Semiconductor Ce-containing materials based on SnO_2 for gas sensitive layers of H_2 sensors

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Introduction

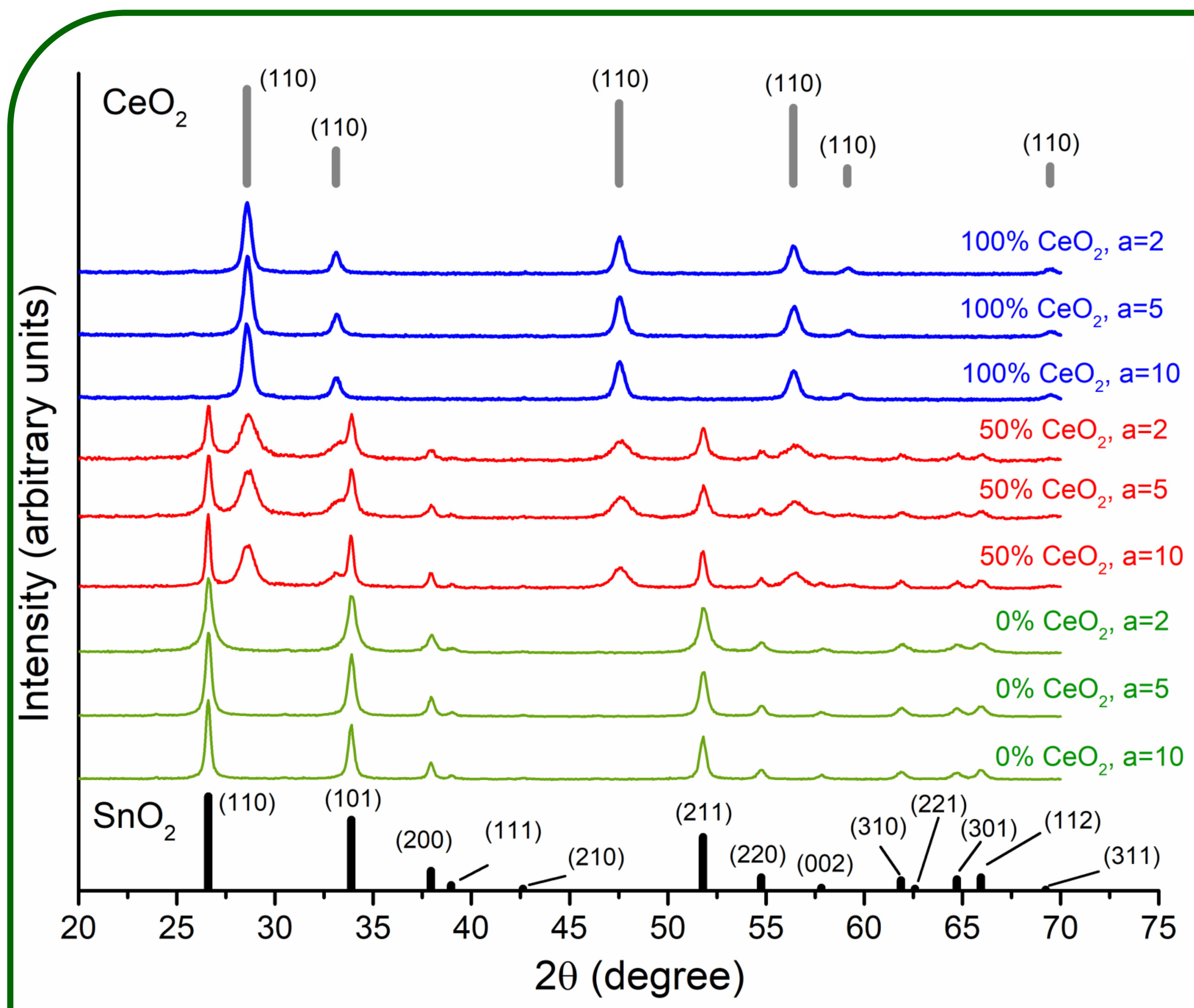
For detection of hydrogen leakages adsorption semiconductor sensors can be used due to their low cost, simple construction, low power consumption and high sensitivity. Their sensing mechanism is based on catalytic oxidation of H_2 molecules on the surface of the semiconductor gas sensitive layer by chemisorbed oxygen, that causes a change of the electrical resistance of the sensor. The most used material for the gas sensitive layer is tin dioxide because of its chemical stability. However, in order to increase sensitivity to hydrogen some catalytically active dopants can be added to the semiconductor gas sensitive material. Cerium can be such additive due to its ability to promote formation of active oxygen during $Ce^{4+} \leftrightarrow Ce^{3+}$ transition and high activity in oxidation reaction. In this work we compare Ce/SnO_2 microcrystalline sensor material obtained by wet impregnation technique and CeO_2-SnO_2 nanocomposite obtained by Pecini synthesis.

Target

The goal of this study was to investigate Ce doped tin dioxide materials obtained by different techniques and study gas sensitive properties to hydrogen of the sensors based on them. To achieve the target next experimental methods and techniques were used:

- Transmission electron microscopy (TEM) to study morphology of Ce/SnO_2 (Selmi TEM – 125K)
- Scanning electron microscopy (SEM) of Ce/SnO_2 (Jeol Superprobe 733)
- X-ray diffraction analysis (XRD) to investigate phase composition of the gas sensitive materials (Bruker D9 Advance, CuK_α radiation)
- Studies of gas sensitive properties to 40 ppm H_2 (were performed on a special electric stand)

Ce-containing sensor materials

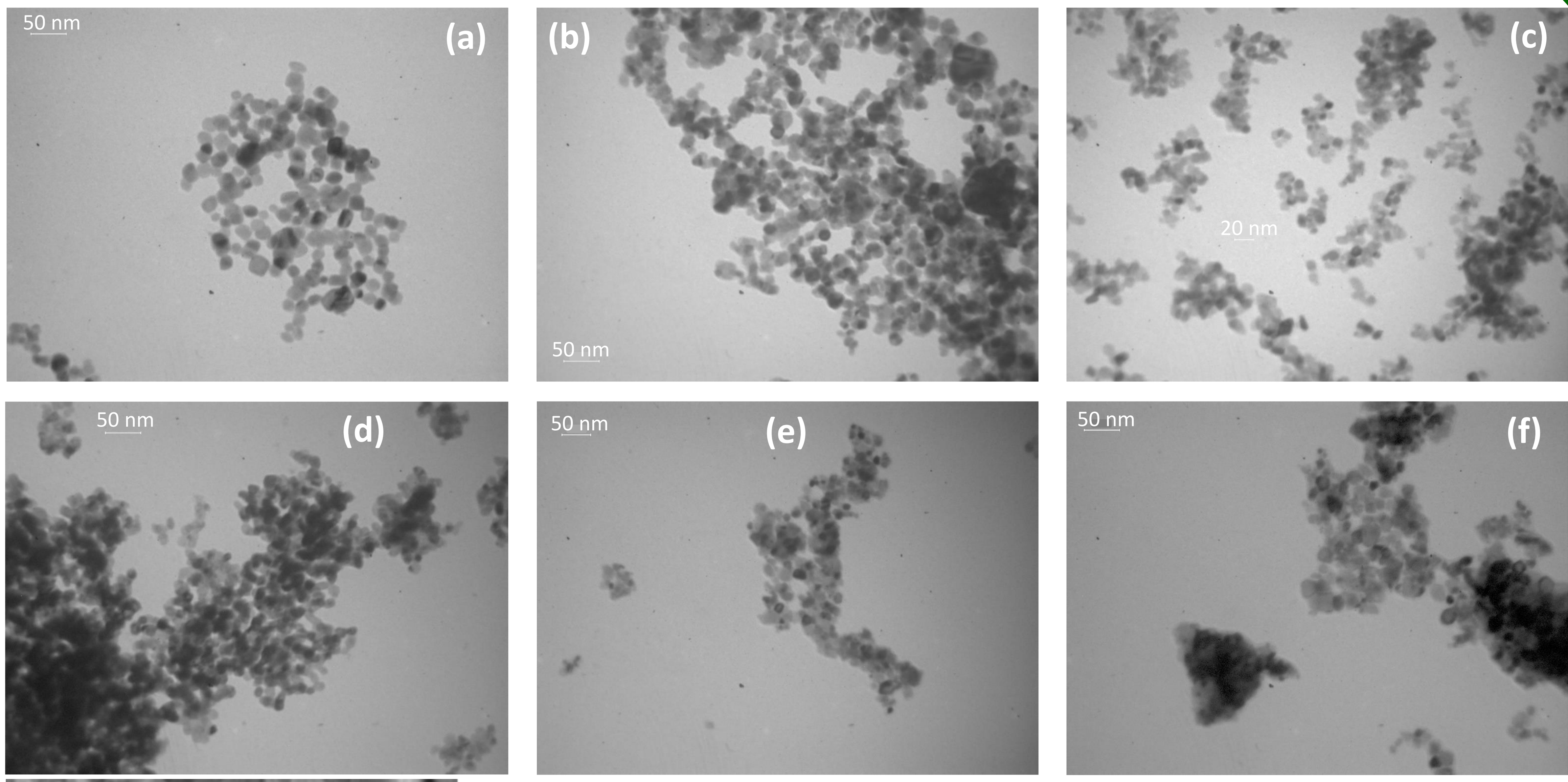


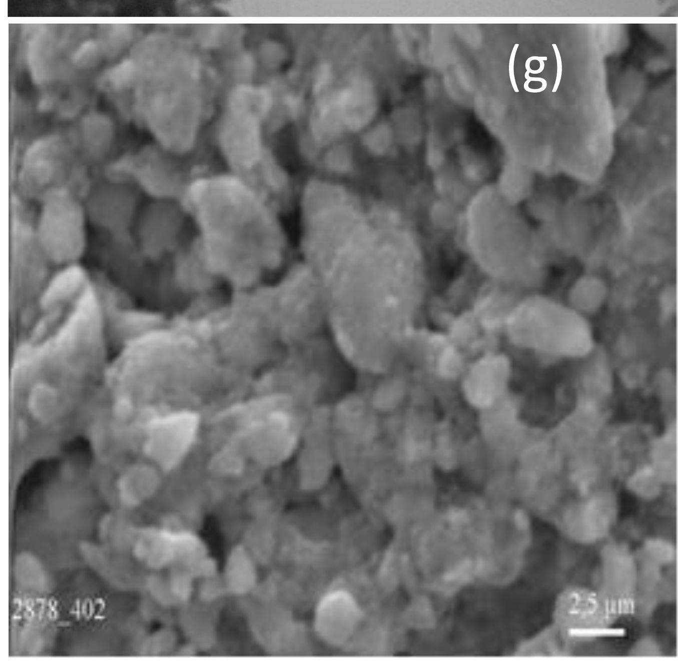
Presence of SnO_2 (cassiterite phase) and CeO_2 was confirmed for the CeO_2-SnO_2 nanocomposite materials by XRD study.

Materials obtained through Pecini synthesis consist of SnO_2 (materials without Ce), CeO_2 (materials without Sn) and both CeO_2 and SnO_2 phases (nanocomposite containing 50 wt.% CeO_2). Materials were synthesized by calcination of xerogels by the following thermal treatment process:

$$\text{room temp.} \xrightarrow{a} 600\,^{o}C$$

where a – is a heating rate (in ^{o}C/min).

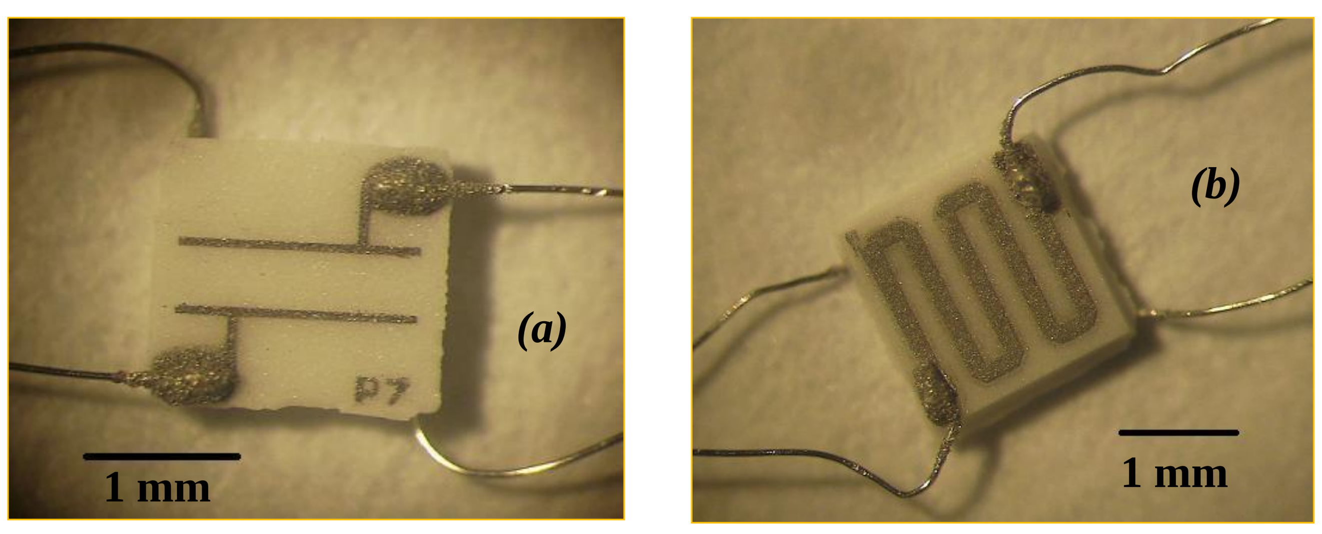




TEM images of the materials obtained through Pecini synthesis: a – tin dioxide obtained with heating rate 10 ^{o}C/min; b – tin dioxide obtained with heating rate 2 ^{o}C/min; c – CeO_2-SnO_2 nanocomposite obtained with heating rate 10 ^{o}C/min; d – CeO_2-SnO_2 nanocomposite obtained with heating rate 2 ^{o}C/min; e – cerium dioxide obtained with heating rate 10 ^{o}C/min; f – cerium dioxide obtained with heating rate 2 ^{o}C/min. SEM image (g) of Ce-containing microcrystalline SnO_2 (obtained through impregnation by 2,5×10^{-2} mol/L $CeCl_3$ solution).

Microcrystalline semiconductor nanomaterial consist of two types of particles: large (diameter 25-30 μm) and small (diameter 1-5 μm). Materials obtained through Pecini synthesis consist of particles with diameter less than 50 nm.

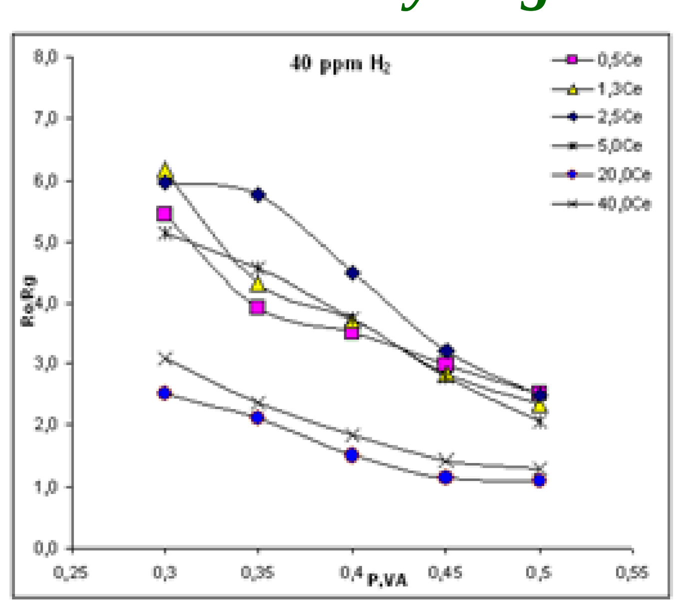
Adsorption semiconductor sensor



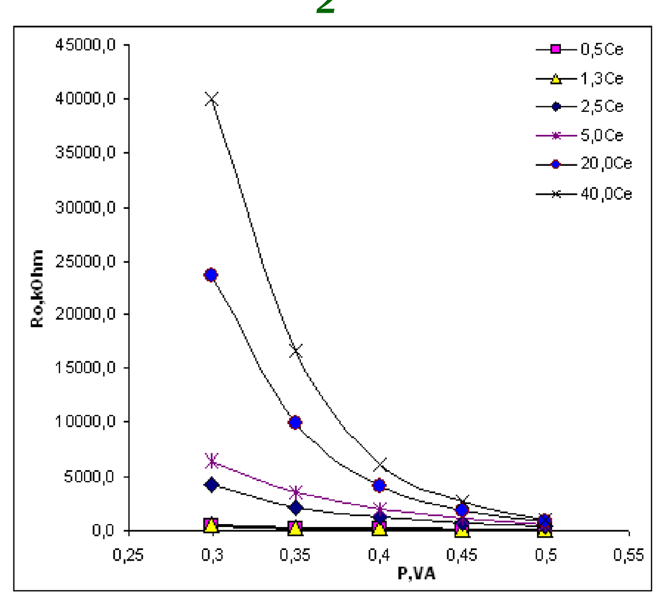
The ceramic plate of the sensor with measuring electric contacts (a) and a heater (b).

The gas sensitive layer of the sensors was created from a paste obtained by mixing semiconductor materials with carboxymethylcellulose (CMC) water solution. Cerium was added into the gas sensing materials based on microcrystalline SnO_2 by impregnation with $CeCl_3$ solutions. The concentrations of $CeCl_3$ were varied from 0.5 × 10^{-2} to 40 × 10^{-2} mol/L. To create the sensors, the plates with the deposited layers were sintered in air up to 620 ^{o}C. A measure of the **sensor response** was taken as a ratio R_0/R_{H2}, where $\mathbf{R_0}$ is a value of electric resistance of the sensor in air and $\mathbf{R_{H2}}$ is a value of electric resistance in the presence of 40 ppm H_2. A temperature of the sensors were controlled by applying power to the heater of the sensor.

Sensors to hydrogen based on the obtained Ce/SnO_2 materials



Dependence of the responses to H_2 of the sensors with Ce additives (a range of $CeCl_3$ impregnating solutions was 0.5÷40.0×10^{-2}M) versus the power applied to the heater of the sensors.



Dependence of the electrical resistances of the sensors with Ce additives (a range of $CeCl_3$ impregnating solutions was 0.5÷40.0×10^{-2}M) versus the power applied to the heaters of the sensors.

Increase in the electrical resistance in air with decrease in the applied heating power (and, thus, decrease in temperature of the gas sensitive layer) is typical for semiconductors. The highest response to hydrogen was observed for the sensors impregnated by 1,3-2,5×10^{-2} mol/L $CeCl_3$ water solution. This fact can be explained by possible formation of an interface between Ce-containing particles and SnO_2 support. The response to hydrogen may be proportional to the interface length and, thus, the highest length should be exhibited by materials obtained from 1,3-2,5×10^{-2} mol/L $CeCl_3$.

Summary

Our study of the CeO_2-SnO_2 nanocomposite materials and Ce/SnO_2 microcrystalline materials confirmed their ability to be used for creation of highly sensitive adsorption semiconductor sensors intended to detect low H_2 concentration in air. Formation of CeO_2 phase in CeO_2-SnO_2 nanocomposite was confirmed by XRD study.