

ZINC OXIDE

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Abstract

The rapid growth of the world population, intensifying industrialization, and increasing environmental challenges are raising the global demand for renewable energy sources. Among these, solar energy is considered one of the most promising and environmentally friendly alternatives. In particular, solar photovoltaic systems provide the possibility of generating stable, affordable, and clean electricity without harming the environment. The role of modern photovoltaic technologies in ensuring continuous, efficient, and eco-friendly energy supply for the population is invaluable, and their improvement and adaptation to local climatic conditions remain important scientific and practical tasks.

Zinc oxide is a well-known compound that has long been widely used in various fields of industry, technology, and medicine. ZnO thin films are weather-resistant, chemically inert, and transparent in the visible and infrared regions of the spectrum. They are used as electrical contacts, reflective coatings for thin-film solar cells, and components in touch screen displays.

Keywords :Solar photovoltaic cell; semiconductor metal oxides; polymers; carbon structures with high electrical conductivity and good optical transparency; tin oxide; zinc oxide.

Introduction

Zinc oxide is a well-known compound that has long been widely used in various fields of industry, technology, and medicine. ZnO thin films are weather-resistant, chemically inert, and transparent in the visible and infrared regions of the spectrum. They are used as electrical contacts, reflective coatings for thin-film solar cells, and components in touch screen displays. Other promising applications of ZnO include transparent thin-film transistors (due to their high optical transparency and high conductivity), acoustic wave devices (owing to their large electromechanical coupling), and nanoscale devices such as nanowire and nanorod-based biosensors and gas sensors, since ZnO nanostructures are easy to form. Moreover, they exhibit high charge-carrier mobility and high crystallinity quality [1], [2].

The limited supply and consequently high cost of indium have motivated extensive research and development aimed at finding alternatives to ITO. AZO and GZO semiconductors are considered the main candidates for replacing this material. In addition, in optoelectronics, ZnO is regarded as a potential substitute for the expensive gallium nitride, since it possesses an exciton binding energy that is 60 meV higher than that of GaN [1].

Zinc oxide is a direct band-gap semiconductor with n-type conductivity and a band-gap energy of 3.36 eV. ZnO belongs to the A₂B₆ group of semiconductor compounds and crystallizes in the wurtzite structure with the space group C_{6v}–C_{6mc}. The lattice parameters (at room



temperature) have the following values: $a = 3.245 \pm 0.0442 \text{ \AA}$, $c = 5.2069 \pm 0.031 \text{ \AA}$, depending on the stoichiometric composition of ZnO.

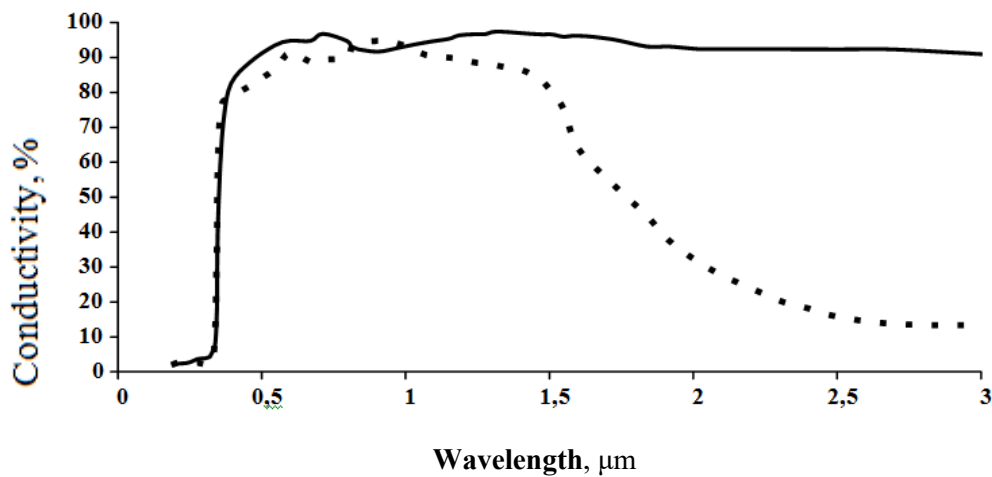
The unit cell contains two ZnO molecules. Oxygen atoms form a dense hexagonal packing, while zinc atoms occupy the centers of the tetrahedra formed by the oxygen atoms. The distance between the oxygen and zinc atoms is 1.992 \AA along the c-axis and 1.973 \AA along the other three directions of the tetrahedral coordination.

The structure of ZnO is characterized by the absence of a center of symmetry, which results in the presence of a polar axis parallel to the [0001] direction. The polarization of oppositely charged zinc and oxygen ions can be described as a network of uncompensated permanent dipole moments, leading to the existence of a single polar axis. Therefore, ZnO crystals exhibit pronounced piezoelectric and pyroelectric properties. No formation of polytypes has been observed in ZnO crystals [2].

TCOs based on ZnO have attracted significant attention due to their good electrical conductivity, high optical transparency, smooth surface, and low deposition temperature. According to [3], transparent amorphous oxides with high electron mobility must contain cations of heavy transition metals possessing an electron configuration of $(n-1)d^{10}ns^0$ (where n is the principal quantum number). MeZO oxide films, where Me = Al, Ga, In, or Sn, are obtained from homogeneous composite targets of $\text{Al}_2\text{O}_3(\text{ZnO})$, $\text{Ga}_2\text{O}_3(\text{ZnO})$, $\text{In}_2\text{O}_3(\text{ZnO})$, and $\text{SnO}_2(\text{ZnO})$ mixtures. In thin AZO ($0.85 \times 10^{-4} \Omega \cdot \text{cm}$) and GZO ($1.2 \times 10^{-4} \Omega \cdot \text{cm}$) films grown by pulsed laser deposition, low resistivity values (below $2 \times 10^{-4} \Omega \cdot \text{cm}$) were achieved together with high charge carrier concentrations exceeding 10^{21} cm^{-3} [4], [5], [6]. For comparison, the specific resistivity of ITO is $0.72 \times 10^{-4} \Omega \cdot \text{cm}$ [7].

Thus, the most promising materials are AZO and GZO, as they possess low resistivity (on the order of $10^{-4} \Omega \cdot \text{cm}$) and their source components are inexpensive and non-toxic. Numerous studies have reported that the electrical properties of TCO films are strongly dependent on the deposition methods and conditions. An increase in gallium concentration shifts the edge of the fundamental absorption band toward the blue region of the spectrum (Figure 1) and reduces the transparency of ZnO films in the infrared region. Modifying the deposition conditions (oxygen and/or Ga concentration) changes both the ZnO lattice parameters and the resistivity. Annealing in an oxygen atmosphere leads to an increase in film resistivity over the entire doping range.

Adds	Concentration, wt. %	Conductivity, $\times 10^{-4} \Omega \cdot \text{cm}$	Charge carrier concentration, $\times 10^{20} \text{ cm}^{-3}$
Al_2O_3 Ga_2O_3	1–2	0,85	15,4
B_2O_3 Sc_2O_3	2–7	1,2	14,5
SiO_2 V_2O_5 F	2	2,0	5,4
No added	2	3,1	6,7
	6	4,8	8,8
	0,5–3	5,0	4,9
	0,5	4,0	5,0
	0	4,5	2,0



Undoped ZnO film ZnO film doped with gallium (2.5 at.%)

Picture 1. Transmission spectra of ZnO films

The industrial implementation of TCO production requires deposition techniques capable of coating large surfaces at high deposition rates. Before the invention of planar magnetron sputtering, thin films were deposited onto substrates by thermal evaporation in vacuum or by chemical vapor deposition techniques. The development and creation of industrial magnetron sputtering systems (MRS) fundamentally changed thin-film deposition technology.

MRS can sputter almost all types of materials, including metals and alloys, simple and complex dielectrics, semiconductors, and ceramics. The sputtering materials can be combined in various configurations and used to form multilayer coatings with thicknesses ranging from several tens of nanometers to tens of micrometers. By modifying and controlling plasma parameters, it becomes possible to precisely regulate the deposition conditions, and thus the electrophysical and structural properties of the resulting coatings [8].

To enable the widespread use of MRS technology for TCO deposition, several scientific and technical challenges must be addressed: reducing equipment costs, shortening deposition time, and solving the issue of adapting power supply systems. Under laboratory conditions, the required characteristics of TCO coatings have often been achieved using complex methods, which limits their industrial applicability. For example, positioning the substrate perpendicular to the MRS target surface significantly reduces the film deposition rate.

Nowdays, the magnetron sputtering techniques that have been developed can ensure low resistivity in ZnO-based TCOs only at substrate temperatures above 200 °C, which limits their practical applications. For example, depositing conductive coatings onto polymer substrates is only possible at temperatures that do not exceed the material's softening point. Therefore, for the manufacturing technology of such coatings, as well as for deposition onto flexible or low-melting substrates, it is necessary to reduce the substrate temperature.

To achieve this, one must determine the optimal plasma parameters—specifically, the density and energy of ions bombarding the substrate—that make it possible to obtain transparent and conductive doped zinc oxide at relatively low substrate temperatures of about 110 °C [9].



Conclusion

1. Methods for comparing various TCO (Transparent Conductive Oxide) materials applied using different techniques have been selected. Approaches for determining the key properties of TCOs — such as transmittance, band gap, the probable type of interband electronic transitions, and electron mobility or concentration — based on the processing of measured optical spectra are examined. For this purpose, algorithms are developed and appropriate software is created.
2. Composite oxide and fluoride materials were synthesized in a solar furnace for use as transparent and electrically conductive coatings.

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