30th Eurosensors Conference, EUROSENSORS 2016

Pt deposition techniques for catalytic activation of nano-structured materials

Ferenc Bíró[a,b,*], György Z. Radnóczi[a], Máté Takács[a,c], Zsófia Baji[a],

Csaba Dücső[a] and István Bársony[a]

[a]*Institute of Technical Physics and Materials Science –MFA, Konkoly-Thege M. u 29-33., Budapest, 1121 Hungary*
[b]*University of Pannonia, Egyetem u. 10., Veszprém, 8200 Hungary*
[c]*Budapest University of Technology and Economics, Műegyetem rkp. 3., Budapest, 1111 Hungary*

Abstract

Various deposition techniques were tested to form Pt catalyst on nano-structured materials characterized by 50-200 nm dimensions. Different layer structures applied in gas sensing were sensitized by Pt sputtering and droplet deposition of Pt nano-particles formed from $H_2[PtCl_6]$ solutions. Besides, atomic layer deposition (ALD) of Pt was also investigated. The layers to be coated were disordered piles of WO_3 nano-rods and sol-gel deposited WO_3 nano-crystals as well as electrochemically formed alumina with high aspect ratio perpendicular pores. Distribution of Pt particles inside these layers was analyzed by scanning (SEM) and transmission electron microscopy (TEM). Demonstration of functionality is also provided.

1. Introduction

Nano-structured materials form the basis of novel gas sensing devices owing to the extreme sensitivity due to their increased surface. Nevertheless, metal-oxide layers of conductivity type sensors generally exhibit low selectivity and response time. Addition of catalytic nano-particles, e.g. Pt may eliminate the selectivity deficit and open the way towards forming devices of appropriate characteristics. Another group of sensors exploits the large catalyst

* Corresponding author. Tel.: (+36)1 3922222/1244; fax: (+36) 1 3922226.
  E-mail address: birof@mfa.kfki.hu

surface and operates with calorimetric principle by measuring the heat generated by the catalytic gas combustion. Both groups of devices require the thin films of nano-porous structure to be covered uniformly by the catalyst across the full depth of the sensitive layer.

2. Experimental and results

2.1. Formation of nano-structured layers

Three types of nano-structured layers were processed for testing Pt deposition techniques.

- To form a micro-pellistor, porous alumina layers were formed by electrochemical etching of 1 µm thick Al layer in oxalic acid, followed by etching in H_3PO_4 to enlarge the diameter of the perpendicular pores to 60-70 nm [1]. Due to the competing effects of the volume increase caused by the Al_2O_3 formation versus the etching during pore enlargement, the final porous layer thickness is 1.2 µm. Note, that the aspect ratio of the pores is at least 17-20 (Fig. 1 and Fig. 2).
- For conductivity-type sensors hexagonal WO_3 nano-rods of 80-150 nm diameter and 4-5 µm length were formed by hydrothermal synthesis [2]. Droplet deposition followed by a drying process leading to a thin layer composed of disordered piles of nano-rods (Fig. 2, center).
- An alternative WO_3 structure was formed by sol-gel deposition from Pluronic F127 block copolymer and tungsten hexa-chloride solution via spin-coating process and final annealing in synthetic air at $300°C$ for 30 minutes. The obtained 200 nm thick layer consists of 50-150 nm large WO_3 grains with embedded pores of 20-50 nm (Fig. 2, right).

2.2. Deposition of Pt particles

- Thin films of 17 nm thickness were deposited by DC magnetron sputtering as reference. For the formation of metal nano-particles the thin Pt layer was annealed in N_2 at $300°C$ for 30 minutes. The well-known coverage characteristics of the sputtered layer is represented in Fig. 1 which shows the inherent limitations to form large surface coverage of Pt in high aspect ratio porous materials. Nevertheless, its application is feasible for extremely thin layers of aspect ratios below 2-3 (Fig. 1, right).
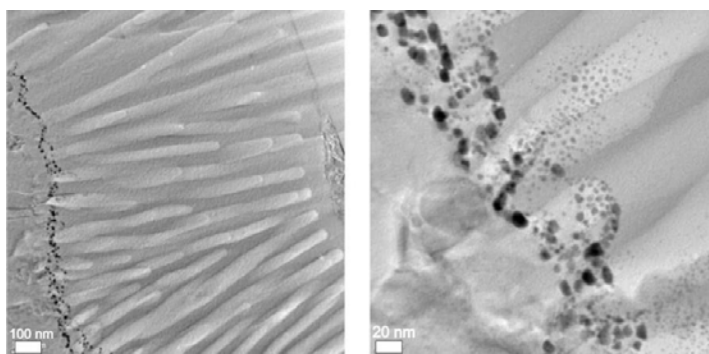

Fig. 1. XTEM views of 17 nm nominal thickness of Pt deposited in porous A_2O_3 layer by DC sputtering followed by annealing at 300ºC. The distribution of Pt particles reveals the strict limitation of the technique. Dark spots: Pt particles.

- Controlled size Pt nano-particles were synthetized for droplet coating of the above described nano-structured layers according to [3]. A mixture of 3.6 ml 0.2 M H_2PtCl_6 and 1.1 ml 1 M sodium citrate in 46.4 ml of boiling DIW was prepared. Quick injection of 0.55 ml 0.08M sodium borohydrate and 1M sodium citrate solution resulted in 1-2 nm Pt seeds. To increase the formed Pt particles to 18-20 nm uniform size, a solution composed of 0.045 ml of a 0.4M H_2PtCl_6, 0.5 ml 1M sodium citrate and 1.25M L-ascorbic acid was added and stirred for 30 minutes. Pt distributions in the three characteristic layers are represented by Fig. 2.
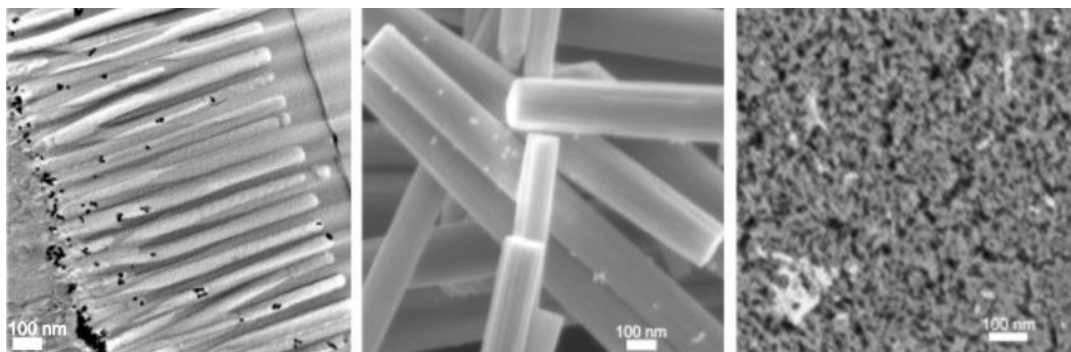
Fig. 2. Distribution of 20 nm average size Pt particles deposited by droplet technique. Particles can be seen on top of the porous alumina layer while some of them are located at the bottom of the pores (left, XTEM). Particle distribution in disordered piles of WO_3 nano-rods (centre, SEM) and in 200 nm thick sol-gel deposited porous WO_3 layers (right, SEM). Due to the different imaging techniques Pt appears as black in TEM whereas white in SEM pictures.

The technique is adequate for sensitizing both metal-oxide structures, as their operation requires small number of noble metal catalytic particles (see Fig. 2, centre and right). When coating perpendicular pores of high aspect ratio, most of the particles are found on the surface and only a limited number at the bottom of the pores (see Fig. 2. left). Due to the moderate increase of the catalytically active surface, this structure is not yet optimized for calorimetric gas sensing.

- The ALD process can be tuned to meet most of the requirements of the above devices. Applying a few deposition cycles, separated Pt nano-particles can be formed even in the case of substrates with pores of the highest aspect ratio (see Fig. 3). With the appropriate number of deposition cycles (>300), contiguous coverage can be achieved. By providing an ideally large surface this can be a potential solution for catalytic combustion.
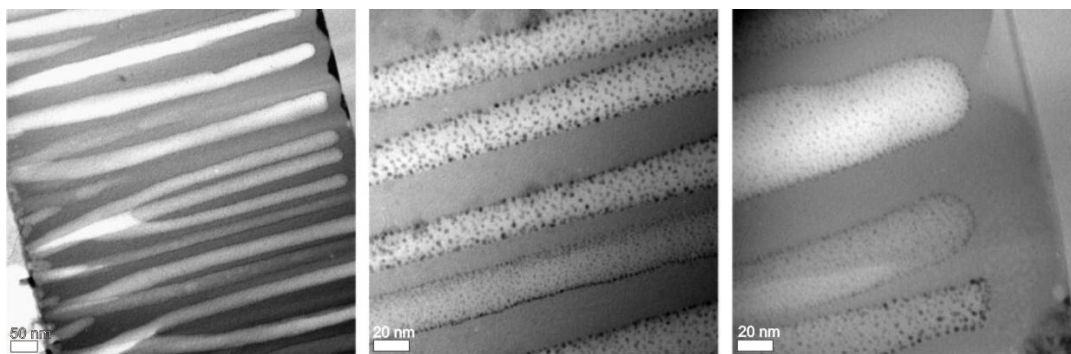

Fig. 3. Distribution of Pt particles deposited by ALD in porous alumina layers. XTEM views of the full layer thickness of 1 um (left), magnified sections from the middle (centre) and at the bottom of the pores (right). The small particle sizes indicate that the ALD process works still in the nucleation phase.

2.3. Functional tests

- Calorimetric sensors operating with catalytic combustion.
  To demonstrate the efficiency of catalytic coating of the micro-pellistor, identical micro-hotplates covered with porous alumina were sensitized by sputtered and droplet deposited Pt as well as by ALD technique. Responses for propane in the range of 20-100% LEL (lower explosion limit) were cyclically measured. The characteristic responses presented in Fig. 4 confirm the difference as expected from TEM images. The higher response of the ALD coated sample is definitely advantageous at 20% LEL concentrations.
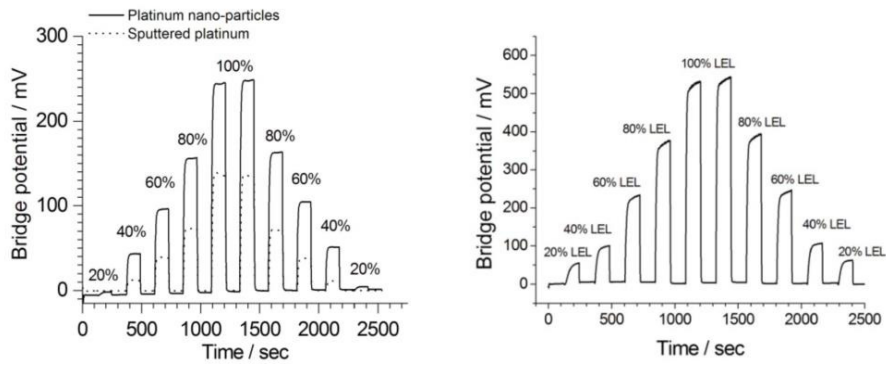
Fig. 4. Pellistor responses on exposure of propane up to 100% LEL in synthetic air. Devices were coated by sputtering and droplet technique (left), or uniformly distributed catalyst by ALD (right). The power dissipation is 2x17 mW of each hotplate-pair.

- Conductivity type WO_3 sensors.
  Nano-rod and sol-gel deposited gas sensor structures were sensitized by the above described techniques. For demonstration we present the effect of droplet deposited Pt nano-particles on both structures (see Fig. 5).
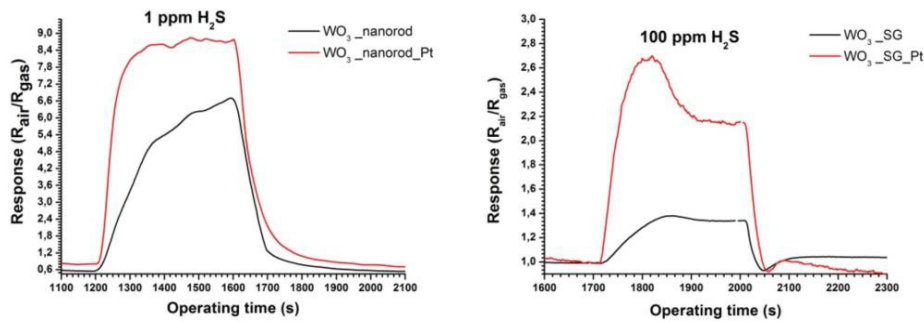

Fig. 5. Responses of non-doped and sensitized WO_3 conductivity type sensors: nano-rod (left) and sol-gel deposited (right) samples.

3. Summary

Alternative routes for sensitizing different nano-structured matrices with Pt nano-crystals for gas sensing were investigated in terms of the feasibility of the activation method and the accessible sensitivity. We demonstrated that with proper selection of the Pt coating technique performance enhancement can be achieved. Optimization of each sensor structure will follow this work.

Acknowledgements

References

[1] F. Bíró, A. E. Pap, I. Bársony, and C. Dücső, Micro-pellistor with integrated porous alumina catalyst support, Proc. Eng. 87 (2014) 200-203.
[2] M. Takács, C. Dücső, A. E. Pap, Fine-tuning of gas sensitivity by modification of nano-crystalline WO_3 layer morphology, Sens. Actuators, B 221 (2015) 281–289.
[3] N. C. Bigall, T. Hartling, M. Klose, P. Simon, L. M. Eng, A. Eychmüller, Monodisperse platinum nanospheres with adjustable diameters from 10 to 100 nm: Synthesis and distinct optical properties, Nano Lett. 8 (12) (2008) 4588-4592.