High temperature electrical conductivity in hydrothermally grown ZnO

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Results of measurements of high temperature electrical conductivity (HTEC) in undoped hydrothermally grown ZnO single crystal are presented. HTEC measurements were made under the Zn component vapor pressure (up to 1 atm) and in the temperature range from 873 K to 1273 K. Reliable thermodynamic equilibrium in the ZnO crystal for HTEC measurements of isotherms and isobars was obtained at the temperatures higher than 873 K. Surprisingly slow chemical diffusion prolonged the high temperature measurement cycles continuously for several weeks. In our experiments the absolute value of HTEC in undoped hydrothermally grown ZnO was several orders of magnitude higher than HTEC in undoped ZnS. Slopes of HTEC isotherms varied with component vapor pressure and changed in the range from 0.2 to 0.4. For HTEC isobar in the temperature range from 1173 K to 1273 K it was found activation energy value 0.3-0.4 eV at zinc vapour pressure 0.092 atm. Defect model for explanation of this high temperature experiment is discussed in connection with impurities.

1 Introduction The hydrothermal method has an advantage to grow large bulk crystals for substrates of ZnO-related devices due to the growth under low supersaturation. The difference in vapor pressure of components above undoped ZnO at elevated temperatures causes a stoichiometric excess of Zn in crystal. Undoped ZnO exhibits n-type electrical conductivity, which may be due to an excess of the metal component or/and by an impurity caused shallow donor. Zn nonstoichiometry may be defined by definitions of two types [1]. Excess Zn in ZnO is built up automatically at high temperatures and growth of more stoichiometric material can be promoted by low-temperature methods. To determine the excess zinc in ZnO, the atomic absorption photometry (AAP) of zinc vapour was used in the conditions of solid-vapour equilibrium [2]. AAP method enables to discriminate the zinc which originates from the ZnO crystal lattice or from zinc inclusions [3]. The analytically determined concentration of the metal component excess appears to be bigger than the concentration of electrically active defects [4]. The reactions of impurity metals with excess Zn in ZnO ceramics were observed in Zn AAP experiments [5]. The solubilities of metal impurity oxides in ZnO are high. Metal impurities form oxides which will reduce during annealing in Zn vapor up to metals form [6]. Although the room temperature properties of crystals are of practical interest, the initial defect structure in equilibrium is formed usually at much higher temperatures during crystal growth or annealing, when the high temperature defect equilibrium (HTDE) is established. The role of native defects caused by excess Zn in ZnO, is not clear until now [7-10].

2 Experimental The sample for high temperature electrical conductivity (HTEC) measurements was cut
from hydrothermally grown ZnO boule. One of the problems in experiments with hydrothermally grown ZnO crystals is to take in consideration the contamination of the crystal with metallic impurities. The concentration of impurities may exceed often the concentration of native defects at room temperature. The colourless crystals used in our experiment are believed with a total impurity content of about 10 ppm [11, 12]. The Li concentration and electrical properties of Li-doped ZnO could be controlled by different thermal processes [13]. The removal of lithium and other group I contaminants from hydrothermally grown ZnO results in significant changes in its characteristics [14]. The HTEC \( \sigma \) was measured as a function of sample temperature \( T \) and component vapor pressure (\( P_{Zn} \)). \( P_{Zn} \) was maintained by controlling the temperature of the reservoir of zinc. In all cases, the ampoule was placed into a quartz furnace tube, which was evacuated to \( 10^2 \) Pa for prevention of oxidation of the electrodes. The four-probe method was used. Tungsten springs gave satisfied ohmic contacts with ZnO at high temperatures as in vacuum as at Zn vapour pressure. \( I-U \) dependences were linear during all measurements cycles. HTEC experiments within ZnO led us to Eq. (1), a power dependence of electron concentration \( n \) on component vapour pressure \( P_{\text{comp}} \) with slopes \( \alpha \) and temperature \( T \) as

\[
n \sim P_{\text{comp}}^{\alpha T + \beta} \exp(-\Delta E/kT) . \tag{1}
\]

The \( T^{3/2} \) dependence of mobility can be accounted by the factor \( T^\alpha \), so that at the first stage the conductivity \( \sigma \) is proportional to the free carrier concentration. Chemical diffusion data were accounted in measurement cycles. There are publications concern HTEC measurements in ZnO in the high temperature region [15, 16, 21]. Measurements of electrical conductivity of ZnO in the region below 800 K has been described in [17, 18].

3 HTEC in ZnO

3.1 HTEC isobars and isotherms At the beginning we supposed that in the course of rising of sample temperature, the concentration of native defects will exceed the concentration of residual impurity defects. The starting resistivity of ZnO object dropped in vacuum from \( \sim 10 \) k\( \Omega \) cm at 673 K to \( \sim 2 \) k\( \Omega \) cm at 873 K. Then the temperature of ZnO was raised step by step from 873 K to 1273 K at constant zinc vapour pressures in Fig. 1. Figure 2 presents the measurements of HTEC isotherms. In [15], \( \sigma \) of highly pure thin ZnO films were investigated in the temperature range 500 to 1000 K under oxygen pressure. In this experiment \( \Delta E = 1.6 \) eV. In our experiment we had also \( \Delta E \approx 1.6 \) eV at around and lower the temperature 873 K (not presented here). Authors [15] explained this value of activation energy as the half of the band gap energy. In comparison: for the same temperature region for undoped ZnS \( \Delta E = 1.4 \) eV was obtained [19]. Hagemark [20] found in ZnO monocrystals and Tomlins et al. [21] found in ZnO ceramics the component vapour pressure \( P_{Zn} = 1/3 \) relationship or corresponding to a \( P_{\text{oxygen}} \sim 1/6 \) dependence on concentration of electrons \( n \). \( \alpha \approx 1/3 \) value for Zn vapour pressure relationship may be a result of an increase in doubly charged dominating native defect (at \( P_{\text{oxygen}} \) conditions it gives slope \(-1/6 \) for n-type ZnO).

![Figure 1](image1.png)

**Figure 1** Experimental data: in the temperature region from 973 to 1073 K at \( P_{Zn} = 0.005 \) atm, the Arrhenius plot gave \( \Delta E \approx 1.25 \) eV. In the next region from 1073 K to 1173 K at \( P_{Zn} = 0.079 \) atm, \( \Delta E \approx 0.7 \) eV and in the region from 1173 K to 1273 K at \( P_{Zn} = 0.092 \) atm, \( \Delta E \approx 0.3 - 0.4 \) eV.

![Figure 2](image2.png)

**Figure 2** At \( T_{\text{ZnO}} = \text{const conditions} \) \( \sigma \sim P_{\text{comp}}^\alpha \) the next slopes were found: at \( T_{\text{ZnO}} = 1073 \) K, \( \alpha \approx 0.29 \); at \( T_{\text{ZnO}} = 1173 \) K, \( \alpha \approx 0.35 \); at \( T_{\text{ZnO}} = 1273 \) K, \( \alpha \approx 0.27 \).

In the first sight one can propose the existence of relation \( n \sim [V_{\text{O}}^\text{a} \] or \( n \sim [\text{Zn}^{\text{a}+}] \) based on the electroneutrality condition approximation for the here presented HTEC isotherms. Although various total energy calculation methods have been applied by many researchers to calculate HTDE models for ZnO, the role of native defects in the results of calculations are interpreted differently [22–25].
3.2 Observation of chemical diffusion

After measurements of HTEC isobars and isotherms we were interested in the chemical diffusion in ZnO at elevated temperatures. During the chemical self-diffusion the crystal changes its level of non-stoichiometry, in this process gradients in the chemical potentials of the constituents of a crystal are removed. Measurements of HTEC as a function of time after step-like change of the crystal temperature \( T_{ZnO} \) is appropriate method to study chemical self-diffusion.

![Figure 3](image-url)

**Figure 3** Example of chemical diffusion: at constant \( P_{Zn} = 8000 \) Pa, part I: \( T_{ZnO} \) change from 1173 K to 1203 K, part II: \( T_{ZnO} \) change from 1203 K to 1243 K, part III: \( T_{ZnO} \) change from 1243 K to 1273 K.

Some doubts in the simple interpretation of HTEC isobars and isotherms of our experiment arose after the investigations of chemical diffusion curves of our ZnO object. Figure 3 characterizes HTEC isobars as function of time after step-like change of ZnO crystal temperature at fixed zinc vapour pressure \( P_{Zn} \). The curves in Fig. 3 characterize two (or more) consecutive processes after step-wise changing of temperature of ZnO crystal. We propose the next explanation to this phenomenon. At first there is the formation of native defects and the next following slower step is the interaction of generated native defects between themselves or between native defects and some impurity defects. Such phenomenon we could not observe in our investigations of chemical diffusion in undoped ZnS and CdSe [26]. There are several high concentration impurities in hydrothermally grown ZnO crystals to connect to this HTEC relaxation phenomenon. Li is the main acceptor in hydrothermal ZnO compensating shallow donors, in addition to being a fast diffuser. The concentrations of Fe, Al, Li, K are detected as functions of the distance from the seed and surface polarity [27]. Li concentration was reduced from \( \sim 10^{17} \) cm\(^{-3} \) in as-grown samples to \( \sim 10^{15} \) cm\(^{-3} \) for samples treated at 1500 °C [28]. On this phenomenon is based the removal of these impurities from the hydrothermal grown ZnO crystal [14]. Hydrogen is also one of most common impurity in hydrothermally grown ZnO. It is believed that hydrogen causes n-type conductivity in ZnO at room temperature [29]. The complex Li-H is highly stable and it can be annealed out only at temperatures above 1100 °C [30]. The result of diffusion of Li in ZnO from interstitial donor to substitutional acceptor depends sensitively on annealing time [31].

4 Conclusion

The concentration of dominating donors at 1273 K and at 1 atm of zinc vapour pressure can be estimated based on the experiment data. For calculations of concentration of dominating donor we use free carriers mobility at elevated temperature as \( \mu_k = 100(T/298)^{3/2} \). Here for temperatures higher than room temperature 298 K, the \( T^{3/2} \) dependence of mobility \( \mu_k \) was expected as a result of phonon scattering. In hydrothermal ZnO crystals electron mobilities of \( \geq 100 \) cm\(^2\)/Vs at room temperature are observed. Taking HTEC value \( \sigma \approx 1 \) S/cm from our experiment we get concentration of dominating donor defects by equation \( n = \sigma/e\mu_k \), the value of \( n \leq 10^{18} \) cm\(^{-3} \). It is approximately the same value as the limit for impurity concentration in hydrothermally grown ZnO single crystals. Can we assign the measured in the region from 1173 K to 1273 K ZnO isobar \( \Delta E \approx 0.4 \) eV value to the native defects generation process? After HTEC measurements, the monitoring of HTEC as a function of time was used for determining of complex behaviour of high temperature processes. These curves characterize consecutive processes in ZnO after step-wise changing of \( T_{ZnO} \). The first high-speed step may be the formation of native defects and the following slower one is the interaction of generated native defects between themselves or between native defects and some impurity defects. The slow component on chemical diffusion curves indicates the existence of slow diffusion processes of some species. After present experiment of HTEC measurements of ZnO isotherms and isobars we got more questions about dominating native defects than before the performance of our measurements. But from our experiments one thing became clear: dominating defects at elevated temperatures and at \( P_{Zn} \) conditions are connected to Zn excess in ZnO. Properties of ordinary hydrothermally grown ZnO at room temperature are determined by residual impurities or their complexes with native defects. To achieve the domination of native defects at room temperature, the lowering of concentration of residual impurities not less than one order must be undertaken.

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References


