Electric transport in 3D photonic crystal intermediate reflectors for micromorph thin-film tandem solar cells

J. Úpping*, A. Bielawny†, S. Lee‡, M. Knez‡, R. Carius‡, and R. B. Wehrspohn†

† Institute of Physics, Martin-Luther-University Halle-Wittenberg, Germany
‡ Max Plank Institute of Microstructure Physics Halle, Germany

ABSTRACT

The progress of 3D photonic intermediate reflectors for micromorph silicon tandem cells towards a first prototype cell is presented. Intermediate reflectors enhance the absorption of spectrally-selected light in the top cell and decrease the current mismatch between both junctions. A numerical method to predict filter properties for optimal current matching is presented. Our device is an inverted opal structure made of ZnO and fabricated using self-organized nanoparticles and atomic layer deposition for conformal coating. In particular, the influence of ZnO-doping and replicated cracks during drying of the opal is discussed with respect to conductivity and optical properties. A first prototype is compared to a state-of-the-art reference cell.

Keywords: photon management, light trapping, tandem solar cells, photonic crystals, atomic layer deposition, inverted opal, current matching, electric transport

1. INTRODUCTION

Micromorph silicon tandems are composed of two cells, an a-Si:H front absorber and a μc-Si bottom absorber (Fig. 1a)). The absorption profiles (Fig. 1b)) of the series-connected cells for typical thickness of the absorbing material lead to an unbalanced distribution of the absorbed photon flux. The front cell produces a lower electrical current than the bottom cell which reduces the overall efficiency since the tandem is a serial connected device.

The combined efficiency of micromorph cells suffers from the difference in absorbed photon flux between a-Si:H and μc-Si under AM1.5 irradiation. Representative currents of the junctions are $j_{sc,a}=10.7\,mA/cm^2$ and $j_{sc,μ}=12.5\,mA/cm^2$ measured within the tandem.\(^1\) To reduce this current mismatch and to operate the tandem at its maximum power point intermediate reflective layers (IRL) can be placed between a-Si:H and μc-Si to alter the photon distribution optically. IRLs have been investigated successfully by several approaches in recent years.\(^2-6\) From the working principle of the micromorph tandem cell, three main requirements for the IRL can be deduced:

- Firstly, the IRL should deliver a spectrally-limited back reflectance for the a-Si:H top cell where the EQE of both junctions overlap.
- Secondly, the IRL should be transparent for red and infrared light in order to avoid a negative impact on the bottom cell.
- Thirdly, the IRL must exhibit a sufficient electrical conductivity as the micromorph tandem is a serial connected device.

Corresponding author information:
J. Úpping: E-mail: johannes.uepping@physik.uni-halle.de
An IRL should reflect photons preferably in the low-absorption regime of a-Si:H (550 nm-700 nm) back into the a-Si:H top-cell. A common approach is the use of thin ZnO layer that generates Fabry-Pérot oscillations enhancing the photon flux in the a-Si:H cell. Three-dimensional thin-film photonic crystals have been suggested as an integrated reflector to optically match the current distribution by appropriate photon management between the two absorbers. Promising candidates for IRL are especially ZnO 3D photonic crystals (PhC) since they do not require additional structuring of the absorber layers. PhCs might offer spectrally-selective reflection as well as a high transmittance in the desired spectral ranges.

In this work, artificial opals using PMMA spheres have been grown via self-organized crystallization and they have been used as templates for the inversion process. After an heat treatment to interconnect the nanospheres to increase the mechanical and thermal stability of the opals atomic layer deposition has been used to fabricate ZnO and Al-doped ZnO inverted opals. Finally, the nanospheres have been removed via wet chemistry methods. This process results in an incomplete inverted opal structure. Due to ZnO as host material and due to the connected structure, the conductivity of the photonic crystal depends on the electrical properties of the ZnO.

2. OPTICAL CURRENT MATCHING

The impact of the reflectance of spectrally selective IRL on current matching within the tandem cell is calculated in order to determine the fundamental spectral properties required for the application of inverted opal filters as IRL. The spectral photon flux density data $\Phi$ of AM1.5 (ASTMG173 illuminance, NREL) multiplied with the EQE allow to determine spectral short-circuit current densities $j_{sc} (\lambda)$ of both junctions (a-Si, $\mu$-Si) which reads:

$$j_{sc} (\lambda) = q_e \Sigma \lambda \Phi(\lambda) EQE(\lambda)$$

In this model, an arbitrary IRL function can be introduced by a reflectivity $R(\lambda)$ in order to obtain its impact on the short circuit currents $j_{sc,a}$ and $j_{sc,\mu}$:

$$j_{sc,a} = q_e EQE_{max} \Sigma \lambda [\phi_0 (\lambda) d\lambda EQE_{n,a}]$$

$$j_{sc,\mu} = q_e EQE_{max} \Sigma \lambda [\phi_0 (\lambda) d\lambda EQE_{n,\mu} \cdot (1 - R(\lambda))]$$

with $d\lambda$ being the step width. We have chosen a measured Bragg peak of an inverted opal thin-film as specular reflection function (Fig. 2b)). The function is characterized by their amplitude $R_{max}$, center position $\lambda_0$ and base width $\Delta \lambda$. The measured reflectance data show a Bragg peak with $R_{max} = 0.73$ and $\Delta \lambda = 175 \text{ nm}$ (sample processed like described in11). Any reflectivity can be described by the variation of the external quantum efficiency $\Delta EQE$, as a change in the quantum efficiencies of both junctions induced by
the altered photon distribution. Thereby, the IRL is directly connected to the impact on current mismatch $\Delta j_{sc} = j_{sc,a} - j_{sc,\mu}$. Photons reflected at the IRL are lost for the absorption in the $\mu$-c-Si cell and can contribute to the a-Si:H top cell current. The absorption in the a-Si:H top cell is below the maximum in the spectral region of overlap and a certain ratio of the light reflected at the IRL adds to back reflection losses:

$$\Delta j_{sc,\mu} = -\Delta j_{sc,a} - \Delta j_{sc,\text{lost}}.$$  

The term $R(\lambda) (1 - EQE_{n,a})$ in Eq. 2 contains the ratio of back-reflected light from the IRL. However, even if the external quantum efficiency contains recombination and electrical losses, it does not allow to quantify them. Therefore, we make use of a normalized EQE. The normalization factor $EQE_{\text{max}} = 0.762$ (i.e. the maximum of the top cell’s EQE (Fig. 1b)) includes the module losses, e.g., front-glass reflection and front-side recombination. Consequently, the absorbance in the a-Si:H top cell for the incident and the reflected light is assumed to be equal. The EQE of the bottom cell has been measured for the same tandem cell. Therefore, it already contains the a-Si:H EQE profile. Thus, the initial flux $\Phi_0$ has to be used in Eq. 3, reduced only by the reflectance function $R$ of the IRL. The investigated spectral range has been limited from 500 nm to 700 nm. Here, the absorption of a-Si:H dominates the EQE response. A calculation towards longer wavelength would leave the range of sufficiently high a-Si:H absorbance. The numerical model does not incorporate absorption by the IRL. This affects the obtained amplitude, e.g., reflectance but does not alter the more important spectral properties.

Keeping $\Delta \lambda = 175$ nm constant, $R_{\text{max}}$ and $\lambda_0$ have been varied (Fig. 3a)). This 2D map shows a similar curve for zero current mismatch $\Delta j_{sc} = 0$ compared to the ideal reflector but a plateau is established already at $R_{\text{max}} = 0.25$. To verify that the absolute current density is not reduced by the IRL compared to the initial device without the IRL, we defined a normalized short circuit current ratio $\zeta$:

$$\zeta = (j_{sc,a,\text{IRL}} + j_{sc,\mu,\text{IRL}})/j_{sc,\text{tandem,initial}}$$  

which yields the ratio of converted photon flux in the tandem with and without the IRL and its dependence on the parameters of the filter. The back reflection losses, which are values under unity of the normalized short circuit current ratio $\zeta$, caused by partial transmission of reflected light in the a-Si:H cell are presented in Fig. 3b). The planar interfaces lead to strong losses at high $R_{\text{max}}$ and large $\lambda_0$.

The results above suggest two favored working regime for the IRL. The first one is the 'green' regime using peak center positions close to 570 nm for values of $R_{\text{max}}$ in the range of 0.6 to 1. High reflectance and short center wavelength of this 'green' regime reduce the back reflection losses down to 1%. The second is the 'red' regime using peak center positions between 640 nm and 700 nm for lower reflectance of about 25%. This will increase back reflection losses to 4%. However, the combination with textured interfaces is expected to compensate this. A significant advantage of this ‘red’ regime is the horizontal plateau of current matching.

<table>
<thead>
<tr>
<th>regime</th>
<th>wavelength range</th>
<th>reflectance range</th>
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<tbody>
<tr>
<td>red regime</td>
<td>640 nm – 700 nm</td>
<td>$\approx 0.25$</td>
</tr>
<tr>
<td>green regime</td>
<td>$\approx 570$ nm</td>
<td>0.6 – 1</td>
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Table 1. Summary of the properties of the two possible working regimes for optimal current matching with their spectral properties.
condition between 640 nm and 700 nm in Fig. 3a).

For effective current matching using an inverted opal PhC a guideline concerning the two regimes can be derived. Working in the ‘green’ regime, where the current mismatch is less dependent on the reflectance \( R_{\text{max}} \), the value of layers of the inverted opal determining \( R_{\text{max}} \) is rather flexible. However, the nanospheres (sphere diameter \( d_{\text{green}} \approx 290 \text{nm} \)) determining the position of the reflection peak should be as monodisperse as possible. Working in this regime the angular dependence of the structure (not presented here) is however disadvantageous, since position of the reflection peak shifts towards the blue spectral for increasing angular incidence. In the ‘red’ regime (sphere diameter \( d_{\text{red}} \approx 360 \text{nm} \)) a change in \( \lambda_0 \) due to the angular dependence of the 3D PhC has almost no effect on the current distribution. A quasi-invariance against angular dependency is observed. For an interference-based IRL, e.g., for systems having an angular blue-shift of a photonic stop gap, the red regime is more robust. Nevertheless, any reflection peak position between both regimes is in principle possible. However, the current mismatch is more sensitive for the peak position and the magnitude of reflection. For example, Bieławny et al.\(^{11}\) realized experimentally a spectral position around (600 nm) has been realized in an IRL prototype.

Since the angular dependence of the EQE of the tandem cell is unknown, our calculation is limited to normal incidence. Furthermore, it is restricted to a perfect conducting and non-absorbing IRL. Nevertheless, our model can be applied to any tandem or even triple cell such as III-V based solar cells using intermediate reflectors.

### 3. ELECTRICAL TRANSPORT

The electrical transport through the intermediate reflector layer is the third critical property for its applicability. From former work it is known\(^{11}\) that the conductivity of plain ZnO by atomic layer deposition (ALD) is too low for being suitable as IRL. A possible solution is the use of Al-doped ZnO (ZnO:Al). To fabricate this material via ALD the normal ZnO cycles (precursor 1: dimethylzinc) is intercepted with single cycles to deposit Al using trimethylaluminum as precursor. In such a way the doping level of aluminum can be tuned by changing the number of Al cycles. To compare plain ZnO with the ZnO:Al, the sheet resistivities are measured. An interdigitated gold mask has been sputtered directly on the thin films with an \( W/L = 36 \). Note that the measured sheet conductivity is a mixture of surface and bulk conductivity. For the electrical measurement thin films with a thickness of about 50 nm had been deposit onto a microscope slide. In Fig. 4, two different samples are compared: a plain ZnO and one Al-doped ZnO:Al with an dopant concentration...
of 3.3%. Both films exhibit an ohmic behaviour (Fig. 4a)). In a corresponding double logarithmic plot the difference of about 4 orders of magnitude in conductivity is observable (Fig. 4b)). An enhancement of the sheet conductivity up to 4 orders of magnitude is observed from a sheet resistivity of $12950 \, \text{M\textOmega/\square}$ for pure ZnO to $3.2 \, \text{M\textOmega/\square}$ for Al-doped ZnO. This enhanced sheet conductivity can also be observed for Al-doped ZnO inverted opal crystals under scanning electron microscopy investigation where nearly no charging effects had been observed.

The rather high sheet resistivity originates from the extremely thin film thickness of 50 nm compared to standard ZnO:Al films of 1-2 $\mu$m which have typically $10 - 100 \, \Omega/\square$. Nevertheless, since the tandem cell is a serious connected device, the IRL layer has only 2 $\mu$m thickness yielding to a rather low potential drop being even enhanced by replicated cracks. An additional enhancement of current flow through an inverted opal replicated via ALD originates from cracks (defects) which occur during the process of drying. The filled cracks form an interconnection grid through the whole layer. To estimate the impact of this interconnected grid to the whole conductivity of the inverted crystal, the normalized area of the cracks $C_A$ is determined by an optical microscopy picture (Fig. 5a)). Using image processing tools the area for this sample can be calculated:

![Optical microscopy picture of an opal](image1.png)

![Sketch of the contribution of the cracks to the current flow within an inverted opal structure](image2.png)

Figure 5. a) Optical microscopy picture of an opal under a magnification of M=400 after drying. Note the regular pattern of the drying cracks. b) Sketch of the contribution of the cracks to the current flow within an inverted opal structure.
\[ C_A = \frac{A_{\text{crack}}}{A_{\text{pic}}} = 0.078 \]  

where \( A_{\text{crack}} \) is the area covered by the cracks and \( A_{\text{pic}} \) is the area of the picture.

This fraction seemed to be very small but within the inverted opal only 26% of the volume are filled with ZnO while 74% are air. Within the core shell structure\(^\text{14}\) additional voids decrease the filling fraction down to 24%. Assuming a isotropic homogeneous ZnO and only bulk conductivity, the overall conductivity scales with the cross-section of the structure. This cross-section depends on the position within the crystal due to its 3D nature. A comparison between cross-sections of different geometric structures involved in the process and the crack-enhanced cross-section of the core shell structure is presented in Fig. 6a). Since the relevant structural information is contained within the first two layers of nanospheres with diameter \( d \) due to periodicity only two layers of nanospheres are shown in Fig. 6. The centres of the nanospheres are located at 0.5\( d \) and \( \sqrt{2/3}+0.5d \) where \( d \) is the diameter of the nanospheres. They define the area of the opal and therewith the area of the complete inverted opal. The shell area is a combination of the opal and the conformally-coated ZnO. Due to the conformal coating the thickness of the shell \( d_S \) is limited to the thickness where the complete area of \( \sqrt{3} \) is filled. This thickness is determined as \( d_S = 0.077d \) in agreement with the analytical value. The area of the conductive material is given by difference of the shell area and the opal area. Even though the cracks are covering only a small area, the massively filled cracks cover a significant part of the cross section area for the current flow. In particular, at positions where the air sphere centres are located [0.5; \( \sqrt{2/3}+0.5; \ldots \) the cracks become very important (Fig. 6b)). At this depth the cross section area of the cracks is comparable to the area of the whole inverted opal. Summing everything up, the cracks contribute to about can transport 45% of the current flow. This value holds for an incomplete filled inverted opal as well as for a perfect inverted opal. Unlike in depth between two layers where the cracks can transport \( \approx 21\% \) of the current flow in the inverted opal and \( \approx 30\% \) of the current flow in the incomplete inverted opal. This difference is caused by the air void between the spheres which occur during the incomplete inversion. In conclusion, the cracks will contribute the lateral current flow by about 45%.

### 4. PROTOTYPING

The first IRL prototype integrated onto the top cell was produced growing an opal template on the back side of an a-Si top cell. The fabrication process run top to bottom starting with the front glass ending with the back contact. Our IRL consists of \( d = 360 \text{ nm} \) air spheres surrounded by undoped ZnO from atomic layer deposition. On the back side of the IRL a thin layer of silicon was deposit to simulate the correct optical
The whole sample was terminated with a metal back contact (Fig. 4a)). To verify the impact of the IRL to the top cell, the external quantum efficiency has been measured in the visible spectrum (Fig. 4b)). Note that the EQE was measured at reversed bias voltage due to the low conductivity of the undoped ZnO. The bias influence has been observed to saturate between 2\( \text{V} \) and 3\( \text{V} \) which is interpreted as a large series resistance in the IRL. In comparison to a high efficient reference cell with randomly textured light trapping surfaces, the flat cell with 3D photonic IRL suffers over nearly the complete absorption region from reduced absorbance. Nevertheless, the proof of concept is given because of the enhanced absorption in the spectral range of design back reflectance of the IRL. In this range both EQE are at the same level (black circle in Fig. 4b)). As a next step, a prototype with the Al-doped ZnO is fabricated.

![Figure 7](image_url)

**Figure 7.** a) Scanning electron microscope image of the profile of the prototype: 1) substrate layer 2) TCO front contact 3) a-Si:H top cell 4) photonic IRL 5) backside silicon and metal back contact. b) Experimentally determined spectral EQE of the prototype and a state-of-the-art reference cell (a-Si:H cell on textured substrate). Note, that in the spectral range, where the back reflectance of the IRL is maximum, the EQEs are comparable (black circle).

### 5. CONCLUSION

In conclusion, we developed an optical and electrical model describing and optimizing intermediate reflectors in tandem solar cells. The aim was to minimize the current mismatch and to maximize the absolute current. Our optical model is based on a parameterized description of the impact of any intermediate reflector for normal incidence. The numerical results identify two possible working points for minimum current mismatch and maximum current: the ‘green’ regime (close to 550 nm) and the ‘red’ regime (650 nm - 700 nm). The green regime offers low back reflection losses while the red regime offers a more robust region for spectral imperfections of the IRL. The green regime reduces thermalization in the bottom cell because it filters at shorter wavelengths. However, it requires sharper band stop filtering and generally higher spectral precision of the IRL properties. The red regime promises more tolerant working conditions for imperfect (thus low-cost) IRL structures and is considered preferable for a realization using inverted opals.

The usage of Al-doped ZnO within the intermediate reflector will decrease the sheet resistivity of the IRL layer by almost four orders of magnitude. The obtained sheet resistivity is about 3.2\( \text{M}\Omega/\square \). We numerically analyzed the impact of cracks in the inverted opal on the current flow. It turned out that about 45% of the current flow is through the cracks for a typical inverted opal. Thus, cracks help to increase the vertical conductance of the layer by a factor of 2 relative to the conductance of a perfectly inverted opal. Finally, we prepared a first prototype tandem cell with IRL consisting of an inverted opal. Though the conductivity is still limiting, in the region of spectral enhancement of the top cell, the prototype has the same performance than state-of-the-art amorphous silicon solar cells.
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