Effects of constant voltage and constant current stress in PCBM:P3HT solar cells

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Abstract

The aim of this work is the investigation of forward and reverse bias stress effects, cell self-heating and annealing in roll coated organic solar cells with PCBM:P3HT active layer. In reverse bias stress cells show a constant degradation over time. In forward current stress cells alternate degradation and annealing phases, which are explained through the high power dissipation during the current stress, and the consequent self-heating. The high temperature is able to recover the cell performances at least until a critical temperature is reached. The degradation can be explained by the following mechanisms: the decrease of the net generation rate (due to formation of exciton quenching centres or the reduction of exciton separation rate); the formation of small leaky paths between anode and cathode, which reduces the total current extracted from the cell. The stress-induced damage can be recovered by thermal annealing at 120 °C.

1. Introduction

Advanced PV is becoming of extreme interest, to overcome some of the limits of conventional solar cells, especially in terms of costs and energy payback time. Conventional silicon cells require very expensive production processes, operating in high vacuum and high temperatures, and materials with very high degree of purity. This makes the final cost unattractive and an energy payback time as long as several years. To reduce the cost and payback time, several approaches have been identified by the scientific community: the thin film concept [1] that reduces the amount of material required; the use of new materials (such as organic small molecule and polymers) that are easier to produce [2]; and adopting completely different working principles, such as in hybrid organic–inorganic cells [3].

Besides the very low-cost production techniques (such as roll-to-roll) the organic/polymeric solar cells have very appealing and peculiar features: tuneable colours, (semi)transparency, flexibility, lightweight, and good performance even under diffused radiation.

Despite these advantages, organic solar cells (OSCs) still have some limitations. In literature, there are several papers focused on OSC stability in different environments (temperature and humidity) or light conditions [4–7], highlighting that organic materials are very sensitive to the high energy part of solar spectrum, as well as high temperatures and humidity. Among the known issues, we may cite: the electrical instabilities of the devices; the degradation processes related to temperature, oxygen, and humidity [4] or electric stress; and the generation of exciton quenching centres. In recent years there have been a number of publication addressing the long term stability of OSCs, where the effects of the environmental factors, such as light, temperature and humidity on the device performance have been addressed [8–16].

In the presented work we focus instead on the effects of the electrical stresses, such as forward and reverse bias stresses, as well as the self-heating and annealing of the device, which may eventually help in the process of developing a methodology for accelerated stress tests and rapid identification of failure mechanisms in organic solar cells.

Moreover, the stress procedure used in this work may also simulate the operation of a cell under non-uniform light illumination. In fact, in real applications, the partial shadowing of the solar cells or a non-uniform illumination on the entire panel can result in reverse biasing of one of the solar cells in the array. In the particular case of total shadowing of a solar cell in a string, the cell will act as a load for the rest of the cells, which force the current through the shaded cell [17]. This may cause breaking of the solar cell, increase of the temperature [18], and possibly degradation of the encapsulation of materials.

Especially since organic photovoltaic is suitable not only for roof mounting, but also for integration in windows, shelters, and facade decorations, the ideal positioning and orientation of the cells or panels cannot always be met. This makes more difficult to assure a uniform illumination of the cells, emphasizing the above-mentioned problem.

In the light of these considerations, the systematic study of solar cells under low illumination levels and under reverse biasing stresses is of particular importance for the reliability of a solar system. The methodology described in Section 2, used to identify the failure points, is a step stress strategy in which the current or voltage levels are increased...
step by step until the failure of the cell is reached. In this way any hard failure and soft pre-failure degradation mechanisms can be revealed and analysed.

2. Experimental and devices

In this work we used organic solar cells with a PCBM:P3HT active layer. The active layer thickness is 300 nm and the active area is 1 cm². The samples have been fabricated by the Energy Department at Technical University of Denmark, and they have been produced by means of slot die coating and flexographic printing using roll coating machinery.

After transportation to Padova the solar cells were subjected to several stress-characterization steps, until the cell breakdown was reached or a maximum stress time was elapsed. The procedure is depicted in Fig. 1 and it consists of a sequence of steps. After the initial characterization, we applied a constant voltage stress (CVS) or constant current stress (CCS) to the cell for 1000 s. After the end of the step, the cell was measured again, the stress voltage/current was increased and a new 1000-s stress step was performed. All stresses were carried out in the dark. During CCS the currents started at 20 mA and were increased by 20 mA after each step. In CVS the voltage was –2 V at the beginning followed by 0.2 V increases after each step.

Electrical characterization included the measurement of the short-circuit current (ISC), the open circuit voltage (VOC) and the I–V curves both in the dark and in the light. All measurements were done using a white LED illuminator. Illumination intensity was calibrated by means of a certified reference solar cell. We corrected the calibration values, taking into account the mismatch of the illumination spectra.

3. Results and discussion

3.1. Stress-induced degradation of the I–V curves

Fig. 2 represents the evolution of the cell I–V curves under CVS. There is a clear degradation of the characteristics as indicated by the arrows, especially in the ISC. For comparison, Fig. 3a–c show the I–V behaviour during the CCS, which is somewhat different from the CVS results. During CCS, we can observe three distinct regions, corresponding to three different degradation phases.

The first region (phase 1), shown in Fig. 3a, corresponds to the stress current from 20 mA to 200 mA. Here the cell undergoes degradation similar to the CVS. In Fig. 3b (phase 2) the opposite trend appears and the curves increase, indicating a recovery process of degradation. This occurs when the stress current ranges from 200 mA to 320 mA. This is followed by the third region (phase 3) of rapid degradation, which starts at a current level of 320 mA and continues until complete breakdown of the device, as shown in Fig. 3c.

Fig. 4 shows the comparison between the ISC behaviours during CVS and CCS plotted against the stress step values: the peculiar fluctuating behaviour of the cells subjected to CCS is clearly observed. In contrast, CVS induces a monotonic reduction of ISC. From Figs. 2 and 3 we observe a very small variation of VOC during CVS. Meanwhile CCS produces larger instability of VOC, especially during phase 3.
3.2. Origin of cell degradation

A careful analysis of the I–V curves during the stress tests showed that CCS and CVS reduce the \( I_{SC} \). The following mechanisms are considered:

1) a decrease of the net generation rate, e.g., due to formation of exciton quenching centres or the reduction of exciton separation rate in the donor/acceptor complexes.
2) the formation of small leaky paths between the anode and cathode, which reduces the total current extracted from the cell.

While the former mechanism is expected to affect only \( I_{SC} \) the latter also impacts the \( V_{OC} \). This suggests that some residual "microshunts" are formed during stress. We believe that as soon as a conductive path is formed a high current will flow, inducing a very large localized power dissipation, which will result in quick burning of the shunts. Small defect-rich and leaky spots are likely to be formed in the neighbourhood of the burned path, increasing the total shunt resistance of the cell, as the stress proceeds. In turn, as the shunt is burned the effective area of the cells is reduced, further decreasing the I–V curve.

To confirm this idea, we used a simple model, by adding a shunt resistance to the fresh device and reducing the effective generation rate. In this simplified picture, we assumed that the photocurrent is given by the Sokel–Hughes model [19], firstly we proposed for insulator and then also adopted in organic solar cells. We adopted the simplest case, which is solved analytically, but it is still adequate to describe the carrier extraction in organic solar cells. Following this model the photocurrent is:

\[
J_{PH}(V) = qGd \left[ \coth \left( \frac{V-V_i}{2V_T} \right) - \frac{2V}{V-V_i} \right]
\]

where \( G \) is the average generation rate, \( V_i \) is the built-in potential, \( V_T \) is the thermal potential, \( q \) is the elementary charge, and \( d \) is the active layer thickness. The complete cell model is shown in Fig. 5a. The photocurrent is represented by the current source, \( R_S \) is the cumulative series resistance, \( R_{sh} \) is the parasitic shunt resistance of a fresh device, and \( R_{P2} \) represents the additional "stress-induced" shunt resistance. Fig. 5b and c shows some examples of fitting of the stressed cell I–V during CCS and CVS, respectively. Despite the simplicity, the model excellently fits the experimental data.

3.3. Role of self-heating in cell degradation

Because we measured a considerable power dissipation during the stress, we attribute the recovery during CCS (phase 2) to thermal annealing due to self-heating. To assess the exact role of the self-heating in cell degradation kinetics, we measured the cell temperature under stress by means of an infrared camera. Some selected temperature images taken during CCS are shown in Fig. 6a, b, and c, corresponding to the three degradation phases depicted in Fig. 3a, b, and c, respectively. Fig. 7a and b represents the calculated power dissipated during CCS and CVS, respectively.

We believe that during phase 2 cells undergo an annealing effect due to the high temperature reached during the stress (between 90–150 °C). On one hand it is enough to recover the active layer, degraded during the previous phase 1, on the other hand it is low enough to prevent further thermal degradation. Of course, we cannot neglect that a current larger than 200 mA in phase 2 also degrades the active layer at a rate faster than phase 1. Hence, the thermally-induced recovery rate must be larger than the stress-induced degradation rate, at least until the current is smaller than 320 mA and the temperature is smaller than 150 °C. Instead, when the stress current exceeds 320 mA and, in turn, temperature exceeds 150 °C, the very high temperature jointly with the high stress current leads again to the cell degradation.

Fig. 4. Short circuit current degradation during CCS (a) and CVS (b). Two samples are shown for each stress.

Fig. 5. Simplified model for the stress induced shunt formation (a) and comparison between degradation model (red lines) and experimental data (symbols) during CCS (b) and CVS (c). The solid blue line is the fresh device. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
self-heating effects. In fact, the maximum power dissipated during CVS barely reaches 350 mW in the worst case. Such a value is much smaller than the power dissipation during CCS, due to the much smaller reverse current value, even at high voltages. Consequently the maximum temperature observed during CVS does not exceed 85 °C, i.e., not sufficient to achieve significant annealing.

To confirm the previous assumptions we performed ageing of stressed cells under thermal heating conditions at 120 °C for 1 h in the dark without applying bias. Fig. 8 shows the I–V curves measured on a fresh cell, after CVS, and after 1-hour thermal annealing. The cell recovers the short circuit current after the annealing, and the ISC appears even larger than the one measured before CVS, indicating that some small process-induced damage may also be present in the fresh cell.

4. Conclusions

We analysed the behaviour of polymeric organic solar cells under electric stresses. In reverse voltage stress, cells show a constant degradation over time. In forward current stress cells exhibit degradation and annealing phases, which are explained through the high power dissipation during the current stress, and the self-heating. The high temperature is able to recover the cell performances, at least until a critical temperature is reached. Degradation involves the formation of leaky conductive paths across the cell and the reduction of the net generation rate likely due to exciton quenching centres.

These findings raise several issues which are still open to debate. For instance, what is the exact role of annealing? Does the high temperature completely restore the cell status or does it simply “patch” the damage? In this regard, it is worth to note that a silicon solar cell may reach a temperature larger than 80 °C during sunlight exposure, which accelerates the degradation of the cell. We demonstrated that, moderately high temperature can recover the damage of organic solar cells. What is the real impact of the temperature in the cell lifetime is a question worth a careful investigation, also in the perspective of assessing if conventional standards for solar cell lifetime testing are still suitable for organic photovoltaics.

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Fig. 7. a) Power dissipation as a function of stress time (bottom scale) and stress current (top scale) during CCS; b) power dissipation as a function of stress time (bottom scale) and stress voltage (top scale) during CVS.

Fig. 6. Infrared camera pictures taken on a cell during CCS at different stress levels.

Fig. 8. I–V curves taken on the same cell: before stress, after CVS, after 120 °C-annealing, and after the second CVS performed after annealing.
References