Resonant Ta Doping for Enhanced Mobility in Transparent Conducting SnO₂ 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^{7,8} was used in order to address the *self-interaction error* thus allowing for an accurate description of the band gap and electronic properties of SnO₂. PBE0 incorporates 25% of exact Fock exchange to the PBE (Perdew Burke and Ernzerhoff) formalism.⁹ Hybrid functionals have consistently displayed improved geometry and electronic properties of semiconductors,^{10–18} and PBE0 has been shown to describe these properties for tin based TCOs with a high degree of accuracy.^{19–28}

An initial relaxation of the conventional cell of rutile SnO_2 was carried out to a force criterion of 0.01 eV atom⁻¹ using a Γ -centred *k*-point grid of 4 × 4 × 6 and a plane wave energy cutoff of 400 eV for accurate convergence.²⁰ The intrinsic defects and extrinsic dopants were simulated using a 2 × 2 × 3 supercell expansion of the conventional cell containing 72 atoms. Γ -centred 2 × 2 × 2 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⁻¹.

1.1 Defect Formalism

The formation energy for a defect in charge state *q* can be defined as:

$$\Delta H_f(D,q) = (E^{D,q} - E^H) + \sum_i n_i (E_i + \mu_i) + q(E_{\text{Fermi}} + \epsilon^H_{VBM} + \Delta E^{\text{pot}}) + q^2 E^{IC}_{\text{corr}} + E^{BF}_{\text{corr}}$$
(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_(s), O_{2(g)} and Ta_(s)) and has an associated chemical potential denoted by μ_i . n refers to the number of electrons

added to or taken away from an external reservoir.²⁹ In this work the Fermi level ranges from the valence band maximum (VBM) at 0 eV (where ϵ_{VBM}^{H} denotes the eigenvalue of the VBM in the host material) to ~ 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 ΔE^{pot} .³⁰

To account for the finite size effects of the defect supercells, two post-processing corrections are applied, E_{corr}^{IC} and E_{corr}^{BF} . The first correction term corresponds to the *image-charge correction* which minimises the long ranged nature of the Coulomb interaction^{31,32} of the charged defect and its periodic images. The implementation used herein uses a formalism based upon the Lany and Zunger correction³⁰ with a 'non-cubic' adaptation as implemented by Hine and Murphy.^{32,33} Lastly a *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'.^{30,34}

1.2 Thermodynamic Limits

The chemical potentials (μ_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, SnO₂:

$$\mu_{\rm Sn} + 2\mu_{\rm O} = \Delta H_f^{\rm SnO_2} = -5.27\,\rm eV$$
⁽²⁾

The experimentally determined standard enthalpy of formation for SnO_2 is -5.98 eV³⁵ 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:

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

$$\Delta\mu_{\rm Sn} = 0; \Delta\mu_{\rm O} = -2.64\,\rm eV \tag{3}$$

and an Sn-poor/O-rich bound limited by the formation of oxygen gas, $\mathrm{O}_{2(g)}$

$$\Delta\mu_{\rm O} = 0; \Delta\mu_{\rm Sn} = -5.27\,\rm eV \tag{4}$$

The solubilities of the dopant related species are restrained by the formation of secondary phase Ta₂O₅ for μ_{Ta} . μ_{Ta} 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:

$$\epsilon_D \frac{q}{q'} = \frac{\Delta H_f(D,q) - \Delta H_f(D,q')}{q' - q} \tag{5}$$

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 μ_0 on the oxygen partial pressures and temperatures can be determined using the equation:³⁶

$$\mu_{O}(T, p^{0}) = \frac{1}{2} [H(T, p^{0}, O_{2}) - H(0K, p^{0}, O_{2})] - \frac{1}{2} T[S(T, p^{0}, O_{2}) - S(0K, p^{0}, O_{2})]$$
(6)

Where *T*, *H* and *S* are temperature, enthalpy and entropy respectively and $p^0 = 1$ atm (with reference to a zero state ; $\mu_0(0K,p^0) = \frac{1}{2}E_{O_2}^{total} = 0$).^{37,38} The temperatures used for the AACVD deposition in this study is ~800 K meaning that μ_0 can be determined from thermochemical

tables³⁹ giving:

$$\mu_0(T, p^0) = -0.85 \,\text{eV} \tag{7}$$

Thus $\mu_{\rm Sn}$ and $\mu_{\rm Ta}$ incur values of -3.57 eV and -8.11 eV respectively.

This methodology has been used successfully in F-doped SnO_2 to determine the experimental conditions of thin films created using atmospheric pressure chemical vapour deposition (APCVD) at thermal equilibrium.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 *primitive* or *conventional* cell, the band unfolding code, *BandUp* was used. Band unfolding is a methodology described by Popescu and Zunger⁴⁰ and is implemented in a python package by Medeiros and Björk.^{41,42}

2 Transition Levels at 800K,1atm

The enthalpies of formation (Δ H_f) under *800K*, *1atm* growth conditions for the TaTO, ATO, FTO and NbTO related defects are given in Table S1 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).

	Charge State	Δ H _f <i>800K,1atm</i> (eV)	Transition levels relative to VBM (eV)	
	-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		
Vo	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		

Table S1: The formation energies of each defect and charge state under *800K*, *1atm* conditions at $E_F = 0$ eV together with the transition levels (relative to the VBM) as shown in the thermodynamic transition levels in Figures 1 (main text) and SI S1.

	Charge State	Δ H _f <i>800K,1atm</i> (eV)	Transition levels relative to VBM (eV)	
	0	13.54	(+1/0)	4.10
	+1	9.43	(+3/+1)	3.79
Τ-	+2	5.74	(+4/+3)	2.77
Ia _i	+3	1.85	(+5/+4)	2.63
	+4	-0.91		
	+5	-3.55		
	0	11.94	(+1/0)	4.23
	+1	7.70	(+2/+1)	3.61
ch	+2	4.09	(+3/+2)	3.33
SD _i	+3	0.75	(+4/+3)	2.89
	+4	-2.13	(+5/+4)	2.56
	+5	-4.69		
	-1	5.91	(-1/0)	2.02
F _i	0	3.88	(0/+1)	1.29
-	+1	2.59		
	0	12.51	(+3/0)	4.11
	+1	8.62	(+4/+3)	1.82
(ML)	+2	4.30	(+5/+4)	1.71
(ND_i)	+3	0.17		
	+4	-1.66		
	+5	-3.36		
	0	5.55	(+1/0)	4.28
	+1	1.27	(+2/+1)	2.64
$[1a_{sn}+v_0]$	+2	-1.37	(+3/+2)	2.59
	+3	-3.95		
	0	3.95	(+1/0)	4.08
	+1	-0.13	(+2/+1)	2.01
$[SU_{Sn}+V_O]$	+2	-2.15	(+3/+2)	1.85
	+3	-4.00		
	-1	6.31	(-1/0)	3.90
[F-F] _O	0	2.41	(0/1+)	0.39
	+1	2.02		
	0	4.94	(+1/0)	3.49
$([Mb + U^{-1}))$	+1	1.46	(+2/+1)	2.63
$([1VD_{Sn}+V_O])$	+2	-1.18	(+3/+2)	2.59
	+3	-3.77		

3 On Nb-doped SnO₂

The transition level diagram under *800K*, *1atm* is shown in Figure S1 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 occuring 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 SnO₂ in accordance with the low conductivities seen in experiment ($\sim 10^{-2} - 10^{-3} \Omega$ cm) and low carrier concentrations ($\sim 10^{19}$ cm⁻³) despite the array of different deposition techniques used.^{43–55}

Figure S2 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 S3 and S4 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 Nb⁴⁺ in SnO₂ and not as Nb⁵⁺ as predicted further solidifying the fact that Nb is highly unlikely to contribute to the conductivity in SnO₂. 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 4*d* states in the band gap of SnO_2 concluding the incorporation of Nb⁴⁺ 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 PBE⁹ 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*, *1atm*. 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 S1: 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.



Figure S2: The unfolded band structure and DOS for the neutral charge state of substitutional Nb_{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_{Sn} and F_O

Figures sS3 and sS4 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 S3: The unfolded band structure and DOS for the neutral charge state of substitutional Sb_{Sn} defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.



Figure S4: The unfolded band structure and DOS for the neutral charge state of substitutional F_0 defect. The band structure is decomposed into both spin up and spin down channels and the VBM is set to 0 eV.

4.1 X-ray Diffraction

Figure S5 shows the XRD patterns for each of the Ta doped, Sb doped and undoped samples as well as the calculated pattern for SnO_2 . All peaks in the diffraction patterns for all the samples can be attributed to SnO_2 as they are present in the calculated pattern. All films are therefore polycrystalline SnO_2 .

A difference in preferred orientation can be seen between the Sb doped and the Ta doped samples. In the Sb doped samples there is significantly less intensity in the peak corresponding to the 200 reflection at 37.9° which is the most intense in several of the Ta doped samples. Sb doped samples also display less intensity in the 301 reflections at 61.7°. The preferential orientation in the Ta doped samples appears similar to that in the undoped sample, tat is (100) texture. The Ta doped samples display a slight increase, compared to the undoped film, in 200 reflection relative intensity with respect to the 101 reflection.

Notably, many of the Ta doped SnO_2 samples with the highest reported mobilities within the literature display (100) preferential orientation.^{58,59} In combination with the XRD patterns shown here there is a clear correlation between the presence of the 200 peak in XRD and improved mobility. Charge transport within SnO_2 has been shown to be anisotropic with the electron effective mass varying depending on the direction.^{60,61} Therefore, it is possible that the differences in orientation contribute to the improvement in carrier mobility seen in the Ta doped samples. However, Sb doped SnO_2 samples in the literature rarely display the (100) texture in XRD and high mobility Ta doped SnO_2 not displaying this preferred orientation has been reported.⁶² Further work looking at samples of Sb and Ta doped SnO_2 with controlled orientation would be required to establish the magnitude of this potential contribution.



Figure S5: XRD for (a) TaTO and (b) ATO under different doping concentrations. Shown in each panel are the XRD for undoped SnO_2 and the calculated XRD of SnO_2 .

5 HAXPES mid-gap 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) at the surface. Figure S6(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.⁶³ As Sn is a component of SnO₂ this state can be seen in all samples regardless of dopant. The Sn(II) states were fitted as shown in figure S6(a) and removed when analysing the data so the Valence band onset could be more clearly seen.

Figure S6 (b) shows the HAXPES spectra for an Sb doped and a Ta doped sample for the region encompassing the conduction band emission. An extra feature 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.. This feature could be caused by a defect present only in the ATO samples or plasmonic losses due to the higher carrier concentrations in the Sb doped samples. It is also possible that it is an artefact from the subtraction of the Sn(II) states withing the bandgap. 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. As a result, comparison of the conduction band emission in the two dopants is not possible.



Figure S6: a) HAXPES spectra for the Ta:SnO₂ 15% sample for the region containing the VBM and conduction band emission. The large mid-gap states shown is attributed to Sn(II). The fit shown is representative of the fits used to subtract the mid-gap states from the data for extracting the VBM to Fermi level separation. b) The normalised HAXPES spectra for the the region containing the conduction band emission for the Ta:SnO₂ 15% (n=2.65×10²⁰ cm⁻³) and Sb:SnO₂ 15% (n=6.26×10²⁰ cm⁻³) samples. A small mid-gap state can be seen just below the CBM in the Sb doped sample but not the Ta sample.

It is also noted that the width of the occupied conduction is estimated according to the measured VBM to Fermi level separation and the semiconductor statistics calculation to be about 0.5 eV (see main manuscript Figure 6(d)). It is however seen in the photoemission data of Figure S6 to be wider than this. This is due to a combination of the instrumental broadening

of the photoemission data and broadening on the high binding energy side associated with a plasmon-loss feature, just as observed for core-level photoemission peaks.

6 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 Φ for convenience when referring to it.

Figure S7 (a) shows the difference between Φ 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_{opt} includes the impact of the valence band dispersion while Φ does not.

Figure S7 (b) shows how Φ was extracted from the HAXPES spectra. The position of $E_{\rm F}$ 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.



Figure S7: a) Diagram demonstrating the difference between the Fermi level, E_F , to VBM, E_V , separation, which has been defined as Φ , and the optical band gap, E_{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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