# IMPURITY DISTRIBUTION IN n-ZnSe CRYSTALS DOPED WITH Au

**D.D. Nedeoglo, N.D. Nedeoglo and V.P. Sirkeli**

*Department of Physics, Moldova State University,*
*A. Mateevich str. 60, MD-2009, Chisinau, Republic of Moldova*
*Tel: +373 22 577586; Fax: +373 22 244248; e-mail: nedeoglo@usm.md*

## Abstract

Hall effect, electric conductivity and mobility of charge carriers in n-ZnSe single crystals doped with Au are investigated in the temperature range from 77 to 300 K. Impurity distribution in the crystals was studied by a method of "layer-by-layer" etching of a sample surface. The model, which explains this distribution by a simultaneous diffusion of Zn and Au atoms during a long-term high-temperature annealing of as-grown crystals in Zn + Au melt, is proposed.

High-quality doping of crystals results in uniform distribution of doping impurity deep into the crystals. This problem is easily solved in case of doping in the process of crystal growth. The homogeneous doping of bulk crystal by the diffusion method, when impurity atoms penetrate through the crystal surface in the process of a long-term thermal treatment, is a difficult problem. The necessity of the investigation of dopant distribution, i.e. the distribution of charge carrier concentration and other electrical parameters deep into the crystal, appears.

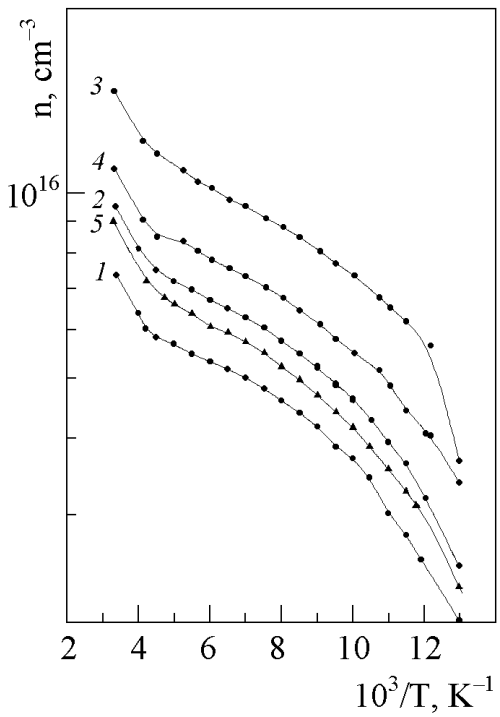



Fig. 1. Temperature dependence of free electron concentration in the n-ZnSe : Zn : 2 at% Au. Etch time, s: 1 – 30; 2 – 120; 3 – 240; 4– 360; 5-420.

Free electron concentration $n$, electric conductivity $\sigma$ and electron mobility $R_H\sigma$ versus etch time $t_{etch}$ of n-ZnSe crystals, doped with Au during a long-term (100 h) high-temperature (950°C) annealing in Zn + 2 at% Au melt, are studied. Temperature dependences of $n$, $\sigma$ and $R_H\sigma$ electrical parameters under the "layer-by-layer" etching of the sample surface were also investigated in the temperature range from 77 to 300 K. 7% bromine-methanol solution [7% Br – $CH_3(OH)$] was used as the etchant. The sample mass, its geometric dimensions, etch rate, and the thickness of the etched layer were measured after every step of the etching.

Fig. 1 shows the temperature dependence of the free electron concentration in the n-ZnSe : Zn : 2 at% Au crystals etched during various time intervals. As the etch time increases (the etch rate is equal to 0.24 μm/s), the curve behaviour is unchanged: the $n$ = f ($10^3$ / $T$) dependence shifts almost parallel in the whole investigated temperature range. However, such a shift is not a monotonous one. As the etch depth increases to 58 μm, the free electron concentration becomes almost twice as large (Fig. 2). The further

increase of the etch time ($t_{etch}$ > 240 s) leads to a decrease of the electron concentration. The electric conductivity of the samples increases as the etch time increases up to 200 s (the etch depth is about 48 μm). The further increase of the etch time leads to a decrease of the electric conductivity (Fig. 2). This type of the $\sigma = f(t_{etch})$ dependence is stipulated mainly by the free electron distribution deep into the sample, because the electron mobility weakly depends on the etch time (Fig. 2).

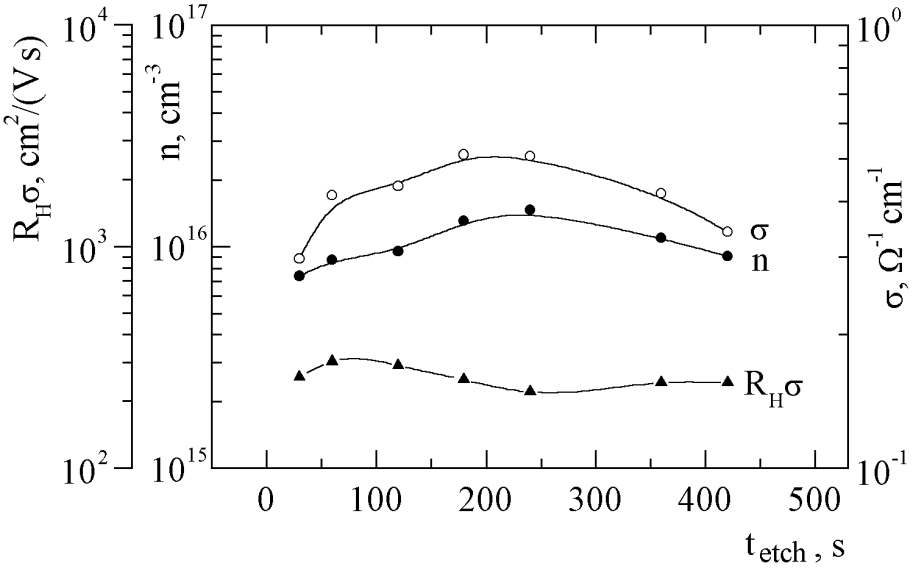



Fig. 2. Electric conductivity, free electron concentration and electron mobility versus etch time. T = 300 K.

The following model, which explains the observed distribution of the dopant impurity deep into the n-ZnSe : Zn : Au crystals, is proposed. A simultaneous diffusion of Zn and Au atoms into n-ZnSe crystals during their annealing in Zn + Au melt takes place. Zn atoms fill zinc vacancies ($V_{Zn}$); as a result, the concentration of acceptor native defects $V_{Zn}$ reduces. At the same time, the concentration of free electrons activated from donor levels to the conduction band increases. Consequently, if we suppose that Zn atoms penetrate deep into the crystal non-uniformly, i.e. Zn atom gradient is observed, then the free electron concentration should decrease as the etch time increases. Such a decrease of the free electron concentration is observed experimentally for the etch times more than 240 s (the etch depth is more than 58 μm). At smaller values of the etch time, the free electron concentration increases with the increasing etch time (Fig. 2).

Au atoms substitute Zn atoms in the sites of Zn sublattice, i.e. fill Zn vacancies, and form $Au_{Zn}$ acceptor defects. These impurity defects, as well as the $V_{Zn}$ native defects, compensate electrically active donors; as a result, the free electron concentration decreases. At non-uniform distribution of Au atoms deep into the crystals (the number of Au atoms is greater near the surface than in the volume of the sample), the free electron concentration should increase as the etch time increases, because the layers with great number of compensating acceptors are removed. Just the same character of the $n = f(10^3/T)$ dependence is observed for the values of the etch time less than 240 s (Fig. 2). The temperature and time modes of thermodiffusion doping of the n-ZnSe crystals with gold, used in this work, allow to dope the samples up to the depth of ~ 60 μm. The decrease of the free electron concentration at $t_{etch}$ > 240 s (Fig. 2) is stipulated by non-uniform diffusion of Zn atoms deep into the

sample, because Au atoms scarcely penetrate to the depth of more than 60 μm. The supposition that the diffusion depth of Au atoms is smaller than that of Zn atoms is in a good agreement with the diffusion constants for Zn and Au atoms in ZnSe crystals at 1000 °C: $D_{Zn} = 2.3 \cdot 10^{-11}$ cm$^2$/s [1] and $D_{Au} \approx 10^{-13}$ cm$^2$/s [2], i.e. the diffusion constant for Au atoms is two orders of magnitude smaller than the diffusion constant for Zn atoms. The doping of ZnSe crystals with Au in the process of their synthesis also causes the great dopant gradient, which is explained by poor solubility of Au atoms [3].

## References

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