

A new encapsulation solution for flexible organic solar cells

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Abstract

We report herein a shelf lifetime study of poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene-vinylene) (MDMO-PPV):1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C₆₁ (PCBM) solar cells encapsulated in a new flexible and transparent poly(ethylene naphthalate) (PEN)-based ultra-high barrier material entirely fabricated by plasma enhanced chemical vapor deposition (PECVD). We have found in this preliminary work that the encapsulation raises the shelf lifetime (50% of the initial efficiency) of 30 × 57 mm² solar cells from a few hours into the range beyond 3000 h, or more than four months.

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1. Introduction

Due to a strong demand for renewable energy [1] and a widespread and growing interest in organic semiconductor based devices [2,3], organic solar cells have been the object of increasing development during the last decade [4,5]. Recently, efficiencies up to 5% have been reported for both conjugated polymer [6] and small molecule based photovoltaic devices (PV) [7]. Considering their intrinsic physical properties such as light-weight, mechanical flexibility and semi-transparency, these devices may open up new opportunities for applications of PV cells. Besides, conjugated polymers can be made soluble [8] in organic solvents, so that low-cost production of polymeric PV can be envisaged by applying common printing techniques [9]. This allows large-scale roll-to-roll processing using flexible substrates. However, to be viable in the market, such products should not only offer high efficiencies and low cost, but also lifetimes (when 50% of the initial performance level is reached) of at least 10,000 h [10].

1.1. Degradation of organic solar cells

Conjugated polymers such as poly(p-phenylene vinylene) (PPV) are known to be rather unstable in air [11], being particularly susceptible to photodegradation induced by oxygen and moisture [12]. The mechanism involves the binding of oxygen atoms to vinyl bonds, which breaks the conjugation and leads to the formation of carbonyl groups [13,12]. Spectroscopic ellipsometry studies showed that during simultaneous exposure to air and light, the thickness of the active layer increases while its refractive index and absorption coefficient drastically decrease [14]. Moreover, the material for the low work function electrode is usually chosen from metals like Al and Ca, in order to minimize the electron injection barrier and to maximize the open circuit voltage of the solar cells [15]. These metals rapidly undergo oxidation when exposed to air. This leads to the formation of thin insulating oxide barriers [16], hindering electric conduction and collection of the charge carriers. Besides, it has been reported that water can affect the interface between the metallic contact and organic semiconductors by an electrochemical process that causes delamination of the electrode [17].

In spite of the fact that the degradation effect is significantly decreased when conjugated polymers are mixed with fullerenes [18], PPV based solar cells usually do not operate for more

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than few hours in air [19]. Therefore, appropriate encapsulation is mandatory for this type of devices.

The ability of oxygen and moisture to cross an encapsulating membrane is represented by the oxygen transmission rate (OTR) and the water vapor transmission rate (WVTR), respectively. It is generally accepted that the lifetime of organic light emitting diode (OLED) devices above 10,000 h requires WVTR and OTR of about $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ and $10^{-3} \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$, respectively [20]. These values, which seem to be on upper limit of organic solar cells requirements, are about six to eight orders of magnitude lower than the corresponding values of commercially available polymer films (Fig. 1). A quite straightforward solution consists in encapsulating the sensitive devices between glass plates [21], which form an optimum barrier even when the plates are very thin. However, this solution obviously sacrifices flexibility and mechanical robustness of the final device, and therefore is not satisfactory for large-scale, low-cost manufacturing.

1.2. Thin film gas barriers on polymers

Thin film barrier coatings against permeation of gases and vapors deposited onto flexible polymer substrates have been intensively studied for applications in food and pharmaceutical packaging, where improving the barrier capabilities of the bare plastic films by 1 to 3 orders of magnitude is usually considered sufficient (Fig. 1). It has been shown that silicon-based dielectric coatings deposited by plasma enhanced chemical vapor deposition (PECVD) on plastic films can be used as single layer permeation barriers [22,23]. Permeation through those barrier materials is a defect-controlled phenomenon. Fig. 2 shows the OTR of a 13 μm thick poly(ethylene terephthalate) (PET) film versus the thickness of a SiO_x coating deposited by PECVD [24]. It can be seen that near the so-called critical thickness, d_c (here about 15 nm) the OTR drops drastically, yet cannot be improved significantly by further increasing the thickness. It has been observed that nanometer-size structural defects present in the barrier coating, which are mainly caused by intrinsic or extrinsic surface roughness [25] account for this limited performance of single-layer gas barrier.

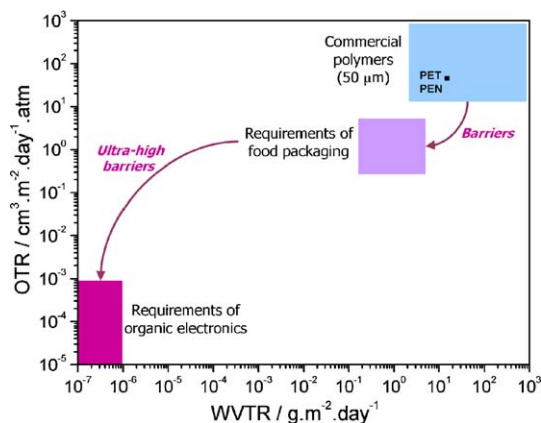


Fig. 1. Oxygen transmission rate (OTR) versus water vapor transmission rate (WVTR) for commercial polymers, encapsulations required for food packaging and for organic electronics purposes.

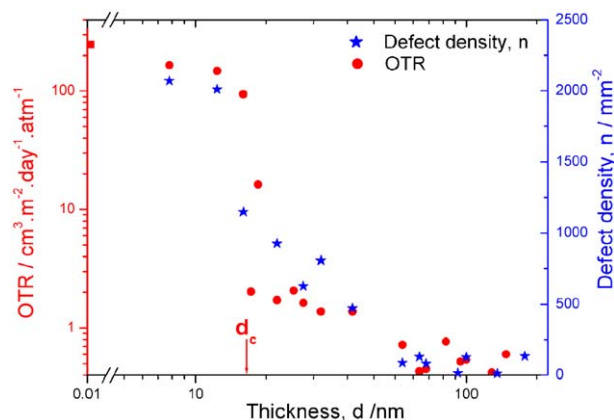


Fig. 2. OTR (●) and defect density (★) versus SiO_x barrier layer thickness deposited by PECVD onto a 13 μm PET film [24].

Theoretical calculations have shown that the total permeation rate through many small pinholes is much higher than that corresponding to the same total pinhole area combined in a few larger defects [26,24]. This can be explained by lateral diffusion and it is of crucial importance when the diameters of defects are small compared with the thickness of the substrate. Finally, it should be noted that deposition of multilayered inorganic films usually improves the barrier performance only slightly [27], mainly because of defect propagation through successive layers during growth.

The most common technique used to achieve ultra-high barrier properties is based on alternating organic–inorganic multilayers: Sandwiching inorganic barriers between polymeric buffers has been reported to reduce the number of pinholes significantly [28]. This can be explained in terms of smoothing of the coated surface, reduction of mechanical damage and increased thermal stability [20]. Moreover, repeating the alternating process yields stacked structures that allow the organic layers to “decouple” the defects from neighboring inorganic layers.

The best flexible barrier materials reported so far are based on polyacrylate/ Al_2O_3 alternating coatings produced in a multi-step process. The organic layer is produced by flash evaporation of an acrylic monomer that is subsequently cured by UV light [29], while the inorganic coating is usually deposited by reactive sputtering. WVTR of about $2 \times 10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ has been reported [30], yielding 5 mm^2 OLED lifetime of 2500 h [31].

We report herein the first shelf lifetime study of conjugated polymer:fullerene solar cells fabricated on, and encapsulated with flexible, transparent ultra-high barrier material produced entirely by PECVD.

2. Experimental

2.1. Plasma enhanced chemical vapor deposition of ultra-high barrier coatings

The encapsulation films used in this study are poly(ethylene naphthalate) (PEN) substrates coated with ultra-high barrier multilayer coatings deposited by PECVD. The choice of PEN

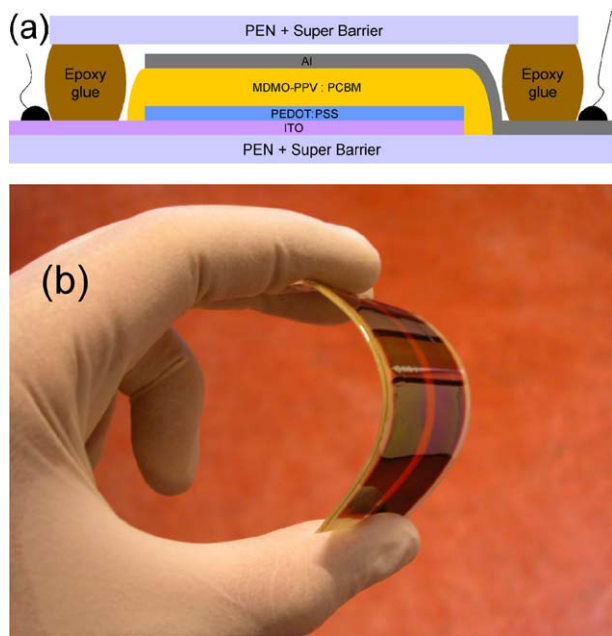


Fig. 3. (a) Cross-sectional view of the conjugated polymer:fullerene solar cells investigated here; (b) picture of a bent device.

instead of PET is justified by its higher temperature of glass transition that allows potential post-treatment of devices. The ultra-high barrier coatings comprise alternating transparent layers of dense inorganic material and plasma-deposited organic material, the hard inorganic material being the first layer in direct contact with the flexible substrate. Inorganic and organic layers, namely SiO_x and PECVD-deposited organosilicon, are grown sequentially on the PEN film in the same deposition chamber. The former (SiO_x) are produced from a volatile organosilicon precursor under oxidative plasma conditions, while the latter are deposited using similar organosilicon precursor but in a non-oxidizing plasma. The final ultra-high barrier consists of five layers of about 100 nm, resulting in a total thickness of about 500 nm, as measured by spectroscopic ellipsometry. These coatings are transparent with optical transmission $T > 85\%$ over the entire visible spectrum, they show good resistance to common organic solvents and do not deteriorate during washing with isopropanol, acetone, chlorobenzene or toluene. Oxygen and water vapor permeation measurements performed with MOCON Oxtran and Permatran instruments are below their detection limits which are $0.005 \text{ cm}^3 \text{ m}^{-2} \text{ day}^{-1} \text{ atm}^{-1}$ and $0.005 \text{ g m}^{-2} \text{ day}^{-1}$, respectively. Our barrier material survives an accelerated “Calcium test” (50 °C, 85% relative humidity) for more than 1000 h, which corresponds to at least 10,000 h under normal ambient conditions.

2.2. Preparation of the solar cells

First, indium tin oxide (ITO) electrodes were sputtered through a mask onto the $75 \times 42 \text{ mm}^2$ barrier substrates. Adhesion was good and sheet resistance was found to be about $60 \Omega/\text{square}$. The transparent substrate was then coated with a thin ($\approx 90 \text{ nm}$) layer of poly(3,4-ethylenedioxythio-

phene) doped with poly(styrene sulfonate) (PEDOT:PSS Baytron®, Bayer AG), deposited by doctor blading. On top, a solution of poly[2-methoxy-5-(3',7'-dimethyloxy)-1,4-phenylene-vinylene] (MDMO-PPV, Covion GmbH):1-(3-methoxycarbonyl) propyl-1-phenyl[6,6] C_{60} (PCBM, Nano-C Inc.) with a mass ratio 1:4, was deposited by the same technique; the resulting active layer was 200 nm thick. Finally, an aluminum electrode was thermally evaporated through a second mask.

Unlike the conjugated polymer deposition procedures that were done in air, the encapsulation step was carried out in a glove box in pure, dry Ar atmosphere. A two-component epoxy resin was used to seal the device with a top cap made of the same barrier material as the substrate (Fig. 3(a)). After curing the epoxy, the overall structure can still bend appreciably, as illustrated in Fig. 3(b). For comparison with commercially available polymers, exactly the same types of devices were produced on and encapsulated with 175 μm thick PET. Independently of the substrate used (PET or ultra-high barrier), the cells showed a quite low efficiency of about 0.035% (fill factor, $\text{FF} = 0.26$; open circuit voltage, $V_{\text{OC}} = 1100 \text{ mV}$; short circuit current $= 0.12 \text{ mA cm}^{-2}$). This is explained by the very large surface area ($30 \times 57 \text{ mm}^2$) made of two non-optimized series connected cells, combined with an ITO having a quite high sheet resistance. However, we believe that this drastic limitation due to an overwhelming series resistance does not influence our lifetime study.

The current–voltage (I – V) measurements were performed with a Keithley 236 measurement unit under simulated AM 1.5 solar irradiation (Steuernagel Lichttechnik GmbH, 100 mW cm^{-2}). Between successive measurements, the solar cells were stored in the dark under ambient air (≈ 20 – $25 \text{ }^\circ\text{C}$; ≈ 35 – 50% relative humidity).

3. Results

Fig. 4 shows the evolution of the normalized open circuit voltage (V_{OC}) and Fill Factor (FF) of a typical solar cell versus

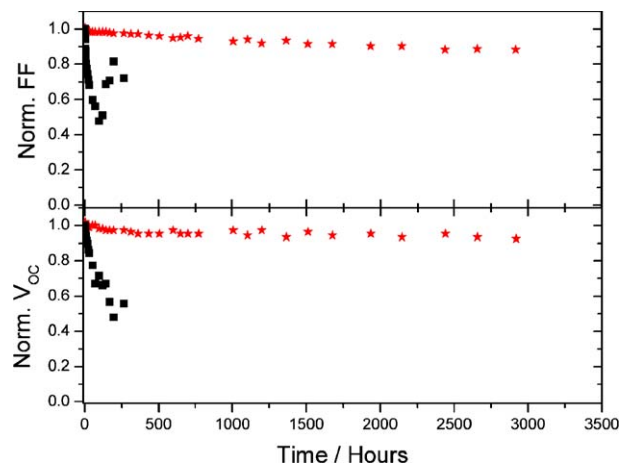


Fig. 4. Normalized V_{OC} and FF of solar cells encapsulated with uncoated PET (■) and with flexible gas barrier material (★) versus storage time in the dark under ambient air.

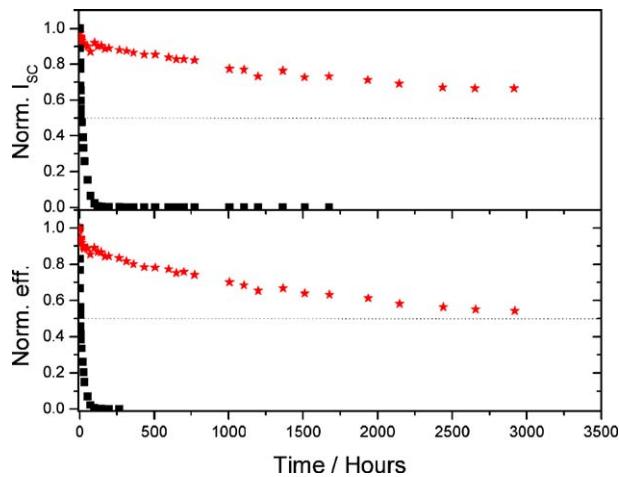


Fig. 5. Normalized I_{SC} and efficiency of solar cells encapsulated with uncoated PET (■) and with flexible gas barrier material (★) versus storage time in the dark under ambient air.

storage time. In the case of PET encapsulation, both V_{OC} and FF decrease by 50% within less than 200 h. We observed that aging of the cells results in the development of a back diode that tends to drastically reduce FF. However, in the case of the flexible barrier encapsulation, V_{OC} remains at about 90% of its initial value after 3000 h, as does FF.

Fig. 5 presents the evolutions of the normalized short circuit current (I_{SC}) and of the efficiency η , calculated by

$$\eta = \frac{V_{OC} \cdot I_{SC} \cdot FF}{P_{in}}, \quad (1)$$

where P_{in} is the incident light power. In the case of PET encapsulation, I_{SC} and η values decrease by 50% in 10 and 6 h, respectively. The difference between their decay rates arises from the fact that η accumulates the decrease of V_{OC} , FF and I_{SC} . However, when the cells are encapsulated in the flexible barrier material, their lifetimes are greatly increased: After 3000 h, I_{SC} and η still possess 67% and 54% of their initial values, respectively, where a significant part of the observed performance drop occurs during the first 50 h of the experiment.

4. Discussion

The flexible gas barrier encapsulation used in this study shows promise to drastically increase the lifetimes of conjugated polymer:fullerene solar cells. While a simple PET film provides a shelf lifetime of less than 6 h, the permeation barrier material produced by PECVD yields organic PV lifetimes that exceed 3000 h, comparable to those reported for the same type of cells encapsulated between glass plates [18]. This suggests that degradation of the device characteristics may not be related to the flexible gas barrier itself, but to intrinsic instability of the photoactive material. The rapid decay observed during the first 50 h that accounts for 20% of the overall performance loss is quite intriguing. We believe that it may possibly be explained by two different phenomena: (i) As mentioned earlier, the cells were produced under normal laboratory ambient conditions, no special measures being taken to remove residual oxygen

adsorbed on the surface or absorbed in the bulk of the device; (ii) the epoxy glue was used as received without any step of degassing before application, though it might contain some traces of moisture or oxygen. One possible solution to minimize these effects could be to use a getter material for moisture and oxygen [20,30]. As known from OLED display manufacturing, getter encapsulated along with the device reacts more rapidly with O_2 and H_2O than do the active semiconducting polymers.

The 3000 h of device stability achieved so far in this study is not sufficient for this type of device on the market, yet it represents a critical first step in the realization of long-lived flexible plastic solar cells. MDMO-PPV is known to be particularly unstable and sensitive to aging. However, new materials like polythiophenes that are much less sensitive to moisture and oxygen and allow even better photovoltaic conversion are becoming available [32]. The combination of such materials with the present flexible gas barrier encapsulation might constitute a very promising advance in this field.

5. Conclusion

A new type of transparent, flexible ultra-high barrier material, entirely produced by PECVD, has been used to encapsulate MDMO-PPV:PCBM solar cells. Shelf lifetimes above 3000 h have been achieved, while bare commercial PET films permit lifetime of less than 6 h. This extended lifetime equals those previously reported for the same type of devices encapsulated between glass plates. The combination of less sensitive materials like polythiophenes and this new transparent flexible gas barrier, that is compatible with roll-to-roll processing, may open the way to long-lived flexible plastic solar cells.

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