

A hard x-ray photoemission study of transparent conducting fluorine-doped tin dioxide

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Abstract — Fluorine-doped tin oxide (FTO) is a commercially successful transparent conducting oxide with very good electrical (resistivities $< 1 \times 10^3 \Omega \cdot \text{cm}$) and optical properties (transmittance $> 85\%$). These properties coupled with cheap and large-scale deposition on float-glass lines means FTO has found commercial use in, for example, low emissivity windows and solar cells. However, despite its widespread application, a detailed understanding is lacking of the doping and defects in FTO. Recent work [1] has suggested that the fluorine interstitial plays a major role in limiting the conductivity of FTO. Here we present synchrotron radiation high energy x-ray photoemission spectroscopy (XPS) of the fluorine 1s core level of FTO films without *in situ* surface preparation. This probes deeper than standard XPS and shows that the fluorine interstitial is present not just at the surface of the films and is not an artefact of argon ion sputtering for surface preparation.

Index Terms — Fluorine-doped tin dioxide, SnO_2 , Transparent conducting oxides, HAXPES

I. INTRODUCTION

Transparent conducting oxides (TCOs) are materials that combine optical transparency and electrical conductivity. The combination of these properties is almost unique to TCOs; many electrical insulators can be made transparent (such as glass and ceramics), whilst materials such as metals are heavily conducting but optically opaque. These properties have seen TCOs being incorporated into many modern technologies including photovoltaic (PV) devices, low-emissivity windows, touch screens, and flat panel displays [2-4]. Currently the market for TCOs is dominated by tin-doped indium oxide ($\text{Sn:In}_2\text{O}_3$, ITO), which boasts the best conductive properties but, due to the high cost of indium, is chosen mainly for consumer electronics and not large scale applications. Fluorine-doped tin dioxide (F:SnO_2 , FTO) is a

cheaper alternative with competitive optoelectronic properties to ITO and is more thermally and chemically robust. FTO has found use in large scale applications such as PV, being produced via cheap and scalable methods such as chemical vapor deposition (CVD) [5].

Whilst FTO is a very successful commercial material in its own right, recent results have indicated that a self-compensation mechanism exists by which the electrical properties of FTO are inherently limited [1]. It was found that the fluorine interstitial is incorporated into the SnO_2 matrix when a heavy doping level is reached. This acts as an electron acceptor and counteracts around half of the substitutional fluorine's donor electrons.

However, these findings were based in part on standard 1486.6 eV Al $K\alpha$ x-ray photoemission spectroscopy (XPS) of FTO films prepared by Ar^+ ion bombardment. Two different chemically shifted species were seen in the F 1s XPS spectra and were attributed to substitutional and interstitial F. As XPS is very surface sensitive (~ 5 nm based on 95% of the signal coming from within three inelastic mean free path lengths) and Ar^+ ion bombardment can change the surface bonding configurations, the question remained as to whether the interstitial F is present in the as-grown film and whether it is present below the first few nanometers of the surface.

Here, therefore, we have employed hard x-ray photoemission spectroscopy (HAXPES), a synchrotron-based technique used to probe the occupied states of samples using high energy photons (6450 eV) and measurement of the kinetic energy of the emitted photoelectrons. This technique gives greater probing depth (~ 25 nm) and enables the films to be studied without Ar^+ ion bombardment. Through this technique we can obtain data to support the claim that the fluorine interstitial exists in FTO, and is present in quantities

of roughly a half of the substitutional fluorine incorporation. This research confirms the previously reported mechanism that inherently limits the conductivity of FTO and indicates that alternative dopants for SnO_2 may produce films with significantly higher conductivities.

II. EXPERIMENTAL METHODS

FTO thin films deposited on a glass float line by the atmospheric pressure chemical vapor deposition (APCVD) method were obtained from NSG Group. Samples were prepared for measurement by mechanically cleaning the surface to remove large particulates and treated in an ultrasonic bath submerged in diluted surface cleaner and then isopropyl alcohol, and rinsed in deionized water. The thickness of FTO films was determined using profilometry to be $\sim 300\text{nm}$.

High resolution x-ray photoemission spectroscopy was performed using a Kratos monochromatic Al $K\alpha$ ($h\nu = 1486.6\text{ eV}$) x-ray source. In-situ surface cleaning was performed via argon ion bombardment at an energy of 200 eV for 600 seconds in cycles. This is a low energy sputter to minimize any damage of the surface of the material.

Hard x-ray photoelectron spectroscopy was performed at the I09 beamline at Diamond Light source. No *in situ* surface preparation was performed. Measurements were performed at 6450 eV . Photoelectrons were collected using a SCIENTA EW-4000 electron energy analyzer mounted perpendicular to the X-ray beam. The sample was irradiated in grazing incidence geometry at an angle of 3° between x-ray beam and sample surface. The energy calibration and resolution of the system were determined from a polycrystalline Au foil.

Both soft and hard XPS spectra were referenced to the measured Fermi level. It is estimated that the HAXPES measurements have a resolution of $\sim 300\text{ meV}$ and $\sim 500\text{ meV}$ for our lab-based XPS system for the setting used, based on measurements of a cleaned silver foil.

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was performed using the ION-TOF 5 (ToF-SIMS) instrument to obtain a compositional positive ion depth profile for each sample. The analysis beam was Bi^{3+} and the sputter beam was 1 keV Cs^+ . For each sample, the sputter beam was rastered over a $200 \times 200\text{ micron}$ area and the bismuth analysis beam was rastered over a $50 \times 50\text{ micron}$ area at the center of the sputtered region.

III. RESULTS AND ANALYSIS

The wide-scan survey spectra of FTO shown in Figure 1 were recorded using hard x-ray (6450 eV) and lab based x-ray (1486.6 eV) sources. Only a low level of carbon contamination is seen in both spectra. Tin and oxygen peaks are present as expected for SnO_2 . The F 1s not well resolved in either survey spectra due both to the small quantity of fluorine in the samples ($\sim 1\text{ at. \%}$) and the low photoionization cross-section of F1s.

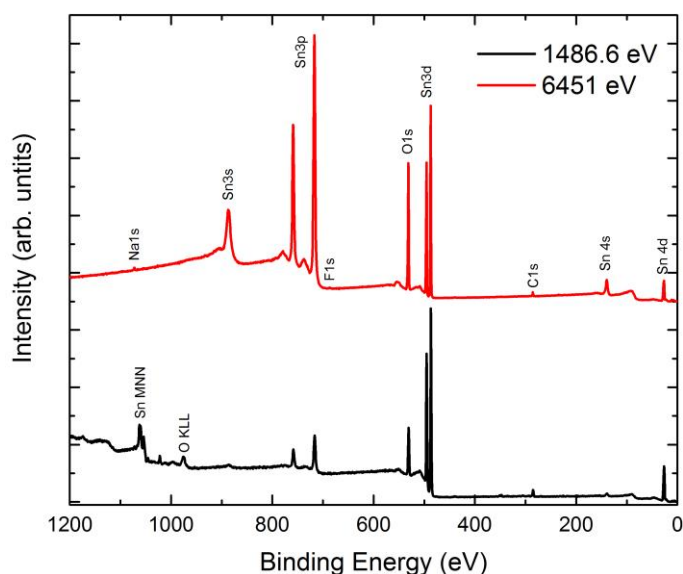


Figure 1. Survey spectra of FTO using lab based source (1486.6 eV) and synchrotron source (6450 eV).

An additional peak due to Na is seen in the HAXPES survey, suggesting a small amount of sodium contamination is present. This is not seen in the low photon energy spectra because *in situ* argon ion bombardment was used to clean the surface (indeed even after very long scan times, no Na signal is discernable after sputtering). This indicates the Na resides at the surface of the material, most likely a result of how the TCO-coated glass is stored/handled and transported. The assignment of Na as a surface feature is supported by the ToF-SIMS measurements, shown in Figure 2.

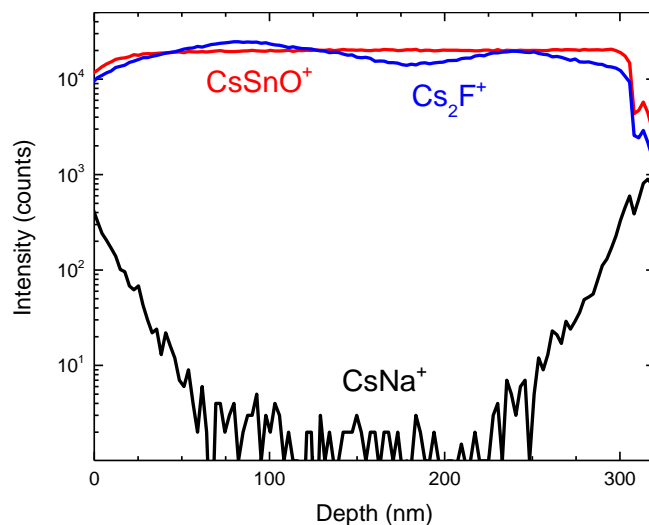


Figure 2. Secondary ion mass spectrometry data of FTO showing signals from tin oxide, fluorine and sodium.

Figure 2 shows Sn and O are distributed evenly throughout the full thickness of the FTO layer of the sample. F is also distributed throughout the film, although the signal displays peaks and troughs over the 300 nm thickness of the films. This

is consequence of the float line CVD deposition method used. The signal due to the Na begins at the surface, but quickly falls away to the level of the noise by a depth of around 50nm. The signal goes to zero until a depth of well over 200 nm is reached, where it is likely a small amount of Na diffusion from the glass occurs. It is important to note that the intensity in Figure 2 is on a logarithmic scale and so even at its maximum the number of counts of the Na signal is very low. This does however explain why Na is seen in the HAXPES spectra but not in XPS spectra from *in situ* Ar⁺ sputtered films.

In order to fully analyze the core levels from the HAXPES spectra, it is important to account for all the physical phenomena present. TCOs that are degenerately doped possess a high density of free electrons ($n > 10^{20} \text{cm}^{-3}$), the collective excitations of which form a conduction electron plasma [6]. During the photoemission process, photoelectrons have a probability to lose energy to the free electron plasma, which then manifests as an energy shifted component in the core level spectra.

In order to model this effect in the subsequent HAXPES spectra, the plasma frequency was obtained by modelling the reflectivity of FTO samples. A two oscillator model was used to simulate the dielectric response of the FTO and subsequent layers, in conjunction with the transfer matrix method for optical modeling multi-layer stacks [7]. A plasma frequency of 0.5 eV was determined [1].

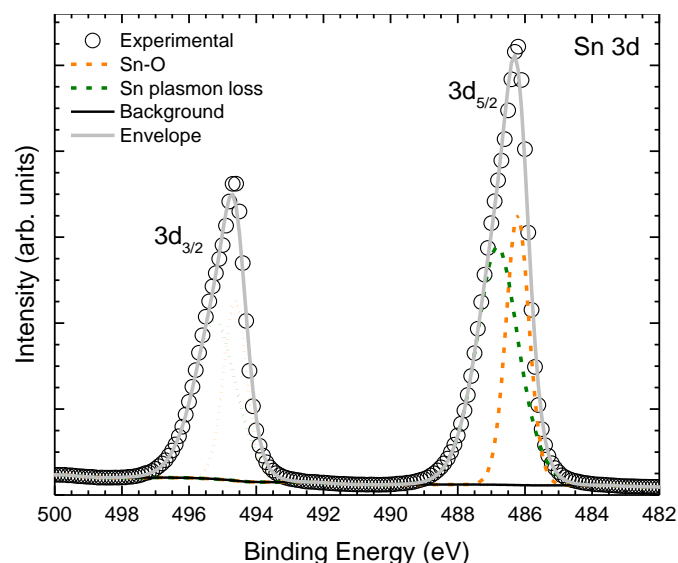


Figure 3. HAXPES spectra of Sn 3d core level region.

The Sn 3d core level region is displayed in figure 3 with associated fit. The core level fits are performed using a Shirley background and Gaussian-Lorentzian line shape. Both $3d_{5/2}$ and $3d_{3/2}$ peaks are shown, allowing us to constrain the core level fits appropriately with equal FWHM and an energy separation of 8.41eV. The plasma loss features have a much broader line shape with more Lorentzian character to account for the finite lifetime broadening of the plasmon. These loss components are constrained to be $\omega_p = 0.5 \text{eV}$ to higher binding energy than the core loss peak. An asymmetric line shape can

be considered for the plasmon loss component, although we opted not to use this line shape as the loss component was not sufficiently separated from the core level peak to necessitate this. An excellent fit to the data is achieved with only two components per peak (a Sn-O (486.3 eV) bond and associated loss peak), as is consistent with SnO₂ [8]. Due to the small fluorine and sodium concentrations neither an F-Sn bond nor any Na-Sn component are discernable.

Figure 4 shows the O1s region HAXPES spectrum. Again an excellent fit is achieved using only two components (a Sn-O bonding component (530.4 eV) and associated plasmon loss component) also consistent with literature [9]. Clearly the asymmetry always seen in photoemission spectra of degenerately doped TCOs can be excellently described using two component fit with energy separation constrained by the plasma frequency determined from infrared reflectance.

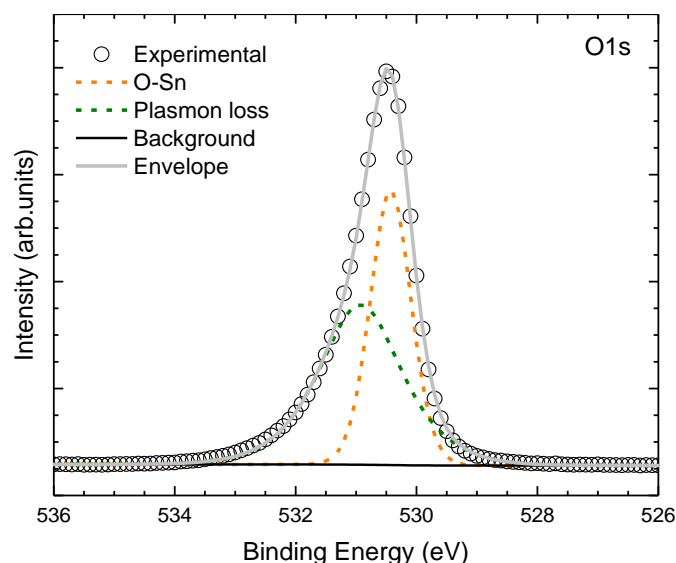


Figure 4. HAXPES spectra of O 1s core level region.

Now we turn our attention to the F 1s core level region of the FTO XPS data (seen in Figure 5). Due to the small concentration of fluorine present in the samples, the signal-to-noise for this region is comparatively worse than for the Sn3d or O1s. The F 1s peak being comparatively weak in intensity means that a longer scan time is required to resolve the peak and its features.

Both the soft XPS spectra (1486.6 eV) and hard XPS spectra (6450 eV) are shown in Figure 5 after background subtraction. The soft XPS F 1s peak is broader and is fairly asymmetric, but with a slight shoulder on the high binding energy side. It was determined that two core level components (and additional associated loss peaks) were required to fit this spectra, in good agreement with Ref. [1]. Using only a single core level-plasmon loss pair produces peaks with unrealistically high full widths at half maximum, and the fits are poor. Hence, it was concluded that an extra set of peaks is required. These are assigned to the F-Sn bond (685.0 eV) consistent with previous measurements of SnF₂ [10], the interstitial fluorine defect (685.7eV), visualized in Figure 6.

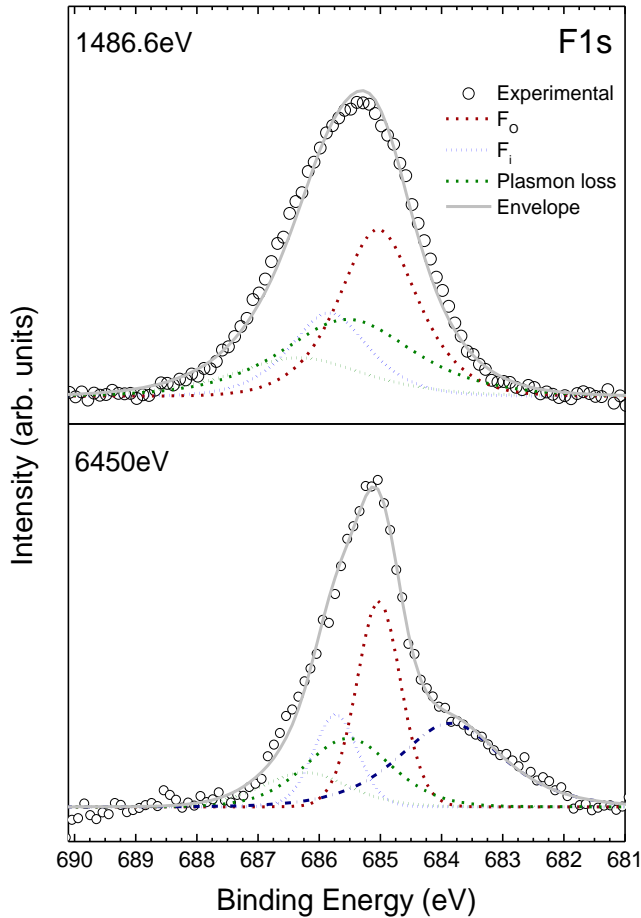


Figure 5. Soft XPS and HAXPES spectra of F1s core level region.

The HAXPES F 1s spectrum is narrower due to the better resolution of HAXPES compared with lab XPS, enabling the peak asymmetry to be seen more clearly. The spectrum can be fitted in exactly the same way, with the high binding energy tail being accounted for with a similar interstitial peak. In the HAXPES F1s spectrum, there is also an additional low binding energy feature that is relatively broad and is situated around ~ 684 eV. This is consistent with Na-F [11] and is supported by the Na peak in the survey spectra. Again this likely originates from Na surface contamination. Being present only at the surface and not throughout the film, confirmed by ToF-SIMS (Figure 2), Na is unlikely to significantly alter the conductivity of the FTO films.

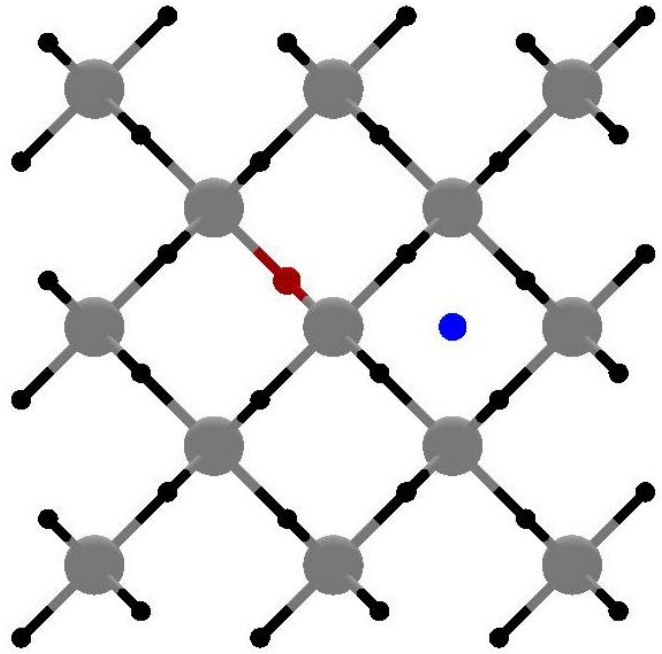


Figure 6. Schematic of interstitial fluorine in the SnO_2 rutile structure. The red circle represents the substitutional F and the blue circle represents the interstitial F atom, with O depicted black and Sn in grey.

Using the same fitting procedure as previously, we find F1s spectra cannot be fitted with a single F-Sn bond (and associated plasmon loss). The peak shape is too wide to be realistic based on the good resolution of the HAXPES. Hence a second component is required at higher energy. The separation between the two peaks was found to be 0.8 eV, consistent with previous XPS measurements [1], and too small a shift to be caused by contaminant species. The higher binding energy of the other peak also helps rule out many contaminant elements based on electronegativity arguments. The quantitative area ratio between the interstitial and substitutional F peaks is 0.46 in the HAXPES and 0.54 in the soft XPS, indicating the interstitial species is incorporated in a roughly 2:1 ratio with the substitutional fluorine. This confirms previous findings and supports the existence of the fluorine interstitial in FTO films.

IV. CONCLUSION

HAXPES is an excellent tool to confirm the fluorine interstitial is present in commercial FTO films and is not just at the surface or created by Ar^+ ion sputter surface preparation. The fluorine interstitial is confirmed as a bulk defect and is present in the predicted 2:1 quantities relative to substitutional fluorine. The presence of this compensating acceptor means fluorine is unlikely to be the most efficient dopant in the SnO_2 matrix indicating further work is required to find a dopant that can be incorporated without also creating compensating acceptor.

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