JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 8, August 2008, p. 2138 - 2141

Synthesis, characterization and gas sensing properties of rutile TiO_2 doped with Pt obtained by sol-gel method

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The gas sensitive oxide TiO_2 doped with Pt was obtained by sol gel polymeric method. The reagents used as precursors were the tetra-iso- propylortotitanate alcoxide, platinum chloride, surfactant butylamonium bromide and polyvinibutyral as polymer. The molar ratio used surfactant/alcoxide=0.1. The materials were obtained as films or powders. The obtained gels were dried at 373 K and heat treated in air between 473-873 K The films were obtained by dipping method and the support was CeO_2-Ta_2O_5 disc. The obtained materials was characterized by XRD, SEM, TEM electron microscopy and N_2 adsorption-desorption. The sensing properties of TiO_2-Pt films were tested in NOx and CO_2.. For the 10 mg/m^3 NO_x and 5000 ppm CO_2 after 5 minutes gas exposure, the sensor voltages were 35 mV for NO_x and 65 mV for CO_2.

(Received April 4, 2008; in revised form June 6, 2008; accepted June 30, 2008)

Keywords: Gas sensors, TiO_2-Pt, Semiconductor oxide, Nanostructure, Sol-gel method

1. Introduction

The development of reliable and selective solid-state gas sensors has great importance both in the field of atmospheric pollution and in the emission control from combustion plants. Recently, many efforts have been aimed to improve the gas sensor performances. Titanium dioxide is a very useful materials and has been extensively investigated for its gas sensitive behavior excellent dielectric property as well as having catalysis applications [1-3]. Rutile TiO_2 is a n type semiconductor oxide with a wide band gap of about 3 eV. TiO_2 in form rutile has a flat tetragonal unit cell with two Ti atoms and four O atoms. The Ti atoms are surrounded by six O atoms and as in many ionic crystals, the geometric structure is determined by the relative size of the ions and the coordination.[4] The octahedral configuration of O atoms around the Ti atom is slightly distorted to accommodate all the ions. Bond lengths between Ti and O atoms are 1.946 Å and 1.983 Å for the four-fold symmetric and two-fold symmetric bonds respectively. In the crystal, the octahedral are stacked with their long axis alternating by 90^o resulting in three-fold coordinated O atoms.[5] The valence band is based predominantly on O 2p orbitals, while the conduction band is Ti 3d based. The ionicity – the degree of ionic bonding-of TiO_2 in form rutile is of the order of 70% meaning that it has a non negligible covalent character.[6] For gas sensing applications many efforts have been aimed to improve the gas sensing performance by preparing porous, high specific surface area TiO_2 films, since the number of gas molecules that interact with the semiconductor can be increased in this way [3]. A wide variety of techniques have been used to prepare porous TiO_2, such as sol–gel , direct deposition from aqueous solutions, sputtering, laser-assisted pyrolysis, co-precipitation and hydrothermal method [1]. Sol–gel techniques offer important advantages due to excellent compositional control, high homogeneity at the molecular level, lower crystallization temperature and, feasibility of producing thin films. The use of a metal-organic precursor as a starting material is an effective way to improve gas sensitivity and selectivity at low temperature. This is because it is possible to form films with controlled microstructure including the hetero components that are homogeneously dispersed and bonded at the molecular level. In our study, a metal-organic precursor containing Ti and Pt was synthesized to disperse Pt particles on the nanoscale throughout the TiO_2 matrix [7,8].

In reactions involving titania, oxygen vacancies are one of the major advantages of such material. However, for better sensing performances, titania surface is decorated with a variety of additives, such as platinum. These additives enhance the material sensitivity and selectivity and reduce the response time and operating temperature of the sensing layer. In this paper, we present the synthesis and characterization of mesoporous porous Pt doped TiO_2 materials and their gas-sensing properties. The sol–gel polymer/inorganic hybrid route capable of producing not only thick enough coatings without cracking but also films with novel properties was used to obtained the films by dip coating method .

2. Experimental

The preparation of TiO_2 with 1% Pt, was realized by sol-gel polymeric method. The surfactant used was cetyltrimethylammonium bromide (CTAB) and polymer was polyvinibutyral. The reagents used as precursors were titanium isopropoxide and $PtCl_2$. The oxides were obtained by partial hydrolysis of alkoxide in the presence of water resulting from an esterification reaction between propylic alcohol and acetic acid. The sols were mixed with CTAB, PVB and $PtCl_2$ solution in alcohol. The molar ratio surfactant/alcoxid was 0.1. The resulting sol-gel was gelled at 313 K in air for hydrolysis and polymerization of the inorganic precursors or supported or supported on the disc of CeO_2-Ta_2O_5 by dipping method. The gels were dried at 373 K and were thermally treated in air at temperature of 473 K, 673 K or 873 K.

The obtained materials were characterized by X-ray diffraction (XRD) (Philips PW 170 diffractometer), 2 adsorption/desorption (Micromeritics), TGA, scanning electron microscopy (SEM) with a PhilipsXL-20 microscope, transmission electron microscopy (TEM) with Philips Tecnai microscope.The sensor support consists by a disc from CeO_2-Ta_2O_5 obtained by sintering method. The raw materials CeO_2-Ta_2O_5 were milling in the ball-mill in moisture atmosphere 6 hours and dried at 373K and pressing into a disc ∅10 x1mm at 20 N/mm^2 and sintering at 1773K for 5 hours. The sensitive element was deposed on the disc by dip coating in 200 nm thickness and calcining at 473K and 873K. The sensor was contacted by 2 metallic blades. The sensing activity was tested in the static system, where the device was placed in an insulated glass test chamber.

The sensing activity was tested in the static system, where the device was placed in an insulated glass test chamber. Electrical characterization was carried out by volt-amperometric technique. Sensor element was connected to a multimeter type EXTECH LASER POINTER for the voltage measurements

3. Results and discussion

XRD patterns of TiO2-Pt oxides reveal the presence of rutil phase and amorphous phase. Rutil phases were clearly observed on the XRD patterns of the calcined mixed oxides at temperature of 873 K. The XRD patterns suggest that oxides gel started to crystallize after 673 K. The diffraction peaks became sharp with a rise in calcination temperature, indicating the grain growth of TiO2 crystallites. In Fig.1 XRD patterns at low angle reflections exhibit the presence of amorphous phase with a mesoporous structure. The low-angle diffraction indicates that mesoscopic order is preserved in the calcined oxides. This is confirmed by transition electron microscopy (TEM, SEM) and nitrogen adsorption-desorption isotherms. No phase other than rutil was observed up to calcination at 673 K, and this phase became prominent for the powder calcined at 873 K. For the as-synthesized powder, it is obvious that fine particles agglomerate to form large secondary particles. The evolution of the mesoporous structure was examined by TEM and SEM for the samples calcined at 873 K and 1273 K. Development of the ordered mesoporous structure in the TiO_2 powder was suggested by its TEM photograph shown in Fig. 2 and 3. The formation of crystallites are evidenced by TEM image (Fig. 3).

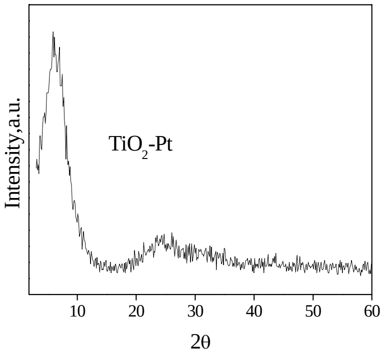

Fig.1. XRD patterns of TiO_2-Pt powder calcined at 473 K.

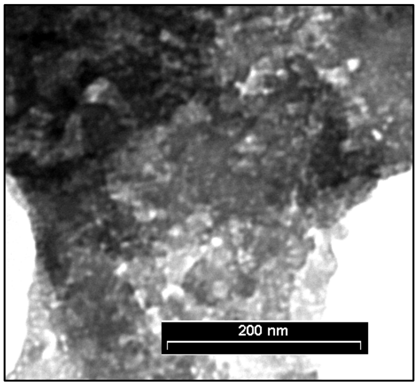

Fig.2.TEM image of TiO_2-Pt powder calcined at 473 K

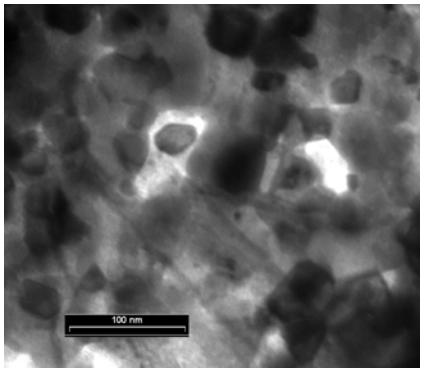

Fig.3. TEM image of TiO_2-Pt calcined at 873 K.

TEM micrographs show that titania structure are not influenced by platinum whereas the size particles increases with the heat treatment temperature. A uniformly dispersion of Pt in titania was obtained by sol-gel method. Fig. 4 shows SEM photographs of TiO_2-Pt calcined al 473 K. The morphology is typically for mesoporous structures and that fine particles agglomerate with increasing of temperature of termic treatment to form large secondary particle with crystalline structure. SEM images of TiO_2-Pt films obtained by coating of CeO_2-Ta_2O_5 support exhibit a similarly spherical morphology (Fig. 5).

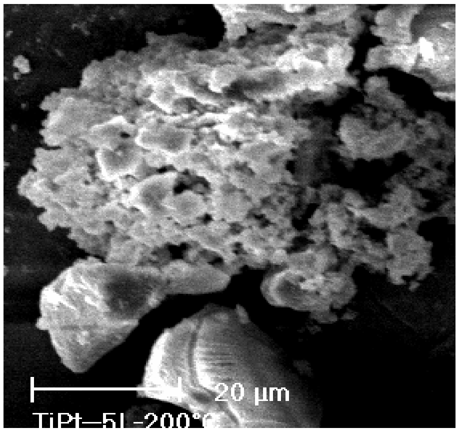

Fig.4 SEM image of TiO_2-Pt calcined at 473 K.

N_2 adsorption-desorption isotherms obtained for the samples calcined at different temperatures confirm modification of structure and formation of a more dense phases with increasing of temperature (Fig.6). The obtained oxides are mesoporous materials with high surface area.

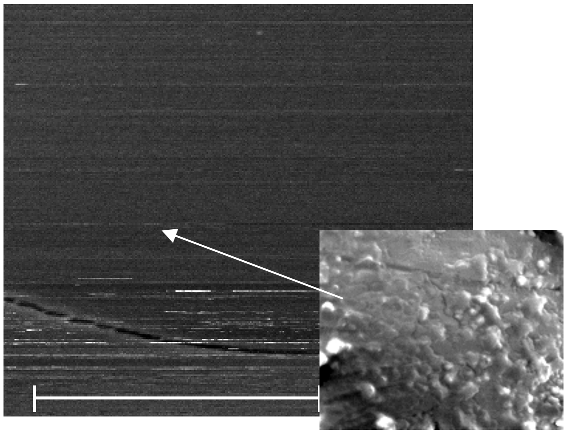

Fig. 5 SEM images of TiO_2-Pt film calcined at 673 K

The formation of low-densified oxides, with mesoporous structure, after 800 K, can be related to the mesopores growing into layer connected channels during calcinations and the decreasing of pores diameters following sintering processes. Almost similar microstructure was observed for the powders calcined at 473 K. However, interconnected spherical particles with smooth surface were observed after calcination at 673 K and the particle size slightly increased after calcination at 873 K indicating rapid grain growth of TiO_2 to micron-size particles. In accordance with these changes, the surface area decreased from 154 m^2/g (for the as-synthesized powder) to 54 m^2/g (for the powder calcined at 873 K). The obtained oxides are mesoporous materials with high surface area and highly stable structure. Characterization revealed that the mesoporous powder, calcined at 873 K was weakly agglomerated and had a high surface area. TG analyses performed in powders calcined at 673 K show a mass loss, 71% of the resin initial mass, occurs up to 873 K due to elimination of water and organic substances. From the above results, the ordered mesoporous structure of TiO_2 was not thermally stable enough, and particle size of both powders apparently grew up to micron order after calcination at 873 K. However, it was confirmed that some fractions of the ordered mesoporous structure still remained even after the calcination at 873 K. This is the main reason for their large surface area enough for sensor application, irrespective of their micron-size particles. Formation of homogeneous mesostructured solid was attributed to the surfactant templating effect during the sol-gel chemistry.

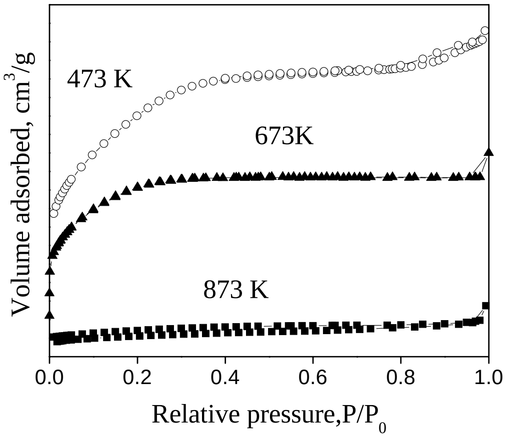

Fig.6. N_2 adsorption-desorption isotherms of the calcined TiO_2-Pt materials

In order to improve the gas sensor characteristics, TiO_2 has been modified by platinum. The efficiency in catalytic introduction has been improved by adding the Pt precursor in the rutil titania phase, whose surface reactivity for the Pt incorporation is better.

The sensors with the sensitive element TiO_2-Pt calcined at 473 K, 673 K or 873 K were exposed in NO_x and CO_2 atmospheres at the room temperature. Fig.. 7 shows the characteristics voltage-time for 10 mg/m^3 NO_x. The sensing properties are higher at 673 K than that at 473 K and 873 K. The same properties were evidenced for CO_2 atmosphere (5000 ppm CO_2). For the NO_x detection, the sensor present a quickly response developing a voltage of 35 mV in the first 5 minutes after exposure and for CO_2 detection the sensor was developed 65 mV in the first 5 minutes. In NO_x atmosphere, the signal of the sensor increase slowly up to 80 minutes of exposure corresponding of the 88 mV follow by the stability and for CO_2 measurement the signal increase quickly up to 20 minutes exposure, follow by a decreased of the signal. The sensor presents a very high sensitivity for the NO_x at small value of CO_2concentration.

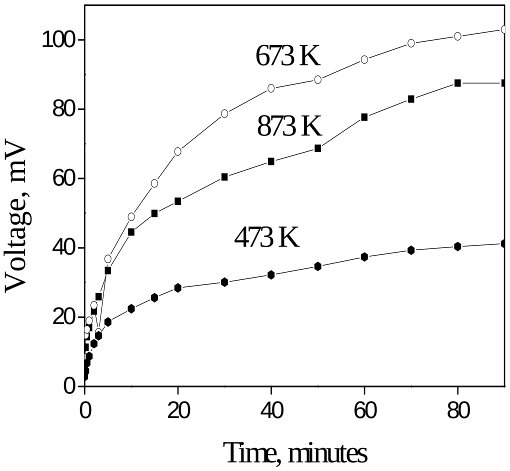

Fig. 7. The characteristic voltage-time in NOx forTiO_2-Pt films calcinated at different temperatures.

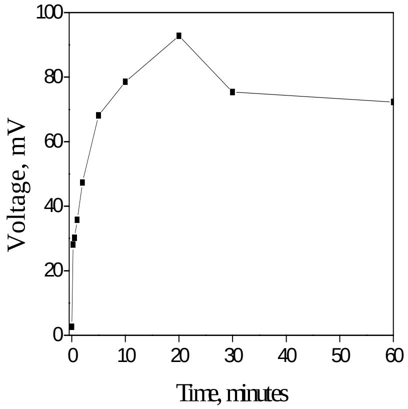

Fig. 8. The characteristic voltage-time in CO_2 for for TiO_2-Pt film calcined at 873 K.

4. Conclusions

The sensors prepared by dipping of TiO_2-Pt gels, synthesized by sol-gel method, in this study, present sensitivities over the NO_x and CO_2. The improved sensitivities arose from the mesoporous structure introduced by the present modified sol–gel method. In order to improve the gas sensor characteristics, TiO_2 surface has been modified by platinum. The efficiency in catalytic introduction has been improved by adding the Pt precursor in the rutil titania phase, whose surface reactivity for the Pt incorporation is better.

The gas sensitive element TiO_2 doped with Pt was obtained by sol gel polymeric method followed by calcination at 473K, 673K and 873K. A mesoporous phase was obtained to 473 K transformed to crystal phase to 873K. After 5 minutes exposure in 10 mg/m^3 NO_x the sensor present a quickly response developing a voltage of 35 mV and for CO_2 exposure the signal of the sensor was 65 mV. The sensor presents a very high sensibility at the small value of NOx concentration.

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