Electrical properties of transparent conductive ATO coatings obtained by spray pyrolysis

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Abstract: Transparent conductive coatings based on thin films of metal oxides have been widely spread in various optoelectronic devices and appliances. It is necessary to determine the influence of preparation conditions on coatings properties for their use in the solution of certain tasks. Thin films of tin dioxide were obtained by the method of spray pyrolysis on glass substrates. Surface resistance and resistivity, concentration and mobility of charge carriers, the conductivity were measured, and the dependences showing the effect of preparation conditions on electrical properties of optically transparent coatings.

Keywords: transparent conductive coating, spray pyrolysis, electrical properties, the method of Van der Pauw, four-probe method, surface resistance, resistivity, concentration of charge carriers, mobility of charge carriers, conductivity.

I. INTRODUCTION

Transparent conductive coatings (TCC) based on thin films of metal oxides (In₂O₃, ZnO, SnO₂, etc.) are widely used today in various appliances and optoelectronic devices: organic light-emitting diodes, liquid crystal displays, touch screens, anti-dazzle panels, elements of flexible electronics, etc. These materials possess a unique combination of the following properties: high electrical conductivity and good optical transparency in the visible region of the electromagnetic spectrum [1]. Parameters depend on the film thickness, the type and the concentration of impurities. The surface resistance of thin films decreases with the increasing thickness [2, 3]. Therefore it is possible to improve electrical and optical properties of TCC by changing the conditions of receiving by any method. Basically the electrical properties of TCC are directly characterized by these parameters: electrical resistivity, concentration and mobility of charge carriers.

Traditionally electrical properties of thin transparent conducting oxide films are studied depending on the influence of the following parameters:
• the type and dopant concentration;
• temperature and the substrate type in the synthesis of TCC;
• methods of TCC working after the synthesis;
• TCC temperatures.

Impurity atoms doping is effective to increase the electrical conductivity of transparent conductive coatings. Impurity atoms doping allow increasing the concentration of charge carriers due to shallow impurity levels in the TCC zonal structure.

However the impurity atoms doping can lead to charge carriers mobility increase [4]. The impurity atom should have a higher valence than the atom forming an oxide compound. For example, the atom of tin has a valence +4, and the atom indium valence +3, in the case of indium oxide doped with tin. An atom of aluminum has a valence of +3, and an atom of zinc has a valence of +2, in the case of zinc oxide doped with aluminum. Also, it is necessary to limit the concentration of impurity atoms to avoid the second phase formation that may affect the TCC final electrical properties.

Moreover electrical parameters influence on the optical properties which are the TCC main characteristics along with their electrical ones. Basically the optical properties are examined to determine the following important parameters:
• the values of the coefficients of transmission and reflection in the ultraviolet, visible and near infrared range of wave lengths;
• the value of the optical forbidden zone;
• the values of refractive index and extinction in the ultraviolet, visible and near-infrared range of wave lengths.

II. EXPERIMENTAL

SnO$_2$ films are obtained by the spray pyrolysis method which is today one of the most promising methods of TCC applying on substrates of a large space. In this work the experimental setup is presented and designed for this method implementing.

This method is mainly used for the formation of thin films of simple metal oxides (ZnO, SnO$_2$, TiO$_2$, ZrO$_2$, etc.) having wide application as transparent conductive and anti-reflective coatings, sensitive elements of gas sensors, structures for optoelectronics, solid oxide fuel cells and photovoltaic converters. By the pyrolysis you can also obtain films of mixed oxides (SrTiO$_3$, Pb(Zr$_{1−x}$Ti$_x$)$_3$O$_3$), binary chalcogenides (CdS, CdSe, CdTe), oxide superconducting films (YBa$_2$Cu$_3$O$_{7−x}$) and others. In the case of spray pyrolysis the films formation occurs due to thermal decomposition of the precursors contained in the aerosol spraying on the heated substrate. Compared to other methods the spray pyrolysis has the advantages such as the simplicity of the used equipment, the efficiency, the easy control of deposition rate, thickness and process of the films modification, the possibility of a complex composition of the films forming, the potential for mass production, etc.

Sodium-calcium-silicate glasses were used as substrates. The substrates were pre-cleaned by ultrasonic working in acetone, ethanol and distilled water. The films application SnO$_2$ was conducted from solutions containing tetrachloride pentahydrate of tin (SnCl$_4$·5H$_2$O) with molar concentration of $C_M$, ethanol (solvent) and antimony chloride (SbCl$_3$) with impurity concentration $\chi$. For this solutions with different volumes $V$ were spraying on the substrates heated to a temperature $T_S=450$ °C. The atomization took place with the help of compressed air supplied to the pneumatic atomizer under the pressure $p=2$ bar. The distance between the sprayer and the substrates was $L=300$ mm. Table 1 shows the values of $C_M$, $V$ and $\chi$. 
The four-probe method and Van der Pauw method were used to determine electrophysical parameters of films SnO2 applied on glass substrates.

Surface resistance (Ω/□) is the main parameter among electrophysical characteristics characterizing the quality of the TCC. It is possible to determine their specific resistance $\rho$ (Ω·cm), if we know values of $R_S$ and the thickness of coatings.

Four-probe method is the most common method of measuring the surface resistance of semiconductor materials. Its use by its high metrological indicators and simple construction of the measuring means.

This research method is based on the phenomenon of the electric current spreading at the contact point of the tip metal with the semiconductor. The calculation of the surface resistance is carried out after the measurement of the potential difference at two points located on a flat surface while passing through two point contacts located on the same surface, current of a certain value [5].

Other electrical parameters have been obtained by Van der Pauw method.

The main feature of the method is a method of the electrical resistivity measuring. The current is passed two adjacent contacts in a magnetic field and the potential difference is measured between the two others. As a result "resistance" is determined according to the obtained results. The procedure is then repeated but for the other pairs of contacts and the "resistance "is determined in the other direction [6].

Installation Ecopia HMS 5000 was used to determine electrical parameters which use the Hall effect.

### III. Results

Electrical parameters were obtained as a result of the research of transparent conductive coatings. As a first step we consider the surface resistance measured by the four-probe method (table 2).

| Sample number | $\chi$, % | $C_{A6}$, mole/l | $V$, ml |
|---------------|-----------|-----------------|--------|
| 1             | 0         | 0,25            | 5      |
| 2             | 0,25      |                 | 5      |
| 3             | 0,025     |                 | 10     |
| 4             | 0,05      |                 | 15     |
| 5             | 0,025     | 0,25            | 5      |
| 6             | 0,05      |                 | 10     |
| 7             | 0,025     |                 | 15     |
| 8             | 0,05      |                 | 5      |
| 9             | 0,025     |                 | 10     |
| 10            | 0,05      |                 | 15     |
Table. 2 - Films thickness SnO₂ and surface resistance measured by four-probe method

| Sample number | d, nm | $R_S$, Ω/□ (four-probe method) |
|---------------|-------|---------------------------------|
| 1             | 115   | 1528                            |
| 2             | 133   | 861                             |
| 3             | 168   | 675                             |
| 4             | 209   | 637                             |
| 5             | 211   | 426                             |
| 6             | 225   | 221                             |
| 7             | 245   | 139                             |
| 8             | 260   | 95                              |
| 9             | 262   | 89                              |
| 10            | 270   | 57                              |

According to the obtained results it can be concluded that the surface resistance decreases with the coating thickness increasing. This dependence is explained by the "size effect" in which there is an increase of surface scattering with thickness decreasing compared to the bulk material.

In table 3 there are the rest of the electrical parameters obtained by Van der Pauw method.

Table. 3 - Electrical parameters of TCC obtained by the method of Van der Pauw

| Sample number | Resistivity, Ω cm | Conductivity, 1/(Ω m cm) | Charge carrier mobility, cm²/(V·s) | Concentration, cm⁻³ |
|---------------|-------------------|--------------------------|-----------------------------------|---------------------|
| 1             | 6.67·10⁻³        | 150                      | 13.25                             | 7.08·10¹⁰           |
| 2             | 6.24·10⁻³        | 160                      | 11.34                             | 8.83·10¹⁰           |
| 3             | 1.46·10⁻²        | 68.4                     | 8.03                              | 5.31·10¹⁰           |
| 4             | 8.41·10⁻³        | 119                      | 9.15                              | 8.11·10¹⁰           |
| 5             | 4.45·10⁻³        | 225                      | 12.24                             | 1.15·10¹⁰           |
| 6             | 2.16·10⁻¹        | 463                      | 8.12                              | 3.56·10²⁰           |
| 7             | 1.45·10⁻¹        | 692                      | 14.75                             | 2.93·10²⁰           |
| 8             | 9.56·10⁻¹        | 2240                     | 7.41                              | 9.04·10²⁰           |
| 9             | 9.16·10⁻²        | 1090                     | 15.91                             | 4.33·10²⁰           |
| 10            | 5.91·10⁻⁴        | 1690                     | 13.56                             | 7.79·10²⁰           |

Dependences were built on the results of obtained parameters from the obtaining conditions.
Surface resistance consistently decreases with the volume of solution increasing, the concentration of precursor and the concentration of impurity. Antimony replaces the tin atoms in the lattice. As a result the antimony atoms act as donors and create the excess number of free electrons. A small increase in the values of $R_s$ above a certain concentration of doping is connected with that the excess antimony atoms do not occupy the correct positions in the lattice; it leads to disruption of the structure and to increase of the surface resistance.

Fig. 2 - Dependence of the resistivity on the concentration of the precursor

Resistivity decreases with the impurity increasing due to the increase of the number of free electrons. With the increase of the impurity concentration the mobility of charge carriers decreases. This is due to the fact that the increase of the charge carrier scattering takes place with the increase of the impurity concentration with the result that the mobility is reduced.

Fig. 3 - The dependence of the charge carriers mobility on the concentration of the impurities

With the increase of the impurity concentration the mobility of charge carriers decreases. This is because of the fact that with the increase of the impurity concentration the scattering of charge carriers is increased resulting in the mobility decreases.
The concentration of charge carriers increases with the increase of the concentration of impurity (Sb). Antimony can be in 2 States: SB$^{5+}$ and Sb$^{3+}$. When antimony (Sb$^{5+}$) is introduced as impurity in the film its atoms replace tin atoms (Sn$^{4+}$) in the lattice. As a result the antimony atoms act as donors and create excess electrons.

**IV. CONCLUSION**

Studies have shown that changing the conditions for obtaining it is possible to adjust the electrical properties of the coating.

1) the surface resistance decreases with the film thickness increasing;
2) the surface resistance consistently decreases with the volume of solution increasing;
3) the resistivity decreases with the impurity increasing;
4) the mobility of charge carriers decreases with the impurity concentration increasing.

Thus, the results obtained in the study can be applied in the development of coatings for certain optoelectronic devices.

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