Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1395 - 1398

NIOBIUM-DOPED TITANIA NANOPOWDERS FOR GAS SENSOR APPLICATIONS

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Pure titania and titania doped with Nb (3%) was synthesised by sol-gel route from alkoxide precursors. The gel obtained was dried to get nanopowders and then calcined at various temperatures. XRD and SEM characterization were made to know the physical properties of these materials. The sensing properties towards O_2 were tested using different concentration of O_2 in N_2.

(Received April 12, 2005; accepted May 26, 2005)

Keywords: Gas sensor, Nano-powder, Nb/TiO_2

1. Introduction

Due to many advantages as low cost, small size and low power consumption, semiconductor sensors appear as a good solution for gas detection. Titanium dioxide is the semiconductor material most widely used for oxygen detection [1]. Titania (usually rutile crystalline phase) based sensors need to work at high temperatures (700-1000ºC), with a high power consumption, which is not desirable for electronic applications.

Oxygen detection, in rutile state, is mainly due to diffusion of oxygen ions in the bulk of the material. This is because rutile is a completely stable phase. For bulk reaction it is necessary to work at high temperatures (700 – 1000ºC). On the other hand, oxygen detection in anatase state titania is mainly due to surface reaction that takes place at not so high temperatures (400 – 500 ºC) [2,3]. So it can be derived that maintaining an anatase structure would allow the detection of oxygen at medium temperatures, which is desirable for sensor design [4].

When titania is doped with pentavalent impurity ions, i.e. Nb^{5+}, such ions get into the anatase titania crystalline structure giving rise to a hindering in the phase transformation to rutile and an inhibition in grain growth. In undoped titania, the change from anatase to rutile starts at about 600 ºC. In doped titania, the temperature to start this change is higher, around 750 ºC. This effect is attributed to the extra valence of niobium ions, in comparison with titanium ones, which reduces oxygen vacancies in the anatase phase, thus retarding the transformation to rutile [5].

Furthermore, grain growth is inhibited due to the stress induced to the anatase structure by the Nb^{5+} substitutional ions, with slightly higher ionic radius value with respect to Ti^{4+}. Small grains mean more active area, which increases sensor sensitivity [2].

It has been also reported that Nb-doped titania shows higher sensitivity towards oxygen and shorter response time than pure TiO_2 [6]. The doped material also shows lower impedance at low operating temperatures and hence, it is easier to design associated electronic circuitry [4]. J. Arbiol [5] reported that there is an optimum range for the concentration of Nb dopant; this range is around unities of atomic percent of Nb^{5+} in titania. The best doping concentration for titania was found around 3 at% of Nb^{5+}.

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2. Synthesis of the active material

Nb-doped titanium was prepared from alkoxides precursors via sol-gel route in dry nitrogen atmosphere. The precursors used were titanium isopropoxide (IV) $Ti[OCH(CH_3)_2]_3$ with a 99,99% purity and niobium ethoxide $Nb(OC_2H_5)_5$ with a 99,99% purity. A solution of these two precursors was made, in proper concentrations for doping, in isopropanol solvent. Then, this solution was added to water containing nitric acid under stirring. The final composition of the constituents was set to satisfy $[Ti]:[HNO_3]:[H_2O] = 1:1:100$ in molar ratio. The initial water concentration is a main factor in average particle size. If it increases, it produces higher nucleation rates, which results in a decrease in average particle size. Based on this, a $[H_2O]:[Ti]$ ratio of 100 was selected. In the presence of such amount of nitric acid, the hydrolysis proceeded without forming a precipitate, leading to a transparent sol. Gellification of the sol was achieved by increasing the pH. This was done by adding a weak alkaline solution, i. e., an aqueous solution (1 M) of Ammonium Carbonate [7].

The gel was dried at a temperature of 80ºC for 72 hours to eliminate organic elements. The obtained precipitate material was milled and then calcined at 600 ºC, 700ºC, 800 ºC and 900ºC. The reason for these different calcination temperatures is to find the maximum temperature in which the material crystalline structure is still mostly anatase. A temperature ramp of 5 ºC per minute was employed to reach calcination temperatures, this slow rate of temperature increment is to hinder grain growth.

3. Experimental

SEM and XRD characterization of the active layers were made. For SEM analysis, the samples were coated previously with a thin gold layer, which was sputtered to avoid charging effects. The samples were observed using a JSM 6400 scanning electron microscope. For XRD characterization, a Siemens D5000 X-Ray diffractometer was used.

For the characterization of the sensing properties, two types of sensors were built. For this, pure titania and Nb-doped TiO_2 nanopowders were dispersed in glycerol and then a drop of the resulting paste of each material was deposited manually over the sensor electrodes. The as-deposited films were dried using a ramp of temperature, from ambient temperature to 300 ºC, with an increment of 20 ºC per minute to avoid cracks in the layer. The active layers were annealed at 600 ºC for 2 hours.

Drying and annealing processes were made in situ using the heater of the sensor. A voltage ramp was applied to the heater of the sensor employing a computer programmable power supply. Finally, sensors were connected into a test chamber (with a volume of 16 cm^3). In a first stage, a mixture of synthetic air and pure nitrogen was set to have an oxygen concentration of 10%. This mixture of gases was input into the test chamber and the sensor base line was established. A constant flow of 140 ml/min was fixed to avoid interference of pressure in the measurements. Different mixing concentration of synthetic air and N_2 were used to obtain and measure oxygen concentration of: 10%, 8%, 6%, 4%, 2% and 1%. The mixtures were set by mass-flow controllers. The accuracy of each mass-flow meter was $\pm$1 % of its full scale. The operation temperature was set at 500 ºC. The acquisition of the sensors' resistance was performed with an Agilent 34970A data acquisition unit.

4. Results

4.1. Structural properties

A comparison between the XRD patterns of Nb-doped titania and pure titania is shown in Fig. 1. It can be seen that in undoped material (Fig 1a.), at 600 ºC, both anatase and rutile phases are present. At 700 ºC the change of phase to rutile is almost complete. Making an extrapolation it is possible to ensure that the beginning of phase transition in undoped material was at about 500 ºC.

On the other hand, in doped titania (Fig 1b.) clear signs of phase transformations appear around 700 ºC. Even at 800 ºC there is presence of titania in anatase phase. These results indicate that the addition of Nb^{5+} to TiO_2 structure retarded the change in crystalline phase from anatase to rutile. This retard in phase change allows the sensor to work at appropriate temperatures and help oxygen catalysis on the active layer surface, avoiding the irreversible change to rutile phase, avoiding the need to work at higher temperatures (~800 ºC) to detect oxygen.

Based on XRD analysis, it is possible to conclude that the maximum annealing temperature of doping material to ensure that a considerable quantity of material remains in anatase state is 700 ºC. Therefore, the maximum working temperature will be 600 ºC. In undoped material, the maximum annealing temperature to ensure that part of the material is in anatase phase and is 600 ºC, and then in this case the maximum working temperature will be 500 ºC.

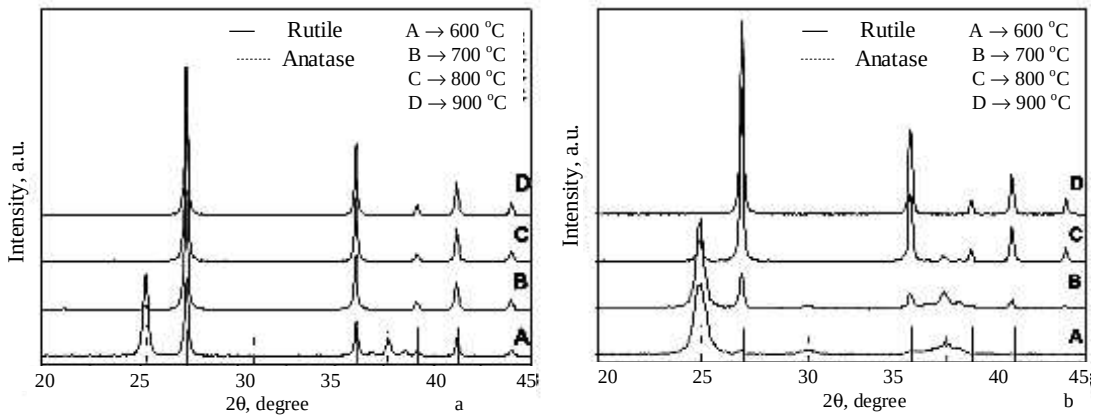

Fig. 1. XRD patterns of a. pure TiO_2 and b. TiO_2 doped with 3 at% of Nb.

It is also possible to see that peaks in Nb-doped titania pattern are wider than those in undoped material. That means that crystal size is smaller in Nb-doped titania, so it can be concluded that grain growth of TiO_2 crystallites is hindered by the addition of Nb. This observation is also supported by SEM photographs of material calcined at 600 ºC, as shown in Fig. 2, where it was observed that the doped material is composed by nanoscale particles of about 50 nm (Fig 2b.) while in undoped material nanoparticles size is about 100 nm (Fig. 2a.).

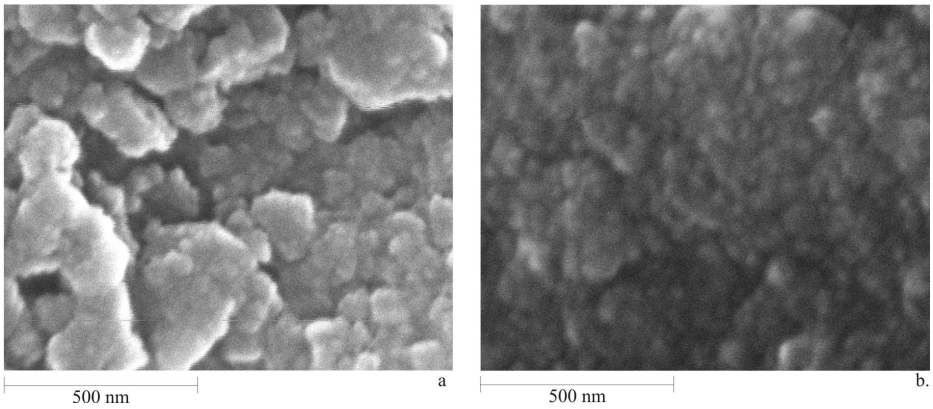

Fig. 2. SEM image of a. pure titania, and b. Nb-doped titania. Both calcined at 600 ºC.

4.2. Sensing properties

Both materials, doped and undoped titania, were tested at 500 ºC, which is the maximum common working temperature to compare the behaviour of sensors. Fig. 3 shows the response of

sensors to different concentrations of oxygen. As it can be seen, both materials, doped and undoped, react to oxygen. At 500ºC this response is attributed mostly to superficial reactions that take place on titania in anatase phase which is present in both materials. The difference is in the resistivity of the materials: while in doped samples, the resistance is in the range of tens of megaohms, in undoped samples it goes up over the hundred megaohms. This lower resistance of doped material was expected because the Nb^{+5} ion acts as a donor type impurity and leads to a decrease in the resistivity of the semiconductor [4,8,9], and is very desirable for electronic designs.

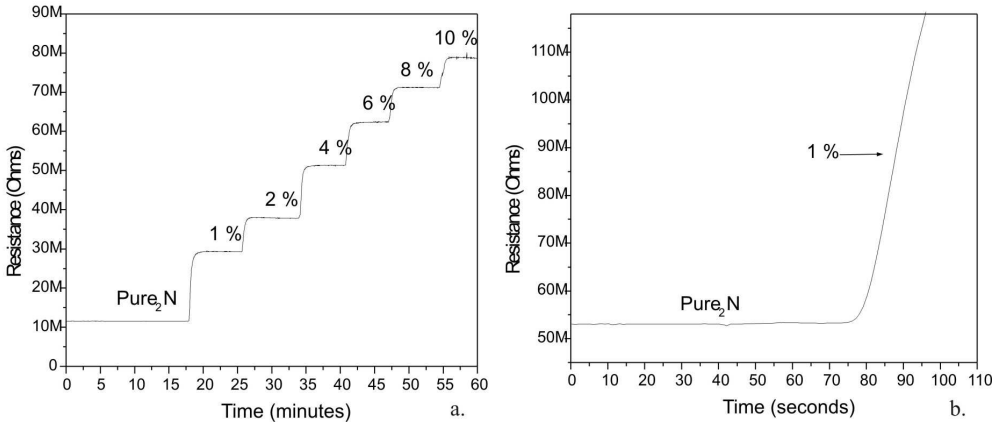

Fig. 3. Response to different oxygen concentration in a flow of N_2 of a. Nb-doped titania sensor, and b. pure titania sensor.

5. Conclusions

Pure titania and Nb-doped titania nanopowders were synthesized by a sol-gel route. XRD and SEM analysis showed that addition of niobium to the titania structure retarded phase change from anatase to rutile. Niobium also hinders grain growth, which results in more active area. The maximum annealing temperature to have a significant part of the material in anatase phase was 600 ºC for pure titania, and 700 ºC for Nb-doped titania. It was also observed that addition of Nb^{+5} reduced the electrical resistivity, so it can be said that niobium acts as an electrical dopant.

Sensitivity of pure and Nb-doped titania to oxygen was tested under different O_2 concentration in a flow of N_2. It was found that pure and Nb-doped titania sensors were responsive to oxygen. In the case of pure titania, only the reaction to 1% of O_2 could be observed, but not the stabilized resistance, this was because of the high electrical resistivity of the material. On the other hand, Nb-doped titania showed a good responsiveness to oxygen in N_2.

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