Radiation-induced deposition of transparent conductive tin oxide coatings

S Umnov, O Asainov and V Temenkov

National Research Tomsk Polytechnic University, 30, Lenin ave., Tomsk, 634050, Russia

E-mail: usp@tpu.ru

Abstract. The study of tin oxide films is stimulated by the search for an alternative replacement of indium-tin oxide (ITO) films used as transparent conductors, oxidation catalysts, material gas sensors, etc. This work was aimed at studying the influence of argon ions irradiation on optical and electrical characteristics of tin oxide films. Thin films of tin oxide (without dopants) were deposited on glass substrates at room temperature using reactive magnetron sputtering. After deposition, the films were irradiated with an argon ion beam. The current density of the beam was (were) 2.5 mA / cm^2, and the particles energy was 300-400 eV. The change of the optical and electrical properties of the films depending on the irradiation time was studied. Films optical properties were investigated by photometry in the range of 300-1100 nm. Films structural properties were studied using 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 has been found that the transmission increases proportionally with the irradiation time, however the sheet resistance increases disproportionally. Tin oxide films (thickness ~ 30 nm) with ~ 100% transmittance and sheet resistance of ~ 100 kOhm/sq. were obtained. The study has proved to be prospective in the use of ion beams to improve the properties of transparent conducting oxides.

1. Introduction

The transparent conductive oxide (TCO) films are widely used in various industries. These optically transparent electrodes are intended for displays, solar panels, photoelectric devices, touch panels, etc. Currently, one of the most widely used TCO substances is indium tin oxide (ITO) because it has high electrical conductivity and optical transparency.

Recently, because of the high cost of indium,the research has been conducted to find an alternative replacement for ITO. In particular, this is a compound based on tin oxide (dopant-Sb, F, As, Nb, Ta), zinc (dopant- Sn, Ge, Mo, F, Ti, Zr, Hf, Nb, W, Te), and other elements. Although, SnO_2 and ZnO impurities increase their conductivity, but it does not reach the values obtained for the ITO films. However, it is not necessary in some practical applications (very large conductivity). So, in paper [1] pure oxide films (SnO_2) prepared by electron beam evaporation had transmittance of 90% and a surface resistance of 200 kOhm /sq. (substrate temperature is 100^{o}C). Originally, pure SnO_2 films are the conductors if they are deposited in a shortage of oxygen, so they are non-stoichiometric.

For deposition of thin TCO films various methods are applied, including thermal, electron- beam, laser vaporization, cathode, a high-frequency or magnetron sputtering and others. Wesuggest focusing on

the film deposition by magnetron sputtering with additional useof the ion beam.The use of ion beams in the film coatings deposition leads to almost all films properties change [2-3].

Papers [4-8] present data showing that the use of an assisting ion leads to the changes in the optical and electrical properties of the deposited ITO thin films. It means that ion beams allow achieving the optimum relationship of the metal and the oxygen components in the film. So, the transmission of the films treated in that wayis about 90%, and the surface resistance of the best samples is 20 Ohms/sq. According to the authors, this is due to such factors as changes in the mobility of ad atoms and crystal lattice damage.

In their works, the authors used different types of ion sources that had been used under different deposition conditions (the ion beam parameters, the temperature of the substrate). In the papers mentioned above,assisting ion beams were used in the deposition of the doped TCO oxides.

Whereas, the energy formation of oxygen vacancies and tin interstitials in SnO_2 is very low and, thus, these defects form readily, explaining often observed high conductivity of pure, but non-stoichiometric, SnO_2 [9], so the ion beams could be a good tool to stimulate this process.

In this paper, we have studied the influence of the irradiation of the pure tin oxide (without dopant) films argon ions after deposition ontheir the optical and electrical properties.

2. Experimental details

Tin oxide films with thickness of about 30 nm were deposited by reactive magnetron sputtering of the target made of tin (99.5 wt.%) on the glass substrates at room temperature. Before the film deposition the glass substrates were purified by a chalk suspension in isopropyl alcohol.

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 speed of the carrier movement was 3.62 cm / second. The working gas was a mixture of oxygen and argon (partial pressure ratio is O_2 – 60%, Ar – 40%). The pressure in the vacuum chamber during sputtering was 0.3 Pa. The gas flow was controlled by an electronic meter and gas pressure was measured by an ionization and thermocouple gauge. After the deposition, tin oxide films were irradiated with argon ions.

The ions were generated by the ion source with a closed electron drift of 2800 V voltage and a 0.28A discharge current. The greatest number of argon ions in the beam hasthe energy of 400-600 eV. The chamber pressure in such case was 0.166 Pa. For measuring surface electrical resistance Rsq. the samples were deposited with aluminum strips, which provided a reliable contact with the film. The thickness of the deposited films was measured using a profilometer‘Micro Measure 3D Station’. To measure the transmission spectrum in the range of 300-1100 nm the spectrophotometer ‘SF-256’was used. The structure and morphology of the films werestudied using the X-ray diffractometer‘XRD6000’ and an atomic-force microscope ‘NT-MDT’.

3. Results and discussion

All freshly prepared tin oxide films were transparent dielectrics. This is due to deposition by reactive magnetron sputtering that was performed in an atmosphere with the excess oxygen content. Under these conditions, there was enough oxygen to have all the metal oxidised to a state of complete oxide, so all the oxygen vacancies, creating conductivity, are busy and a SnO_2 semiconductor film is deposited as a dielectric. After the deposition of the tin oxide films, the samples were irradiated with argon ions. Figure 1 shows the results of measurement of the films transmittance of both non-irradiated and irradiated samples. As it is seen from the figure the transmission is strongly dependent on exposure time.

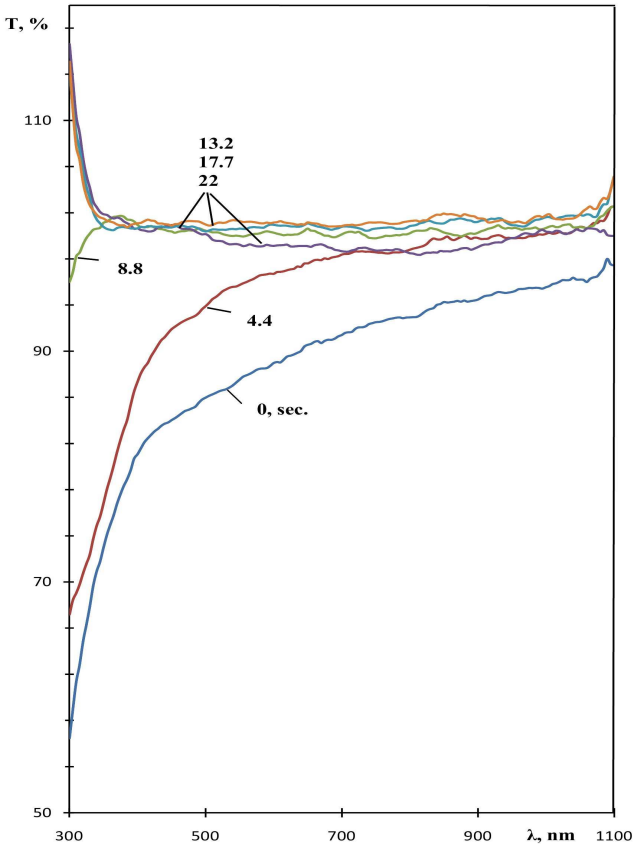

Figure 1.Dependence of the transmissionon the irradiation time

So, when the exposure time is less than ~ 4.5 sec. the transmission slightly improves. For longer times (≥ 8,8 sec.) the transmission is increased to 100% in almost the entire range of the wavelengths. It should be mentioned that when the irradiation time is 13 - 22 seconds, there is an increase in transmittance under wavelengths less than 360 nm and a slight increase in the infrared region. The increase in transmission, especially in the short-wavelengths region, of the irradiated films is related to the change of the plasma frequency [10-12]. This change is a consequence of increasing the electrons concentration.

However, the nature of the transmission is defined by the frequency of the incident light wave and the plasma frequency.

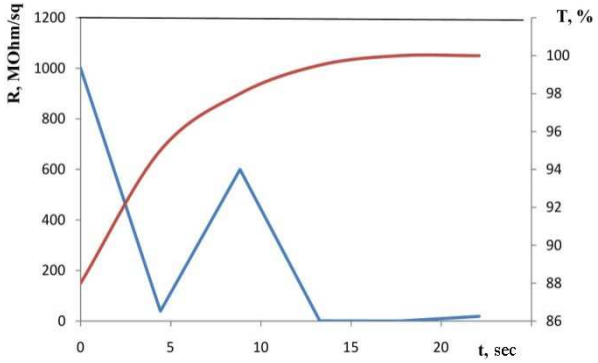

Figure 2. Dependence of the transmission on the irradiation time

Figure 2 shows the results of the surface resistance measurements, an average transmittance value at various irradiation times. The figure shows that the film surface resistance is disproportionately

dependent on the exposure time. With the exposure time increase, the resistance initially decreases and then increases again. The film transmittance almost uniformly increases and quickly reaches 100%.

As the deposition was carried out under the excess oxygen content, the films were deposited in the SnO_2 stoichiometric form which is a good insulator.

During the Ar ions irradiation there is their collision with the film surface and the power transfer in the local area to the neighbouring atoms of the crystal lattice, imbedded and adsorbed on the grains boundary. As a result, there are physical and chemical processes that lead to break or reduction of chemical bonds, causing desorption or chemical reaction that alters the structure of the coating.

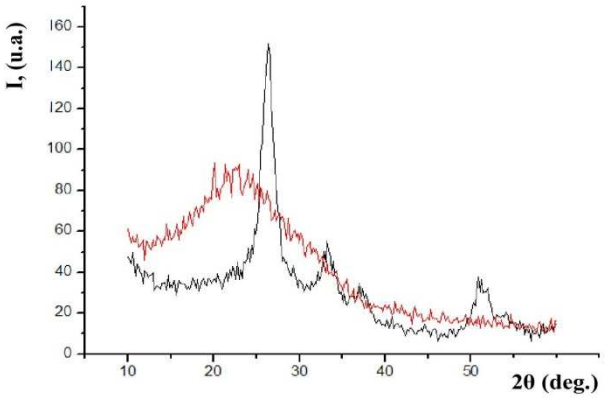

Figure 3.XRD diagram samples of SnO_2

The concentration of the increasing number of electrons is connected with both the break of the Sn-O chemical bonds and desorption of oxygen, which leads to the formation of non-stoichiometric tin oxide. Thus, the film exposure leads to an increase in the number of oxygen vacancies, which, in its turn, leads to a reduction in the films electric resistance. However, a further irradiation time increase leads to the film resistance increase. This is, possibly, connected with the formation of Sn self-point defects [11-12]. Whereas, the point defects interact with all conductive electrons, so the electrons, located near the defects, are 'bound' and do not participate in conductivity. As a result, the film resistance increases.

Figure 3 shows the results of the study of the deposited films structure. The figures show that the deposited tin oxide films have a crystal structure (tetragonal) with the grain size bottom of ~ 9.8 nm. After argon ions irradiation the structure becomes quasi-crystalline (amorphous - a red curve). This is due to the opening of the crystal lattice chemical bonds and forming new ones, which lead to formation of a quasi-crystalline structure.

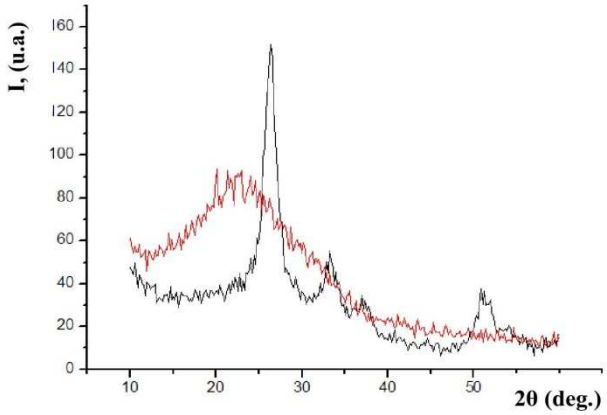

Figure 3.XRD diagram samples of SnO_2

4. Conclusions

Pure SnO_2 films were deposited at room temperature by reactive magnetron sputtering, followed by Ar ions beam irradiation with energy of 400-600 eV. It allows obtaining the films with 100% of transmittance and satisfactory surface resistance of 100 kOhm/sq. The surface resistance value can be reduced by optimizing the deposition conditions and ion beam parameters. Thereby, transmission increases proportionally with the irradiation time increase, while the surface resistance disproportionately. The crystal structure of the SnO_2 film after ion irradiation is transformed into a quasi-crystalline one.

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