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Nanocomposite based on semiconductor oxides SnO_2/WO_3

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ABSTRACT

Nanocrystalline SnO_2 and WO_3 and nanocomposite with Sn:W ratio 1:9, 1:1, 9:1 were prepared by co-precipitation of α -stannic and tungstic acids. Phase composition and average crystallite size were determined from XRD data. Presence of the second component results in the reduction of the crystallites growth rate, giving rise to the enhancement of thermal stability of nano-scaled system. TGA data allowed to estimate the concentration $v_{\text{H}_2\text{O}}$ of water adsorbed on nanocomposite effective surface. Maximal $v_{\text{H}_2\text{O}}$ value and the highest resistance were observed for nanocomposite with Sn:W = 1:1. The temperature dependence of resistance R reveals its activation character. The current-voltage curves are interpreted in terms of electrochemical capacitor recharge.

INTRODUCTION

Metal oxides SnO_2 , ZnO , In_2O_3 in ultradispersed form are widely used as resistive type gas sensors. High values of gas sensitivity may be regarded as their main advantage, while microstructure stability being their main deficiency. The stability of the ultradispersed systems is heightened in more complicated materials containing an additional phase and characterized by non-homogeneous structure and composition: nanoheterogeneous materials or nanocomposites [1-3]. The reduction of the total area of the crystallite surface contacts for each of the ultradispersed phases slows down the growth of the grains. If the grain size of the oxides is comparable with the Debye length the introduction of new phases may also result in qualitative modification of material properties. Nanocomposites based on semiconductor metal oxides $\text{Me}_1\text{O}-\text{Me}_2\text{O}$ with low mutual solubility are of a special interest as gas sensing materials. The present work deals with the synthesis, structure characterization and electric properties of $\text{SnO}_2 - \text{WO}_3$ nanocomposites. The influence of the high temperature anneal together with the composition variation on the grain size in each phase is studied. The charge transport is found to involve ionic component, the conductivity activation energy is estimated.

EXPERIMENTAL

Nanocrystalline SnO_2 , WO_3 and nanocomposite with Sn:W ratio 1:9, 1:1, 9:1 (samples Sn_1W_9 , Sn_1W_1 and Sn_9W_1 respectively) were prepared by co-precipitation of α -stannic and tungstic acids. α -stannic acid was prepared by conventional hydrolysis of SnCl_4 in ammonia water solution. Tungstic acid was obtained by hydrolysis of $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ in HCl water solution. Gels of the acids mentioned above were co-precipitated from the solution containing $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41}$ and $\text{Na}_2[\text{Sn}(\text{OH})_6]$ prepared by reaction of α -stannic acid with 1 M NaOH. The precipitates were

centrifuged, washed with deionized water until the absence of chloride ion (AgNO_3 test) and dried at 80°C for 24 h.

Thermal anneals have been undertaken to study the microstructure stability of the individual nanocrystalline oxides and nanocomposites. The samples were annealed at $T=80, 150, 300, 600, 800^\circ\text{C}$ during 24 h. After the annealing procedure the samples color varied from white to yellow depending on the composition and annealing temperature.

Phase composition and microstructure of the powders were studied by X-ray diffraction (XRD) (STOE) with use of $\text{Cu}(\text{K}\alpha)$ radiation. The average grain size of SnO_2 and WO_3 was estimated from diffraction patterns using the Sherrer's equation.

Mass loss during the annealing procedure was studied by means of thermogravimetry (TGA-7, Perkin-Elmer) in air, the temperature was varied from 35 up to 900°C with the heating rate of $10^\circ/\text{min}$.

Electrophysical properties were measured for ceramic pellets of 6 mm in diameter and 1.5 mm thick prepared by pressing at 700 MPa with subsequent annealing in air at 600°C for 24 h. The golden contacts were deposited on the pellet surface by thermal evaporation technique. The distance between the contacts was 2 mm. The resistance of the samples was studied in static electric fields up to 10 V in temperature interval 200 -300 K.

RESULTS AND DISCUSSION

Phase composition of the investigated samples determined from the diffraction XRD patterns is given in the Table. The following phases are found: SnO_2 , $\text{WO}_3 \cdot \text{H}_2\text{O}$ and WO_3 . Phases of ternary compounds were not observed. In the samples SnO_2 and Sn_9W_1 annealed at $T \geq 150^\circ\text{C}$ the cassiterite (SnO_2) phase alone was found. The degree of crystallization rises with the annealing temperature increase. For WO_3 and Sn_1W_9 samples the increase of the annealing temperature results in the change of phase composition. At low annealing temperatures 80 and 150°C $\text{WO}_3 \cdot \text{H}_2\text{O}$ phase is observed, at $T \geq 300^\circ\text{C}$ this phase falls down and at the same time WO_3 phase appears. In diffraction patterns of the Sn_1W_1 nanocomposite the reflexes corresponding to both the phases of SnO_2 and WO_3 exist. However, the interpretation of the XRD spectra and quantitative calculations of the peaks positions are complicated due to the superposition of triplet peaks of WO_3 ($2\theta = 26.49, 26.62, 26.84$) and SnO_2 peak ($2\theta = 26.61$), and the group of lines WO_3 ($2\theta = 33.00, 33.58, 33.92, 34.11, 34.49$) and SnO_2 peak ($2\theta = 33.89$).

Table. Phase composition of SnO_2 - WO_3 nanocomposites

Sample	W:Sn ratio	Annealing temperature, T ($^\circ\text{C}$)					E_a , eV
		80	150	300	600	800	
WO_3	1:0	$\text{WO}_3 \cdot \text{H}_2\text{O}$	$\text{WO}_3 \cdot \text{H}_2\text{O}$	WO_3	WO_3	WO_3	0.12-0.14
Sn_1W_9	9:1	$\text{WO}_3 \cdot \text{H}_2\text{O}$	$\text{WO}_3 \cdot \text{H}_2\text{O}$	WO_3	WO_3	WO_3	0.15-0.18
Sn_1W_1	1:1	Amorph.	Amorph.	SnO_2	$\text{WO}_3 + \text{SnO}_2$	$\text{WO}_3 + \text{SnO}_2$	
Sn_9W_1	1:9	SnO_2	SnO_2	SnO_2	SnO_2	SnO_2	
SnO_2	0:1	SnO_2	SnO_2	SnO_2	SnO_2	SnO_2	0.035

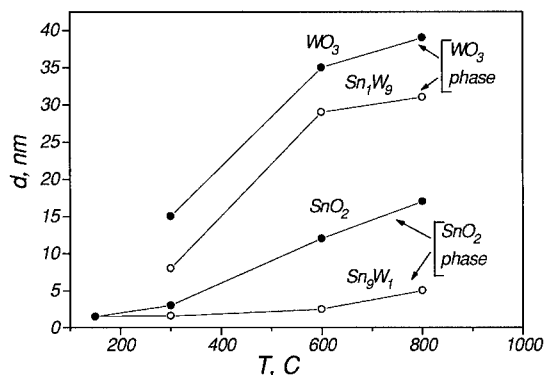


Figure 1. Crystallite size of SnO₂ and WO₃ phases in nanocomposites vs annealing temperature.

In contrast with the data for WO₃ and Sn₁W₉ samples the crystallization of tungstic acid was not observed in Sn₁W₁ nanocomposite. Comparison of the XRD patterns for all the investigated samples annealed at 600 C shows that in nanocomposites the degree of crystallization of the individual oxides reduces. The annealing temperature increase leads to the grain size growth for both the SnO₂ and WO₃ phases (Fig.1). WO₃ crystallites are of 10-50 nm that significantly exceeds the size of SnO₂ crystallites (2-15 nm) at the same annealing temperature. It is important that the introduction of an additional component results in the reduction of the crystallite growth rates for both the phases.

The thermogravimetry (TGA) analysis data are in good accordance with the XRD results. For the samples SnO₂ and Sn₉W₁ two characteristic temperature regions may be regarded: 35 - 175 C and 175 - 800 C. Low temperature region is characterized by a pronounced peak at the DTG curves at 90 C. This peak may be attributed to surface water desorption. High temperature region is smooth and the mass loss for this case may be due to a gradual water removal during the transformation of α -stannic acid into β -form.

Therefore it may be concluded that up to the temperatures ~800 C tin dioxide exists in partially hydrated state. For the samples WO₃ and Sn₁W₉ TG curves also may be characterized by two temperature regions of mass loss. The low temperature region (35 - 150 C) with a peak at 50 C corresponds to desorption of water molecules slightly bonded at the surface by physical adsorption mechanism. Another peak at 250 C corresponds to transformation of tungstic acid into tungsten oxide. The mass loss at this temperature range equals to 6.75% for WO₃ sample that corresponds to removal of 0.96 mole of H₂O from 1 mole of WO₃. At the DTG curve for Sn₁W₁ high temperature peak was not observed in agreement with XRD data since the crystallization of tungstic acid was not found. The low temperature region of the DTG curve for this sample is characterized by mass loss significantly exceeding the values obtained for all other samples. The estimation of the adsorbed water quantity ν_{H_2O} (mole per 1 mole of the nanocomposite) as a function of SnO₂ mole fraction in the nanocomposite is shown in Fig.2. The non-linear character

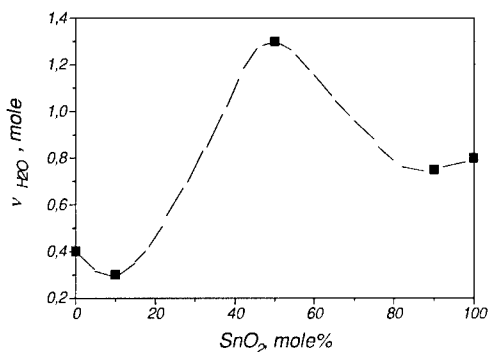


Figure 2. Calculated quantity of surface adsorbed H₂O as a function of sample composition. Line is a guide for eye.

of this dependence may be attributed to grain size reduction and possible increase of effective surface in nanocomposites compared to individual oxides.

The charge transport is characterized by electric current instabilities for all investigated samples. A typical current –voltage (I-U) curve is shown in Fig.3 for Sn₁W₁ sample. The arrows indicate the order of voltage switching. In low fields $U < 1$ V current is unstable reducing down to values, which registration is eliminated by the device sensitivity (10^{-3} μ A). Thus current values at low fields may be considered as some effective data taken at a gradual field switching. At $U > 3$ V the current stabilizes and I-U curve transforms into a linear one. The current was stable while the sample was kept under $U = 5$ V for 5 minutes. After what the field was gradually switched off.

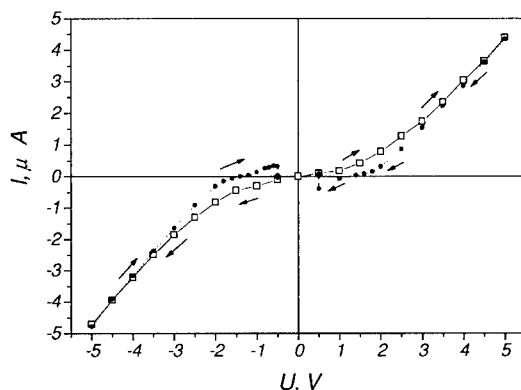


Figure 3. Current - voltage characteristic of Sn₁W₁ nanocomposite.

The hysteresis at I-U curve appears at $U \leq 3$ V, and at $U=1.4$ V current reaches zero and then changes the sign. At the same time the current instabilities appear. To illustrate the relaxation process the sample was kept under the fixed voltage $U=0.5$ V. In 5 minutes I relaxes to a value shown on Fig.3 as a rhombus. In the field of opposite direction the picture is the same. The observed peculiarities of the I-U curves may be explained in terms of electrochemical capacitor. Charge accumulation on the capacitors electrodes may be associated with ionic component in charge transport. It involves the dissociated water and, possibly, Na^+ and Cl^- ions, which presence is related to the synthesis methods. Charge accumulation process in the nanocomposite seems to be of special interest, since the voltage corresponding to the change of current sign is high enough.

Strongly identical conditions were chosen to estimate and compare the conductivity of the samples with different composition. The measurements were performed in the dry helium atmosphere. The voltage $U=0.5$ V was applied to the samples contacts. Two current values were registered: immediately after the field switching on and 5 minutes later. Resistance R was calculated for both current values, the results are shown in Fig4. Solid line corresponds to the values taken at the first moment after field switching, dotted line - to the data obtained 5 minutes later. The resistance measured at the first moment seems to be closer to the electronic component of conductivity. After some time passes the external field is reduced by the ions accumulated on the electrodes (the charging of electrochemical capacitor). Though the data shown in Fig.4 are only an estimation, the uncertainty in determination of R is significantly less than resistance change under composition variation. Maximal ability for charge accumulation (and maximal resistance value) is observed in nanocomposite with $\text{Sn}:\text{W} = 1:1$ ratio. That may be related at least to two self-consistent factors: maximal water adsorption ability and minimal grain size. It should be mentioned that for nanocrystalline SnO_2 films according to [4] the reduction of grain

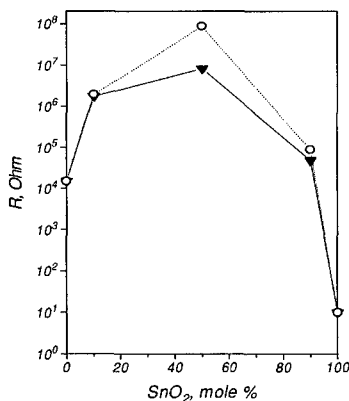


Figure 4. Resistance R as a function of sample composition. Solid line corresponds to the values taken at the first moment after field switching, dotted line - to the data obtained 5 minutes later.

size from 10 down to 6 nm results in resistance growth from $2 \cdot 10^4$ up to $6 \cdot 10^4$ Ohm at the room temperature. Under cooling this difference increases and at $T=77$ K reaches $8 \cdot 10^4$ and $3 \cdot 10^6$ Ohm respectively.

The temperature dependence of the resistance R have been measured only for the samples, where current instabilities may be neglected at a first approximation. The dependencies $R(T)$ were taken in dry helium atmosphere under a fixed voltage $U=1$ V. The criterion of the measurements trust-worth was the coinciding of the curves taken during the temperature cycling from cooling to heating. All the plots $\ln R-1/T$ demonstrate the linear behavior. The activation energies E_a were calculated with use of the equation $R \sim \exp(E_a/kT)$ (see Table). The activation character of the conductivity process reveals the barrier mechanism, the barrier height E_a rises with the resistance increase.

CONCLUSIONS

The presented results confirm the possibility to obtain more stable microstructure in nano-scaled systems. Introduction of an additional component whether to WO_3 or to SnO_2 results in slowing down of the crystallite growth rates. Microstructure of investigated nanocomposites practically does not change under thermal annealing in temperature interval 100-600 C. Just this range is important in gas sensor applications. Water adsorption ability, grain size and electrical properties correlate and depend on the composition of the samples. Nanocomposite with metals ratio 1:1 is of special interest as the most stable and possessing the highest adsorption ability.

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