Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2018, **28**, 164–166

Mendeleev Communications

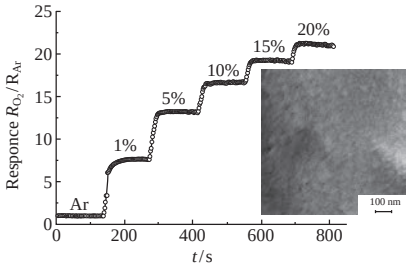
Sol-gel made titanium dioxide nanostructured thin films as gas-sensing materials for the detection of oxygen

Vladimir G. Sevastyanov,* Elizaveta P. Simonenko, Nikolay P. Simonenko, Artem S. Mokrushin, Vitaliy A. Nikolaev and Nikolay T. Kuznetsov

N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 495 954 4126; e-mail: vg_sevastyanov@mail.ru

DOI: 10.1016/j.mencom.2018.03.018

The titanium dioxide nanostructured thin films have been obtained using a sol-gel process at different crystallization temperatures. The influence of both the phase composition and the particle dispersity of 2D nanomaterials on their gas-sensing properties has been evaluated. The TiO_2 nanostructured thin film prepared from xerogel under the mildest crystallization conditions (500 °C, 1 h) exhibited high sensitivity and selectivity in oxygen detection within a broad range of its concentrations at 350 °C.



Oxygen sensors are widely used in processes of environmental monitoring, medicine and other fields. In particular, the defects of intercalation sites within the structure of TiO_2, which result from intercalation of oxygen vacancies, the great fraction of oxygen nonstoichiometry within a crystal lattice and the n-type semiconductor properties have made titanium dioxide capable of detecting oxygen[1] in addition to other analyte gases (hydrogen and nitrogen dioxide).[2,3] The photocatalytic,[4] electrophysical and gas-sensing[5,6] properties of functional materials based on TiO_2 are greatly affected by phase composition,[7] dispersity and microstructure.

A sol-gel process allows one to prepare nanomaterials as both powders and nanostructured metal oxide thin films. In this case, the product parameters and sensor characteristics can be adjusted by changing xerogel thermal treatment conditions during the crystallization of a target phase.[8]

The aim of this work was to prepare the nanostructured thin films of titanium dioxide as receptor material for oxygen detection and to determine the dispersity effect varied by changes in thermal treatment conditions on its gas-sensing properties.

As a precursor, the solution of a heteroligand complex in butanol (0.25 mol dm^{-3}) was prepared by the addition of acetylacetone to titanium tetrabutoxide [$n(Ti^{4+}) : n(C_5H_8O_2) = 1 : 0.47$] followed by agitation for 10 min to decrease the hydrolytic activity of the compound and to obtain transparent and uniform gel by hydrolysis.[9] To activate the hydrolysis, an ethanol–water solution [$V(H_2O) : V(EtOH) = 1 : 1$, $n(H_2O) : n(Ti^{4+}) = 18 : 1$] was added. After agitation (2 min), special aluminum oxide substrates (roughness, 0.4 μm) were dipped into the colloid system – substrates were fitted with interdigital electrodes and a microheater on the reverse side[8] – and a thin gel film was deposited by a dip-coating method (the withdrawing rate was 0.5 mm min^{-1}). The samples were dried (24 h) and thermally treated in air at 500 and 800 °C for 1 h. It was shown[8] that, for chemically similar precursors under the same conditions of hydrolysis and gelling, as a result of the thermal treatment of films at 500 °C, an anatase phase crystallized, whereas a rutile phase was formed at 800 °C with a considerable coarsening of the particles. To reveal the effect of this phase transformation on the gas sensitive properties of thin TiO_2 films, the temperatures of 500 and 800 °C were chosen. Since the deposition of the second layer increases the gas sensing metal oxide thin films on the surface of the sensor ceramic substrate with high roughness,[8] the algorithm described was repeated.

For comparison, the thermal treatment of a xerogel powder was studied (Figure 1). It is evident from the X-ray pattern (Bruker D8 Advance diffractometer) of the powder obtained by the thermal treatment of xerogel in air at 500 °C (1 h) that the only anatase phase was formed; as the crystallization temperature

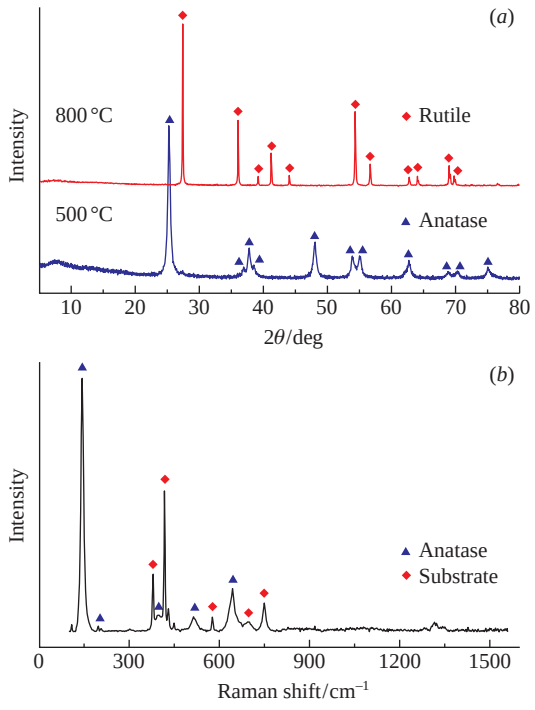


Figure 1 (*a*) X-ray diffraction patterns of TiO_2 powders prepared by thermal treatment of xerogel powder in air at 500 and 800 °C (1 h); (*b*) Raman spectrum of TiO_2 film on Al_2O_3/Pt substrate obtained at 800 °C (1 h).

was increased to 800 °C, anatase completely converted into rutile. The average crystalline grains of nanostructured powders obtained at 500 and 800 °C were evaluated by Scherrer's formula at 21 and 65 nm, respectively, *i.e.*, unit cell volumes differed by a factor of 3.

When the titanium dioxide nanostructured thin films formed on the surface of an Al_2O_3 polycrystalline substrate fitted with interdigital platinum electrodes and a microheater, the X-ray pattern of the sample prepared by thermal treatment at 500 °C involved a little reflection with (101) indices of the anatase phase, which was probably due to both the high dispersity of TiO_2 particles and the small thickness of a coating.

If the crystallization temperature was raised to 800 °C, the intensity of this reflection increased, while those corresponding to the rutile lattice were absent. In this case, the absence of a rutile phase was corroborated by Raman spectroscopy (Senterra Bruker).

Figure 1(*b*) shows that the anatase[10] crystal lattice has peaks at 144, 199, 395, 514, 644 (E_g, B_{1g}, A_{1g}, B_{1g}, E_g and E_g modes) in addition to a background pattern corresponding to the substrate. The essential difference in the behaviors of powders and thin films during TiO_2 crystallization resulting from xerogel heating confirms the effect of film thickness on the anatase–rutile phase transition.[11]

Scanning electron microscopy (Carl Zeiss NVision 40 triple-beam workstation) demonstrated that, because of small sizes, one cannot determine particle size for the titanium dioxide nanostructured thin films supported on an Al_2O_3 polycrystalline substrate obtained at 500 °C. However, the samples obtained at 800 °C formed a nanostructured coating (Figure 2), which had an average particle size of ~50 nm. In this case, there were some gaps due to the great height drop (up to 0.5–1 μm) between Al_2O_3 grains.

It is known[1] that the presence of defects and oxygen vacancies within the TiO_2 crystal lattice allows oxygen to be detected with high accuracy; therefore, gas-sensing properties in oxygen detection for the samples obtained were studied. The resistance of TiO_2 films in air and argon atmospheres was measured with a Fluke 8846A digital multimeter (6.5 Digit Precision Multimeter). The gaseous medium was made in a special quartz cell using two Bronkhorst gas controllers with flow capacities of 200 and 100 ml min^{-1}. The response to oxygen (R_{O_2}/R_{Ar}) (where R_{O_2} and R_{Ar} are the resistance of oxide film in an air–argon mixed flow and in an argon flow, respectively) was recorded at 1, 5, 10, 15 and 20% oxygen concentrations in gas mixtures; the resistance in high-purity argon (99.99995%) was used as a reference line. The calibrated sensor element was heated by a platinum microheater on a reverse side of a substrate.

The response to oxygen was detected at three working temperatures of 350, 400 and 450 °C. For the sample crystallized at 500 °C (1 h), the response (R_{O_2}/R_{Ar}) at 350 °C was 7.73±0.02 to 1% O_2 and 21.30±0.01 to 20% O_2 [Figure 3(*a*)].

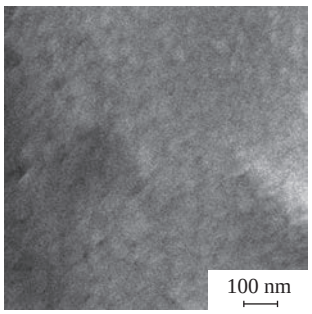


Figure 2 Microstructure of a TiO_2 thin film on the surface of a ceramic sensor prepared by thermal treatment at 800 °C (SEM).

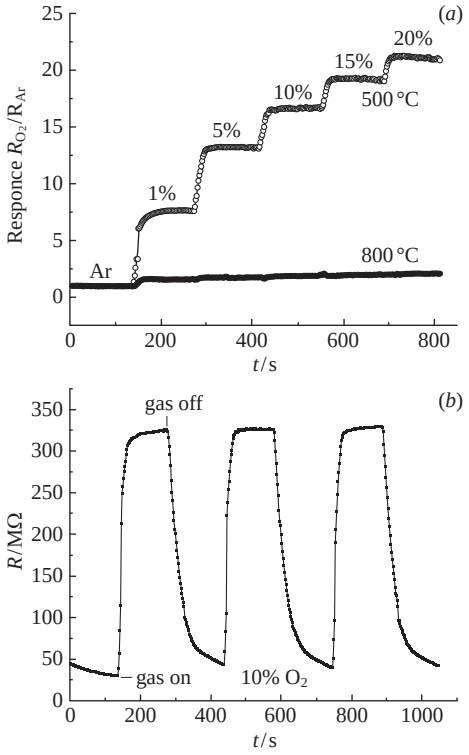


Figure 3 (*a*) Response at working temperature 350 °C of TiO_2 nanostructured thin films prepared at 500 and 800 °C to different oxygen concentration; (*b*) reproducibility of TiO_2 film signal to 10% O_2 at T = 400 °C (preparation conditions: 500 °C, 1 h).

When the working temperature of detection increases, the response to oxygen essentially decreases within the entire concentration range. When this temperature increases up to 400 and 450 °C, the response to 1% O_2 decreases by 12 and 40% or by 30 and 63% to 20% O_2. The larger oxygen concentrations, the higher temperature influence on the oxygen detection. Response time does not change with detection temperature, and it was 22–25 s for working temperatures of 350, 400 and 450 °C.

The TiO_2 nanostructured thin film crystallized in air at 800 °C (1 h) showed essentially lower response to oxygen within the entire concentration range at three working temperatures. The change in the detection temperature does not essentially affect the signal [the response to 1% O_2 (R_{O_2}/R_{Ar}) is 1.5±0.1, and 2.1±0.1 to 20% O_2]. Thus, the response to 1% O_2 (R_{O_2}/R_{Ar}) and to 20% O_2 at 350 °C decreases by 80 and 90%, respectively, in comparison with the sample prepared under milder conditions.

It is evident that a radical decrease in the response to oxygen when the temperature of thermal treatment was raised from 500 to 800 °C was due to the growth and aggregation of particles composing thin films. Although the phase composition of the film obtained at 800 °C was constant, an increase in sample calcination temperature led to a decrease in both the particle dispersity and the sensitivity to oxygen.

Semiconductor properties of TiO_2 enable it to be used in the detection of other analyte gases,[12,13] oxidizers (NO_2) and reducers (CO, H_2 and organic compounds). The experiments performed testify that only the sample whose TiO_2 receptor layer was crystallized from xerogel at 500 °C in air showed some sensitivity to H_2, CO, CH_4 and NO_2 (Figure 4). The response of this sample to hydrogen (100–2000 ppm) occurred at working temperatures of 350, 400 and 450 °C. At 350 °C, the response to hydrogen (R_{air}/R_{H_2}) at 100 or 2000 ppm was 1.26 or 2.53, respectively. The sample sensitivity to CO (200 ppm) (R_{air}/R_{CO}) was 1.7 at 400 and 450 °C; the response to 2000 ppm of CH_4 (R_{air}/R_{CH_4}) was 1.35 at 400 and 450 °C, and the response to 100 ppm of

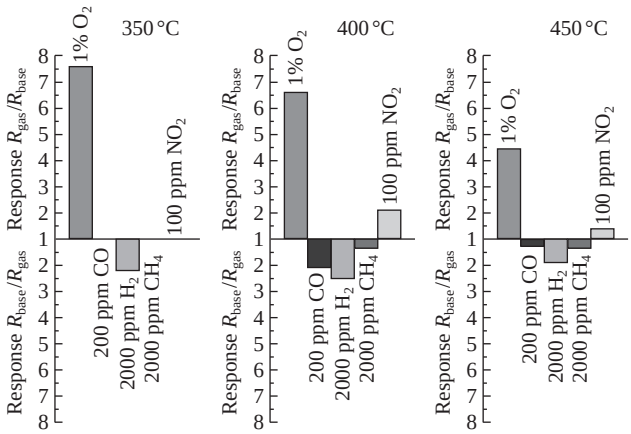


Figure 4 Responses R_{gas}/R_{base} (to analyte oxidizers of 1% O_2 and 100 ppm NO_2) and R_{base}/R_{gas} (to analyte reducers of 200 ppm CO, 2000 ppm H_2 and 2000 ppm CH_4) at detection temperatures of 350, 400 and 450 °C.

NO_2 (R_{NO_2}/R_{air}) decreased from 2.09 to 1.38 as the working temperature increased from 400 to 450 °C.

Thus, the sol-gel TiO_2 nanostructured thin film prepared under the mildest crystallization conditions from xerogel (500 °C, 1 h) exhibited both high sensitivity and selectivity in oxygen detection (1–20% at working temperatures of 350–450 °C) due to the increased dispersity of composing particles. Note that the value of R_{O_2}/R_{Ar} essentially decreased with raising the detection temperature from 350 to 450 °C.

This work was supported by the Russian Foundation for Basic Research (grant nos. 15-29-01213 ofi_m and 18-03-00992 a).

References

1 R. Ramamoorthy, P. K. Dutta and S. A. Akbar, *J. Mater. Sci*., 2003, **38**, 4271.
2 L.-X. Yang, S.-L. Luo, Q.-Y. Cai and S.-Z. Yao, *Chin. Sci. Bull*., 2010, **55**, 331.
3 Y. Li, W. Wlodarski, K. Galatsis, S. H. Moslih, J. Cole, S. Russo and N. Rockelmann, *Sens. Actuators B*, 2002, **83**, 160.
4 I. V. Baklanova, V. N. Krasil'nikov, O. I. Gyrdasova and L. Yu. Buldakova, *Mendeleev Commun*., 2016, **26**, 335.
5 D.-H. Kim, W.-S. Kim, S. Kim and S.-H. Hong, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11817.
6 Z. M. Seeley, A. Bandyopadhyay and S. Bose, *Mater. Sci. Eng. B*, 2009, **164**, 38.
7 N. Luo, H. W. Jing, Z. G. Ma, W. Liu, L. Zhang and G. Sun, *Mendeleev Commun*., 2016, **26**, 157.
8 N. P. Simonenko, E. P. Simonenko, A. S. Mokrushin, V. S. Popov, A. A. Vasiliev, V. G. Sevastyanov and N. T. Kuznetsov, *Russ. J. Inorg. Chem*., 2017, **62**, 695 (*Zh. Neorg. Khim*., 2017, **62**, 707).
9 N. P. Simonenko, V. A. Nikolaev, E. P. Simonenko, V. G. Sevastyanov and N. T. Kuznetsov, *Russ. J. Inorg. Chem*., 2016, **61**, 929 (*Zh. Neorg. Khim*., 2016, **61**, 975).
10 K. Ishioka and H. Petek, *Phys. Rev. B*, 2012, **86**, 205201.
11 N. P. Simonenko, V. A. Nikolaev, E. P. Simonenko, N. B. Generalova, V. G. Sevastyanov and N. T. Kuznetsov, *Russ. J. Inorg. Chem*., 2016, **61**, 1505 (*Zh. Neorg. Khim*., 2016, **61**, 1566).
12 H. J. Kim and J. H. Lee, *Sens. Actuators, B*, 2014, **192**, 607.
13 S. J. Patil, A. V. Patil, C. G. Dighavkar, K. S. Thakare, R. Y. Borase, S. J. Nandre, N. G. Deshpande and R. R. Ahire, *Front. Mater. Sci*., 2015, **9**, 14.

Received: 7th June 2017; Com. 17/5273