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Metal oxide-based gas sensor research: How to?

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Abstract

The paper critically reviews the state of the art in the field of experimental techniques possible to be applied to the study of conductometric gas sensors based on semiconducting metal oxides. The used assessment criteria are subordinated to the proposed R&D approach, which focuses on the study, and subsequent modelling, of sensors' performance in realistic operation conditions by means of a combination of phenomenological and spectroscopic techniques. With this viewpoint, the paper presents both the to-date achievements and shortcomings of different experimental techniques, describes – by using selected examples – how the proposed approach can be used and proposes a set of objectives for the near future.

Keywords: Metal oxide; Gas sensor; Transduction; Spectroscopy; Operando

1. Introduction

Conductometric gas sensors based on semiconducting metal oxides are actually one of the most investigated groups of gas sensors. They have attracted the attention of many users and scientists interested in gas sensing under atmospheric conditions due to the: low cost and flexibility associated to their production; simplicity of their use; large number of detectable gases/possible application fields [1–4]. The initial momentum was provided by the findings of metal oxide-gas reaction effects of Heiland [5], Bielanski et al. [6] and Seiyama et al. [7] and the decisive step was taken when Taguchi brought semiconductor sensors based on metal oxides to an industrial product (Taguchi-type sensors [8]). Nowadays, there are many companies offering this type of sensors, such as Figaro, FIS, MICS, UST, CityTech, Applied-Sensors, NewCosmos, etc. [9–13]. Their applications span from "simple" explosive or toxic gases alarms (see information provided by the gas sensors manufacturers on their homepages) to air intake control in cars [14] to components in complex chemical sensor systems [15].

On the side of the R&D work the most visible result is a large number of publications, generally reporting excellent individual gas sensing performance. The latter is obtained mainly by measuring the signals of laboratory samples (change of sample/sensor's electrical resistance) in quite unrealistic environments from the viewpoint of real sensors' working conditions, id est. in the absence of changing background conditions (e.g. humidity, presence of interfering gases, temperature, etc.). Sometimes, especially when the understanding of the sensing is targeted, some spectroscopic input is also provided. This type of approach, which is still dominant for the time being, is at the basis of most of R&D shortcomings and explains why, in spite of so many excellent laboratory results, the choice of devices to be used in real applications is still rather limited. It also explains why the modelling of gas sensing with metal oxide-based gas sensors is still in its infancy.

To understand what is wrong with the above-mentioned approach we need to realise that the reasons for high sensitivity to a particular gas and, simultaneously, low selectivity are related to the metal oxides-based sensors working principle. The cause of the change of sensor resistance (sensor signal) can be traced down to a ionosorption process and explained in terms of a free charge carriers (electrons) transfer from the semiconductor to adsorbed surface species or the other way around. The adsorption process that is responsible for the sensor signal is strongly influenced by the presence of the pre-adsorbed species (like ionosorbed oxygen, hydroxyl groups, carbonates, etc.) and by only measuring the change of resistance upon exposure to the target gas we will only record the overall electrical effect of quite complex surface reactions; summarizing, by only measuring the resistance change we do not have the needed discrimination for the correlation between surface species and their electrical effect. In principle, the discrimination we are missing should be provided by the results obtained by applying

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