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Surface Chemistry of Semiconducting Metal Oxides, Viewed at the Atomic Scale

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Abstract:
The adsorption of molecules at the surfaces of semiconducting metal oxides, and the related charge transfer to and from the material, lies at the heart of chemical sensing. With surface-science techniques such process can be directly followed, one molecule at a time,. Although these experiments are conducted in conditions that are remote from 'real' systems, i.e., usually on flat, macroscopic, single crystals and in ultrahigh-vacuum conditions, they give powerful insights into fundamental processes and phenomena, especially when combined with first-principles theory. We discuss recent results from atomically resolved Scanning Probe Microscopy, with special emphasis on the adsorption and charge transfer of O_2, water, CO, and small organic molecules on TiO_2, In_2O_3, and iron oxide surfaces.

Key words: Metal oxides, surface science, adsorption, charge transfer, Scanning Probe Microscopy.

Gas sensing with semiconducting materials is based on the charge transfer that occurs when molecules adsorb on the surface [1].

Recent progress in the surface science of metal oxides shows how one can give direct and unequivocal insights into such processes. As a precondition for such experiments, 'well-characterized' systems are needed, i.e., samples - usually macroscopic single crystals - with flat surfaces that have a known structure and can be prepared with controlled types and amounts of defects. It is now known how to reproducibly prepare the low-index surfaces of relevant metal oxides, including TiO_2 [2], SnO_2 [3], ZnO [4], Fe2O3 [5] or In_2O_3 [6].

Equally important is a controlled gas atmosphere. Surface-science experiments are usually conducted in ultrahigh vacuum, i.e., at pressures of 10^{-10} mbar or less. This allows taking images with atomic resolution in Scanning Tunneling Microscopy (STM), and more recently, non-contact Atomic Force Microscopy (AFM). Here the adsorption of single molecules can be followed, the adsorption site can be identified, and reactions can be monitored, or even instigated, using the STM tip. The microscopic information is best supplemented by area-averaging spectroscopies, based on, e.g., photoemission or thermal desorption. The experimental results are then directly comparable to computational modeling using density functional theory (DFT) based methods.

A recent overview of these developments is provided in ref. 6, which discusses the importance of point defects for surface chemistry. Typically O vacancies are considered [2] but cation vacancies [8] or adatoms [6] are often equally important. The interaction between the surface and the bulk of the material is highly relevant in oxidation and reduction processes.

Figure 1 shows one example of the type of results that can be obtained. Here, nc-AFM is used to image the (101) surface of single-crystalline anatase TiO_2 [8]. To slow down diffusion, and to suppress thermal noise, experiments are conducted at low sample temperatures (here 5 K). Shown in Fig. 1b is the surface after exposure to a small amount of molecular O_2. Most molecules physisorb, but a few of them become spontaneously charged. Likely, the electrons stem from Nb impurities in the sample [9]. The charged and neutral O_2 are easily identified according to their interaction with the tip, as is shown in representative force-distance curves taken on top single molecules (Fig. 1c). While the physisorbed O_2 desorbs around 70 K, the negatively charged species are strongly chemisorbed and do not leave the surface when the sample temperature is raised

to 300 K and above; these also give rise to a small but significant upwards band bending of ~0.2 eV.

The AFM image in Fig. 1b was taken under conditions where no current flowed between the tip and the sample. When a small positive sample voltage was applied, and electrons were injected into the O_2, molecules could be charged judiciously. Interestingly, the bias voltage needed for charging increased with the number of O_2^- already present on the surface. Reversing the sample bias and thus discharging the O_2^- results in desorption; irradiation with UV light instigates both processes simultaneously.

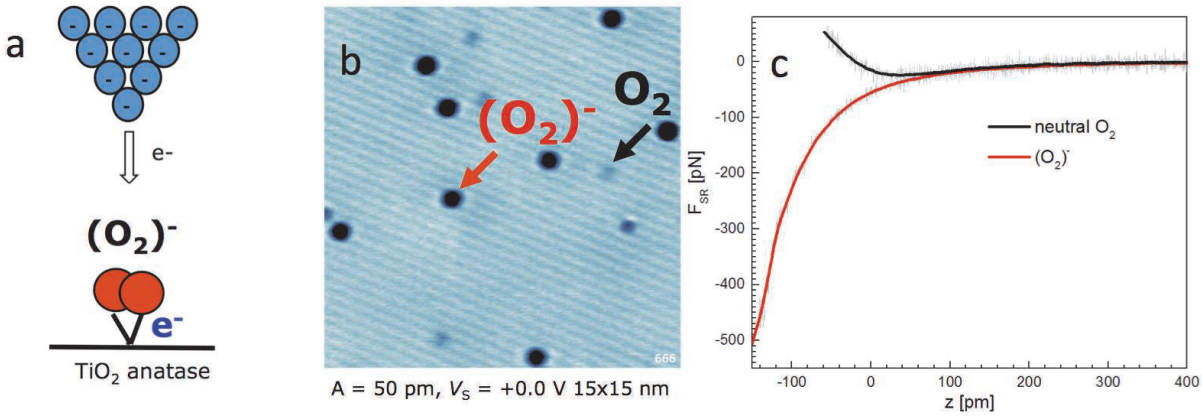

Figure 1. Example of atomically-resolved information that can be gained with surface-science techniques. (a) Schematic of the experiment. The sharp tip of an atomic force microscope (AFM) is used to sense the presence of molecular oxygen, adsorbed on a single-crystalline TiO_2 anatase (101) surface. (b) Atomically-resolved AFM image, taken at 5 K. Two types of O_2 molecules, charged, chemisorbed and neutral, physisorbed species, exhibit a clear contrast in frequency shift. (c) Force-distance curves taken on top of the two types of O_2 molecules. For a full description of the work, see ref. [8].

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