

## Ta<sub>2</sub>O<sub>5</sub> nanoporous membrane for chemical sensing in harsh environment

Alexander Imbault<sup>1</sup>, Yue Wang<sup>1</sup>, Peter Kruse<sup>1</sup>, Evheni Strelcov<sup>3</sup>, Elisabetta Comini<sup>2</sup>,  
Giorgio Sberveglieri<sup>2</sup>, and Andrei Kolmakov<sup>3</sup>

<sup>1</sup>McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4M1, Canada

<sup>2</sup>University of Brescia, CNR-IDASC, Brescia, Italy

<sup>3</sup>Department of Physics, Southern Illinois University at Carbondale, Carbondale, Illinois 62901, USA

Corresponding e-mail address: [akolmakov@physics.siu.edu](mailto:akolmakov@physics.siu.edu)

### Abstract

The conductometric gas sensors made of nanoporous oxide ultrathin membranes can be particularly promising for the active sampling of the diluted analytes. Here we report the case study of the electron transport and gas sensing properties of such a membrane made of Ta<sub>2</sub>O<sub>5</sub>. In spite of well-known high thermal and chemical stability, Ta<sub>2</sub>O<sub>5</sub> membranes appear to exhibit noticeable chemical sensitivity at high temperatures above 300 °C. The proposed suspended architecture of the gas penetrable Ta<sub>2</sub>O<sub>5</sub> membranes as active sensing element, may lead to the new designs of the ultrasensitive analytical systems operating at high temperature and harsh environments.

**Key words:** metal oxide, nanoporous membranes, chemical sensing, gas permeation

### Introduction

The sensitivity of the conductometric metal oxide sensors increases with decreasing of the size (or dimensionality) of the sensing element. However, as it has been pointed in [1], the principal limitations of the miniaturization can be imposed at nanoscale, especially for strongly diluted analytes and the response time of nanoscopic sensing element increases significantly and can reach hours when the concentration approaches sub ppb level. Therefore there exists a principle limit of the size of the individual sensing element where its further reduction is not feasible any more while using the standard sampling. High yield protocols to fabricate and transfer the nanoporous ultrathin oxide membranes became recently available [2]. The nanoscopic thickness of such membranes preserves advantages of the effective transduction of the surface reactivity to electrical signal while their macroscopic lateral dimensions eliminate the aforementioned limitations as an effective receptor. An additional potential advantage of such membranes is their inherent nanoporosity which: (i) increases the surface area of the sensing element and (ii) controls its gas

permeability. The latter offers the implementation of the advanced device architectures and active analyte sampling approaches. In this communication we have tested the electron transport and gas sensing properties of Ta<sub>2</sub>O<sub>5</sub> -the first synthesized membrane of that type.

### Experimental

The tantalum pentoxide membranes were prepared by electro-polishing and anodization of tantalum sheets in accordance to protocols described in [3, 4] [2, 5]. Two probe transport measurements were performed in vacuum inside the probe station in the temperature range from RT to 400 °C. Gas sensing tests were conducted using the flow-through technique at atmospheric pressure. A constant synthetic air flow 300 sccm as carrier gas was used for the analyte dispersion. The sensor was stabilized at operational temperature for a few hours. Measurements were performed in the 300-500 °C temperature range under a constant humidity level of 40%, in an isothermal chamber maintained at a fixed temperature of 20 °C throughout the experiment. The sensor resistance was monitored by means of the volt-ampometric technique at constant bias

voltage. The sensor material was tested against  $\text{NH}_3$ ,  $\text{CO}$ ,  $\text{H}_2$ ,  $\text{NO}_2$ , ethanol and acetone analytes with concentrations ranging from 3 ppm to 3000 ppm.

## Results and discussion

Figure 1a depicts an optical image of the part of the membrane deposited on to an array of Pt

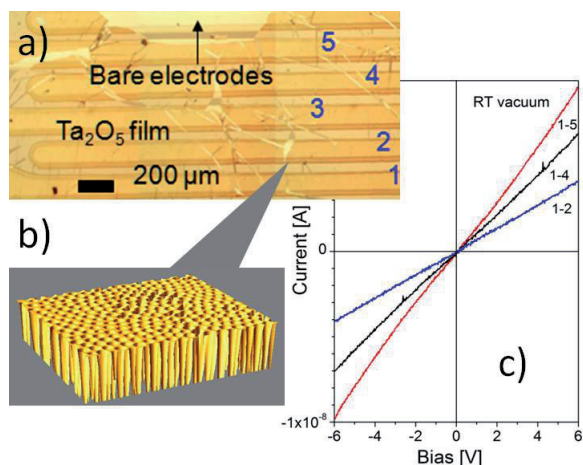


Fig. 1: a) Optical image of few Pt electrodes coated with  $\text{Ta}_2\text{O}_5$  membrane; b) The morphology of the nanoporous membrane; c) I-V characteristics of the  $\text{Ta}_2\text{O}_5$  membrane measured between different electrodes at room temperature

electrodes using Lift-Off-Float technique. I-V curves in the Fig.1b indicate the rather high sheet resistance (in the order of  $10^{10}$ - $10^{11}$   $\Omega/\text{sq}$ ) of as grown tantalum pentoxide membranes at room temperature. More detailed analysis reveals that the increase of the resistance with the length of the membrane is not linear what presumably is due to cracks and wrinkles in the conducting path between the tested Pt leads. The Arrhenius plot for conductance indicate the existence of two types of activation processes responsible for conductivity at low (below 200  $^\circ\text{C}$ ) and at high (above 250  $^\circ\text{C}$ ) temperatures. The transition threshold coincides with surface water dissociation temperature range and formation of strongly bonded hydroxyl groups. The latter points toward the involvement of the molecular water in the conductance at lower temperature range (see discussion and refs. in [6]).

As it was expected, tantalum pentoxide membrane as a sensor material has no or very poor response to any of the tested analytes at low temperature (below 300  $^\circ\text{C}$ ) but sensitivity improves noticeably above 400  $^\circ\text{C}$ . Fig. 2 depicts the kinetics of conductance response of

the membrane to square concentration pulses of tested analytes at 400  $^\circ\text{C}$ . The responses are typical for n-type semiconductor material. The sensors has reasonable response time in the order of few seconds and good baseline

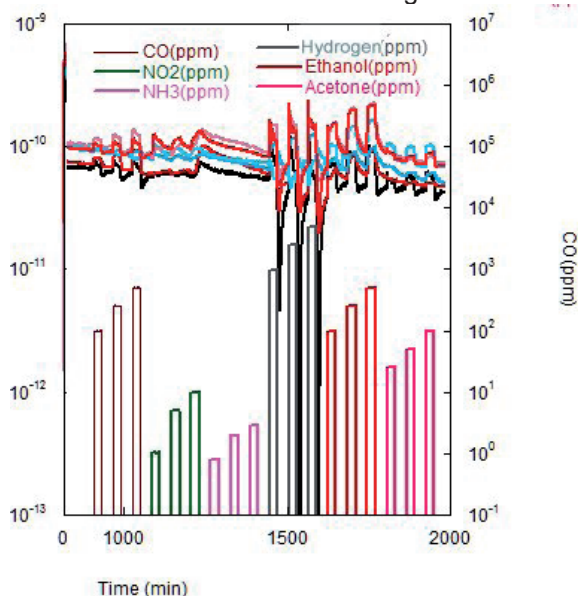


Fig.2 Dynamic response of tantalum oxide membrane at a working temperature of 400 $^\circ\text{C}$  to pulses of a number of analytes diluted in air

recovery at the end of each exposure cycle (except the case of  $\text{NO}_2$ ). The latter indicates a reversible adsorption/desorption of the analyte or reaction products.

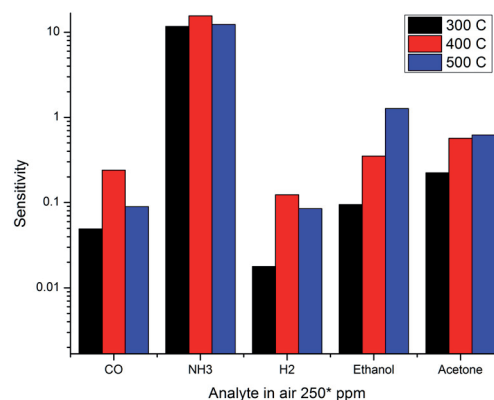


Fig.3. Effective sensitivities of the sensor towards few common analytes as a function of temperature. All responses were reduced to a single value of 250 ppm assuming its linear dependence on analyte concentration.

Figure 3 displays the relative selectivity of the sensors to a particular analyte from the tested set. The membrane sensor has rather high sensitivity to ammonia in entire tested temperature range. The sensitivity to  $\text{NH}_3$ ,  $\text{H}_2$

and CO has a peak around 400 °C while it keeps growing with temperature for ethanol and acetone.

### Conclusions and outlook

Nanoporous ultrathin tantalum pentoxide membranes exhibit low reactivity toward common redox gases at low temperature but demonstrate good performance at high temperatures. The latter makes this material more suitable for high temperature and harsh environment applications. The porous morphology of such free standing membranes makes such a material to be a promising platform for devices which combine pre-concentration and sensing functions. The fabrication of the suspended membranes made of traditional sensing oxides such as SnO<sub>2</sub>, ZnO, WO<sub>3</sub> and *etc* is feasible and will reveal the full capacity of this approach

### References

- [1] P. R. Nair and M. A. Alam, "Performance limits of nanobiosensors," *Applied Physics Letters*, vol. 88, 2006.
- [2] S. Singh, M. Festin, W. R. T. Barden, L. Xi, J. T. Francis, and P. Kruse, "Universal Method for the Fabrication of Detachable Ultrathin Films of Several Transition Metal Oxides," *ACS Nano*, vol. 2, pp. 2363-2373, 2008.
- [3] S. Singh, W. R. T. Barden, and P. Kruse, "Nanopatterning of Transition Metal Surfaces via Electrochemical Dimple Array Formation," *ACS Nano*, vol. 2, pp. 2453-2464, 2008.
- [4] H. El-Sayed, S. Singh, M. T. Greiner, and P. Kruse, "Formation of Highly Ordered Arrays of Dimples on Tantalum at the Nanoscale," *Nano Letters*, vol. 6, pp. 2995-2999, 2006.
- [5] S. Singh, M. T. Greiner, and P. Kruse, "Robust Inorganic Membranes from Detachable Ultrathin Tantalum Oxide Films," *Nano Letters*, vol. 7, pp. 2676-2683, 2007.
- [6] N. Barsan and U. Weimar, "Conduction model of metal oxide gas sensors," *Journal of Electroceramics*, vol. 7, pp. 143-167, 2001.