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Introduction

With today’s detector techniques and electronics we are able to record signals from our surroundings much in the same way as the living body does it with its five senses. In this view a gas sensor is an electronic nose. Similarly, a microphone is an electronic ear, and further, thermometers, various pressure sensors, different types of cameras and chemical sensors are other electronic senses. Some of these operate in close analogy with human senses like the CCD image sensor that records the visual information in the same way as the retina does it in our eye. There are, of course, many signals which we are able to electronically detect beyond the ability of human sensing, such as electric and magnetic fields, different kinds of radiation, etc.

A common feature in the human and electronic sensing is the transducing of signals to the electrical form. Further similarities are found in the signal transfer, there the main difference being that in a living body the electrical signals are mostly carried by ions instead of electrons. But, in processing and storing of the information the analogies are less. However, it seems that sometimes we can find solutions to technical problems by imitating biosystems.

Electronic nose

An electronic nose is used to recognize simple or complex odors. It is an instrument, which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern-recognition system, which may be based on neural networks. The partial specificity means response broadly to a range or a class of gases. This is unlike to the ideal gas sensor, which should respond to a single gas only with a unique output. One can imagine a broad field of applications for such a nose, that range from replenishment or replacing the human nose on areas of food testing (freshness) or perfume industry, to many others in recognition, forewarning and control applications.

Computational models and methods

In a semiconductor gas sensor, the chemical signal is transduced through the microstructure of the ceramic semiconductor into the resistance change. Therefore, the metal-oxide n-type semiconductors are common sensing materials. For basic understanding of a chemical sensor one needs to separate the receptor function which recognizes the chemical substance, and the transducer function which transforms the chemical signal into an electric output signal. Catalytic surface reactions form the basis for the receptor function of the sensor. The natural diversity of semiconductor surfaces for different catalytic reactions makes semiconductor gas sensors very promising for different electronic-nose applications.
Localized structures and phenomena ignore the periodicity, and thus, yield a molecular electronic structure with discrete one-electron levels. If the band structure of the continuum levels at the surface is essential, one has to invoke the slab models and intrinsically periodic methods.

The case we have chosen to present here is the stannic oxide (SnO₂) and (110) surface to illustrate some basic aspects of the gas sensor surface phenomena. SnO₂ is one of the most applied materials and the stable (110) face is its nonpolar surface that can be studied even in its bulk derived geometry without relaxation. Nitrogen oxide (NO molecule) is taken as an example of the adsorbate and chromium (Cr atoms) as an example of an impurity used to dope the SnO₂ semiconductor. The adsorption and doping effects can be examined as local phenomena to the extent where a cluster model in Fig. 1 is adequate [1].

For such a large cluster the density functional method with the local density approximation (LDA) is the method of choice, if an ab initio level approach is desired. CSC offers a collection of good commercial software, of which we have mostly been using DMol and DSolid from Biosym, but also academic codes have been employed for more specific purposes. Very briefly, these SCF ab initio methods are based on the linear-combination-of-atomic-orbitals (LCAO) theory and basis functions in numerical form from atomic and ionic calculations. A description of the methods can be found from CSC News, March 1995 issue, for example.

Cr-doped SnO₂

The band gap of bulk SnO₂ is about 3.6 eV, and roughly, the valence band maximum is created from 2p levels of oxygen and the conduction band minimum from 5s levels of tin. There are some surface states (levels) in the band gap, of which many are related to the missing bridge oxygen atoms. There are also gap levels arising from the finite size effect of our small cluster, i.e., there is more surface than only the intended (110) surface. All this can be nicely seen in the level map in Fig. 1. Chromium impurities in SnO₂ have a strong effect on the electrical properties both in the bulk and at the surface.

Fig. 1. Geometry of the Sn₂₈O₇₁Cr₄ cluster (in C₂ᵥ symmetry) modeling the (110)-1x1 surface of SnO₂. Cr atoms as dopants substitute some of the Sn sites and a NO molecule is placed as an adsorbate on a probable surface site. The bridge oxygen sites are assumed to be occupied in usual conditions. The calculated "molecular" one-electron level structure (without the adsorbate) at the "band gap" region is shown below. Part of the population analysis (the strongest atomic orbital component of each level) is also shown [1].
face. It is a consequence of Cr 3d levels, which emerge in the band gap. The bulk impurities cause the deep levels near the valence band and the surface impurities create levels in the middle part of the gap. Both of these level types behave as conduction electron trap in an n-type SnO₂ semiconductor. This explains, for example, why Cr impurities have so strong effect on the conductivity of polycrystalline SnO₂ film.

**NO dissociation on SnO₂ surface**

Chromium impurities in SnO₂ have a strong effect on the catalytic properties, too. It seems that the high reactivity of Cr ions at the surface is responsible for the enhanced adsorption and dissociation of NO. We can start the analysis from the one-electron orbitals of the NO molecule, shown in the Fig. 2.

The bond in the NO is formed by the fully occupied bonding 1p and 5s orbitals and weakened by one electron in the antibonding 2p* level. Thus, the bond is something between the triple bond of N₂ and double bond of O₂. Further occupation of antibonding levels would weaken the bond, and in fact, dissociation of free NO implies degeneration of the 1p, 5s, 2p* and 6s* levels to the atomic 2p levels, thus decreasing (increasing) the occupation of bonding (antibonding) levels. This is also the mechanism of the NO disso-

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**Fig. 2.** Calculated one-electron levels of free NO molecule and the SnO₂-Cr clusters with and without the NO adsorbate. Only the levels originating from NO or Cr are shown explicitly [1].

**Fig. 3.** Conductance of pure, Sb- and Al-doped SnO₂ thick-film samples in dry synthetic air as a function of inverse temperature measured at acooling (- - -) and heating (___) rate of 2.4 Kmin⁻¹ [2].
cation on the Cr activated SnO$_2$ surface, though energetically much more favorable than the dissociation of free NO. In Fig. 2 it is seen how NO 1p, 5s and 2p* orbitals hybridize with the Cr 3d levels leading to slightly decreased occupation of bonding and strongly increased occupation of antibonding molecular orbitals. This is actually the conventional picture of transient formation of an NO- ion with increased occupation of 2p* in catalytic reduction of NO.

**What next?**

Surface relaxation and even reconstructions are known to be large for some compound semiconductor surfaces. Usually they are also essential in tuning the catalytic activity through adjusting the polarity and dangling bonds and other factors in the surface density of states. In the present case removal or adding the bridging oxygen atoms, the pink ones in Fig. 1, change the surface relaxation considerably. This is under investigation at the moment. For instance, we want to establish the role of the bridging oxygen atoms in the irreversible conductance behavior of different doped SnO$_2$ samples in Fig. 3 [2]. During heating, the conductance of all the four samples with very different surface concentration of electrons turn to decrease at exactly the same temperature of 280 °C. Therefore, the behavior origins from structural surface changes which naturally relate to oxygen balance at ionic oxide surfaces. In the case of CO exposure, for instance, conductance changes of the samples in Fig. 3 follow the exposure only at temperatures above 280 °C, and now the structural surface changes have also a close relation to the catalytic properties of the surfaces.

Though static geometries give certain understanding of surface processes in the long run with increasing computational resources we will be able to study more dynamical aspects at the *ab initio* level. This could be done by *ab initio* molecular dynamics or through evaluation of potential energy hypersurfaces, for example.

**References**
