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Chemical and device degradation in PCPDTBT:PCBM solar cells using XPS and TOF-SIMS

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Abstract

Analysis of the degradation routes for PCPDTBT-based solar cells under illumination and in the presence of air have been conducted using a combination of X-ray Photoelectron Spectroscopy (XPS), Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) and solar cell device data. After ageing, XPS studies show that PCPDTBT appears as an oxygen-containing polymer, with data indicating that a break-up in the aromatic rings, formation of sulphates at the thiophene ring, chain scission in the polymer backbone and also loss of side chains. XPS studies on active layers blends of PCPDTBT and PCBM also show significant changes in the vertical composition during ageing, with increased enrichment of PCPDTBT observed at the top surface and that the use of a processing additive (ODT) has a negative impact on the morphological stability. TOF-SIMS has been used to study electrode degradation during ageing experiments leads to migration of indium and tin ions into the active layer in non-inverted devices, but is eliminated for inverted devices.

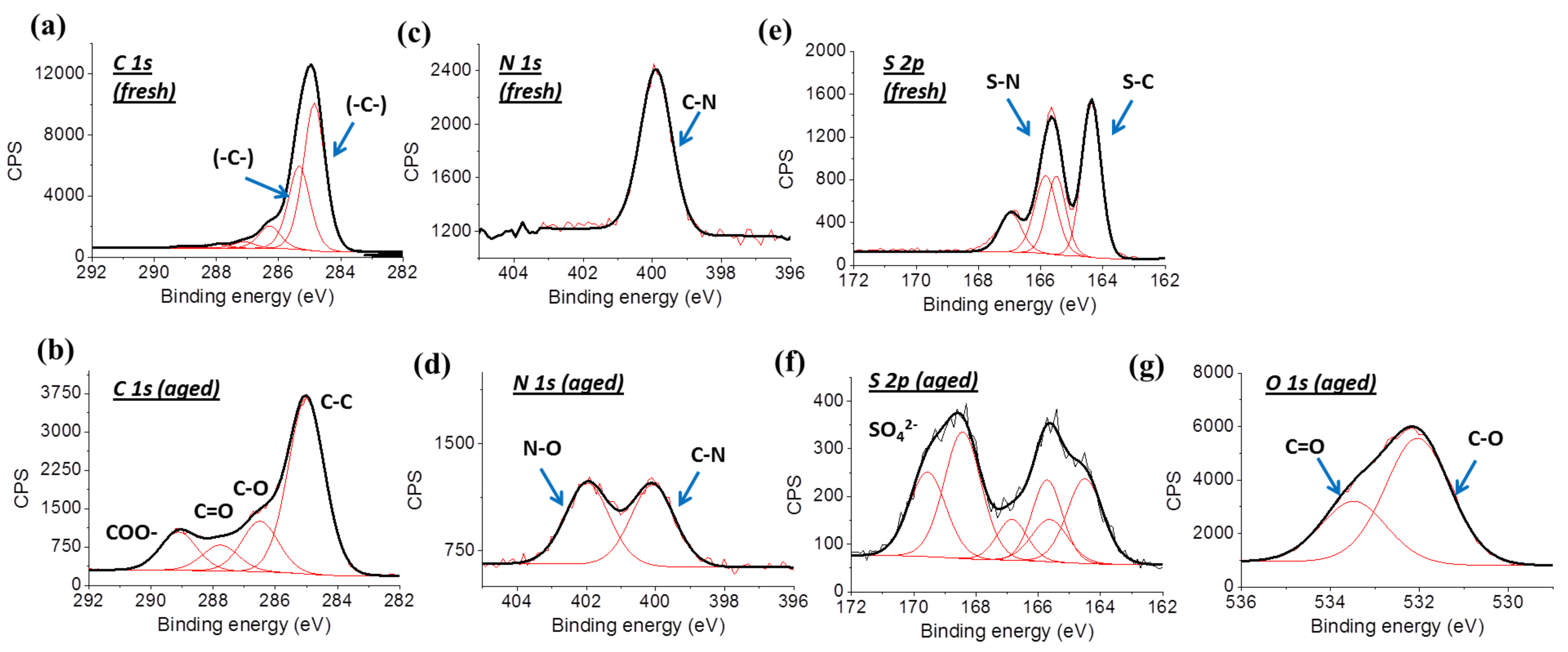
Experimental

- Samples were prepared on glass samples; PCPDTBT, $PC_{71}BM$, PCPDTBT:$PC_{71}BM$ (1:3 ratio) with the process additive 1,8-octanedithiol (ODT).
- ODT or similar alkanethiols are used in almost all reports of high efficiency OPVs and acts as a second non-reacting solvent. It has been shown that the incorporation of a few volume percent of ODT into the blend improves the Power Conversion Efficiency (PCE) by about a factor of two
- XPS conducted using using a bespoke UHV fitted with a Specs GmbH Focus 500 source and Specs GmbH hemispherical analyser with 9-channeltron. Survey spectra were acquired over the binding energy range 1100 – 0 eV
- TOF-SIMS imaging was conducted using a using a 25kV pulsed gallium ion beam with a Phi Thift III

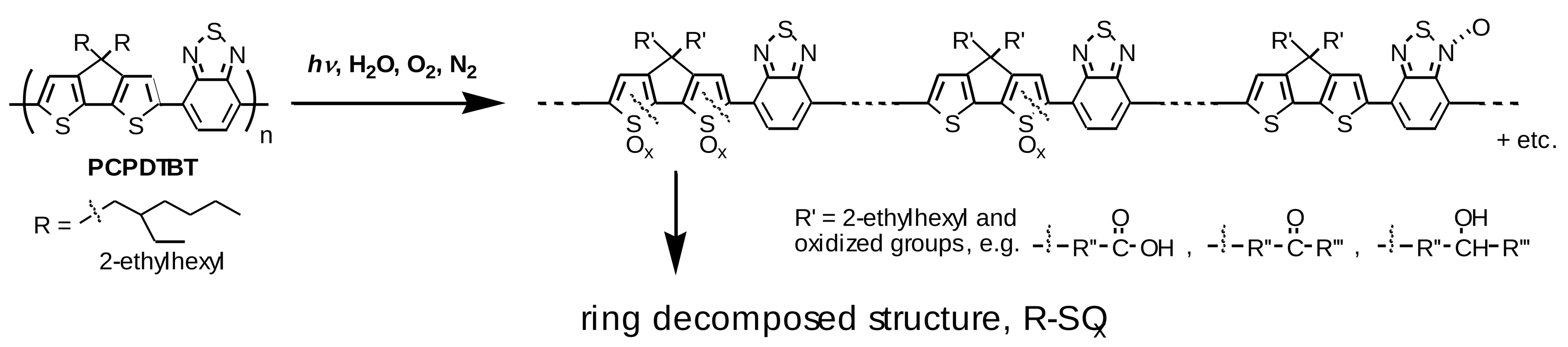
Results – *XPS data for PCPDTBT after 300 hours ageing in ambient air*

Time 0 h

300 h



- Composition at 0 hours; composition was expected to be approximately 86% C, 6% N and 8% S
- After ageing in ambient air over a 300 hour time span, the amount of O and N is increased, with decreases in sulphur (S) and carbon (C).
- After ageing, the C 1s spectrum appears typical of an oxygen-containing polymer with well-defined symmetric components at 285 eV (C-C), 286.5 eV (C-O), 287.9 eV (C=O) and 289.2 eV (COO- or C(=O)O)
- The most drastic changes occur within the first 100 hours of light soaking
- N 1s spectrum indicates possible N-O or quaternary N formation, S 2p spectrum indicates aromatic structure is broken and the formation of $R\text{-}So_x$
- Plausible change of chemical structure of PCPDTBT after light soaking in normal atmospheric conditions shown below. The side chain is oxidized to form carboxylic acid, carbonyl, or hydroxyl groups. The ring structure decomposes into R-SOx

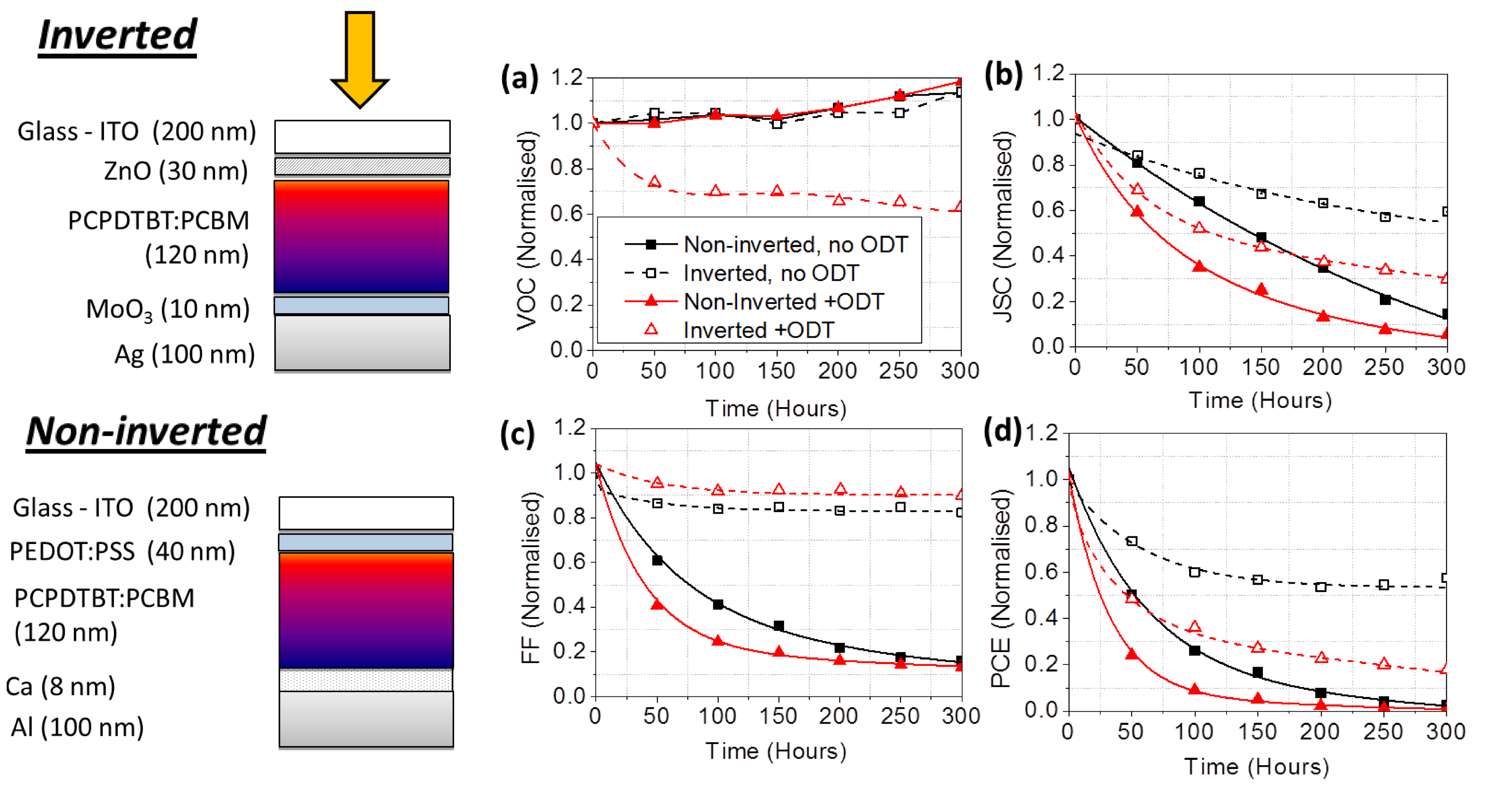


PCPDTBT, Atom % concentration				
	0 hours	25 hours	100 hours	300 hours
C 1s	86.52	78.04	62.07	60.58
N 1s	4.03	4.49	6.04	6.28
S 2p	9.2	7.71	6.45	6.27
O 1s	0.25	9.75	25.44	26.87

Table shows how elemental composition changes as a function of time

OPV stability testing

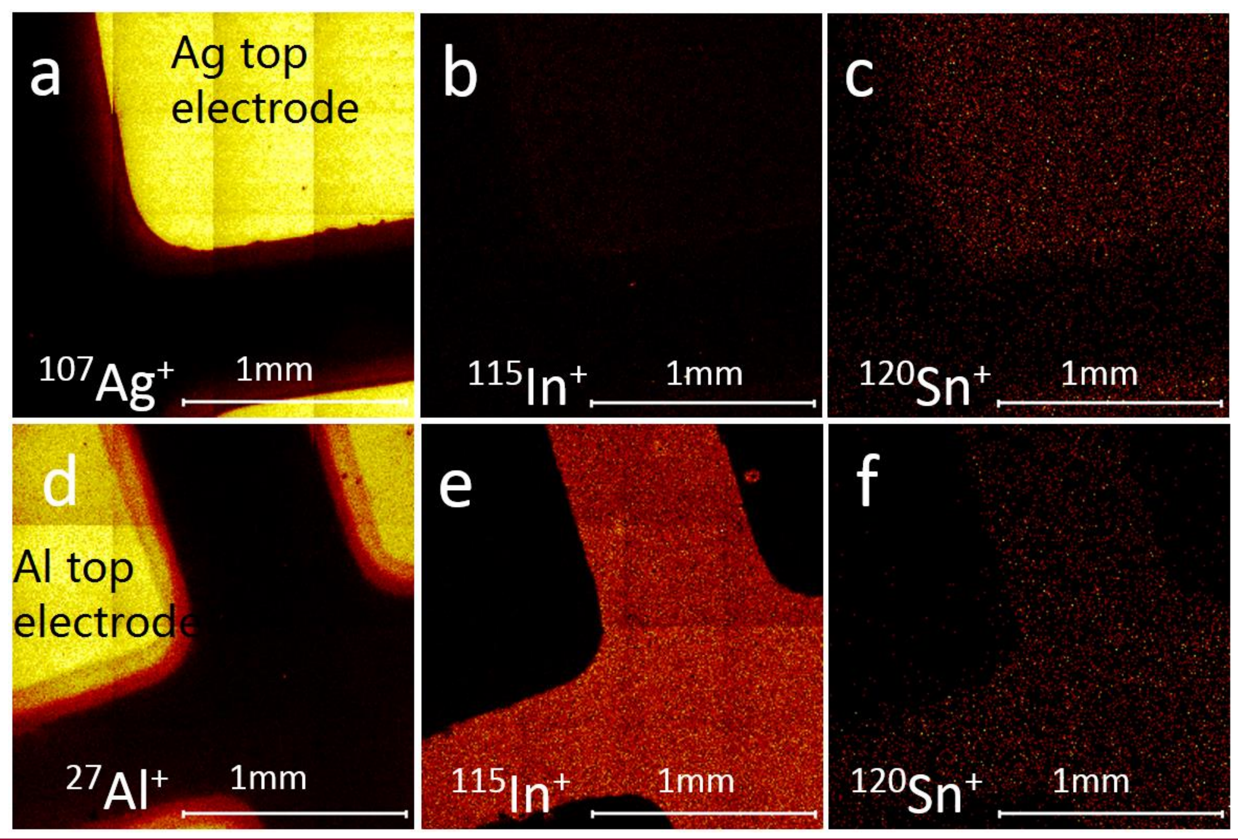
- XPS measurements made on active layers with PCPDTBT:$PC_{71}BM$ (1:3 ratio) with and without the process ODT.
- Data shows polymer enrichment is observed at the 'top' surface; 40% of top surface is PCPDTBT for samples with no ODT, 68% for samples with ODT
- In addition, the morphology is shown to alter drastically during light soaking, with fullerene aggregation occurring at the surface. This appears to be more severe for samples with ODT



- OPV lifetime data using ISOS-L-2 standard testing, supports XPS data; samples made with ODT degrade quicker

Results – *Electrode degradation studies using TOF-SIMS*

- TOF-SIMS images show the ion distribution of $^{107}Ag^+$ (a); $^{115}In^+$ (b) and $^{120}Sn^+$ (c) on the surface of an aged, inverted cell and the distribution of $^{27}Al^+$ (d); $^{115}In^+$ (e) and $^{120}Sn^+$ (f) on the surface of an aged non-inverted cell
- In and Sn ions present on the non-inverted device surface after aging (none present on fresh device surface), indicating that the electrode material is degrading and migrating through the active layer
- Ion migration is due to 'etching' by PEDOT:PSS
- Ions could form trap sites Inverted devices showed no electrode migration, due to the absence of PEDOT:PSS or the 'ion blocking effect' of ZnO layer on top of ITO electrode



Conclusions

The data presented shows the chemical changes that occur in PCPDTBT under illumination, in the presence of air. After ageing, the PCPDTBT appears as an oxygen-containing polymer with numerous chemical changes on the polymer backbone and sidechains. . The XPS results support device data and shows the use of a processing additive (ODT) has a major impact on the lifetime stability of the devices. TOF-SIMS data shows the electrode ion migration issue is eliminated by using an inverted structure.

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