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Formation of Porous ZnO Nanosystems for Potential Use in Sensor Electronics

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The semiconducting ZnO is a very promising material for applications in UV light emitters, optical detectors, solar cells, piezoelectric transducers, transparent electronics, gas sensors etc. It is known that physical properties, and as a result areas of applications, are strongly determined by morphology and size of the material's structural elements. Therefore, the development of a technology that allows formation of nanoporous metal oxide structures with a high surface to volume ratio is of great interest nowadays. The aim of this work was to develop technology for selective formation of porous ZnO nanosystems and to determine the relationship between morphological characteristics of the layers obtained and their optical and electrical sensor properties with the aim of potential applications in optoelectronics and sensor electronics.

Keywords: Metal Oxides, Sensors, Porous Nanostructures, Magnetron Sputtering, Photoluminescence.

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1. INTRODUCTION

The metal oxide ZnO is widely used in photocatalysis, gas sensors and light emitting diodes. Nowadays much attention is devoted to the investigation of sensor properties of ZnO. This is due to the fact, that this material has high sensory sensitivity, rate of response and recovery rate. Moreover, it is shown, that it has high sensitivity to the "invisible gases" such as CO, H_2, alcohol, toluene and methanol. The operation efficiency of ZnO based devices depends on the layer crystalline phase state, dimension and morphology. It is known, that sensitivity is significantly enhanced with increasing porosity of the three-dimensional system, and with decreasing in size of the structural elements to the nanoscale. Therefore, in order to improve the efficiency, much attention is paid to the development of the technology which allows the formation of nanostructures with desired morphology and dimension.

Our previous experiments have shown that under conditions of quasi-equilibrium steady-state condensation the self-organization of three dimensional micro- and nanosystems on substrates can be observed. These structures have complicated architectures with narrow size and shape distributions of the structural elements. In this work the two-stage fabrication of porous metal oxide structures is proposed.

2. EXPERIMENTAL PROCEDURE

At the first stage highly porous zinc nanostructures with different morphologies have been obtained using condensation under conditions close to thermodynamical equilibrium in plasma-condensate system. The principle components of the device are the magnetron sputterer in combination with the hollow cathode which operate under high pressure of highly refined argon. It is worthwhile to point out that almost all atoms of inert gas and sputtered substance become ionized when get inside the hollow cathode. Under increased pressure, plasma particles collide so frequently and intensively to average their energy effectively.

The mentioned above technology is characterized by two main peculiarities: the condensation process goes at sufficiently low supersaturation to provide a proximity to the phase equilibrium between condensate and depositing substance; this supersaturation remains stable in time to guarantee the steady-state conditions of the condensation process. Due to above conditions adsorbed atoms can attach to the growth surface only if the strongest chemical bonds are realized to minimize the free energy. As a result adjacent local parts of the condensate grow at different rates. Spatially-distributed growth selectivity of such type is named structural selectivity. The second mechanism contributing to different growth rates of adjacent local surface parts is field selectivity. It is caused by focusing of depositing ion fluxes by electric field onto projecting parts of the growth surface. Obviously, the field selectivity is implemented only provided growth surface is negatively biased and depositing substance is mainly ionized.

It should be noted that structural and morphological characteristics of the condensates are easily controlled by varying such technological parameters of the experiment as working gas argon pressure and power of discharge. The typical morphologies are shown in Fig. 1. Elemental analyses have shown that the zinc layers obtained have no significant admixtures.

At the second stage, Zn samples were oxidized in a CVD device for three hours in 99,9 % oxygen under a pressure of 800 mbar and at temperatures of 200 °C, 350 °C and 400 °C. Elemental analysis also have been made after the oxidations. They show, that the composition varies from 43.1 to 46.2 at% oxygen. XRD investigations have been made to observe the transformation of zinc to ZnO. For the samples oxidized at 350 °C and 400 °C all diffraction pattern correspond to ZnO while zinc peaks have completely disappeared. Samples oxidized at 200 °C show characteristics of both species. The results of SEM and X-ray diffraction

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investigations have shown that the most effective mode of oxidation corresponds to a temperature of 350 °C because here the full transformation of zinc into ZnO occurs without any changes in the condensates morphology. Finally sensing and optical properties of three-dimensional metal oxide nanostructures have been investigated depending on their morphology.

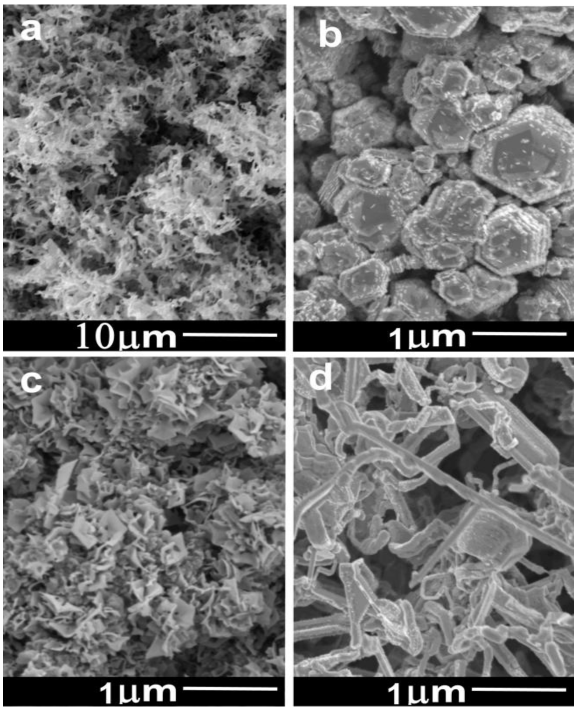

Fig. 1 – Some typical morphologies of Zn layers obtained.

3. RESULTS AND DISCUSSION

The photoluminescence properties of ZnO nanostructures have been investigated in this work. The spectra obtained (Fig. 2) show narrow peaks in UV range (374 nm) and broad in green range (510 nm). Spectral analyses have shown that the optical properties of the nanostructures depend on the ZnO morphology and oxidation temperature. In the case of oxidations at 350 °C the maximum luminescence intensity for most of the samples occurs in the UV range. Oxidations at 400 °C lead to a decrease in UV peak intensity while the green peak becomes dominant. For some morphologies the UV peak almost disappears. Thus, the proposed technological approach allows the formation of highly porous ZnO nanostructures with different morphologies and adjustable optical properties.

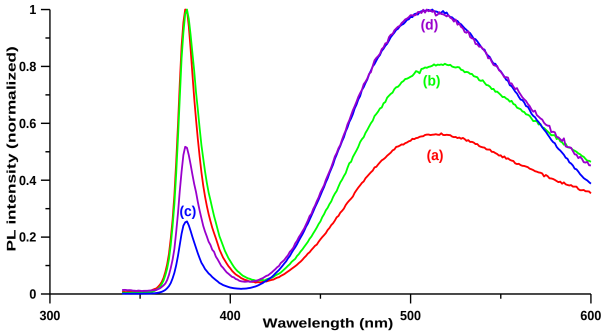

Fig. 2 – Photoluminescence spectra of the samples 1 and 2 (a) and (b) oxidized at 350 °C; (c) and (d) oxidized at 400 °C.

The sensing properties have been studied depending on the morphology. The methodology of the sensing experiments was as follows: current-voltage curves between contacts on surface were measured for a range of temperatures from 20 °C to 200 °C with an increment of 10 °C first in air and then in CO atmosphere. Then for each temperature the resistivity was determined. The sensor response or sensitivity (S) was calculated as the ratio of resistivity in CO and in air. In figure 3 one sees the sensitivity S in respect to the temperature.

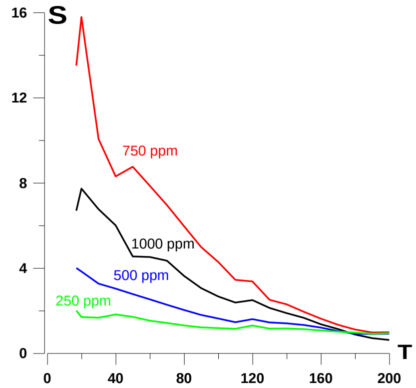

Fig. 3 – ZnO gas sensor measurements for CO concentrations 1000 ppm, 750 ppm, 500 ppm and 250 ppm.

Comparing our results with literature, it should be noted that usually the sensitivity has large values at high temperatures of 200 °C and more. For our samples there is a high response even at low temperatures about 20 °C to 30 °C, so they can be potentially used as CO sensors at room temperature.