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Spark discharge synthesis of semiconductor nanoparticles for thick-film metal oxide gas sensors

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Abstract

Traditional methods of synthesis of metal-oxide gas sensing materials for semiconductor sensors are based on wet sol-gel processes. However, these processes lead to the formation of hydroxyl groups on the surface of oxide particles being responsible for the strong response of a sensing material to humidity. In this work, we investigated the possibility to synthesize metal-oxide materials with reduced sensitivity to water vapors. Dry synthesis of SnO_2 nanoparticles was implemented in the gas phase by spark discharge, which allowed us to produce powder with specific surface area of about 40 m^2/g after additional annealing at 610°C. The drop of sensor resistance does not exceed 20%, when air humidity increases from 40 to 100%, whereas the response to 100 ppm of hydrogen is of a factor of 8 with very short response time of about 1 s.

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Keywords: gas sensor; nanoparticles; spark discharge

1. Introduction

One of the most important obstacles limiting the application of metal-oxide (MOX) gas sensors for contaminant trace detection is the humidity dependence of sensor response. For example, according to recent rules, it is necessary to detect 100 ppm of methane in industrial safety systems. According to datasheet of Figaro Inc., the sensor response to this concentration is ~ 10%; at the same time, the response to the variation of relative humidity from 20 to 100% is 30–40%. According to a recent point of view [1], the response to humidity is due to the presence of OH-groups on

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the surface of metal oxide. Several methods were suggested to decrease the concentration of superficial hydroxyl groups, for example, high-temperature annealing of sensing material, hydrothermal treatment, functionalization with SO_4^{2-} ions, etc. To decrease the concentration of OH-groups, we used dry synthesis of SnO_2 material.

2. Experiment

The gas sensing material was synthesized by spark discharge. This method is very promising for producing various nanoparticles from any parent bulk materials (electrodes) with satisfactory conductivity ($\rho < 0.2\ \Omega\cdot$cm) [2]; this condition is fulfilled for all metals and some semiconductors such as doped Si, Ge, and Sb [2–5]. In this work, we used a custom-built multi-spark discharge generator [6] containing 12 pairs of serially connected cylindrical electrodes powered by a 12-nF capacitor charged by a high-voltage source (Fig. 1, left). The electrodes made of pure tin (purity ~ 99.95%) with a nominal diameter of 6 mm were aligned axially at a distance of 0.5 mm and blown out continuously with dry (RH = 20–30%) clean air at a rate of 15 m/s. The optimum values of the source output voltage and the pulse repetition frequency providing reasonable combination of the mean size (< 100 nm) and the production rate (> 1 g/h) of airborne nanoparticles were found to be 4.5 kV and 2.5 kHz, respectively. The airborne nanoparticles were deposited onto the air filter made of porous stainless steel. In order to reduce the metallic phase content, the as-synthesized powder was annealed in air atmosphere as follows: i) heating up to 610ºC at a constant rate of ~ 5 K/min.; ii) keeping 610ºC for 2 h. The sensing ink was prepared by mortar mixing of pure SnO_2 powder (without any catalyst decoration) with a solution of ethyl cellulose in terpineol. The ink droplet was deposited onto sensor chip by dispensing. The ink was dried at 300ºC (15 min.) and then fired at 720ºC for 15 min.

The phase composition of produced materials was retrieved from X-ray diffraction (XRD) spectra measured with Bruker D8 DISCOVER. The particle size distribution was determined from transmission electron microscopy (TEM) images obtained with JEOL JEM-2100. The specific surface area was estimated by BET method with the use of Micromeritics TriStar 3000. The size distribution of nanoparticles was measured just prior to their deposition with AeroNanoTech DAS 2702 aerosol spectrometer. Gas sensitivity was studied using Microgas-F setup (Russia).

3. Results and discussion

It was found from XRD phase analysis that the as-synthesized powder is comprised of the following crystalline phases: SnO_2 (93.2±0.5 wt. %), SnO (5.4±0.1 wt. %), and metallic Sn (1.5±0.1 wt. %).

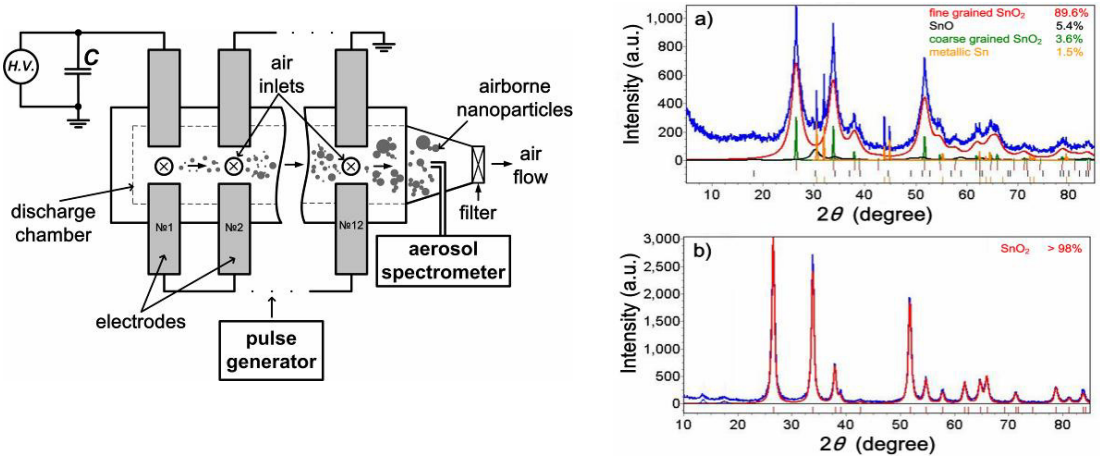

Fig. 1. (Left) Scheme of the multi-spark discharge generator. (Right) Results of XRD phase analysis of as-synthesized (a) and annealed (b) powders: the measured spectra are shown in blue, other spectra calculated by Rietveld method correspond to crystalline phases indicated in the upper right area of each figure.

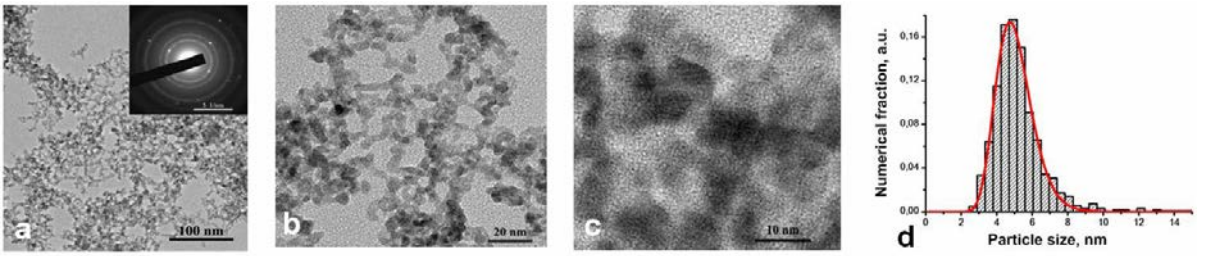

Fig. 2. TEM images of as-synthesized nanoparticles at different magnifications (a, b, c), electron diffraction pattern (inset of figure a), and particle size distribution (d).

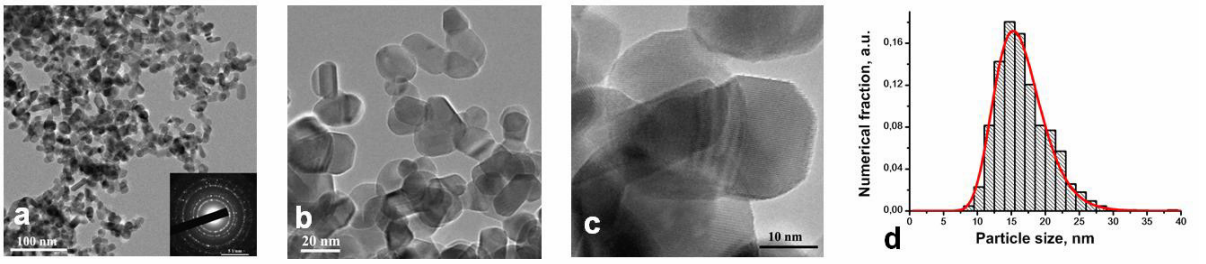

Fig. 3. TEM images of annealed nanoparticles at different magnifications (a, b, c), electron diffraction pattern (inset of figure a), and particle size distribution (d).

The annealed (610°C) powder contains only SnO_2 phase (> 98%) and traces of unidentified phases. The measured XRD spectra together with the calculated spectra of constituent crystalline phases are presented in Fig. 1.

The as-synthesized powder is represented by primary near-spherical particles and their aggregates of irregular shape (Fig. 2). The histogram obtained from the analysis of TEM images of primary particles is well described by the log-normal distribution with the modal size of about 4.7 nm (Fig. 2d). The annealed powder used for patterning the gas sensing layer is represented by near-spherical and slightly elongated particles (Fig. 3) possessing certain surface faceting. The corresponding histogram is well described by log-normal distribution with the modal size of about 15.3 nm (Fig. 3d). According to the electron diffraction patterns (insets of Figs. 2a, 3a), particles in both materials have a crystalline structure; it is also evidenced by TEM images at high magnification (Figs. 2c, 3c). The specific surface area of as-synthesized and annealed powders is found to be about 130 and 40 m^2/g, respectively. These values are well correlated with the size parameters retrieved from TEM images.

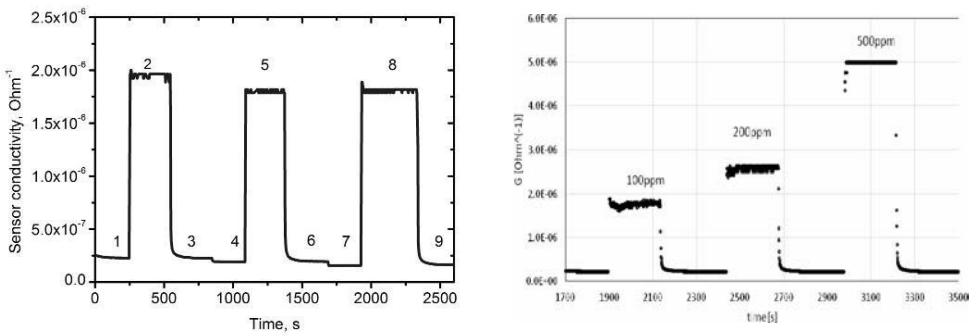

Fig. 4. (Left) Sensor response to 100 ppm of hydrogen at different values of relative humidity (RH): 1 – air @ 80%; 2 – 100 ppm H_2 @ 80%; 3 – air @ 80%; 4 – air @ 60%; 5 – 100 ppm H_2 @ 60%; 6 – air @ 60%; 7 – air @ 40%; 8 – 100 ppm H_2 @ 40%; 9 – air @ 40%. (Right) Sensor response to different concentrations of hydrogen at RH = 60%.

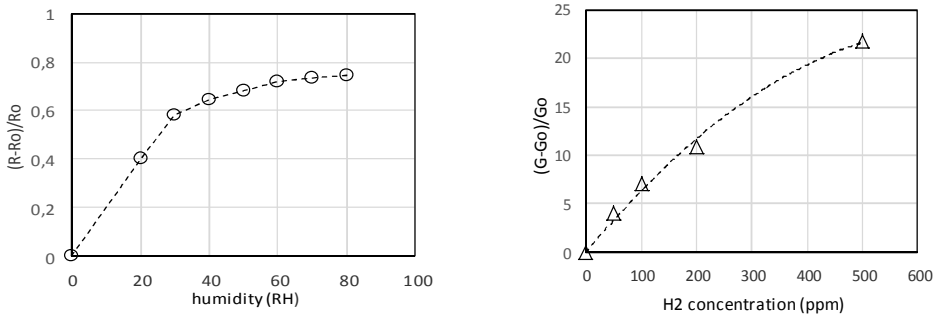

Fig. 5. (Left) Relative change of sensor resistance as a function of relative humidity. (Right) Relative change of sensor conductance at RH = 60% as a function of hydrogen concentration.

The sensor resistance was measured at different concentrations of hydrogen in the air and different values of relative humidity of the air. At a working temperature of 450°C, the resistance drop does not exceed 20% in the humidity range 40–100% (Fig. 5, left). The concentration dependence of relative change of sensor conductance has a usual power law (Fig. 5, right), which is typical of such sensors [7]. At the same time, the sensor response (Figs. 4, 5) to hydrogen concentration of 100 ppm exceeds a factor of 8 in this humidity range. Taking into account random variations of ambient humidity, the hydrogen detection limit is estimated at 1 ppm (3σ). Very fast response to the humidity (~ 10 s) and the hydrogen (~ 1 s) can be considered as outstanding feature of such sensors as compared to the conventional metal-oxide sensors prepared by wet sol-gel processes.

4. Conclusion

The metal oxide gas sensing material (SnO_2) with a reduced sensitivity to water vapors was investigated. To decrease the concentration of OH-groups, dry synthesis based on spark erosion of tin electrodes in air atmosphere was employed. The fabricated sensors demonstrated outstanding characteristics: very fast and stable response to hydrogen (~ 1 s) and humidity (~ 10 s). Together with moderate sensitivity to the humidity, this enables accurate correction of gas concentration measurement results by using an additional humidity sensor. Thus, the metal oxide materials produced by spark discharge have obvious advantages over materials synthesized by wet sol-gel processes used in the conventional MOX sensors.

Acknowledgements

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