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Influence of light on electrophysical properties of thin films of mixed zinc and tin oxides

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Introduction

Two component oxide system ZnO-SnO_2 has good electrical conductivity, high optical transmittance, good chemical stability. It can be used in variety of applications such as energy conversion, optical materials, sensors, catalysts, etc.

The ZnO-SnO_2 films can be formed by various methods: magnetron sputtering, pulsed laser deposition, sol-gel technique. Depending on the synthesis method, the resulting materials may have different physicochemical and electrophysical properties, therefore, one of the pressing issues of modern research is the optimal choice of method and conditions for obtaining materials. In the framework of this work, we studied the properties of nanoscale zinc and tin oxides obtained by low-temperature pyrolysis.

The chemical pyrolysis is alternative technique to previously indicated methods with its simplicity and cheapness for formation of films on large surfaces.

Experimental

1. Synthesis of intermediate products

1.1 Synthesis of Zn^{2+} and Sn^{4+} intermediate organic compounds (molar ratios of Zn^{2+} and Sn^{4+} were 99:1, 95:5, 5:95 and 1:99)

1.2. Dissolution of intermediate organic compounds in organic solvents

2. Synthesis of mixed zinc and tin oxides films

2.1 Ceramic alumina-based substrates preparation

2.2 Applying an intermediate products solution on the pre-prepared substrate

2.3. Substrates calcination

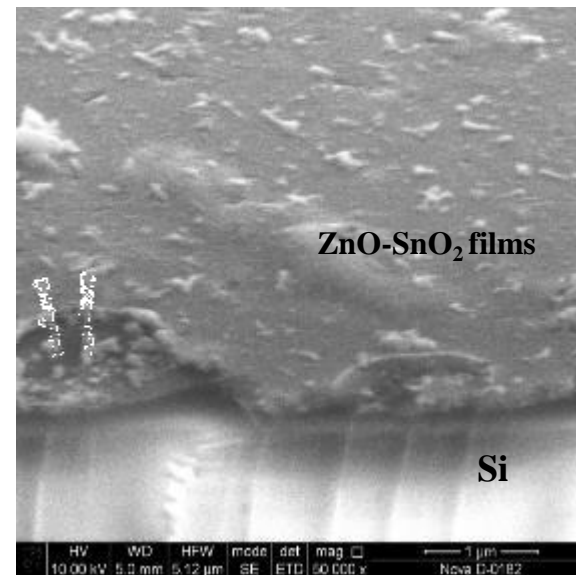
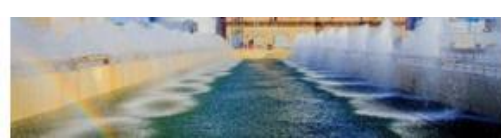


Fig. SEM image film $ZnO-SnO_2$ (99:1 in solution)



Results and discussion

X-ray diffraction

ARL X'TRA diffractometer,
CuK_{α1}-radiation

Obtained materials contain single-phase, hexagonal wurtzite structure ZnO and single-phase tetragonal cassiterite SnO₂ structure.

$D = \frac{k\lambda}{\beta \cos \theta}$ Scherrer equation
ze - 10-17 nm.

where k is the shape factor ($k=0.9$), λ is the X-ray wavelength ($\lambda = 0.1540562$ nm), β is the full width at the half maximum of the diffraction line and θ is the diffraction angle.

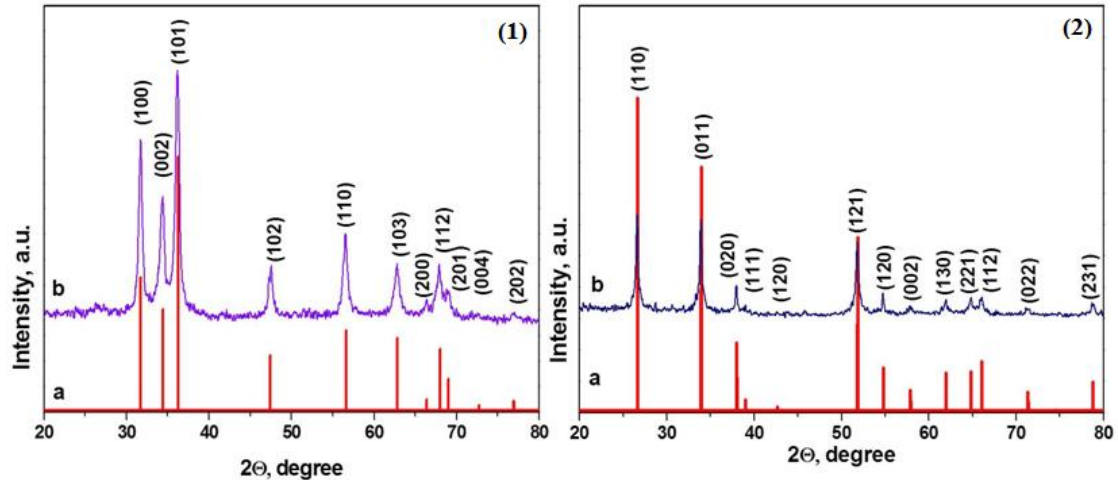
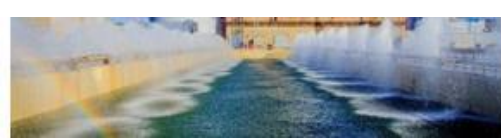
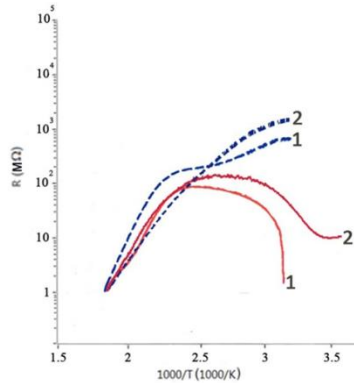


Fig. XRD- patterns of ZnO-SnO₂ films:

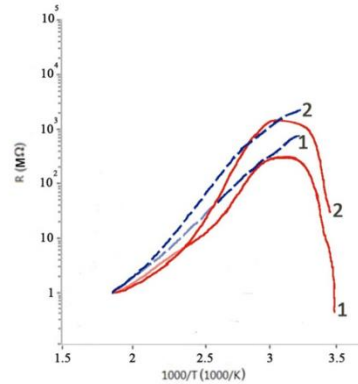
- (1): a - ZnO phase COD ID 2300113, b - 99Zn:1Sn;
- (2): a - SnO₂ phase COD ID 1521419, b - 1Zn:99Sn.



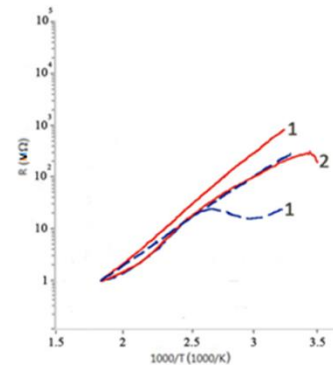
Results and discussion



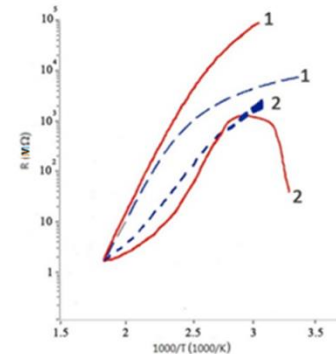
(a)



(b)



(c)



(d)

The resistance dependence of the formed structures on the reverse temperature were measured after exposure to daylight and after exposure to darkness for 24 hours.

Resistance (R) dependences on reverse temperature ($1000/T$) of ZnO-SnO₂ films with the Zn:Sn ratio 1:99 (a), 5:95 (b), 95:5 (c) and 99:1. (1 – after light irradiation, 2 – after dark exposure; (—) – heating, (---) – cooling)



Results and discussion

It is seen that during heating, the resistance of all samples first increases, then, in the temperature range 80-180 °C, a change in the nature of the temperature dependence of the resistance is observed - a smooth transition through the maximum occurs. The increase in resistance during heating can be explained by the effect of adsorbed oxygen. Oxygen molecules in the atmosphere are adsorbed on the oxide surface and become negatively charged due to the capture of electrons from the surface ZnO layers. This leads to the formation of a depletion layer in the surface region of the film and a decrease in its conductivity. As the temperature rises, the thermal generation of carriers begins to exert an increasing influence on the resistance of the material, and the character of conductivity changes.

With further heating from 180 to 300 °C, a linear section of the temperature dependence of the resistance is well approximated by the Arrhenius law: $\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$.

where ρ_0 is preexponential factor, E_a is activation energy of conductivity and k is Boltzmann constant. The activation energy calculated for samples with Zn:Sn ratio 5:95 and 95:5 is 0.7 eV and for samples with Zn:Sn ratio 1:99 and 99:1 is 1.1 eV. Since for oxide semiconductors, the electrical conductivity is determined by intrinsic defects, primarily oxygen vacancies, this energy corresponds to the levels of these defects in the band gap of the semiconductor.

At temperatures below 180 °C, the heating and cooling curves do not coincide. This difference in the course of the curves may be due to the lack of desorption of molecular oxygen ions from the surface of the films.



Conclusions

The thin films of mixed zinc and tin oxides obtained by low-temperature pyrolysis contain phases of zinc oxide and tin dioxide and have nanocrystalline structure with crystallite size about 10-17 nm.

A significant effect of daylight on the temperature dependences of the film resistance has been established. The temperature dependences of the resistance of ZnO-SnO₂ films, measured in the range from room temperature to 300 °C, show the difference between the heating and cooling curves, that can be explained by two competing processes - thermal activation mechanism of conductivity and adsorption-desorption of oxygen particles on the surface of the oxide film.

The activation energy calculated for samples with Zn:Sn ratio 5:95 and 95:5 is 0.7 eV and for samples with Zn:Sn ratio 1:99 and 99:1 is 1.1 eV for heating region from 180 to 300 °C.

Thus, taking into account the effects found, the synthesized films of zinc and tin oxides can be recommended for use in the functional elements of alternative energy.



Thanks