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Fabrication and characterization of transparent tin dioxide films with variable stoichiometric composition

Abstract. *Tin dioxide films with variable stoichiometric composition were fabricated by means of DC magnetron sputtering followed by a 2-stage annealing process. The structural and electrical properties of tin dioxide films were investigated by means of Raman spectroscopy and impedance spectroscopy, respectively. It was found that crystallinity and grain size of tin dioxide films increase with the increasing of annealing temperature. The most conductive samples were obtained at the annealing temperature 375°C on the 2-nd stage of the heat treatment procedure. Increasing of the impedance of films annealed at higher temperatures is explained by decrease of the concentration of oxygen vacancies.*

Streszczenie. *Folie z dwutlenku cyny o zmiennym składzie stechiometrycznym zostały wytworzone za pomocą rozpylania magnetronowego przy użyciu prądu stałego oraz poddane dwuetapowemu wygrzewaniu. Właściwości strukturalne oraz elektryczne folii zostały zbadane przy użyciu spektroskopii ramanowskiej i spektroskopii impedancyjnej. Ustalono, że krystaliczność oraz rozmiary ziaren folii z dwutlenku cyny zwiększają się wraz ze wzrostem temperatury wygrzewania. Najbardziej przewodzące próbki zostały poddane wygrzewaniu w temperaturze 375°C w drugim etapie obróbki cieplnej. Wzrost impedancji folii wygrzanych w temperaturach wyższych jest związany ze zmniejszeniem koncentracji wakansów tlenu. (**Wytwarzanie i charakterystyki przezroczystych folii z dwutlenku cyny o zmiennym składzie stechiometrycznym**).*

Keywords: stoichiometric composition, magnetron sputtering, electrical properties, impedance spectroscopy.
Słowa kluczowe: skład stechiometryczny, rozpylanie magnetronowe, właściwości elektryczne, spektroskopia impedancyjna.

Introduction

Coexistence of excellent optical transparency in the visible range of electromagnetic spectrum and high electrical conductivity of tin dioxide films provides possibility for applications as transparent conducting electrodes in optoelectronic devices such as flat panel displays, light-emitting diodes, and solar cells [1, 2]. One of the main reason of the enhanced electrical properties of tin dioxide films is the presence of native defects causing existence of n-type conduction (due to states formed by oxygen vacancies and tin interstitials near the conduction band) and p-type conduction (due to states formed by tin vacancies near the valence band) [3, 4]. According to the first-principles calculations both oxygen vacancies and tin interstitials cause nonstoichiometry in SnO_2 due to suprisingly low formation energy and strong mutual interactions [5]. Therefore possibility of tuning of stoichiometric composition of tin dioxide films during fabrication process is a crusial task for wide range of their applications. Inspite of various techniques and methods used to prepare tin dioxide films a fabrication of samples with desired physical and chemical properties still remains a challenge. Here we report fabrication method of tin dioxide films with variable value of electrical conductivity. For the characterization of structural and electrical properties of tin dioxide films Raman spectroscopy and complex impedance measurements technique were utilized.

Experimental methods

In order to fabricate $SnO_{2-\delta}$ films with variable stoichiometric composition DC magnetron sputtering of tin target in Ar atmosphere with the following 2-stage annealing procedure in air was used. The 1st stage includes heating up to 200°C and isothermal annealing during 2 hours, the 2nd stage – heating and subsequent isothermal annealing at different temperatures in the temperature interval 375°C - 450°C during 1 hour. Raman spectra were recorded using 3D confocal Raman spectral-analytical system Nanofinder HE with laser source with λ=532 nm. Measurements of the frequency dependences of the impedance $Z=Z'+iZ''$ of tin dioxide films in the frequency interval 20 Hz – 2 MHz were used for electrical characterization of the samples annealed at different temperatures. LCR meter Agilent E4980A was used for the measurements of frequency dependences of real Z' and imaginary Z'' components of the impedance of tin dioxide films. Amplitude of the sinusoidal signal was 40 mV.

Experimental results and discussion

In order to vary electrical conductivity of tin dioxide films different annealing procedures were used. It was found that 2-stage heat treatment process with the isothermal annealing at 200°C (near the melting temperature of Sn) followed by high temperature annealing in the temperature interval 375 - 450°C provides possibility to fabricate conductive and transparent tin dioxide films. Variation of oxidation temperature allows to change in wide range stoichiometric composition and structural characteristics of tin dioxide films as far as during oxidation process the phase transformations of films from metallic tin to the higher oxides occur.

Raman spectra for samples annealed on the second stage at 375°C and 450°C are shown in Fig. 1. It is well known that the frequencies of vibration modes of SnO_2 depend on the crystal's size, shape and aggregation [6].

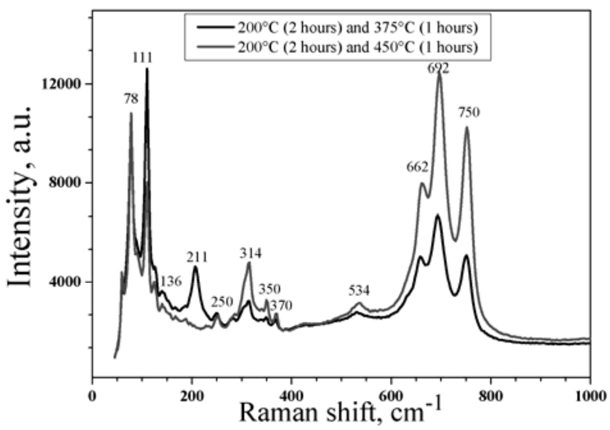

Fig.1. Raman spectra of $SnO_{2-\delta}$ films fabricated by DC magnetron sputtering of tin target followed by a 2-stage heat treatment procedure

In our spectra several peaks (for example, at 111 cm^{-1} and at 750 cm^{-1}) in the vicinity of the classical vibration modes B_{1g} (theoretically predicted at 121 cm^{-1} [7]) and B_{2g} (theoretically predicted at 760.8 cm^{-1} [8]) for single SnO_2 crystal were observed. Besides that, peaks at 314 cm^{-1} and 692 cm^{-1} can be attributed to vibration modes E_u (3) of transverse optical phonons and A_{2u} of longitudinal optical phonons, respectively [9]. Peaks near 250 cm^{-1}, 350 cm^{-1} and 370 cm^{-1} can be also assigned to vibration modes E_u [3, 6, 10]. A peak at 211 cm^{-1} is present in the spectra of film annealed on the second stage at 375°C. This peak corresponds to the Sn-O vibrations in tin oxide phase [11] formed as a result of oxidation in air of Sn film. Due to complete oxidation of metallic film at higher annealing temperature (450 °C) and formation of tin dioxide phase this peak corresponding to SnO phase was not observed.

It should be noted that natural oxygen deficiency in structure of tin dioxide films can be explained not only by the existence of oxygen vacancies in crystalline structure but by the presence of tin interstitials as well. The unusual stability of Sn interstitials inside SnO_2 is caused by the multivalence of tin (Sn(IV) in SnO_2 and Sn(II) in SnO). Moreover, tin interstitials strongly reduce the formation energy of oxygen vacancies acting thus as additional factor of nonstoichiometry of SnO_2 [5]. Therefore vibration mode B_{1g} near 111 cm^{-1} can be assigned both for SnO [12] and SnO_2 [7] crystalline structure. The structural similarity to SnO implies that the interstitial tin atom in SnO_2 has an effective oxidation state Sn(II). As far as the annealing temperature is raised the amplitude of the peak at 111 cm^{-1} is reduced assuming thus decreasing of concentration of defect pairs oxygen vacancy – tin interstitial. On the other hand, amplitudes of inherent for SnO_2 structure peaks near 250 cm^{-1}, 350 cm^{-1}, 370 cm^{-1}, 692 cm^{-1} and 750 cm^{-1} are increased.

The existence of peaks at 136 cm^{-1}, 534 cm^{-1} and 662 cm^{-1} might indicate other tin oxide stoichiometry (Sn_2O_3, Sn_3O_4, SnO_x ($1<x<2$)) [3, 13, 14].

Thus, according Raman spectra we can assume that polycrystalline tin dioxide films with different stoichiometric composition were fabricated as a result of variation of annealing procedure.

This assumption was confirmed by the results of the complex impedance of tin dioxide films measurements. Impedance spectroscopy is one of the most useful and informative method for investigation of electrical properties of polycrystalline materials. Dependences of the real $Z'(f)$ and imaginary $Z''(f)$ parts of impedance on frequency are determined by the prevailing charge transport mechanisms which depends on stoichiometric composition and crystalline structure of the samples. Modeling of the experimental results by the equivalent circuits allows to divide contribution from the grain volume and grain boundaries in the polycrystalline films [15].

Impedance diagram of $SnO_{2-\delta}$ films fabricated by DC magnetron sputtering of tin target followed by heat treatment in air at 200°C during 2 hours and at 375 °C during 1 hour is shown in Fig. 2. The points correspond to the experimental data while solid lines represent the results of the calculations by means of complex nonlinear least-square method (CNLS) [15]. Best fitting results were obtained by simulation of the experimental data with an equivalent scheme shown in the inset to the Fig. 2. According to this scheme resistors *R1*, *R2* and capacitances *C1*, *C2* simulate resistance and capacitance of the grain volume and grain boundaries, respectively.

Impedance diagram of tin dioxide films annealed on the 2nd stage of heat treatment procedure at 450°C is shown in Fig.3. It was found that real part of impedance of the samples increased in comparison with Z' value of $SnO_{2-\delta}$ films annealed at 375°C on the 2nd stage of heat treatment procedure. This can be explained by decrease of the oxygen vacancies concentration which provide n-type conductivity of tin dioxide films [4].

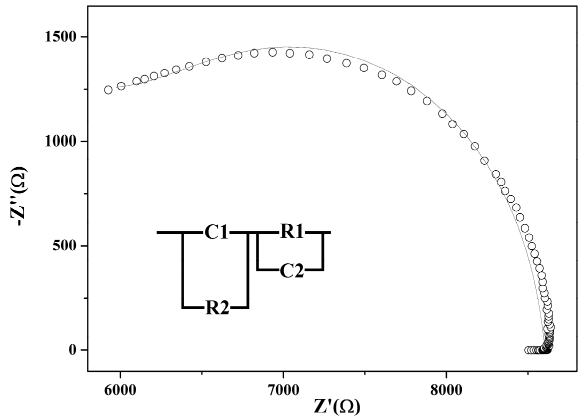

Fig.2. Impedance diagrams of $SnO_{2-\delta}$ films fabricated by DC magnetron sputtering of tin target followed by heat treatment in air at 200°C during 2 hours and 375°C during 1 hour. Line is the approximation of the experimental data by an equivalent circuit shown in the inset

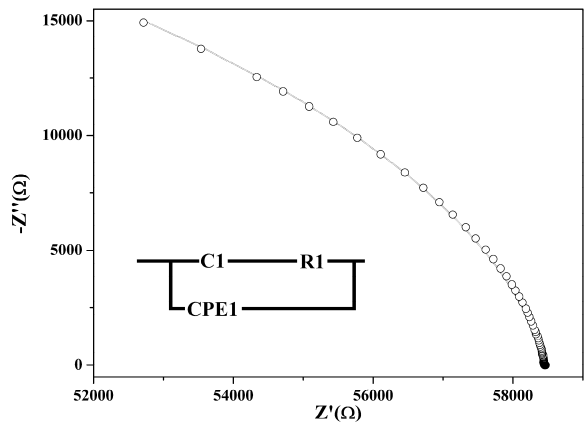

Fig.3. Impedance diagrams of $SnO_{2-\delta}$ films fabricated by DC magnetron sputtering of tin target followed by heat treatment in air at 200°C during 2 hours and 450°C during 1 hour. Line is the approximation of the experimental data by an equivalent circuit shown in the inset

On the other hand, rising of the annealing temperature induces increase of the size of grains and reduces potential barriers between them. As a result equivalent scheme for these samples shown in the inset to Fig.3 was modified in comparison with the equivalent scheme of tin dioxide films annealed at 375°C on the 2nd stage of heat treatment procedure. Resistors *R1* and capacitances *C1* in this scheme simulate resistance and capacitance of the grain volume. Constant phase element (CPE) used in an equivalent scheme takes into account distribution in values of the resistance and capacitance of the grain boundaries. The admittance of the CPE is defined as [15]:

$$(1)\quad Y_{CPE} = A_0(i\omega)^{\alpha} = A_0 i\omega^{\alpha}[\cos(\alpha\pi/2) + i\sin(\alpha\pi/2)]$$

where A_0 is the coefficient with the dimensionality depending on the α value. In the case α=1 the value A_0 has the dimensionality of capacitance while in the case α=0 the value A_0 has the dimensionality of resistance. In the intermediate case dimensionality of A_0 can be considered as $\Omega^{-1}\cdot s^{\alpha}$ [16]. As a result of modelling it was found that α=0.94, this means that *CPE1* element corresponds to capacitance.

In order to enhance conductivity of the tin dioxide films annealed on the 2nd stage of heat treatment procedure at 450°C these samples were subjected to the additional annealing in vacuum (10^{-4} mbar) at 450°C during 1 hour. Typical impedance diagram for these samples is presented in Fig.4.

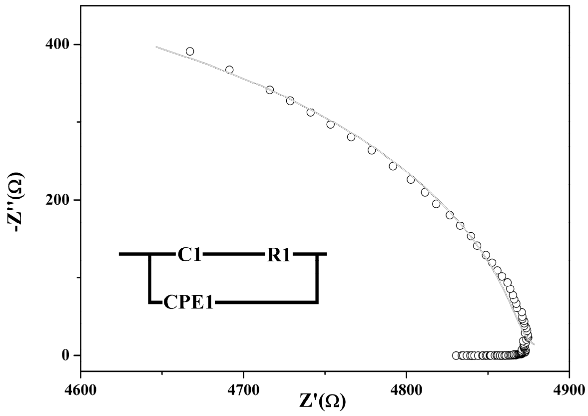

Fig.4. Impedance diagrams of $SnO_{2-\delta}$ films fabricated by DC magnetron sputtering of tin target followed by heat treatment in air at 200°C during 2 hours and 450°C during 1 hour and in vacuum at 450°C during 1 hour. Line is the approximation of the experimental data by an equivalent circuit shown in the inset

Best fitting results were obtained by simulation of the experimental data with the same equivalent scheme as for the samples fabricated without vacuum annealing. However, it was found that parameter α is close to 0 (α~10^{-3}) assuming that *CPE1* element corresponds to resistance. Essential variation of parameter α can be explained by increase of size of grains, decrease of potential barriers between them, redistribution of oxygen vacancies and rising of their concentration.

Conclusion

Fabrication procedure for preparation of $SnO_{2-\delta}$ films with different stoichiometric composition was developed. Tin dioxide films were synthesized by means of DC magnetron sputtering followed by a 2-stage annealing procedure. As a result of analysis of the Raman spectra and impedance diagrams of the samples it was found that polycrystalline tin dioxide films with different sizes of grains were obtained. Electrical properties of tin dioxide films were found to depend on the oxygen vacancies and tin interstitials defect pairs concentration as well as on the grain volume and grain boundary contribution to conductivity. According to the analysis of Raman spectra and impedance measurements we assume that at 375°C annealing temperature on the 2-nd stage of heat treatment procedure the tin interstitials and oxygen vacancies dominate in the defect structure of SnO_2 due to the multivalence of tin, explaining the natural nonstoichiometry and high conductivity of films. Rising of the annealing temperature up to 450°C at the 2-nd stage of heat treatment procedure induces decreasing of the concentration of the oxygen vacancies and tin interstitials defect pairs. Additional annealing in vacuum was found to enhance tin dioxide films conductivity as a result of increase of size of grains, decrease of potential barriers between them and rising of the oxygen vacancies concentration.

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