

Fully Integrated Electrochemical Sensors: a Disruptive Alternative Compatible With Microelectronics Procedures

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Abstract:

Solid-state gas sensors are required to undergo a profound renovation in the next years in order to respond to new challenges in terms of portability, start-up response, sensitivity. In the present contribution, a novel approach for lambda sensors based on a nanometric, free-standing, full-ceramic membrane is presented. State-of-the-art, advantages and the challenges of such a technology, which combines advanced material engineering with low cost and batch production, are highlighted.

Key words: electrochemical sensor, thin film, microintegration, ceramic, yttria-stabilized zirconia.

Introduction and Motivation

The gas sensor market, whose size was estimated at USD 1.8 billion in 2013 [1], is expected to undergo a huge increment in the next years in view of the increasingly stringent legislations in terms of health, safety and emission control.

State-of-the-art solid state gas sensors (lambda sensors), which are based a bulky charge selective barrier (most commonly ionically conductive yttria-stabilized zirconia (YSZ)), are affected by a series of intrinsic limitations related to their size (about 2 cm), to the operating temperature (above 400 °C) and to the start-up response (≈ 10 s), which make them insufficient to respond to the future demands. For these reasons, great attention has been put in recent years in the development of new architectures for gas sensors: Among these, one of the most promising technologies is based on free-standing ceramic membranes of nanometric size.

Even though such an approach, which combines thin-film techniques and microfabrication steps, has shown enormous

potential in the field [2], some key challenges related e.g. to the chemical compatibility and the thermal stability of the components need to be overcome.

In the present contribution, the latest advances towards the realization of reliable, long-term stable and highly performant micro-gas sensors integrated in Si are presented.

Results

In Fig. 1a, the configuration of a micro gas-sensor integrated in Si is shown. Si micromachining (chemical and reactive ion etching) of a Si wafer, on top of which a ceramic-based thin structure is deposited by means of large area deposition methods (pulsed laser deposition or atomic layer deposition), allows for exposing the functional layers (total thickness ≈ 200 nm) to the reference and to the measured atmospheres (cross-plane configuration). Solid-gas reactions take place at the electrode-gas interface whereas charge separation by the electrolytic membrane allows for the built-up of the electrical signal.

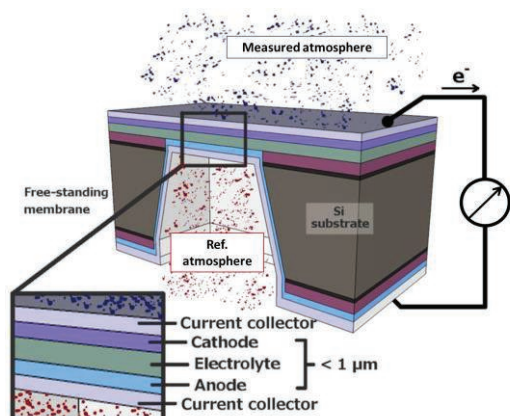


Fig. 1. Sketch of micro-gas sensor integrated in Si.

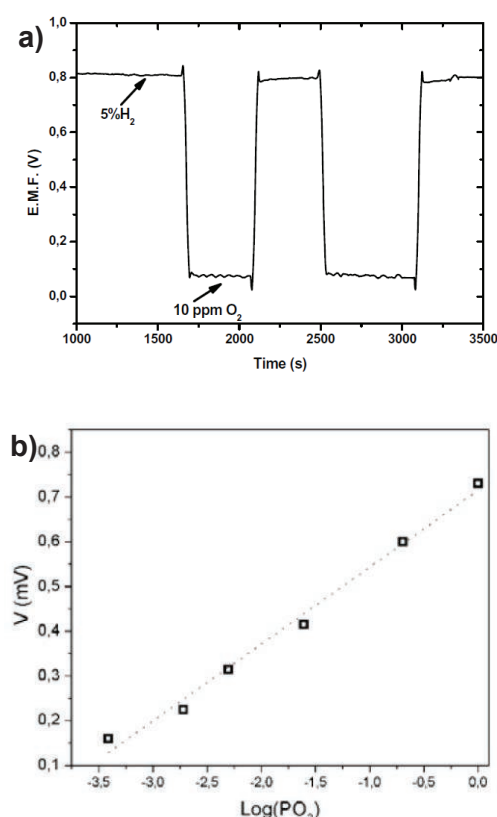


Fig. 2. Electrochemical performance of a Pt-YSZ microsensor

In Fig. 2, the sensor response to the application of different oxygen partial pressure is shown for a YSZ-based microsensor with porous Pt electrodes [3]. One can notice that the response is stable over different cycles (Fig. 2a) and that the expected linear correlation vs $\text{Log}(p\text{O}_2)$ is obtained (Fig. 2b). However, a series of limitations should be highlighted: i) the E.M.F. is reduced with respect to the theoretical value. Moreover, as highlighted by a number of reports [2,4], ii) the long-term thermal stability of such metal electrodes is deeply affected by degradation phenomena (dewetting). Moreover,

iii) the different thermal expansion coefficient between YSZ and Si, which may cause the mechanical failure of the membrane, should be taken great care of.

Such technology will be addressed in the present contribution and effective strategies, which we implemented in order to overcome its crucial issues, will be explained.

In particular, I show that thin film technology offers great flexibility in order e.g. to tune the strain state of the layers by varying the process parameters and to minimize the concentration of extended defects by combining different fabrication techniques. Remarkably, all such processes are realized at wafer level, thus giving the opportunity of scaling-up. Moreover, I will show the enormous potential which nano-engineering of ceramics (e.g. the control of the chemistry by the changing the microstructure or the fabrication of nano-composites) [5] has in the realization of materials whose electrical and structural properties are comparable, if not superior, to the “classical” metallic materials which are nowadays employed in sensors (see e.g. Fig. 3). This paves the way towards “full-ceramic” microdevices possessing unprecedented performances and long-term stability.

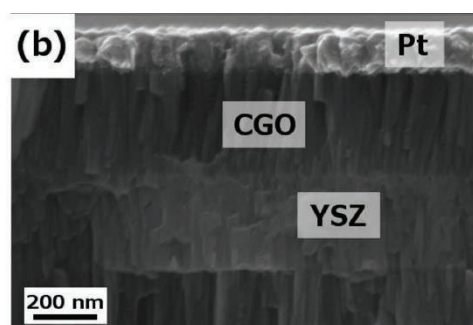


Fig. 3. SEM picture of a “full-ceramic” free standing membrane for micro gas sensors

References

- [1] Grand View Research
- [2] I. Garbayo et al., Energy Environ. Sci. 7, 3617-3629 (2014); doi: 10.1039/C4EE00748D
- [3] I. Garbayo et al., Procedia Eng. 87, 927-930 (2014); doi: 10.1016/j.proeng.2014.11.307
- [4] A. Evans et al., J. Power Sources 194, 119-129 (2009)
- [5] F. Chiabrera et al., Solid State Ionics 299, 70-77 (2017)