Surface studies of gas sensing metal oxides†

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The relation of surface science studies of single crystal metal oxides to gas sensing applications is reviewed. Most metal oxide gas sensors are used to detect oxidizing or reducing gases and therefore this article focuses on surface reduction processes and the interaction of oxygen with these surfaces. The systems that are discussed are: (i) the oxygen vacancy formation on the surface of the ion conductor CeO$_2$(111); (ii) interaction of oxygen with TiO$_2$ (both adsorption processes and the incorporation of oxygen into the TiO$_2$(110) lattice are discussed); (iii) the varying surface composition of SnO$_2$(101) and its consequence for the adsorption of water; and (iv) Cu modified ZnO(0001)-Zn surfaces and its interaction with oxygen. These examples are chosen to give a comprehensive overview of surface science studies of different kinds of gas sensing materials and to illustrate the potential that surface science studies have to give fundamental insight into gas sensing phenomena.

1. Introduction

Of all the gas sensing solid state materials, metal oxides were one of the first considered$^{1,2}$ and are still the most widely used gas sensing materials. This choice is partially due to the chemical stability of oxides at the operation conditions of gas sensors. Commonly, the dependence of the material’s conductance on the gaseous environment results in their applications as gas sensing materials. We may distinguish between two fundamentally different kinds of conductors that give rise to different gas sensor designs and applications: (i) ion conductors such like ZrO$_2$ and CeO$_2$ and (ii) semiconductors with in principle n- or p-type conduction. In practice most gas sensing materials are n-type due to strong n-type doping of the oxides as a consequence of intrinsic defects. Typical materials of the latter kind are SnO$_2$, In$_2$O$_3$, ZnO, and TiO$_2$. One main application of both kinds of metal oxide gas sensors is the detection of oxidizing and reducing (combustible) gases and this is what this review is focusing on. Instead of trying to give a complete summary of all the surface science studies performed on metal oxide gas sensing materials we selected a few systems that we consider to be well-suited models for the different kinds of gas sensing materials. A comprehensive review of oxide gas sensing materials with much insightful information on operation conditions, e.g. temperature, can be found in ref. 3. This review attempts to demonstrate that surface science experiments are important to find a better fundamental understanding of gas sensing mechanisms.

This article is organized as follows. First, we give a brief introduction to gas sensing with ion conductors and discuss the oxygen vacancy formation on CeO$_2$(111). Then a more comprehensive review of surface science studies of materials whose electrical conductivity depends on the gaseous environment is presented. In the latter case we distinguish between bulk and surface sensitive materials. The different phenomena relevant for these gas sensing mechanisms are discussed on the examples of TiO$_2$ and SnO$_2$, respectively. Finally, the influence of additives for surface sensitization is highlighted using the example of Cu deposits on ZnO(0001) surfaces.

2. Ion conductors

Ion conductors, or solid electrolytes, are used in a design where the gas sensing material acts as a membrane separating two gases with differing chemical potentials. One gas is usually the reference with a known chemical potential while the other gas is the analyte. The solid electrolyte material is coated with porous metal electrodes that serve two purposes: (i) the metal acts as a catalyst, which ensures a chemical equilibrium between the gases and the ions in the ion conducting membrane; and (ii) the potential difference measured between the electrodes serves as the sensing signal. To obtain a sizeable potential difference between the electrodes it is required that the solid electrolyte which separates them is a poor electron conductor.

In most cases the conduction-ions are also the species that are being detected. For instance ZrO$_2$ (usually Y$_2$O$_3$ stabilized zirconia is used) or CeO$_2$ can be used for oxygen sensing and LaF$_3$ for fluorine sensing. A popular example is the use of ZrO$_2$ membranes coated with Pt electrodes to measure the oxygen content in automobile exhausts. In this case the atmosphere acts as the reference gas and the engine exhaust is the analyte. For a more detailed discussion of the applications of ion conductors as gas sensing materials the interested reader is referred to ref. 4 and 5.

Here we focus on surface science studies of ion conducting gas sensing materials. Recently there has been increased interest in the study of the surface properties of ceria.$^{6,7}$ Many of these studies are motivated by the catalytic properties of
ceria and its oxygen storage capability, which is closely related to its application as a gas sensing material. As pointed out above it is critical for an ion conducting gas sensing material that it is a poor electron/hole conductor. Consequently low sample conductivities often complicate surface science studies on these materials. One solution is to grow model systems of thin oxide films on metal supports and there are numerous studies of thin ceria or zirconia films on metal substrates. For some materials like CeO$_2$ it has also been shown that it becomes conductive enough if it is reduced by annealing in vacuum and measured at elevated temperatures. In this case charging effects can be avoided and even scanning tunneling microscopy (STM) studies are possible on bulk samples.

The variable valency of cerium of (IV) and (III) is responsible for its high oxygen storage and release capacity that is exploited in heterogeneous catalysis and gas sensing. The valencies of Ce suggest that every O-vacancy in CeO$_2$ is associated with two reduced Ce$^{3+}$ ions. The oxygen vacancy formation on CeO$_2$ (111) surfaces was studied at elevated temperature with STM. These studies, in combination with DFT calculations, revealed that the formation of surface and subsurface vacancies are almost equally likely. Furthermore, there is a strong preference to forming vacancy complexes consisting of surface and subsurface vacancies in such a constellation that exclusively Ce$^{3+}$ ions are exposed. STM images of a surface exhibiting oxygen vacancies are shown in Fig. 1a and b. The atomic model for a hypothetic single O-vacancy that would expose only two Ce$^{3+}$ sites is illustrated in Fig. 1c. The observed surface-subsurface O-vacancy complex that exposes three Ce$^{3+}$ sites is shown in Fig. 1d. The formation of surface and subsurface oxygen vacancies is shown in (e). Further removal of oxygen vacancies appear for strongly reduced surfaces. Ball and stick models of the O-vacancies are shown in (c)–(e). In (c) a hypothetical single surface O-vacancy is shown that would reduce two adjacent Ce-atoms to 3+ indicated as yellow balls. Experimentally, all three Ce-atoms next to an O-vacancy sites favours the formation of linear oxygen vacancy chains at the surface upon further reduction of the sample. This can be seen in Fig. 1b and is indicated in Fig. 1c. The observation that only Ce$^{3+}$ ions are coordinated to vacancies required complexes of at least two vacancies (surface and subsurface). It was pointed out that this requirement may hamper the nucleation of O-vacancies. Once these two-vacancy complexes are formed further O-release is favoured by the formation of linear oxygen vacancy chains. It has also been pointed out that, for example, Zr$^{4+}$-dopants in ceria are not being reduced upon O-vacancy formation. This can lift the requirement for nucleating two-vacancy complexes in the neighborhood of a Zr-dopant. Consequently such dopants may facilitate O-vacancy nucleation.

Studies on the oxygen vacancy formation processes are of obvious relevance for a basic description for oxygen sensors. The formation and annihilation of oxygen and variation in the O-vacancy concentration as a function of the oxygen chemical potential are at the heart of the gas sensor. Only surface science studies can provide insight at these atomic scale processes. The surface oxygen concentration and defect formation are also important for conductivity gas sensors. These studies are being reviewed next.

3. Surface science studies of conductivity gas sensors

The gas response to oxidizing or reducing gases can be conveniently detected by measuring the conductivity of metal oxide gas sensing materials. This change in the conductivity upon exposure to gases may have two different contributions: (i) a change of the bulk charge carrier concentration due formation or annihilation of intrinsic dopants by reduction and oxidation of the gas sensing material; and (ii) a surface band bending induced by chemisorbed (or ionosorbed) charged surface species, or the reaction of gas molecules with such adsorbed species. The surface band bending induced shift of the energy levels (relative to the Fermi level) results in a change of the charge carrier population. In addition it also induces barriers at grain boundaries that influence the charge transport in porous films. The amplifying effect of the gas
response due to grain boundaries in porous gas sensing materials has been extensively investigated by the gas sensing community.\textsuperscript{22–25} Most practical gas sensors are porous metal oxides to increase the interaction with the gas phase and thus the grain boundary effects are important in these devices. Here we concentrate on the surface science studies of single crystal surfaces and thus we will not consider the influence of grain boundaries any further. It is interesting to mention, however, that highly sensitive gas sensors have been fabricated by either using epitaxial single-crystalline films or by utilizing single-crystalline oxide nanobelts. These devices have in some cases shown even a higher sensitivity than conventional porous thick film sensors.\textsuperscript{26} Thus this demonstrates that grain boundaries are not essential for the operation of conductivity gas sensors.

Depending on which of the two mechanisms mentioned above is dominant one distinguishes between bulk sensitive and surface sensitive gas sensing materials. From the three oxides we will discuss in the following in some more detail it is generally accepted that TiO\textsubscript{2} is more bulk sensitive, \textit{i.e.} it exhibits conductivity changes due to variations in intrinsic dopants as a consequence of the formation of oxygen vacancies and Ti interstitials, while SnO\textsubscript{2} and ZnO are considered surface sensitive materials. In the case of surface sensitive oxides for the detection of oxidizing and reducing gases the adsorption of charged surface oxygen species plays a central role. Negatively charged surface oxygen species introduce an upward band bending that reduces charge carriers in the conduction band and therefore causes a drop in the conductivity. The concentration of these charged oxygen species depends on the equilibrium conditions with the gas phase.\textsuperscript{4}

Reducing gases may react with these pre-adsorbed oxygen species and thus reduce their concentration which results in an increase in the gas sensor’s conductivity. Therefore for both cases, bulk and surface sensitive metal oxide gas sensors, the interaction with oxygen from the atmosphere is crucial. This warrants a close look at the interaction of oxygen with metal oxide sensing surfaces. The interaction of O\textsubscript{2} with TiO\textsubscript{2} is discussed in sub-section 3.1 and with SnO\textsubscript{2} in sub-section 3.2. In addition, we will review the interaction of water with SnO\textsubscript{2} surfaces in sub-section 3.3. Water is omnipresent in the use of sensor materials and thus it is important to understand how and where water is adsorbed on surface sensitive gas sensing oxides. The interaction of O\textsubscript{2} with TiO\textsubscript{2}(110) surfaces has been investigated by electron energy loss (ELS) spectroscopy,\textsuperscript{29} surface sensitive methods without complications due to surface charging. The re-oxidation mechanism of TiO\textsubscript{2} in an oxygen atmosphere has been investigated by surface science studies and we will review these processes, which are particularly relevant to explain the gas response of this bulk sensitive gas sensor, below. Before we discuss the incorporation of gas phase oxygen into the TiO\textsubscript{2} lattice, we first turn to the adsorption of oxygen species at the surface of TiO\textsubscript{2}(110).

\textbf{3.1 Interaction of oxygen with TiO\textsubscript{2}}

Titania is the most widely studied transition metal oxide material.\textsuperscript{27} The main motivation for studying titania comes, however, not from its use as a gas sensing material but rather because of its importance as a photocatalyst. Nevertheless, many of the surface science studies can also be related to gas sensing applications and a great deal about fundamental gas sensing processes can be learned from these studies. The fairly easy preparation of well defined rutile TiO\textsubscript{2}(110) surfaces makes it the model system of choice for surface science investigations of transition metal oxides. Vacuum annealing reduces TiO\textsubscript{2} and creates bulk O-vacancies and Ti-interstitials. These intrinsic defects make the material strongly \textit{n}-type and a fair conductor, which allows the applications of surface science methods without complications due to surface charging. It is reasonable to assume that similar bulk reduction processes, to the one observed by vacuum annealing, result in the conductivity change in gas sensing applications of titania. The interaction of reduced titania with oxygen causes a re-oxidation of the sample and consequently a decrease in conductivity. The re-oxidation mechanism of TiO\textsubscript{2} in an oxygen atmosphere has been investigated by surface science methods without complications due to surface charging. The re-oxidation mechanism of TiO\textsubscript{2} in an oxygen atmosphere.

\textbf{(i) Chemisorption of oxygen on TiO\textsubscript{2}(110).} The TiO\textsubscript{2}(110) surface is an autocompensated bulk truncation consisting of rows of fivefold coordinated Ti atoms and two-fold coordinated, so called bridging O-atoms. The structure of this surface is illustrated in Fig. 2. Critical to the understanding of the chemical properties of TiO\textsubscript{2}(110) surfaces prepared by sputtering and annealing in UHV is the presence of O-vacancies at the surface. From STM imaging it is known that after annealing to 850 K the surface exhibits \textuparrow{~8}\% missing bridging oxygen atoms.\textsuperscript{28} The interaction of O\textsubscript{2} with a vacancy containing TiO\textsubscript{2}(110) surface has been investigated by electron energy loss (ELS) and temperature programmed desorption (TPD). These studies indicated that O\textsubscript{2} adsorbs and dissociates at surface O-vacancies,\textsuperscript{29,30} suggesting that one oxygen atom ‘heals’ the surface defect and the other O-atom is adsorbed at the fivefold Ti-row. TPD studies showed an O\textsubscript{2} desorption peaks at 410 K upon exposure to above 4 \times 10\textsuperscript{7} molecules cm\textsuperscript{-2} at 120 K.\textsuperscript{29} Furthermore, isotopic labeling experiments demonstrated that there is no scrambling between dosed O\textsubscript{2} and the lattice.

![Fig. 2](image-url)
oxygen, suggesting the combination of O-atoms chemisorbed at the five-fold Ti-rows. No molecular O\textsubscript{2} adsorption down to 100 K was found on defect free surfaces. Evidence for O-adatom formation was also found from co-adsorption experiments with water.\textsuperscript{30} ELS measurements showed a disappearance of a peak at 0.8 eV and the appearance of a loss peak at 2.8 eV upon O\textsubscript{2} exposure.\textsuperscript{29} This was interpreted as the formation of O\textsuperscript{2−} at the surface. It is well established that oxygen vacancies are extremely reactive towards water adsorption, which also dissociates at O-vacancies.\textsuperscript{31–34} Thus these O-vacancies are easily hydroxylated due to residual water even under best UHV conditions. This suggests that although O\textsubscript{2} does not adsorb on the perfect TiO\textsubscript{2} surface at 120 K it can interact with hydroxyls at the surface. Thus there still remains some uncertainty of the surprisingly complex oxygen chemistry even for the fairly well defined single crystal TiO\textsubscript{2}(110) surface, especially if more complex, but more realistic conditions are considered.

How do the surface science studies described above relate to a fundamental understanding of gas sensing materials? The advantage of TiO\textsubscript{2}(110) over most other metal oxide surfaces is that it can be prepared with well defined surfaces and although it exhibits defects (oxygen vacancies), these defects themselves are well defined. This allows an almost unique opportunity to study defect chemistry of a metal oxide surface. Defects, such as oxygen vacancies, are thought to be an important component to the chemical and gas sensing activity of many metal oxide gas sensors. This gives TiO\textsubscript{2} a special standing as a general metal oxide model system. In this respect, we can learn from the above studies about formation mechanisms of O ad-species on metal oxide surfaces that might be relevant for other metal oxide gas sensing materials as well. It may be expected that under real gas sensing conditions additional effects become important. Co-adsorption, for instance, of different gases will alter the interaction of oxygen with TiO\textsubscript{2}. Above, we have already alluded to the influence of water adsorption and consequently the formation of hydroxyls, which is changing the interaction of oxygen with the surface. Thus the above studies illustrate that with a multitechnique surface science approach we can come closer to an atomic level understanding of complex, entwined processes at metal oxide surfaces. The next section will give a more tangible example of the relevant connection between surface science studies and TiO\textsubscript{2} gas sensing materials.

(ii) Incorporation of gas phase oxygen into the TiO\textsubscript{2} lattice. Above we described an approach aiming at understanding the chemisorption of oxygen on TiO\textsubscript{2} surfaces. Although we saw that O\textsubscript{2} heals surface O-vacancies there was no indication of a bulk re-oxidation process at or below room temperatures. Bulk oxidation and thus a change in the intrinsic doping level is, however, believed to be the dominant mechanism by which a TiO\textsubscript{2} gas sensor changes its conductivity. Therefore, in this section, we will review surface science studies that provide insight in re-oxidation mechanisms of TiO\textsubscript{2}.

The change in the defect concentration of TiO\textsubscript{2} single crystals after reduction in vacuum can be seen by optical inspection of the samples.\textsuperscript{35} TiO\textsubscript{2} crystals change their colour from transparent for a stoichiometric sample to dark blue for a heavily reduced sample. This optical change is due to the formation of colour centres in the material. Oxidation by annealing of the single crystal in an oxidizing atmosphere restores the transparency. Naively, one may expect that the oxidation of a reduced TiO\textsubscript{2} crystal occurs via diffusion of oxygen species into the crystal and subsequent annihilation of bulk O-vacancies. Surface science studies on single crystal TiO\textsubscript{2}(110) surfaces have, however, demonstrated that there exists an additional mechanism that needs to be taken into account to explain the reduction and re-oxidation of bulk TiO\textsubscript{2}.

It has been shown by STM,\textsuperscript{36,37} low energy ion scattering (LEIS), static secondary ion mass spectroscopy (SSIMS) (by using isotopic labeled \textsuperscript{18}O\textsubscript{2} as the oxidation gas),\textsuperscript{36} and low energy electron microscopy (LEEM)\textsuperscript{38} that re-oxidation of slightly reduced TiO\textsubscript{2−x} predominantly occurs at the surface by diffusion of bulk Ti-interstitials to the surface and reaction with adsorbed oxygen. These studies have been performed by exposing a TiO\textsubscript{2}(110) sample to 2 × 10\textsuperscript{−7} to 10\textsuperscript{−6} mbar O\textsubscript{2} within an UHV chamber and simultaneous annealing of the sample in a temperature range between 470 and 1000 K. From SSIMS and LEIS it was concluded that the oxygen uptake initially increases with temperature, reaches a maximum for 570–670 K, and then decreases again. The results of a SSIMS experiment is shown in Fig. 3. In this experiment the samples are exposed to \textsuperscript{18}O for 260 s, while simultaneously monitoring the \textsuperscript{18}O uptake. From the low temperature increase in the oxygen uptake an oxygen activation energy of above 19 kcal mol\textsuperscript{−1} was estimated. It was also observed that more reduced TiO\textsubscript{2} crystals show a higher \textsuperscript{18}O surface concentration for otherwise the same exposure parameters.

STM and LEEM have been used to study the surface morphology evolution during re-oxidation of the sample. A restructuring of the surface in 1 × 2 surface structures that is known to also form for heavily reduced samples and formation of ‘rosette’-structures have been observed. These are sub-stoichiometric TiO\textsubscript{2−x}, possibly Ti\textsubscript{2}O\textsubscript{3} structures. Fig. 4 shows an STM image of a surface restructured into ‘rosettes’ and the proposed atomic model of these structures derived from DFT calculations.\textsuperscript{36} Stone \textit{et al.} performed high temperature STM measurements on heavily reduced TiO\textsubscript{2} surfaces to observe the oxidation process \textit{in situ}. They found nucleation and growth of 1 × 1 islands within the initially 1 × 2 reconstructed surfaces followed by formation of a second layer 1 × 2 structure on these 1 × 1 islands.\textsuperscript{37} These scenarios were confirmed by low-energy electron microscopy studies (LEEM)\textsuperscript{38} that showed step edge flow growth at high-temperature and nucleation and islanding at lower temperatures. For both temperature regimes a layer-by-layer growth mode was observed.

The relevant picture for gas sensing applications that evolves from these surface science studies is that the surfaces of TiO\textsubscript{2} act as the source\textsuperscript{39} or sink for bulk Ti-interstitials. Thus it has been demonstrated that Ti interstitials are the most active species in the oxidation of reduced TiO\textsubscript{2}. Although these studies do not address why Ti-interstitials play an apparently larger importance compared to oxygen vacancies in the formation of non-stoichiometry of the bulk, calculations have shown that Ti-interstitials can diffuse easily along open channels in the [001] direction of rutile.\textsuperscript{40} This may imply that a reduction of a TiO\textsubscript{2} surfaces results in Ti-species, rather than
As pointed out above, chemisorption of oxygen is crucial for the gas response mechanism of surface sensitive materials. From electron paramagnetic resonance (EPR) measurements at SnO$_2$ powders it has been established that different oxygen species form at the surface at different temperatures. The following conversion scheme of adsorbed oxygen to charged O-species has been proposed:

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O_2(\text{gas}) \leftrightarrow O_2(\text{ad}) \leftrightarrow O^- (\text{ad}) \leftrightarrow O^{2-} (\text{ad}) \leftrightarrow O^{2-} (\text{lattice}).
\]

These transformations occur at critical temperatures at a given pressure. The transformation temperatures of the O-species determined by EPR also compare favourably to separately obtained changes in the measured conductivity of a SnO$_2$ gas sensor. Thus these measurements appear to demonstrate the correlation between the gas response signal and the chemisorbed O-species. Recently, Gurlo strongly questioned this paradigm. Of particular concern in Gurlo’s review are experimental ambiguities and misinterpretation. Also sample preparation in many studies including the EPR study cited above may not reflect realistic operation conditions. Details of Gurlo’s criticism would take us too far a field and the interested reader is referred to the original paper.

Single crystal surface science experiments under UHV conditions are more ambiguous for SnO$_2$ than those described above for TiO$_2$. This is mainly because the SnO$_2$ surfaces cannot be prepared with the same degree of perfection as TiO$_2$ surfaces. This is particularly true for stoichiometric SnO$_2$ surfaces, which, as we will discuss below, only form at elevated O-pressures or by formation with efficient oxidants such as ozone, NO$_2$, or O-plasma. Presence of charged oxygen adspecies has however been deduced from band bending measurements in photoemission experiments after exposure to O-plasma. Unlike for TiO$_2$ there exist very little information on atomic scale features of chemisorbed oxygen on single crystal SnO$_2$. Such information would be desirable for a surface science description of these gas sensors, but the difficulties in preparing well defined SnO$_2$ surfaces have prevented such studies up to date.

In addition to chemisorbed oxygen the surface lattice oxygen concentration may be important for gas sensing mechanisms. Unlike the TiO$_2$(110) surface that shows a substoichiometric $1 \times 2$ surface reconstruction only if the bulk is reduced, the SnO$_2$(110) surface is easily reduced, independent of its bulk state. This easy surface reduction has been observed for all SnO$_2$ surfaces studied so far. For the SnO$_2$(110) surface the surface reduction causes a $1 \times 2$ surface reconstruction that is not well understood. For this reason we will focus on the SnO$_2$(101) surface in the following. The (101) surface can form bulk truncations for both a stoichiometric and reduced surface without the formation of complex surface reconstructions. These bulk truncations are illustrated in Fig. 5.

The SnO$_2$(101) surface prepared in vacuum by sputtering and annealing to $\sim 900$ K exhibits a $1 \times 1$ LEED pattern and in atomic resolved STM images a surface unit cell that is consistent with a bulk truncation can be discerned. LEIS experiments indicate that this surface can take up a significant
amount of oxygen if annealed to 500 K in an oxygen atmosphere. If such an oxidized sample is subsequently annealed in vacuum it loses surface oxygen, again, at around 600 K.

Similarly, the surface electronic structure can be monitored as a function of vacuum annealing temperature. Fig. 6 shows angle resolved ultraviolet photoemission data at normal emission. It is apparent that coinciding with the surface reduction observed in LEIS a new electronic state appears on top of the valence band maximum. In angle resolved photoemission measurements this state shows dispersion with the symmetry of a $1\times1$ surface Brillouin zone. Therefore, a two-dimensional surface state is formed indicating a uniform reduction of the surface in agreement with STM measurements that also indicate a uniform surface.

All the experimental evidence points to one model: The stoichiometric surface, as shown in the ball and stick model in Fig. 5a, is prone to reduction at elevated temperature under UHV conditions. Reduction converts the surface into an alternative bulk truncation by complete removal of the terminating oxygen atoms. The resulting surface is shown in Fig. 5b. This surface still has a $1\times1$ surface unit cell but the surface Sn atoms have to change their charge state in order to maintain overall charge neutrality. This is, however, easily

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**Fig. 4** STM image of a TiO$_2$ surface exposed to $10^{-6}$ mbar oxygen for 10 min at 550 K. The surface structure formed is indicated in the model. It is shown that the structure can be constructed of a bulk TiO$_2$ lattice with missing O and Ti atoms. Taken with permission from ref. 36. © Elsevier 1999.

**Fig. 5** Ball-and-stick model of a cross-section through the SnO$_2$ crystal with the (101) surface on top. The stoichiometric bulk termination is shown in (a) and the reduced surface with a Sn(II) surface layer is indicated in (b).
accomplished for Sn, with its dual valency of (ii) and (iv). From the representation of SnO₂ in Fig. 5 it is apparent that it can be described as a stacking of O–Sn–O trilayers along the (101) direction. Removal of the topmost oxygen layer from the stoichiometric SnO₂ surface thus leaves a terminating SnO surface layer. This implies that the surface Sn adopts a Sn(ii) valency for the reduced surface. A conversion from Sn(iv) for the stoichiometric surface to Sn(ii) for the reduced surfaces further suggests the occupation of Sn-5s states. This is in agreement with the new electronic states observed in the UPS measurements shown in Fig. 6.

With respect to gas sensing it has to be remarked that the conversion of the surface layer from Sn(iv)O₂ to a Sn(ii)O surface is not expected to directly influence the sample conductivity and thus is not expected to cause a gas response. This conclusion has been reached for two reasons: (i) No net surface charge, which could cause a band bending and thus a change in charge carrier concentration, is formed by the described reduction process. This is consistent with the lack of any detectable band bending in photoemission experiments. (ii) The surface band formed by the mainly Sn-5s states lies deep in the band gap (2 eV below the conduction band). Therefore these electrons will not contribute to the conductivity.

Although this change in the surface composition and structure does not directly change the sample conductivity the surface composition is important for understanding the interaction of molecules with the material. Therefore a changed surface composition may determine the gas sensitivity of the material through the altered chemical/adsorption properties of the surface. Thus in the case of SnO₂ we have a special opportunity to study molecular adsorption on the same material with different bulk truncations. This influence of the tunable surface properties on the gas response is studied on the example of water adsorption in the next section.

### 3.3. Water adsorption on SnO₂

From the very beginning it was recognized that humidity had a profound effect on the gas sensitivity of SnO₂ gas sensing material. Usually these effects are unwanted side effects that reduce the sensitivity to the targeted gas. This resulted in numerous studies of the effects of water adsorption on the gas sensing properties of SnO₂. A brief summary of these studies can be found in ref. 44. Here we concentrate on the SnO₂(101) surface as an example of how surface science can contribute to an understanding of molecular adsorption on gas sensing metal oxide surfaces.

As outlined above, two kinds of SnO₂(101) surfaces can be prepared. The stoichiometric Sn(iv)O₂ and the reduced Sn(ii)O surface. Water adsorption on both these surfaces was studied by UPS. Fig. 7 shows the results for water dosed at both surfaces under UHV conditions at 110 and 160 K. At 110 K water adsorbs on both surfaces readily. A shift in binding energy of the HOMO of water by 0.9 eV on the two surfaces is due to a changed work function of the reduced and stoichiometric SnO₂ surfaces. Interestingly, only the stoichiometric surface shows some signal at the position of the OH-3σ orbital, indicating dissociation of water. This difference between the two surfaces is more clearly observable for water dosed at 160 K. Both surfaces have been dosed with 2 L water. At this temperature only minute changes are observed for the reduced surface before and after water exposure indicating essentially no water adsorption. On the stoichiometric surface, on the other hand, the spectrum changes significantly. This change is attributed to formation of OH and possibly also some adsorption of molecular water. Therefore, these measurements indicate that the reduced surface does not chemisorb water and only at low temperatures (110 K) is water condensed. The stoichiometric surface, on the other hand, interacts more strongly with water and dissociates the molecule. These results are also confirmed by DFT calculations. Fig. 8 shows the proposed monolayer adsorption geometry of water on the reduced surface and for molecular and dissociated water on the stoichiometric surface. The calculated adsorption energies for the different adsorption models are also indicated, showing the weak interaction of water with the reduced surface and the preference for dissociation on the stoichiometric surface.

This result is different from what is commonly observed for other metal oxide surfaces where a surface reduction causes an increase in surface reactivity. This is, however, not surprising because in these cases reduction forms oxygen vacancies, with under-coordinated cations, which consequently are quite reactive. In the case of SnO₂, the reduced surface may be viewed as a fully-coordinated Sn(ii) surface. In this case the Sn-5s lone pair electrons are rather inactive towards the adsorption of water. Furthermore, the reduced surface does not have any surface lattice oxygen that could act as a Lewis base site to accept hydrogen atoms from water. This will also contribute to the lack of any dissociation on the reduced surface. On the stoichiometric surface, on the other hand, water can adsorb in the position of the broken Sn–O bond and there are surface O-sites available that make a dissociation of water possible (see Fig. 8c). A similar adsorption behaviour on the two surfaces of SnO₂(101) may be expected for other weak Bronsted acids.
Important for the gas response is the adsorbate induced band bending. This was also evaluated from photoemission experiments. Monitoring the Sn-4d core level position during water dosing allows measuring of the amount of band bending. This is shown in Fig. 7c for water adsorption at 110 K on the two surfaces. It is apparent that the stoichiometric surface exhibits a four times larger band bending effect than the reduced surface. This is consistent with the stronger interaction of water with the reduced surface and agrees with previous results which suggested that water dissociation and formation of hydroxyls cause the conductivity to increase due to humidity in SnO$_2$ gas sensors.

For a complete removal of hydroxyls under UHV conditions from the stoichiometric surface the samples had to be annealed to above 400 K. This indicates the problems gas sensing materials face under atmospheric conditions. Although these devices are commonly operated at $600 \text{ K}$, a presence of hydroxyls is likely and therefore their influence needs to be considered in gas sensing applications.

### 3.4 Surface modification of ZnO with Cu

To increase gas sensitivity and/or selectivity, metal oxide gas sensors are modified by a variety of different additives. A fundamental understanding of the function of many of these additives is lacking. Additives can be present as dopants in the

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**Fig. 7** Ultraviolet photoemission spectra for water adsorption on a reduced (a) and (d) and a stoichiometric surface (b) and (e) at a sample temperature of 110 (a) and (b) and 160 K (d) and (e). Water interacts more strongly with the stoichiometric surface than with the reduced surface. At 160 K water adsorbs dissociatively on the stoichiometric surface while no water adsorption is detected on the reduced surface. Water induced band bending is also stronger on the stoichiometric surface. The band bending measured as a function of water exposure is shown in (c). Taken with permission from ref. 55. © Elsevier 2006.

**Fig. 8** Density functional theory calculations for one monolayer of water on the reduced surface (a) and molecular (b) and dissociated water (c) adsorption on the stoichiometric surface. These calculations confirm the weak water adsorption on the reduced surface and the preferred dissociative adsorption of water on the stoichiometric surface. Calculated adsorption energies (in eV) are indicated. Taken with permission from ref. 55. © Elsevier 2006.
metal oxide bulk or reside at the surface in the form of clusters. Surface clusters are commonly differentiated into chemical and electronic sensitizers. This differentiation is made depending on their dominant mechanism to increase gas sensitivity. Chemical sensitizers act mainly as heterogeneous catalysts, i.e., they activate the target gas by, for example, dissociation and subsequent spill over of dissociation fragments onto the gas sensing material, which then causes the gas response. An example of this would be Pt clusters that dissociate H₂ in a hydrogen sensor. This is closely related to the area of heterogeneous catalysis that is extensively studied in the surface science community and thus is not further considered in this review. Electronic activation is due to a changing Schottky barrier at the interface between a supported cluster and the semiconducting metal oxide gas sensing material as a consequence of the interaction of the additive with the gas phase. This is, for example, the case in oxidation and reduction reactions of late transition metal additives such as Pd or Cu. Sometimes a strict differentiation into chemical and electronic sensitizers may not be possible, however. For example, it has been proposed that hydrogen sensing with Pd sensitizers may involve both processes, i.e., dissociation of hydrogen and diffusion of hydrogen to the Pd/metal oxide interface.

Here we concentrate on the simple case, where the additive will change its charge state depending on the oxidative or reduction potential of the gas phase. Formation of oxides increases the Schottky barrier at the interface, which is equivalent to saying that it induces a band bending in the gas sensing material. Consequently, the conductivity of the gas sensing material is changed. This mechanism is sensitively dependent on the interface composition between the clusters and metal oxide. These properties are difficult to study on polycrystalline or powder samples and therefore studies of metal clusters supported on single crystal metal oxide supports will be a way to increase our fundamental understanding of the complex interplay between cluster, support and gas phase.

In this review we describe a system that has been studied for other reasons as well as gas sensing. The Cu/ZnO system is of great importance because of its use as the methanol synthesis catalyst in low-temperature water–gas shift reactions and for hydrogen production from methanol in the reverse water–gas shift reaction. No matter what the original motivation, the outcome allows us to demonstrate the usefulness of these kinds of model system studies not only for applications in heterogeneous catalysis but also for gas sensing applications.

Physical vapour deposition of copper on the clean Zn-terminated polar ZnO(0001) surface has been demonstrated to proceed via a 3-D cluster growth mode (earlier studies suggested an initial 2-D growth, which was suggested to be possibly related to surface roughness of the sample). The clusters have a clear orientational relationship with respect to the hexagonal ZnO(0001) surface. This is apparent from three independent measurements: STM measurements, shown in Fig. 9a, of Cu clusters show hexagonal cluster shapes with the same orientation for all the clusters. For higher Cu-coverage LEED spots from the top face of the Cu-clusters are observed. These LEED spots correspond to a Cu(111) face and are superimposed on the LEED pattern of the ZnO(0001) substrate. The quite different lattice constants of the substrate and copper give a larger reciprocal space vector for Cu, but the relative orientation of the hexagons is the same (Fig. 9b). Finally X-ray photoelectron diffraction (XPD) also indicates the strict orientational relationship between the cluster and the substrate with the Cu(111) plane parallel to the substrate surfaces. XPD, however, also shows that there exist two cluster orientations rotated by 180° relative to each other.

The influence of Cu adsorption on the band bending and work function changes was investigated by photoemission spectroscopy. Fig. 10 shows the shift of the Zn-2p₃/₂ binding energy as a function of Cu coverage on the ZnO(0001) surface.

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**Fig. 9** (a) Scanning tunneling microscopy image of Cu-clusters grown by vapour phase deposition of Cu on a ZnO(0001) surface. The scan area is 70 x 70 nm. All the Cu-clusters show a hexagonal shape indicating that the clusters expose the Cu(111) face. Low energy electron diffraction (LEED) pattern of a Cu-deposit on ZnO(0001) is shown in (b). LEED spots from both, the ZnO substrate as well as from Cu(111) faces are present. Figure (b) modified from ref. 70.

**Fig. 10** Work function and binding energy of Zn 2p₃/₂ core level as a function of Cu coverage on the ZnO(0001) surface. The change in the Zn-core level position is due to a Cu-induced band bending. The difference between band bending and the change in work function is also indicated. The latter indicates the contribution of the surface dipole layer to the change in the work function. Taken with permission from ref. 66. © Elsevier 1998.
core-level and the change in work function as a function of Cu coverage. The shift in the Zn 2p\textsubscript{3/2} core level represents the Cu induced band bending in the ZnO substrate. The change in the work function has two contributions, the band bending and the interface dipole moment. In the case shown in Fig. 10 the change in the work function is an almost perfect mirror image of the band bending, indicating that the band bending is almost entirely responsible for the observed change in the work function. The sum of the negative band bending and the change in the work function is also indicted in the same figure. This curve represents the dipole moment at the surface. After a small initial increase in the band bending, possibly due to charge transfer from ZnO substrate to Cu, the substrate bands are bent upward by up to $-0.4$ eV. This upward band bending is explained by an alignment of the Fermi levels in the substrate and the Cu-deposit. Band bending is an accurate measure of the change in charge carrier concentrations in the valence band. An upward band bending causes a depletion of charge carriers in an $n$-type semiconductor. Therefore Cu deposition on ZnO should decrease the conductivity within the depletion zone, which commonly extends several hundred nanometers from the surface into the bulk.

In gas sensing applications we are interested in how the band bending induced by an additive changes due to its interaction with the gas phase. The most obvious chemical change of the additive is its oxidation or reduction as a consequence of a change in the oxidation potential of the gas phase. This has been examined by oxidizing Cu clusters similar to those shown in Fig. 9 in a UHV chamber by exposing the sample to an O-plasma. After oxidation the upward band bending was increased to $-1.6$ eV. This is a huge effect considering the band gap of ZnO of $\sim 3.4$ eV. Therefore this should result in a drastic reduction of the conductivity of ZnO gas sensors. For some samples charging of the surface was observed in XPS measurements after Cu-oxidation. This is additional evidence for a drastic decrease in surface conductivity.

In addition to measuring the band bending, photoemission spectroscopy can analyze the oxidation state of Cu. This is especially useful in the case where several oxidation states of the same element exist as is the case here. CuO and CuO have characteristic Cu-2p satellite-peaks and Auger LMM lines that allow discriminating the different oxides. The plasma treatment produces mainly CuO. Deposition of additional metallic Cu, by physical vapour deposition, allowed to reduce CuO to CuO. This is possible because the reaction of CuO $+$ Cu $\rightarrow$ CuO is exothermic and thus the surface copper oxide can be converted into CuO. The formation of CuO was confirmed by XPS. In this case the band bending decreased to $-0.9$ eV. Therefore, an upward band bending of $-0.4$ eV, $-0.9$ eV, and $-1.6$ eV is observed for Cu, CuO, and CuO clusters at the surface of ZnO, respectively.

It is also interesting to investigate the uniformity of the Cu-oxide formed at the surface. XPS at different emission angles of the Cu-2p core level. The sample was prepared by vapour depositing three monolayers of copper and subsequent oxidation in an O-plasma. The characteristic Cu-2p satellite peak for CuO is suppressed at larger polar angles. XPS is more surface sensitive at larger polar angles and therefore these results indicate that CuO is at the interface to ZnO and the surface contains Cu in a lower oxidation state, most likely Cu$_2$O.

Recent advances in the surface science of metal oxides and metal clusters supported on metal oxide surfaces have been supported sensitizers. Therefore more surface science studies of late transition metal sensitizers supported on single crystal metal oxide gas sensing materials are needed to gain insight in what phase and interface states result in what kind of gas response. Combinations of UHV sample preparation with controlled high pressure experiments may also be a way forward for studying the influence of different gases on the interface composition and structure of supported sensitizers.

4. Conclusions

Recent advances in the surface science of metal oxides and metal clusters supported on metal oxide surfaces have
increased our understanding in the interaction of the gas phase with these systems. Most of the research effort in this field has been motivated by applications in heterogeneous catalysis. Many of the questions that are being asked in catalysis research are, however, similar to the questions that need to be addressed to understand metal oxide gas sensing materials. Therefore many of the techniques and methods that are employed for model catalysts can also be applied to the study of metal oxide gas sensors. We are now at a stage where surface science studies can significantly contribute to our understanding of the relevant gas sensing processes. Ultimately, gas sensing is a molecular scale process. Consequently, to gain a basic understanding we need to investigate molecular/surface interactions at this length scale. Only the well-defined conditions UHV affords will allow us to make further progress for obtaining the sought fundamental description of gas sensing materials.

In this review we focused on two main aspects that are critical for metal oxide gas sensors. One is the formation and annihilation of oxygen vacancies and the other the importance of metal/oxide interfaces for sensitization of gas sensors. In both cases we have shown that surface science has the tools to address fundamental questions successfully. However, even apparently simple systems such as well-defined TiO$_2$(110) surfaces show complexity even for the interaction with a small molecule like O$_2$. Attempts to simulate more realistic environments by co-adsorption of more than one gas cause even more ambiguities and thus test our capabilities as surface scientists to understand processes occurring in real applications. Similarly, the interfaces between metals and oxides are extremely complex if we take the gas phase into account. For example, years of studies of the industrially important and here-discussed Cu/ZnO system by many surface scientists has not allowed us to come up with a consistent model for describing the synergy between the metal and the oxide for the gas phase shift reaction. Sensitization of metal oxides by late transition metals for gas sensing applications are potentially simpler than those in heterogeneous catalysis where complex reactions need to be activated at special surface sites. Nevertheless, more research is needed to fully understand the interaction of metal clusters with gas phase molecules and the dependence of the gas response on these interactions. It has been shown that the different oxidation states of the metal cluster and the associated change in band bending can be conveniently prepared under UHV conditions. This allows employing all the strength of surface science techniques for elucidating gas sensing mechanisms.

Many metal oxide gas sensing materials are polycrystalline and porous films. Therefore one may expect that other sites than those encountered on single crystal surfaces may become important, for example for O-adsorption. It appears, however, that single crystalline materials show the same gas responses$^{7,72}$ as these polycrystalline materials and thus no special sites need to be taken into account for explaining gas responses. The good gas sensing properties of novel single crystalline materials justifies the study of single crystal surfaces and in addition it has the prospect of building real gas sensing devices based on, for example, single crystalline epitaxial films. This would allow correlation of surface science characterization of the single crystal films with the actual gas response of the film. The measurement of the gas response is the information needed to truly combine surface science studies with gas sensing research.

References
