Influence of the Type of Metal Contact and Post-deposition Treatment on the Performance of P3HT:PCBM Organic Solar Cells

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Abstract. Bulk-heterojunction solar cells based on P3HT:PCBM with Al or Ag electrodes deposited either by magnetron sputtering or by thermal evaporation were produced and their performance compared. The best results were obtained with thermally evaporated Al electrodes. Post-production annealing was applied to the already encapsulated samples and significantly enhanced the efficiency of all four types of cells. For both Ag and Al electrodes deposited by thermal evaporation post-annealing improved the I-V characteristics eliminating the S-shape usually typical for as deposited samples.

1. Introduction

Organic solar cells based on the concept of the donor-acceptor heterojunction have attracted wide interest [1,2]. The efficiency of such solar cells depends strongly on the effectiveness of the photogeneration of excitons and their subsequent dissociation into free electrons and holes. To facilitate rapid dissociation of the excitons and fast transport of the released charges to the electrodes, interpenetrating networks of organic electron donor and acceptor materials are used as the absorbing layer in organic solar cells. Mixtures of semiconducting conjugated polymers serving as electron donor and fullerene derivatives serving as electron acceptor are the constituents of bulk heterojunction (BHJ) structures. The blend of poly(3-hexylthiophen) (P3HT) and the fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is a popular donor-acceptor couple which has been successfully used according to the literature. In most reported cases, indium tin oxide (ITO), covered with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as an intermediate hole-conducting layer, have been used as the transparent positive electrode either on glass or on flexible polyester substrates. Aluminium is often used as the negative electrode. Silver is more stable against oxidation and is also a prospective candidate for the role of the negative electrode. The almost standard method for cathode deposition is the thermal evaporation of Al in high vacuum [3]. Magnetron sputtering is better suited for large-scale production, but is usually avoided because of the potential sputter damages to the organic absorber layer. However, as shown in [4], magnetron sputter deposition can be an alternative deposition technique, if adequate post-annealing is applied.

The purpose of the present contribution is to test, characterize and compare polymer/fullerene bulk-heterojunction solar cells of identical structure and production technology avoiding production steps in
glove box, and using Al or Ag electrodes deposited either by magnetron sputtering or by thermal evaporation.

2. Experimental

Test solar cells were produced using the substrate packs purchased from Osilla. A thin layer (≈ 90 nm) of PEDOT:PSS Clevious P, purchased from K.C. Stark was deposited from water dispersion onto pre-patterned ITO/glass substrates by spin coating at 1750 rpm for 60 s. The films were subsequently annealed for 30 min at 130°C in argon atmosphere. P3HT and PCBM, purchased from Rielke Metals and Solenne, respectively, were dissolved in chlorobenzene (1:1 weight ratio with concentration 12 mg/ml) by stirring for 48 hours at 50°C in argon. The photoactive layer was deposited onto the substrate by spin-coating at 400 rpm for 80 s and the thickness obtained was 80-90 nm as measured by a Talystep stylus profilometer. The samples were kept for 10 min in a closed vessel with solvent-vapor atmosphere to assure slow drying of the polymer for better thin-film morphology [5]. Finally, Ag or Al metal electrodes were deposited by thermal evaporation or sputtering through a steel shadow mask, thus yielding 6 small solar cells on each substrate with surface area of 0.045 cm² each. In the sputtering chamber the samples were subjected to thermal drying in Ar for 10 min at 100°C before sputtering and thermal annealing at 140°C for 15 min after the deposition. No thermal treatments were applied to the samples in the vacuum evaporation chamber. The active area of the samples was encapsulated using a thin glass plate and UV curable epoxy resin. Finally, electrical connection legs were mounted to provide reliable electrical contact for the measurements. Post-production annealing of some of the samples was performed by heating the already encapsulated samples on a hot plate at 150°C for 10 min.

Current-voltage (I-V) measurements with and without illumination were carried out by a computer controlled home-made potentiostat. The voltage scan rate was 20mV/s in the range from -0.5V to +0.6V. A 50W tungsten-halogen lamp powered by a regulated d.c. power supply served as illumination source. Impedance spectroscopy measurements were performed at different bias voltages using a fast Fourier transform (FFT) impedance spectrometer [6, 7] in the frequency range 1.5 Hz – 50 kHz with a 15 mVp-p perturbation voltage.

3. Results and discussion

3.1. Current-voltage measurements

The I-V characteristics obtained in a technological batch showed some deviations from cell to cell and from sample to sample, most probably due to inhomogeneities of the absorbing layers. Here data and results for typical of the respective batch representative single cells are presented and discussed.

I-V curves measured upon illumination of the four types of samples before post-annealing are depicted in figure 1, curves (1). For both metals evaporation leads to significantly higher photocurrents compared to sputtering with the used processing. Structure damages in the thin absorbing layer during the sputtering deposition cannot be excluded. The parameters obtained from the characterization of the cells are presented in table 1.

A look at the curves for the samples before post-annealing in figure 1 reveals not only low photocurrent values at short circuit, but also very low fill-factors and the existence of a characteristic S-shape close to the open-circuit voltage regime. This S-shape kink has been repeatedly mentioned in the literature [1,4,8-10] and several models have been proposed, but as of now this effect is not completely explained for both planar and bulk heterojunction organic solar cells. Often the existence of barriers at the metal contacts is considered. An attempt to model the I-V characteristics of BHJ organic solar cells is presented in [9], where the authors mention that non-ohmic contacts can strongly limit the current flow and lower the fill-factor. According to [8] the appearance of an S-shape I-V characteristic indicates slow charge transfer at one of the electrical contacts of the absorber layer. Further, these authors suggest an effect of possible corrosion of the Al electrode.
The samples with evaporated Al and Ag electrodes worked better than the ones with sputtered electrodes but their photovoltaic performance was also disappointing, especially because of the low fill-factors and the S-shaped I-V characteristics. So the samples were annealed on a hot plate in air at 150°C for 10 min after encapsulation. Representative results are shown in figure 1, curves (2) and table 1. Very significant improvement of the photovoltaic parameters resulted for all of the samples. Short-circuit currents and open-circuit voltages increased markedly. The S-shape feature in the I-V characteristics of sputtered samples, unfortunately, remained, thus their fill-factors were still low. The improvement of the samples with evaporated metal electrodes was less pronounced, but their S-shape kink fully disappeared and fill-factors as high as 60% were calculated.

Using the data for the post-annealed cells with evaporated Al and Ag electrodes, which do not show S-shape near the open-circuit voltage, the series and the shunt resistances were calculated from the respective slopes of the I-V curves, as can be seen in table 1. If the I-V data sets which show an S-kink are evaluated in the same way series resistances in the range of kOhms would result, but the reasons behind the S-shape feature are more complex and not well understood, and thus, it is not correct to apply the slope-method for the estimation of the series resistance. Alternatively, we have tried to obtain some information about the series and shunt resistance values of the cells using impedance spectroscopy.

3.2. Impedance spectroscopy
The series resistance is an important parameter for solar cells of any kind. A number of methods for the estimation of the series resistance of semiconductor p-n junction solar cells are known from the literature [11], however, still further investigations are necessary to prove their validity for organic donor-acceptor solar cells.
Table 1. Parameters obtained from the I-V characterization of the cells and $R_{ser}$ and $R_{sh}$ from the impedance spectra.

| Batch                      | $U_{oc}$, mV | $J_{sc}$, mA/cm$^2$ | FF, % | $R_{ser}$, Ω (I-V) | $R_{sh}$, Ω (impedance) | S-shape |
|----------------------------|--------------|----------------------|-------|--------------------|--------------------------|---------|
| Ag, sputtered              | 375          | 0.93                 | 19    | -                  | -                        | yes     |
| Ag, sputtered, post-annealed | 452         | 4.44                 | 32    | -                  | -                        | yes     |
| Ag, evaporated             | 429          | 3.33                 | 32    | -                  | -                        | yes     |
| Ag, evaporated, post-annealed | 508       | 5.1                  | 53    | 760                | 50                       | no      |
| Al, sputtered              | 409          | 0.82                 | 17    | -                  | -                        | yes     |
| Al, sputtered, post-annealed | 518        | 3.55                 | 32    | -                  | -                        | yes     |
| Al, evaporated             | 496          | 3.33                 | 33    | -                  | -                        | yes     |
| Al, evaporated, post-annealed | 529       | 4.2                  | 60    | 552                | 100                      | no      |

The series resistance of BHJ solar cells should include at least contributions from the ITO and PEDOT:PSS layers, the contact resistance in-between, plus the resistance of the metal electrode, plus the two contact resistances at both sides of the absorbing layer. At least partly, the bulk resistance of the active layer could also contribute to the estimated value of the series resistance.

Several authors have applied impedance measurements to characterize solar cells. Information on carrier lifetime and electron density-of-states [12], mobility [13], density and energetic position of defect states in the absorber [14], etc. can be obtained applying proper calculation models to measured impedance spectra in a wide frequency range, at different bias voltage, with or without illumination.

Often the impedance spectra of a solar cell exhibit a single semicircle in the complex plot of the imaginary part vs. the real part of the complex impedance. A simple equivalent circuit consisting of a series resistor, $R_{ser}$, connected to a capacitor, $C_p$, and a resistor, $R_{sh}$, in parallel to $C_p$, can be used to fit the measurement results obtained for different measurement conditions, i.e. illumination intensity and voltage bias. In most cases, however, the semicircle appears to be somehow depressed. A so called constant phase element (CPE) is then used to replace the capacitance and take account of the distributed nature of the non-ideal capacitance. More generally this effect is attributed to the distribution of time-constants, due to distributions of physical properties such as: structure, dielectric constants, and/or resistivity over the surface of an electrode and/or normally to the electrodes [15]. The impedance of the CPE is defined as $Z_{CPE} = \frac{1}{\sqrt{Q_p(j\omega)^\alpha}}$, where $j = \sqrt{-1}$, $\omega$ is the circular frequency. For $\alpha=1$, $Q_p$ has capacitance dimension and the impedance spectra plot is a semicircle in the complex plane. For higher frequencies (up to 1 MHz), a second partial arc can appear and a more complex equivalent circuit has to be used [12, 16].

The impedance spectra of the samples were measured upon illumination in the range from 1.5 Hz to 50 kHz. The impedance spectra obtained depended strongly on the bias voltage, illumination level and markedly – on post-production annealing. Here only data for the best performing sample, the one obtained with thermal evaporation of Al are presented. Figure 2 shows data measured at reverse bias of -0.3V from the as-prepared sample (curve 1) and the one after post-production annealing (curve 2).
Figure 3 presents data acquired close to the open-circuit voltage. The spectra are shown in the complex plane (figure 2a and figure 3a) and as Bode-plots in figure 2b,c and figure 3b,c to show explicitly the frequency dependence of the real and imaginary parts of the impedance. The equivalent circuit as described above with a CPE instead of capacitance gave a good fit. Even without looking at the fit parameters it can be seen that for both bias voltages used the effect of post-production annealing is very strong.

**Figure 2.** Impedance spectra obtained at reverse bias of -0.3V of the as-prepared sample with evaporated Al contacts (1) and after post-production annealing (2).

**Figure 3.** Impedance spectra obtained close to the respective open-circuit voltage of the as-prepared sample with evaporated Al contacts (1) and after post-production annealing (2).

The shunt resistance obtained from the fit of measured impedance data is representative of the bulk resistivity of the P3HT:PCBM layer due to recombination of charge carriers in the absorbing layer and possibly existing conductive paths between the two metal electrodes across the absorbing layer. The voltage and illumination dependence of $R_{sh}$ is attributed to the photogeneration and/or injection of charge carriers. Measurements at reverse bias of -0.3V (cf. figure 2a) showed almost no significant change in the value of $\alpha$ (ca. 0.95) after post-annealing and the shunt resistance increased from 12.7 kOhm to 31.7 kOhm after annealing. Close to open circuit voltage the shunt resistance decreased from 3.07 kOhm to 1.76 kOhm after annealing. The depression of the semicircles (cf. figure 3a) decreased from $\alpha = 0.89$ before to 0.96 after post-production annealing for measurement close to open-circuit conditions. These data are in good correspondence with the observed improvement of the short-circuit current, the open-circuit voltage and the fill-factor. The accepted opinion, that post-annealing leads to improvement of the morphology of the absorption layer (crystallinity, phase separation etc.) can also be confirmed by the increased value of $\alpha$. The series resistance, as revealed from the fit, is in the range of 100 Ohm, a value much less than the one obtained from the I-V curve slope (552 Ohm, cf. table 1). Obviously, the slope of the I-V curve at open-circuit voltage depends also on other structural and/or interface factors. The value of $R_{ser}$ obtained from the impedance spectra possibly does not account for any resistive effects due to the absorbing layer and its interface to the electrodes. Discussions
concerning the nature of the CPE and its parameter $Q_p$ would be very speculative, due to lack of further data for the absorbing layer morphology, and are beyond the scope of this note.

4. Conclusion
In this contribution bulk heterojunction organic solar cells with sputtered metal contacts are studied and compared to samples with evaporated metal contacts. The photoactive thin film consisting of mixed P3HT and the fullerene derivative PCBM was deposited by spin coating on patterned ITO covered glass plates coated with PEDOT:PSS. Metal electrodes of aluminium or silver were sputtered or evaporated through a shadow mask. The active area was encapsulated using a thin glass plate and UV curable epoxy resin. After encapsulation the samples were subjected to thermal annealing in air. The solar cells were characterized by current-voltage measurements and attempts were made to determine their effective series and shunt resistances by means of impedance spectra measurements. The results of the investigation indicate that cells with both sputtered and evaporated contacts improve their performance significantly after annealing but for sputtered contacts the S-shape of the I-V characteristic and resulting lower fill-factor values are not fully overcome.

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References
[1] Deibel C, Dyakonov V and Brabec C J 2010 IEEE J. Sel. Top. Quant. 16 1517
[2] Wang Y, Wei W, Liu X and Gu Y 2012 Sol. Energ. Mat. Sol. C. 98 129
[3] Singh V, Thakur A K, Pandey S S, Takashima W and Kaneto K 2008 Org. Electron. 9 790
[4] Ahlswede E, Hanisch J. and Powalla M 2007 Appl. Phys. Lett. 90 063513
[5] Chen F-C, Ko C-J, Wu J-L and. Chen W-C 2010 Sol. Energ. Mat. Sol. C. 94 2426
[6] Popkirov G and Schindler R-N 1992 Rev. Sci. Instrum. 63 5366
[7] Popkirov G and Schindler R-N 1993 Electrochim. Acta 38 861
[8] Glatthaar M, Riede M, Keegan N, Sylvestre-Hvid K, Zimmermann B, Niggemann M, Hinsch A and Gombert A 2007 Sol. Energ. Mat. Sol. C. 91 390
[9] Kumar P, Jain S C, Kumar V, Chand S and Tandon R P 2009 J. Phys. D: Appl. Phys. 42, 055102
[10] Tress W, Petrich A, Hummert M, Hein M, Leo K and Riede M 2001 Appl. Phys. Lett. 98 063301
[11] Bashahu M and Habyarimana A 1995 Renew. Energ. 6 128
[12] Garcia-Belmonte G, Boix P P, Bisquert J, Sessolo M, Bolink H 2010 J Sol. Energ. Mat. Sol. C. 94 366
[13] Garcia-Belmonte G, Munar A, Barea E M, Bisquert J, Ugarte I, Pacios R 2008 Org. Electron. 9 847
[14] Khelifi S, Decock K, Lauwaert J, Vrielinck H, Spoltoire D, Piersimoni F, Manca J, Belghachi A and Burgelman M 2011 J. Appl. Phys. 110 094509
[15] Hirschorn B, Orazem M E, Tribollet B, Vivier V, Frateur I and Musianid M 2010 J. Electrochem. Soc. 157 C452
[16] Leeve B J, Bailey C A, Marks T J, Hersam M C and Durstock M F 2012 Adv. Energy Mater. 2 120