ELSEVIER

Materials Science and Engineering B91–92 (2002) 534–536

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Computer image HRTEM simulation of catalytic nanoclusters on semiconductor gas sensor materials supports

J. Arbiol [a,*], F. Peiró [a], A. Cornet [a], J.R. Morante [a], J.A. Pérez-Omil [b], J.J. Calvino [b]

[a] *Departament d'Electrònica, Universitat de Barcelona, EME, Martí i Franquès, 1, 08028 Barcelona, Spain*
[b] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Cádiz, Spain*

Abstract

In the present work, we have analyzed the feasibility of several metal/semiconductor systems for metal additive superficial clustering. To this aim, we have selected the most common semiconductors (SnO_2 and TiO_2) and catalytic metal species (Pt, Pd and Nb) used for gas sensing. The application of nanoscopical techniques such as high resolution electron microscopy and the complementary use of the digital image processing (DIP) and computer image simulation (CIS) have shown the morphological characteristics of the metal additive nanoclusters attached to the semiconductor surface. While the natural distribution for Pt on semiconductor nanopowders (SnO_2, TiO_2...) is as metal nanoclusters, Pd atoms tend to disperse on semiconductor surface and Nb tends to diffuse into the semiconductor bulk. In this work, we show that metal nanoclustering is also possible in the latter cases under special growing conditions such as high metal additive doping or submitting the sample to thermal or reducing processes.

Keywords: Catalysis; Diffusion; Doping effects; Electron microscopy; Semiconductors

1. Introduction

In the last few years, there has been an increasing interest in the field of electronics for gas sensors based on semiconducting materials [1,2]. In view of the increasingly strict legal limits for polluting gas emissions, there is a great interest in developing high performance gas sensors for applications such as control of air pollution and exhaust gases. In this way, semiconductor gas sensors (SGS) offer advantages due to their simple implementation, low cost and good reliability for real-time control systems. The introduction of catalytic additives to the SGS materials has been reported by several authors to improve the sensitivity and selectivity of the sensor, and to reduce the response time and operating temperature of the device [3,4]. The amount and distribution of the metal is the most important parameter to be controlled in order to obtain the highest sensitivity [5].

Although there exist many works in literature devoted to the electrical and general analytical characterization as well as to the understanding of the physical mechanisms that control the gas sensing behavior, only a few works have been dedicated to the nanostructural characterization of semiconductor nanopowders and metal additives morphology and distribution in the SGS systems. We have applied those nanoscopical techniques that allow the further studies needed in the SGS materials field. TEM and HRTEM observations and the complementary use of the digital image processing (DIP) and computer image simulation (CIS), have given us a good understanding of the nanoscopic characteristics and behavior of our materials. In this work, we have summarized the most important results found recently about superficial clustering in different catalytic metal additives when added to SGS materials.

2. Experimental details

SnO_2 and TiO_2 samples have been doped with different catalytic metals such as, Pt; Pd; and Nb. The samples have been prepared following different growing

* Corresponding author. Tel.: +34-93-402-1141; fax: +34-93-402-1148.

E-mail address: arbiol@el.ub.es (J. Arbiol).

0921-5107/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0921-5107(01)01067-4

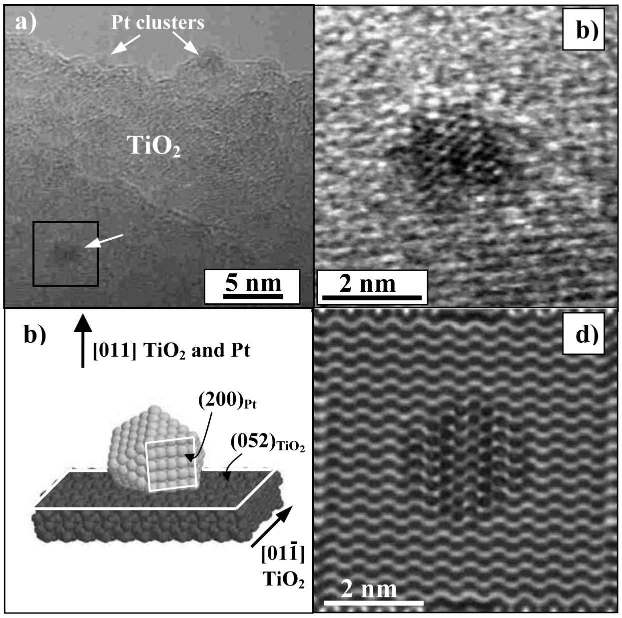

Fig. 1. (a) HRTEM micrograph of a TiO_2 rutile nanoparticle surface with the presence of Pt nanoclusters. (b) Magnified detail of the selected area in (a). (c) Supercell model of one of this cuboctahedral Pt nanoclusters and (d) CIS of the supercell model.

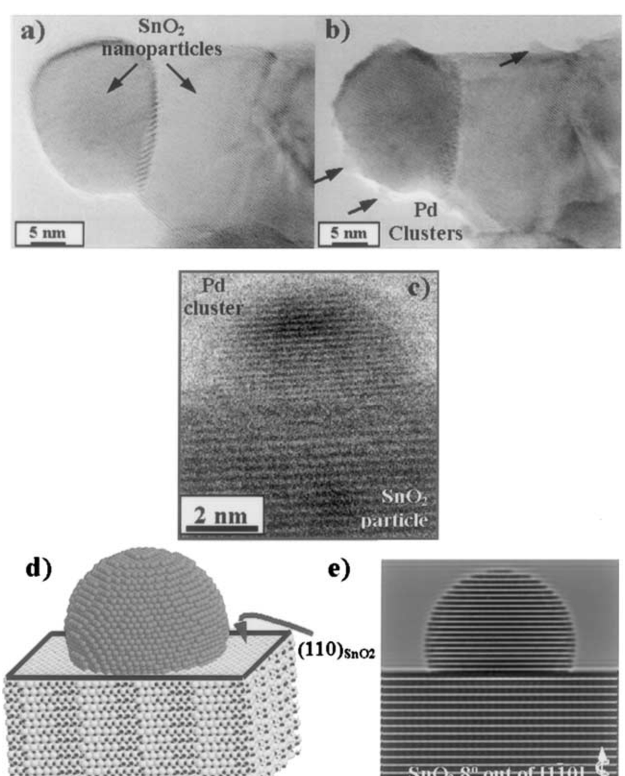

Fig. 2. (a) HRTEM image of the Pd/SnO_2 nanopowders in as-grown sample. (b) HRTEM micrograph of the same nanoparticles after the reduction process. A few Pd clusters appear in the image. (c) HRTEM micrograph of a Pd nanocluster on a SnO_2 nanoparticle surface. (d and e) Supercell model and CIS of the Pd cluster shown in (c).

methods, selecting the most appropriate in every case, such as the impregnation method for Pt/TiO_2 systems [6,7], the electroless and microwave methods for low and high doped Pd/SnO_2 systems [6,8,9], respectively, and the laser induced pyrolisis for the Nb/TiO_2 systems [6,10]. HRTEM observations have been performed in a Philips CM30 microscope operated at 300 kV with 0.19 nm point resolution. For CIS, the EMS software package [11], installed in a *Indy R5000 Silicon Graphics* workstation, has been used. Supercell files used in EMS have been built using the RHODIUS program [12].

3. Results and discussion

One of the most common examples of catalytic metal distribution in gas sensor materials is superficial nanoclustering in the as-grown samples. This is the case of Pt noble metal added to TiO_2 [13,14]. In recent works [7], we have shown that those nanoclusters nucleated as cuboctahedral clusters for diameter sizes smaller than 3 nm (cuboctahedrons with triangular and square faces) and in non-regular faceted shapes, which tended to be spherical for bigger diameter sizes (≥ 3 nm). We also showed the feasibility of obtaining a good Pt nanocluster dispersion and high percentage of metal active atoms. As an example, in Fig. 1, we present a HRTEM micrograph of few Pt nanoclusters distributed on a TiO_2 rutile nanoparticle surface. The subsequent modelling and simulation of the selected cluster/support structure let us obtain important information about the epitaxial relationship, $[11-1](011)_{Pt}\|[200](052)_{TiO_2}$ in this case, and the nanocluster morphology. CIS shown in Fig. 1d has been obtained in the Scherzer defocus, at 300 kV and $C_s = 1.2$.

Besides this natural formation of nanoclusters, we can find catalytic metal distributed in other ways. However, we can enhance superficial nanoclustering by an appropriate modification of the growing conditions. A second distribution mode is observed when Pd is added in low concentrations to the semiconductor substrate. In that case, the metal can be dispersed as monoatomic centers, giving rise to ultradispersion or atomically dispersion of the additive metal on the semiconductor surface, as found in the case of Pd on SnO_2 [15,16]. Nevertheless, for higher concentrations (> 5 wt.% Pd) or even at low concentrations but after a reduction treatment, we could obtain Pd nanoclustering on the semiconductor surface [6,8,9]. In Fig. 2, we show an example of the reduction treatment effects on Pd/SnO_2 nanopowders. The SnO_2 nanoparticles surface appears 'clean' of clusters before reduction (Fig. 2a), while after an in situ reduction process a few Pd clusters sinter on surface (Fig. 2b). The in situ reduction process has been widely described elsewhere [8]. In Fig. 2c, we show a magnified HRTEM detail of a Pd nanocluster on the

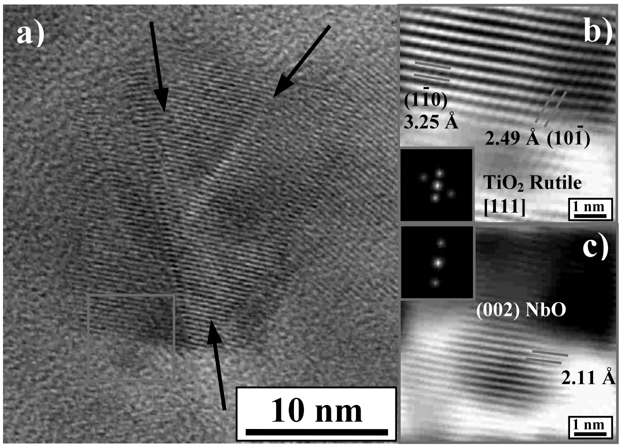

Fig. 3. (a) HRTEM micrograph showing the formation of a NbO cluster on TiO_2 surface. (b and c) DIP of the area squared in (a). Black arrows mark the presence of twins in the TiO_2 nanoparticle.

surface of a SnO_2 nanoparticle. In Fig. 2d and e we show the supercell model and the CIS of the Pd cluster shown in Fig. 2c. In this case, the study of the cluster morphology reveals a semispherical shape with a perfect epitaxy with the following relationship: $[11-2](111)_{Pd}||[1-10](110)_{SnO_2}$. CIS shown in Fig. 2e has been also obtained in the Scherzer defocus conditions, at 300 kV and $C_s = 1.2$.

Finally, a third metal distribution mode is found when additives can diffuse into the semiconductor. An example is found for Nb added to TiO_2, which diffuses by entering substitutionally into the semiconductor bulk or occupying interstitial positions or inducing structural changes in metal oxide structure [17,18]. In this case, we have found that metal clustering is possible when submitting the Nb/TiO_2 nanopowders to an annealing process. The Nb superficial clustering has been found to be related to the anatase-to-rutile phase transition and dramatically accelerated when increasing the metal addition percentage, as shown recently [6,8]. In Fig. 3 there is an example of a TiO_2 rutile nanoparticle showing a NbO nanocluster on its surface. The image has been digitally processed obtaining the material phase separation by filtering the digital diffraction pattern after FFT of the HRTEM experimental image. In this way, in Fig. 3b and c we show the atomic planes corresponding to the TiO_2 rutile phase and the NbO nanocluster phase, respectively.

4. Conclusions

The feasibility of several metal/semiconductor systems for metal additive superficial clustering has been studied by means of HRTEM, DIP and CIS. The use of complex supercell models let us to simulate the nanostructures studied, obtaining a good understanding of the experimental results. The most common semiconductors (SnO_2, TiO_2) and catalytic metal species (Pt, Pd, Nb) used for gas sensing have been selected. In this work, we show that metal nanoclustering is also possible not only in the as-grown state as in the case of Pt/TiO_2, but also in other systems as Pd/SnO_2 and Nb/TiO_2 under special growing conditions such as high metal additive doping or after sample submission to thermal or reducing processes.

Acknowledgements

This work has been partially funded by the EU INCO project ICA2-CT-2000-10017 and by the Spanish CICYT program MAT 99-0435-C02-01.

References

[1] A. Cirera, A. Vilà, A. Diéguez, A. Cabot, A. Cornet, J.R. Morante, Sens. Actuat. B 64 (2000) 65.
[2] K. Sekizawa, H. Widjaja, S. Maeda, Y. Ozawa, K. Eguchi, Catal. Today 59 (2000) 69.
[3] M. Gaidi, B. Chenevier, M. Labeau, Sens. Actuat. B 62 (2000) 43.
[4] A. Cabot, J. Arbiol, J.R. Morante, U. Weimar, N. Bârsan, W. Göpel, Sens. Actuat. B 70 (2000) 87.
[5] V.A. Chaudhary, I.S. Mulla, K. Vijayamohanan, Sens. Actuat. B 55 (1999) 154.
[6] J. Arbiol, Ph.D. Thesis Work, Universitat de Barcelona, Barcelona, 2001.
[7] J. Arbiol, A. Ruiz, A. Cirera, F. Peiró, A. Cornet, J.R. Morante, A. Alimoussa, M.-J. Casanove, Institute of Physics Conference Series, in press.
[8] J. Arbiol, R. Díaz, A. Cirera, F. Peiró, A. Cornet, J.R. Morante, F. Sanz, C. Mira, J.J. Delgado, G. Blanco, J.J. Calvino, Institute of Physics Conference Series, in press.
[9] J. Arbiol, A. Cirera, F. Peiró, A. Cornet, J.R. Morante, J.J. Delgado, J.J. Calvino, Appl. Phys. Lett. 80 (2) (2002) 329.
[10] J. Arbiol, J. Cerdà, G. Dezanneau, A. Cirera, F. Peiró, A. Cornet, J.R. Morante, J. Appl. Phys.
[11] P. Stadelmann, Ultramicroscopy 21 (1987) 131.
[12] J.A. Pérez-Omil, Ph.D. Thesis, Universidad de Cádiz, Cádiz, 1994.
[13] M. Labeau, M. Vallet-Regí, V. Ragel, J. Román, J. Martínez, J. Peña, E. García, A. Varela, B. Gautheron, J.M. González-Calbet, Proceeding of EUREM92, 2, Granada, Spain, 1992, p. 655.
[14] M. Labeau, B. Gautheron, F. Cellier, M. Vallet-Regi, E. García, J.M. González-Calbet, J. Solid Stat. Chem. 102 (1993) 434.
[15] M.H. Madhusudhana Reddy, A.N. Chandorkar, Thin Solid Films 349 (1999) 260.
[16] R. Cavicchi, V. Sukharev, S. Semancik, Surf. Sci. 418 (1998) L81.
[17] D. Mardare, P. Hones, Mater. Sci. Eng. B 68 (1999) 42.
[18] J. Marien, T. Wagner, G. Duscher, A. Koch, M. Rühle, Surf. Sci. 446 (2000) 219.