TEMPERATURE DEPENDENCE OF THE EPR SIGNAL IN ZnO

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Ceramics based on zinc oxide doped with lithium was fabricated. It is shown that an increase in the lithium content in an amount up to 0.1% leads to a decrease in electrical conductivity, and then in the range up to 3% to its increase. The real and imaginary parts of the permittivity decrease with increasing lithium concentration over the entire range of measured frequencies (50 kHz - 3 MHz). Similarly, the signal of the EPR line with g-factor ~ 1.96 decreases.

An analysis of the temperature dependence of the EPR signal intensity with a g factor of ~ 1.96 gives an activation energy of 0.06 eV, which practically coincides with the depth of shallow donors in ZnO. This makes it possible to identify the EPR signal with g-factor ~ 1.96 with oxygen vacancies.

1. Introduction

As of today, progress in the field of semiconductor materials is impossible without studying their electrophysical properties and the influence of both external factors and doping on them [1]. In addition, information on the energy state of certain point defects is not complete, studied and systematized. To obtain more reliable data, it is advisable to use a combination of a highly sensitive research method, such as electronic paramagnetic resonance, and the study of electrical properties of materials [2, 3].

Zinc oxide belongs to a wide class of semiconductor compounds of the A^2B^6 group, with a band gap close to 3.43 eV (300 K) and has n-type conductivity. The specific electrical conductivity can vary widely depending on the preparation method and mainly depends on the stoichiometry and surface condition of the samples (adsorption of gases). The variety of paramagnetic centers in ZnO is quite wide. The internodal oxygen atom O_i^x creates a paramagnetic center with the configuration $1s^2 2s^2 2p^4$ (triplet state). The successive capture of electrons on these centers gives paramagnetic defects O_i^{1-} ($1s^2 2s^2 2p^5$) and diamagnetic O_i^{2-} ($1s^2 2s^2 2p^6$). Removal of oxygen from the lattice site will create a doubly positive Vo^{2+} vacancy, which is surrounded by four Zn^{2+} cations. The capture of one electron by such a center will lead to the appearance of a Vo^{1+} paramagnetic center (F^+–center). The subsequent capture of one more electron will transfer such a vacancy to the neutral Vo^x state, which can be either paramagnetic (triplet state $s =1$), if the electron spins are directed in the same way, or diamagnetic in the case of electron spin compensation.

The zinc vacancy V_{Zn}^{2-}, which is surrounded by four oxygen ions O^{2-} in the nodes of the anionic sublattice, creates a diamagnetic defect. Capture of a hole by an oxygen ion neighboring an empty cation site forms a paramagnetic center of the V_{Zn}^{1-} type [4] with the configuration of an oxygen ion ($1s^2 2s^2 2p^5$). The neutral zinc vacancy V_{Zn}^x corresponds to the capture of two holes by oxygen ions surrounding the vacancy and is a center with spin s = 1, the properties of which depend on the interaction of the magnetic moments of localized unpaired electrons on two neighboring O^{1-} ions. Thus, intrinsic point defects with spin $s = 1/2$ (Zn_i^+, O_i^+, V_{Zn}^{1-}, and Vo^{1+}), as well as centers with spin $s = 1$ (triplet state) of type O_i^x, V_{Zn}^x, and Vo^x are paramagnetic [5-7].

In zinc oxide, one can observe signals from defects in which the value of g-factors is both greater and less than that of a free electron (g_e=2.00229). Usually, centers with $g > g_e$ are classified as acceptor-type defects, while signals with $g < g_e$ correspond to donor defects [3].

One of the first EPR signals detected in zinc oxide was a signal with a factor g≈1.96, the intensity of which is closely related to the value of the electrical conductivity of the sample.

The absence of an allowed ultrafine structure led most researchers to the conclusion that the g ≈ 1.96 signal is caused by free carriers in the conduction zone and electrons in the impurity donor zone. Recent results on the temperature dependence of the signal intensity g ≈ 1.96 in the temperature range 77-300 K indicate the predominant role of donor electrons.

The work [4] reported the observation of an EPR signal with $g_\parallel=1.9557$, $g_\perp=1.9576$, which was attributed to the V_O^+ oxygen vacancy (F^{1+} center), and the g–factor shift was explained by the anisotropy effect. Similar studies of ZnO single crystals [3] also showed that annealing relatively high-resistivity samples in a zinc atmosphere at temperatures $t >$ 1200 K is accompanied by a significant increase in their conductivity and the appearance of a line with $g_\parallel=1.956$. Heat treatment of the obtained samples in air ($t = 920$ K for 48 hours) leads to an increase in their specific resistance and the complete disappearance of this signal. In this case, the EPR signal with $g_\parallel=1.956$ was attributed to free carriers in the conduction band and electrons in the impurity donor band.

In the paper [7], devoted to the study of EPR of ZnO powder heat-treated under reducing and oxidizing conditions, it is reported on the observation of three lines with $g_1=1.955$ (V_O^{1+}), $g_2=1.958$ ($V_O+O_i^{2-}$) and $g_3 = 1.987$ (O_i^{1-}).

In all studied ZnO single crystals, the F^{1+}–center signal can be detected only after optical excitation in the range of energies $h\nu \geq 1.7$ eV, and its magnitude depends on the intensity of the excitation light [8]. At the same time, the maximum signal intensity is observed at the photon energy $h\nu \approx 2.5 \div 2.65$ eV, $T = 77$ K. Therefore, according to the authors of [8], the V_{Ox} oxygen vacancy is a deep donor with photoionization energy $E \approx 2.5 \div 2.65$ eV ($T = 77$ K). This conclusion is confirmed by theoretical estimates of the depth of the ground state of the F^{1+} center, which give a value of 2.7–3.2 eV below the bottom of the conduction band [6].

Studies of the ZnO surface were carried out in [9], after grinding a ZnO single crystal, an EPR line with g = 2.005 and a width of $\Delta H = 8$ E was observed. A line with g ≈ 1.96 and a width of $\Delta H \leq 6$ E occurs after heating the samples at temperature $T \geq 800$ K in vacuum and is observed at $T = 77$ K. This line is intensified when the sample is irradiated with light with a quantum exceeding the band gap ($E_g \approx 3.435$ eV) and weakens under the action of various gases adsorbed on the surface. Despite the large number of works [10-12] dedicated to elucidating the nature of this line, there is still no unambiguous model of the resonance source.

In some cases, there is even doubt as to whether this line belongs to the surface center. Regarding the nature of the resonant spin, there are three points of view: these are conduction electrons that arose in the conduction zone or the impurity zone; these are electrons captured on an oxygen vacancy (local centers of the F^{1+}–center type); these are interstitial Zn^{1+} ions. It was noted [10] that with certain thermal and gas-vacuum treatment, the line with g ≈ 1.96 can split into two lines (with $g_1=1.965$ and $g_2=1.961$). It is assumed that the line with g_1 is responsible for Zn^{1+} and the line with g_2 –for vacancy O^{1-}.

On the basis of the data given above, it is possible to conclude that the spectra of electron paramagnetic resonance in metal oxide materials are insufficiently studied.

The purpose of the work was to study the nature of the EPR signal with g-factor ~ 1.96 in zinc oxide and to investigate the influence of lithium-doping on the electrical properties of zinc oxide.

2. Samples and method of investigations
2.1. Sample manufacturing technology

Experimental samples were made of pure zinc oxide and lithium-doped zinc oxide. The starting materials were powders of zinc oxide (chemically pure) and lithium

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carbonate (Li_2CO_3) (chemically pure). Traditional ceramic technology was used. It consisted of the following stages: weighing the components, liquid mixing, drying the charge, forming under a pressure of 10 MPa, firing and applying electrodes using silver paste [13]. The samples were discs with a diameter of 10.5-12 mm and a thickness of 1-2 mm. Ceramic blanks were fired at a temperature of 900°C for 1 hour. Silver electrodes were ignited at a temperature of 750°C for 20 minutes. The electrodes were located on the ends of the discs.

2.2. Method of dielectric measurements

The complex dielectric permittivity of the experimental samples was investigated using a standard BM 560 Q-factor meter, which allows measurements in the range of 50 kHz – 35 MHz.

The values of the capacity of the ceramic sample (X) and the *Q*-factor values were measured: Q_1 – *Q*-factor without the sample, Q_2 – *Q*-factor with the ceramic sample. The values of complex permittivity were calculated using the following formulas:

$$\varepsilon' = C_x/C_g \tag{1}$$

where ε' is the real part of the complex dielectric permittivity; C_g is calculated according to the formula

$$C_g = \varepsilon_0 \cdot S/d \tag{2}$$

where ε_0 is electrical constant; S is cross-sectional area of the ceramic sample; d is of the ceramic sample thickness,

$$\varepsilon'' = 1/(2\pi\nu R C_g) \tag{3}$$

where ε'' is the imaginary part of the complex dielectric permittivity; ν denotes frequency; R stands for the sample resistance calculated by the formula

$$R = Q_1 Q_2/(2\pi \, \nu C_1(Q_1 - Q_2)). \tag{4}$$

The measurement conditions were the same for all samples.

2.3. Method of measuring electrical conductivity

The electrical conductivity of the samples was measured using industrial devices: digital voltmeters V7-27A/1 and V7-35 and adjustable sources of constant voltage TV-3, TV-42. The coefficient of non-linearity of the current-voltage characteristic (CVC) b was determined in the range of current densities through the sample from 4 to 40 A/m^2 according to the formula [14]:

$$\beta = \frac{\lg(J_1/J_2)}{\lg(E_1/E_2)} \tag{5}$$

where $J_1 = 40$ A/m^2; $J_2 = 4$ A/m^2; E_1 and E_2 are electric field strengths corresponding to these current densities.

The temperature dependence of the specific electrical conductivity σ was approximated by the phenomenological expression:

$$\sigma\ (T) = \sigma_0 \cdot \exp(-E_a/kT), \qquad\qquad (6)$$

where σ_0 is a certain constant; k is Boltzmann's constant; E_a denotes the activation energy.

2.4. Method of measuring spectra of electronic paramagnetic resonance

All measurements of the EPR spectra were carried out with the radiospectrometer EPR "RADIOPAN" SE/X-2543 according to standard methods.

Measurements for ceramic samples were carried out at liquid nitrogen temperature. To study the temperature dependence of the EPR signal, pure ZnO powder calcined at a temperature of about 400°C in ethanol vapor was used. This made it possible to increase the signal amplitude and measure it already at room temperature. A ball with a diameter of about 5 mm was formed from the powder treated in this way using an adhesive that did not give an EPR signal. A nichrome spiral was mounted inside the ball, which served for electrical heating of the experimental sample, as well as a thin chromel-copel thermocouple for temperature control. By varying the voltage applied to the coil, the temperature was stabilized, and then the EPR signal was measured. For such samples, studies of the signal g ≈ 1.96 were carried out in the temperature range 296 K – 450 K.

3. Experimental results and discussion

3.1. Dielectric properties

Concerning frequency dependences of the real and imaginary parts of the dielectric permittivity for all samples, a decrease in the measured value with increasing frequency was observed (Fig. 1). This type of dependence is characteristic for polycrystalline materials and may testify them in favor of the existence of intercrystalline potential energy barriers.
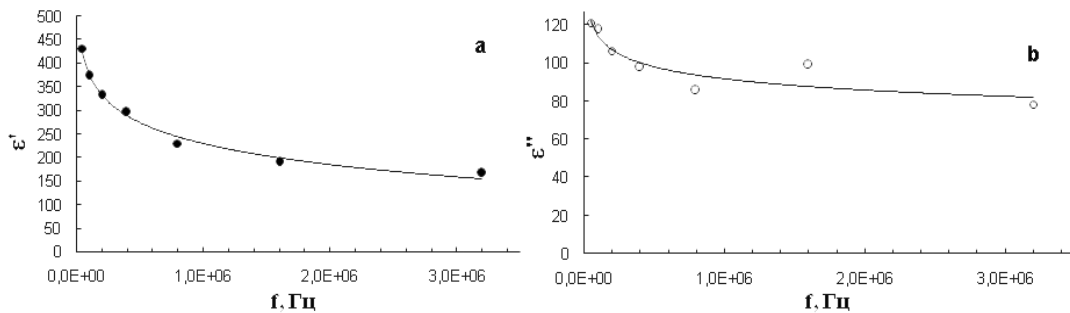

Fig. 1. Frequency dependence of the real (a) and imaginary (b) parts of the complex permittivity of ZnO ceramics without impurities Li_2CO_3.

An increase in the amount of lithium carbonate admixture leads to a decrease in the values of ε' and ε'' at the same frequency values. This may be due to an increase in the width of the intercrystalline potential barrier at the ZnO grain boundaries. An increase in the amount of the Li_2CO_3 impurity, which is an accessory to zinc oxide, leads to an expansion of the intercrystalline potential barrier region due to an increase in the Debye screening length. Since ε'' is inversely proportional to the resistance of ZnO grains, a decrease in the electrical conductivity of the semiconductor will lead to a corresponding

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decrease in the values of the imaginary part of its complex dielectric conductivity with an increase in the lithium content in the samples.

3.2. Electrical conductivity

The current-voltage characteristics of the experimental ceramic samples were weakly nonlinear with b = 2,0 – 2,6. With an increase in the amount of lithium carbonate impurity, there is first a decrease in the specific electrical conductivity of the samples, and then, after a value of 0.1%, its slow increase (Fig. 2).
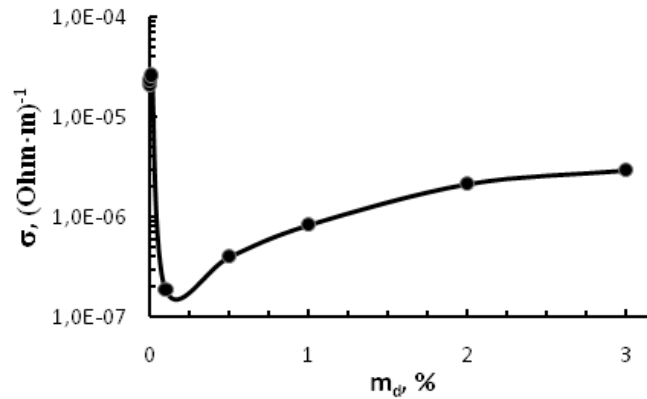

Fig. 2. Dependence of the specific conductivity of ceramics based on ZnO on the amount of additive Li$_2$CO$_3$ at *E* = 1 V/mm.

This may be due to the fact that lithium forms acceptor-type defects in the ZnO structure, which leads to a sharp decrease in electrical conductivity. Further, some increase in electrical conductivity values can be explained by the formation of a Li-based phase in the intergranular space of ceramics, or by the formation of insertion defects.

The activation energy of electrical conductivity calculated on the basis of expression (6), ranged from 0.2 eV to 0.26 eV and can be interpreted mainly as the height of the intercrystalline potential barrier between the ZnO grains.

3.3. Spectra of electronic paramagnetic resonance

The most intense line of the EPR spectrum signal was the line with g ≈ 1.96 for all samples. For ceramic samples doped with lithium, a decrease in the signal amplitude was observed with an increase in the content of the Li additive.

EPR spectra were measured for samples made from ZnO powder calcined in ethanol vapor according to the method described in point 2.4 at different temperatures from 296 K (Fig. 3) to 450 K (Fig. 4). As can be seen, the signal intensity (*dI*/*dH*) decreases with increasing temperature.

On the basis of the obtained data, the values of the relative magnitude of signals at different temperatures were calculated. Experimental data were presented in Arrhenius coordinates (Fig. 5). This made it possible to calculate the activation energy of the EPR signal for a line with the g-factor of 1.96 in ZnO according to the relation similar to that used to calculate the activation energy of electrical conductivity (6). The calculated activation energy value of the EPR signal magnitude for a line with the g-factor of 1.96 is 0.06 eV. It practically coincides with the value of the depth of occurrence of the small donor level in ZnO [15]. This makes it possible to identify the EPR signal with the g-factor of 1.96 with oxygen vacancies (Vo$^+$) in zinc oxide.
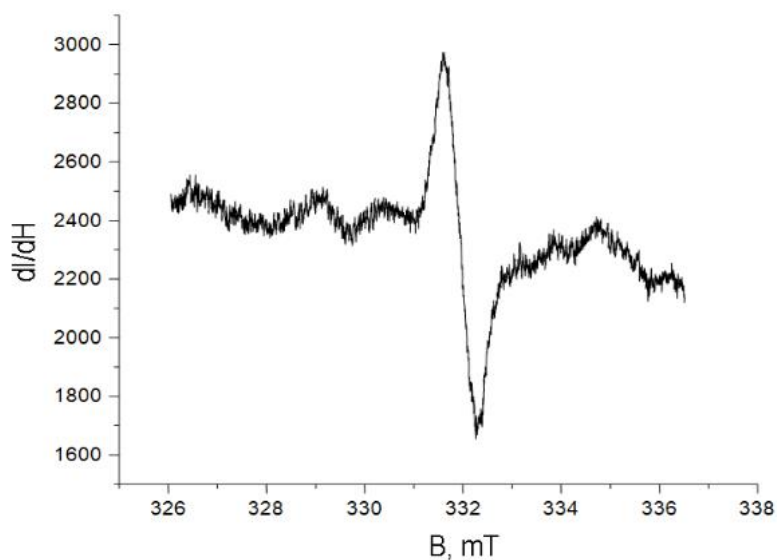
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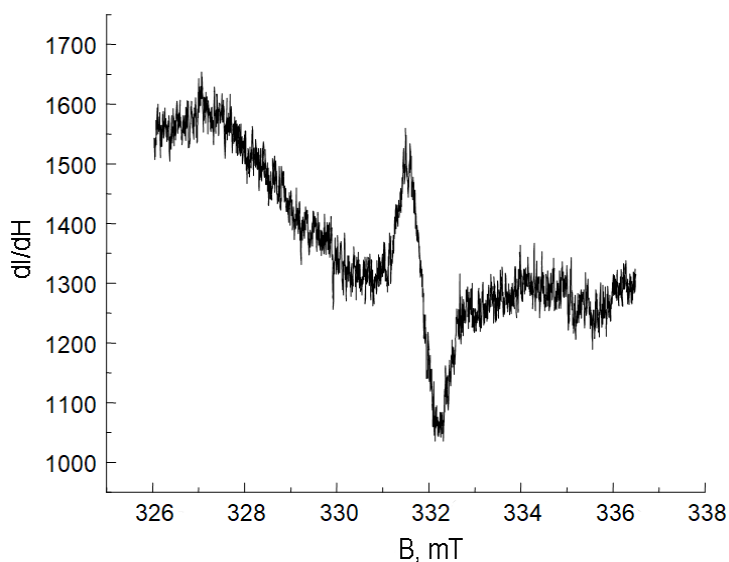**Fig. 3. EPR spectrum of ZnO powder at temperature 296 К.**

Fig. 4. EPR spectrum of ZnO powder at temperature 450 К.

To check whether heating during the experiment did not lead to the adsorption of oxygen on the surface of zinc oxide, which would lead to a decrease in the EPR signal, the spectrum was measured after cooling the experimental sample. It was found that after the experiment, the signal returned to its initial value. This may indicate that chemisorption of oxygen on the surface of ZnO particles was not the factor responsible for the decrease in the EPR signal with increasing temperature.
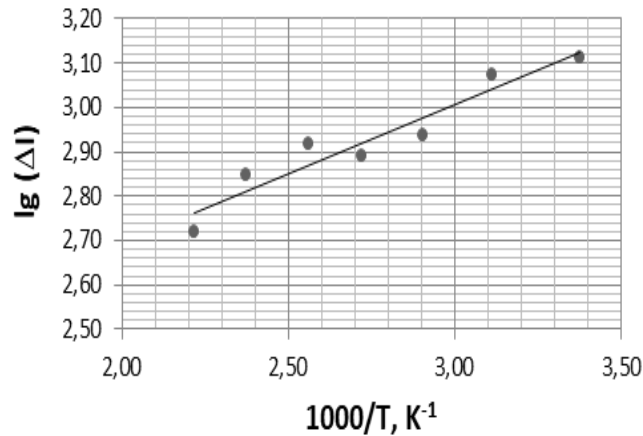
Fig. 5. Temperature dependence of the relative value of the EPR signal for the line with g-factor 1.96 of ZnO powder (dots – experimental values; line – approximation).

Intercrystalline potential barriers, the existence of which in ceramics and powders is proved by the shape of the frequency dependences of dielectric permittivity and height, according to measurements of the temperature dependence of electrical conductivity, ~ 0.2 eV, apparently do not influence the formation of an EPR signal with the g-factor of 1.96.

4. Conclusions

The decrease in electrical conductivity, the real and imaginary parts of the complex dielectric constant with increasing amounts of lithium carbonate impurity is associated with the formation of acceptor-type defects in the ZnO structure.

The value of the activation energy of the EPR signal value of the line with a g-factor of 1.96 in ZnO practically coincides with reference data on the depth of the shallow acceptor level (0.005 eV), which is associated with oxygen vacancies and interstitial zinc. Taking into account that the signal is amplified after heat treatment in a reducing environment, the EPR line with a g-factor of 1.96 can be identified as a signal from single-charge oxygen vacancies V_O^+.

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