Multilayer broadband anti-reflective coatings for bulk heterojunction polymer solar cells

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Abstract
The photocurrent produced by solar cells is limited by reflection losses for all types of photovoltaic devices. The first reflection loss occurs at the glass/air interface of the photovoltaic device. A solar cell without a light trapping mechanism in place loses around 4% of the solar energy at this interface. To minimise the losses, a broadband multilayer thin film anti-reflection (MAR) coating has been designed and deposited onto the glass surface of a solar cell. The coating consisted of four dielectric layers of alternating thin films of ZrO₂ and SiO₂. The layers were deposited by using high rate pulsed DC magnetron sputtering using time only for nanometre thickness control. Spectrophotometer measurements confirm that the transmission increased over the spectrum utilized by the bulk heterojunction (BHJ) solar cell (350nm-700nm). The weighted average reflection reduced from 4.22% to 0.99%. BHJ solar cells with a PCDTBT:PCBM blend serving as the active layer were prepared on a MAR coated soda lime glass slides to verify the effectiveness of the coating. The efficiency increased by 0.18% at STC from 4.98% to 5.17% (a 3.7% relative increase). The gain was achieved by increasing the photocurrent from 11.96 mA/cm² to 12.36 mA/cm².

I. Introduction
Photovoltaics (PV) is a technology perceived as a credible alternative source of energy for the future, it is anticipated that up to 50% of the global energy needs will be met by energy generated by solar technologies by 2050 [1]. All the flat panel PV technologies share a very similar structure, with a glass cover at the top, underneath which a PV device is located. Because of the refractive index difference between the glass (n=1.52) and air (n=1) reflection losses occur. A glass surface reflects around 4% of the light across the spectrum used in a solar cell. This reflection loss is common for all PV technologies. These reflection losses can be reduced by glass surface modification or by applying an antireflective (AR) coating on the surface of the glass.

The simplest AR coating which can be used is a single layer refractive index matching coating. This coating is designed based on refractive index matching and quarter wavelength destructive interference. The biggest challenge of this approach is the availability of material with refractive index lower than that of glass. Magnesium Fluoride (MgF₂) is a commonly used material for single layer AR [2]. The drawback of the MgF₂ is the low durability which would not allow the AR surviving the 25 years lifetime of the module. Another drawback of the single layer AR is limited efficiency of the design by the “V” characteristics of the coating.

Multilayer AR design is a more promising solution to the problem. The advantage of this approach is the fact that material with refractive index lower than glass is no longer required; pairs of low and high refractive index materials are used instead. The low index material is usually silicon dioxide (SiO₂). The high index material is usually chosen from a range of metal oxides including zirconium dioxide (ZrO₂), hafnium dioxide (HFO₂), titanium dioxide (TiO₂), niobium pentoxide (Nb₂O₅) and tantalum pentoxide (Ta₂O₅). The choice is dictated by the level of anti-reflection required, lifetime, durability and by cost. Careful design of the thickness of each layer in a multilayer stack allows the interference of light to be controlled and used to reduce the reflection losses. These dielectric metal-oxide materials are hard and scratch resistant and adhere well to glass surfaces. Their durability and environmental stability is exceptional and already well proven in the ophthalmic and precision optical applications even on plastic substrates [3].
Polymer solar cells have recently attracted much attention due to the solution processed nature of their photoactive layer, which allows for compatibility with roll-to-roll processes such as printing or spray-coating on cheap, flexible substrates [4], [5]. Due to the short diffusion length of excitons in typical organic semiconductors (around 10nm [6]), a bulk heterojunction (BHJ) design is typically used for the photoactive layer. This involves an inter-penetrating mixture of donor (in this case the polymer PCDTBT) and acceptor (PC70BM) domains with length scale comparable to the exciton diffusion length.

II. Anti-Reflective Coating design

The reflection of light is a result of the difference in the refractive index between two mediums. The amplitude of the reflected waves at the medium boundary can be calculated using Fresnel equations. Single layer AR utilise material with refractive index between the glass and the air, lowering the amount of the light reflected at the surface of the glass. The coating also uses interference between the light reflected from the glass and AR surfaces to reduce the total amount of light reflected.

Light interference

Anti-reflection coatings, single and multi-layer, utilise interference to control the reflection. In a thin film stack system the waves reflected between different medium boundaries can interfere. The interference can occur under the condition that the thickness of the film is less than the coherence length. When the phase difference is equal $\Delta = k\pi$ (where $k$ is any integer), destructive interference occurs and results in the amplitude of light being reduced to a minimum (equals 0 when $A_1 = A_2$). The phase change is a function of the distance travelled. Therefore the phase difference between waves can be controlled by selecting the refractive index and adjusting the thickness of the layer. The single layer ARC uses this interference mechanism by depositing a layer with a thickness equal to a quarter wavelength, $\lambda/4$. This results in a phase change equal to $\pi$ and thus the destructive interference occurs between the light reflected back toward the top surface of the ARC and the light reflected from the ARC coating surface. This enables the reflection to be reduced at a chosen wavelength with the effect diminishing gradually for shorter and longer wavelength. This type of coating is referred to as a “V” coating since the reflection rises rapidly at each side of the chosen wavelength. The MAR coating uses coupled medium boundaries and this way the efficacy of the anti-reflection effect can be greatly improved and extended across a wavelength range. The performance of the MAR is adjusted by tuning the thickness of each layer. The performance of the MAR can be improved by increasing the number of layers in the multilayer stack. However, increasing the number of layers increases the materials usage and the thin film deposition process time. This work has focused on the development of a 4 layer broadband design.

“Essential Macleod” optical modelling software package was used to design MAR coating for the BHJ solar cell [7]. The software models the optical coating using the transfer matrix method to predict propagation of electromagnetic wave through the thin film stack. In this work, Zirconia ($ZrO_2$), a relatively low cost material, was chosen as the high refractive index material, with silica ($SiO_2$) as the low index material. The design was optimized to minimise the reflection for wavelengths in the range between 350 nm and 700 nm. The limits are set by the BHJ solar cell spectral response and the solar spectrum. The design of the MAR coating used for a thin film BHJ solar cell is shown in Table 1, the total thickness is only 241nm and of which 133nm is zirconia.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Refractive Index</th>
<th>Extinction Coefficient</th>
<th>Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medium</td>
<td>Air</td>
<td>1.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>SiO$_2$</td>
<td>1.45</td>
<td>0.0</td>
<td>81.56</td>
</tr>
<tr>
<td>2</td>
<td>ZrO$_2$</td>
<td>2.13</td>
<td>0.0</td>
<td>117.18</td>
</tr>
<tr>
<td>3</td>
<td>SiO$_2$</td>
<td>1.45</td>
<td>0.0</td>
<td>25.57</td>
</tr>
<tr>
<td>4</td>
<td>ZrO$_2$</td>
<td>2.13</td>
<td>0.0</td>
<td>16.68</td>
</tr>
<tr>
<td>Substrate</td>
<td>Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A weighted average reflection (WAR) is a more representative measurement of the reflection loss for a solar cell, since it includes the importance of the photon flux $\Phi$ in the AM1.5G solar spectrum. WAR is calculated using equation:

$$WAR(\lambda_{\text{min}}, \lambda_{\text{min}}) = \int_{\lambda_{\text{min}}}^{\lambda_{\text{min}} + \Phi_\lambda R} d\lambda$$

The model shows that the WAR (350,700) for reflection from the front surface of a glass slide
is reduced from 4.22% to 0.99% after applying the MAR coating. This corresponds to a possible short circuit current gain of 0.68mA/cm².

III. Experimental

Pattered glass-ITO substrates (20 Ω/□) from Ossila Ltd were cleaned by sequential sonication in Helmanex solution, IPA and DI water before being dried with compressed nitrogen. At this point the substrates were transferred to a nitrogen atmosphere for the remainder of the processing. Firstly, a 10nm layer of molybdenum oxide was evaporated onto the ITO to act as a hole transport layer. A blend of PCDTBT:PC 70BM (both from Ossila) in a ratio by weight of 1:4 at a concentration of 20mg/ml was spin-coated to create the active layer of the device, with a thickness of 70nm. The reflective rear electrode was then deposited by sequential evaporation of 6.5nm calcium and 100nm aluminium. All evaporations were performed at <10⁻⁶ mbar. Encapsulation was achieved using a glass slide and a UV epoxy (Ossila), cured under a UV lamp for 30 minutes. Only after encapsulation were the devices removed from the nitrogen atmosphere.

The thin film stacks for the AR coating preparation were deposited by pulsed DC magnetron sputtering in a “PV Solar” deposition system from Power Vision Ltd., (Crewe, UK). The system was designed specifically for the deposition of multilayer thin film stacks. The system can be equipped with up to four 6 inch circular magnetrons mounted vertically around a circular chamber. During reactive sputtering growth of the dielectrics one of the magnetrons is replaced with an oxygen plasma source. The samples are mounted vertically on a rotatable carrier, designed for mounting 5cm x 5cm substrates. The carrier rotates typically at 120rpm during the deposition process. Two magnetrons fitted with 6 inch diameter silicon and zirconium planar metallic targets are used during the growth. In each pass of the carrier a thin layer of metal ~1nm is deposited. The metal layer is then exposed to oxygen plasma located at a third position allowing the metal films to be converted into the optical quality metal-oxides required for the MAR design.

The layers for this study were sputtered using a pulsed DC power supply (Advanced Energy Inc. Pinnacle plus 5kW) in an argon/oxygen environment. The zirconium was sputtered at 1kW using a 1.5µs reverse time, whilst the silicon was deposited at 1.5kW and 2.5µs reverse time. The frequency of the pulse was set to 150 kHz for both materials. The strategy of separating metal deposition from the oxidation process in separate zones avoids reactive sputtering hysteresis effects and also allows high deposition rates to be obtained [8]. The films were first deposited on 1mm thick soda lime glass slides to allow measurement of the optical properties of the materials deposited and the establishment of their deposition rates. The complete MAR coating was then deposited on a glass slide to assess its performance against the model and then onto a top surface of a BHJ solar cell. The refractive index, extinction coefficient and thickness of the deposited films were measured using a Horiba Jobin Yvon UVISEL iHR320FGAS spectroscopic ellipsometer. The anti-reflection performance of the coatings deposited was tested by measuring the light reflection spectrum using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The MAR coating was deposited on the front surface of thin film BHJ solar cells. The efficiency of the cell was measured at STC conditions, using a Oerlikon-WACOM solar simulator, before and after applying the broadband AR coating. An aperture mask was used to define an active area of 0.0256cm².

Figure 1 Refractive index film dispersions of SiO₂ and ZrO₂ films deposited in the PVSolar sputtering system.

IV. Results

Spectroscopic Ellipsometer

The spectroscopic ellipsometer showed that the deposition rate of the Zirconia and Silica were 0.7nm/s and 0.66nm/s respectively (measured for rotating substrate holder). The dispersion of the refractive index of the films used for preparation of the AR coatings is shown in Figure 2.
Spectrophotometer

Figure 3 shows reflection spectra measured for an uncoated and AR coated 1mm thick soda lime glass. The comparison shows a significant reduction in reflection measured across the considered spectrum.

Figure 2 Reflection Spectrum measured for uncoated and MAR coated soda lime glass

Solar simulator

The AR coating was deposited onto a substrate with six solar cells. The efficiency of the solar cells was measured before and after depositing the coating. Figure 4 shows I-V curve measured at STC before and after applying the coating to the surface of the solar cell.

Figure 3 I-V curves measured for solar cell before and after applying the AR coating.

Table 2 Average change in short circuit current and relative change photon conversion efficiency measured before and after applying the coating

<table>
<thead>
<tr>
<th></th>
<th>Change in $\eta$ [%]</th>
<th>Change in $J_{sc}$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>average</td>
<td>3.20</td>
<td>3.12</td>
</tr>
<tr>
<td>Best</td>
<td>3.68</td>
<td>3.33</td>
</tr>
<tr>
<td>Worst</td>
<td>2.88</td>
<td>2.90</td>
</tr>
<tr>
<td>std. dev.</td>
<td>0.28</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The change in the short circuit current and photon conversion efficiency is listed in Table 2.

V. Summary

A four layer antireflective coating for BHJ solar cells was designed, deposited and tested. The coating was designed using Essential Macleod software; the modelling showed that the WAR can be reduced from 4.22% to below 1%. The total thickness of the AR coating was only 241nm, with 133 nm of Zirconia.

The coatings were deposited using Pulsed DC magnetron sputtering system. The films were deposited at ~0.7nm/s deposition rate (on rotating octagonal sample holder). Spectroscopic ellipsometry showed that the films did not absorb light in the considered spectrum.

The coating was deposited on solar cells, and resulted in an increase in the short circuit current of 3.3%.

References