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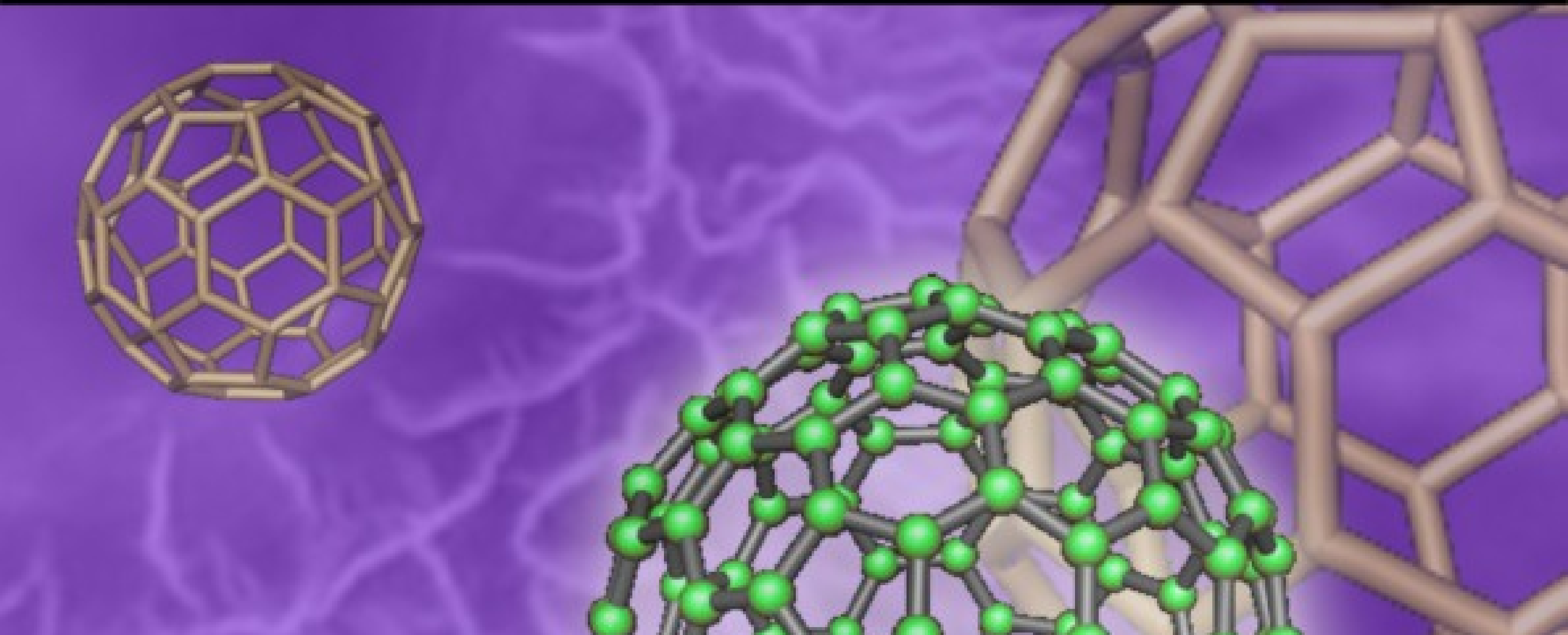

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Synthesis and Properties of Thin Film Nanocomposites Sn-Y-O for Gas Sensors

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Abstract: Three-component thin film nanocomposites Sn-Y-O were prepared by RF reactive ion-beam sputtering of metal target in the ambient of $Ar+O_2$. Amorphous films were thermal treated at 400 ^{o}C for crystallization and stabilization of electrical properties. Atomic composition and morphology of thin films were investigated by X-ray microanalyzer, high-resolution transmission electron microscopy method, atomic force microscopy. It was determined that the presence of Y_2O_3 additive in composites on the base of SnO_2 prevents the growth of big grains up to 3 nm, and can be used for the control of thin film structure. Electrical properties and gas sensitivity of nanocomposite samples were studied and the correlation between grain size and gas sensitive parameters was found. *Copyright © 2009 IFSA.*

Keywords: Reactive sputtering, Metal oxides, Composition and morphology, Electrical properties, Gas sensitivity

1. Introduction

Semiconducting thin films SnO_2 are often used as gas sensitive elements in solid state gas sensors for environmental monitoring, for determining of toxic and explosive gases, in medicine and in other fields of gas control [1].

There is possibility to control the value of gas sensitivity by changing grain sizes of polycrystals and initial electrical conductivity of the films [2, 3]. Gas absorption leads to the modulation of potential barrier's height on the grains boundary for drift of charge carriers, therefore the most effective are materials with Debye length comparable with grain diameter. The decreasing of grain size causes the increasing of polycrystal surface deposit into the total electrical conductivity of the samples. More over the promotion of surface activity of nanosize polycrystals leads to the increasing of gas sensitivity as well as to the decreasing of energy threshold of gas ions reaction with surface states, i.e. to the diminishing of temperature of maximal gas sensitivity of the film to different gases in the air [4].

Tin oxide is usually doped with metal oxides [4, 5] and rare earth oxides [6] in order to obtain smaller grain size. For instance sensors based on SnO_2 with Y_2O_3 additive present a good sensitivity to CO [7].

The aim of this work is to investigate the influence of composition, morphology and electrical-physical properties of film nanocomposites Sn-Y-O on the absorption activity of surface states.

2. Experimental

Film nanocomposites Sn-Y-O were prepared by radio frequency (RF) reactive ion-beam sputtering of composite target from tin and unequally situated on the surface of the target yttrium stripes. Sputtering ambient was $Ar+O_2$, sputtering equipment was built on the base of vacuum post UVN-2M [8]. It was possible to prepare 15 samples with different correlations between Sn and Y oxides in dependence on target composition simultaneously.

Thickness of the films was measured by interference microscope MII-4. Element composition of nanocomposites was determined with the help of X-ray microanalyser JEOL JXA-840 on the 15 reference-samples situated through 1.5 cm along the substrate, the samples of pure metal tin and yttrium were used as standards. Surface morphology of annealed films was studied by scanning atomic force microscope (AFM) FemtoScan-001. High-resolution transmission electron microscopy (HRTEM) was performed on Philips Tecnai F30 FEG-TEM (USA) operated at 300 kV. Samples for the HRTEM were prepared by means of Argon Ion Thinning. Electrical resistance of the films was measured by four-point method (apparatus CIUS-4) or by Van-der-Pauw method. Concentration and mobility of free charge carriers were determined with the help of Hall effect according to Van-der-Pauw method.

Gas sensitivity S_g of the films was measured by standard method as a ratio of film resistance in the air R_a and film resistance in the mixture of investigated gas and the air R_g: $S_g = R_a/R_g$ [1].

3. Results and Discussion

It was found that films just after RF ion-beam sputtering had mostly amorphous structure. Isothermal treatment method elaborated earlier [4] was used for stabilization of surface resistance and crystallization of SnO_2 films doped with yttrium. Samples were annealed in the air at T = 400 ^oC during 13 to 29 hours with every-hour control of surface resistance.

Film nanocomposites Sn-Y-O prepared by RF ion-beam reactive sputtering have thickness of 1.6 – 4.3 μm.

Fig. 1 presents the element distribution of metals and oxygen in 15 nanocomposite samples with different content of metal oxide additives prepared simultaneously. X-ray analysis data show that yttrium-dopant concentration in investigated films SnO_2 changes from 0.4 to 6.0 at.%. AFM-study of 7 nanocomposites Sn-Y-O gives pictures of surface morphology and distribution of grain sizes in films SnO_2 with different dopant content. Fig. 2 presents two typical picture of the samples with Y 0.4 at.%

(a) and Y 1,0 at.% (b), that reflects the common tendency of decrease grain size with increase contence of yttrium in SnO_2. The average height of the grains was calculated according to the probe moving at AFM-investigations. The high of surface roughness in sample Sn-Y-O with 0.4 at.% Y is about 40 nm, and in the sample with 1.0 at.% Y is about 5 - 7 nm. We can see that the increase of dopant amount causes the decrease of grain sizes in 7 investigated samples (Fig. 3). Doping with yttrium more than 2 at. % does not lead to the change of grain size.

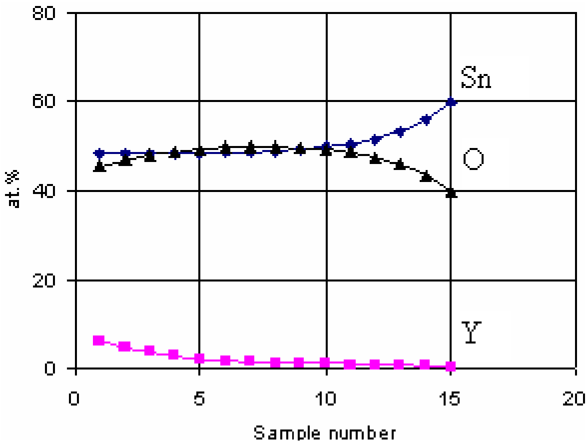
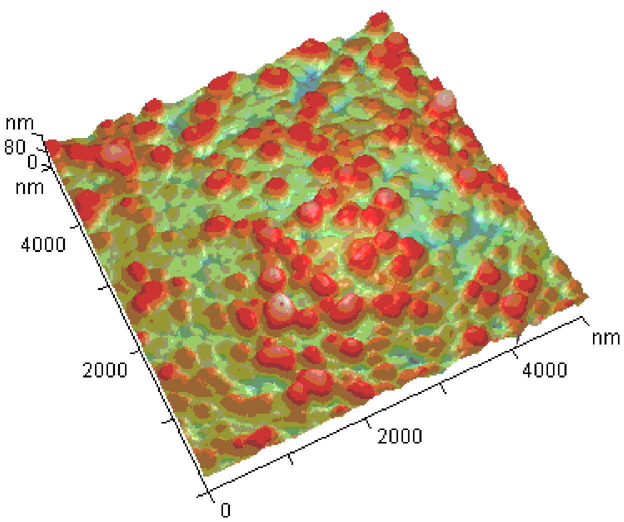
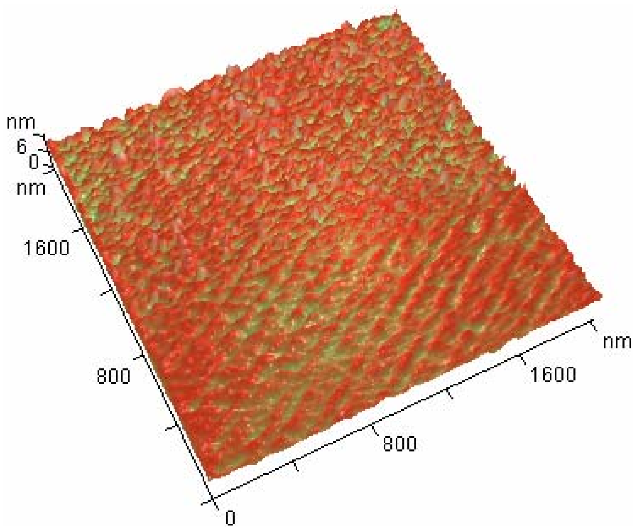


Fig. 1. Element composition (at.%) in nanocomposites Sn-Y-O.



(a)



(b)

Fig. 2. AFM images of nanocomposite Sn-Y-O: a – 0,4 at.% yttrium; b – 1,0 at.% yttrium.

HRTEM measurement was conducted to direct characterize the morphology and structure of the film. A typical HRTEM image of the sample with 5 at.% yttrium, shown in Fig. 4, indicates that the RF ion-beam reactive sputtering film consists of well-crystallized grains as well as amorphous areas. The measured average grain size is about 3 nm that is in agreement with AFM-data. The lattice fringes in the HRTEM image confirm the single crystalline nature of the SnO_2 grains. The spacing between the adjacent lattice fringes is 0.330 nm, corresponding to the (110) facet of tetragonal SnO_2 [9].

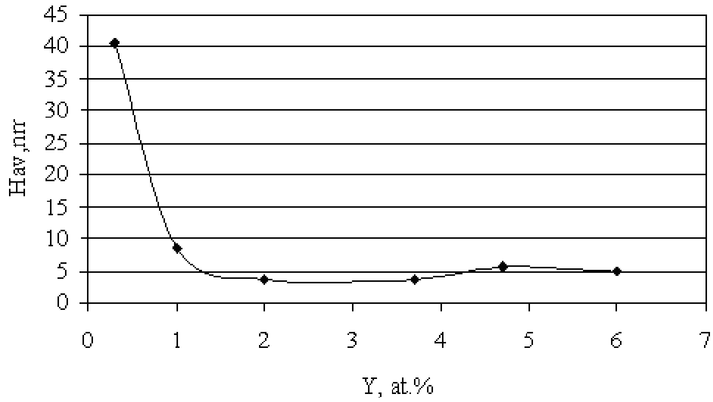


Fig. 3. Average high of grains (H av, nm) in nanocomposite Sn-Y-O in dependence on yttrium content (Y, at.%).

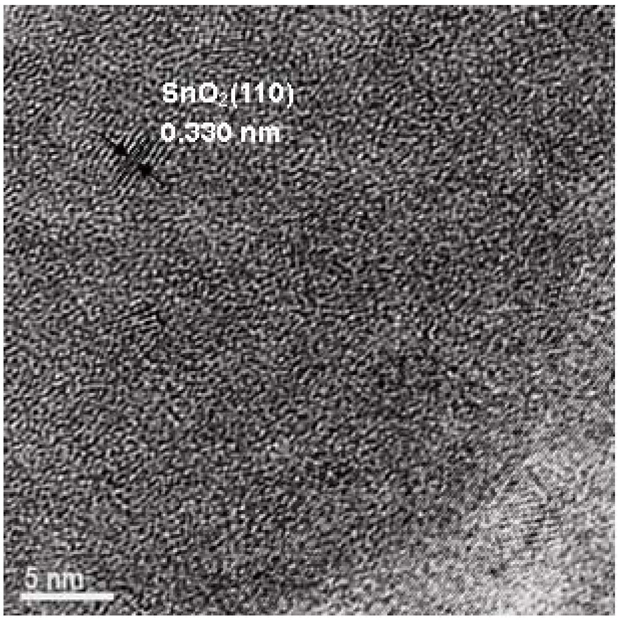
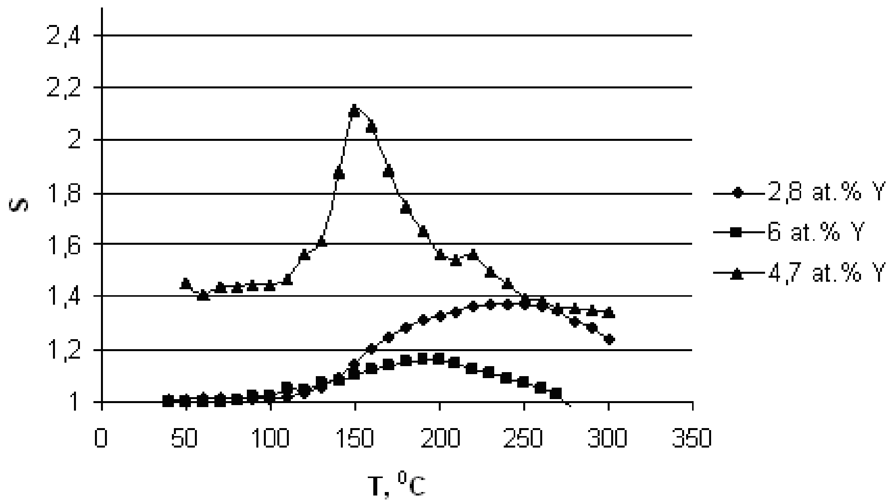


Fig. 4. HRTEM micrograph of nanocomposite Sn-Y-O (5,0 at.% Y).

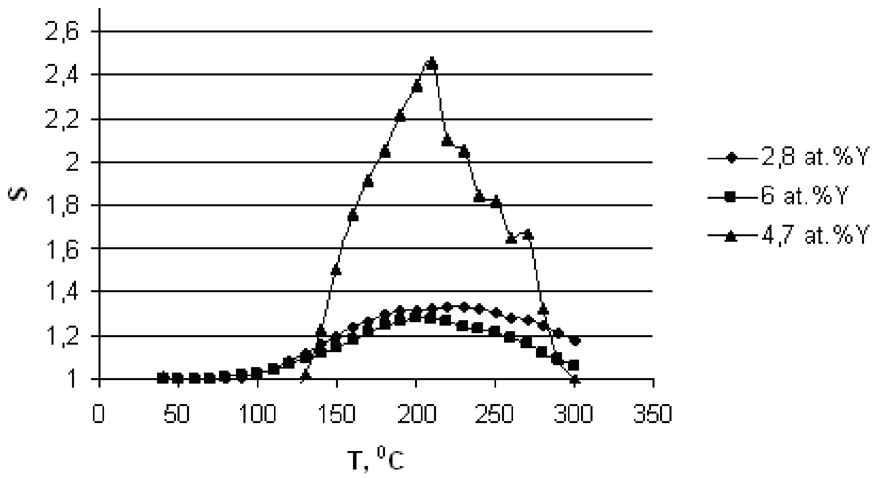
Y ion has a bigger radius (0,09 nm) than Sn ion (0,071 nm), so it has a smaller solubility in SnO_2 lattice, and the excess content simply acts as a stabilizer of the SnO_2 crystallites [10], therefore Y doped SnO_2 in our study shows a small crystallite size. AFM-pictures present the film surface as conglomerates of grains (Fig. 2). The presence of yttrium-additive prevents growth of big grain's conglomerates as it was found earlier in nanocomposites Sn-Si-O, Sn-Mn-O [4, 11].

Measurements of concentration and mobility of free charge carriers show that the initial samples are characterized by concentration value $n = 10^{16} - 10^{17}$ cm^{-3} and mobility $\mu = 9 – 30$ $cm^2/V \cdot s$ at room temperature. These experimental results allow to estimate the value of Debye length L in the grains and to compare it with grain sizes of nanocrystals in order to estimate the efficiency of modulation of intergrain potential barriers during changing of gas sensitivity. For estimation of $L = (\varepsilon\varepsilon_0 kT/e^2 n)^{1/2}$ we used $\varepsilon = 13.5$ for SnO_2 [12] and experimental data of electron concentrations: $n = 10^{17}$ cm^{-3}, T = 20 °C, therefore L = 13.7 nm. In order to determine the main mechanism of charge carrier transport in nanocrystalline films the value of L was compared with grain diameter D [2]. Calculations show that electroconductivity is carried out mostly according to the model of ultrafine particle mechanism (2L = 27.4 nm, D ≈ 5 nm).

Temperature dependences of gas sensitivity towards vapors of ethanol and acetone in the air (2000 ppm), for SnO_2 films undoped and doped with 2.8 at.%, 4.7 at.%, 6 at.% yttrium have been studied. Undoped films SnO_2 have a maximal sensitivity to ethanol at T = 330 ^oC, to acetone at T = 360 ^oC [13]. SnO_2 films doped with 2.8 at.% Y have a maximal sensitivity to ethanol at 230 ^oC, to acetone at 220 ^oC. Figs. 5 a, b show that SnO_2 films doped with 2.8 at.% Y have a maximal sensitivity to ethanol at 230 ^oC, to acetone at 220 ^oC; SnO_2 films doped with 4.7 at.% Y have a maximal sensitivity to ethanol at 150 ^oC, to acetone at 210 ^oC; SnO_2 films doped with 6.0 at.% Y have a maximal sensitivity to ethanol and to acetone at 220 ^oC. It was found that the increasing of yttrium content in SnO_2 films has a tendency to the further decreasing of temperature of maximal gas sensitivity of nanocomposite towards all investigated gases (Fig. 6). This effect displays differently for different gases, which may be used for the increasing of film selectivity to different gases. This result shows that investigated nanocomposites used in gas sensors allow to diminish value of consumed power of sensor at the gas control in the air.



(a)



(b)

Fig. 5. Temperature dependence of gas sensitivity of nanocomposite Sn-Y-O towards vapor of ethanol (a); and acetone (b) in the air 2000 ppm.

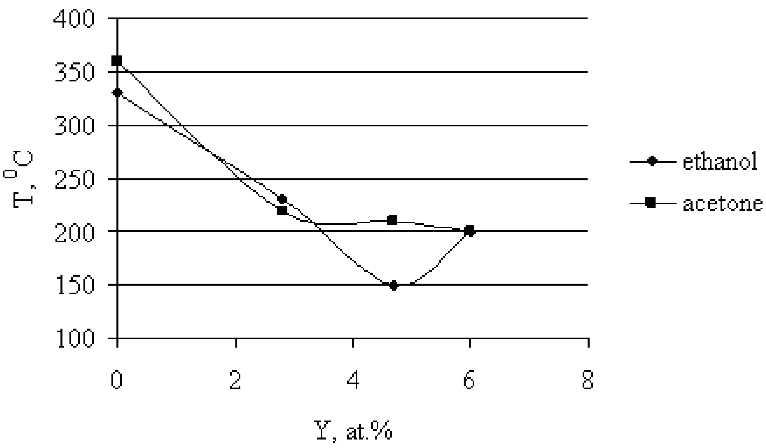


Fig. 6. Temperature of maximal gas sensitivity of nanocomposite Sn-Y-O to ethanol and acetone in the air (2000 ppm) in dependence on yttrium content.

4. Conclusions

Film nanocomposites Sn-Y-O with yttrium content from 0.4 to 6.0 at.% were prepared by RF reactive ion-beam sputtering method.

Surface morphology in dependence on yttrium content in the films was investigated. On the base of HRTEM- and AFM-data the average grain height in dependence on yttrium percentage in the films was calculated. Yttrium content evidently influence on the grain size of polycrystals. Increasing of yttrium concentration leads to the decreasing of average grain size of polycrystals in the films.

With the help of Hall effect the concentration and the mobility of free charge carriers in Sn-Y-O nanocomposites in dependence on yttrium percentage were measured. The Debye length was calculated and the mechanism of charge carrier transport according to ultrafine particle model was determined.

Gas sensitivity of film nanocomposites Sn-Y-O towards different reducing gases as well as changing of temperature of maximal gas sensitivity of Sn-Y-O films to detected gases in dependence on dopant amount were investigated. Increasing of yttrium concentration leads to the decreasing of temperature of maximal gas sensitivity of nanocomposite to different gases up to 100 – 200 °C, that can be used for improving of film selectivity towards different gases.

Thus film nanocomposites Sn-Y-O are perspective material for gas sensitive elements of gas sensors, as they have good sensitivity and selectivity towards different gases and allow to control gases at lower temperatures than undoped films SnO_2.

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- Sensor instrumentation;
- Virtual instruments;
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