Characterizing solid state gas responses using surface charging in photoemission: water

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LETTER TO THE EDITOR

Characterizing solid state gas responses using surface charging in photoemission: water adsorption on SnO$_2$(101)

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Abstract
A novel experimental approach for studying the gas response mechanism of semiconducting gas sensor materials is demonstrated using the example of water adsorption on SnO$_2$(101). In this approach, valence band photoemission as a chemical probe is combined with photocurrent induced surface charging as a basis for contactless sample conductivity measurement.

(Some figures in this article are in colour only in the electronic version)

Solid state gas sensors, based on the adsorbate dependent electrical conductivity of semiconducting metal oxides, are widely used for detection of harmful gases. In spite of this important application, there remain open questions regarding the interaction of molecules with gas sensing materials. Simultaneous measurement of the gas response and the determination of molecular adsorption properties are required for a better understanding of gas sensing mechanisms. In this letter, we introduce a novel experimental approach as a basis for a contactless measurement of a gas sensing material's conductivity change upon gas exposure. It can easily be implemented in a conventional photoemission experiment and provides valuable insights into the molecular mechanisms that govern gas sensing.

Stannic oxide (SnO$_2$) is the prototypical solid state gas sensor material. Acceptor-like or donor-like adsorption of molecules results in charged adsorbates, which induce a band bending of the energy levels in semiconductors [1, 2]. The resulting variation of charge carriers in the conduction band causes a detectable change in conductivity or 'gas response'. The sensitivity of SnO$_2$ to humidity in ambient air is an unwanted side-effect for many applications. It is well established that water adsorption on SnO$_2$ results in an increased conductivity and generally the formation of OH$^-$ surface species is invoked [3–6]. The presence of water at the surface also influences the detection of other gases [7, 8]. Thus for fundamental as well as practical reasons it is important to understand the interaction of water with SnO$_2$ surfaces and the gas response that it induces.

Commonly the conductivity change of the gas sensing material upon gas exposure is studied by means of four-point probe measurements. This method, however, does not contain any information about the chemical state of the adsorbate. Such data are often gathered

independently, from electron spin resonance measurements, and subsequently correlated with the conductivity changes [9]. Photoelectron spectroscopy can be used to evaluate the band bending induced by adsorbates via measuring the shift in core level positions and simultaneously obtain information on the alignment of the adsorbates' orbitals with respect to the valence band of the solid. Although the band bending is directly related to the conductivity change in most practical applications it is impossible to deduce the magnitude of the conductivity change from the amount of band bending alone. This is mainly because of unknown defect levels in the semiconducting oxides that preclude calculating the change in charge carrier concentration from a shift in the Fermi level. Here we utilize surface charging to evaluate the conductivity change of $SnO_2(101)$ single-crystalline samples. Charging effects are usually considered a nuisance in photoelectron spectroscopy studies of poorly conducting materials and they are rarely used as a basis for an analytical technique. Exceptional cases are the use in surface charge spectroscopy in evaluating insulator/semiconductor interfaces [10, 11] and in depth profiling in mesoscopic layers, by exploiting a linearly decaying electrical potential perpendicular to a thin film [12]. The principle of the technique described here is simple (see figure 1). The withdrawn photoelectrons are replaced by a photocurrent through the sample. According to Ohm's law, the current results in an increase in potential between the sample's surface and the sample holder that is held close to the ground potential. For good conductors, this potential increase is negligible. For highly resistant materials, however, it can result in a substantial build-up of surface potential. As a consequence, the kinetic energy (relative to the ground potential) of the photoemitted electrons shifts uniformly. By measuring the shift in photoelectron spectra (the surface potential) in conjunction with the photocurrent and applying Ohm's law, we obtain a measure for the sample resistance. For typical photocurrents of $\sim$10 nA a resistance of 10^8–10^9 Ω allows observing a finite peak shift; this range may be extended by choosing an appropriate photon flux. In this study the resistance of a single-crystal SnO_2 sample was controlled by annealing it in 10–100 mbar O_2 at $\sim$600 K.

Photoemission measurements were carried out in the end station of the 3 m TGM beamline at CAMD, Baton Rouge, LA. The samples were cleaned in UHV by 1 keV Ar^+ sputtering and annealing to $\sim$900 K. Subsequently, the sample was transferred to an attached chamber without breaking vacuum and was exposed to 10–100 mbar O_2 at $\sim$600 K sample temperature. Upon re-transfer into the end station the sample was briefly annealed to 600 K to desorb any water that may have adsorbed during the high pressure treatment and then cooled to $\sim$110 K and photoemission spectra were acquired. The sample preparation procedure was repeated until the conductivity was low enough for observing significant surface charging. Oxygen annealing was also necessary to obtain a stoichiometric (101)-1 $\times$ 1 surface [13–15]. Water was dosed via a precision leak valve. The valence band spectra shown were taken for conductive samples that did not exhibit charging even at low temperatures. These spectra were compared to valence band spectra from highly resistant samples. For such samples the binding energies were referenced to the known Sn 4d core level position. This procedure gave for the valence band of highly resistant samples results identical to those obtained for conductive samples. The work function was evaluated by measuring the secondary electron cut-off. Difference spectra were calculated by subtracting a normalized reference spectrum of a clean surface from spectra of samples with different water exposures.

Figure 2(a) shows photoemission and difference spectra taken at a photon energy of $h\nu = 65$ eV for a conducting sample without peak shifts for reduced and stoichiometric surfaces. Water was adsorbed at 160 K. At this temperature multilayers do not form and monolayer adsorption is characterized. In the difference spectrum a signal for the OH 3σ orbital is observed. This is a clear fingerprint for dissociative water adsorption [16, 17]. Figure 2(b) shows the change in work function and the band bending upon water adsorption at 110 K.
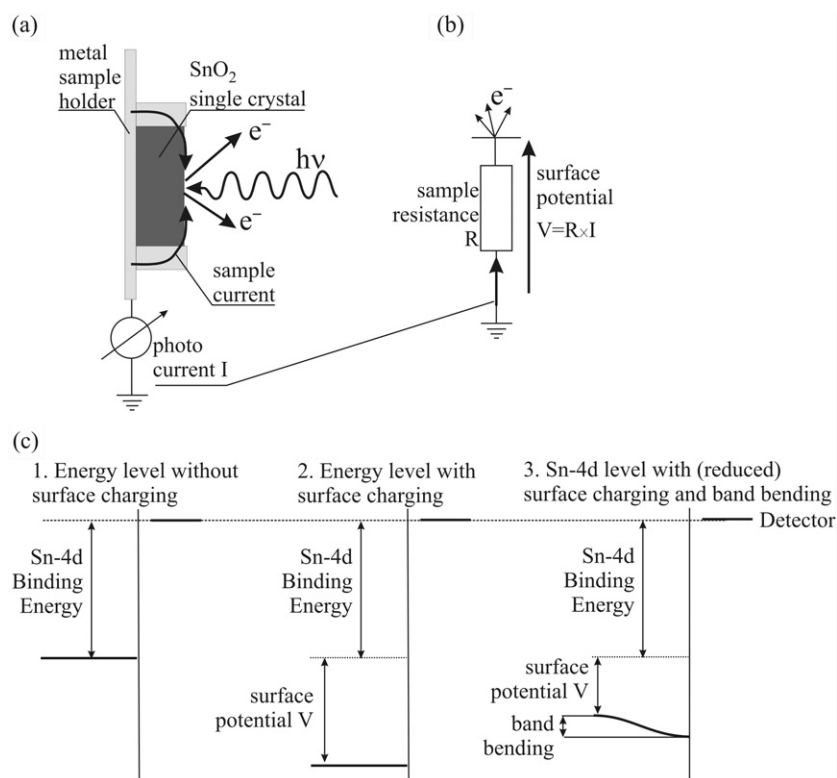
Figure 1. Schematic diagrams of the experimental set-up and measurement of the sample resistance. Photoemitted electrons are compensated by a current through the sample. This photocurrent is measured between ground and the sample holder (a). For a non-negligible sample resistance the withdrawn photoelectrons from the sample surface result in surface charging (surface potential) (b). This surface potential causes a shifting of the energy levels of the sample relative to the ground potential of the detector and thus measuring of e.g. the Sn 4d level allows detection of the surface potential (c). Increased sample conductivity caused by an adsorbate induced downward band bending results in a reduced surface charging as is indicated in (c-3). In this latter case the measured energy level is the sum of the charging induced surface potential and band bending.

The change in work function can be almost entirely attributed to the downward band bending induced by water adsorption. Thus the adsorbed water is not expected to have a net dipole moment normal to the surface. The strong downward band bending implies an increased conductivity of the sample. This was evaluated for a sample that was made less conductive by annealing in oxygen, and which consequently exhibited significant surface charging. The inset in figure 3 shows the kinetic energy of photoelectrons emitted from the Sn 4d core level. At room temperature the sample does not charge up and the core level is at its expected position. Cooling the sample causes a drop of the sample conductivity and consequently a significant peak shift is observed[1]. Subsequent exposure to water reduces this shift indicating an

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[1] Pure SnO_2 is an n-type semiconductor with its charge carrier originating from intrinsic dopants such as oxygen vacancies and Sn interstitials. Oxygen annealing decreases the defect concentration and thus the n-type dopant level. Theoretical results predict donor levels due to Sn interstitials to lie 203 meV above the CBM and thus to spontaneously ionize and donor levels due to oxygen vacancies to lie 114 meV below the CBM (Kiliç and Zunger [18]). Experimental results suggest an activation energy for charge carriers of ∼150 meV (Marley and Dockerty [18]). Our observation that surface charging in photoemission spectroscopy is strongly dependent on the sample temperature is consistent with a thermally activated charge carrier concentration.
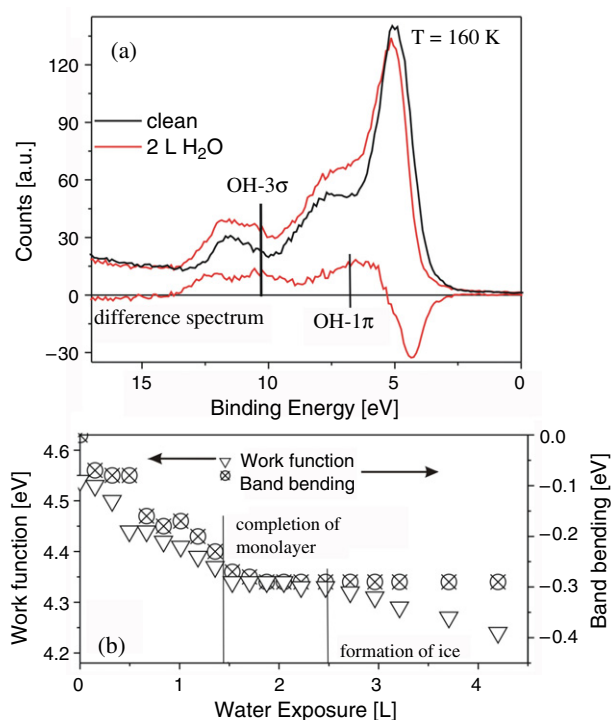
Figure 2. (a) Valence band photoemission and difference spectra for water exposures at 160 K sample temperature for the $SnO_2(101)$ sample. The orbitals for dissociated water (OH^-) are indicated. (b) Work function and band bending measured with photoemission as a function of water exposure at 110 K.

increase in the sample conductivity. The peak shift ceases upon adsorption of ∼1 L and further adsorption only results in the expected attenuation of the core level intensity with increasing water coverage. Figure 1(c) illustrates schematically the different contributions to the Sn 4d energy level position relative to the potential of the electron detector. In the data presented in figure 3 the sample resistance never attains a low enough value to avoid sample charging entirely. Figure 3 also shows the sample resistance, estimated from the amount of peak shift (surface potential) and the photocurrent drawn from the sample, as a function of water exposure. It changes by about one order of magnitude as a response to adsorption of ∼1 L of water.

In order to apply surface charging correctly for evaluating gas sensing responses, one needs to consider other effects that might change the position of core levels. Firstly, the amount of core level shift is the sum of the surface charging plus the amount of band bending. Consequently, the band bending has to be evaluated independently from the surface charging and subtracted from the peak shift. Here this is done by measuring the band bending for a conductive sample; however, the correction is small for large charging shifts. Secondly, the measured photocurrent may contain a 'leak' current due to for example photoelectrons returning to an incompletely screened sample holder. Thus the true photocurrent from electrons photoemitted from the sample may be higher than the measured current, implying an underestimation of the sample resistance. An estimate of the contribution of the 'leak' current can be obtained by measuring the sample resistance for different photocurrents. In our set-up an increase of the photocurrent from 2.5 to 5.4 nA resulted in an apparent decrease of the sample resistance of 10%. Thirdly, a photovoltage effect can reduce the band bending [19]
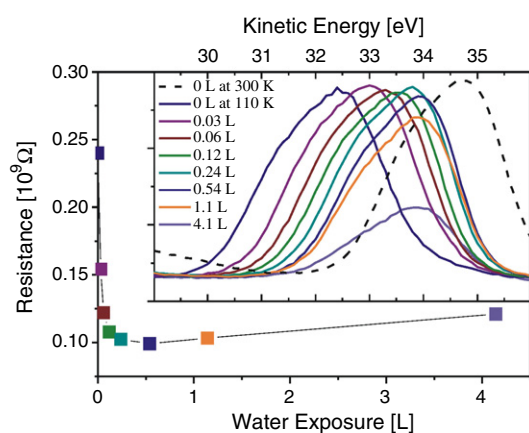
Figure 3. Effect of water adsorption on sample conductivity of stoichiometric $SnO_2(101)$. The inset shows the shift of the Sn 4d core level measured in UPS for different water exposures.

and thus alter the conductivity. This effect can be expected if photoexcited electron–hole pairs recombine only slowly and separate in the potential of the Debye layer. In order to test for this possibility band bending and conductivity measurements should be obtained at various photocurrents. In our study we measure a slightly lower sample resistance for larger photocurrents which is opposite to a photovoltage induced unbending of bands. Thus we believe that this effect is unimportant for SnO_2. Lastly, a change in the sample's work function can alter the photocurrent and therefore the surface potential, even without a change in sample resistance. In the case reported here the downward band bending upon water adsorption causes a decrease in the work function and thus an increased photocurrent. In the data reported in figure 3, for instance, the photocurrent increases from 10 to 12 nA. The contribution of the increased photocurrent to surface charging is negligible, however, and the concurrent increase in sample conductivity is dominant. In general, measuring the charging shift alone will not give an accurate measure of the change in conductivity. If the sample resistance is, however, evaluated in conjunction with the photocurrent, then work function changes should not introduce any measuring artefacts.

In conclusion, we have demonstrated that surface charging in photoemission spectroscopy can be utilized to evaluate the gas response of semiconducting oxide gas sensing materials. This technique has the advantage that it also gives information on the molecule–surface interaction. In the case reported here dissociation of water has been observed and this implies that the formation of OH^- is responsible for the strong gas response of water on SnO_2. Surface charging in photoemission as a probe of sample conductivity may find applications for other semiconducting surfaces. A particularly exciting possibility is using epitaxial thin films [20] for such experiments. Furthermore it may be possible to refine the experimental set-up by using a gate voltage to control the charge carrier concentration in the film or by adding an electron flood gun to control the surface charging. This would allow turning charging on and off and switching between a high resolution photoemission mode and a conductivity measurement mode. Possible phenomena that can be addressed with this technique are adsorbate induced conductivity changes, as we have demonstrated here, and temperature dependent phase transitions.

References

[1] See e.g. Madou M J and Morrison S R 1989 *Chemical Sensing with Solid State Devices* (Boston, MA: Academic)
[2] Batzill M and Diebold U 2005 *Prog. Surf. Sci.* **79** 47
[3] Yamazoe N, Fuchigami J, Kishikawa M and Seiyama T 1979 *Surf. Sci.* **86** 335
[4] Williams D E 1987 *Solid State Gas Sensors* vol 71, ed P T Moseley and B C Tofield (Bristol: Hilger IOP Publishing) chapter 5.1
[5] Bârsan N and Ionescu R 1993 *Sensors Actuators* B **12** 71
[6] Hahn S H, Bârsan N, Weimar U, Ejakov S G, Visser J H and Soltis R E 2003 *Thin Solid Films* **436** 17
[7] Tamaki J, Nagaishi M, Teraoka Y, Miura N, Yamazoe N, Moriya K and Nakamura Y 1989 *Surf. Sci.* **221** 183
[8] Ionescu R, Vancu A, Moise C and Tomescu A 1999 *Sensors Actuators* B **61** 39
[9] Chang S C 1980 *J. Vac. Sci. Technol.* **17** 366
[10] Lau W M 1989 *Appl. Phys. Lett.* **54** 338
[11] Chan R W M, Kwok R W M and Lau W M 1996 *J. Appl. Phys.* **79** 3635
[12] Doron-Mor I, Hatzor A, Vaskevich A, van der Boom-Moav T, Shanzer A, Rubinstein I and Cohen H 2000 *Nature* **406** 382
[13] Batzill M, Chaka A M and Diebold U 2004 *Europhys. Lett.* **65** 61
[14] Bergermayer W and Tanaka I 2004 *Appl. Phys. Lett.* **84** 909
[15] Batzill M, Burst J M, Katsiev K, Chaka A M, Delley B and Diebold U 2005 *Phys. Rev.* B **72** 165414
[16] Thiel P A and Madey T E 1987 *Surf. Sci. Rep.* **7** 211
[17] Henderson M A 2002 *Surf. Sci. Rep.* **46** 1
[18] Kiliç C and Zunger A 2002 *Phys. Rev. Lett.* **88** 095501
    Marley J A and Dockerty R C 1965 *Phys. Rev.* **140** A304
[19] Alonso M, Cimino R and Horn K 1990 *Phys. Rev. Lett.* **64** 1947
[20] Batzill M, Burst J M and Diebold U 2005 *Thin Solid Films* **484** 132