and $FF>82\%$.


