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# DEVELOPMENT OF TRANSPARENT, CONDUCTIVE THIN FILM COATINGS ON THE BASIS OF METALS

**Abstract:** The object of the study are thin films of metal oxides (zinc, tin), obtained by magnetron deposition. The electrophysical properties of thin films of metal oxide semiconductors ZnO and $SnO_2$ are investigated.

Technological regimes for obtaining metal oxide films by the method of reactive magnetron sputtering are worked out. In the process of obtaining the films, the technological parameters-the substrate temperatures, the pressure and the gas atmosphere during the deposition process, the discharge power, were changed. The dependences of the transparency and resistivity of tin oxide and zinc oxide films on the temperature of the substrate and the concentration of oxygen in the working gas are investigated, and the optimal parameters of the film production process are determined. The observed dependences are explained by the change in the composition of the films and by the deviation from stoichiometry.

The dependences of the film properties on the annealing temperature, on the gas composition of the atmosphere during annealing are determined. High-transparency metal oxide films with low electrical resistance were obtained.

**Keywords:** ZnO and $SnO_2$ metal oxides, electrical resistance, electrophysical properties.

## Introduction

In recent years widely studied transparent semiconductor oxides, such as $In_2O_3$, ZnO, $SnO_2$, CdO, $Ga_2O_3$, $TiO_2$ and more complex binary and ternary oxides. There is a great interest in production of transparent conducting oxide (TCO) and transparent oxide semiconductors for the development of photonic devices and transparent conducting electrodes (TCE) for solar cells[1].

ZnO is one of the most promising materials for the creation of nanoelectronic devices and nanosystem technology [2]. Interest is due to a number of the electrical properties of ZnO: high melting point and thermal conductivity, photosensitivity, piezoelectric and pyroelectric effect, a wide band gap, chemical stability, biocompatibility, that allows the use of ZnO as a transparent conductive oxide material. Zinc oxide has a low resistivity and good optical properties and is one of the most promising materials for creating transparent conductive coatings. The problem of obtaining coatings with high conductivity at low substrate temperatures (below 300 ° C) and without subsequent step of annealing is relevant, for example, in the manufacture of solar multilayer coatings (as at low temperatures retard the mutual diffusion layer), or by sputtering conductive coatings polymeric substrate at a temperature not exceeding the softening temperature of the material [3]. Global growth in demand for energy-efficient and compact devices stimulates the deep interest of researchers in this class of materials. From a scientific point of view, these materials are also of significant interest. It may be noted the problem of obtaining n-type conduction by doping acceptors and donors. Such alloying lowers the energy of the introduction of acceptors and allows you to enter them with a higher concentration, but its mechanism is not fully understood. In addition, features of the band structure, for example, single-valley valence band in ZnO allows the use of these materials as a model to test in theory calculations. Among the transparent thin-film materials, some compounds, for example, $In_2O_3$, ITO ($IN_{2-x}Sn_xO_3$) are relatively well studied and widely used in practice. Others, for example, ZnO, $SnO_3$ and double and triple solid solutions, much less studied, but have the promising properties. By changing the composition of the solution, can achieve the desired band gap, as well as other physical and chemical properties [4-6].

## Materials and methods of research

Obtaining transparent conductive thin ZnO and $SnO_2$ films was carried out in three ways: by reactive magnetron sputtering in an oxygen atmosphere, and sputtering in an inert atmosphere followed by annealing in air, as well as by reactive ion beam sputtering. Magnetron sputtering was carried out in a chamber where vacuum is achieved beforehand about $7^{-10}$ Torr. When the discharge capacity of about 30 W deposition rate was 0.5-1 nm/c. The physicochemical properties of the target surface are not changed due to the thermal diffusion, chemical interaction. Therefore, a sputtering process permits layered remove atoms from the target surface and thus obtain a uniform film. Uniformity is also achieved by rotating the substrate at a speed of 30 rev / min. Continuouslybombarding of neutral atoms deposited films and the negatively charged argon ions and atoms of the reactive gas is oxygen, which leads to the fact that the film captures a large amount of gas and impurity atoms.

As the oxygen pressure was measured manometer to measure the partial pressure of the second gas was shut off the flow necessary - argon, and wait for pressure stabilization. Therefore, to measure the partial pressure of oxygen flow rate used. Checking the partial pressure of oxygen, depending on the size of the flow showed that this dependence is almost linear. Therefore, the partial pressure is determined by the flow-largest.

The samples were placed on a rotating table, which temperature can vary from room temperature to 450°C. Next to the table for the thickness patterns placed measuring, which measures the thickness of the layer deposited on it by the density of the sprayed material and changing the resonance frequency of the quartz resonator, one side of which was deposited measurable layer. The relative accuracy of the thickness was 1 A. However, the absolute accuracy of the thickness depends on how many different particle flow, causing film growth, at the site of the substrate and location of the thicknessmeasuring.

Measurements were performedZnO film deposition rate of discharge power and gas pressure (total pressure, oxygen partial pressure). In the 4% oxygen concentration observed deposition rate drop further stabilization deposition rate observed with increasing oxygen concentration. This is due to the oxidation of zinc misheniiz the appearance of oxygen in the gas atmosphere in the processing chamber.

Rate of sputtering for a fixed total pressure and partial pressure of oxygen increases with increasing discharge power monotonically as a value of ~ 15-25 watts of power, a sharp increase in deposition rate due to changes in discharge conditions, the modified surface of the target: the speed of the target of oxidation at this power spraying rate becomes smaller. Therefore, to obtain high deposition rates need to use higher discharge power 25 W.

By changing the partial pressure of oxygen in the growth process can be controlled by the properties of films obtained by reactive magnetron sputtering. Another method of forming metal oxide films was magnetron sputtering in an inert atmosphere. After deposition on the substrates formed high-quality metal film, which is oxidized in air and in oxygen atmosphere during subsequent thermal annealing.

A third method of producing the films were ion-beam sputtering, using a special vacuum chamber. Formation of a beam of Ar and $O_2$ ions occurred in the ring system of electrodes, forming a complete cathode to the anode, and magnets with crossed electric and magnetic fields. The total discharge capacity was about 300 watts. The targets of high-purity zinc or tin sprayed beam bombardment of ions Ar and $O_2$ variations in oxygen partial pressure of 0% to 100%. Used glass, quartz and silicon substrates. Before coated substrates were cleaning and degreasing the surface of the procedure. The temperature of the substrate during the deposition process was maintained may vary from room temperature to 400°C.

## Results and discussion

Obtaining of thin ZnO films was carried out at various deposition conditions. The results of this experiment are shown in Figure 1. As seen from the figure for optimal reduction of the resistivity were the total pressure in the chamber $1{,}1 \times 10^{-2}$ Torr and the volume content of oxygen partial pressure of 3-4 percent by volume. Further decrease the total pressure in the chamber leads to deterioration of film transparency. Increasing the total pressure from the optimal values results in a sharp increase in resistivity.

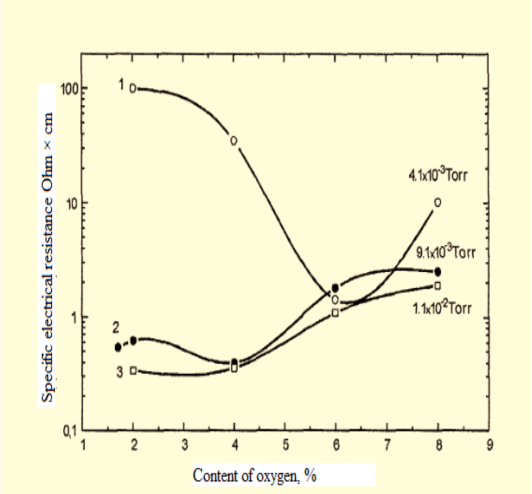

Figure 1 - The dependence of the specific resistance of ZnO oxygen partial pressure and the total pressure in the chamber.

The existence of the optimum value of oxygen concentration due to the fact that at low oxygen content of the zinc is not in spraying time to react with oxygen, and the metal inclusions are generated, leading to additional scatteringof carriers and growth of specific resistivity. When an excess of oxygen concentration of oxygen vacancies, which are donorsof electron, drops sharply, which again leads to an increase in resistance of the films. At the optimum pressure of oxygen, apparently, the conditions for the growth of stoichiometric film growth. On the electrical properties of ZnO films deposited by magnetron sputtering, are greatly influenced by the substrate temperature. Immediately after the deposition of the film have a resistivity of about 10 ohm×cm. Analysis of the temperature dependence indicative of the prevailing influence of the scattering mechanism of carriers by ionized impurities specific resistance dependence on temperature of the substrate is shown in Figure 2. As seen from the figure the resistivity first increases up to a certain temperature, equal to 240°C, while then decreases. When heating of the substrate increases the grain size, thus increasing the concentration, however with increasing the carrier concentration and mobility first decreases and then increases. This kind of dependence explained by carrier trapping grain boundaries. The obtained ZnO film with a grain size of about 10 nm are shaped stolbchatayu and grains axis oriented perpendicular to the substrate plane. After film deposition characteristics were stable at room temperature in air. This demonstrates that the composition of the films is in the region of homogeneity. Research shows influence subsequent thermal treatments (Figure 3), the annealing of the films (grown under optimal for low resistance conditions) under vacuum resulting in a further reduction of resistance. Therefore, annealing accompanying the change in the phase composition of the films, increasing the concentration of oxygen vacancies. This agrees with literature data shear stoichiometric excess ZnO in the direction of metal. Aligning the phase composition may also lead to reduction in the number of scattering centers. There was a decrease in resistance after annealing in vacuum is approximately two orders of magnitude compared with the initial value immediately after spraying. A significant decline was observed in the resistance in range 250-350°C. Also performed and a reverse process of annealing in a vacuum, where observed to return to the original resistance value.

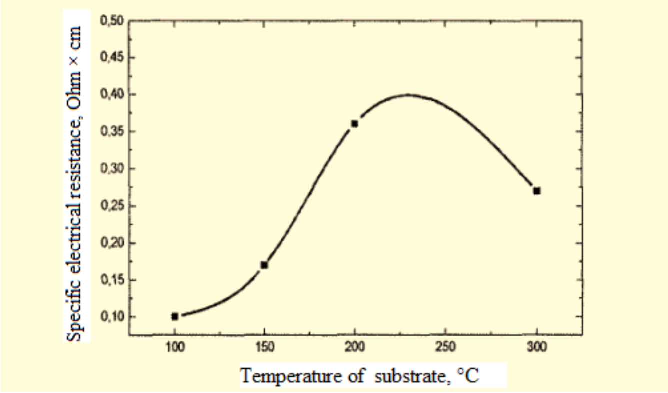

Figure 2 – The dependence of the specific resistance of ZnO on the substrate temperature.

When the atomic defects are mobile enough, their concentration can be changed by the reaction between the film and the surrounding atmosphere. Adjusting the concentration of intrinsic defects in the binary compound by annealing them in the air can be changed in a wide range of electrical properties of ZnO films. Figure 4 shows the dependence of the resistivity of the annealing temperature in air. As seen from the figure annealing in air leads to a sharp increase in resistivity. When growing, and heat treatment of initial ZnO films often realized conditions when the vapor pressure of the metalloid less pressure necessary for the stoichiometric composition and therefore excess or deficiency of one of the connection components provides one or the other type of conductivity. ZnO film is annealed at high temperatures above 300°C, contain an excess of zinc and as a consequence, have electronic conductivity.

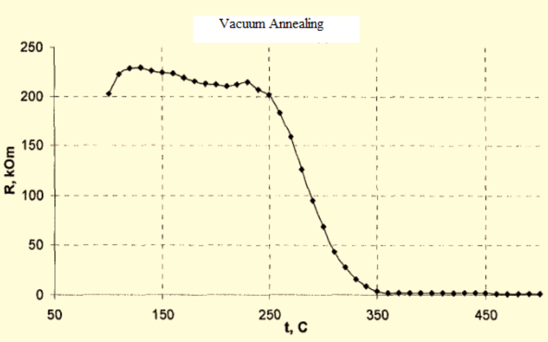

Figure 3 – The dependence of the specific resistance of the ZnO temperature annealing in vacuum.

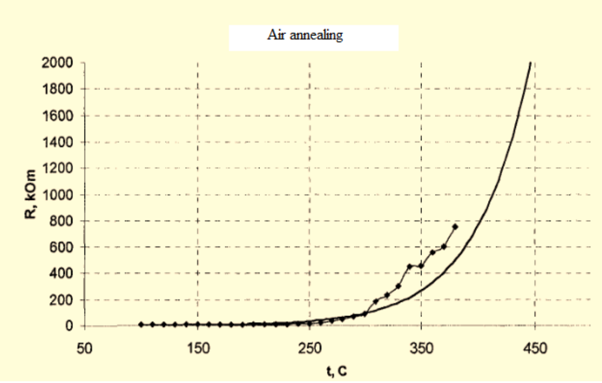

Figure 4 – The dependence of the specific resistance of the ZnO annealing temperature in air.

The main reason for determining the propensity for the electronic conductivity type is that the metalloid present in molecular form. Thermodynamic analysis gives an indication of ratio various defects and their behavior in a steady state of equilibrium.

The repeated annealing films in a vacuum after annealing in the atmosphere also leads to the opposite effect, ie, film resistance returns to its original value. After subsequent heat treatment had stable film properties, i.e. resistivity retains its value and at room temperature. Thus, by varying the annealing temperature in a vacuum of ~10$^{-}$3 Pa in the atmosphere and can be adjusted over a wide range of films and set the desired resistance value of the specific resistance. With the use of silicon as substrate p-type heterostructure p-Si – n-ZnO. Obtained structures have diode current-voltage characteristics (CVC). Typical results are shown in Figure 5. Immediately after deposition the CVC were less pronounced diode character. The series resistance and leakage currents heterostructures fell sharply during the annealing in air at 750 and 900°C. This indicates homogenization interface Si-ZnO, a sharp decrease during the annealing of the concentration of surface defects and lowering the electrical resistance of the interface. Note that the resulting heterostructure had a significant photosensitivity. Measurement of spectral dependences of photosensitivity of the structures obtained show that the highest photosensitivity is observed in the range from 400 to 700 nm. This area is an area of silicon self-absorption, and for ZnO - region of impurity absorption. Consequently, the photosensitivity is provided by light generation of electron-hole pairs in silicon and exploded in heterojunction Si-ZnO due to the built-in electric field. Figure 6 shows the photosensitivity of the two samples after annealing at 300°C (curve 1) and 400°C (curve 2). Annealing at a higher temperature of 400°C results in a greater photosensitivity is apparently due to annealing of defects at the interface Si-ZnO.

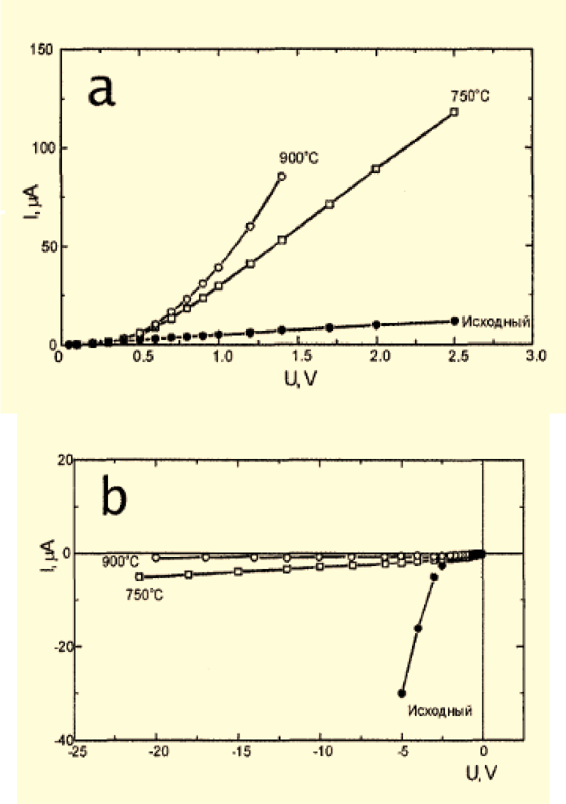

Figure 5 – Current-voltage characteristics of structures p-Si – n-ZnO (line (a) and inverse (b) branch) immediately after annealing in air at 750 and 900°C.

Further increase of the annealing temperature leads to the disappearance of the photosensitivity, it is possible to explain the formation of a high concentration of defects at Si-ZnO boundary due to thermal stresses arising from different thermal coefficient expansion materials.

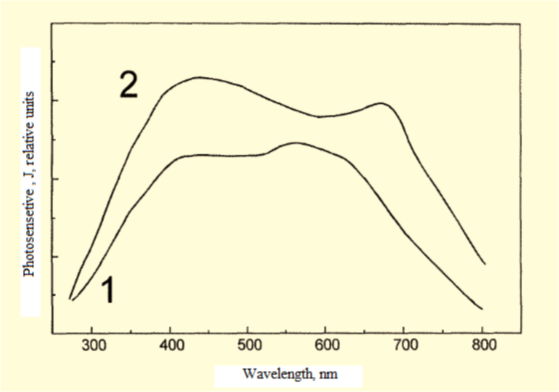

Figure 6 – Photosensitivity spectra of the sample Si-ZnO, the last annealing at 300°C (curve 1) and 400 ° C (curve 2).

From the data obtained it can be concluded that under conditions where sufficient atomic defects are mobile, their concentration may vary within wide limits by torate between the film and the surrounding atmosphere. And annealing the ZnO films SnOx air and vacuum can change the electrical properties over a wide range by controlling the concentration of intrinsic defects in binary compounds and receive the desired value of the resistivity.

## Conclusions

In this work studied the change property of electric metal-oxide films deposited by reactive magnetron sputtering during subsequent thermal annealing in a wide range of temperatures. The dependence of the film properties of the annealing temperature in the annealing process. Obtained highly transparent metal oxide film with low electrical resistance detected electric characteristics unique correlation ZnO film during annealing in vacuum and in air.

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## МЕТАЛЛ НЕГІЗІНДЕГІ МӨЛДІР ЖӘНЕ ӨТКІЗГІШ ЖҰҚА ҚАБЫҚШАЛЫ ЖАБЫНДАРДЫ ӘЗІРЛЕУ

**Аннотация.** Зерттеу объектісі магнетрондық тозаңдату арқылы қондырылған (мырыш, қалайы) металл тотықтары. Бұл жұмыста ZnO және $SnO_2$ металл тотықты жартылайөткізгіштерінің жұқа қабықшалардың элетрофизикалық қасиеттері зерттелінді.

Реактивті магнетрондық тозаңдату әдісі арқылы металл тотықты қабықшалар алудың технологиялық режимі жасалынды. Қабықшаларды алу процессі кезінде төсеніш температурасы, шаңдату процецінде қысым мен газдық атмосфера, разряд қуаты сияқты технологиялық параметрлер өзгертіліп тұрды. Қалайы мен мырыш тотықтарының мөлдірлік коэффициенті мен меншікті кедергілерінің төсеніш температурасы мен жұмыс газындағы оттегі концентрациясынан тәуелділігі зерттелінді, қабықшаларды алу процесінің оңтайлы параметрлері анықталды. Байқалатын тәуелділіктер қабықшаның құрамының өзгеруімен және стехиометриядан ауытқуымен түсіндіріледі. Қабықшалар қасиетінің жасыту температурасынан, жасыту процесі кезінде атмосфераның газдық құрамынан тәуелділігі анықталды. Электрлік кедергілері төмен жоғары мөлдір металл тотықты қабықшалар алынды.

**Түйін сөздер:** ZnO және $SnO_2$ металдарының тотықтары, электрлік кедергі, электрофизикалық қасиеттер.

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## РАЗРАБОТКА ПРОЗРАЧНЫХ, ПРОВОДЯЩИХ ТОНКОПЛЕНОЧНЫХ ПОКРЫТИЙ НА ОСНОВЕ МЕТАЛЛОВ

**Аннотация.**Объектом исследования являются тонкие пленки оксидов металлов (цинк, олово), полученное магнетронным осаждением. В работе исследованы электрофизические свойства тонких пленок металлооксидных полупроводников ZnO и$SnO_2$.

Отработаны технологические режимы получения металлоокисдных пленок методом реактивного магнетронного распыления. В процессе получения пленок менялись технологические параметры –температуры подложки, давление и газовая атмосфера в процессе напыления, мощность разряда. Исследованы зависимости от температуры подложки и концентрации кислорода в рабочем газе коэффициента прозрачности и удельного сопротивления пленок оксида олова и цинка, определены оптимальные параметры процесса получения пленок. Наблюдаемые зависимости объясняются изменением состава пленок и откланением от стехиометрии.

Определены зависимости свойств пленок от температуры отжига, от газового состава атмосферы в процессе отжига. Получены высокопрозрачные металлооксидные пленки с низким электрическим сопротивлением.

**Ключевые слова:** Оксиды металлов ZnO и$SnO_2$, электрическое сопротивление, электрофизические свойства.