The study of the optical properties of transparent conductive oxides SnO$_2$:Sb, obtained by spray pyrolysis

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Abstract. The study results of the dependences of the refractive index and samples transmittance of transparent conductive films of tin dioxide depending on wavelength are presented. Films with different doping levels, with different solutions volumes were synthesized on an automated installation by spray pyrolysis. It is shown that the transmittance practically does not depend on the amount of substance sprayed onto the substrate; the transmittance practically does not depend on the solution volume, but depends on the impurity concentration. The chemical composition and temperature of film deposition influence on its refractive index is established. The research results can be used in the development of technologies for the manufacture of optoelectronic structures containing transparent conductive coatings.

1. Introduction

Transparent conductive oxides (TCO) of metals have high transparency and conductivity. Most widely used today are TCO based on metal oxides (MeO). Most of them are binary compounds (In$_2$O$_3$, ZnO, SnO$_2$ and CdO) containing one metallic element. In the stoichiometric composition, these compounds are dielectrics, however, due to the large number of internal defects, which are expressed in the presence of oxygen vacancies or in the presence of interstitial metal atoms, they can become semiconductors with a wide forbidden band (E$_g$ > 3 eV). The formation energy of vacancies and atoms in the interstitial is very low; therefore, these defects are easily formed, which explains the relatively low resistance of non-stoichiometric metal oxides [1]. In addition to high conductivity, TCO also have a good optical transparency (transmittance T > 80%) in the visible and near infrared regions of the electromagnetic spectrum. Therefore, the TCO transmission window is in the range $\lambda$ from 400 nm to 1500 nm. This is explained by the fact that in the region of long waves ($\lambda$ > 1500 nm) light is reflected as a result of the appearance of a plasma edge when the light frequency $\omega$ coincides with the frequency of collective oscillations of charge carriers in a material (plasma frequency $\omega_p$). While the light transmission in the near ultraviolet ($\lambda$ <350 nm) is limited by the forbidden band, since photons with energy $\omega$ > E$_g$ are absorbed. Also, tin dioxide has important physical properties for use in TCO [2]. For the promising TCO application in the field of transparent electronics, for example in thin-film transparent transistors [3] or hetero-structures to create light-emitting diodes, it is necessary to measure and study the dependences of the complex refractive index on the wavelength, which allow to obtain data on the optical width of the forbidden zone, defect levels, phonon and plasma frequencies. To control the optical characteristics, it is necessary to investigate the laws governing the optical TCO properties of the formation obtained by the spray pyrolysis method depending on the deposition parameters, and also to take into account the interrelation of the optical and electrical TCO properties [4].

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2. Experiment

The deposition of tin dioxide films with different doping levels was carried out using the developed spray pyrolysis installation [5]. The conditions for applying all the films are the same and are summarized in the Table 1.

| Parameter                        | Value                        |
|----------------------------------|------------------------------|
| Precursor №1                     | SnCl4 · 5H2O                 |
| Precursor №2                     | SbCl3                        |
| Precursor №2, concentration Npec2| 0, 0.1, 0.25 mol.%           |
| Vrast (volume of solutions)      | 5-20 ml                      |

Figure 1 shows the dependence of the films transmittance on the wavelength for pure tin dioxide with a different volume of the sprayed solution.

When an impurity is introduced into the semiconductor, the charge carrier concentration in the TCS will lead to a change of the plasma frequency. As the charge carrier concentration in the TCS increases, the plasma frequency will shift towards the visible range, and the corresponding transparency window will decrease significantly. The plasma frequency and charge carrier concentration in the material is related as follows [6]:

\[
\omega_p = \sqrt{\frac{n e^2}{m^* \varepsilon_0 \varepsilon_\infty}} \tag{1}
\]

where \( n \) is the concentration of free charge carriers, \( e \) is the electron electric charge (1.6·10\(^{-19}\) CI); \( m^* \) is the effective electron mass in the material, \( \varepsilon_0 \) is the electric constant (8.85·10\(^{-12}\) F/m), \( \varepsilon_\infty \) is the dielectric constant of the material at high frequencies.

Electromagnetic waves of a lower frequency are absorbed by the material, and for waves of a higher frequency, it becomes much more transparent. In practice, it is more convenient to use the plasma length, which is easier to count as:

\[
\lambda = \sqrt{\frac{\pi}{n^*re}} \tag{2}
\]

where \( re \) is the classical electron radius, equal to 2.818·10\(^{-15}\). If we take the working wavelength more than the critical one, then there will be no reflection, and the layer for this wavelength will be transparent. The results are described in detail in [7].
Reducing the transparency window is an undesirable effect in solar photovoltaic applications [8, 9]. This change in transmittance is due to the Burstein-Moss effect, which is associated with the filling of the conduction band with electrons. The absorption and emission of light by any substance is determined by three factors — the energy structure of the substance, the population of the energy levels, and the probabilities of optical transitions. Any effect on a substance, leading to a change in its spectra or other absorption and emission characteristics, primarily affects the value of these factors. When impurities are introduced into a semiconductor, especially in large quantities, all three characteristics of a substance can change significantly. First, new levels and even zones of permissible energy values appear in the forbidden zone. Secondly, the distribution of electrons and holes in levels changes dramatically; the Fermi level is shifted to the forbidden zone in the transition from one type of semiconductor to another. Third, because of the perturbation of the wave functions describing the electrons motion in the zones, the probabilities of optical and non-optical transitions change, new channels of light absorption and recombination radiation are opened [10].

![Graph](https://via.placeholder.com/150)

**Figure 2(a, b).** (a) Dependences of the samples transmittance with different doping levels (volume 5 ml on the wavelength); (b) Transmittance of samples with different doping levels (volume 10 ml): 1) impurity concentration 0%; 2) impurity concentration 0.1%; 3) impurity concentration 0.25%.

![Graph](https://via.placeholder.com/150)

**Figure 3.** Dependences the refractive index of samples at different solution volumes on the wavelength: 1) solution volume 10 ml; 2) solution volume 15 ml; 3) solution volume 20 ml.

The refractive index of experimental samples differs only in the region of ultraviolet radiation, and in the visible region the refractive index tends to one value, being in the range of 2.4-2.7. This is due to the fact that the refractive index depends on the material being sprayed, as well as on the deposition temperature. As the deposition temperature increases, the refractive index decreases. This is explained by a decrease in the sizes of sub-grains and the formation of a polycrystalline, rather than an amorphous film.
Figure 4 shows that the refractive index does not change linearly. The reason for the decrease in the refractive index is the decrease in the number of defects and the compaction of films as a result of doping with antimony [11]. When spraying 10 ml of the solution, a thin defect-free film with a crystal structure is obtained (as evidenced by the correspondence of the refractive index to the theoretical data). With an increase of the solution volume, the film acquires an inhomogeneous structure: due to the long application of a large volume of solution, the substrate surface cools to a temperature below 450 °C, which accordingly leads to the formation of an amorphous structure [12].

3. Conclusion

The transmittance is almost independent on the amount of substance sprayed onto the substrate. However, the transmittance is strongly influenced by the chemical films composition. The transmittance also weakly depends on the sprayed solution volume. In this case, a clear dependence of the transmittance on the impurity concentration in the films is observed. This phenomenon is associated with a change in the frequency of the plasma, which depends on the charge carriers concentration. The higher the concentration of charge carriers in the semiconductor, the more the plasma frequency will shift towards the visible range, which accordingly reduces the range in which the TCS is transparent. The refractive index of the samples also depends on the impurity concentration in the initial solution. With increasing impurity concentration, the refractive index decreases slightly and is in the range from 2 to 2.7. The minimum refractive index is observed for samples obtained by spraying 10 ml of the precursor solution.

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