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Transparent conducting oxides (TCOs) are ubiquitous in modern consumer electronics. SnO2 is an earth abundant, cheaper alternative to In2O3 as a TCO however, its performance in terms of electrical properties lags behind that of In2O3. Based on the recent discovery of mobility and conductivity enhancements in In2O3 from resonant dopants, we use a combination of state-of-the-art hybrid density functional theory calculations, high resolution photoelectron spectroscopy and semiconductor statistics modelling to understand what the optimal dopant is to maximise performance of SnO2-based TCOs. We demonstrate that Ta is the optimal dopant for high performance SnO2, as it is a resonant dopant which is readily incorporated into SnO2 with the Ta 5d states sitting ~1.4 eV above the conduction band minimum. Experimentally, the electron effective mass of Ta doped SnO2 was shown to be 0.23m0, compared to 0.29m0 seen with conventional Sb doping, explaining its ability to yield higher mobilities and conductivities.

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Resonant Ta Doping for Enhanced Mobility in Transparent Conducting SnO$_2$

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Abstract

Transparent conducting oxides (TCOs) are ubiquitous in modern consumer electronics. SnO$_2$ is an earth abundant, cheaper alternative to In$_2$O$_3$ as a TCO however, its performance
in terms of mobilities and conductivities lags behind that of In$_2$O$_3$. Based on the recent discovery of mobility and conductivity enhancements in In$_2$O$_3$ from resonant dopants, we use a combination of state-of-the-art hybrid density functional theory calculations, high resolution photoelectron spectroscopy and semiconductor statistics modelling to understand what is the optimal dopant to maximise performance of SnO$_2$-based TCOs. We demonstrate that Ta is the optimal dopant for high performance SnO$_2$, as it is a resonant dopant which is readily incorporated into SnO$_2$ with the Ta 5$d$ states sitting ~1.4 eV above the conduction band minimum. Experimentally, the electron effective mass of Ta doped SnO$_2$ was shown to be 0.23$m_0$, compared to 0.29$m_0$ seen with conventional Sb doping, explaining its ability to yield higher mobilities and conductivities.

**Introduction**

Transparent conducting oxides (TCOs) are materials which possess the generally mutually exclusive properties of high electrical conductivity and optical transparency. These properties are achieved through degenerate doping of wide band gap semiconductors ($E_g > 3.1$ eV) giving rise to applications in a variety of crucial modern technologies such as touch screen displays, solar cells low emissivity windows and gas sensors.$^{1-6}$

Arguably the most successful TCO in terms of both optoelectronic properties and commercial success is In$_2$O$_3$ doped with Sn (ITO) which demonstrates resistivities as low as $\sim 8 \times 10^{-5}$ $\Omega$ cm, carrier concentrations exceeding $10^{21}$ cm$^{-3}$ while retaining $>90\%$ visible light transparency.$^{7,8}$ ITO dominates the electronics market, however, due to the scarcity and high cost of indium, there is a pressing need to move towards alternative earth abundant TCOs particularly for applications requiring large surface areas such as photovoltaic devices and low emissivity glass coatings.$^9$

SnO$_2$-based TCOs are often used in such applications due to both their durability as well as the abundance and low cost of Sn. With a suitably wide fundamental band gap of $\sim 3.6$ eV, undoped SnO$_2$ has been reported to have resistivities of $\sim 10^{-2} - 10^{-3}$ $\Omega$ cm$^{10}$ while $n$-type doping
has achieved resistivities of $\sim 10^{-4}$ $\Omega \text{cm}$.$^{4,11}$ Such doping is achieved by the intentional substitution of Sn or O by elements with a higher oxidation state than the element they are replacing ((V) cations for the Sn(IV) site or (VII) anions for the O(VI) site). Traditional wisdom dictates that the best choice of dopant is the element positioned directly to the right of the host element in the periodic table. This represented a logical choice as they should possess both the correct oxidation state and similar ionic radii thus minimising lattice distortion which can lower solubility.$^4$ Thus Sb (on the Sn-site) or F (on the O site) have typically been the dopants of choice.

Both F-doped SnO$_2$ (FTO) and Sb-doped SnO$_2$ (ATO) thin films have displayed resistivities of $\sim 5 \times 10^{-4}$ $\Omega \text{cm}$.$^{4,12}$ and have been successfully deposited with a wide range of techniques including pulsed laser deposition,$^{13,14}$ spray pyrolysis,$^{15,16}$ sol-gel$^{17,18}$ and sputtering.$^{19}$

Recent reports show that FTO is inherently self-limiting as mobilities fail to surpass $\sim 35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for carrier concentrations $> 3 \times 10^{20} \text{ cm}^{-3}$.$^{20,21}$ The mechanism for this self-limitation was recently shown to be due to the formation of negatively charged fluorine interstitials; as the Fermi energy rises (due to doping) to $\sim 0.5$ eV above the conduction band minimum (CBM) it becomes more energetically favourable for fluorine to incorporate interstitially thus acting as an acceptor rather than as a donor, as is the case when incorporated substitutionally.$^{20}$ ATO also undergoes self-compensation, arising due to the multivalency of Sb (Sb(III) and Sb(V)), which have both been observed using both Mössbauer spectroscopy$^{22,23}$ and XPS studies. Recent DFT studies have proposed two ways in which self-compensation may occur in ATO. Firstly substitutional Sb defects can only act as a donor when in the (V) oxidation state and as an acceptor when in the (III) oxidation state.$^{24,25}$ The second limitation, which was originally proposed from an X-ray absorption fine structure (EXAFS) analysis$^{26,27}$ and confirmed through density functional theory calculations, was that the clustering of a substitutional Sb (Sb$_{\text{Sn}}$) adjacent to an oxygen vacancy ($V_O$) leading to the formation of Sb(III) and a trapped electron in the oxygen vacancy, similar to an F-centre.$^{11}$

Recently however, we have proposed and demonstrated a new doping mechanism for In$_2$O$_3$ which yields mobilities and conductivities superior to those reported for ITO. We have demon-
Stratified that Mo-doped In₂O₃ (IMO) outperforms ITO as Mo behaves very differently from Sn in In₂O₃. In ITO, Sn is in the (IV) oxidation state, and the Sn 5s orbitals mix with the In 5s states at the bottom of the conduction band of In₂O₃. As the concentration of Sn is increased, the mixing at the CBM increases, increasing the effective mass of the CBM and lowering the overall mobility of the system. Mo in the (IV) oxidation state on the other hand, possesses localized donor d-orbitals that sit resonant in the conduction band, well separated from the CBM. This and reduced mixing of orbitals due the lack of overlap between the host s states in the CBM and the dopant d states due to their different shapes ensure that minimal hybridisation takes place between the dopant states and the CBM. Increasing the concentration of Mo therefore has no adverse effect on the effective mass of the CBM, allowing higher mobilities and conductivities. Other transition metals which have donor d states and incorporate in the (IV) oxidation state in In₂O₃ are Ti, Zr, Hf and W. Doping In₂O₃ with these have all demonstrated higher mobilities than ITO indicating similar behaviour to Mo.

For SnO₂, the ideal donor dopant should therefore be of a similar ionic radius to either Sn or O, possess donor states that sit high in the conduction band, not hybridise with the host Sn 5s states, while being in the correct oxidation state. Based on the successful dopants in In₂O₃, likely candidates would be transition metals which are stable in a (V) oxidation state. Three such elements exists, V, Nb and Ta. Previous experimental studies have shown V to not be a shallow donor in SnO₂ with V 3d states sitting 1.1 eV above the valence band maximum (VBM). As such, V can be ruled out as a dopant. Nb doping of SnO₂ has demonstrated moderate results experimentally, with high mobilities for SnO₂ but suffering from low carrier concentrations, in most cases failing to reach 1×10²⁰ cm⁻³. Therefore, Nb doping warrants further investigation here from a theoretical perspective. The last of the three (V) oxidation state candidate dopants, Ta, has shown significant promise experimentally. Thin films of Ta-doped SnO₂ (TaTO) have displayed resistivities as low as 1.8×10⁻⁴ Ω cm and have been fabricated by a wide array of deposition methods. TaTO also displays exceedingly high mobilities of up to 83 cm² V⁻¹ s⁻¹ when deposited by pulsed laser deposition in particular and up
to 49 cm² V⁻¹ s⁻¹ when deposited by sputtering⁴⁶ (at carrier concentrations of 2.7×10²⁰ cm⁻³ and 2.2×10²⁰ cm⁻³ respectively). This surpasses the upper mobility limits displayed by both ATO and FTO. Indeed, in cases where TaTO does not surpass the upper reported mobilities, comparative studies show that TaTO deposited by the same method as ATO displayed higher mobilities⁴⁴ for the same carrier concentrations. Crucially, the origin of this improvement in performance of TaTO films over other doped SnO₂ alternatives has never been elucidated.

In this study, we use hybrid density functional theory to examine the suitability of Nb and Ta as an alternative dopant for SnO₂, and compare it to conventional Sb and F dopants. A consistent picture emerges of Ta as the ideal dopant for SnO₂, possessing resonant donor states high above the CBM and minimal hybridisation with CBM states. We probe the electronic structure differences between Ta and Sb dopants using semiconductor statistics modelling and hard X-ray photoelectron spectroscopy (HAXPES) of aerosol assisted chemical vapor deposition (AACVD) grown TaTO and ATO thin films. Crucially, our experimental characterisation supports our computational analysis, indicating that Ta is the optimum dopant for high performance SnO₂.

**Methods**

**Computational Methodology**

*Ab-initio* density functional theory (DFT) calculations were carried out on SnO₂ using a plane-wave basis within the periodic code, VASP.⁴⁷⁻⁵⁰ The projector-augmented wave method (PAW)⁵¹,⁵² was used to describe the interaction between the core electrons (Sn[Kr], O[He] and Ta[Xe]) and the valence electrons. The hybrid functional used was PBE0 developed by Adamo and Barone⁵³,⁵⁴ which partially addresses the self-interaction error present in local functionals thus allowing for an better description of the band gap and electronic properties of SnO₂. PBE0 incorporates 25% of exact Fock exchange to the PBE (Perdew-Burke-Ernzerhoff)⁵⁵ formalism. For Sn-based TCOs in particular, PBE0 has been shown to yield electronic structure in excellent agreement with experiment.¹¹,²⁰,⁵⁶–⁶⁵
A full description of all calculations performed is provided in the supplementary information (SI Section 1) and includes the calculation of the formation energies of each defect and its charge state through the methods described by Neugebauer and Van de Walle. The relative dopant concentrations used in the cells corresponds to ~4% for Ta and Sb and ~2% for F respectively. To account for the finite size effects of the defect supercells, both an image-charge correction and band filling correction were used. The image-charge correction used herein was formulated by Lany and Zunger and adapted for non-cubic systems by Hine and Murphy. This correction accounts for the interaction of a charged defect with its periodic images. The latter correction remedies the unphysical band filling present in finite-sized supercells in order to regain the dilute limit and is implemented in the scheme by Lany and Zunger. Simulation of the experimental conditions under which the samples were deposited (800 K, 1 atm) was performed using formalism developed by Reuter and Scheffler (SI equation 6) which has been used to successfully simulate F-doped SnO$_2$ films deposited by atmospheric pressure chemical vapour deposition (APCVD) in our previous work. Due to the folded nature of the energy bands present in large supercells, the band unfolding code ‘BandUP’ by Medeiros et al. was utilised to obtain a primitive cell representation of the band structure of the doped supercells.

**Thin Film Fabrication**

Thin films of SnO$_2$:Ta and SnO$_2$:Sb were deposited by aerosol assisted chemical vapour deposition (AACVD). All precursors were purchased from Sigma-Aldrich and used as received. AACVD depositions were carried out on a custom built cold-wall reactor where the substrate (~50 nm SiO$_2$ barrier-coated float glass) was positioned on a graphite block containing a Watmann cartridge heater regulated by a Pt-Rh cartridge heater. A stainless steel top plate was positioned 0.8 cm above the substrate to promote laminar flow. The tantalum doped SnO$_2$ films were grown using a dual pot AACVD process using butyltin trichloride (0.3 mL, 1.77 mmol) dissolved in dry methanol (10 mL, 394 mmol) and tantalum (V) ethoxide (5, 10, 15, 20 mol.%) dissolved in dry toluene (10 mL, 124.7 mmol). The two solutions were atomized using a John-
son Matthey Liquifog® piezoelectric ultrasonic humidifier with the tin precursor flow rate kept at 0.6 L min\(^{-1}\) using air (BOC, 99.99\%) and the tantalum precursor flow rate was kept at 0.6 L min\(^{-1}\) using nitrogen (BOC, 99.99\%). The two flows were then mixed at a Y junction and delivered to the CVD reactor. The glass substrate was maintained at 500 °C. The antimony doped SnO\(_2\) films were grown similar to our previously reported method\(^1\) on glass substrates at 450 °C using a one-pot AACVD process where the butyltin trichloride (0.2 mL, 1.06 mmol) and antimony(III) ethoxide (2, 6, 9, 11, 15 mol.%) were dissolved in methanol (10 mL, 394 mmol). The carrier gas was air and the flow rate was 1 L min\(^{-1}\). At the end of the depositions for both systems, the reactor was turned off and cooled under a flow of nitrogen until 100 °C after which point the samples were removed. The coated substrates were handled and stored in air.

**Thin Film Characterisation**

Hall effect measurements were carried out in the van der Pauw geometry to determine the sheet resistance, free carrier concentration and mobility. A square array of Ohmic contacts was arranged on 1 cm\(^2\) samples that were subjected to an input current of 1 mA and a calibrated magnetic field of 0.58 T.

Transmission spectra were obtained using a Shimadzu UV-Vis-IR 3700 spectrophotometer with an integrating sphere detector and were measured over a range of \(\lambda = 250 - 2500\) nm to cover the visible and near infra-red regions.

IR reflectance measurements were performed using a Bruker Vertex 70v Fourier-transform infrared (FTIR) spectrometer. A CaF\(_2\) beam splitter and DLaTGS detector were used and spectra were recorded over an energy range of 0.25 - 1.25 eV so the plasma resonance cut off could be observed for all samples.

Hard X-ray photon emission spectroscopy (HAXPES) was performed at the I09 beamline at the Diamond Light Source (Didcot, UK). A photon energy of 5.95 keV was selected using a Si(111) double-crystal monochromator and a Si(004) channel-cut crystal as a post monochromator. The beam size at the sample was 40×20 \(\mu\)m\(^2\) with a grazing incident angle of 87.5° with respect
to the surface normal. Photoelectrons were detected using a EW4000 photoelectron analyser from VG Scienta (Uppsala, Sweden). Calibration of the binding energy scale was performed using the Fermi edge and the 4f core level lines of a gold reference sample. The gold Fermi edge was fitted to obtain an experimental resolution of \( \sim 200 \text{ meV} \).

**Results and Discussion**

**Defect Thermodynamics and Band Structure**

Defect thermodynamics and band structures have been calculated for Nb and Ta doped SnO\(_2\). As described in detail in the SI, Nb is found to be neither a shallow nor a resonant donor. Therefore the remainder of this work focuses on Ta doping.

To understand why Ta has the potential to surpass Sb and F as a dopant in SnO\(_2\), the thermodynamic transition levels of the Ta-related species were calculated and are presented in Figure 1, showing the formation energy of a defect and its respective charge states as a function of Fermi energy. Also shown are the Sb and F defect species together with the dominant intrinsic defect species (\( V_{\text{Sn}} \) and \( V_{\text{O}} \)) as reported previously in refs. 11 and 20. The transition levels shown are presented under \( 800 \text{ K/1 atm} \) conditions in order to represent the growth conditions of the AACVD grown films in this work.

The substitutional impurity Ta\(_{\text{Sn}}\) is found to be the dominant tantalum species in SnO\(_2\) and acts as a resonant one-electron donor transitioning from the 1+ charge state to the 1- charge state at around \( \sim 0.5 \text{ eV} \) above the CBM. These results are in line with the high conductivities seen in experiment both here and elsewhere.\(^{35-45}\)

The ability to push the Fermi level high into the conduction band is critical for maximising the charge carrier concentrations and thus conductivities. In Sb-doped SnO\(_2\), despite Sb\(_{\text{Sn}}\) acting as a resonant donor, the 1+ charge state transitions to the neutral charge state at \( \sim 0.15 \text{ eV} \) above the CBM. In F-doped SnO\(_2\), the Fermi level also reaches \( \sim 0.5 \text{ eV} \) above the CBM before self-compensation from fluorine interstitial defects occurs, thus making Ta competitive as a
Figure 1: The calculated formation energies for the TaTO (red), ATO (grey) and FTO (green) related defects as a function of Fermi energy under experimental synthesis conditions (800 K and 1 atm). The VBM is set at 0 eV and the conduction band is depicted by the graded orange area. A full discussion of the Sb and F related defects can be found in Refs 11 and 20 respectively.
replacement. Reaching this Fermi level is also dependent on the solubility of Ta in SnO$_2$. At the CBM it can be seen that although Ta$_{Sn}$ ($\sim 1.27$ eV) possesses a higher formation energy than Sb$_{Sn}$ ($\sim 0.40$ eV) at the CBM it is still lower than F$_O$ ($\sim 1.33$ eV). As this level is reachable in FTO thin films it is highly likely that TaTO thin films will also reach high carrier concentrations. Indeed, it can be expected that under non-equilibrium conditions such as CVD, the solubility will be enhanced due to the inclusion of kinetic effects. As previously stated, both F-doped SnO$_2$ and Sb-doped SnO$_2$ undergo defect compensation mechanisms that can severely limit the electron mobility and thus the conductivity of tin dioxide. From our calculations it is shown that the only limiting factor to Ta as a dopant is the transition to the 1- charge state whereby Ta(V) accepts two electrons to become Ta(III) and thus acts as an acceptor. Additionally, the formation of Ta$_i$ is prohibitively high ($\sim 13.54$ eV in the neutral charge state) under 800 K/1 atm growth conditions and acts as a donor and thus is not expected to form or act as a mechanism for self-compensation.

Similarly, it was found that the clustering of Ta$_{Sn}$ and V$_O$ was found to be highly unfavourable ($\sim 13.54$ eV in the neutral charge state) and prefer to dissociate from each other with associated formation energy being $\sim 0.38$ eV higher for the neutral charge state respectively. Unlike in ATO therefore, it is highly unlikely that these clusters will exist.

The high mobilities reported in TaTO thin films are indicative of the lack of dopant hybridisation at the CBM as seen in Mo-doped In$_2$O$_3$ (IMO) resulting in no increase in effective mass with increased carrier concentration. The effect of Ta on the band structure of SnO$_2$ is shown in Figure 2 which displays the unfolded supercell band structures of substitutional Ta (Ta$_{Sn}$) in the 1+ (ionised) charge state in both the spin-up and spin-down configurations. Also shown is the density of states (DOS) pertaining to the Ta states. Unfolded band structures are given for Sb$_{Sn}$ and F$_O$ for comparison and are found in SI Figure 3 and 4 respectively.

In both spin-up and spin-down configurations, there is no hybridisation of the Ta states with the CBM which is dominated by Sn 5s and O 2s states which gives rise to its highly dispersive character and low effective mass of $\sim 0.26m_e$ typical of n-type metal oxides. In TaTO
Figure 2: The unfolded band structure and DOS for the ionised (1+ charge state) substitutional Ta$_{Sn}$ defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.

It can be seen that the Ta 5d states occur $\sim 1.40$ eV above the CBM in both spin configurations with further Ta 5d “bands” appearing $\sim 2.47$ eV above the CBM. These bands have 70% Ta $d$ character mixed with Sn $s$ and O $s$ states. For TaTO, the CBM has $<1\%$ Ta $d$ character, indicating minimal perturbation of the CBM states by Ta doping. Conversely, in the band structures for Sb$_{Sn}^{1+}$ and F$_{O}^{1+}$ (SI Figures 3 and 4 respectively) there is around 3% Sb and F character at the CBM. This is shown pictorially in Figure 3(a), (b) and (c) by the partial charge densities of each system (TaTO, ATO and FTO respectively) at the CBM. The lack of charge density observed around the Ta$_{Sn}$ site (red) indicates there are no Ta states at the CBM. Meanwhile, charge density can been seen around the Sb$_{Sn}$ (blue) and F$_{O}$ sites indicating that Sb and F contribute states at the CBM. It is clear that for both ATO and FTO there is significant mixing of the dopant...
states with those of the host. It is expected, therefore that no perturbation of the host effective mass will be observed with Ta doping which gives rise to the high mobilities seen.

**Figure 3:** The partial charge densities at the CBM of SnO$_2$ for Ta$_{Sn}$ (a), Sb$_{Sn}$ (b) and F$_O$ (c). The densities highlight the fact that Sb and F both hybridise with the CBM thus providing a detrimental effect to the band curvature with increased doping concentrations and that Ta does not undergo this same effect.

**Experimental results**

To experimentally confirm the resonant behaviour of Ta in SnO$_2$ as predicted by the calculations, Ta and Sb doped SnO$_2$ films were deposited by AACVD. The thin films displayed a wide range of electrical properties as shown in Figure 4 and in the supplementary information in Table 2. For the Sb doped films, the highest mobility is $17.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at a carrier concentration of $3.44 \times 10^{20} \text{ cm}^{-3}$, corresponding to the lowest resistivity of $10.3 \times 10^{-4} \Omega \text{ cm}$. In the Ta doped films, the highest mobility observed was $25.9 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at a carrier concentration of $2.65 \times 10^{20} \text{ cm}^{-3}$, corresponding to a resistivity of $9.1 \times 10^{-4} \Omega \text{ cm}$. Films with higher carrier density of up to $3.70 \times 10^{20} \text{ cm}^{-3}$ and slightly lower mobility gave resistivities down to $7.4 \times 10^{-4} \Omega \text{ cm}$. Literature values for TaTO and ATO are also shown in Figure 4. The literature shows a trend of TaTO achieving higher mobilities than ATO at comparable carrier concentrations, similar to the samples studied in this work. Some exceptions to this are the TaTO samples deposited onto seed a layer to promote preferred orientation and increased crystallinity, which
display significantly higher mobilities than seen else where and highlight the potential of Ta as a dopant.\textsuperscript{35,46}

**Figure 4:** The mobility for samples with a range carrier concentrations deposited by AACVD (This work) and Hall properties of ATO and TaTO samples reported throughout the literature.\textsuperscript{19,44,74–76} Dashed lines display lines of constant resistivity. Triangular points are TaTO films deposited on seed layers as reported in the literature.\textsuperscript{35,46}

Experimentally, the difference in the conduction band dispersion expected due to differences in hybridisation with the Sn 5s states can be observed as changes in band filling as a function of carrier density. This can also be seen as a difference in the electron effective mass as the carrier effective mass and band dispersion are related.

Transmission spectra for examples of TaTO and ATO of comparable carrier concentrations, $3.66 \times 10^{20}$ and $3.44 \times 10^{20}$ cm$^{-3}$ respectively, are shown in Figure 5 (a). The transmission at high energies is comparable for the two samples. However at lower energies TaTO displays superior transmission. For photovoltaic application, depending on the absorber used, transparency in the near infra-red at energies as low as 1.1 eV can be important. Currently, one of
the main applications of FTO is as a transparent electrode in thin film solar cells, so it is likely that commercially TaTO would be used in similar applications so the increased transmission in the near-IR is important. It should be noted that Zr-doped In$_2$O$_3$ thin films with improved IR transparency have been reported to yield an improvement in power conversion efficiency of perovksite solar cells, due to the lack of parasitic losses in the IR region.$^{77}$

The reflectivity spectra in the near IR range for the same samples is shown in 5(b). Reflectivity in this range is caused by scattering of light by free carriers and the onset of reflection is determined by the plasma frequency, $\omega_p$. The energy at which this onset occurs is described by

$$\omega_p = \sqrt{\frac{ne^2}{m^*\varepsilon_{\infty}\varepsilon_0}}$$  \hspace{1cm} (1)

For these samples of similar carrier concentration, the ATO sample has a reflection onset at a lower energy than the TaTO sample. Based on equation 1 this must be due to variation in the carrier effective mass. As $\omega_p$ is proportional to the inverse of the square route of $m^*$ a higher plasma frequency is expected for a lower effective mass. This is indicative that carriers in ATO have a higher effective mass than those in TaTO.

Differences in band filling can be observed as changes in the relationship between the Fermi level and carrier concentration in the film. It was not possible to optically measure the gap for the samples in this study as the absorption edge of the glass substrate is at a lower energy than that of the doped SnO$_2$ films. However, the Fermi level to valence band maximum separation, $\Phi = E_F - E_V$, can be observed in the HAXPES spectra as emission from the conduction band up to the Fermi level can be observed, as shown in Figures 6(a) and 6(b). The value obtained will be close to the optical band gap, $E_{\text{opt}}$, but will vary from it slightly as valence band dispersion does not contribute to $\Phi$, as illustrated in 6(d). A full description of how the $\Phi$ values were obtained is given in the supplementary information. HAXPES is used rather than conventional XPS due to the increased relative cross-section of s states compared with p and d states at higher photon energies and the increased intensity obtained from synchotron radi-
Figure 5: (a) The wide range transmission spectra for TaTO and ATO samples with carrier concentrations of $3.66 \times 10^{20}$ and $3.44 \times 10^{20}$ cm$^{-3}$ respectively. (b) The IR reflectivity spectra for the same two samples showing different onsets for plasma edge. The expressions for plasma frequency is shown, showing that at constant carrier concentrations the plasma frequency will depend on the inverse of the carrier effective mass.

As the conduction band minimum is primarily of Sn 5s character, the relative intensity of the signal from the conduction band is therefore a lot higher in HAXPES. This enables the $\Phi$ values to be determined more easily and the results are plotted in Figure 6(c).

The carrier concentration, $n$, of the films is related to the Fermi energy, $E_F$ by

$$n = \int_0^{\infty} D(E)f(E)dE$$  \hspace{1cm} (2)

Where $D(E)$ is the energy dependent density of states and $f(E)$ a Fermi function which is dependent on $E_F$. $D(E)$ is dependent on $m^*$, therefore the relationship between carrier concentration and Fermi level is dependent on the carrier effective mass.

The carrier concentrations of the samples are known from Hall effect measurements and are plotted against $\Phi$ in Figure 6(c). A clear difference between the relationships between $E_{opt}$ and $n$ for the two differently doped materials can be seen with larger optical gaps being observed.
for similar carrier concentrations in TaTO compared to ATO.

Figure 6: (a) The fitted VB edges for HAXPES spectra for a range of carrier concentrations in (a) TaTO and (b) ATO respectively. A Fermi edge has been fitted to the conduction band emission in each spectrum and set to 0 eV. The values presented are $\Phi$ for each data set. (c) The optical gaps as calculated from valence band and conduction band HAXPES spectra of TaTO and ATO film with a range of carrier concentrations. Fitted lines are calculated using the non-parabolic alpha approximation. (d) The calculated band dispersion for band edge effective masses 0.23$m_0$ (red) and 0.29$m_0$ (blue) demonstrating the difference in band filling by showing the different Fermi levels (Dashed Lines) for a carrier concentration $3.6 \times 10^{20}$ cm$^{-3}$. The optical gap, $E_{opt}$ and the Fermi level to VBM separation, $\Phi$, are demonstrated for the band edge effective mass of 0.23$m_0$. 

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was calculated as a function of \( n \) using equation 2 for a range of band edge effective masses, \( m^*_{BE} \), while accounting for conduction band non-parabolicity using the alpha approximation.\(^{78}\) The calculated lines that fit the data are shown in Figure 6(c) and the values of \( m^*_{BE} \) for TaTO and ATO were found to be \( 0.23m_0 \) and \( 0.29m_0 \) respectively.

The shape of the conduction band close to the CBM is described by \( E(1 + E/E_g) = \hbar^2k^2/2m^* \). An increase in band edge effective mass is therefore indicative of a more dispersed conduction band. Figure 6(d) shows the calculated band dispersion, using the alpha approximation to account for non-parabolicity, for the effective masses obtained for TaTO and ATO. The Fermi levels shown are calculated for a carrier concentration of \( 3.6 \times 10^{20} \text{ cm}^{-3} \).

The different CB dispersion should result in discernible differences in HAXPES CB emission as previously shown for a comparison of IMO and ITO.\(^{29}\) However, the presence of Sn(II) and Sb(III) lone pairs introduces intense subgap states, the intensity of which merges into the weak CB emission, as shown in Figure 5 in SI. This makes detailed comparisons of the conduction band emission as a function of carrier density and dopant type impossible in this case.

The increase in the band edge effective mass and change in dispersion in ATO compared to TaTO is due to hybridisation of the Sb 5s with the Sn 5s at the conduction band minimum. Notably, the ATO sample with the highest carrier concentration does not fall on the fitted line for \( m^*_{BE} = 0.29m_0 \) in Figure 6(C). This is likely due to higher Sb incorporation causing further hybridisation with the CBM, further increasing the band-edge effective mass.

While these values can explain the increase in mobility observed in these Ta doped AACVD films with respect to Sb doping, the differences in effective mass is not enough to explain the high mobilities observed in previous literature. It is of note that the highest mobility samples reported in the literature have all been grown on seed layers promoting a (200) preferred orientation and increased grain size.\(^{35,46}\) While the mechanism behind these higher mobilities is not fully understood, as at the high carrier concentrations observed grain-boundary scattering is expected to have minimal contribution,\(^{79}\) these samples highlight the potential of TaTO to surpass other SnO\(_2\)-based TCOs. While CVD FTO has benefitted from decades of empirical op
timization, it has reached the peak of its self-compensation-limited performance. Meanwhile CVD of TaTO is in its infancy, but our results and those from other deposition techniques\textsuperscript{35,39,46} indicate that the conductivity of CVD TaTO could exceed that of FTO by a factor of five or six with improved IR transparency.

These observations made from the HAXPES data in combination with the results from DFT calculations show clear benefits of the position of the Ta donor states with respect to the CBM. The Ta \textit{d} states sit resonant in the conduction band meaning that there is minimal mixing with the host states at the CBM. As a result, the shape of the conduction band is maintained and carrier effective mass is not increased as occurs with traditional dopants and higher mobilities can be achieved.

**Conclusion**

Using a combination of hybrid density functional theory calculations, IR reflectivity and hard x-ray photoelectron spectroscopy, we have demonstrated conclusively that Ta is a resonant donor in SnO\textsubscript{2}. These findings, in combination with previous literature on Ta-doped SnO\textsubscript{2} indicate that Ta is a superior dopant to both fluorine and antimony, with the capability to yield higher conductivities, higher mobilities and better IR transparency than either FTO or ATO. These findings suggest that TaTO has the potential to replace FTO as the industrial standard for large surface area applications where a low cost TCO is required.

**Conflicts of Interest**

There are no conflicts to declare
Supporting Information

Supporting information is provided containing the computational methodology, Nb-doped SnO$_2$, Unfolded bandstructures of ATO and FTO and the full method for experimentally determining Fermi Level to VBM separation.

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Resonant Ta Doping for Enhanced Mobility in Transparent Conducting SnO$_2$

Supporting Information

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1 Computational Methodology

Ab-initio calculations were performed using density functional theory (DFT) implemented using the periodic code, VASP.$^{1-4}$ The projector-augmented wave method (PAW)$^{5,6}$ was used to
describe the interaction between the core electrons (Sn[Kr], O[He] and Ta[Xe]) and the valence electrons. The hybrid functional PBE0 developed by Adamo and Barone\textsuperscript{7,8} was used in order to address the \textit{self-interaction error} thus allowing for an accurate description of the band gap and electronic properties of SnO\textsubscript{2}. PBE0 incorporates 25\% of exact Fock exchange to the PBE (Perdew Burke and Ernzerhoff) formalism.\textsuperscript{9} Hybrid functionals have consistently displayed improved geometry and electronic properties of semiconductors,\textsuperscript{10–18} and PBE0 has been shown to describe these properties for tin based TCOs with a high degree of accuracy.\textsuperscript{19–28}

An initial relaxation of the conventional cell of rutile SnO\textsubscript{2} was carried out to a force criterion of 0.01 eV atom\textsuperscript{-1} using a Γ-centred \textit{k}-point grid of \(4 \times 4 \times 6\) and a plane wave energy cutoff of 400 eV for accurate convergence.\textsuperscript{20} The intrinsic defects and extrinsic dopants were simulated using a \(2 \times 2 \times 3\) supercell expansion of the conventional cell containing 72 atoms. Γ-centred \(2 \times 2 \times 2\) \textit{k}-point meshes and 400 eV plane wave energy cutoffs were applied for geometry optimisations. All the defect calculations were spin-polarised and the individual systems were deemed to be converged when the forces on all the atoms were less than 0.01 eV atom\textsuperscript{-1}.

\subsection{Defect Formalism}

The formation energy for a defect in charge state \(q\) can be defined as:

\[
\Delta H_f(D, q) = (E_{D,q} - E^H) + \sum_i n_i (E_i + \mu_i) + q(E_{\text{Fermi}} + e_{\text{VBM}}^H + \Delta E_{\text{pot}}^\text{corr}) + q^2 E_{\text{ICcorr}}^2 + E_{\text{BFcorr}}^2
\]  

(1)

Where \(E^H\) is the total energy of the host supercell, \(E_{D,q}\) is the total energy of the defective supercell in charge state \(q\). \(E_i\) corresponds to an elemental reference energy (Sn\textsubscript{(s)}, O\textsubscript{2(g)} and Ta\textsubscript{(s)}) and has an associated chemical potential denoted by \(\mu_i\). \(n\) refers to the number of electrons added to or taken away from an external reservoir.\textsuperscript{29} In this work the Fermi level ranges from the valence band maximum (VBM) at 0 eV (where \(e_{\text{VBM}}^H\) denotes the eigenvalue of the VBM in the host material) to \(\sim 3.4\) eV above the conduction band minimum (CBM) which occurs at
3.6 eV. The potential of the defect supercell bar the immediate vicinity of the defect is averaged and aligned to the host supercell and is described by $\Delta E_{\text{Pot}}$.\textsuperscript{30}

To account for the finite size effects of the defect supercells, two post-processing corrections are applied, $E_{\text{corr}}^{IC}$ and $E_{\text{corr}}^{BF}$. The first correction term corresponds to the \textit{image-charge correction} which minimises the long ranged nature of the Coulomb interaction\textsuperscript{31,32} of the charged defect and its periodic images. The implementation used herein uses a formalism based upon the Lany and Zunger correction\textsuperscript{30} with a ‘non-cubic’ adaptation as implemented by Hine and Murphy.\textsuperscript{32,33} Lastly a \textit{band-filling} correction is applied to shallow and resonant defects to account for the high carrier concentrations present in supercell calculations so as to regain the ‘dilute limit’.\textsuperscript{30,34}

### 1.2 Thermodynamic Limits

The chemical potentials ($\mu_i$) can reflect the equilibrium growth conditions which can be varied to simulate the experimental partial pressures. This is all determined relative to the calculated enthalpy of the host, SnO$_2$:

$$\mu_{\text{Sn}} + 2\mu_{\text{O}} = \Delta H_f^{\text{SnO}_2} = -5.27 \text{ eV}$$

(2)

The experimentally determined standard enthalpy of formation for SnO$_2$ is -5.98 eV\textsuperscript{35} in agreement with our calculated value at 0 K. This formation enthalpy allows for the calculation of a range of growth conditions bounded by two growth conditions which are:

\textit{Sn-rich/O-poor} bound limited by the formation of metallic Sn (Sn$_{(s)}$):

$$\Delta \mu_{\text{Sn}} = 0; \Delta \mu_{\text{O}} = -2.64 \text{ eV}$$

(3)

and an \textit{Sn-poor/O-rich} bound limited by the formation of oxygen gas, O$_2$\textsuperscript{(g)}:

$$\Delta \mu_{\text{O}} = 0; \Delta \mu_{\text{Sn}} = -5.27 \text{ eV}$$

(4)
The solubilities of the dopant related species are restrained by the formation of secondary phase Ta₂O₅ for μ₉. μ₉ is limited by the formation of Ta₂O₅ giving rise to values of -3.64 eV and -10.23 eV under Sn-rich/O-poor and Sn-poor/O-rich conditions respectively.

The ionisation levels or thermodynamic transition levels are presented in Figure 1. For a given defect the transition from charge state q to q′ can be calculated at a specific Fermi-level position by:

$$\epsilon_D^{q\rightarrow q'} = \frac{\Delta H_f(D, q) - \Delta H_f(D, q')}{q' - q}$$  \hspace{1cm} (5)

These transition levels can be observed using techniques such as deep level transient spectroscopy (DLTS) as the final charge state can relax to its equilibrium configuration after the transition.

1.3 Dependence on Oxygen Partial Pressure and Temperature

In order to simulate the experimental conditions under which the aerosol-assisted chemical vapour deposition (AACVD) thin films were carried out at, the dependance of μₒ on the oxygen partial pressures and temperatures can be determined using the equation:  \hspace{1cm} (6)

$$\mu_o(T, p^0) = \frac{1}{2} [H(T, p^0, O_2) - H(0K, p^0, O_2)] - \frac{1}{2} T[S(T, p^0, O_2) - S(0K, p^0, O_2)]$$

Where T, H and S are temperature, enthalpy and entropy respectively and p^0 = 1 atm (with reference to a zero state ; μₒ(0K,p^0)=1/2ε_{O_2}^{total} = 0). The temperatures used for the AACVD deposition in this study is ~800 K meaning that μₒ can be determined from thermochemical tables giving:

$$\mu_o(T, p^0) = -0.85 \text{ eV}$$  \hspace{1cm} (7)

Thus μ₉ and μ₉ incur values of -3.57 eV and -8.11 eV respectively.

This methodology has been used successfully in F-doped SnO₂ to determine the experi-
mental conditions of thin films created using atmospheric pressure chemical vapour deposition (APCVD) at thermal equilibrium.\textsuperscript{19}

1.4 Band-Unfolding

Due to the shrinking of the Brillouin zone, supercell calculations result in folded band structures. In order to regain a representation of the \textit{primitive} or \textit{conventional} cell, the band unfolding code, BandUp was used. Band unfolding is a methodology described by Popescu and Zunger\textsuperscript{40} and is implemented in a python package by Medeiros and Björk.\textsuperscript{41,42}

2 Transition Levels at 800K,1atm

The enthalpies of formation (\(\Delta H_f\)) under 800\textit{K},1\textit{atm} growth conditions for the TaTO, ATO, FTO and NbTO related defects are given in Table 1 and their respective charge states at \(E_F = 0\) eV. The associated transition levels of that defect are also given relative to the VBM (0 eV).
### Table 1: The formation energies of each defect and charge state under $800K,1atm$ conditions at $E_F = 0 \text{ eV}$ together with the transition levels (relative to the VBM) as shown in the thermodynamic transition levels in Figures 1 (main text) and SI 1.

| Charge State | $\Delta H_f$ $800K,1atm$ (eV) | Transition levels relative to VBM (eV) |
|--------------|-------------------------------|--------------------------------------|
| $V_{Sn}$     |                               |                                      |
| -4           | 19.01                         | (-4/-3) 2.81                         |
| -3           | 16.20                         | (-3/-2) 2.45                         |
| -2           | 13.75                         | (-2/-1) 1.93                         |
| -1           | 11.82                         | (-1/0) 1.75                          |
| 0            | 10.07                         |                                      |
| $V_{O}$      |                               |                                      |
| 0            | 3.68                          | (+2/0) 2.84                          |
| +1           | 0.67                          |                                      |
| +2           | -2.00                         |                                      |
| $Ta_{Sn}$    |                               |                                      |
| -1           | 5.83                          | (-1/+1) 4.10                         |
| 0            | 1.78                          |                                      |
| +1           | -2.37                         |                                      |
| $Sb_{Sn}$    |                               |                                      |
| -1           | 4.61                          | (-1/0) 4.06                          |
| 0            | 0.55                          | (0/+1) 3.80                          |
| +1           | -3.25                         |                                      |
| $F_{O}$      |                               |                                      |
| -1           | 6.67                          | (-1/0) 4.58                          |
| 0            | 2.09                          | (0/+1) 4.36                          |
| +1           | -2.27                         |                                      |
| ($Nb_{Sn}$)  |                               |                                      |
| -1           | 5.32                          | (-1/0) 4.05                          |
| 0            | 1.26                          | (0/+1) 3.45                          |
| +1           | -2.19                         |                                      |
|                  | Charge State | ΔH_f \(800K,1atm\) (eV) | Transition levels relative to VBM (eV) |
|------------------|--------------|--------------------------|----------------------------------------|
| \(Ta_i\)        | 0            | 13.54                    | (+1/0) 4.10                            |
|                  | +1           | 9.43                     | (+3/+1) 3.79                           |
|                  | +2           | 5.74                     | (+4/+3) 2.77                           |
|                  | +3           | 1.85                     | (+5/+4) 2.63                           |
|                  | +4           | -0.91                    |                                        |
|                  | +5           | -3.55                    |                                        |
| \(Sb_i\)        | 0            | 11.94                    | (+1/0) 4.23                            |
|                  | +1           | 7.70                     | (+2/+1) 3.61                           |
|                  | +2           | 4.09                     | (+3/+2) 3.33                           |
|                  | +3           | 0.75                     | (+4/+3) 2.89                           |
|                  | +4           | -2.13                    | (+5/+4) 2.56                           |
|                  | +5           | -4.69                    |                                        |
| \(F_i\)         | -1           | 5.91                     | (-1/0) 2.02                            |
|                  | 0            | 3.88                     | (0/+1) 1.29                            |
|                  | +1           | 2.59                     |                                        |
| \((Nb_i)\)      | 0            | 12.51                    | (+3/0) 4.11                            |
|                  | +1           | 8.62                     | (+4/+3) 1.82                           |
|                  | +2           | 4.30                     | (+5/+4) 1.71                           |
|                  | +3           | 0.17                     |                                        |
|                  | +4           | -1.66                    |                                        |
|                  | +5           | -3.36                    |                                        |
| \([Ta_{sn}+V_{O}]\) | 0            | 5.55                     | (+1/0) 4.28                            |
|                  | +1           | 1.27                     | (+2/+1) 2.64                           |
|                  | +2           | -1.37                    | (+3/+2) 2.59                           |
|                  | +3           | -3.95                    |                                        |
| \([Sb_{sn}+V_{O}]\) | 0            | 3.95                     | (+1/0) 4.08                            |
|                  | +1           | -0.13                    | (+2/+1) 2.01                           |
|                  | +2           | -2.15                    | (+3/+2) 1.85                           |
|                  | +3           | -4.00                    |                                        |
| \([F-F]_0\)     | -1           | 6.31                     | (-1/0) 3.90                            |
|                  | 0            | 2.41                     | (0/1+) 0.39                            |
|                  | +1           | 2.02                     |                                        |
| \([Nb_{sn}+V_{O}]\) | 0            | 4.94                     | (+1/0) 3.49                            |
|                  | +1           | 1.46                     | (+2/+1) 2.63                           |
|                  | +2           | -1.18                    | (+3/+2) 2.59                           |
|                  | +3           | -3.77                    |                                        |
3 On Nb-doped SnO$_2$

The transition level diagram under 800K,1atm is shown in Figure 1 for the Nb-doped SnO$_2$ (NbTO) related defect species as well as the dominant intrinsic defects, V$_{Sn}$ and V$_{O}$.

Despite possessing a low formation energy (1.26 eV for the neutral charge state), Nb$_{Sn}$ acts as a deep donor with a +1/0 transition level occurring around -0.20 eV below the CBM trapping the Fermi level at this point. It is highly unlikely that Nb will be a source of conductivity in SnO$_2$ in accordance with the low conductivities seen in experiment (~ $10^{-2} - 10^{-3}$ Ω cm) and low carrier concentrations (~ $10^{19}$ cm$^{-3}$) despite the array of different deposition techniques used.$^{43-55}$

Figure 2 shows the unfolded band structures and DOS for the neutral charge state of Nb$_{Sn}$ decomposed into both spin-up and spin-down configurations. Unlike in Figures 2 (main text) and Figure 3 and 4 where the defects are shown in their ionised form (i.e. +1 charge state), here as the +1/0 transition level happens in the band gap Nb$_{Sn}$ remains in the neutral charge state. It can clearly shown that in the spin-up configuration, there is a filled localised gap state attributed to Nb 4d (~ 80%) around 2.5 eV above the VBM. This means that Nb in fact incorporated as Nb$^{4+}$ in SnO$_2$ and not as Nb$^{5+}$ as predicted further solidifying the fact that Nb is highly unlikely to contribute to the conductivity in SnO$_2$. As with Ta$_{Sn}$, further Nb 4d bands are shown ~ 2.4 eV above the CBM in both spin-up and spin-down configurations.

Few DFT studies on Nb doped SnO$_2$ have been carried out, agreement with a study by Behtash et al. who, using the HSE06$^{56,57}$ functional see filled Nb 4d states in the band gap of SnO$_2$ concluding the incorporation of Nb$^{4+}$ into the SnO$_2$ lattice.$^{47}$ A recent review of n-type defects in SnO$_2$ using the PBE0 functional similar to this work, show that Nb is a resonant defect with the 1+/0 transition level around 0.5 eV above the CBM suggesting that thin films of SnO$_2$:Nb will provide high conductivities with larger doping concentrations.$^{28}$ This study however relaxed with PBE$^9$ then shifted the lattice parameters using PBE0 thus not fully relaxing the defect supercells likely giving the different results.

As in TaTO, interstitial Nb (Nb$_i$) is a high formation energy defect with the neutral charge
state possessing a formation energy of 12.51 eV under 800K, 1 atm. Nb$_i$ undergoes two transitions in the band gap: +5/+4 (1.89 eV below the CBM) and +4/+3 (1.78 eV below the CBM) and a further transition, +3/0 at 0.51 eV above the CBM. Despite Nb$_i$ being a shallow defect, the formation is prohibitively high and if forms, compensation from tin vacancies (V$_{Sn}$) will occur around 0.93 eV below the CBM.

From our calculations we find that [Nb$_{Sn}$+V$_O$] prefers to dissociated from each other with the associated formation energies being ~0.39 eV higher for [Nb$_{Sn}$+V$_O$] similar to TaTO.

![Figure 1: The calculated formation energies for the Nb-dopant related defects as a function of Fermi energy under experimental synthesis conditions (800 K and 1 atm). The VBM is set at 0 eV and the conduction band is depicted by the graded orange area.](image-url)
Figure 2: The unfolded band structure and DOS for the neutral charge state of substitutional Nb$_{\text{Sn}}$ defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.

4 Unfolded bandstructures of Sb$_{\text{Sn}}$ and F$_{\text{O}}$

Figures s3 and s4 show the unfolded band structures of Sb doped and F doped SnO$_2$ respectively. Discussion of these figures is included in the main manuscript.
**Figure 3:** The unfolded band structure and DOS for the neutral charge state of substitutional Sb\textsubscript{Sn} defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.
**Figure 4:** The unfolded band structure and DOS for the neutral charge state of substitutional \( \text{F}_0 \) defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.
5 Thin Film Properties

The properties of the TaTO and ATO thin films studied in this work are given in table S2. The samples are labeled by the percentage of Ta or Sb in the precursor solution.

Table 2: Electrical properties of the ‘undoped’, Ta doped and Sb doped SnO$_2$ films used in this work as determined by room temperature Hall effect measurements. Percentages given are the Ta or Sb concentration in the precursor solution.

| Sample            | Sheet resistance ($\Omega/\square$) | $\rho$ ($\Omega \cdot \text{cm}^{-1}$) | $\mu$ ($\text{Vcm}^{-1}\text{s}^{-1}$) | $n$ ($\text{cm}^{-3}$) |
|-------------------|-------------------------------------|----------------------------------------|----------------------------------------|------------------------|
| ‘undoped’ SnO$_2$ | 35                                  | 2.97×10$^{-3}$                         | 17.2                                   | 1.21×10$^{20}$         |
| Ta:SnO$_2$ (5%)   | 14                                  | 1.09×10$^{-3}$                         | 21.3                                   | 2.68×10$^{20}$         |
| Ta:SnO$_2$ (10%)  | 8                                   | 7.42×10$^{-4}$                         | 22.5                                   | 3.66×10$^{20}$         |
| Ta:SnO$_2$ (15%)  | 8                                   | 9.08×10$^{-4}$                         | 25.9                                   | 2.65×10$^{20}$         |
| Ta:SnO$_2$ (20%)  | 11                                  | 8.65×10$^{-4}$                         | 19.7                                   | 3.73×10$^{20}$         |
| Ta:SnO$_2$ (40%)  | 13                                  | 1.29×10$^{-3}$                         | 15.7                                   | 3.10×10$^{20}$         |
| Sb:SnO$_2$ (2%)   | 11                                  | 1.03×10$^{-3}$                         | 17.7                                   | 3.44×10$^{20}$         |
| Sb:SnO$_2$ (6%)   | 23                                  | 1.40×10$^{-3}$                         | 11.3                                   | 3.94×10$^{20}$         |
| Sb:SnO$_2$ (9%)   | 33.5                                | 1.49×10$^{-3}$                         | 13.0                                   | 2.38×10$^{20}$         |
| Sb:SnO$_2$ (11%)  | 128                                 | 7.72×10$^{-3}$                         | 5.0                                    | 1.63×10$^{20}$         |
| Sb:SnO$_2$ (15%)  | 23                                  | 1.49×10$^{-3}$                         | 6.7                                    | 6.26×10$^{20}$         |

6 Sn(II) and Sb(III) midgap states

As mentioned in the main text comparison of the shape of the conduction band emission from TaTO and ATO was not possible due to mid-gap states due to Sn(II) and Sb(III) at the surface. Figure 5 (a) shows the HAXPES spectra for a Ta doped sample for the region cover the VBM and conduction band. The mid-gap state can be clearly seen and is regularly attributed the Sn(II) forming due to surface termination. As Sn is a component of SnO$_2$ this state can be seen in all samples regardless of dopant. The Sn(II) states were fitted and removed when analysing the data so the Valence band onset could be more clearly seen.

Figure 5 (b) shows the HAXPES spectra for an Sb doped and a Ta doped sample for the region encompassing the conduction band emission. Extra states can be seen at a slightly
higher binding energy than the conduction band emission in the Sb doped sample but not the Ta doped sample. The origin of these states are not as clear as the origin of the states attributed to Sn(II) but it is likely they are due to Sb at the surface as they are only present in the ATO samples. The low signal of this feature, along with its close proximity to the conduction band emission makes fitting and subtracting of this feature to compare the shapes untenable.

![Figure 5](image)

**Figure 5:** a) HAXPES spectra for the Ta:SnO$_2$ 15% sample for the region containing the VBM and conduction band emission. The large mid-gap states shown is attributed to Sn(II) b) The normalised HAXPES spectra for the the region containing the conduction band emission for the Ta:SnO$_2$ 15% and Sb:SnO$_2$ 15% samples. A small mid-gap state can be seen just below the CBM in the Sb doped sample but nor the Ta sample. This state is attributed to Sb(III) at the surface.

7 Determining Fermi Level to VBM separation

To demonstrate the difference in the carrier effective mass for Ta doped and Sb doped SnO$_2$ the Fermi level, $E_f$ to valence band maximum, VBM, was obtained from HAXPES spectra for a range of samples. This quantity has been labelled $\Phi$ for convenience when referring to it.

Figure S6 (a) shows the difference between $\Phi$ and the optical band gap, $E_{opt}$. The optical
band gap also measures the separation between the Fermi level and valence band but in a degenerately doped semi-conductor excitations will not occur from the VBM. Therefore $E_{\text{opt}}$ accounts for valence band dispersion while $\Phi$ does not.

Figure S6 (b) shows how $\Phi$ was extracted from the HAXPES spectra. The position of $E_F$ was extracted by fitting a Fermi function to the edge of the conduction band emission. Linear fitting of the VBM gave an intercept of -0.1 eV for all samples when fitted to the DOS with the DOS VBM set to 0 eV. This difference is due to instrumental broadening. The position of the VBM was extracted using a linear fit the increased by 0.1 eV to account for this.

![Diagram](figure6.png)

**Figure 6:** a) Diagram demonstrating the difference between the Fermi level, $E_F$, to VBM, $E_V$, separation, which has been defined as $\Phi$, and the optical band gap, $E_{\text{opt}}$. b) Example of extracting the Fermi level using a Fermi function and valence band maximum using a linear fit from a narrow HAXPES spectra of the region.

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