

Modification of optical and electrical properties of SnO₂ under the influence of argon ion beam

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Abstract. Thin films of tin oxide were deposited on the glass substrates at a room temperature using reactive magnetron sputtering. The ratio between O₂/Ar and the discharge voltage is maintained in such a mode when the deposited films are dielectrics. After the deposition, the films were irradiated with an argon ions beam. The modification of the optical and electrical properties of the films depending on the irradiation time was studied. Optical properties of the films were analyzed in the range of 300-1100 nm using photometry and structural X-ray diffraction. The diffractometric research showed that the films, deposited on a substrate, had a crystal structure, and after argon ions irradiation they became quasi-crystalline (amorphous). It was found that the modification in the transmittance was correlated with modifications in the meaning of surface resistance. The dielectrics films SnO₂ with increasing exposure time became conductive and then the electrical resistance decreased and reached a minimum at 13.2 seconds. Then resistance films began to increase.

1. Introduction

The transparent conductive oxide films are widely used in various industries [1-4]. These optically transparent electrodes are used in displays, solar panels, photoelectric devices, touch panels, etc. One of them is tin oxide, which has found wide practical application. In some practical applications, there is no need to simultaneously achieve the high value of transmittance and low resistance. In such cases it is possible to use an undoped tin oxide. Pure tin oxide has conductivity and transparency. This is due to the existence of intrinsic point defects that act as vacancies [5,6]. Annealing deposited films leads to the modification of the optical and electrical properties. The ratio of oxygen to stannum changed under SnO₂ film annealing at atmosphere and it leads to a decrease in their resistance [7,8]. In this case, the transmission and resistance depend on the duration of the annealing. Annealing the tin oxide films in a vacuum results in a significant reduction of resistance [9]. In work [10] it is shown that when optimizing the oxygen content and the substrate temperature one can receive films with improved transmittance and resistance values. Tin oxide can be in the form of SnO₂ and SnO. Under heating, these phases interact with one another that leads to the modification of films properties [9,11,12]. The effect of films annealing in various atmospheres (air, vacuum or hydrogen atmosphere) is studied in work [9]. The correlation was found between the structural and optical properties of SnO₂ films. In the work [11] tin oxide films were annealed at different time period, however the correlation between the electrical specific resistivity and optical and structural properties was not found. In works [13], the effect of oxygen content in a reactive gas mixture on the properties of the deposited tin oxide films was studied. It is shown that films consist of an amorphous and crystal phase [14]. The formation of textured films in the course of the deposited of tin oxides and its transformation into polycrystalline



SnO₂ at a low temperature (~ 200 ° C) is investigated in [15]. Stoichiometry of films depending on the oxygen content and its influence on electric properties were investigated in [16]. The influence of deposited rate of a film on specific electric resistance has been studied in [17]. The mechanism of conductivity of pure oxide tin films deposited at various temperatures of a substrate has been investigated in work [18]. In work [19] the influence of the application of an external constant magnetic field on resistance and an optical transmission of the deposited films are investigated. Oxygen negative ions of the magnetron discharge [20] also have an impact on the films properties. The influence of ionic stimulation in the course of films deposition on optical properties of a film is considered in [21]. The properties modification of already deposited films happens at the irradiation by an ionic beam of already deposited films [22,23,24]. In this research, the tin oxide films were deposited by a reactive magnetron dispersion, and the films after sedimentation were irradiated by a bunch of argon ions.

2. Experimental details

Thin films of tin oxide were deposited on the glass substrates using reactive magnetron sputtering. The size of Sn target (99.5%) was 700x100x5 mm³. The sputtering was carried out at a working pressure of 0.3 Pa in the gas mix O₂ and Ar (O₂ – 60%, Ar – 40%). The voltage of the magnetron discharge was ~ 275 V. Under these conditions the deposited films were dielectric. The power of the discharge at sedimentation was stabilized at the level 1.2 kW. The heating of substrates was not carried out. The substrates were placed on a carrier that was able to carry out a reciprocating motion under the magnetron and the ion source in a vacuum chamber. The distance between a sample and a target was 8 cm. Speed movement of the carriage was 3.62 cm/sec. After the deposition, tin oxide films were irradiated with argon ions. The ions beam was located at an angle 90° to a substrate surface. Ions were generated by a source of ions with the closed drift of electrons at a voltage 2800 V and discharge current 0.28 A. The current density on a surface of samples was 2.4·10⁻³ A/cm². However, the pressure in a chamber was 0.166 Pa. The thickness of the deposited films was measured using profilometer MicroMeasure 3D Station. For measuring a spectrum of a transmission in the range of 300-1100 nanometers the spectrophotometer SF-256 was used. The structure of films was studied on the x-ray diffractometer XRD6000 . The average size of crystallites was estimated by half of width of x-ray diffraction lines.

3. Results and discussion

Dielectric films of tin oxide were deposited on glass substrates. For study of the film structure, SnO₂ coatings with thickness of 800 nm were deposited. To measure optical and electrical characteristics, the film thickness was 200 nm.

Figure 1 shows the diffractogram films of tin oxide before and after irradiation by Ar ions. It is found that the films SnO₂ after magnetron deposition have crystal structure with shares of amorphous (quasicrystal). The analysis of XRD data showed that the deposited films consist of pure SnO₂ tetragonal structure without the presence of other phases – SnO and Sn. Similar results were observed in work [21]. Moreover, the presence of other phases of tin oxide in films was not revealed. The size of crystallites makes ~ 10 nm. After irradiation of structure became quasicrystal (amorphous).

In Fig. 2 the transmission measurements of SnO₂ films at various periods of irradiation time are presented. According to the figure, the transmission $T(\lambda)$ depending on irradiation time has different nature. On the impact at 0 to 13.2 sec., the dependences $T(\lambda)$ have similar qualitative nature.

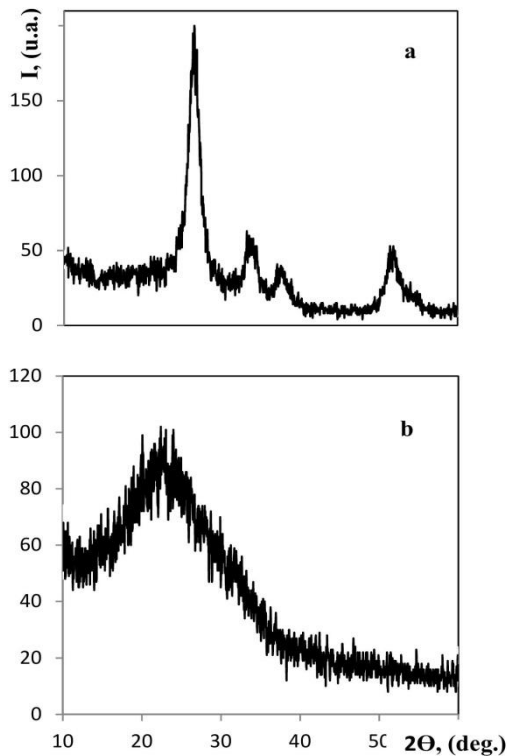


Figure 1. XRD diagram samples of SnO₂: a- before irradiation: b-after irradiation.

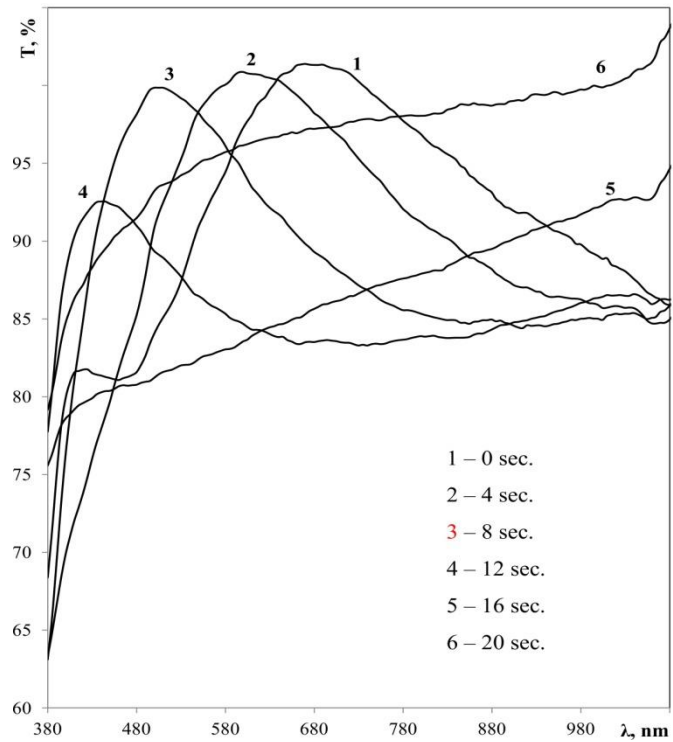


Figure 2. Dependence of the transmission on the irradiation time.

In this time range, the maximum of transmission is existed. The shift of the transmission maximum to the area of short waves during ionic beam exposure time less than 13.2 second is probably connected with the formation of SnO₂ polycrystalline structure [12] of nanodisperse sizes.

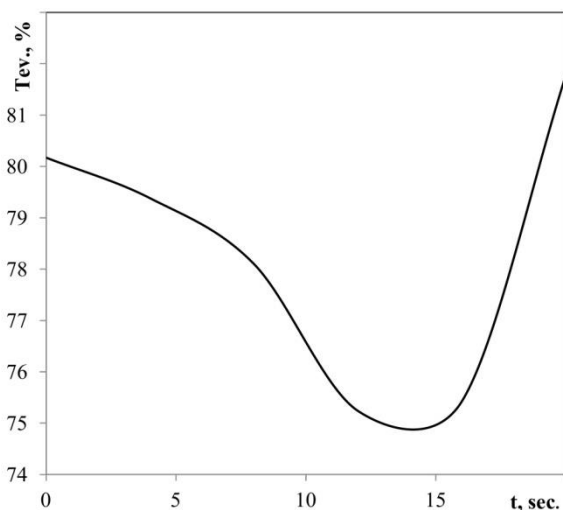


Figure 3. Dependence of the average value of the transmission on the irradiation time.

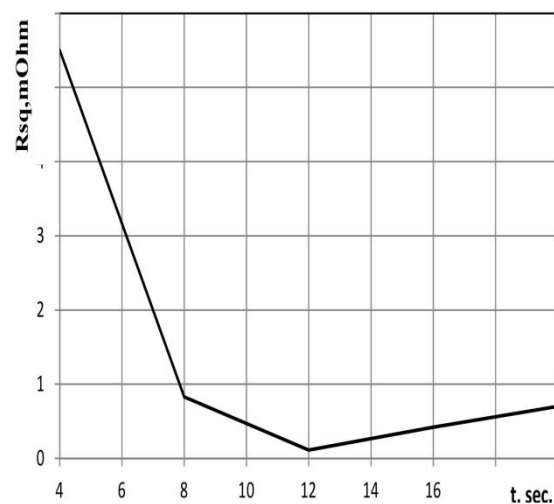


Figure 4. Dependence of surface resistance on the irradiation time.

On the ionic beam impact less than 13.2 sec., the values of a transmission maximum are changed slightly which is perhaps connected with a minor change in a stoichiometric structure of a film. The film transmission decreases under the ion irradiation more than 13.2 sec. This is due to the

fact that on the ions influence a SnO₂ dissociation with formation of metal phase takes place [12]. At ion irradiation time more than 13.2 sec., the dependence $T(\lambda)$ has different character – a rather gradual transmission growth depending on the wavelength. However, the transmittance of SnO₂ films grows with the future increase of ion irradiation time.

Fig. 3 shows the average value change of samples transmission of a deposited SnO₂ film in the range of 380-1100 nm depending on Ar ions irradiation time. As it is seen in Fig. 3, at first the transmission decreases with the increase under the ions irradiation and then increases. The transmission minimum is observed after the irradiation during 13.2 sec. The further growth takes place mostly due to the transmission improvement in a long-wave area relatively to the transmission maximum.

Fig. 4 demonstrates the measurements of a film surface resistance depending on the influence time of an ion beam. It correlates with the change of average transmission. Initially, the film resistance decreases and reaches the minimum value at the argon ions influence time of ~ 13.2 sec. As it has been noted above, at such ion beam influence time the content of small particles of metal tin reaches the highest value in the surface layer of a film. As a result, the film resistance decreases [10] since metal tin particles participate in conductivity. Further impact on an ion beam film leads to the metal component dispersion that reduces its contribution to conductivity, and as a consequence the film resistance increases.

4. Conclusions

Pure SnO₂ dielectric polycrystalline films were deposited at a room temperature by means of reactive magnetron sputtering. After deposition, SnO₂ films were irradiated by argon ions generated by an ion source of with the closed electrons drift. After the irradiation, the film became quasicrystal. It was found that at the increase in ions influence time there is a slightly gradual decrease in average transmission value (from 80 to 75%), which reaches a minimum at ~ 13.2 sec. The further ion beam influence leads to the transmission increase up to 82%. The correlation between optical and electric properties of SnO₂ films is observed. Thus, at first with the increase in Ar ions influence time on the film the film electric resistance decreases and then increases.

Therefore, the optical and electric properties of deposited films can be corrected by means of an argon ions beam impact on the SnO₂ deposited film.

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