Do we need 'ionosorbed' oxygen species? (Or, "A surface conductivity model of gas sensitivity in metal oxides based on variable surface oxygen vacancy concentration")

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Abstract

The author provides opinion on direct experimental evidence available to support the 'ionosorption theory' often employed to interpret 'electrophysical' measurements made during a gas sensing experiment. This article then aims to provide an alternative framework of a 'surface conductivity' model based on recent advances in theoretical and experimental investigations in solid state physics, and to use this framework as a guide towards design rules for future improvement of gas sensor performance.

Background

Many papers on chemoresistive gas sensors employ 'ionosorption theory' to post-rationalise 'electrophysical' gas sensing measurements (conductivity, work function). Such electrophysical measurements provide a changing value (on varying gas exposure) that is a composite of factors, which have been termed 'receptor', 'transducer' and 'utility' [1]. The utility factor describes the diffusion of gases to and from the reactive surface of the gas sensing material, which is affected by parameters such as pore size, film thickness and crystallite packing, whilst the transduction function relates how chemical changes at the surface of the gas sensing material are converted to the measured electrophysical property, which is a function of the grain size and crystallite network (grain boundaries) (Figure 1). However it is the receptor function which describes the interaction of the gas sensitive material with the ambient atmosphere and it is here that ionosorption theory is commonly invoked for phenomenological descriptions of gas sensing.
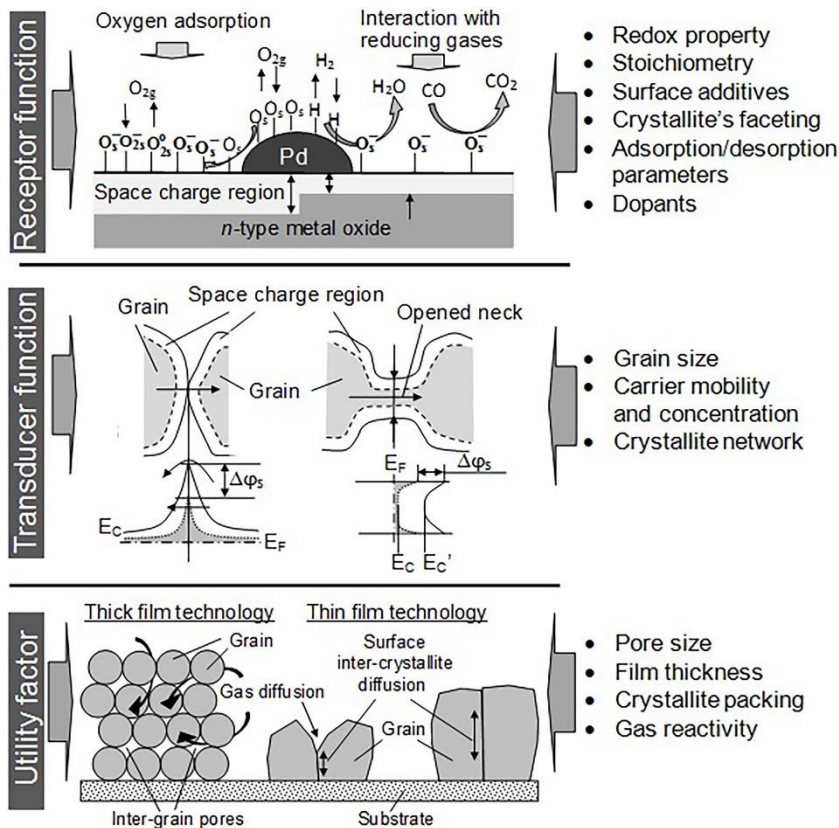
Figure 1. Receptor function, transducer function and utility factor for a chemoresistive gas sensor, and their relation to relevant material properties (reproduced with permission from [1])

Much of the framework for ionosorption theory was developed before the advent of modern surface science analysis techniques and the insight that has been gained from their application (interested readers are directed towards the excellent review by Gurlo which provides a description of the history of development of ionosorption theory [2]). It is therefore perhaps surprising that such ideas have not been generally superseded in the gas sensing community. This matters, because if improved gas sensing materials are to be developed then understanding and accurately describing their mechanism of operation is essential. An important point to highlight is that a 'mechanism' for oxygen adsorption cannot be determined by simple electrophysical measurements, and in the absence of direct (spectroscopic) evidence the following description of ionosorption can therefore only be inferred; an oxygen molecule is initially physisorbed at the surface of the metal oxide (although the 'active site' at the surface for this interaction is rarely described) followed by electron transfer from the metal oxide to form a negatively charged chemisorbed dioxygen molecule, locating negative charge at the surface. [2]. This has been formulated as the following (where the exact nature of the ionosorbed oxygen species, i.e. O_2^-, O^-, O^{2-}, is considered to predominantly be a function of the temperature of the system) [2]:

$$O_2(gas) \rightleftharpoons O_2(ads) \text{ physisorbed} \tag{1}$$

$$O_2(ads) + e^- \rightleftharpoons O_2^-(ads) \text{ ionosorbed} \tag{2}$$

$$O_2^-(ads) + e^- \rightleftharpoons O_2^{2-}(ads) \text{ ionosorbed} \tag{3}$$

$$O_2^{2-}(ads) \rightleftharpoons 2O^-(ads) \text{ ionosorbed} \tag{4}$$

$O^-(ads) + e^- \rightleftharpoons O^{2-}(ads)$ ionosorbed (5)

$O^{2-}(ads) \rightleftharpoons O^{2-}(lattice)$ (6)

In a semiconductor the presence of charged surface states causes carriers in the near-surface region to rearrange in order to screen the surface charge, which is witnessed as an upward (negatively charged surface states) or downward (positively charged surface states) bending of the conduction and valence bands (relative to the Fermi level) [3]. In the framework of ionosorption theory (for *n*-type semiconductors) the negative surface charge resulting from charged oxygen adsorbates is therefore compensated by positive charge resulting from exclusion of electrons in the near surface (electron depletion layer). This is represented as the band edges at the surface bending upwards with respect to the Fermi level, with barrier height qVs (where q is the charge of an electron) as shown in Figure 2 [2].
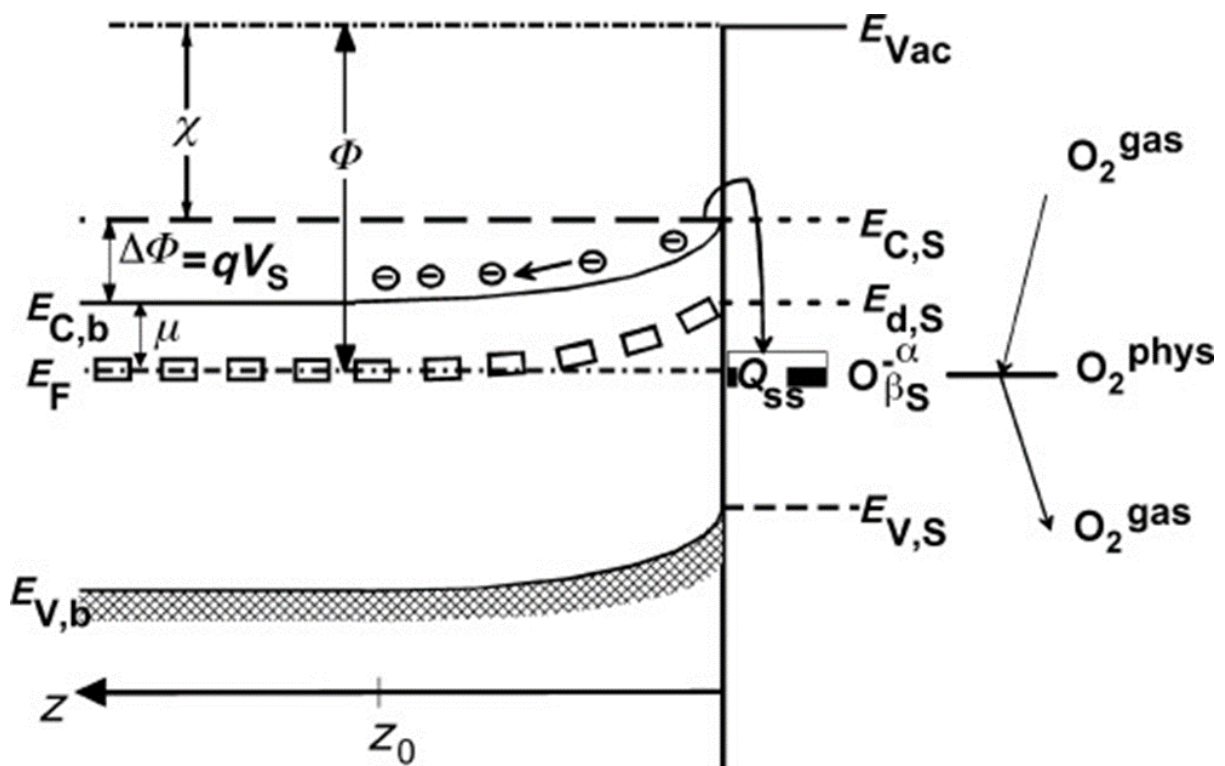

Figure 2. Band bending on an n-type semiconductor after ionosorption of oxygen (reproduced with permission from [2])

The inference of this is that the 'flat band' condition is realised in the absence of oxygen (as oxygen causes bands to bend upwards). It is also worth highlighting that in ionosorption theory the species that are considered neutral with respect to their standard charge state, i.e. physisorbed O_2 and lattice O^{2-}, play no role in conductivity change [2].

When considering direct experimental evidence for the charged surface adsorbed oxygen species inferred in ionosorption theory nothing has significantly changed since Gurlo's brilliantly researched and insightful commentary published in 2006 [2]. Gurlo's conclusions after reviewing available literature were that the only commonly invoked charged oxygen species to have been directly experimentally observed (via electron paramagnetic resonance (EPR) spectroscopy) on SnO_2 under

realistic sensor operating conditions are O_2^- superoxide species (Figure 3), which appear only when O_2 is adsorbed at temperatures below 150°C on freshly vacuum-reduced SnO_2.
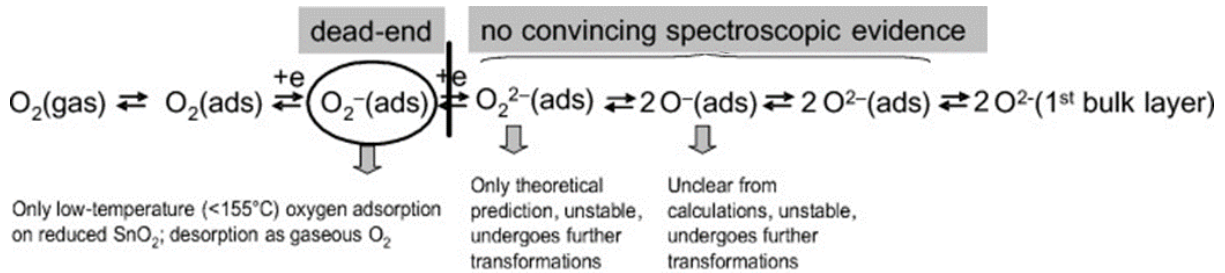

Figure 3. Scheme showing oxygen interaction with metal oxides (adapted with permission from [2])

A very recent review on surface oxygen species on metal oxides reaches similar conclusions [4]; there is no evidence for formation of the atomic oxygen species O^- via the redox processes commonly formulated in ionosorption theory (equations 3-5), and their appearance is associated only with photoexcitation or reductive decomposition of N_2O. So direct spectroscopic evidence for one of the key charged surface adsorbed oxygen species of ionosorption theory, O^-, has never been observed experimentally under normal sensor operating conditions.

There are numerous articles in the gas sensing community which have already addressed the fact that ionosorbed oxygen species are unlikely to be the (main) actors for conductivity change in several common gas sensing materials but these seem in general to have been ignored, or at least their important conclusions missed. For instance the work of Barsan *et al* using diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) on In_2O_3 [5], SnO_2 [6] and WO_3 [7] demonstrates that it is surface lattice oxygen not surface adsorbed charged oxygen species that are responsible for sensor response to CO in these materials, the work of Elger and Hess using *in situ* UV/vis, Raman and FTIR spectroscopies demonstrating the cause of conductivity change in SnO_2-based sensors is varying concentration of surface oxygen vacancies [8] and the work of Koretcenkov *et al* using near-ambient pressure XPS that again demonstrates the importance of surface oxygen vacancies in the gas sensing mechanism of In_2O_3 [9]. In addition there are also now a rather large number of computational modelling studies that describe the interaction of dioxygen with the surface of gas sensing metal oxides, in particular SnO_2, in detail (e.g. [10], [11], with earlier work reviewed in [2]), which explicitly demonstrate the role of surface oxygen vacancies as the active site for oxygen adsorption.

The question that then arises is how changes in work function (band bending) and conductivity measured during a gas sensing measurement are realised as a function of variable surface oxygen vacancy concentrations (but in the absence of charged surface adsorbed oxygen species)?

In fact such mechanisms have been proposed and discussed in the gas sensing literature in the past. Maier and Göpel describe a vacancy-based model, albeit with the caveat that it applies to operation at sufficiently high temperature that vacancies are mobile [12], Zemmel has formulated a model based explicitly and only on oxygen vacancy concentrations [13], and Izydorczyk *et al* have computed the influence of oxygen vacancies on the electronic properties of SnO_2 in the near-surface region [14]. Erickson and Semancik have also described a vacancy-based model on the basis of spectroscopic results obtained from XPS and surface conductivity measurements [15], and more recently Frederick *et al* have formulated a mechanism of gas sensing based explicitly on oxygen

vacancy diffusion ('bulk conduction') and demonstrated its relevance for tungsten oxide-based sensors [16]. However most previous descriptions of defect chemistry in the common gas sensing materials In_2O_3, SnO_2 and ZnO, have been based on the presumption of shallow bulk oxygen defect donor levels providing the (surprisingly high) electronic conductivity observed in these materials [e.g. 7]. More recent theoretical studies have demonstrated that the bulk defect level in In_2O_3 [17] (and SnO_2 and ZnO [18]) is actually deep in the bandgap, i.e. bulk oxygen defects are NOT ionised at normal gas sensor operating temperatures. Consequently in these materials on forming a bulk oxygen vacancy defect the two electrons that would have been donated to the O^{2-} anion remain localised at the vacancy (except at very high temperature) [17, 18] (it is in fact this process that leads to the characteristic yellow colour of reduced SnO_2 via formation of a Farbe-centre (F-centre) [19]). This means that bulk oxygen defects (in In_2O_3, SnO_2 and ZnO) are not expected on their own to significantly contribute to the materials conductivity. Consequently the previous vacancy models mentioned above do not adequately describe the relationship between partial pressure of oxygen, vacancy concentration and material conductivity.

So how can a description of oxygen defects lead to conductivity in such 'deep' oxygen-vacancy materials, and more importantly how might gas sensitivity be developed?

Evidence of surface conductivity

In 2008 McConville *et al* published experimental work on In_2O_3 showing there is downwards bending of the bands at the In_2O_3 surface leading to an increase in surface electron density (electron accumulation layer) as shown in Figure 4 [20]. This observed electron accumulation layer is in direct contrast to the depletion layer assumed in ionosorption theory. Electronic surface states in semiconductors result from the termination of the periodic lattice and can be neutral (for occupied donor-like states, or unoccupied acceptor-like states), positively charged (for unoccupied donor-like states) or negatively charged (for occupied acceptor-like states, like the charged surface adsorbed oxygen species in ionosorption theory); formation of an electron accumulation layer therefore must result from screening of positive charge arising from unoccupied donor-like surface states.
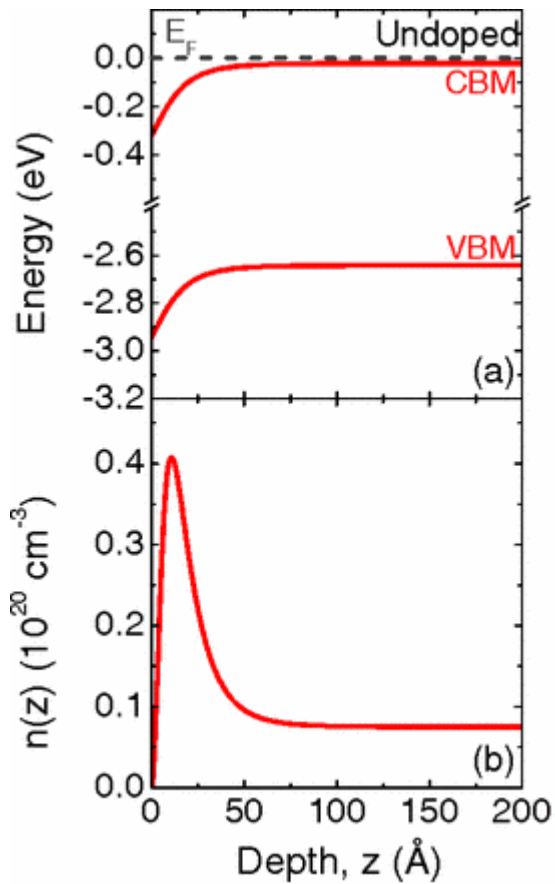
Figure 4. (a) Band bending and (b) carrier concentration profile in the near-surface region of undoped In_2O_3 (reproduced with permission from [20])

So what is the nature of these unoccupied donor-like states? Lany *et al* calculated the energy of electronic states introduced by a surface oxygen vacancy [17] and found the vacancy creates a doubly occupied state that lies considerably higher in energy than the deep lying O-vacancy in the bulk, with an energy nearly degenerate with that of the surface conduction band minimum (Figure 5). Consequently the oxygen vacancy electrons are easily thermally excited (donated) into the surface conduction band at room temperature leaving an unoccupied state. The surface conduction band is localized perpendicular to the surface but has considerable dispersion parallel to it and hence thermal excitation of electrons from these donor-like surface oxygen defects creates a two-dimensional surface conductivity layer in In_2O_3, providing an explicit description for the electron accumulation layer observed by McConville.
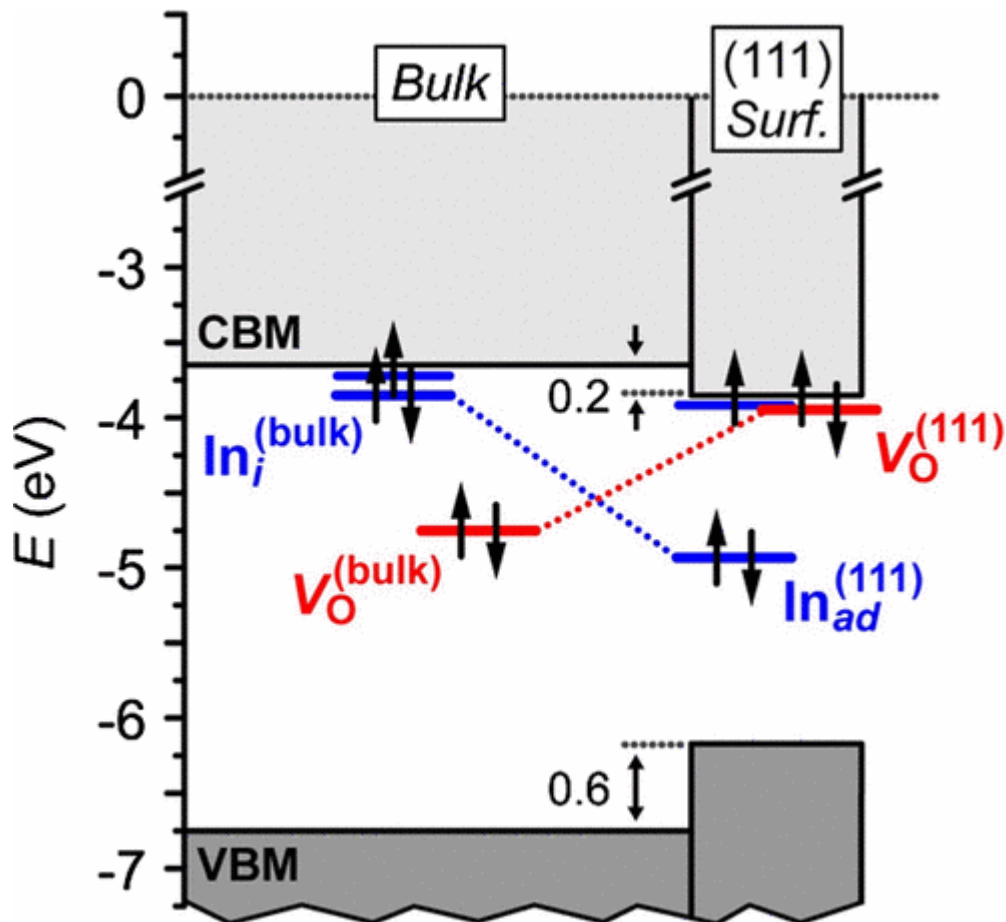
Figure 5. Band diagram for bulk In_2O_3 and the stoichiometric (111) surface, showing the energy positions of the occupied single-particle states created by oxygen vacancies in the bulk (V_O) and at the surface ($V_O^{(111)}$) (reproduced with permission from [17])

Calculation of the bulk and surface carrier densities by Lany *et al* demonstrated that the surface carrier concentration is around three orders of magnitude greater than the bulk carrier concentration, i.e. conductivity in In_2O_3 is expected to be dominated by this surface conductivity layer, and it was further calculated that the surface carrier density is intrinsically dependent on the oxygen partial pressure (during material growth) varying with a power law exponent of -1/6 (as observed by Maier and Göpel for gas sensing measurements on SnO_2 [12], which was related to an oxygen vacancy-based sensing mechanism).

To state this explicitly, surface oxygen defects are expected to significantly contribute to the surprisingly high (given the deep nature of the bulk oxygen defect) conductivity measured in In_2O_3 and, under an assumption of dynamic exchange of ambient oxygen with surface oxygen vacancies, they would control the degree of band bending and hence material conductivity as a function of oxygen partial pressure. In other words this gives rise to a material in which measured conductivity would vary as a function of ambient oxygen partial pressure due to dynamic exchange of ambient dioxygen with surface oxygen vacancies (the surface oxygen vacancy concentration varies).

Experimental verification of this 'surface conductivity' in In_2O_3 was supplied by Egdell *et al* using angle-resolved photoelectron spectroscopy (ARPES) to directly image the surface electron accumulation conductivity layer (two-dimensional electron gas), conclusively identifying the source

of the conductance electrons to be doubly ionised surface oxygen vacancies [21]. They also demonstrated that band-bending decreased (became less bent down, or restating became relatively bent upwards) and the carrier concentration of the surface conductivity layer decreased (i.e. conductivity decreased) as oxygen vacancies were healed (partial pressure of oxygen increases).

These findings were extended by elegant and visually beautiful experimental work by Jovic *et al* in which ARPES was used to directly image the electronic states forming the surface conductivity layer. These were shown to vary in intensity (i.e. surface conductivity varies) as a function of dynamic dosing of oxygen, as shown in Figure 6 [22].
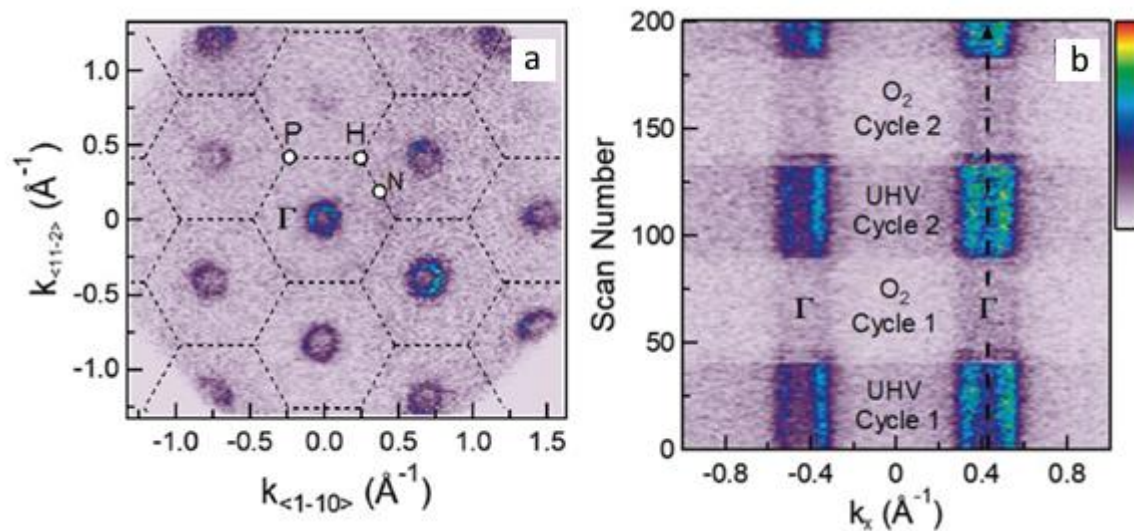

Figure 6. (a) ARPES in-plane Fermi surface map. The surface Brillouin zone boundaries are shown in black. (b) Variation in the two-dimensional electron gas intensity with sequential exposure to UHV and oxygen. A linear colour scale of intensity is shown at the inset (reproduced with permission from [22])

One might then ask whether such findings are limited to In_2O_3? In fact, similar experimental and theoretical work has demonstrated the presence of a surface conductivity layer in SnO_2 [23], which has very recently been directly experimentally imaged using ARPES [24]. In addition such surface conductivity has also been demonstrated in ZnO [25], (anatase) TiO_2 [26], $SrTiO_3$ [27] and $KTaO_3$ [28]. These findings, then, seem universal, at least to many of the commonly employed gas sensing materials (and to several that are not).

Mechanistic description of oxygen/surface interaction in the absence of 'ionosorption'

The next step in considering the ideas of a 'surface conductvity' model is whether a clear mechanism that describes the interaction of dioxygen with the surface, resulting in variation of the surface vacancy concentration, can be developed in the absence of ionosorbed oxygen species?

Considering the most common gas sensing material, SnO_2, and its stable (110) surface termination (Figure 7) we can identify a number of distinctly different surface sites, e.g. bridging oxygen (O_b), in-plane oxygen (O_{ip}), 6-coordinate tin (Sn_{6c}) and 5-coordinate tin (Sn_{5c}) [10].
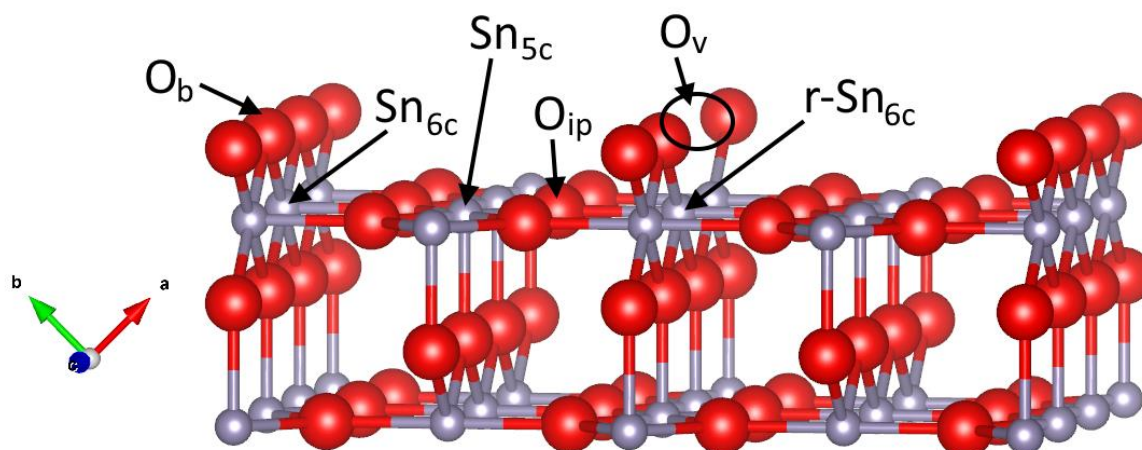
Figure 7. Stable (110) surface of SnO_2 with one vacancy (O_v), labelled to identify different oxygen (O_b, O_{ip}) and tin sites (Sn_{5c}, Sn_{6c}, r-Sn_{6c}); the generation of a vacancy by removal of a bridging oxygen forms a second distinct 5-coordinate tin site by reduction of the coordination sphere of two Sn_{6c} (r-Sn_{6c}).

No significant interaction between gaseous O_2 and a perfect (non-defective) (110) SnO_2 surface is found to occur in the majority of computational studies [29], i.e. Sn_{5c} is not an active site for O_2 adsorption (although it should be noted that the van der Waals interactions associated with physisorption are typically neglected in many such computational studies). It is also worth noting that even under oxygen concentrations consistent with those found in ambient atmosphere a fully oxidised surface is not expected [18] and therefore if we consider adsorption on a partially reduced (defective) SnO_{2-x} surface, computational modelling reveals the active site for initial O_2 adsorption on the (110) surface of SnO_2 to be a bridging oxygen vacancy, O_v, (explicitly highlighted in Figure 7 and shown in blue in Figure 8) [30]. The initial chemisorbed (superoxo-)dioxygen sits with one end of the molecule in the vacancy associated with the r-Sn_{6c} sites, aligned almost perpendicular to the surface (labelled O_2-stand in Figure 8). Subsequently it transitions to a lower energy configuration in which each oxygen atom in the molecule is associated with adjacent under-coordinated tin sites (one r-Sn_{6c} and one Sn_{5c}) with this (peroxo-)dioxygen sitting nearly parallel to the surface (labelled O_2-lie in Figure 8). The final step is cleavage of the chemisorbed O_2, with one O-atom healing the vacancy (O_v → O_b).
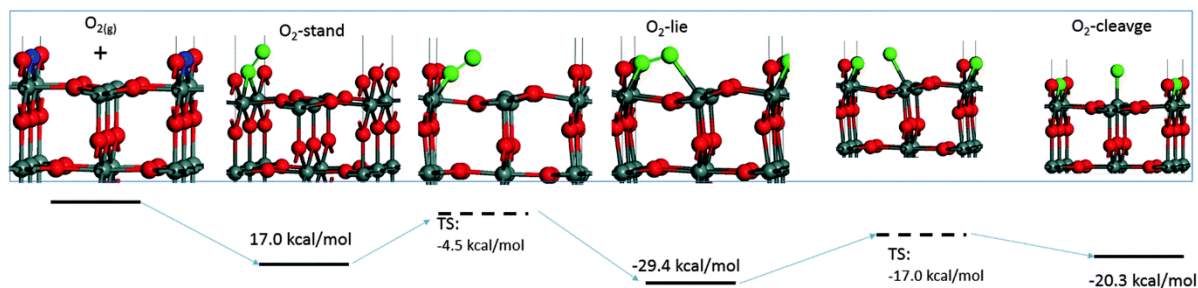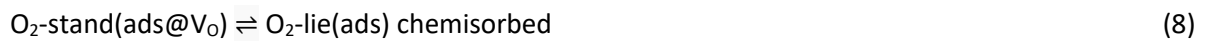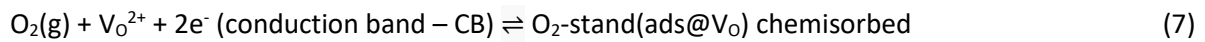

Figure 8. O_2 adsorption on SnO_{2-x} (reproduced with permission from [30]). Blue spheres indicate oxygen vacancies.

Whilst in the pictorial model shown in Figure 8 the other O-atom remains on the previously under-coordinated Sn_{5c} site, in the presence of additional vacancies this O_2-cleavage reaction results in two vacancies being filled, i.e. $O_2(gas) \rightarrow 2O_b$, as this results in a lower energy final state than leaving an O-atom on Sn_{5c} [30]. That is to say adsorption of dioxygen ultimately leads to healing of two vacancies (dependent on relevant activation barriers being overcome), i.e. thermodynamically this description describes an equilibrium between $O_2(g)$ and two O_v, although under a given condition some intermediary distribution of the 'intermediate' O_2-stand and O_2-lie surface adsorbed oxygen species is expected due to the barrier heights encountered along the reaction coordinate.

An attempt to illustrate this schematically (for an *n*-type semiconductor with ionised surface oxygen vacancies) is shown below:

$$O_2(g) + V_O^{2+} + 2e^- \text{ (conduction band – CB)} \rightleftharpoons O_2\text{-stand(ads@}V_O) \text{ chemisorbed} \tag{7}$$

$$O_2\text{-stand(ads@}V_O) \rightleftharpoons O_2\text{-lie(ads) chemisorbed} \tag{8}$$

$$O_2\text{-lie(ads)} \rightleftharpoons O_{br} + O(\text{ads@}Sn_{5c}) \text{ chemisorbed} \tag{9}$$

$$O(\text{ads@}Sn_{5c}) + V_O^{2+} + 2e^- \text{ (CB)} \rightleftharpoons O_{br} \tag{10}$$

$$\text{Overall: } O_2(g) + 2V_O^{2+} + 4e^- \text{ (CB)} \rightleftharpoons 2O_{br} \tag{11}$$

It is worth highlighting that in such a 'covalent' (as opposed to ionic) model of oxygen chemisorption the action of the adsorbed oxygen is to localise electrons in the lattice and hence reduce the positive surface charge arising from pre-existing oxygen vacancies, in the limit producing a neutral surface. This provides an important distinction between the ionosorption model of oxygen chemisorption that is in general ignorant of the surface active site and in which adsorbed oxygen acts to localise electrons outside the lattice producing a negatively charged surface after oxygen adsorption (neutral before), and a covalent model that accounts explicitly for the surface active site and predicts a neutral surface after oxygen adsorption (positive before).

Surface conductivity vs ionosorption comparison

For clarity it is worth stating clearly that when this covalent model is applied to a 'surface conductivity' model, such a description would lead to the bands unbending (bending upwards) for an *n*-type semiconductor, and hence conductivity being expected to decrease, as the partial pressure of oxygen increases (oxygen vacancies are healed). This then allows us to compare the phenomenological description provided under ionosorption theory with that obtained under surface conductivity theory with the following key comparisons.

Surface Conductivity Theory	Ionosorption Theory
The origin of (positive) surface charge is ionised surface oxygen vacancies	The origin of (negative) surface charge is surface adsorbed charged oxygen species
In lower partial pressures of oxygen bands bend downwards from flat band condition	In lower partial pressures of oxygen bands are at flat band condition
In lower partial pressures of oxygen an electron accumulation layer exists	In lower partial pressures of oxygen no electron accumulation/depletion layer exists
In higher partial pressures of oxygen bands are at flat band condition	In higher partial pressures of oxygen bands bend upwards from flat band condition

In higher partial pressures of oxygen no electron accumulation/depletion layer exists	In higher partial pressures of oxygen an electron depletion layer exists
In higher partial pressures of oxygen conductivity decreases	In higher partial pressures of oxygen conductivity decreases

It is worth highlighting that functionally surface conductivity provides the same outcomes as described under ionosorption theory, with the key fundamental difference being the microscopic origin of the band bending and conductivity change. In a surface conductivity model the origin of conductivity change in the material is the change in 'intrinsic' oxygen vacancy concentration whilst in ionosorption theory it is the change in 'extrinsic' charged oxygen species concentration. This matters, because in terms of materials design ionosorption theory provides no indication of how to engineer a material for higher performance (although a very recent article by Sopiha and Wu *et al* [31] has tried to address this) whilst under a surface conductivity model it is clear that manipulating the surface vacancy concentration/stability will directly influence the expected sensing properties of the material.

A phenomenological description of gas sensitivity under surface conductivity

As noted above, surface conductivity has been experimentally observed (via ARPES) in quite a wide range of materials and its magnitude shown to vary as a function of oxygen partial pressure, however how this might apply to interaction with/sensing of other gases is not yet clear. However I conjecture that the surface conductivity model described above should not invalidate previous phenomenological work carried out in the framework of ionosorption theory, but rather it is expected that it simply changes the actor for conductivity change from surface adsorbed O^{x-} (in ionosorption) to lattice-O (in surface conductivity). By way of example, considering the response of a thin film single crystal *n*-type semiconducting metal oxide to increasing concentrations of CO in a background of O_2 (air), in ionosorption theory it is suggested that CO abstracts O^- from the surface (typically formulated as forming CO_2) hence decreasing surface charge, which leads to an increase in measured conductivity [32]. In the framework of surface conductivity the CO would instead abstract O-lattice from the surface (again expected to form CO_2) hence increasing the surface vacancy concentration, which leads to an increase in measured conductivity (readily ionised surface vacancy concentration increases and hence surface conductivity increases). This comparison is shown schematically in Figure 9.
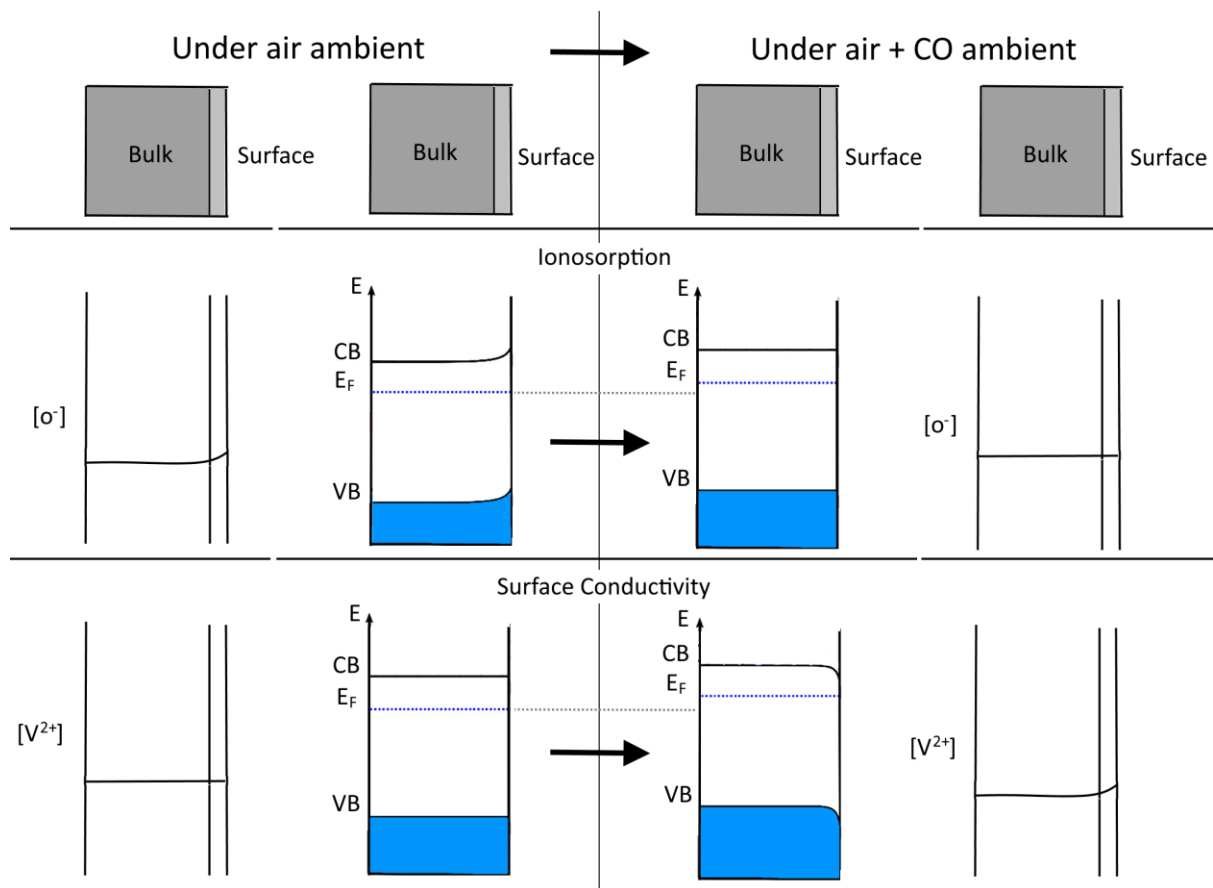
Figure 9: Schematic of band bending expected for exposure of thin film *n*-type semiconducting metal oxide on exposure to CO (in air ambient) under both ionosorption (shown with change in concentration of charged surface adsorbed oxygen, [O⁻]) and surface conductivity (shown with change in concentration of doubly ionised shallow donor vacancies, [V²⁺]), where CB = conduction band minimum, VB = valence band maximum and E_F is the Fermi energy; the downwards band bending in each instance leads to an increase in the Fermi level and hence an increase in conductivity is predicted

It is worth highlighting that in both cases the bands are expected to bend relatively downwards on exposure to CO; in ionosorption the bands are bent up in air and unbend towards flat band on addition of CO, whilst in surface conductivity the bands are at flat band (in the limit) in air and bend downwards on exposure to CO. Hence in both cases conductivity in the sensor body is expected to increase and bands are expected to bend downwards (Fermi level increases) on exposure to CO (Figure 9). The influence of band bending on relative conductivity for single crystal thin films of SnO_2 has recently been illustrated in detail by Barsan *et al* [33]; as shown in Figure 10, e.g. for Ld/D=0.2 (relative) conductivity is expected to increase whenever the bands bend relatively downwards, whether that is from a positive value of band bending towards flat band (0 eV), as would be the case for CO dosing under ionosorption theory, or whether that is from flat band towards a negative value, as would be the case for CO dosing under surface conductivity.
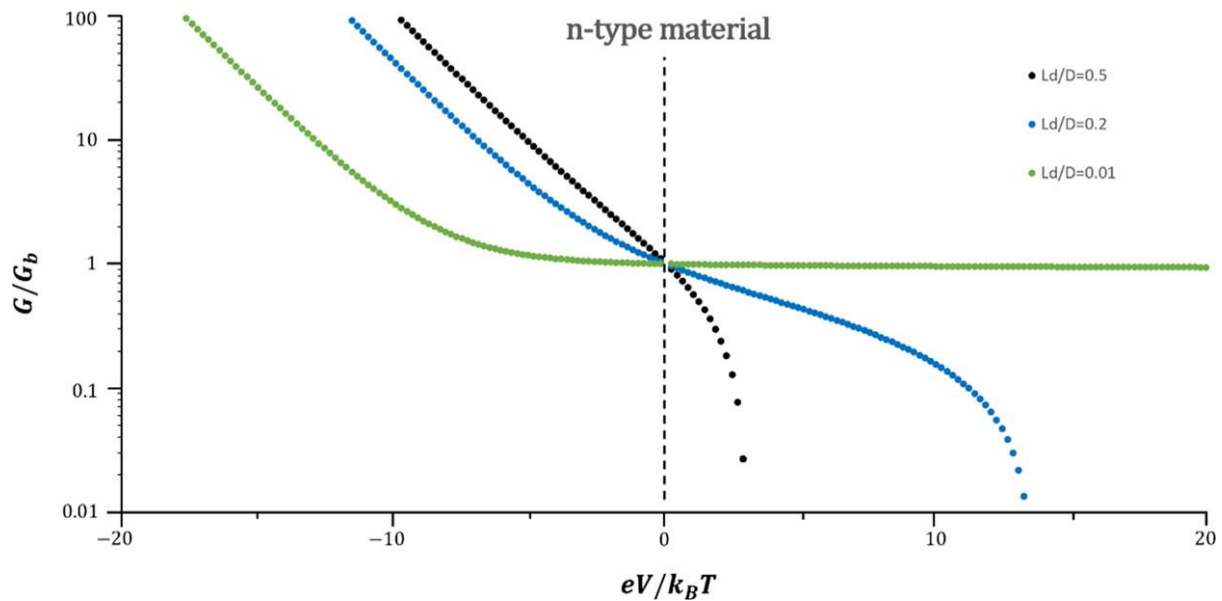
Figure 10: Normalized conduction of an *n*-type chemoresistive sensing layer as a function of surface band bending for three different values of Debye length (Ld)/grain size (D); negative values of the band bending correspond to the formation of a surface accumulation layer, whereas positive values of the band bending correspond to the formation of a surface depletion layer (reproduced with permission from [33])

In a similar way, it is proposed that other phenomenological descriptions from ionosorption theory can also be applied under surface conductivity simply by changing the actor for conductivity change. For example decoration of the sensing body, e.g. with noble metal particles, has commonly been used to modify the sensitivity and selectivity of gas sensing materials [34], and it is envisaged that both the commonly described 'electronic sensitisation' and 'chemical sensitisation' mechanisms could function in a similar way to as they are currently described. For example in chemical sensitisation, rather than the enrichment of the gas sensing material surface with the surface adsorbed O^- species invoked under ionosorption (bending bands relatively upwards compared to the undecorated surface) the surface would instead be 'enriched' with lattice oxygen, i.e. vacancy concentration would be reduced (bending bands relatively upwards compared to the undecorated surface).

Other descriptions, such as the influence of grain size [34], are also expected to hold, with a decrease in grain size reaching a point where the entire particle was enriched with electrons (in surface conductivity; fully depleted of electrons in ionosorption theory) and hence the bands would be essentially flat throughout the particle in both descriptions, with the whole particle expected to change vacancy concentration (Fermi level) as a function of the gas ambient in surface conductivity (whole particle is responsive to changes in surface charge in ionosorption).

Conclusions

To summarise this article, I have attempted to present recent theoretical and experimental findings that show that the origin of gas sensitivity in the common *n*-type gas sensing oxides is unlikely to be ionosorbed oxygen species (for which there is no persuasive experimental evidence for their

existence under normal sensor operating conditions) but is rather more likely due to the presence of a surface conductivity layer formed due to the presence of surface oxygen vacancies (for which abundant experimental evidence has been presented in recent literature and is discussed herein), at least for metal oxide semiconductors in which bulk oxygen defects are 'deep' whilst equivalent defects near the surface are 'shallow'. In preparation of this perspective I was struck by the prescient comments of Erickson and Semancik in their article on SnO_2 published more than 30 years ago [14], "(our data) indicates qualitatively that oxygen vacancies have a characteristic small net positive charge which alters the surface potential to bend the bands downward. The increase in the surface conductivity is attributed to both an increased density of donor states and to an increased occupancy of these states which occurs when the bands bend down", and also by the recent work of Koretcenkov et al that demonstrates downwards band bending in In_2O_3 gas sensors [8].

Reflecting on these findings, it then becomes evident why the most successful gas sensing materials (SnO_2, In_2O_3, ZnO) also happen to be transparent conducting oxide (TCO) materials. From a materials design perspective one would never choose to restrict materials choice by requiring a redundant material parameter, such as including transparency for a gas sensing material. However the TCO materials all gain their unusual properties of being both transparent and conductive due to their particular electronic structure. This same electronic structure also happens to provide a material with conductivity governed by a surface conducting layer, which in turn is controlled by the surface vacancy concentration. It should therefore be no surprise that such materials would also be expected to show rapid and large changes in conductivity in response to changes in gas ambient.

I hope that an important outcome of this article could be that authors think very carefully about recourse to 'charged oxygen species on the surface', unless of course they have direct primary evidence (not just electrophysical measurements) of their presence. In addition I hope this will prompt renewed discussion of the most appropriate theory to describe the gas sensitive properties of metal oxides, which rather seems to have waned in the last decade or two. There is of course the question of the general applicability of the discussion above; the main limitation is that surface conductivity would only be expected to apply to materials in which the bulk oxygen defect is deeper (relatively less ionised) than at the surface (relatively more ionised), and one assumes it requires that the oxygen vacancies are relatively immobile at the sensor operating temperature (to prevent dynamic exchange between the bulk and the surface, which would lead to flattening of the bands). Such a distinction between SnO_2 ('band bending transduction') and WO_3 ('bulk conduction') sensing mechanisms has already been discussed by Frederick [16]. Another important outcome should be that a surface conductivity model provides guidance towards new design rules that might be applied to gas sensing materials. For instance Santander-Syro has demonstrated that surface decoration of SnO_2 with aluminium particles can increase the surface oxygen vacancy concentration and hence the surface conductivity, providing a route to tuning this parameter [24]. Further experimental studies would allow the applicability of the surface conductivity model to be tested in gas sensing measurements and subsequently provide a route to advance in the field by allowing a $priori$ design of higher performance materials.

Acknowledgements

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