

Accepted Manuscript

Oxygen-controlled structures and properties of transparent conductive SnO₂:F films

Fayu Wu, Xinru Tong, Zhuo Zhao, Jianbo Gao, Yanwen Zhou, Peter Kelly



PII: S0925-8388(16)32492-6

DOI: [10.1016/j.jallcom.2016.08.114](https://doi.org/10.1016/j.jallcom.2016.08.114)

Reference: JALCOM 38616

To appear in: *Journal of Alloys and Compounds*

Received Date: 19 April 2016

Revised Date: 5 August 2016

Accepted Date: 14 August 2016

Please cite this article as: F. Wu, X. Tong, Z. Zhao, J. Gao, Y. Zhou, P. Kelly, Oxygen-controlled structures and properties of transparent conductive SnO₂:F films, *Journal of Alloys and Compounds* (2016), doi: 10.1016/j.jallcom.2016.08.114.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Oxygen-Controlled Structures and Properties of Transparent Conductive SnO₂:F films

Fayu Wu, Xinru Tong , Zhuo Zhao, JianboGao, Yanwen Zhou * , Peter Kelly**

School of Materials Science and Metallurgy, University of Science and Technology Liaoning

**zhouyanwen@ustl.edu.cn*

No. 185 Qianshan Road, Hi-tech District, Anshan, Liaoning, China 114051

***peter.kelly@mmu.ac.uk*

Surface Engineering Group, Manchester Metropolitan University, Chester Street, Manchester

M1 5GD, UK

Abstract: The morphology and properties of the transparent SnO₂:F (FTO) films, deposited by RF magnetron sputtering at varying oxygen flows from 0~3sccm, were examined. For FTO films deposited with 0~1sccm O₂, the polar unsaturated (101) planes were the preferred orientation, resulting in resistivity values as low as 10⁻³Ω·cm, and the transparency of 86.5% in the visible range. The saturated (110) orientation planes associated with {101} facets formed knee twin crystallites for the FTO film prepared at 2sccm O₂. Further increases of O₂ led to severe mis-orientation of the crystals. The average transparency in the visible range increased up to 95%, but these FTO films were hardly conductive due to the oversupply of O₂. The optical band gaps became wide at first and then narrow again as the increases of the oxygen flow rates.

Key words: FTO, Structures, TCO materials, Magnetron Sputtering, Oxygen Flow

1. Introduction

Fluorine doped tin oxide (FTO) can be prepared by several techniques, such as the pyrolysis process¹, laser ablation deposition^{2,3}, evaporation⁴, magnetron sputtering⁵ and spray pyrolysis^{6,7}. Semi-conductive transparent FTO coatings can be used as window electrodes, and insulating FTO coatings can form barrier layers in electronic devices^{9, 10}. Also, by engineering the nanocrystalline structure, tin oxide films can effectively emit UV light and used in LED fabrication due to tailing the band edge state¹¹. Tin oxide is much cheaper than indium oxide and can be used in place of it as an electrode¹². It is worth mentioning that chemical vapor deposition (CVD)¹³ is currently the most widely used industrial scale technique to produce FTO glass¹⁴, but environmental pollution from this process may threaten its continued use.

Studies of FTO films show that the textures of the films can be controlled by the preparation processes, such as the choice of precursors in the spray pyrolysis method^{6,7}. As a semi-conductive oxide, the dopant atom, F, takes the place of the O atoms in the SnO₂ lattice, and provides a free electron. Oxygen content is a critical parameter as an oversupply of oxygen might force the F atoms into lattice spaces as an interstitial atom, or in the domain boundaries, where the F atom will lose its role as a donor. In magnetron sputtering, the mean free path of 'light' O and F atoms is normally much larger than that of the 'heavy' Sn atoms, and they can be more easily pumped out of the vacuum chamber. FTO films deposited in a pure Ar atmosphere are likely to be oxygen deficient and form O vacancies. Also, the ratio of fluorine in the films might slightly different with that in the target, which would not affect it, as the donor, to take over the oxygen position, especially to occupy the oxygen vacancy. Such oxygen vacancies would cause deformation of the lattice, and if the deformation was sufficiently severe, this might reduce the mobility of the charge carriers in the FTO

films. Therefore oxygen and fluorine contents are the main factors affecting the conductivity of FTO films. It was found that the morphology of FTO films deposited by magnetron sputtering is also influenced by oxygen content, indicating a strong relationship between structure and the properties.

2. Experimental

FTO films were prepared from powder targets by RF magnetron sputtering in this study, as described elsewhere¹⁵⁻¹⁷. Briefly, 99.99 % SnF₂ powder (Aladdin) was mixed into 99.99 % SnO₂ powder (Aladdin) to give a target content of 2.5 at% fluorine, which kept no change during the preparation of the films. It is presumed that the ratio of fluorine in the films should also be kept constant. The mixed powders were then spread onto the copper backing plate, and slightly tamped by a stainless steel disc to form a uniform and smooth surface, without further processes. This technique has been described in more detail by Kelly and Zhou elsewhere¹⁸. The glass slides were cleaned ultrasonically in alcohol and then deionized water, before drying in pure N₂. The coatings were deposited at a target power of 300W for 2 hours, at varying oxygen partial flows, with a 180mm substrate-target separation; see table 1 for full details. Coating composition was determined by X-ray photoelectron spectroscopy (XPS). Depth profiling of the FTO films was undertaken to 200nm depths to determinate the Sn/O atomic ratios. The structures of the FTO films were characterized by field-emission scanning electron microscopy (FEG-SEM) at 10kV, X-ray diffraction (XRD) in θ - 2θ mode and high resolution transmission electron microscope (HRTEM). The thicknesses of the films were measured by an Alpha Step D100 profilometer, and the optical and electrical properties were determined by a spectrophotometer and a Hall Effect measurement system, respectively.

3. Results and discussion

3.1 Composition and Structure

The O₂:Sn atomic ratios for the FTO films increased as the O₂ partial flow rates increased from 0 to 3sccm in the Ar sputtering atmosphere, changing from approximately stoichiometric to O-rich. The composition data are included in table 1 and illustrated in figure 1. Increasing the O₂ flow rate would also be expected to lead to reductions in the sputtering rate at the target and, therefore, decreasing deposition rate, which is included in figure 1 in terms of film thickness. As shown in figure 2, AFM and SEM analysis indicated distinct changes in surface morphology as a function of oxygen flow rate, with the stoichiometric FTO films revealing polygon-type textured surfaces with pyramid shape grains, whereas the O-rich films appeared to have twin crystallites, changing to rod-like prismatic grains at the highest O₂ flow rate. Figure 2 also indicates that the grain size tended to decrease with increasing O₂ flow rates, which is comparable due to the same magnification times of the a~d AFM and SEM images, respectively.

In order to find the reason that the grain sizes decreased as the increases of the oxygen flow rates, STEM method was applied onto the O-rich film deposited at 3sccm O₂ flow to analyze the distributions of F atoms. The components of the red-cross point in figures 3a and 3b were including tin and oxide elements (figure 3c). The distribution of fluorine along the orange line in figure 3a was shown by the middle orange line in figure 3d. Three peaks pointed by the blue circles were able to be observed, which indicated the fluorine fluctuations in strength. Comparison with the orange line in figure 3a and the blue circles in figure 3d, it could be seen these blue circles were corresponded to the domain boundaries. That is to say, 'F' atoms may participate within the domain boundaries, which blocked the grain growth for the O-rich FTO films.

Another aspect of the structure of the films influenced by oxygen flow rate was the preferred orientation, or crystalline texture, which is shown in figure 4. The main preferred orientations were (101) and (211) when the films were deposited with 0 to 1 sccm of oxygen in the Ar atmosphere. The (101) planes contain either tin or oxygen atoms, which indicates that (101) planes are polar and unsaturated. A shift in texture was then observed for the higher oxygen flow rate coatings to (110), with several other peaks, including the (211) and (301) peaks, also observed. The lattice structure of rutile SnO₂ shows that there are two possible positions to locate oxygen atoms: one is (0.306a, 0.306b, 0c), and the other is (0.184a, 0.816b, 0.5c)¹⁹. The second position is within the (110) planes, which contain both oxygen and tin atoms. Therefore (110) planes are un-polar and saturated ones.

3.2 Optical Property

The average transmittance of the films increased as the increases of the O₂ partial flow rates from 0 to 3 sccm in the Ar sputtering atmosphere, changing from approximately 86.5% to 95% within the visible range (table 1 and figure 5). The absorption edges obviously shifted towards large band gaps as the increases of the oxygen flows up to 2 sccm, showed in the inner graph in figure 5. Then the band gap of the film decreased again when the oxygen flow rate increased to 3 sccm. In optical theory of thin films, the total incident light to be 1, then

$$T=1-R-A-S \quad \dots\dots(1)$$

in which, 'T' presents transmittance, 'R', reflectivity, 'A', absorptivity, and 'S', scattering ratio.

As mentioned in 3.1 section, the O₂:Sn atomic ratios for the FTO films changed from approximately stoichiometric to O-rich as the increases of the O₂ flow rates, which would lead to the loss of the metallic property and the increase of the dielectric property for the semi-conductive oxide films. The

reflectance of the films caused by metallic property would be reduced. The scattering ratio is decreased in the case of the film surfaces are dense and smooth²⁰. It can be seen in table 1, the roughnesses, in term of the root mean square roughnesses, reduced abruptly when the O₂ partial flow rate in the sputtering atmosphere raised up to 2sccm. Additionally, the absorptivity of the semi-conductive films in the visible range mainly depended on the absorption by charge carriers¹⁹, i.e. the higher the charge carrier concentration is, the more the absorption of the visible light is. The carrier concentrations of the FTO films dropped down by three orders as the oxygen flow partial increased up to 2sccm, refer to table 1. Therefore, the decreases of the 'R', 'S' and 'A' as the increases of the O₂ flow partial rates would lead to the increases of the transmittance of the films.

3.3 Electrical Property

The resistivities of the films increased as the O₂ partial flow rates increased from 0 to 3sccm in the Ar sputtering atmosphere, changing from approximately 10⁻³ohm-cm to 10²ohm-cm (table 1 and figure 6). The charge carrier concentrations and mobilities decreased as the O₂ partial flow rates increased from 0 to 3sccm, varying from 10¹⁹/cm³ and 14cm²/V-s to 10¹⁶/cm³ and 1cm²/V-s, respectively. The sudden changes of the resistivity, charge carrier concentration and mobility occurred at the point of 2sccm O₂ partial flow rate. Just at this point, the composition of the FTO film showed O-rich, the crystalline texture changed from polar unsaturated (101) to un-polar saturated (110) plane. It is known that the electrical property of the FTO film depended on the free electron concentration provided by fluorine doping and oxygen vacancies, and on the carrier mobility which affected by lattice deformations and crystalline sizes. The O₂ partial flow in the sputtering atmosphere was up to 2sccm, the compositions of the FTO films were O-rich, which resulted in the

loss of oxygen vacancies, and the participation of the fluorine atoms within the domain boundaries, and the growth of the crystalline domains blocked. The fluorine atoms not only lost their role as a dopant, but also hindered the combination of the crystal grains. Therefore, the charge carrier concentrations and mobilities dropped, the crystalline texture changed to unpolar saturated (110) plane, and the semi-conductive FTO films transformed into insulated films.

3.4 Discussion

The changes in microstructure and texture can be clearly observed in figures 2 and 4, which related to the significant changes of the optical and electrical properties of the FTO films, refer to figures 5 and 6 and table 1.

In figure 7, the TEM images detailed the changes of the crystalline and the nano-domain sizes to clearly explain and accurately predict the properties. As shown in figure 7, the domain sizes of all the films were less than 20nm, and the mis-orientated domains were only about 5nm for the oxygen rich film deposited at 3sccm of oxygen. In Figures 7a and 7b, the selected area electron diffraction (SAED) spots showed that the crystals had strong (101) orientations, which are in accordance with the XRD patterns. The crystalline grain sizes for the film deposited without additional oxygen in the sputtering atmosphere were larger than those with 1sccm O₂ flow, which may account for the lower charge carrier mobility. The fact was the charge carrier mobility decreased from 14cm²/V-s to 3.4cm²/V-s.

The typical rutile SnO₂ knee twin crystal, which is a naturally existing SnO₂ crystal type, can be seen in figure 7c, the FTO film deposited with 2sccm O₂ flow. The parallel (110) planes were perpendicular to the (101) twin planes, indicated in the figure by the red lines with 120° angles on top

planes, which is why the resistivity of the film increased dramatically from 10^{-2} to 10^2 $\Omega\cdot\text{cm}$. The {101} plane group made a (110) orientation, which was consistent with the results in the references of 13, 21 and 22.

The O-rich nature of the FTO film deposited with 3sccm O_2 might lead to the participation of fluorine atoms within the domain boundaries or forced into interstitial lattice spaces. Further growth of the domains was then blocked. Also, the crystallites were tilted and mis-orientated, refer to figure 7d. A study by F.A. Garces²³ showed that the mis-orientation or tilting would reduce the conductivity of the film. Correspondingly, the O-rich films (7c and 7d), with un-polar saturated (110) preferred orientations and small tilting grains, showed very low conductivity.

In general, the polygon-type pyramid shape grains with (101) preferred orientation would lead to high conductivity and relatively low transmittance of the FTO films because the oxygen vacancies existed and fluorine atoms acted as donors. The knee twin crystal shape indicated the O-rich in the FTO films and the un-polar saturation (110) orientation and therefore, resulted in the low conductivity and high transmittance. The rod-like prismatic grain with very fine domain sizes would further decrease the conductivity, increase the transparency and narrow the optical band gap because the movements of the charge carriers were limited by the increasing domain boundaries.

4. Conclusions

The morphological and micro-structures of the FTO films changed as a function of the oxygen:tin atomic ratio in the films, which could be controlled by additional oxygen flow in the sputtering atmosphere. The polar unsaturated (101) planes were the mainly preferred orientation at low additional oxygen flow rates, and polygon grains could be identified. These films were

conductive, but relatively low transmittance. Higher oxygen in the sputtering atmosphere led to a shift in the main orientation to un-polar saturated (110) planes, and mis-orientation or titling of the grains. These FTO films were almost insulating with transmittance up to 95% in the visible range.

This work was supported by the National Science Funding China in Nos. of 51172101 and 51372109 and by National Undergraduate Training Program for Innovation and Entrepreneurship of the University of Science and Technology Liaoning in No. of DC 2014004.

References

- ¹A. Smith, J.-M.Laurent, D.S. Smith, J.-P.Bonnet, R.-R. Clemente, *Thin Solid Films*, 266 (1995) 20-30.
- ²H. Yang, D. Fu, M. Jiang, J. Duan, F. Zhang, X. Zeng, U. Bach, *Thin Solid Films*, 531 (2013) 519-524.
- ³Z. Dai, A. Miyashita, S. Yamamoto, K. Narumi, H. Naramoto, *Thin Solid Films*, 349 (1999) 51-55.
- ⁴P. Jalkanen, S. Kulju, K. Arutyunov, L. Antila, P. Myllyperkiö, T. Ihalainen, T. Kääriäinen, M.-L. Kääriäinen, J. Korppi-Tommola, *Thin Solid Films*, 519 (2011) 3835-3839.
- ⁵X.-X. Ding, F. Fang, J.-Q. Jiang, *J. Vac. Sci. Technol. Chin.*, 32(2012) 379-384.
- ⁶S.-Y.Lee, B.-O. Park, *Thin Solid Films*, 510 (2006) 154-158.
- ⁷B. Thangaraju, *Thin Solid Films*, 402 (2002) 71-78.
- ⁸C. Quintana, P. Atienzar, G. Budroni, L. Mora, L. Hernández, H. García, A. Corma, *Thin Solid Films*, 519 (2010) 487-493.
- ⁹H. Widiyandari, A. Purwanto, K. Diharjo, Suyitno, E. Hidayanto, *AIP Conference Proceedings*, 1554 (2013) 147-149.
- ¹⁰A. Muthukumar, G. Rey, G. Giusti, V. Consonni, E. Appert, H. Roussel, A. Dakshnamoorthy, D. Bellet, *AIP Conference Proceedings*, 1512 (2013) 710-711.
- ¹¹Y. F. Li, W. J. Yin, R. Deng, R. Chen, J. Chen, Q. Y. Yan, B. Yao, H. D. Sun, S. H. Wei and T. Wu, *NPG Asia Materials* (2014) 4, e30.
- ¹²W.-H. Baek, M. Choi, T.-S.Yoon, H.H. Lee, Y.-S. Kim, *Appl. Phys. Lett.*, 96 133506 (2010) .
- ¹³R.Y. Korotkov, P. Ricou, A.J.E. Farran, *Thin Solid Films*, 502 (2006) 79-87.
- ¹⁴Q. Gao, H. Jiang, C. Li, Y. Ma, X. Li, Z. Ren, Y. Liu, C. Song, G. Han, *J. Alloys Compd.*, 574 (2013) 427-431.
- ¹⁵Y.-W.Zhou, X. Liu, F.-Y.Wu, C.-K.Zhang, X.-Y. Zhang, *Surf.Coat.Technol.*, 228, Supplement 1 (2013) S150-S154.
- ¹⁶Y.-W.Zhou, F.-Y.Wu, C.-Y.Zheng, *Chin. Phys. Lett.*, 28(2011) 107307-1~3.
- ¹⁷Z.Banyamin, P.J. Kelly, G.T. West, J. Boardman, *Coatings*, 4 (2014) 732-746
- ¹⁸P.J. Kelly, Y. Zhou, *J. Vac. Sci. Technol. A*24(5) 2006, 1782-1789.
- ¹⁹J. Xu, D.-X.Lu, T.-S.Yuan, *ACTA Physica.Sinica.*, 56 (2007) 7195-7200.
- ²⁰J. Ru, W. Liu, Y. Qiang, *Techniques of Optical Films*, Publishing House of Electronics Industry, 2nd edition, 141-142, in Chinese.
- ²¹A.-V.Moholkar, S.-M.Pawar, K.-Y.Rajpure, C.-H.Bhosale, *Mater.Lett.*, 61 (2007) 3030-3036.
- ²²C.-Y.Kim, D.-H.Ru, *Thin Solid Films*, 519 (2011) 3081-3085.

²³ F.-A.Garcés, N. Budini, R.-R.Koropecki, R.-D. Arce, Thin Solid Films, 531 (2013) 172-178.

Figure caption

Figure 1: Variation with oxygen flow rate of coating stoichiometry and thickness for FTO thin films.

Figure 2: AFM and SEM morphologies of the FTO films via various oxygen flows: a) 0, b) 1, c) 2 and d) 3sccm.

Figure 3: The distribution of fluorine across several crystal domains: a) drift corrected spectrum profile scanning image; b) STEM HAADF detect image; c) EDX drift corrected spectrum profile and d) line scanning profiles of Sn-L (in green), F-K (in orange) and O-K (in red)

Figure 4: XRD patterns of the FTO films

Figure 5: Optical spectra of the FTO films

Figure 6: Electrical properties of the FTO films

Figure 7: TEM images of the FTO films via various oxygen flows: a) 0, b) 1, c) 2 and d) 3sccm.

Table caption

Table 1 The Sn/O and properties of the FTO films with the variations of O₂ partial flows

Table 1 The Sn/O and properties of the FTO films with the variations of O₂ partial flows

No.	O ₂ sccm	Sn/O	d nm	ρ ohm-cm	n /cm ³	μ cm ² /V-s	T %	Sq nm
a	0	33.42 /66.58	827	5.4E-3	8.4E+19	1.4E+1	86.5	2.16
b	1	33.11 /66.89	680	8.1E-2	2.3E+19	3.4E+0	88.7	2.73
c	2	32.53 /67.47	430	1.8E+2	3.0E+16	1.1E+0	93	0.65
d	3	31.61 /68.93	310	2.1E+1	2.9E+16	1.0E+0	95	1.27

Note: Sn/O--Sn/O Atomic ratio; d--Thickness; ρ --Resistivity; n--Carrier concentration;
 μ --Carrier mobility; T-- Transmittance; Sq--Root mean square

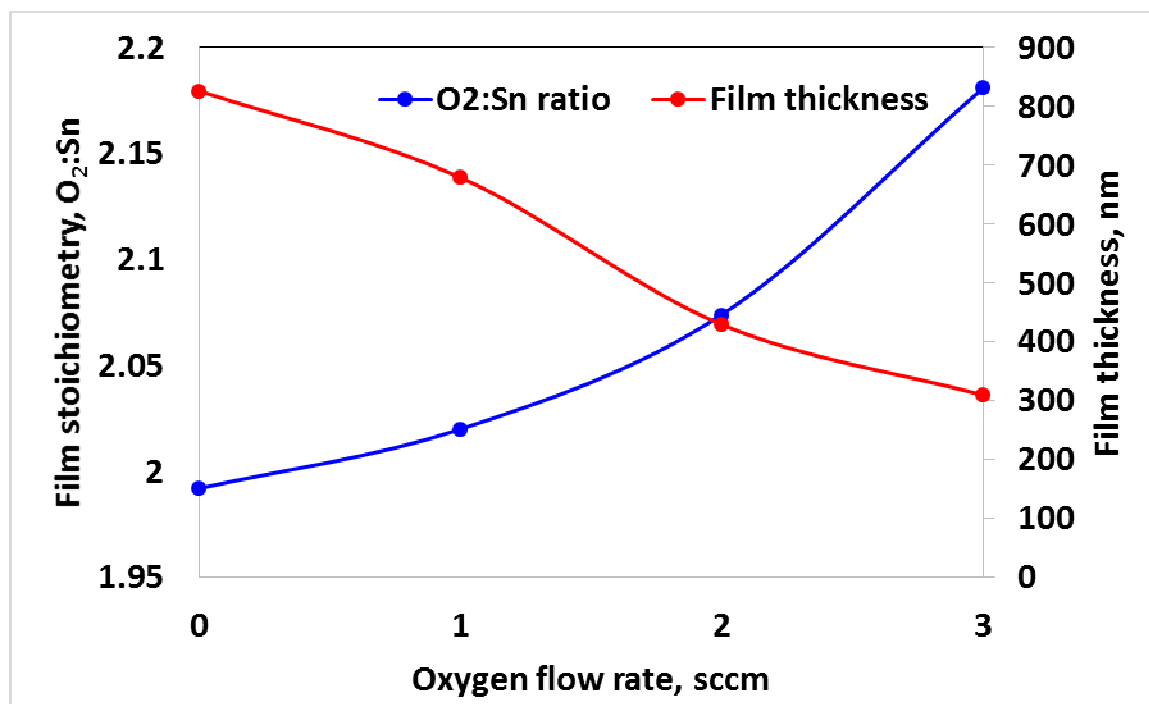


Figure 1

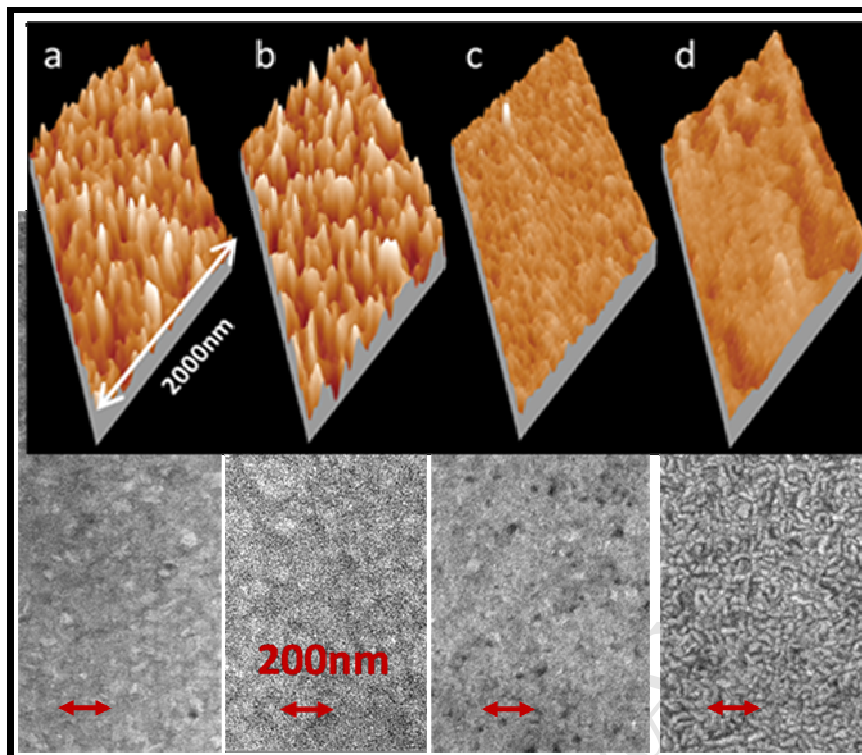


Figure 2

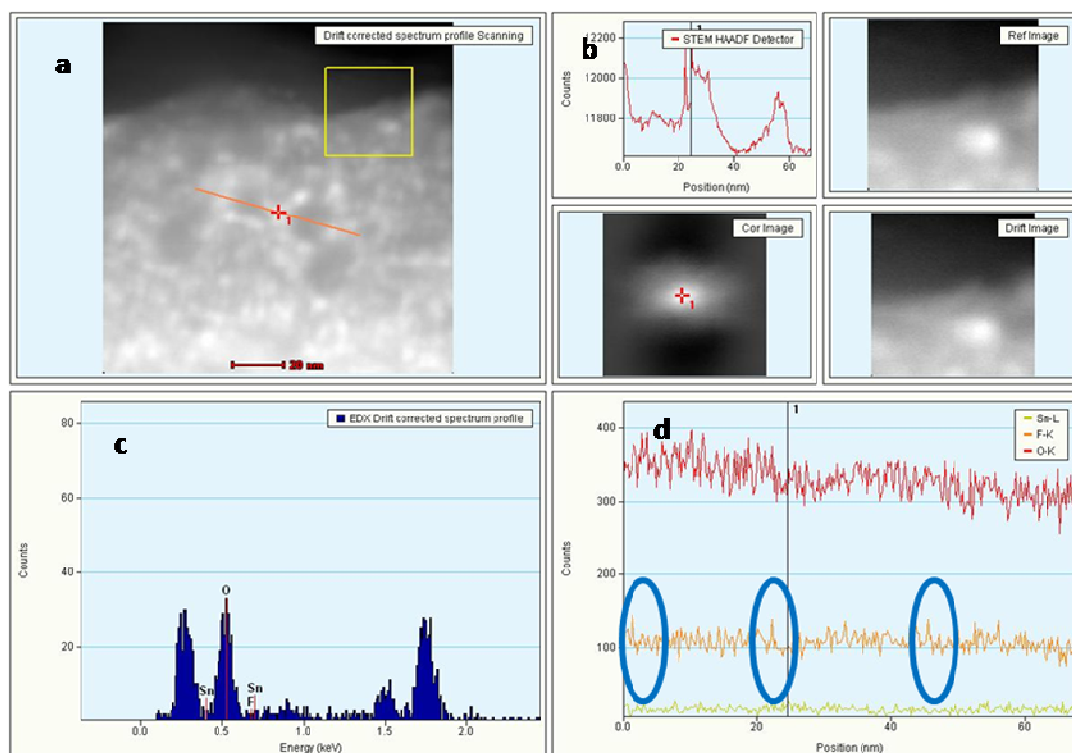


Figure 3

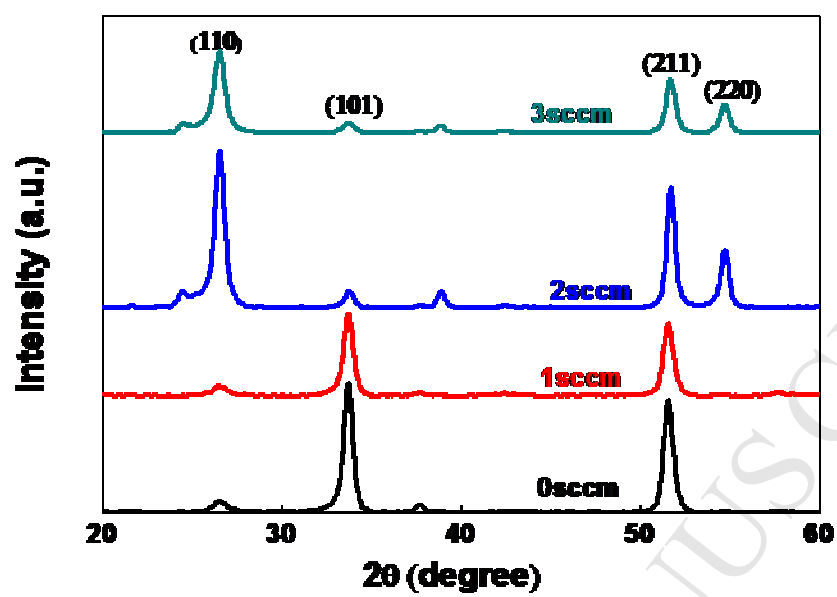


Figure 4

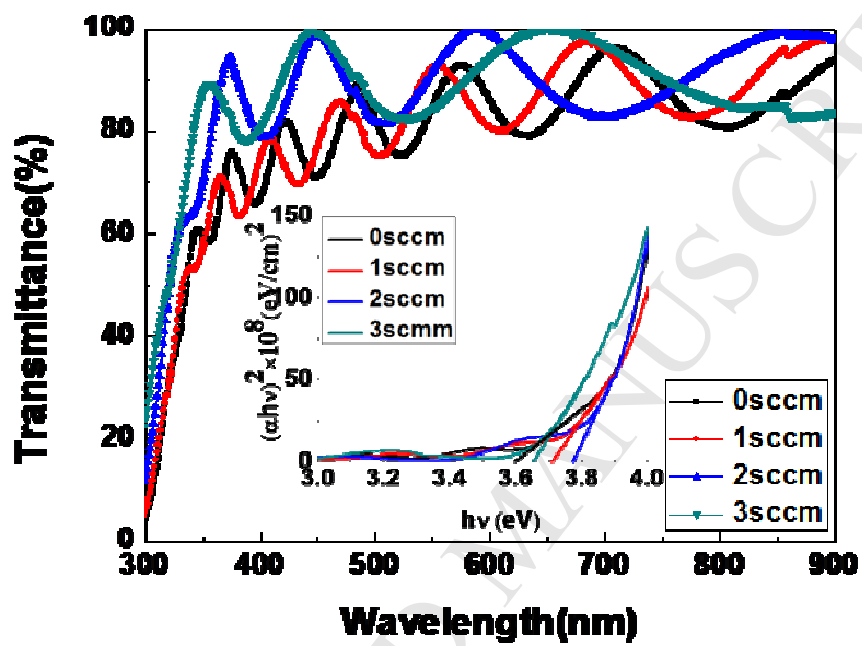


Figure 5

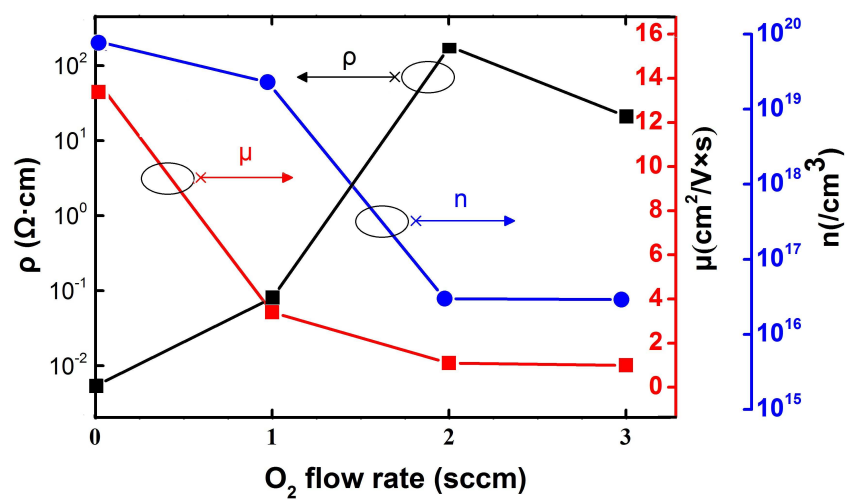


Figure 6

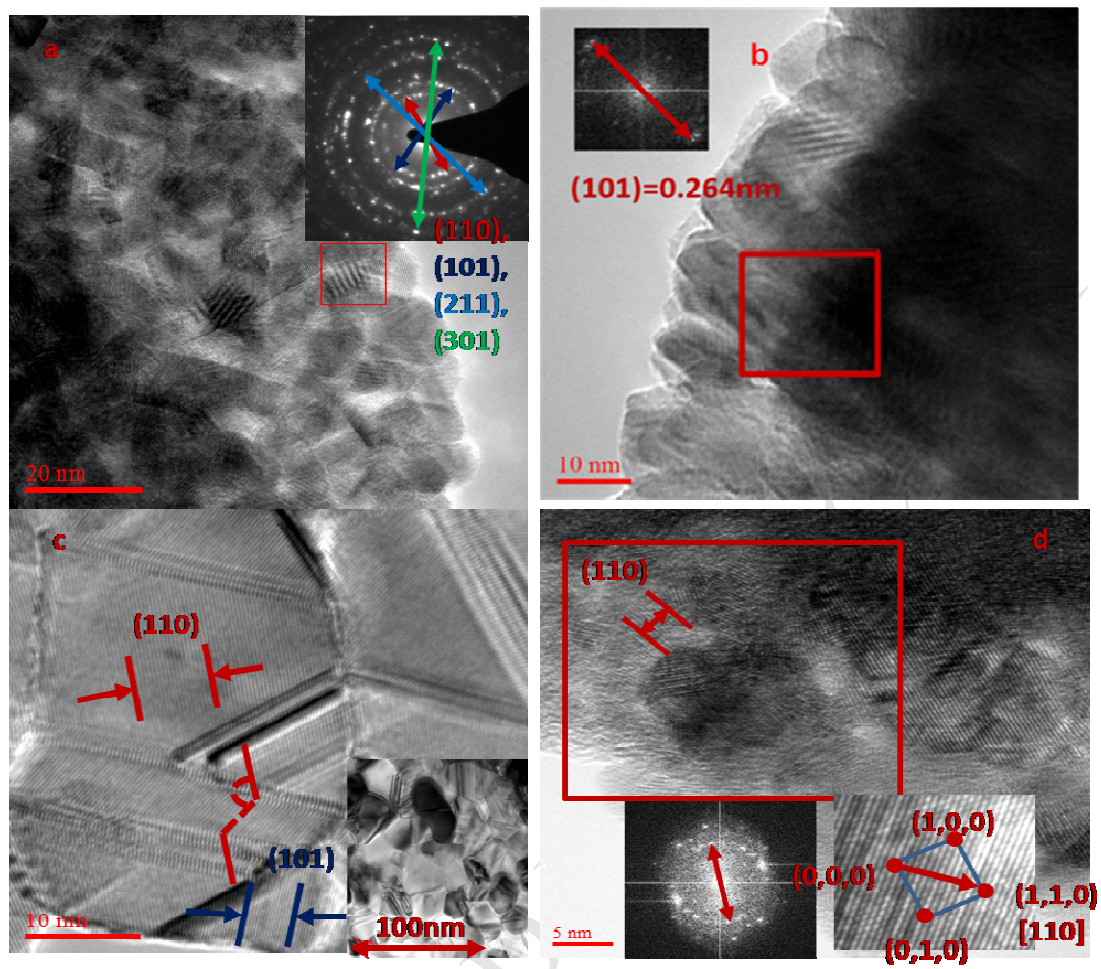


Figure 7

1. The FTO structures could be controlled by O- flow in the sputtering atmosphere.
2. The properties of the FTO films could be customerized by combination Sn with F/O.
3. The slightly O-deficient FTO films were with polar structure and low resistivity.
4. The O-rich FTO films were with un-polar structure and high transparency.