Transparent back contacts for P3HT:PCBM bulk heterojunction solar cells

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Abstract. A new combination of layers functioning as a transparent contact is proposed and tested in real solar cells. The contacts consist of TiO₂ layers and thin metal layers (Ag, Cu) and are deposited by magnetron sputtering. The optical transmission and electrical conductivity of the transparent contact layers (TCL) are measured. The TCLs are applied as back contacts in bulk heterojunction polymer solar cells deposited on ITO covered glass and consisting of the following layers: ITO/PEDOT:PSS/P3HT:PCBM/back contact. The organic layers are deposited by spin-coating. For comparison, the same bulk heterojunction polymer solar cells are prepared with a sputtered Ag back contact. The first results show a dependence of the current-voltage parameters of the studied solar cells on the thickness of the different component layers of the transparent back contacts. There is a balance that has to be observed between the electrical characteristics of the contacts and their optical transparency. Future plans involve their inclusion as intermediate contacts in tandem organic solar cells.

1. Introduction
A large number works have been recently devoted to the development of transparent conductive layers (TCLs) suitable for use as electrodes in organic photovoltaic cells. These include the proposition to use three-layer structures consisting of a thin metal film (Ag, Au, Cu) sandwiched between metal oxide layers (ZnO, ZnO:Al, ITO etc.) [1] The advantages of these TCLs are that they can be thinner and more transparent than ITO for the same conductivity and avoid the use of the expensive element indium. Moreover, they can be deposited by sputtering at a low temperature, which is an advantage when fabricating organic solar cells. A number of papers have been published on the dependence of the conductivity and transparency of such films on the deposition method, composition, thickness of the constituent layers, etc. [2,3]. Such layers have been successfully applied in polymer-based solar cells.

TiO₂ and TiOₓ layers have been used in organic solar cells mostly as single hole-blocking layers [4,5]. There are few publications on TiO₂/Ag/TiO₂ multilayers. They include a study of their optical properties and their application in dye-sensitized solar cells [6,7].

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Another incentive for the development and application of TCLs has been the attempt to develop inverted organic solar cells in which the solar light falls through the cathode instead of through the anode [4,5]. An advantage of such a structure is the higher stability under ambient conditions.

Transparent contact layers are also necessary for the implementation of tandem organic solar cells as the intermediate contact between two cells connected in series. This contact layer should consist of a hole transporting layer (HTL), an electron transporting layer (ELT) and a recombination layer between them which is often implemented as a thin metal layer or a layer of metal nanoparticles [8]. A number of materials have been experimented in view of these applications, e.g. NiO, MoO₃, V₂O₅, WO₃, ITO as hole transporting layers and ZnO, TiO₂ and Cs₂CO₃ as electron transporting layers. ZnO is not very suitable for some of these applications as it is attacked by the very acidic PEDOT:PSS used as a hole transporting layer in many experimental solar cells.

In this contribution, we present results obtained when transparent conducting layers consisting of multilayer structures of TiO₂ and metal components (Ag or Cu) are used as the cathode back contact of a polymer solar cell with a P3HT:PCBM bulk heterojunction active layer.

2. Experimental
The polymer solar cells studied were prepared in the following manner. Structured ITO covered glass slides from Ossila were used, ITO being the front anode layer. They were cleaned using a 10 % NaOH solution in an ultrasound bath, deionized water and isopropyl alcohol and dried in N₂ gas. Then a layer of PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) Clevious P, purchased from K.C. Stark, was deposited by spin-coating at 1750 rpm for 60 s. After deposition, the film was annealed in Ar for 30 min at 130 °C. Next, the active layer was deposited by spin-coating from a 12 mg/ml 50:50 weight ratio solution in chlorobenzene of rr-P3HT (poly(3-hexylthiophen)) from Rielke Metals and PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) from Solenne. The solution was obtained by stirring for 48 hours at 50 °C under argon and deposited at 400 rpm for 80 s. After deposition, the layer was kept for 10 min under the solvent vapor.

The back cathodes of the solar cells were deposited by magnetron sputtering in a Tokuda CFS-4ES sputtering equipment from two targets. They were either the transparent conductive layers studied in this contribution or a metal Ag contact for comparison. The Ag contact was sputtered for 5' at 200 W from a Kurt J. Lesker 99.99% silver target. The transparent contacts were deposited in one of the following sequences of material and times of deposition: 1) Ag 7"/TiO₂ 6'/ Ag 7"/ TiO₂ 4', 2) Ag 15'/TiO₂ 90'/ Ag 15'/TiO₂ 90', 3) Ag 7'/ TiO₂ 45'/ Ag 7'/ TiO₂ 45' and 4) Ag 15'/ TiO₂ 60'/ Cu 15'/TiO₂ 60'. The TiO₂ and Cu depositions were carried out at a power of 300 W from Kurt J. Lesker 99.99% targets without heating the substrates, while the Ag deposition was conducted as described above.

The solar cells prepared in this way were immediately encapsulated with a cover glass attached using a UV-light curable resin provided by Ossila. No glove box was used in the preparation process. The solar cells were further annealed in air on a hot plate for 10 minutes at 150 °C. This has been found [9] to improve greatly the characteristics of the solar cells. In this way, six solar cells, each with an area of 1.5×3 mm, were produced on the same substrate.

Finally, electric contacts were attached and the I-V characteristics were measured using a halogen lamp for illumination.

Separately, the transparent back contact layers were deposited on glass for measuring their conductivity and optical transmission. The sheet resistance was measured by the four-probe method and the optical transmission, using a Shimadzu UV-3600 spectrophotometer.

3. Results
Figure 1 shows the transmission spectra of the transparent back contacts studied. The absorption spectrum of the active layer of the polymer solar cell is also given for comparison with the transparency range of the conducting films. The films are used as back contacts in this instance, but
the solar cell could be inverted and illuminated from the back through the contact. The next step of this work is planned to be the construction of tandem solar cells in which this transparent contact would be the recombination layer between the two cells and the second cell would be a P3HT:PCBM bulk heterojunction.

Table 1 shows the conductivity measured by the four-probe method of the different films studied. It should be noted that although we present data for the sheet resistance, measured horizontally, the vertical resistance of these layered films would be low enough. The thickness of the films is between 20 nm and 40 nm.

Figure 2 shows the current-voltage characteristics of typical solar cells made using the films considered as back contacts. The characteristic of an identical cell made with a sputtered Ag back contact is shown for comparison.

4. Discussion
The data presented in the previous section demonstrates that a very careful optimization has to be carried out on the structural, optical and electrical properties of the TCLs proposed for use in polymer solar cells. TCO1 shows a very high transparency but the corresponding solar cell has poor performance. TCO1 and TCO3 have in common the quite high transparency, which is connected with the very thin Ag layers used – sputtered only for 7". However, in both cases, in spite of the good planar conductivity, the current-voltage characteristics demonstrate low $V_{oc}$ and $J_{sc}$ as well as an S-shape deformation. It is interesting to note that the large difference in the thickness of the TiO$_2$ layers in the two cases has no effect on the planar conductivity and little effect on the $I-V$ characteristics.

![Figure 1. Transmission curves of the TCLs studied. The absorption spectrum of the polymer solar cells’ active layer is also shown for comparison.](image1)

![Figure 2. Current-voltage characteristics of polymer solar cells made using the studied TCLs as back contacts. The characteristic of a cell made using sputtered Ag as back contact is given for comparison. The inset shows more details of the characteristics at smaller short current densities.](image2)
A thicker metal component sputtered for 15" improves the $J_{sc}$ but lowers the transmission of the layers, as demonstrated by TCO2 and TCO4. The use of Cu in TCO4 leads to a flat transmission spectrum in the region where the P3HT:PCBM active layer has its maximum absorption. Unfortunately, the transmission is less than 40%. The planar conductivity of that film is the best amongst the TCLs studied. However, the solar cell characteristics in this case are not much better than the ones for TCO1 and TCO3.

The best solar cell parameters, which are comparable to those of the cell with the Ag back contact, are observed for TCO2. In this case, the two metal component layers of the TCL are thicker and both composed of Ag. However this TCL does not exhibit a very good transparency. Its planar conductivity is also not the best one. As a whole, there is no correlation between the planar conductivity of the TCLs and the quality of the $I$-$V$ characteristics of the respective solar cells. On the other hand, no great variation in the planar conductivity of the studied TCLs is observed.

One should bear in mind that the metal Ag back contact of the cell used for comparison serves as a mirror and reflects back to the active layer the light passing through, thus increasing the proportion of light utilized by the solar cell. This would increase the short-circuit current of the device in comparison with the ones with a transparent back contact. Therefore, the $I$-$V$ characteristics of the cells with the TCO2 and the Ag back contacts can be considered comparable.

5. Conclusions

Four types of TCLs consisting of alternating metal and TiO$_2$ layers deposited by sputtering were studied as a back cathode of P3HT:PCBM bulk heterojunction organic solar cells. They all show a very good planar conductivity of between 4 and 9 Ω/sq. As they could be used as front contacts in inverted solar cells or as intermediate layers in tandem solar cells, their transparency was measured and compared. The best transparency is demonstrated by TCO1 (table 1). On the other hand, the best solar-cell characteristics are observed for the TCO2 containing a thicker Ag component next to the active layer of the solar cell.

References
[1] Guillén C and Herrero J 2011 Thin Solid Films 520 1
[2] Shen L, Ruan S, Guo W, Meng F and Chen W 2012 Solar Energ. Mater. Solar Cells 97 59
[3] Vedraine S, Hajj A E, Torchio P and Lucas B 2013 Org. Electron. 14 1122
[4] Yeo K S, Nakao S, Hirose Y, Hasegawa T and Matsuo Y 2013 Org. Electron. 14 1715
[5] Mohd Yusoff A R B, Kim H P and Jang J 2013 Solar Energ. Mater. Solar Cells 109 63
[6] Dima I, Popescu B, Iova F and Popescu G 1991 Thin Solid Films 200 11
[7] Ito S, Takeuchi T, Katayama T, Sugiyama M, Matsuda M, Kitamura T, Wada Y and Yanagida S 2003 Chem. Mater. 15 2824
[8] Sista S, Park M-H, Hong Z, Wu Y, Hou J, Kwan W L, Li G and Yang Y 2010 Adv. Mater. 22 380
[9] Sendova-Vassileva M, Popkirov G, Vitanov P, Dikov Ch, Gancheva V, Tsocheva D and Mokreva P 2012 J. Phys.: Conf. Series 398 012049