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CONDUCTIVITY MECHANISM IN THIN NANOCRYCTALLINE TIN OXIDE FILMS

Structural properties of tin oxide nanocryastalline films have been investigated by means of atomic force microscopy (AFM) and X-ray diffraction (XRD) methods. Surface morphology, roughness, crystalline size and lattice strain have been estimated. Current-voltage characteristics (I-V) have been measured at different temperatures. Temperature dependence of current has been studied. Activation energies have been evaluated and conductivity mechanism has been proposed.

1. INTRODUCTION

Tin oxide SnO_2 is well known as material for gas sensors [1-8]. The most important reasons of tin oxide use in sensor applications are chemical stability to different aggressive chemical pollutants and high temperature treatment [1]. Those advantages allow fabricating different types sensors, based on tin oxide to different gases [2]. Another application of tin oxide thin films is optics where they have been successfully used as transparent conducting electrodes in optical devises [2-7]. Tin oxide thin films have been successfully used for measurements in liquids to detect ammonia in water [2].

It was published that tin oxide films consisting of nanoparticles showed different properties from typical polycrystalline films [3-8]. The optical characterization of the films was performed in [4]. The thickness and refractive index have been calculated. The crystalline size was estimated by means of optical methods using the absorption spectra [4]. It was observed blue shift of optical absorption spectra in comparison with polycrystalline samples [4]. The value of band gap estimated from optical absorption spectra was 0,2-0,6 eV bigger, than to tin oxide single crystal (E_g=3,6 eV).

Electrical characterization of nanocrystalline tin oxide films has been performed in [3, 4]. No Shotky barriers have been observed and non ohmic behavior was verified [3]. However, the correct explanation of charge transfer in tin oxide tin oxide nanocrystalline films has not been performed.

In this work experimental results of investigation of electrical properties are reported. Current-voltage and temperature dependence of current have been performed. Results of structural properties of the films have been reported. Activation energies were determined. Conductivity mechanism in tin oxide nanocrystalline films has been proposed.

2. EXPERIMENTAL

Tin oxide thin films were deposited with electrostatic spray pyrolysis technique, described in [1-3]. For deposition, tin chloride (IV) ethanol solution was used [2]. Tin chloride concentration of sprayed solution and sprayed solution volume were kept constant and equaled c=0,01 mol/l and v=10 ml, correspondently. Glass substrates, with pretreatment in ethanol and ultrasonic bath, were used for films' fabrication. Applied static voltage between capillary and glass substrate was 17 kV. After deposition, the obtained samples have been annealed at 793 K during 1 hour.

I-V characterization was measured in the range of 0-200 V under different temperatures 293-393 K. Temperature dependence of current was performed at the same temperature range and with applied voltage kept constant 60 V.

Atomic Force Microscopy (AFM) has been performed on the deposited SnO_2 layers in order to investigate the surface morphology of the films.

XRD measurements have been performed with Philips X'Pert-MPD (CuK_α, λ=0,15418 nm) difractometer to identify the nature of deposited material and determine crystalline size.

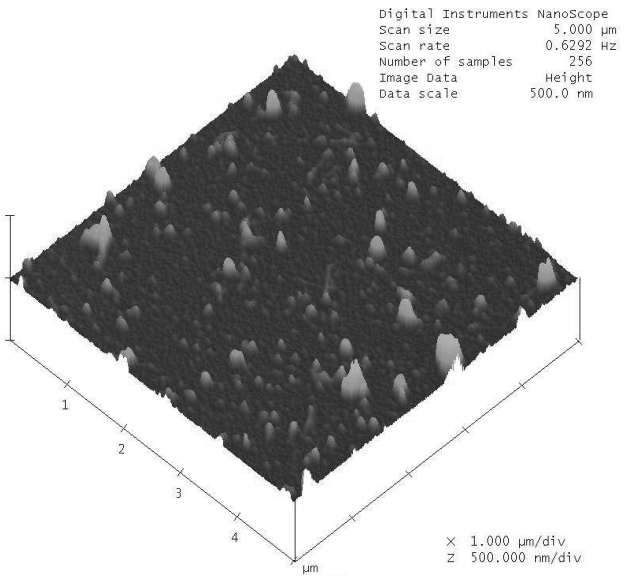

Fig. 1. AFM image of tin oxide film.

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3. RESULTS AND DISCUSSION

The thickness of obtained films, estimated by means of profilometer Tencor P7, was 310 nm. AFM images of tin oxide nanocrystalline films are presented in figures 1, 2. The images refer to 5x5 μm^2 and 800x800 nm^2 areas of tin oxide surface. The one can see that the film had polycrystalline structure with well shaped grains. Wiskers of 200-250 nm height were observed on the surface of the film. It points to high concentration of point defect on the surface of thin films [2]. Surface roughness (Rms) of the films was 26,2 nm, what seems to be suitable for sensor application.

XRD data is presented in figure 3. The one can see peaks at 2θ: 26,5 , 34,5, 37,8 , 51,4, corresponding to tetragonal crystalline phase of tin oxide and one peak at 2θ=65,2, which represents orthorhombic phase of tin oxide [7,8].

Crystalline size and lattice strain have been determined in figure 4, according to equation [7, 8]:

$$\frac{\beta \cdot \cos(\theta)}{\lambda} = \frac{0,9}{d} + \frac{\varepsilon \cdot \sin(\theta)}{\lambda} \qquad (1)$$

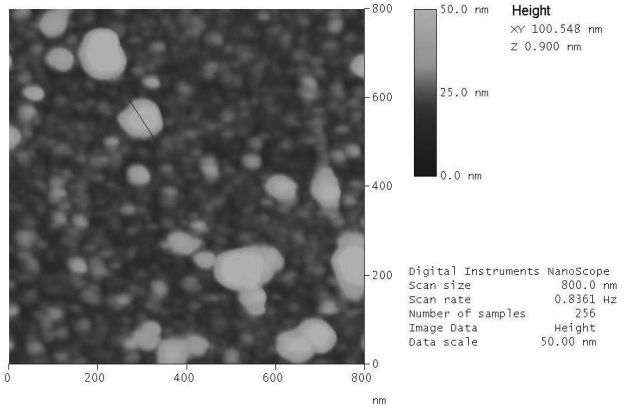

Fig. 2. 2-DAFM image of surface of tin oxide films.

Previously [4], the crystalline size of tin oxide, deposited at the same conditions, determined from optical absorption spectra was 5,2 nm. However analysis of the AFM data showed surface agglomerates with average size of about 20 nm (fig. 2). On the other hand, crystalline size value, determined by XRD method, was compatible with optical absorption data. Similar behavior has been observed in [7], when electron microscopy images gave crystalline size of 100 nm whereas XRD analysis showed particles with 10 nm size. This phenomenon can be explained by formation of agglomerates by low size crystallites.

I-V characteristics are presented in fig.5. In order to analyze charge transfer mechanism they have been plotted in different scales (fig.6, 7). At low voltages (U<50 V) the one can see linear parts in Frenkel-Pool's scale [3]. It may say that under low applied voltages the dominant mechanism is hoping conductivity within surface trapping states. Calculated value of trapping potential was 0,25 eV. The nature of the trapping levels have been discussed in [3, 8]. It is said that trapping states can be formed tin oxide biographic defects at grain boundaries and crystalline interfaces [8].

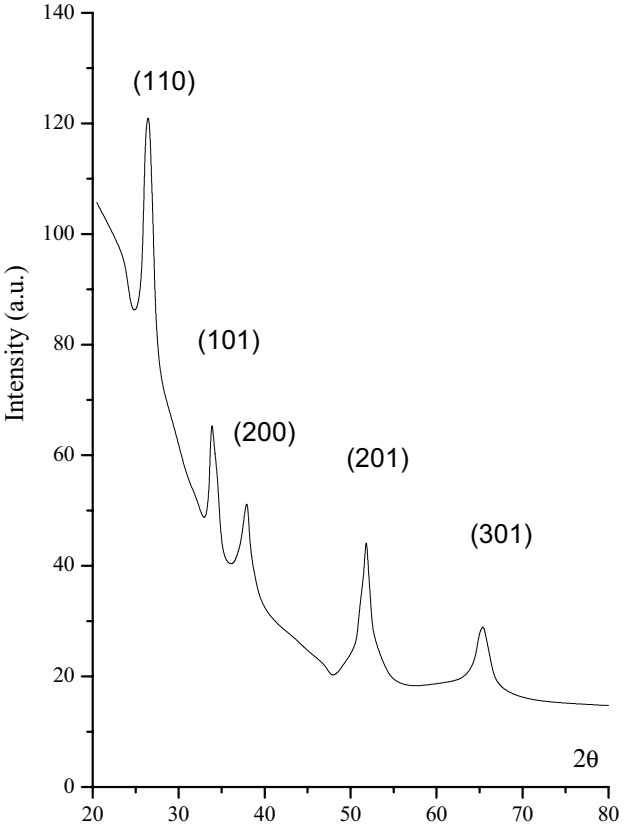

Fig. 3. XRD data of tin oxide thin films. where d-crystalline size in nanometers, λ=0,154 nm, θ — diffraction angle, corresponding to XRD peak, β–peak width at half maximum, ε –lattice strain [8]. The obtained values were 5,54 nm and 0,027 for d and ε, correspondently.

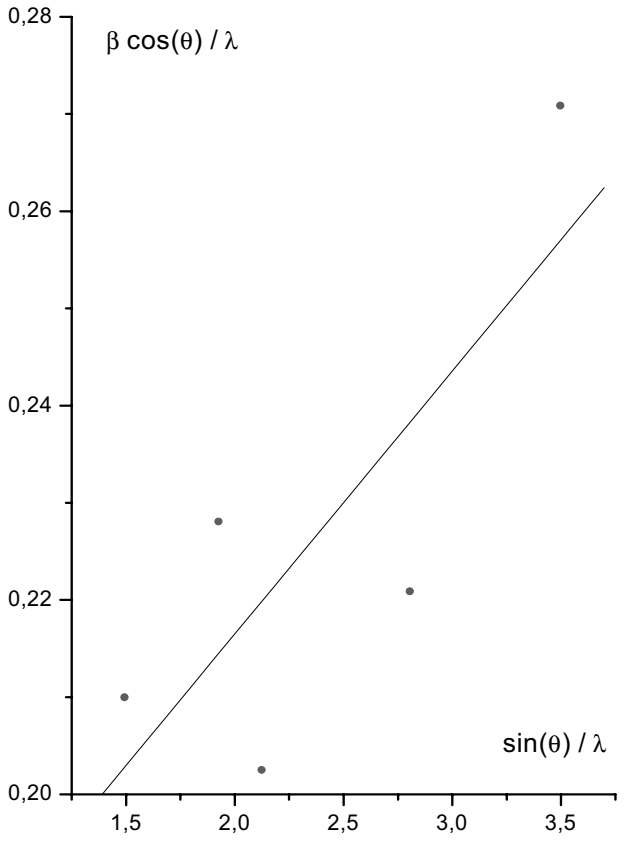

Fig. 4. Determination of crystalline size and lattice strain of tin oxide thin films.

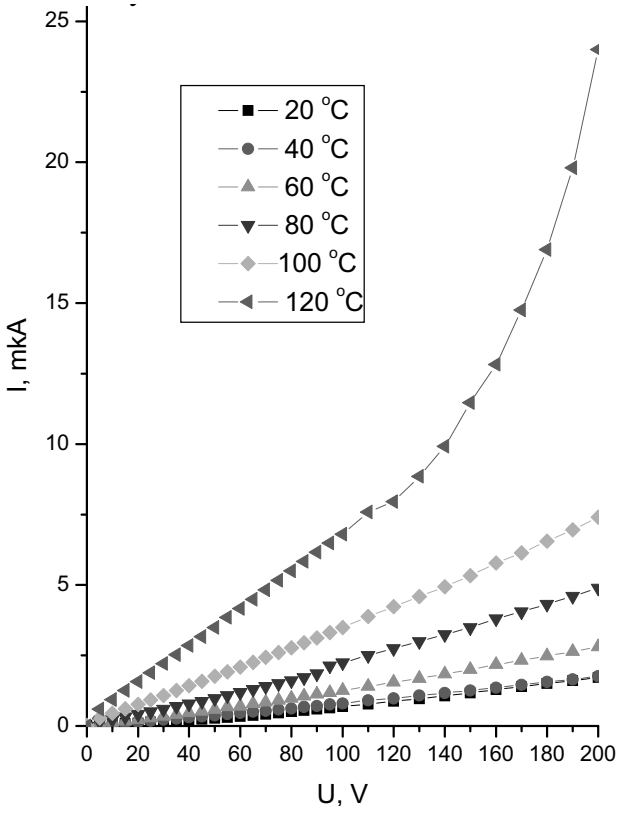

Fig. 5. I-V plots of tin oxide thin films.

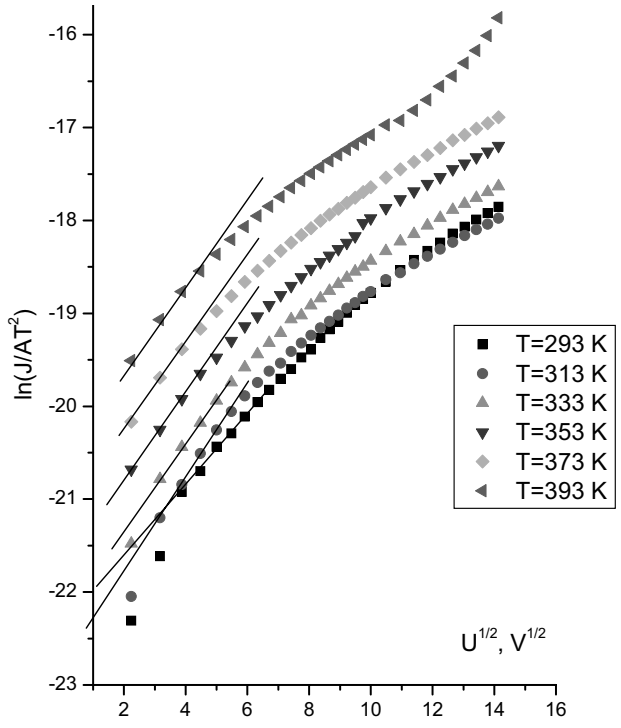

Fig. 6. I-V plots, rebuilt in Frenkel's-Pool scale.

With increase of applied voltage (U>50 V) measured I-V data showed Ohmic behavior. Only at T>353 K nonlinear part was observed.

Temperature dependence of current, measured under constant value of applied voltage U=60 V, was plotted in $\ln I \sim \frac{1}{T}$ scale and two linear parts were found (fig.8). Activation energy values were 0,16 eV and 0,24 eV for low and high temperature regions correspondently. The activation energies E_1=0,16 eV and E_2=0,24 eV correspond to double ionized oxygen vacancies and defect states [8]. The one can see good correlation between energy values determined from I-V measurements and temperature dependences of current. In both cases the same surface states have been observed.

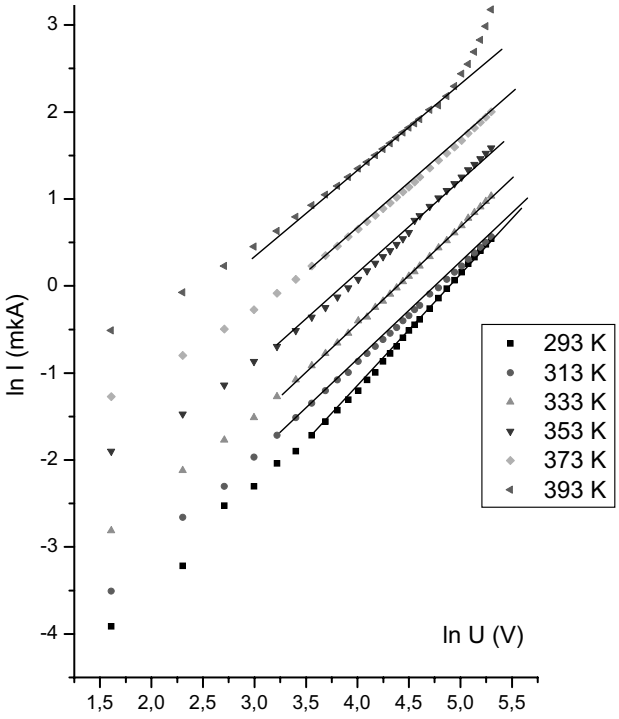

Fig. 7. I-V plots, rebuilt in double logarithm scale.

CONCLUSION

Electrical and structural properties of tin oxide nanocrystalline films have been investigated. AFM analysis showed that the obtained films had polycrystalline nature with rough surface and wiskers, what makes these films attractive for sensor applications.

XRD measurements showed peaks, typical for tin oxide. Crystalline size, determined from XRD measurements, was 5,54 nm. T

I-V data showed two main charge transfer mechanisms. Under applied voltages U<50 V at room temperatures the charge transfer mechanism satisfies Frenkel-Poole equation for hopping conductivity, within surface states with activation energy 0,25 eV. Under U>50 V the Ohm's mechanism dominates.

The temperature dependence of current had two linear parts in Arrenius scale. The activation energies E_1=0,16 eV and E_2=0,24 eV concerned with oxygen vacancies and surface state defects.

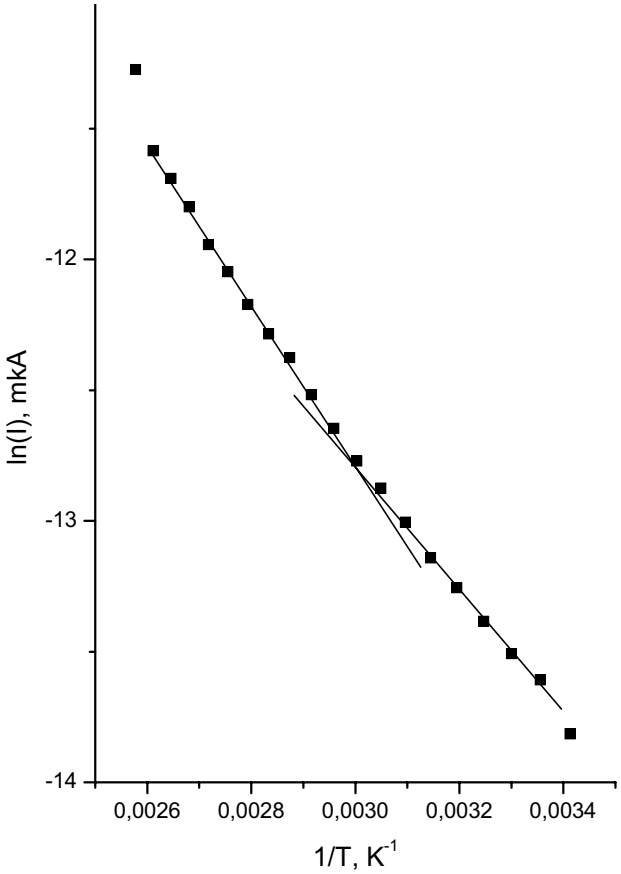

Fig. 8. Temperature dependence of current of tin oxide nanocrystalline films.

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Key words: tin oxide, nanocrystalline films, I-V characterization, XRD, AFM.

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МЕХАНИЗМ ПРОВОДИМОСТИ В ТОНКИХ НАНОКРИСТАЛЛИЧЕСКИХ ПЛЁНКАХ ОКСИДА ОЛОВА

Резюме

Структурные свойства нанокристаллических плёнок оксида олова были изучены при помощи методов атомной силовой микроскопии и дифракции рентгеновского излучения. Были определены морфология поверхности, величины ее шероховатости, размеров кристаллитов и механического напряжения кристаллической решетки. Вольт-амперные характеристики образцов были изучены при разных температурах. Температурная зависимость темнового тока была изучена. Энергии активации проводимости были определены.

Ключевые слова: оксид олова, вольт-амперные характеристики, атомная силовая микроскопия и дифракция рентгеновского излучения.

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МЕХАНІЗМ ПРОВІДНОСТІ В ТОНКИХ НАНОКРИСТАЛІЧНИХ ПЛІВКАХ ОКСИДУ ОЛОВА

Резюме

Структурні властивості нанокристалічних плівок оксиду олова було досліджено за допомогою методів атомної силової мікроскопії та дифракції рентгенівського випромінювання. Було визначено морфологія поверхні, величини її неоднорідності, розмірів кристалітів та механічного напруження кристалічної гратки. Вольт-амперні характеристики зразків було досліджено при різних температурах. Температурну залежність темнового струму було побудовано. Енергії активації провідності були визначені.

Ключові слова: оксид олова, вольт-амперні характеристики, атомна силова мікроскопія та дифракція рентгенівського випромінювання.