Investigation of gas sensing phenomena of SnO_2 via Near Ambient Pressure XPS

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Conductometric gas sensors (CGS) are small, dependable and inexpensive devices that transduce the concentration of surrounding gases into a measurable electrical response. Although improved significantly in the last five decades, CGS still suffer from limited sensitivity and selectivity, which stems largely from our insufficient understanding of the underlying chemistry. Since the advent of operando spectroscopy, the new analytical techniques, such as Near Ambient Pressure (NAP) XPS, allow observation of sensors under conditions much closer to their normal working environment, which can shed light onto the actual phenomena that govern the sensor's response instead of comparing the sensitive material in UHV before and after a dosing cycle. To that end, we have developed a method for in situ resistance measurements simultaneous to the NAP XPS analysis of a real sensor, which allows us to track which microscopic changes in the sensitive material correspond to the observed macroscopic sensor behaviour. We have performed several experiments on SnO_2-based CGS in which we measured the photoelectric emission and resistance simultaneously under the atmospheres of O_2, as a ubiquitous baseline gas, and CO, as a target gas of particular interest. In our numerous experiments we found no direct evidence of monoatomic oxygen adsorbates, which are often quoted as the species responsible for the observed sensor behaviour even without any supporting evidence in the literature [1]. However, our results are consistent with a sensing mechanism based on a variable density of near-surface oxygen vacancies, which act as a self-doping mechanism in SnO_2, therefore providing a mechanism for resistance change following surface reduction by a target gas. Although formerly discounted as a possible reaction pathway [2], direct reduction of the surface by CO and reoxidation by the ambient O_2 are now emerging as the leading theories explaining the transduction behaviour of SnO_2-based CGS [3]. We observed such behaviour in the XPS spectra as a variable O/Sn ratio corresponding to the predictable resistance change of the sensor under UHV and O_2 and CO atmospheres. Our results support the notion of a dynamically changing stoichiometry of the SnO_2 surface in place of the conventional view of a stoichiometric surface with a wealth of monoatomic oxygen adsorbates.

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