An Angular Dependent X-ray Photoemission Study of Indium-Tin-Oxide Surfaces

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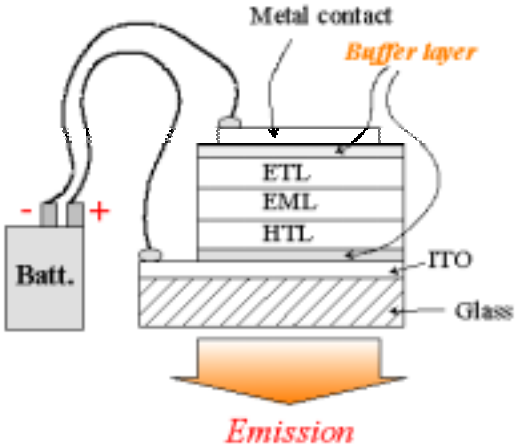
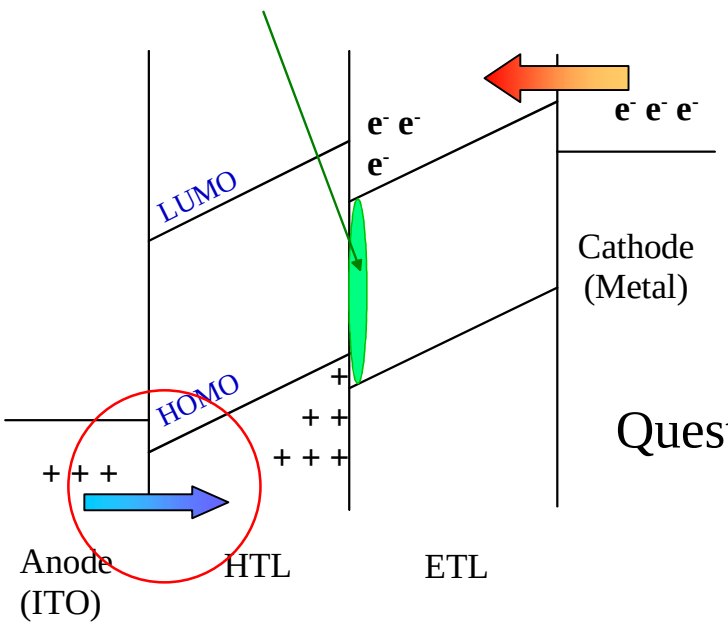
Introduction – Indium-Tin-Oxide (ITO)





Features of ITO

Composition	Sn-doped In_2O_3 (In:Sn ~ 9:1)
Electrical	Degenerate n-type (Free electron - oxygen vacancies / interstitial Sn atoms
	Resistivity ~ 10^{-3} – 10^{-4} Ωcm
Energy gap	Undoped In_2O_3 ~3.8 eV
Free electron conc	$1 – 4 \times 10^{20}$ cm^{-3}
Work function ϕ_{ITO}	~ 4.4 – 4.8 eV

Question: Overcome energy barriers at the interfaces

Aim: ***Increase device efficiency***
Increase hole injection

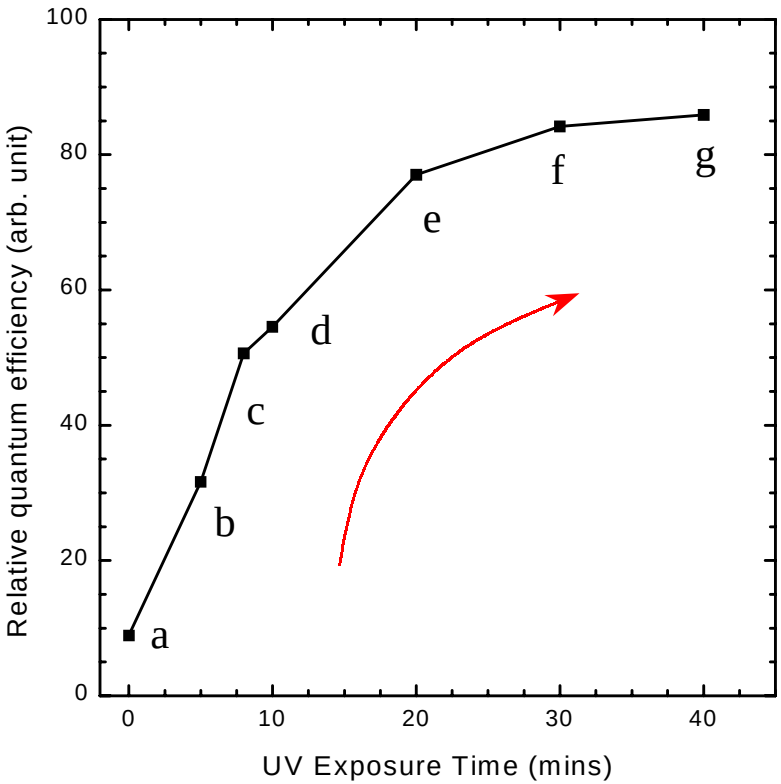
S.K.So, Appl. Phys. A 68, 447 (1999)

Effect of UV-ozone treatments on ITO substrate

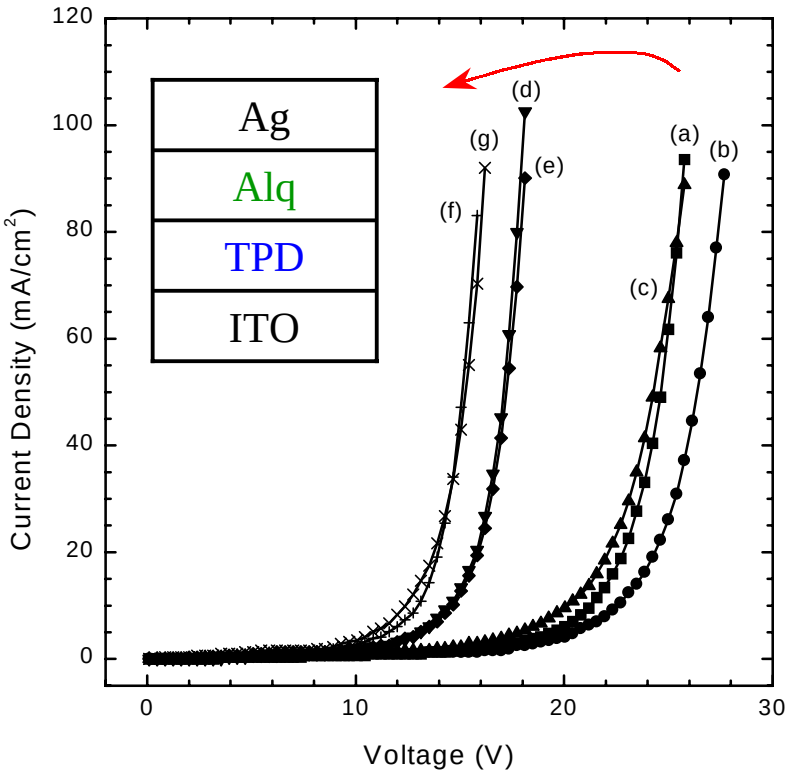
Treatment time

a	b	c	d	e	f	g
0	5	8	10	20	30	40

Brightness vs UV exposure time



Current-voltage characteristics

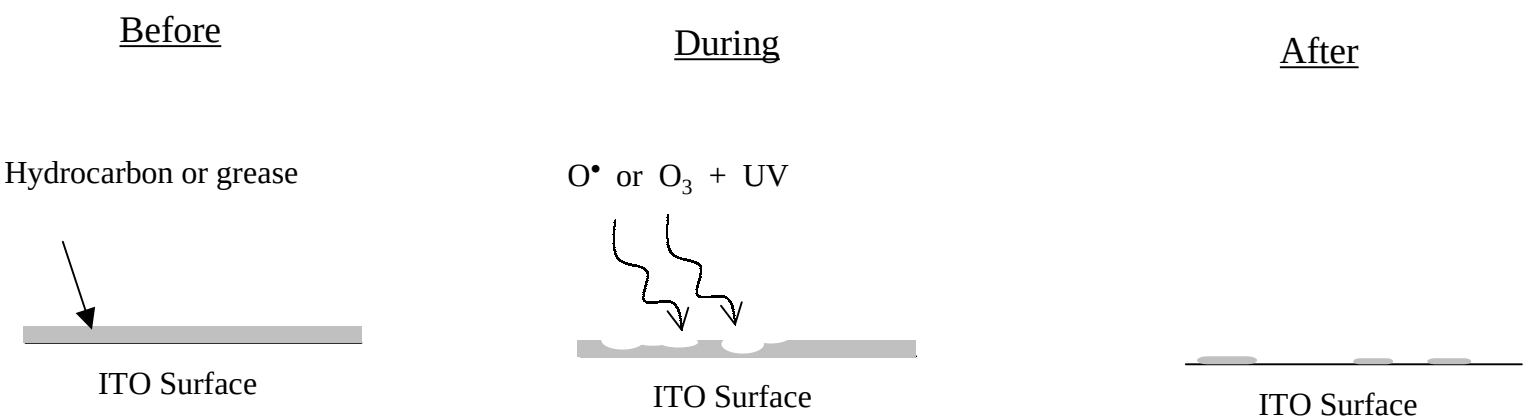


20 – 30 % carbon contamination under long UV exposure

Understanding of the ITO surface

Before & after surface treatments
- Solvent cleaning
- Plasma – Oxygen, Nitrogen, Argon
- Sputtering
- UV-ozone

Why is the ***UV-ozone*** or ***oxygen plasma*** treatment required?



Methodology

Angular dependent X-ray photoelectron spectroscopy (ADXPS)

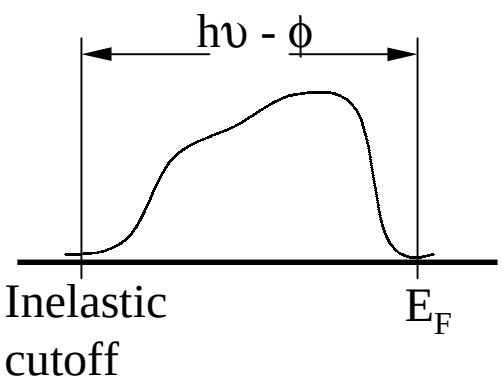
[Take-off-angle (TOA): 5^o, 15^o, 45^o, 90^o Electron mean free path λ ~23Å]

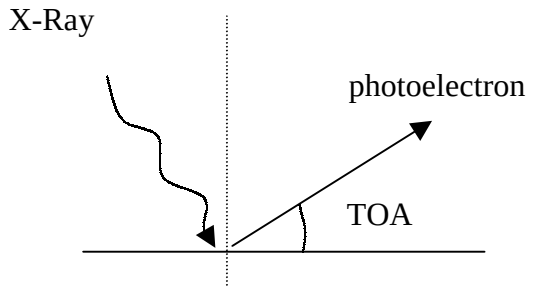
Determine the composition of surface & bulk ITO (In_{3d}, Sn_{3d}, O_{1s})

Determine the surface contamination (C_{1s})

Ultraviolet photoelectron spectroscopy (UPS)

Determine ITO work function (ϕ_{ITO})





Angular-resolved photoemission study

$$I_d = I_\infty [1 - \exp(-d / \lambda)]$$

λ– inelastic mean free path (IMFP) or escape depth

λ(23Å for ITO)

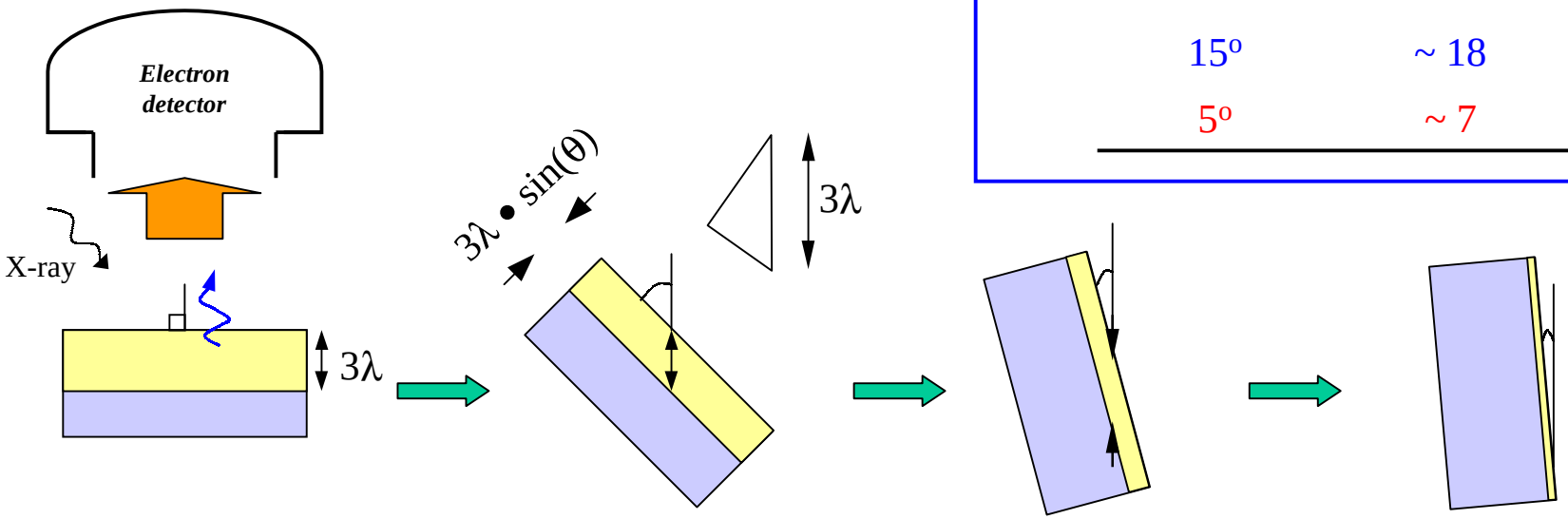
Detection depth of XPS

d	I_d / I_∞
λ	63 %
2λ	87%
3λ	95 %

Surface sensitivity by Angular-resolved XPS

Information depth (95%) = 3λ • sin(θ)

TOA	Information depth (Å)
90°	~ 70
45°	~ 50
15°	~ 18
5°	~ 7



TOA 90° *TOA 45°* *TOA 15°* *TOA 5°*

Bulk **Surface !**

Experimental setup

ITO glass	Sanyo Vacuum 11.4Ω/sq.
	Thickness: 1500 Å
UV-ozone	Jelight UV grid lamp, Model 42-220
	UV dosage 18 000 μW/cm^2
	Peak wavelength 253.7 nm
Plasma	PLASMA-PREEN system
	Gas: O, N, Ar
	Flow rate: 2.0 scfh @ 5 psi
XPS / UPS	Al K_α - 1486.6 eV
	He (I) - 21.22 eV
	PHI Quantum 2000, VG-CLAM+4LH multi-channel hemispherical analyzer

Results & Discussion

A. Plasma treatments (O, N, Ar, Ar^+ sputtering)

Surface elemental changes (15^o, 90^o) [In], [Sn], [O], [C]

XPS spectra – surface carbon (C) & oxygen (O) composition

Carbon contaminations (C-H, C-O)

UPS data – ITO *work function* (ϕ_{ITO}) changes with *surface stoichiometry*

B. UV-ozone (UVO) treatment *(after solvent cleaning)*

Detailed surface elemental changes (5^o, 15^o, 45^o, 90^o)

Surface charging on ITO surface ***before*** and ***after*** UVO

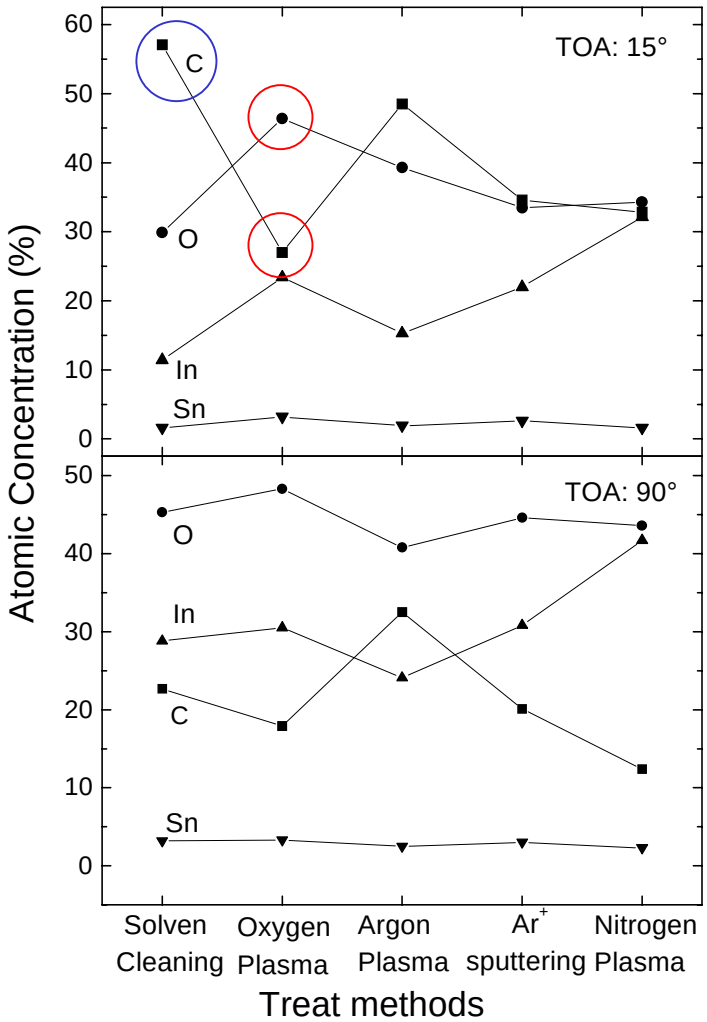
"Before" – surface carbon contamination

"After" – Reduction of oxygen vacancies due to oxygen ions diffusion

C. Proposed model – Explanation of improvement on device efficiency

Plasma treatments

Surface elemental changes (15°, 90°) [In], [Sn], [O], [C] after plasma treatments



[C] Carbon inside ITO bulk

$[C]_{surface} > [C]_{bulk}$ – a layer of carbon contamination

Solvent cleaning – less effective

O-plasma – most effective

[O] O-plasma - highest $[O]_{surface}$

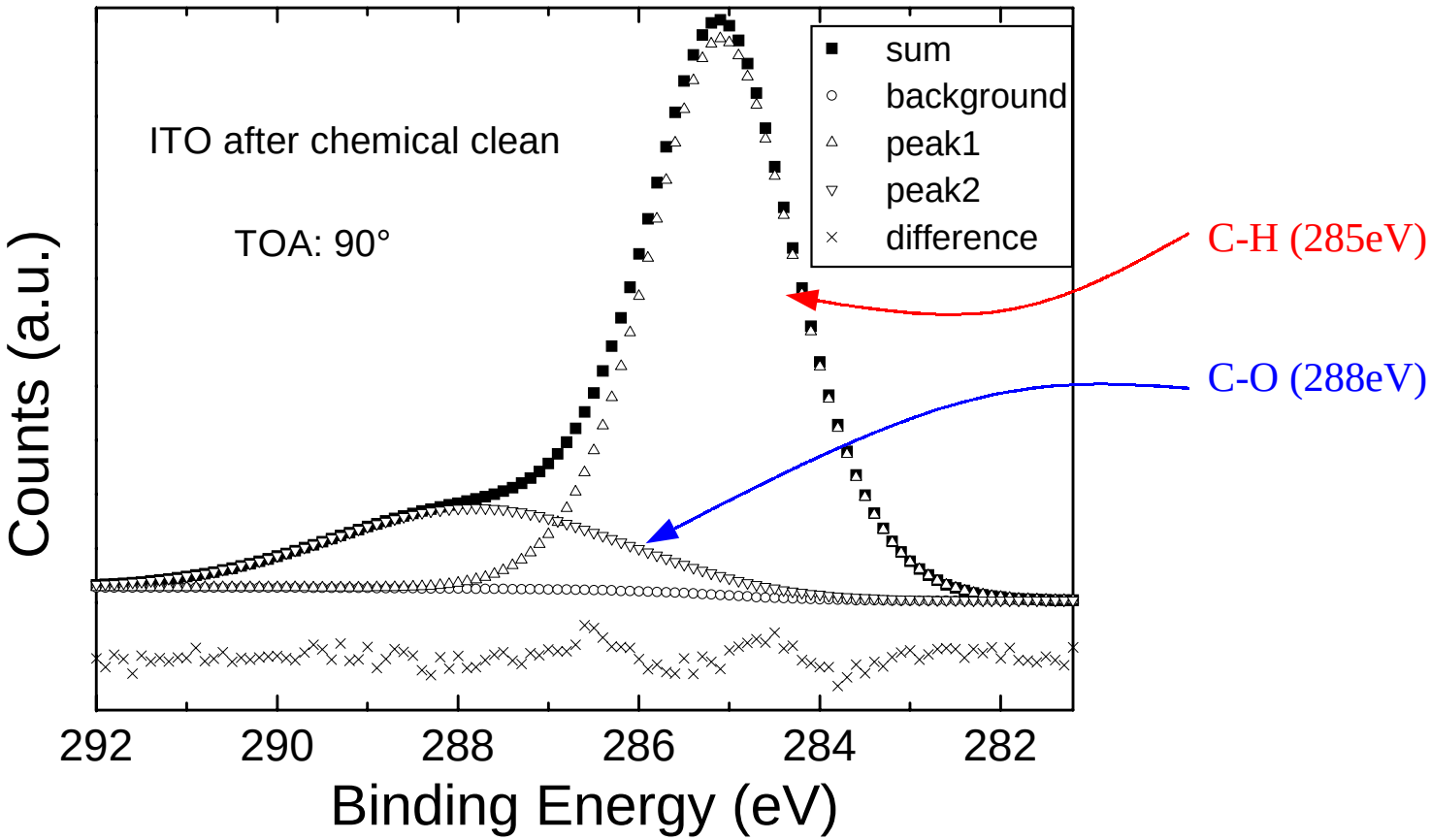
In:Sn	*Solvent cleaning*	*O-plasma*	*Ar-Plasma*	*N-plasma*	*Sputter-ing*
TOA 90°	**9**	**9**	10	10	18
TOA 15°	**7**	**7**	8	8	19

O-plasma & N-plasma introduce oxygen & nitrogen to the ITO surface.

Generally, Ar^+ sputtering reduces the In:Sn ratio

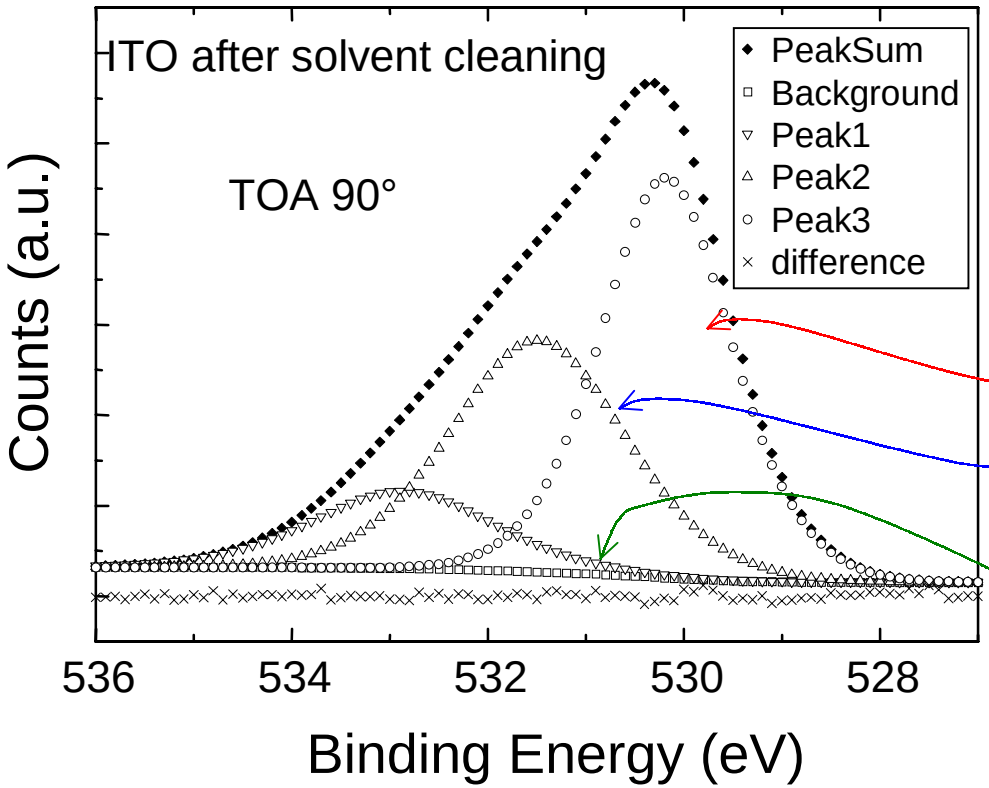
Plasma treatments

Representative XPS spectra – Surface Carbon Composition



Plasma treatments

Representative XPS spectra – Surface Oxygen Composition



O^{2-} ions bonded to In^{3+} (530.3eV)

O bonded to In & Sn or
O associated with C-O
contamination (531.5eV)

O associated with C-O
contamination (532.8eV)

W. Song, Appl. Phys. A 72, 361 (2001)

Plasma treatments - Summary

Carbon contamination

Methods	Carbon atomic concentration (%)			
	90° TOA (***Bulk***)		15° TOA (***Surface***)	
	Hydrocarbon	C-O	Hydrocarbon	C-O
Solvent cleaning	18.2	4.3	48.9	8.2
Oxygen plasma	15.5	2.4	**23.1**	**3.9**
Nitrogen plasma	17.1	3.0	**29.5**	**5.1**
Argon plasma	27.6	4.9	40.7	7.8
Ar^+ sputtering	11.6	0.9	29.4	3.4

Chemistry & work function of ITO

Treatments	Carbon removal	$[O_{InSn}]/1.5[In]+2[Sn]$		Work function (eV)
		90° TOA (***Bulk***)	15° TOA (***Surface***)	
Solvent cleaning	No	0.70	0.64	4.15
Oxygen plasma	Yes	0.75	**0.76**	**4.40**
Nitrogen plasma	Yes	0.72	**0.68**	**4.32**
Argon plasma	No	0.72	0.62	4.26
Ar^+ sputtering	Yes	0.64	0.59	3.90

Factors affected ϕ_{ITO}: a. carbon contamination on ITO surface

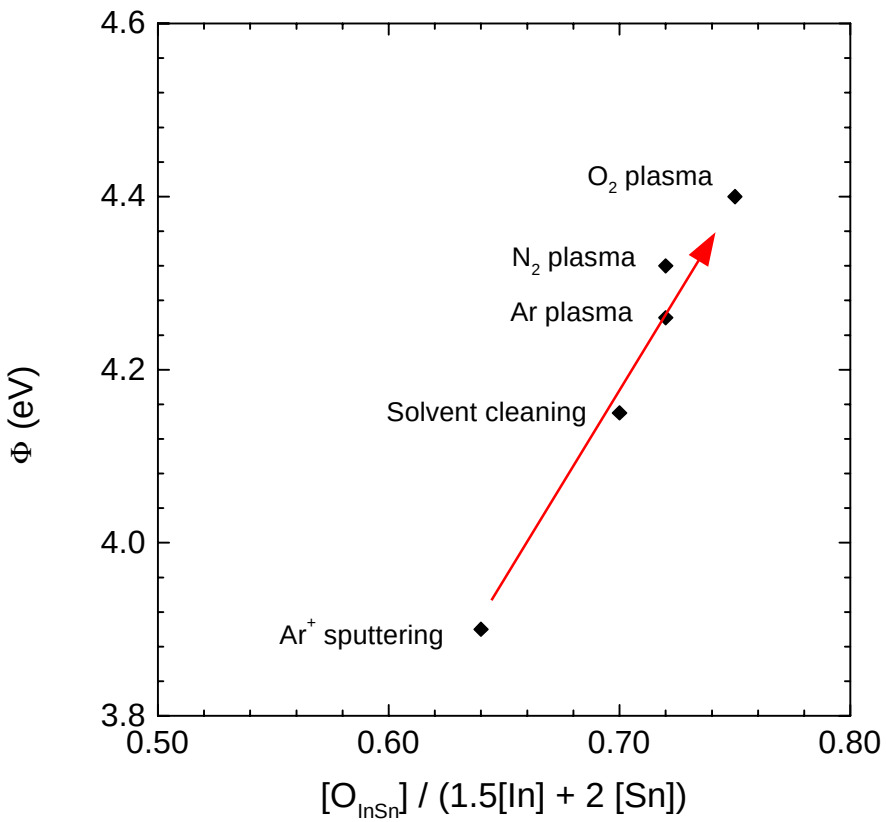
b. the stiochiometry of ITO

W. Song, Appl. Phys. A 72, 361 (2001)

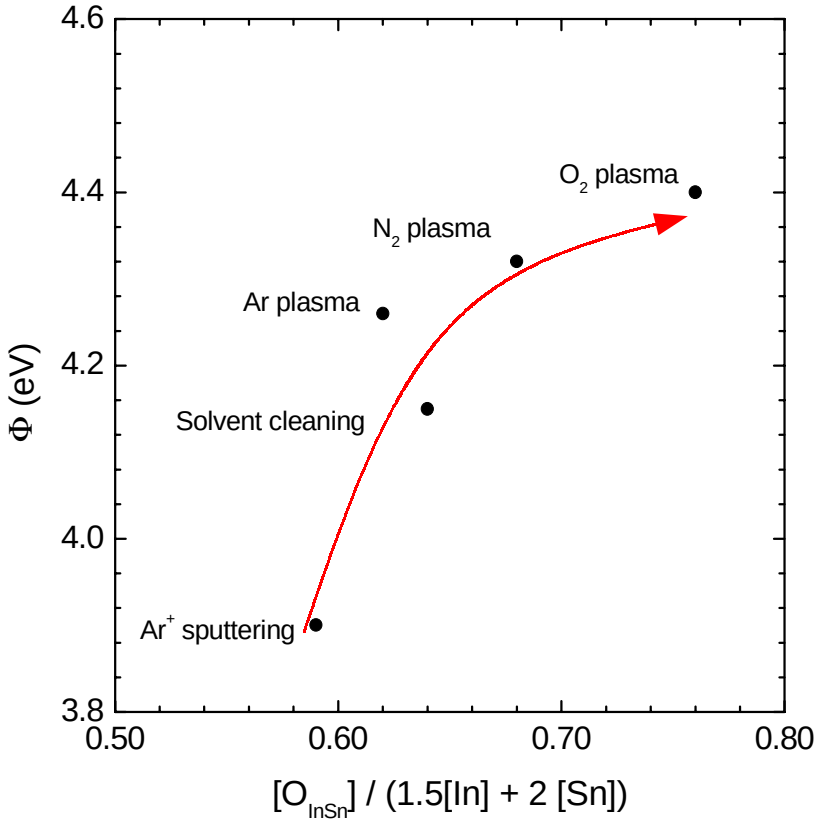
Plasma treatments

Work function of ITO – Prefer lower C contamination & higher stoichiometry

Work function of ITO after various treatments
90° TOA

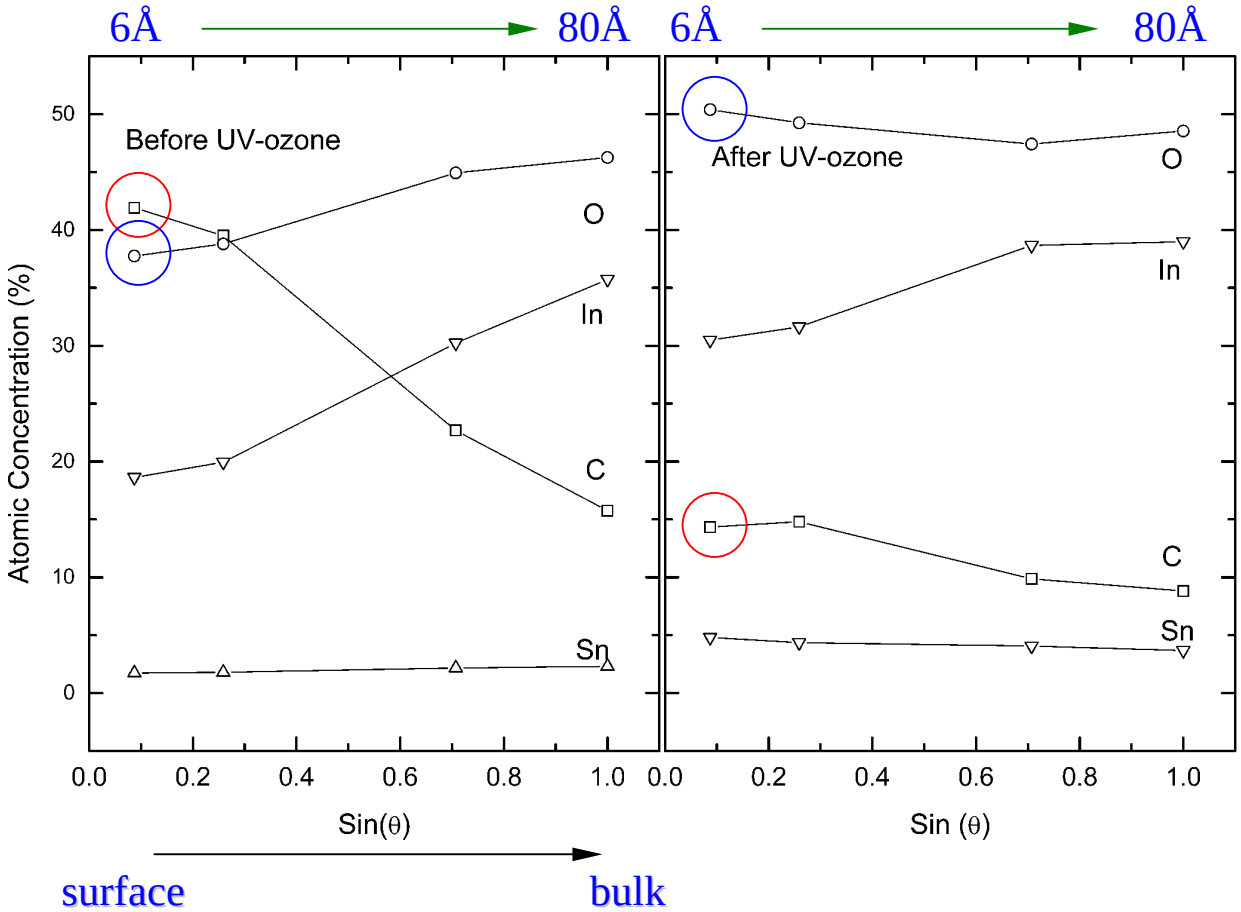


Work function of ITO after various treatments
15° TOA



W. Song, Appl. Surf. Sci. 177, 158 (2001)

UV-ozone treatments



[C]	Before	After
Surface	40%	**15%**
Bulk	15%	10%

[O]	Before	After
Surface	42%	**50%**
Bulk	47%	47%

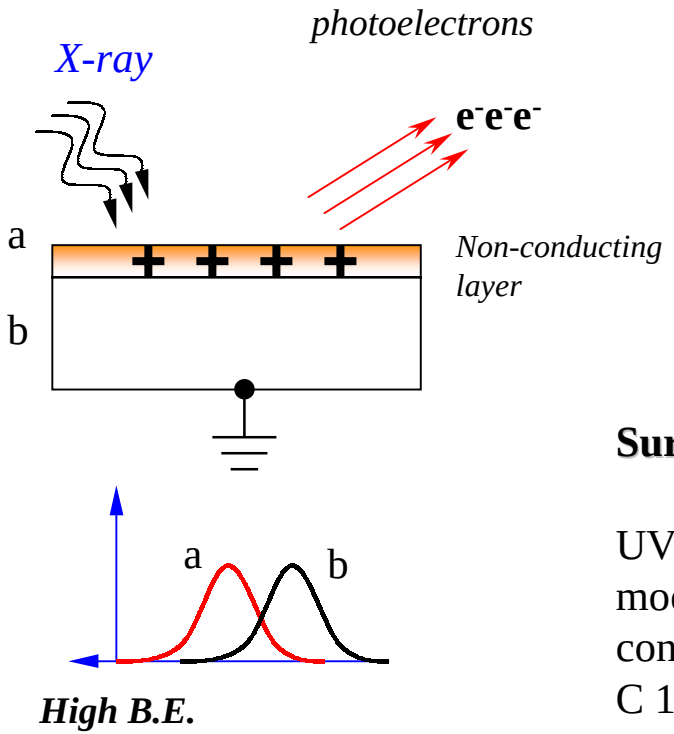
[In]:[Sn] *surface < bulk*

After UVO: a. Significant **reduction** of ***carbon*** *contamination*
b. **Increase** in ***oxygen*** *concentration*

UV-ozone treatments

Charging effects in XPS

Non-conducting sample bulk or surface
Positive holes accumulated due to photo-emitted or Auger electrons
Shift of XPS peaks towards high B.E.



Surface charging effect on untreated ITO [C 1s]

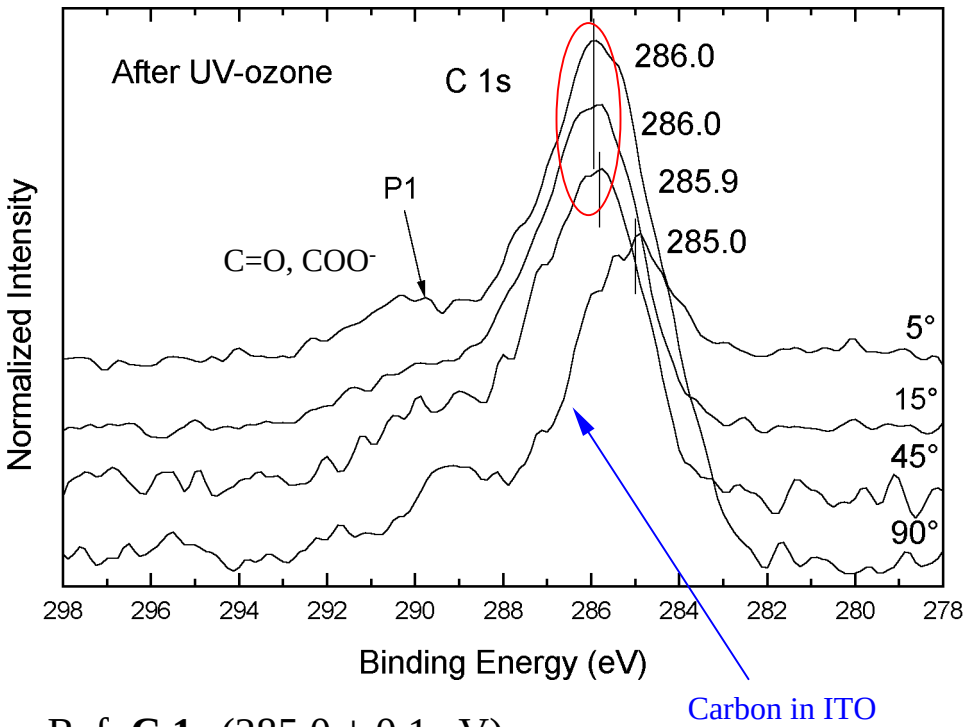
Before UVO treatment, a thin layer of 7Å (charging at 5º TOA only) only ***nonconducting carbon contamination*** is found on the ITO surface.

Surface charging effect on UVO treated ITO [C 1s, O 1s]

UV-ozone treatment introduces ***O^{2-} ions into ITO surface*** with modification depth ~50Å. The ITO surface become less conductive and charging effect is observed in terms of shift of C 1s. (5º – 45º TOA, C 1s peak shifts to 286 eV; 90º TOA, C 1s = 285eV no charging)

UV-ozone treatments

XPS spectra - C 1s



Ref. **C 1s** (285.0 ± 0.1 eV)

Depth (Å) [θ]	Before	After
7 [5°]	285.6	286.0
18 [15°]	285.1	286.0
50 [45°]	285.0	285.9
70 [90°]	285.2	285.0

C 1s acts as *surface potential indicator*

Before UVO

A thin layer of 7Å (charging at 5° TOA only) only non-conducting carbon contamination is found on the ITO surface.

After UVO

Charging occurred from 5° to 45° TOA.

NOT from contamination

Depth (Å) [θ]	In 3d After UVO
7 [5°]	445.25
18 [15°]	445.10
50 [45°]	445.05
70 [90°]	444.70

UV-ozone treatments

XPS spectra – O 1s
Surface Oxygen Composition

P1 (530.3eV): O^{2-} in the tetrahedral interstics of FCC In^{3+} ion array

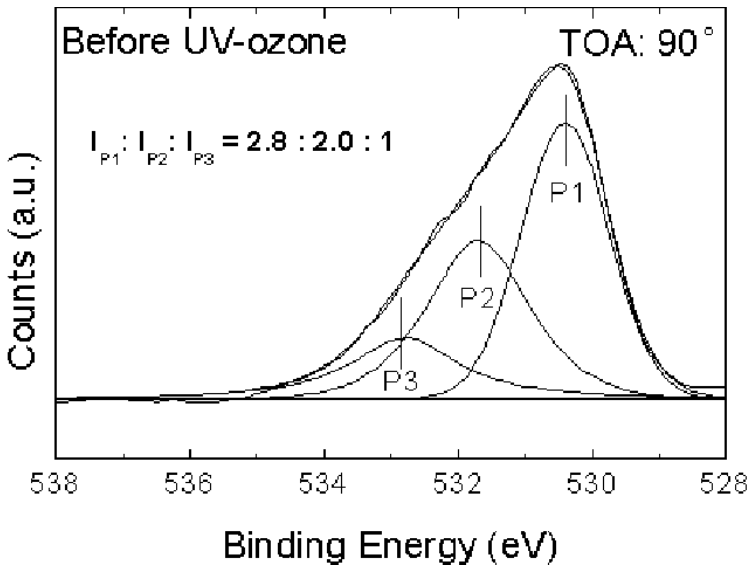
P2 (531.8eV): O from C-O contamination. O bond to In & Sn in ITO.

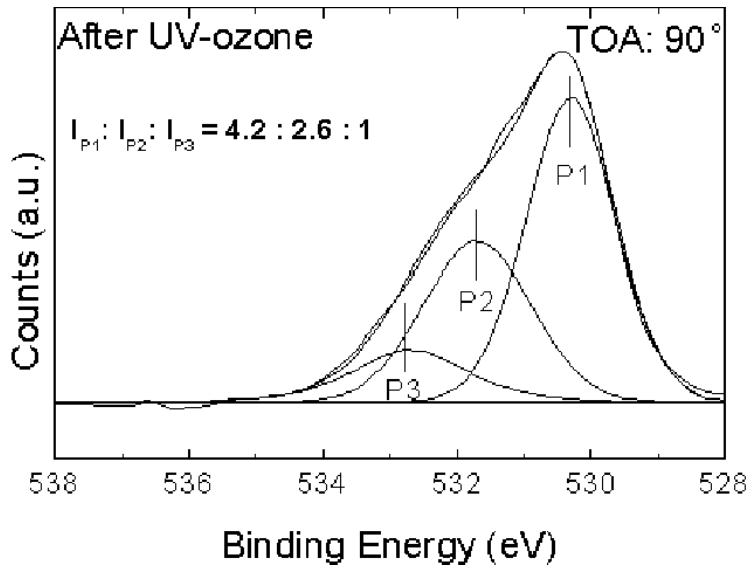
P3 (532.8eV): loosely bonded O^{o} from contamination

Depth (Å) [θ]	P1 : P2 : P3	
	Before	After
7 [5°]	1.1 : 1 : 1	1.3 : 1.2 : 1
18 [15°]	1.4 : 1.3 : 1	1.2 : 1.5 : 1
50 [45°]	2.3 : 1.8 : 1	2.8 : 2.2 : 1
70 [90°]	2.8 : 2.0 : 1	4.2 : 2.6 : 1

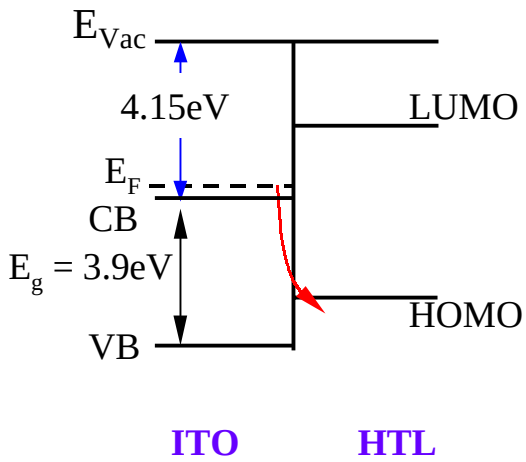
Increase of oxygen concentration - contributed to the increase of **P1(O^{2-})** & **P2(C-O)**.

i.e. UVO introduces **O^{2-} ions** into ITO surface.

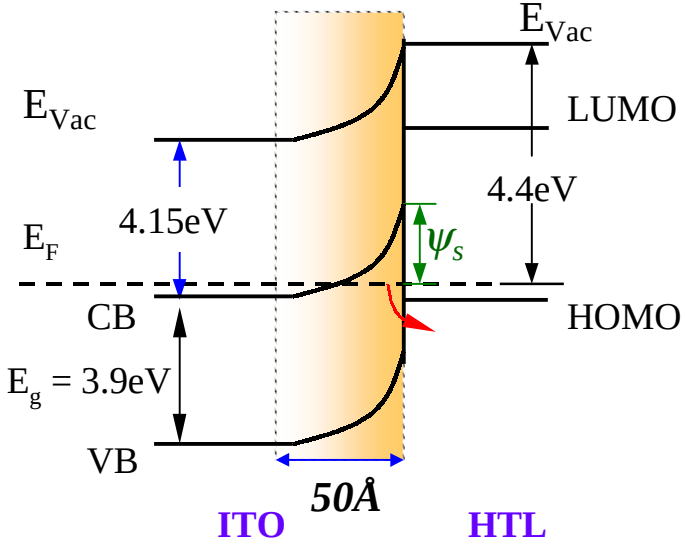




Proposed model



Before UV-ozone treatment



After UV-ozone treatment

Surface band bending

$\phi_{surface}$ = 4.4eV (UPS)

ϕ_{bulk} = 4.15eV (UPS)

Surface potential ψ_s = 0.25eV

Bandgap = 3.9eV (PDS, Absorption spectra)

Ionization potential I_p > 8.1eV

In $3d_{surface}$ *(TOA 15°, 7Å)* = 445.25eV (ADXPS)

In $3d_{bulk}$ *(TOA 90°, 50Å)* = 445.05eV (ADXPS)

Shift in In 3d within ~50Å = 0.2 ± 0.02eV

Conclusion

ADXPS indicates ITO surface is Sn-rich (In:Sn=7:1) & In on ITO surface exists in more complex chemical states than in the bulk.

O-plasma & N-plasma *effectively* remove ITO surface carbon contamination.

Work function of ITO can be increased by *reducing surface carbon contamination* & *increasing the surface stoichiometry* of ITO.

Before UVO treatments, a non-conducting thin layer of carbon contamination (~7Å) at ITO surface. UVO removes most carbon contamination at ITO surface, The residual carbon at ITO surface is partially oxidized.

After UVO treatments, ITO surface (~50Å) is modified through introducing O^{2-} ions on the ITO top surface. The conductivity of ITO surface is decreased.

Acknowledgements

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