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Breaking mechanism of indium tin oxide and its effect on organic photovoltaic cells

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ABSTRACT

Indium Tin Oxide (ITO) is one of the most used anode materials in organic solar cells. ITO is a brittle material, however, in roll-to-roll manufacturing plants and final applications material flexibility is beneficial. This study examines the flexibility limits of ITO in applications manufacturing photovoltaic cells. First, ITO was bent using different cylinders to achieve different sample bending curvatures and thus different stages of breaking. Next, the conductivity of ITO was measured and surface topology was profiled. As a result, it was discovered that samples start to break even with low bending curvatures, and while no changes are detected in the surface profile, conductivity starts to decrease. When the cracks start to appear on the surface of ITO, a specific radius of curvature is discernible. In this critical bending curvature resistance and its relative standard deviation start to increase faster. Optical profilometer examination revealed that the cracks reach the ITO surface at the same moment. After this critical bending curvature, clear positive correlation was observed between the conductivity and the number of cracks. To test the effect of cracked ITO on the performance of solar cells, solar cells were produced on top of the cracked ITO layer. The measurements showed that cracks did not decrease the performance of solar cell. This fact supports the use of ITO-based organic photovoltaic cells in applications where flexibility is required as well as in roll-to-roll manufacturing.

1. Introduction

Transparent conductive films are used in many different applications, *e.g.* in low-emissivity windows in buildings, solar cells, flat-panel displays, electro chromic mirrors and windows, defrosting windows, oven windows, static dissipation, touch-panel controls, electromagnetic shielding and invisible security circuits [1–7]. Indium Tin Oxide (ITO) is one of the most widely used transparent conductor material owing to its good transparency in visible wavelengths, great electrical conductivity and high work function and relatively wide band gap. However, ITO is a brittle material, which property is expected to limit its suitability in flexible electronics applications. With no better replacement, ITO is widely used in flexible solar cells [8–11]. Due to the cost structure and functional limitations, this technology has not yet gained wide-spread commercial application [11–14]. Detailed cost analysis of organic photovoltaic (OPV) fabrication has shown that ITO constitutes the major part of the total cost (*e.g.* over 30% of material cost of OPV). Despite its high cost [12], it is still the most common transparent conductor [11].

When ITO is used for a flexible component's part, it is important to understand how mechanical stress affects its properties. ITO can be bent either during manufacturing or in the final applications. Studies [15–20] have investigated ITO's resistance change under various conditions When ITO was bent, its resistance increased notably between 5 mm and 8.9 mm bending diameter [15]. ITO samples with cracks have been shown [15–17,19,20]. These cracks appear on ITO when the bending has reached critical point [15]. The most dominant factors for the cracks are bending diameter and number of bendings; however, bending frequency and sample thickness also have an effect on cracks and thus on ITO's resistance [15]. ITO's surface profiles have also been studied in repeated bendings, up to 4000 bendings. ITO breaks more, when the number of cycles increases [15,19]. In these studies surface profiles were measured by using optical microscopy and Atomic Force Microscope (AFM). It has also been suggested that ITO's increased resistance comes from micro-defects such as micro-cracks and the micro-detachment on ITO and polyethylene terephthalate (PET) substrate films [20].

The aim of this study was to get a more comprehensive understanding of ITO's breaking mechanism and its limitations, especially in flexible electronics. Therefore, we needed to generate a methodology to treat the samples and measure the conductivity changes from ITO in such a way that it would be possible to get

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repeatable data. To understand the breaking mechanism of ITO, it was also necessary to study its surface, which was done by using an optical profilometer. By bending the sample it is possible to study the critical bending diameter and ITO's cracking mechanism. The practical meaning of ITO cracks was seen when solar cells were produced on top of cracked ITO. This data is important when planning the processes for ITO-based solar cells in roll-to-roll manufacturing conditions or in solar cell applications where flexibility is needed.

2. Materials and methods

The samples were made from commercial PET–ITO sheets. Optical grade PET was produced by DuPont (article code of DuPont Teijin film: Melinex ST 504). ITO was coated on top of PET by Solutia Performance Films (CPFilms), article type OC50. Final PET–ITO product was produced by vacuum sputter deposition of ITO onto the adhered side of PET. Nominal resistance of ITO was 40–60 Ω/square and its nominal thickness was 125 nm, likewise nominal thickness of PET was 125 μm. Visible light transmission was 85%. These ITO/PET sheets were cut to samples. The first sets of dimensions were used to study the breaking mechanism of ITO. Unfortunately, these sample sizes were unsuitable for solar cell preparation and a different set of dimensions had to be used. These dimensions are summarized in Table 1. The main difference was that ITO was etched away from the sides leaving only a stripe of ITO in the middle. All resistance measurements were done before bending, immediately after bending, 2 and 24 h after bending, and measurements were made for 5 parallel samples. During the measurements, the room temperature varied between 21.1 °C and 22.7 °C and humidity varied between 36.8% and 55.1%. It is known that the variations from temperature and humidity have some effect on the performance of ITO [21]. However, in these measurements the variations did not significantly influence the results.

2.1. The sample handling device

The radius of bending curvature was controlled by the cylinder diameter. The layout and photograph of the sample bending device is shown in Fig. 1. Resistance measurements and sample surface profiling were made later in planar orientation, i.e. the sample was not bent during the measurements. Surface roughness is known to affect the strength of ITO [16]. Therefore the samples were placed onto the sample handling device in the direction where the PET substrate was in contact with the cylinder and ITO remained safe, free from accidental attrition, scratches or depression. ITO was cracked in the sample handling device by the bending force. In this device the stable cylinder was placed vertically and the film was hanging from the cylinder with specified gravity force. The weight of the lower cylinder and additional weight was defined as 1 kg after test parameter optimization (Section 2.3).

Table 1
Selected dimensions for samples and bending cylinders for breaking mechanism and solar cell studies.

Parameter	Breaking mechanism study (mm)	Solar cell study (mm)
Sample length (total)	305 ± 0.5	315 ± 5
Sample width	35 ± 0.5	31 ± 0.5
ITO width	35	13
Sample bending cylinder diameters	15, 20, 25, 30 and 53	10

2.2. The measuring devices

The resistance measuring probes were placed in the unbent area of ITO. The largest cylinder had 53 mm diameter, which corresponds to 83.25 mm (53 mm × π÷2) bent length of ITO. Therefore the distance between the probes was selected to be 100 mm. Having detected the exact effective sample bending length, it was possible to calculate the resistance changing ratio (CR_R) on the sample bending area. The premises of the calculations are

- The square resistance of unbent sample is uniform.
- It is only the square resistance of the bent area that changes

Therefore all resistance changes happen on the length of bending $L_2(d)$, but the resistance of the unbent length of the sample (L_{NB}) remains unchanged. When the diameter of the bending cylinder is known, it is possible to calculate CR_R by dividing the resistance of the sample before and after bending on the length of half cylinder. Fig. 2 illustrates the resistance measurement setup, where the distance between the resistance measuring probes (L_1) and the length of bending $L_2(d)$ are marked. CR_R was calculated by using the following equation (1)

$$CR_R = \frac{R_1}{R_2} = \frac{R_{M1} - R_{NB}}{R_0} = \frac{R_{M1} - R_{M0} \times (L_{NB}/L_1)}{R_{M0} \times (L_{2(d)}/L_1)} = \frac{R_{M1} - R_{M0} \times (L_1 - L_2(d)/L_1)}{R_{M0} \times (L_{2(d)}/L_1)} \quad (1)$$

where

R_1 = Calculated resistance of sample after bending on affected sample length.
R_0 = Calculated resistance of sample before bending on affected sample length.
R_{M1} = Measured resistance of sample after bending on total measuring length.
R_{NB} = Resistance of unbent part of bent sample. Resistance did not change in this part of the sample.
R_{M0} = Measured resistance of the sample before bending on total sample length.
L_1 = Distance between probes, 100 mm.
$L_2(d)$ = Length of the active sample bending, $L_2(d) = \pi \times d/2$, where d = cylinders diameter.
L_{NB} = Not bent part of the sample, $L_{NB} = L_1 - L_2(d)$.

The resistance was measured by using Agilent 34401 A 6½ digit multimeter by using 2 W power. Each resistance measurement point was measured with five parallel samples. All measurements were made for all of the samples at three different times after sample bending to validate the data with these time dependent measurements. Measurement times were: immediately after bending (0 h), 2 h after bending and 24 h after bending. Between these measurements, the samples were kept in planar orientation, which was not stretching or stressing the samples. The profilometer measurements were made using Brucker Contour GT profilometer with the following parameters: measurement type: Phase-Shifting Interferometry (PSI), green light, objective 20 × and measurement area X: 0.158 μm, Y:0.119 μm. For measuring the photovoltaic characteristics of solar cells, an Air Mass 1.5 Global (AM1.5G) a solar simulator was employed as light source, and light intensity was calibrated to 100 mW/cm^2 using a NREL calibrated crystalline Si reference cell. Power conversion efficiency (PCE) was obtained from corresponding current density, J [mA/cm^2]–voltage, V [V] curves (J–V curves).