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STRUCTURAL PROPERTIES OF NANOCRYSTALLINE TIN DIOXIDE FILMS DEPOSITED BY ELECTROSTATIC SPRAY PYROLISIS METHOD

This paper describes investigation of structural properties of nanocrystalline tin dioxide films deposited by electrostatic spray pyrolisis method. Average crystalline size measured from XRD methods was 3,5±0,8 nm and 5,8±0,9 nm for films deposited on glass and alumina substrates. Sensitivity of tin dioxide thin films to ethanol was measured under different ethanol concentrations. Annealing temperature influence on crystalline size and sensitive properties was studied.

Key words: SnO_2 thin films, gas sensitivity, ethanol.

INTRODUCTION

Metal oxides are well known as good material for different purposes in semiconductor physics. Because of wide band gap ($E_g = 3,6$ eV) tin dioxide was widely used as optical electrode [1]. Investigations of electrical properties of tin dioxide showed the property to change its resistance under gas adsorption. This phenomenon was put in gas detecting principle and since the sixties tin dioxide has been used as base material for gas sensors [2].

Many technological methods have been developed to deposit thin tin dioxide. The most well known methods are chemical vapor deposition, sol-gel technology and magnetron sputtering. These methods allow to obtain thin films with well predicted structure and stoichiometry [3, 4].

To lower deposition time and costs alternative technological methods were developed such as spray and electrostatic spray pyrolisis methods [5]. They are based on pyrolitical decomposition of chemical compound on heated substrate with metal oxide film formation. The most important advantage of electrostatic spray pyrolisis method is varying of technological parameters such as substrate temperature, distance between high voltage source and substrate and value of high voltage. Variation of these parameters allows to define structure and stoichiometry of thin films.

It was shown that structural properties of thin films strongly influenced their sensitive properties. The more active surface was the higher sensitivity observed. Nowadays one can see attempts to obtain films with high-developed surface to increase sensor's response to detecting gases. The solution of this problem is creation thin films with nanocrystallites [6]. Decreasing crystalline size leads to enhancing active adsorption area and therefore to higher sensitivity.

This paper was devoted to investigation of deposition peculiarities and applications of thin nanocrystalline SnO_2 films as sensors to ethanol.

EXPERIMENTAL

Deposition setup is shown in fig. 1. It consists of vessel with solution *1*, high voltage source *2*, kilovoltmeter *3*, capillary with diameter 0,3 mm *4*, heater *5* with substrate *6* upon. Heater was operated from voltage source *7*. Temperature was measured by thermocouple *8*. For thin SnO_2 films deposition ethanol solution of $SnCl_4$ was prepared with constant concentration 0,05 mol/l. Voltage value was 17±0,1 kV. The distance between capillary and substrate was 30 mm. Thin SnO_2 layers were deposited on glass and alumina substrates.

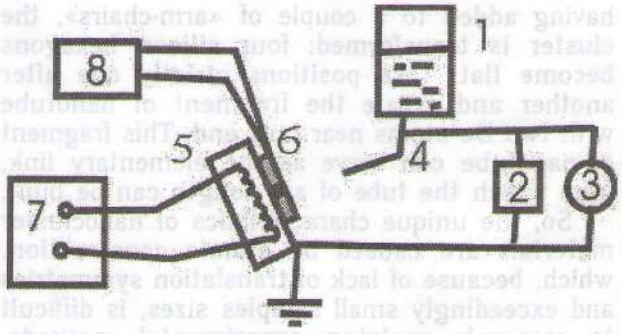

Fig. 1. Experimental deposition setup:
1 — vessel with solution; *2* — high voltage source; *3* — kilo voltmeter; *4* — capillary with diameter 0,3 mm; *5* — heater; *6* — substrate; *7* — voltage source; *8* — thermocouple

It is well known that substrate temperature is one of ruling factors of deposition [4]. It determines structure of samples and crystalline size. Usually SnO_2 thin film deposition by electrostatic pyrolisis method was provided at 420 °C. It was shown that temperature declining on 50 °C led to decreasing crystalline size. According to this, deposition was proceeded under constant temperature 310 °C.

Tin dioxide thin film was formed according to reaction:

$$3SnCl_4 + 2C_2H_5OH + 6O_2 \rightarrow 3SnO_2 + 4CO_2 + 12HCl \quad (1)$$

After deposition thin films were annealed under different temperatures.

Structural characterization was performed by XRD measurements. For XRD analysis Siemens 5000 apparatus with X-ray wave length Cu K_α $\lambda = 0{,}154$ nm was used.

Gas sensitivity measurements were provived at 200 °C under different ethanol concentrations. Gas sensitivity value was calculated as

$$\gamma = R_a / R_g, \qquad (2)$$

where R_a and R_g are the thin film resistance, measured in air and gas mixture, correspondently.

Annealing temperature influence on the thin film structure and gas sensitivity was also studied. For these purposes fresh obtained samples were annealed at temperatures from 420 to 1100 °C at air during 2 hours.

RESULTS AND DISCUSSION

SnO_2 nanocrystalline thin films were deposited on alumina and glass substrates. Both samples were deposited under the same conditions and had the thickness 2 μm. XRD data of tin dioxide thin films deposited on glass and alumina substrates are plotted in fig. 2 and 3, correspondently.

As one can see there are diffraction peaks at 2 θ equaled 26,5, 34,8 и 51,2. These peaks are typical for tetragonal SnO_2 phase [7]. The width of XRD peaks in case of samples deposited on glass substrates is wider than for SnO_2 films upon alumina. It means that films' structure is different and affected by substrate structure. In case of glass substrates SnO_2 films should be amorphous whereas SnO_2 films deposited on alumina were polycrystalline.

Crystallite size was calculated from Scherer's equation [4]

$$d = \frac{0{,}9 \cdot \lambda}{\beta \cdot \cos\theta}, \qquad (11)$$

where λ was X-ray wave length, θ — diffraction angle, β — XRD peak's width on semi height Average crystallite sizes for fresh prepared samples, determined from eq. (3), were 3,5±0,8 nm and 5,8±0,9 nm for films deposited on glass and alumina substrates. Average crystalline sizes were smaller in comparison with results obtained in [8], where these values were 4,5 nm and 9 nm for samples on glass and alumina substrates.

During deposition it's possible to appear two tin oxide phases SnO and SnO_2 [4]. Annealing of fresh prepared samples is necessary measure to oxidize SnO_x compound $(1 < x < 2)$ to SnO_2. Despite SnO phase wasn't observed in XRD spectrum annealing procedure was provided to investigate structural changes and their influence on adsorptive properties of SnO_2 thin films.

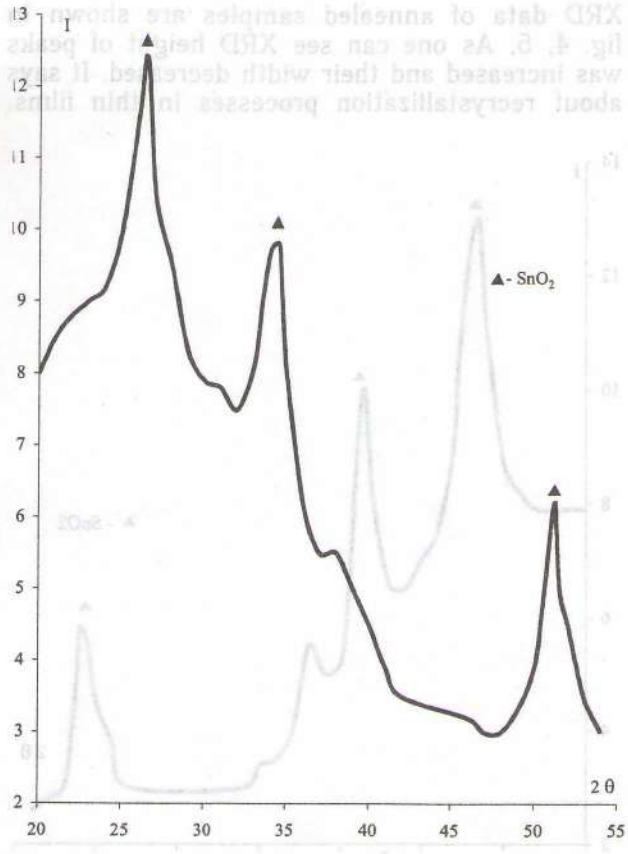

Fig. 2. XRD data of fresh prepared samples deposited on glass substrates

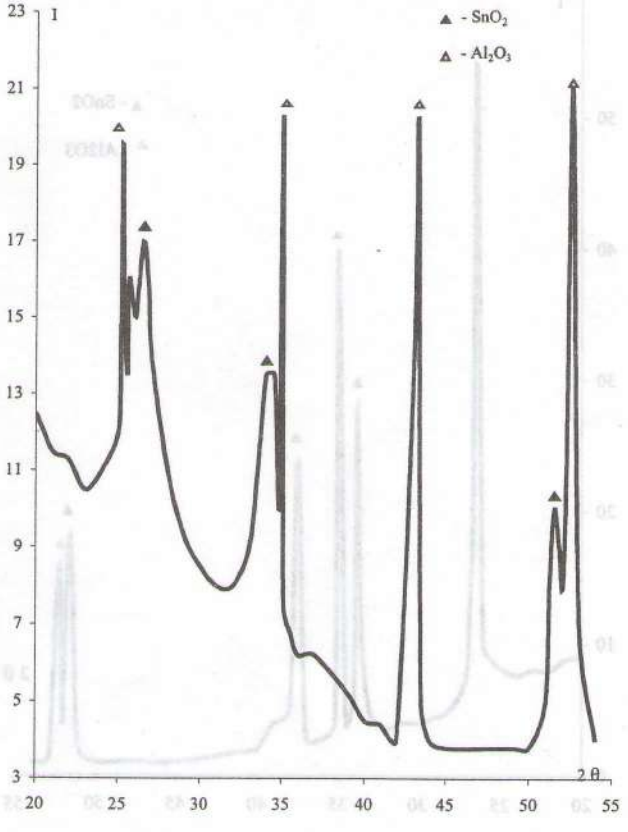

Fig. 3. XRD data of fresh prepared samples deposited on alumina substrates

XRD data of annealed samples are shown in fig. 4, 5. As one can see XRD height of peaks was increased and their width decreased. It says about recrystallization processes in thin films.

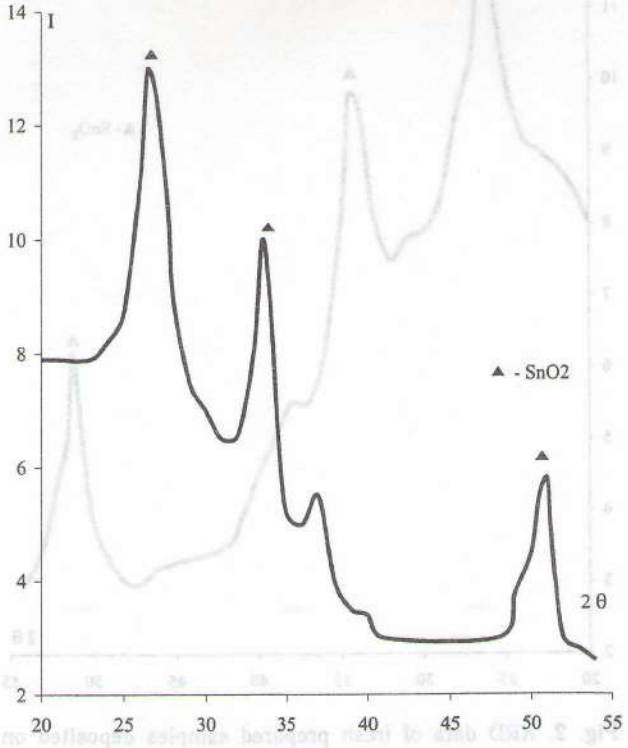

Fig. 4. XRD data of tin dioxide thin films deposited on glass substrates and annealed at 1050 °C

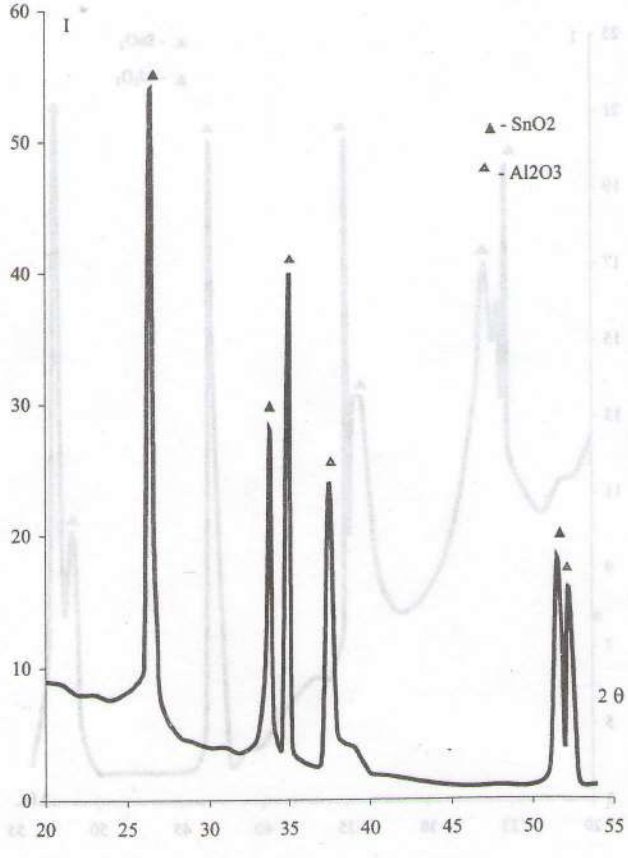

Fig. 5. XRD data of tin dioxide thin films deposited on alumina substrates and annealed at 1050 °C

Crystalline size for annealed samples was determined from (3). Temperature dependence of crystalline size is plotted in fig. 6. Crystalline growth for used samples was different as it can be seen from fig. 6 (curve *1*, *2*). Probably, it's

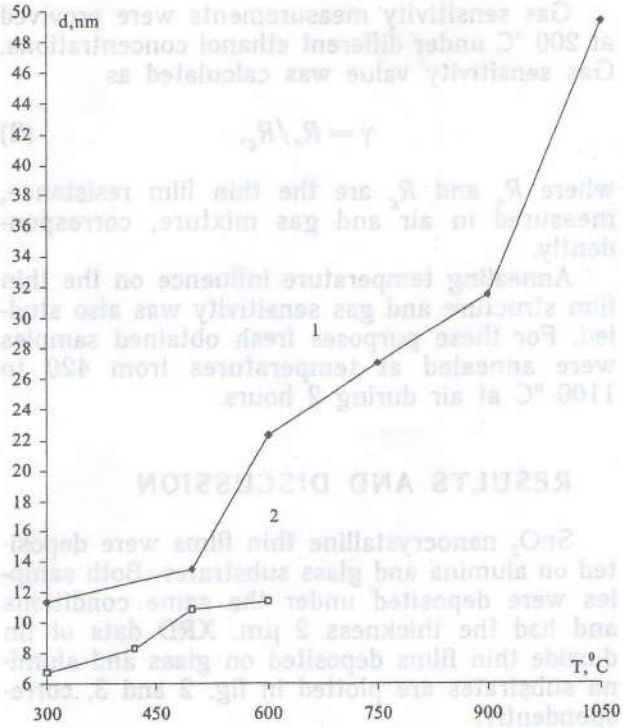

Fig. 6. Crystalline growth diagram:
1 — samples on alumina; *2* — samples on glass

explained by thermal properties of used substrates. It's clear seen (fig. 6, curve *2*) that crystalline growth rate for samples on glass was about saturation at high temperatures. It can result from structural changes of glass substrate. On the other hand, crystalline growth rate for samples on alumina substrate was increasing at the whole temperature range. Curve *1* of fig. 6 was rebuilt in $\ln d \sim T$ terms where d is crystalline size and T — temperature (K). Fig. 7 seems to be linear. It means that we can verify temperature dependence of crystalline growth as $d(T) = d_0 \exp(\eta T)$, where d_0 — crystalline size of fresh deposited samples and η-logarithmic growth rate. In our case η equaled 0,0019 K^{-1}.

Analyzing crystalline growth of SnO_2 thin films one can see that strong structural changes become at temperatures higher than 600 °C. With concern to that gas sensitive measurements were provided to fresh prepared samples and 600 °C annealed samples. All the samples had the same thickness 280±20 nm.

Gas sensitivity dependences versus gas concentration are plotted in fig. 8. Annealed films got less sensitivity than fresh prepared ones. Sensitivity mechanism of SnO_2 was described in [9]. It is based on interaction between gas molecules and previously adsorbed oxygen species:

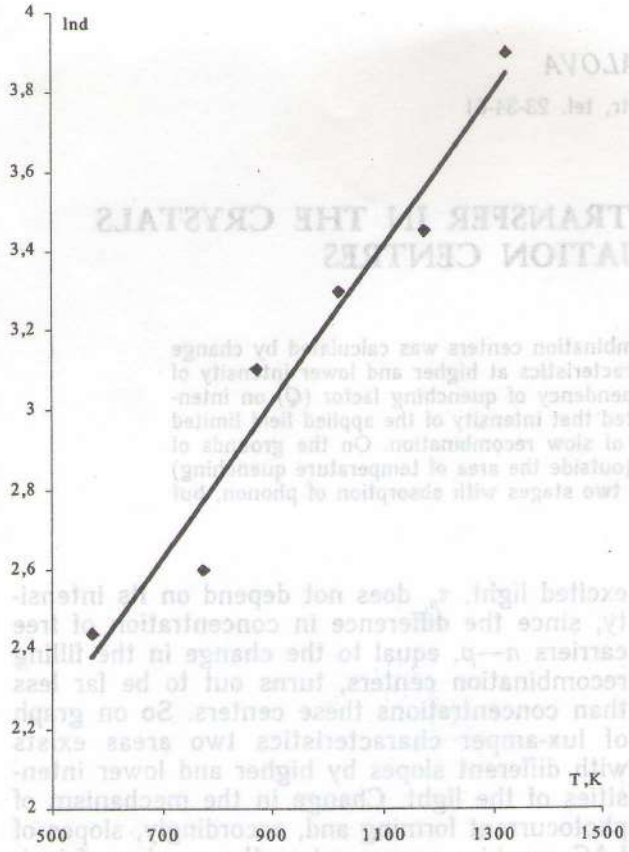

Fig. 7. Crystalline growth diagram of samples on alumina built in semi logarithmic scale

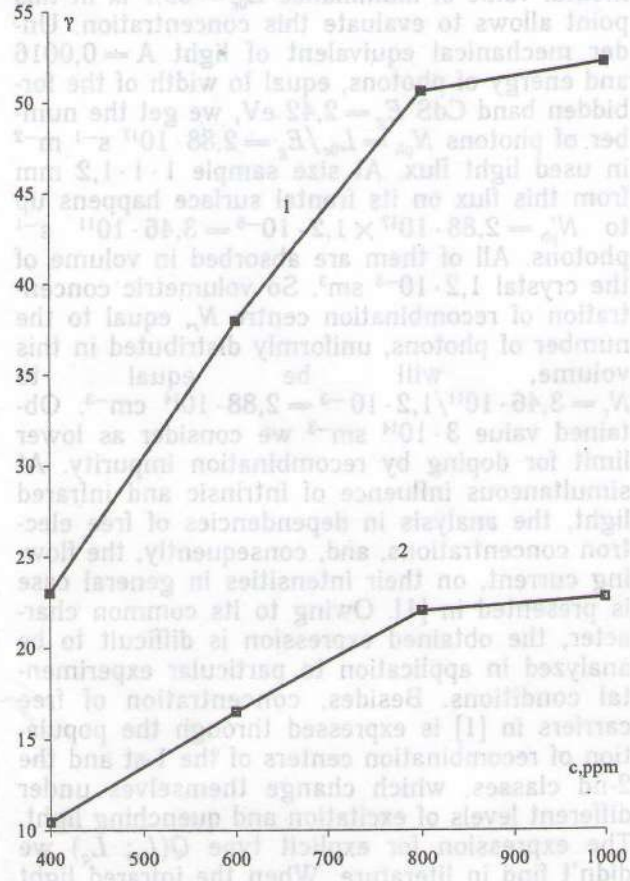

Fig. 8. Gas sensitivity to ethanol of fresh prepared (*1*) and annealed at 600 °C (*2*) thin tin dioxide films

$$R + O_2^- \rightarrow RO_2^- + e^-, \quad (4)$$

$$R + O^- \rightarrow RO + e^-, \quad (5)$$

where *R*-gas molecule, O^{-2} and O^- adsorbed oxygen molecules and atoms. Annealing of thin films led to decreasing active surface area. It lowers surface concentration of adsorbed oxygen and declines interaction rate value. All that reflects in sensitivity value before and after calcinations.

Both dependences get to saturation at high concentrations. It results from finite surface area of the film. As it was previously said surface area affects adsorbed oxygen concentration and surface reaction rate. Under high gas concentration all adsorbed oxygen atoms are involved in interaction and saturation becomes.

CONCLUSION

Thin tin dioxide films deposited by electrostatic spray pyrolisis method consisted of crystallites with average size 3,5±0,8 nm and 5,8±0,9 nm for samples deposited on glass and alumina substrates. Decrease of deposition temperature let us decline crystalline size. Annealing procedure led to increasing crystalline size. Annealed samples had lower sensitivity resulted from crystalline growth and adsorption surface area decrease. To prevent sensitivity fall sensors should be annealed at temperatures less than 500 °C.

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