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## **ELECTROPHYSICAL PROPERTIES OF ZINC OXIDE THIN FILMS OBTAINED BY CHEMICAL METHODS**

The electrophysical characteristics comparative studies were carried out for ZnO films obtained by chemical precipitation from zinc acetate solutions and thermal oxidation of zinc films. The ZnO films showed optical absorption and band gap (2.9 to 3.2 eV) specific for this material, which indicates the presence of crystalline structure in them. The use of polyvinyl alcohol made it possible to obtain samples with the highest values of  $E_g$  and electrical resistance, which is caused by the nanosize crystallites of the films. The investigated electrophysical characteristics of the ZnO films made it possible to establish the contribution of their own defects and surface states to the conductivity.

### **Introduction**

Recently, interest in zinc oxide has increased due to the possibility of using this material to create cathodoluminophores, electroluminescent screens, acoustoelectronic amplifiers, gas detectors, various types of photo- and optoelectronic devices [1,2], as well as in the composition of electronic materials [3]. Often this is possible due to the special properties of the surface and grain boundaries of the material, which can be further modified by targeted alloying, as well as by change in the synthesis conditions. [4-6]. High values of transparency and refractive index of ZnO films in the visible spectrum region makes it possible to use them as illuminating coatings for interference optical elements, as well as to create a transparent conductive electrode in solar cells. [7,8]. Currently, interest to ZnO films has increased due to their possible application to photoelectronic devices such as LEDs with ultraviolet radiation, blue fluorescent ultraviolet emitters and lasers [9]. The need to reduce the costs and to improve the quality of optoelectronic devices necessitates the development of new methods in the manufacturing of ZnO films.

Known from the literature methods for producing thin films of zinc oxide are: atomic layer deposition technique [10,11], and magnetron sputtering in many of its modifications [12,13]. However, these methods require quite energy-intensive technical support. Another used meth-

od is sol-gel technology, which, unfortunately, involves the application of relatively expensive and at the same time harmful reagents, such as  $\alpha$ -terpineol, 2-methoxyethanol, 2-aminoethanol, etc.

In this paper zinc oxide films were obtained by relatively simple methods, in particular, chemical precipitation from zinc acetate solutions, thermal oxidation of zinc films, and subsequent comparative studies of their electrophysical characteristics.

### **Samples preparation**

The studied zinc oxide films were obtained in three different ways, which are hereinafter arbitrarily designated as groups A, B and C. To obtain samples of group A, an aqueous solution of zinc acetate ( $\text{Zn}(\text{O}_2\text{CCH}_3)_2$ ) with a concentration of 0.25 mol was used. Glass substrates were immersed in an aqueous solution of zinc acetate, dried at room temperature in air, and again immersed in the solution. After that, the obtained films were annealed in an air atmosphere at a temperature of 310 °C for 20-60 min.

Samples of group B were also obtained from an aqueous solution of zinc acetate, but with the addition of an aqueous 1% solution of polyvinyl alcohol ( $\text{C}_2\text{H}_4\text{O}$  - PVA) for the purpose of additional structuring of the films, in equal proportions of 2 ml each. Then, the substrates were immersed several times in the solution according to the procedure described above and annealed

in air at a temperature of 310 °C for 60 min.

To obtain group C samples, thin films of zinc metal were deposited on a cleaned glass substrate by thermal spraying in high vacuum. Further, zinc films were annealed in a muffle furnace in air at 570 °C for 10-30 min. As a result, the oxidation process occurred and translucent whitish zinc oxide films were created.

For conducting electrophysical measurements, samples of each of the groups of zinc oxide films were provided with ohmic contacts. For this, indium in the form of parallel strips was deposited on the samples by thermal spraying in high vacuum.

### Results and Discussion

A typical edge of the optical absorption spectra of ZnO films (group A) is shown on Fig. 1. The satisfactory straightening in the coordinates of  $D^2$ - $h\nu$  (here  $D$  is the optical density) is evident. This fact indicates direct allowed optical transitions in the films. The extrapolation of the linear section of the dependences to the energy axis gives the band gap for various samples ranging from 3.02 to 3.06 eV, which satisfactorily coincides with the band gap data for zinc oxide films either calculated [14] or obtained from optical measurements [15,16] by other authors. Extrapolation was carried out taking into account the subtraction of the apparent absorption, which is due to scattering and reflection of the incident light from the film surface. The plateau near the absorption edge at low energies is due to the presence of an amorphous phase in the studied ZnO films.

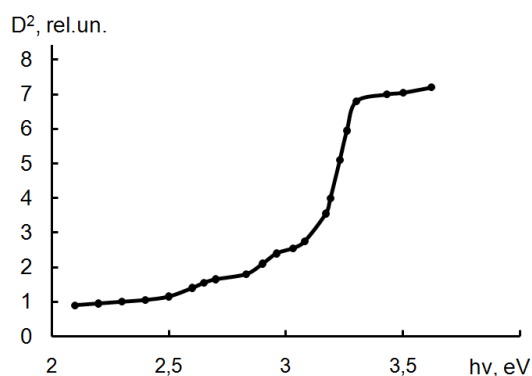


Fig. 1. Typical spectra of the optical absorption of ZnO films (group A)

Figure 2 shows a typical absorption spectrum

of a zinc oxide film (group B). The band gap,  $E_g = (3.15-3.2)$  eV was found by extrapolating its linear section to the energy axis. It can be argued that it is noticeably larger than the band gap of the group A zinc oxide films. This means that the sizes of ZnO crystallites obtained in a solution of zinc acetate with polyvinyl alcohol impurities are smaller than crystallites of ZnO films obtained from a solution without PVA impurities.

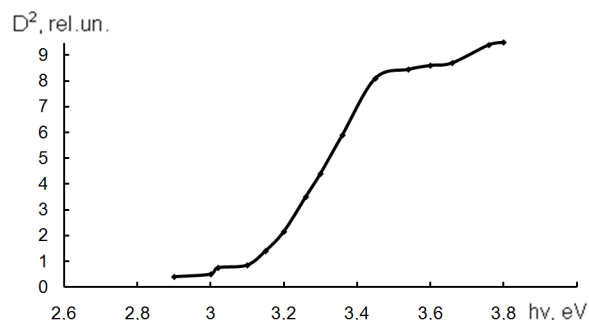


Fig. 2. Typical spectra of the optical absorption of ZnO films (group B).

Figure 3 shows a typical edge of the absorption spectra of zinc oxide films (group C). The band gap, obtained from the extrapolation of their straight section is (2.9-2.96) eV. Thus, the zinc oxide films obtained by oxidizing a metal zinc film in air atmosphere have the smallest band gap. However, the shape of the optical absorption edge indicates their most perfect crystalline structure compared to films obtained from a solution of zinc acetate.

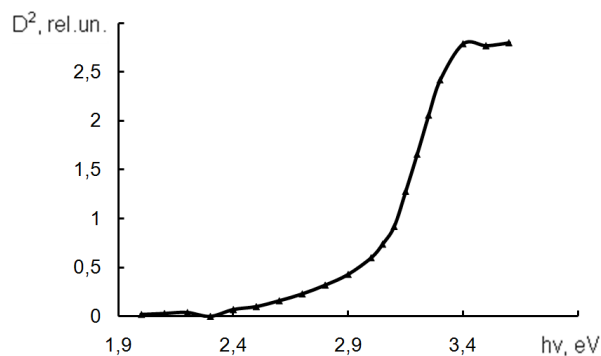


Fig. 3. Typical spectra of the optical absorption of ZnO films (group C).

The band gap of ZnO films obtained with PVA admixture is greater than that of similar films obtained without PVA admixture. The reason is that the PVA polymer matrix limits the size of the reaction volumes where zinc oxide crystallites are synthesized, and thus inhibits the growth of ZnO crystallites.

The current-voltage characteristics and the dark current temperature dependences were investigated in order to assess the electrophysical properties and the presence of their own defects in the band gap of zinc oxide films

Current-voltage characteristic (CVC) of the ZnO film (group A), measured in air (Fig. 4), shows the current linear dependence on the applied voltage, which indicates the electrical uniformity of the film. The inter electrode resistance calculated from the CVC is about  $4 \cdot 10^7$  Ohms.

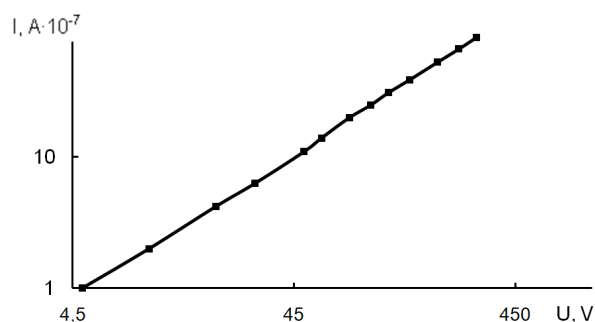


Fig. 4. Current-voltage characteristic of ZnO film (group A), measured in air ( $T = 293\text{K}$ )

The dark current temperature dependence of ZnO film (group A), measured in vacuum at heating of the film is shown at Fig.5. It can be distinguished three characteristic areas. The current at all these sites grows with temperature exponentially. The first section, located in the low-temperature region, has the conductivity activation energy of 0.08 eV, which, with increasing temperature, changes the line slope to the activation energy of 0.16 eV. At a temperature of about  $105^\circ\text{C}$ , this section is replaced by a section with a sharp rise of current with the conductivity activation energy of 1.6 eV.

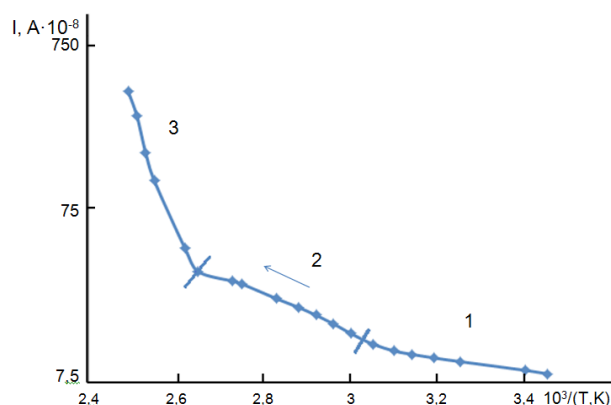


Fig. 5. The dark current temperature dependence of the ZnO film (group A) measured in vacuum. ( $U = 10\text{ V}$ ).

The first and the second temperature-dependent regions may correspond to donor levels formed in the films' volume by single- and double-ionized oxygen vacancies, just as in the case with tin dioxide films. The sharp increase in the current at a temperature above  $105^\circ\text{C}$  is caused by oxygen desorption from the surface of ZnO films. It is known that an oxygen atom adsorbed on the surface of a ZnO film captures one electron from the conduction band thus transforming into a single negatively charged ion, or captures two electrons and becomes a twice negatively charged ion. This leads to a current locking type bending of the surface energy zones and to the appearance of local levels (0.7-0.76) eV and (1.4-1.6) eV, respectively with energy distances from the bottom of the conduction band on the surface of the film. At high temperatures electrons, trapped by oxygen atoms, are thermally released into the conduction band, and oxygen atoms are desorbed from the film surface.

The current-voltage characteristic of the ZnO film (group B) (Fig. 6) is slightly superlinear and has a tendency to an exponential current-voltage dependence. Such dependence is inherent to the barrier current flow mechanism. That is, in the films obtained with PVA admixtures, the intercrystalline potential barriers affecting the current flow are more pronounced. The average value of the inter-electrode resistance, calculated from the initial linear section of the CVC, is

about  $2.8 \cdot 10^9$  Ohms. Therefore, the presence of PVA impurity increases the film resistance by almost 2 orders of magnitude. The reason is, that the PVA evaporates during the annealing, thus increasing the porosity of these films, and they become nanostructured with a more developed surface. Nanometer crystallites can create a quantum well effect for carriers [17], which also lead to greater resistance.

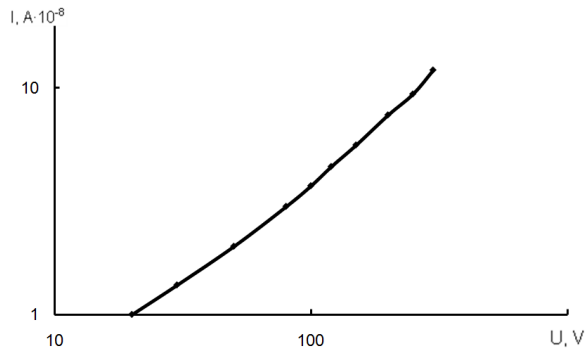


Fig 6. The CVC of the ZnO film (group B) measured in air ( $T = 293\text{K}$ ).

Fig. 7 shows the temperature dependence of the current measured during heating and cooling of the ZnO film (group B). It also contains low-temperature sections with activation energies of 0.08 eV and 0.15 eV associated with oxygen vacancies. There is also a high-temperature region with an activation energy of about 1.6 eV, caused by the desorption of double charged oxygen ions from the ZnO film surface. At the same time, the only one section with activation energy (0.14-0.16) eV is observed in the current temperature dependence curve, measured at cooling. If the film is being cooled to room temperature, then the current remains almost 60 times greater than at heating. This is due to the fact that, when the film is heated in vacuum oxygen desorbes and the conductivity is controlled only by donor vacancies of oxygen in the volume of the film. However, when the air is let into the chamber, then the current decreases to almost the original value. Moreover, the decrease of the current strength in “e” times occurs very rapidly over a period of about 35 s. (Fig. 7).

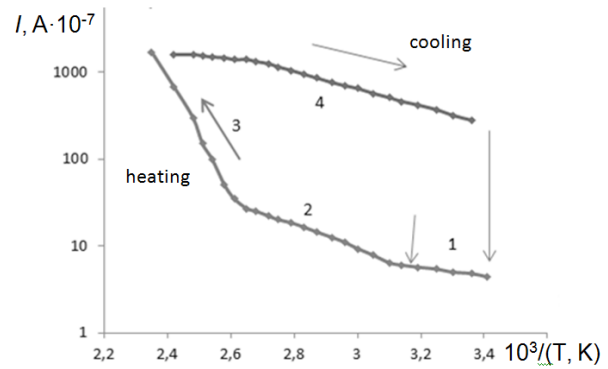


Fig. 7. The dark current temperature dependence of the ZnO film (group B)

When in the Fig. 8 a slower relaxation region is observed, then the straightening of the curve in the coordinates ( $\ln I - t$ ) indicates that relaxation follows the law  $I(t) = I_0 \exp \frac{-t}{\tau}$ , where the characteristic time constant  $\tau$  is 150 s.

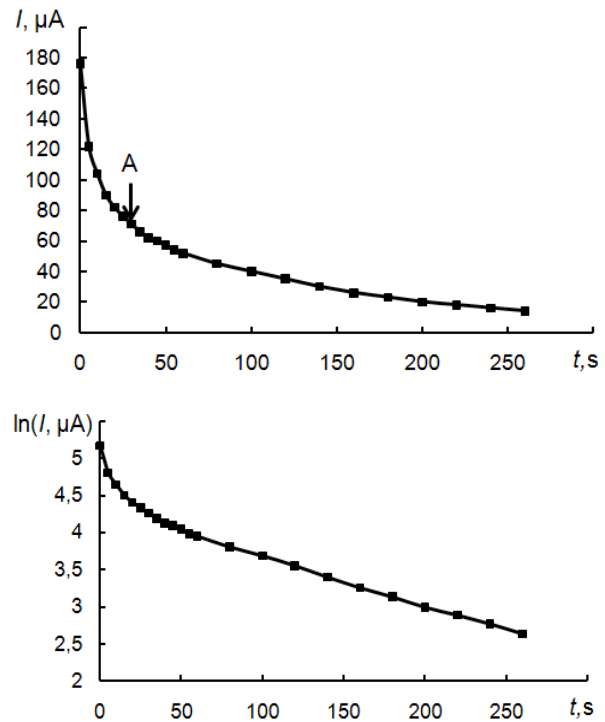


Fig. 8. Relaxation of the current in the film (group B) at letting the ambient air into the chamber ( $T = 298\text{ K}$ ,  $U = 150\text{ V}$ ).

The interelectrode resistance of zinc oxide (Group C) films calculated from the current-

voltage characteristic (Fig. 9) has of about  $2 \cdot 10^5$  Ohms, which is also much lower than for Group A and Group B films.

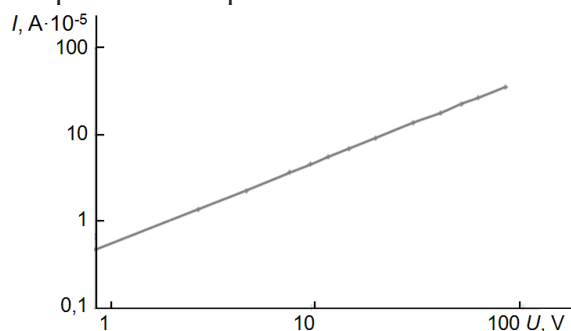


Fig. 9. The CVC of the ZnO film (group C) measured in air ( $T = 290$  K).

Comparison of the calculation results for zinc oxide films' parameters obtained by different chemical methods is shown in table 1.

Table 1

Type of films	A	B	C
Bandwidth	(3,06-3,02) eV	(3,15-3,2) eV	(2,9-2,96) eV
Inter-electrode resistance	$4 \cdot 10^7$ Ohm	$2,8 \cdot 10^9$ Ohm	$2 \cdot 10^5$ Ohm

Zinc oxide films obtained from a solution of zinc acetate with admixtures of polyvinyl alcohol have a much higher resistance than similar films obtained without PVA admixture. This happens in the process of high-temperature annealing of PVA, playing the role of a polymer matrix, with the consequent evaporation of the decay products and hence, the zinc oxide films become porous with a more developed surface.

The ZnO film, obtained by oxidation of zinc metal films appeared low-resistance and have the smallest band gap. However, the shape of the optical absorption edge indicates their most perfect crystalline structure compared to films obtained from a solution of zinc acetate.

### Conclusion

The zinc oxide films obtained by three different methods showed typical for them

optical absorption and bandgap (2.9 to 3.2 eV) characteristic for this material, which indicates the presence of crystalline structure in them. Moreover, the use of polyvinyl alcohol made it possible to obtain samples with the highest values of  $E_g$  and electrical resistance, which is caused by the nanosize crystallites of group C films. The investigated electrophysical characteristics of the obtained zinc oxide films made it possible to establish the contribution to the conductivity of their own defects and surface states.

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PACS 73.61.Le, 73.63.Bd

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### Summary

The electrophysical characteristics comparative studies were carried out for ZnO films obtained by chemical precipitation from zinc acetate solutions and thermal oxidation of zinc films. The ZnO films showed optical absorption and band gap (2.9 to 3.2 eV) specific for this material, which indicates the presence of crystalline structure in them. The use of polyvinyl alcohol made it possible to obtain samples with the highest values of  $E_g$  and electrical resistance, which is caused by the nanosize crystallites of the films. The investigated electrophysical characteristics of the ZnO films made it possible to establish the contribution of their own defects and surface states to the conductivity.

**Key words:** zinc oxide, thin films, electrophysical properties

PACS 73.61.Le, 73.63.Bd

## ЭЛЕКТРОФИЗИЧЕСКИЕ СВОЙСТВА ТОНКИХ ПЛЕНОК ОКСИДА ЦИНКА, ПОЛУЧЕННЫХ ХИМИЧЕСКИМИ МЕТОДАМИ

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### Резюме

Проведены сравнительные исследования электрофизических характеристик пленок ZnO, полученных химическим осаждением из растворов ацетата цинка и термическим окислением пленок цинка. Пленки ZnO показали оптическое поглощение и ширину запрещенной зоны (2,9-3,2 эВ), характерные для этого материала, что свидетельствует о наличии в них кристаллической структуры. Использование поливинилового спирта позволило получить образцы с наибольшими значениями  $E_g$  и электросопротивления, что обусловлено наноразмером кристаллитов в пленках. Исследованные электрофизические характеристики пленок ZnO позволили установить вклад собственных дефектов и поверхностных состояний в проводимость.

**Ключевые слова:** оксид цинка, тонкие пленки, электрофизические свойства

## ЕЛЕКТРОФІЗИЧНІ ВЛАСТИВОСТІ ТОНКИХ ПЛІВОК ОКСИДУ ЦИНКУ, ОТРИМАНИХ ХІМІЧНИМИ МЕТОДАМИ

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### **Резюме**

Проведено порівняльні дослідження електрофізичних характеристик плівок ZnO, отриманих шляхом хімічного осадження з розчинів ацетату цинку та термічного окислення плівок цинку. Плівки оксиду цинку демонстрували специфічне для цього матеріалу оптичне поглинання та ширину забороненої зони (2,9-3,2 еВ), що вказує на наявність у них кристалічної структури. Використання полівінілового спирту дозволило отримати зразки з найвищими значеннями  $E_g$  та електричного опору, що спричинені нанорозміром кристалітів плівок. Досліджені електрофізичні характеристики плівок ZnO дали змогу встановити внесок власних дефектів та станів поверхні в електропровідність.

**Ключові слова:** оксид цинку, тонкі плівки, електрофізичні властивості