

Factors Governing Gas Sensing Characteristics of some Transition Metal Oxides

Pooja Nag and Kapil Sadani*

Abstract: Gas sensing with transition metal oxides is basically a surface phenomenon and an in depth understanding of the sensing mechanisms becomes necessary to analyse and model their adsorption characteristics. In this review article a study on the fundamentals of gas sensing principles in transition metal oxides (TMO) are presented.

Keywords: Transition Metal Oxides (TMOs), Doping, Adsorption.

1. INTRODUCTION

Transition metal oxides are technologically important materials that have found many applications e.g., in electronics, they are employed to make various thin and thick films for photovoltaics, as transistors, in gas sensing etc; in the chemical industry, these oxides are the functional components of catalysis used in large number of processes to convert hydrocarbons to other chemicals. Multicomponent transition metal oxides have also been employed to make high temperature superconductors.

Conductometric (resistive) metal oxide sensors comprise a significant part of the gas sensor component market. While many different approaches to gas detection are available [1– 23], metal oxide sensors remain a widely used choice for a range of gas species [1–5, 15, 24–34]. These devices offer low cost, fast response, high sensitivity and relative simplicity. With new varied applications of gas sensors emerging, these advantages make the use of metal oxide semiconductors almost indispensable especially in the field of portable devices. In the presence of a target analyte, a shift in the equilibrium state of the surface oxygen reaction is observed which in turn results in a change in the concentration of chemisorbed oxygen. This change is measured and recorded as a change in the conductance (resistance) of the metal oxide semiconductor gas-sensing material.

2. SURFACE REACTION MECHANISMS

When it comes to gas sensing, the diagram in the next page illustrate the factors which controls the rate of sensor response.

Possible processes, by which the gas-sensing properties can be controlled, have been presented in Fig. 1 [24]. The probable consequences of these processes for electro-physical and surface properties of metal oxides are presented in Fig. 2. It has been confirmed by research that the processes indicated in Fig. 1, including catalysis, reduction/reoxidation, diffusion and adsorption/desorption are relevant in gas sensors and influenced by structural parameters of the sensor material. This affirms that gas-sensing effects are structurally sensitive.

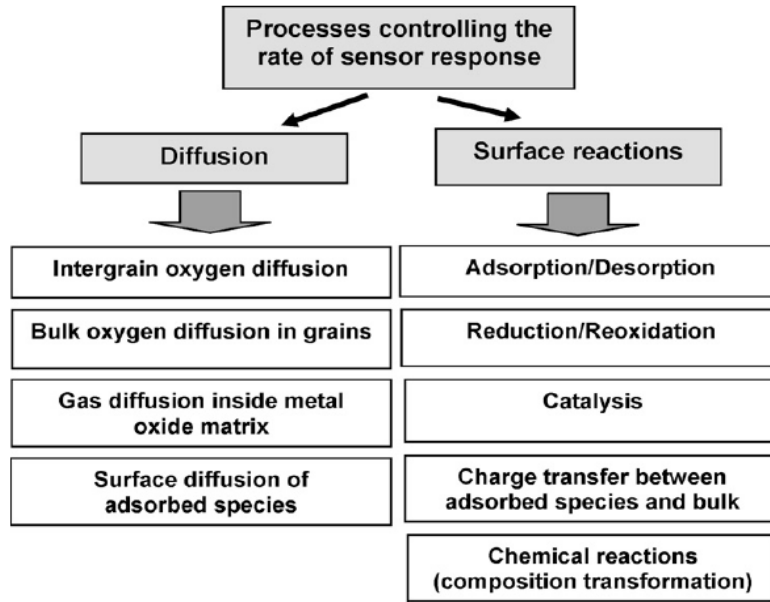


Figure 1: Processes controlling the rate of sensor response

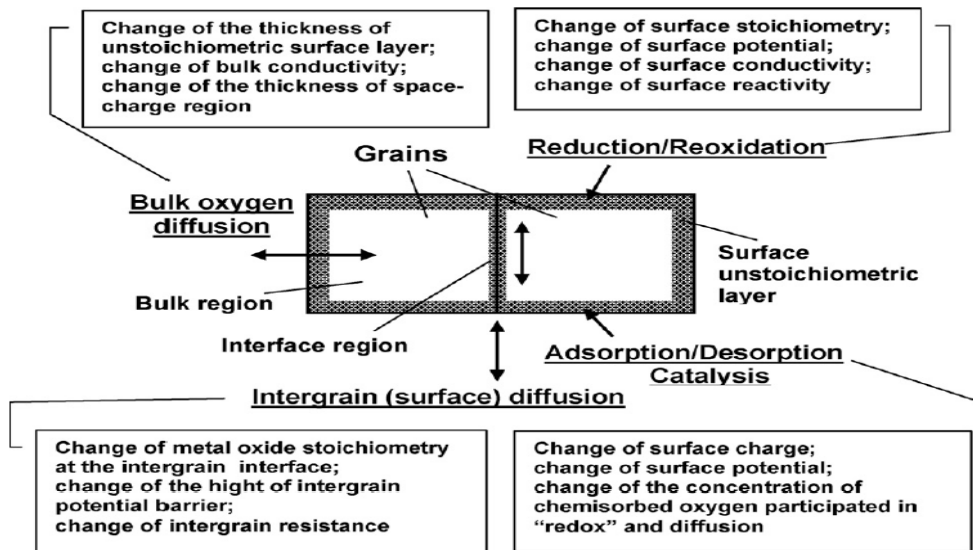


Figure 2: Gas Sensing Mechanism

Taking into account the complexity of the gas-sensing mechanism and its dependence on numerous factors, it becomes clear that we have to consider the influence of a great number of various structural parameters of metal oxide matrix on gas sensors' parameters. It has been shown in Refs. [25,35,36,37,38] that the influence of the above-mentioned parameters on gas-sensing characteristics takes place through the changes in the effective area of inter-grain and inter-agglomerate contacts, energetic parameters of adsorption/desorption, number of surface sites, concentration of charge carriers, initial surface band bending, etc.

3. CRYSTAL STRUCTURAL CLASSES OF SOME TMOS

An examination of the known structures shows that transition metal oxides exist in many different crystallographic forms. There does not appear to be a simple generalization that relates the structure

to the stoichiometry or the position in the periodic table. In fact, it is not uncommon to find a certain oxide in more than one crystal structure at ordinary temperatures. Oxides commonly studied as catalytic materials belong to the structural classes of corundum, rocksalt, wurtzite, spinel, perovskite, rutile, and layer structure. The rocksalt structure is made up of a three-dimensional array of alternating cations and anions (Fig. 3a). Each ion is in the centre of an octahedron whose vertices are ions of the opposite type. The structure can be viewed as being made up of corner-sharing octahedra (Fig. 3b). A wurtzite structure is made up of a three-dimensional net of corner-sharing tetrahedra (Fig. 3 c, d). Each ion is in the centre of a tetrahedron in which the opposite ions are at the vertices.

Many transition metal ions possess multiple stable oxidation states. Among these elements, four have unusually large number of stoichiometries - they are Ti, V, Mo and W. The structures are very similar and can be constructed from the same building blocks. This contributes to the easy conversion of one oxide to another of adjacent stoichiometry by oxidation or reduction. The easy oxidation and reduction, and the existence of cations of different oxidation states in the intermediate oxides have been thought to be important factors for these oxides to possess desirable properties in selective oxidation catalysis. Zinc oxide which happens to be the focus of this thesis exists primarily in two forms: a) the zinc-blende and b) wurzite as illustrated in Fig. 3c .

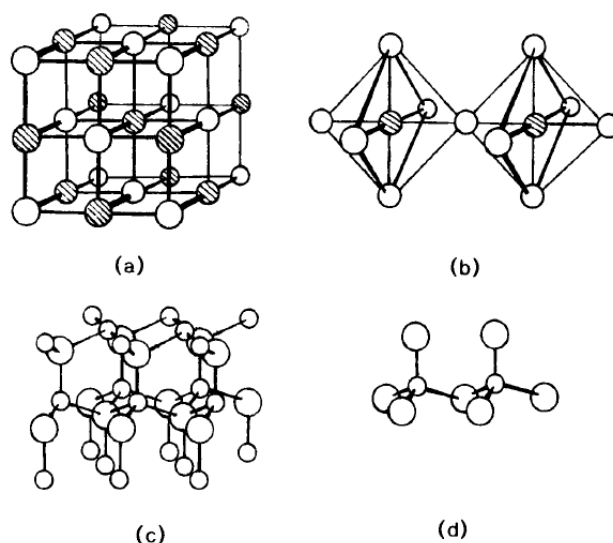


Figure 3: (a) A rocksalt structure (b) Two corner-sharing octahedra, one centered around ion A. (c) A wurtzite structure (d) Two corner-sharing tetrahedra, one centered around ion C.

Sensing properties of zinc have been in study for almost seven decades. Various dopings, electrode geometries, specific orientations of films and sensor technologies with optimum performance have been tried with zinc oxide, however all of the above requiring very costly infrastructure and facilities added to the cost of the noble metal dopants which are no way cheap. Our focus is primarily to develop very low cost but new sensor materials. Going by the above crystal theory it may be noted that Mo and W, theoretically would enhance the selective response of zinc oxide to various analytes and hence this study focuses on the effect of doping Mo and W in the sensing characteristics of ZnO.

4. STABILITY AND RECONSTRUCTION OF METAL OXIDE SURFACES

The positions of the surface ions may or may not be the same as those defined by simple extension of the bulk structure, depending on whether the free surface reconstructs or not. The driving force for

reconstruction is to lower the surface Gibbs energy per unit surface area to attain a thermodynamically more stable system. A thermodynamically stable surface structure will not reconstruct on heating, provided that the temperature is not too high, while a metastable surface would usually undergo reconstruction. In the absence of knowledge of surface Gibbs energy, it is useful to develop qualitative guidelines as a first approximation to compare the stabilities of different surface structures. If the surface plane contains a stoichiometric ratio of cations and anions, the surface will be dipoleless and it is called a nonpolar surface. If they are not, the surface will probably (but not necessarily) possess a strong dipole and the surface is a polar surface. Examples of polar surfaces are wurtzite (0001) (ZnO polar surfaces) and (0001) and rocksalt (111) surfaces.

5. SURFACE COMPOSITION AND ORIENTATION: IONICITY AND MAGNETISM

The surface composition of a single component oxide is determined by the surface anion to cation ratio, which, for an ideal surface, depends on the stoichiometry of the oxide and the orientation of the exposed crystal plane. It is often important to determine whether or not a surface is stoichiometric. Nonstoichiometry often arises from preferential removal of surface oxygen leading to a slight reduction of the surface. The extent of nonstoichiometry depends on the pretreatment of the sample. Stoichiometric surfaces can often be obtained for surfaces that have low surface energies (the stable surfaces) by low temperature annealing.

The magnetic properties of an ion or atom are determined by the orientation and the number of its electron spins. For transition metal oxides, the individual electrons are so strongly correlated in their motion that the spin of an ion is better characterized by one total spin (atomic spin) than the individual electron spins. Fig. 4 shows the types of magnetism commonly found in transition metal oxides, and the associated spin orientations.

Diamagnetism is related to changes in the orbital motion of electrons that occur when atomic systems are placed in a magnetic field. This induced motion of electrons (or currents) is set up in such a direction as to oppose the change in the magnetic flux, and persists as long as the magnetic field is present.

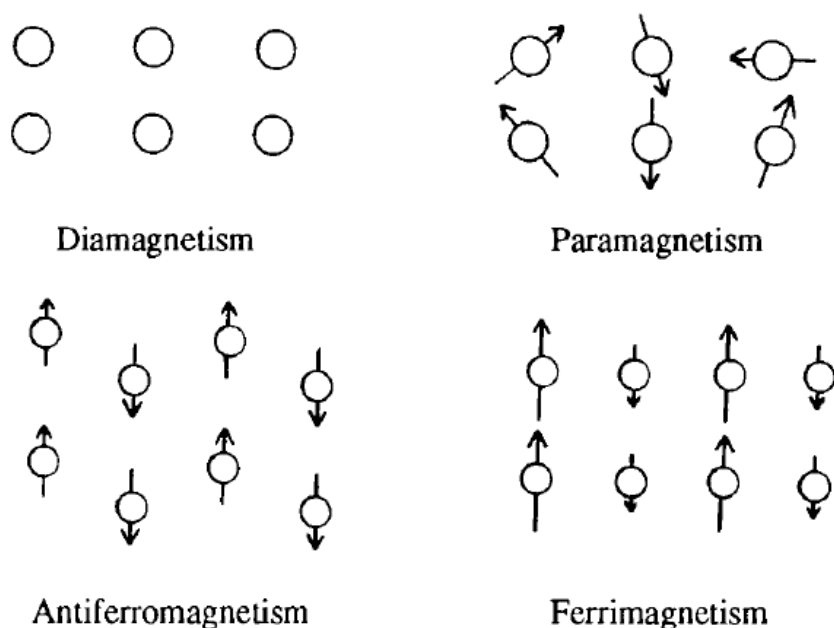


Figure 4: Types of magnetism present in oxides: Direction of arrows indicate spin directions

Paramagnetism is related to the tendency of a permanent magnetic dipole to align itself parallel to a magnetic field. In transition metal ions, the permanent magnetic moment is associated with coupled electron spin and orbital motion of partially filled shells. The magnetic susceptibility decreases with increasing temperature because thermal motion tends to randomize any spins that are aligned by the external field.

In a ferromagnetic material, the interaction among spins is so strong that the magnetic moments are aligned parallel to each other. Such an internal interaction is called exchange field. However, few oxides are ferromagnetic. In a simple antiferromagnetic material, there are two sets of strongly correlated spins that form two spin sublattices of equal magnitude but opposite orientations.

The magnetic susceptibility of such transition metal oxides is a strong function of temperature and thus has a very strong influence of their sensing characteristics. The temperature dependence of the magnetic susceptibilities is depicted in the following figure.

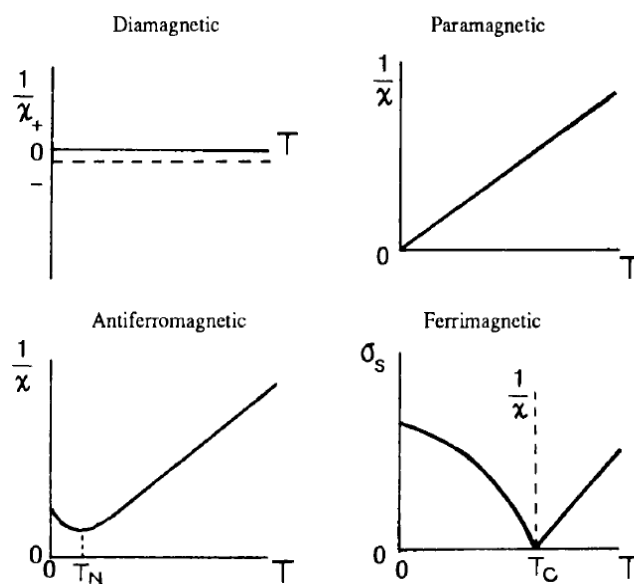


Figure 5: Temperature dependence of magnetic susceptibility for different types of magnetism.

6. SURFACE ELECTRONIC STRUCTURE

Knowledge of the detailed surface electronic structure is critical in the understanding of the chemisorptive and catalytic properties of oxides. The bulk electronic structures have been studied for a number of oxides [39]. Studies on surfaces have been concentrated on the detection of electronic states not found in the bulk that are generated by the presence of the surface. These states are called surface states. The energy of the surface states of interest in catalysis commonly lies near the Fermi energy of the solid (or valence states). These surface states are either partially filled with electrons so that they can both donate and accept electrons from the molecules interacting with the surface, or close enough to the filled valence band (or empty conduction band) such that together, they provide a pair of states to accept and donate electrons to the interacting molecules simultaneously. Consideration of electron bands in the solid is also important in photo-enhanced adsorption, desorption, and catalysis. The reduction of the ionic charges of the surface results from the downward shift in energy of the surface orbitals compared to the corresponding bulk orbitals and the enhanced covalency of the cation-anion bond, as well as the polarization of the surface orbitals by the surface electric field. The surface-induced changes in the electronic properties are strongly localized in the outer few layers of the surface regions.

7. ADSORPTION OF SMALL MOLECULES

In general, molecules may interact with an oxide surface in the following different ways:

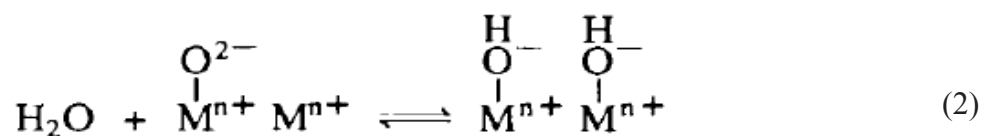
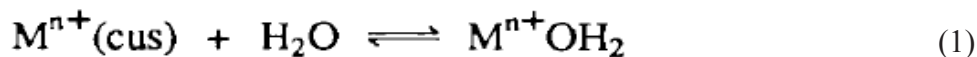
- (1) Molecular (nondissociative) adsorption in which the interaction is mainly by σ -donation and/or π -bonding interaction. This can take place on a single surface coordinatively unsaturated ion.
- (2) Dissociative adsorption in which a molecule dissociates upon adsorption. Dissociation of H_2O into H^+ and OH^- upon adsorption is an example of heterolytic dissociative adsorption in which the molecule is dissociated into charged species. This type of adsorption usually requires an anion-coordinatively unsaturated pair site. Homolytic dissociative adsorption in which neutral species are formed may also occur but less frequently.
- (3) Abstractive adsorption in which the adsorbate abstracts a species from the surface (often a proton). This commonly occurs on acidic oxides. If a proton is abstracted from the surface and the adsorbed species becomes cationic, the adsorbate could be held to the surface by electrostatic forces, and coordinatively unsaturated ions might not be involved.
- (4) Reductive adsorption in which an adsorbed molecule is oxidized while the surface is reduced. It may also be abstractive as in the case when a hydrocarbon molecule is oxidized on adsorption to a carboxylate utilizing the lattice oxygen while reducing the cation.

7. THE ROLE OF ADSORBED OXYGEN

Adsorbed oxygen may be present as atomic or molecular species with various charges. On transition metal oxides, the most common species are O , O^- , O_2 and O_2^- . Depending on the sample history, it is possible that there are oxygen atoms, either neutral or charged, on an oxide surface that are in positions different from the positions of surface lattice oxygen ions. These oxygen atoms and ions may have different charges than the lattice oxygen, have different energies of binding (or adsorption), and be desorbed at different temperatures. Adsorbed oxygen on a stoichiometric surface of a fully oxidized oxide is readily identifiable. It is usually desorbed at temperatures lower than the sublimation temperature of surface lattice oxygen. On a partially reduced surface, adsorbed oxygen may result in re-oxidation of the surface cations to different degrees, depending on the extent of charge transfer between the reduced centre and the adsorbed oxygen. If the charge transfer is such that an adsorbed oxygen atom acquires the same electron density as a surface lattice oxygen ion, and it occupies a lattice site, the surface is reoxidized and the adsorbed oxygen becomes a lattice oxygen. If the charge transfer is less extensive and/or the oxygen species occupies a site different from a surface lattice site, it is adsorbed oxygen. In general, atomic oxygen species are adsorbed more strongly than molecular species. This is because strong surface-atomic oxygen bonds are needed to compensate for the energy required to break the double bond of the oxygen molecule. The rate of dissociative adsorption of oxygen to atomic species is expected to be lower than that of molecular adsorption. Adsorbed O^- is a very reactive species. It reacts readily with alkanes at low temperatures on a number of oxides including ZnO , vanadia, and molybdena.

8. THE ROLE OF ADSORBED WATER

Co-ordinatively unsaturated sites are responsible for chemisorption and binding of molecules to a surface in most instances. Indeed this explains very well a variety of phenomena including poisoning of a surface, competitive adsorption, and the common requirement of heating of an oxide to activate it for chemisorption and catalysis. Activation of an oxide by heating is needed because of the strong adsorption of water on oxides. Thus an oxide surface becomes fully covered with adsorbed water and hydroxyl groups once it is exposed to the moisture in the atmosphere. This process is shown by eq. 1 and 2:



In eq. (1), water is adsorbed molecularly to satisfy the coordinative unsaturation of the metal ion. In eq. (2) the coordinatively unsaturated cation and anion pair adsorbs a water molecule dissociatively as OH⁻ and H⁺. These surface ions become coordinatively saturated and unable to adsorb other molecules. Heating causes removal of water and formation of surface coordinative unsaturation. The extent of dehydroxylation depends on the sensor operating temperature, and is found to be especially true for ZnO. The water that is lost at low temperature are weakly adsorbed water. It is probably non-dissociatively adsorbed water that is lost by a process similar to the reverse of eq. (1), as well as water held to the surface by hydrogen bonding. A rapid loss of water occurs around 200 to 350°C and this thus explains the higher operating temperatures of some TMO's.

9. ADSORPTION OF CO_x AND NO_x

Oxides of carbon (especially carbon-monoxide) is a rather common probe molecule in the study of the surface chemistry of transition metal oxides. Adsorption of CO on noble metal sites in nanostructured oxides is much stronger than on undoped oxides. CO is adsorbed dissociatively on transition metals at the left of the Periodic Table. Dissociative adsorption of CO on oxides has not been reported. Instead, oxidation of CO to CO₂ or carbonate occurs. NO is another probe molecule commonly used to study transition metal oxides. Except for one additional unpaired electron, it has an electronic structure similar to CO. Thus in many ways its adsorption is similar to that of CO, and occurs on surface Mⁿ⁺(cus) ions, although its adsorption is often stronger.

10. CONCLUSION

Currently metal oxide semiconductor sensors find limited commercial use; other types of sensor are favoured for many applications. However, with recent advances in understanding of materials chemistry and synthetic techniques, their properties, coupled with their relative low cost could lead them to becoming ever more important devices in industrial and / or environmental online monitoring or for customised electronic nose or biological samples' studies. In this paper are compiled principles of surface science which I believe are very significant when it comes to sensor development using transition metal oxides.

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