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# The Effect of Surface Preparation on Physical Properties of Ni–ZnSe Junctions

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We report on optical and photovoltaic properties of Ni–ZnSe junctions. We demonstrate that the preparation method of the ZnSe surface determines luminescence, optical transmission of ZnSe substrates and photovoltaic spectra of the Ni–ZnSe junctions. The observed effects are explained by formation of low-dimensional quantum structures on the ZnSe surface in result of the surface preparation procedure. This is confirmed by atomic force microscopy studies, which show the presence of grains with lateral dimensions of 30–300 nm on ZnSe surface. The smallest grains are responsible for a wide spectral band observed in photoluminescence at 3.4 eV, i.e., at much higher energies than the energy gap of bulk ZnSe, $E_g \approx 2.7$ eV.

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## 1. Introduction

The prospect of zinc selenide (ZnSe) in the short optoelectronics stimulates research aimed at improving search technology parameters of the material and devices based on it. The major obstacles for obtaining ZnSe-based $p$–$n$ junctions are low electronic conductivity of ZnSe and the lack of a $p$-type II–VI heteropair compound. As alternative rectifying contacts to ZnSe there may be used metals. Such metal–ZnSe junctions are employed for broadband prebreakdown electroluminescent diodes (PED) and UV photodetectors [1, 2].

Further improvement of the performance and operating parameters of such devices can be obtained by special preparation, i.e., modification of the surface layer of the ZnSe substrate. In this regard very promising seems to be any procedure that leads to formation of low-dimensional quantum structures on the surface. Such an approach applied to Au–CdTe contacts resulted in an significant increase of the potential barrier height $\varphi_0$ of the junction and in reduction of the surface recombination of photoexcited carriers [3, 4]. The present work is devoted to the influence of the ZnSe surface preparation method on the optical, fluorescent and photovoltaic properties of Ni–ZnSe junctions.

## 2. Experimental

As substrates, we used $4 \times 4 \times 1$ mm$^3$ platelets cut from bulk ZnSe single crystals. The crystals were doped by isovalent tellurium impurity, which ensured high temperature and radiation stability of the optical properties of material. In result of a thermal annealing of the substrates in saturated vapor of Zn their electron conductivity considerably increase to $\approx 10\Omega^{-1}$ cm$^{-1}$ at 300 K. Low-resistance $n$-type ZnSe substrates were chemically etched in various solutions. In result the ZnSe surfaces became either mirror-like (type 1 surface) or matt (type 2 surface). To create mirror surface used etchant composition $CrO_3$:HCl = 2:3, and matt — $H_2SO_4$:$H_2O_2$ = 3:1. Removal of etching products was done by prolonged rinsing (10–15 min) in boiling distilled water. The ohmic contacts were formed on the back side of the wafers. On the front side rectifying contacts were deposited. For rectifying contacts semitransparent layers of Ni were employed. The Ni layers exhibit high transmittance in the energy range from 1 eV to 6 eV. This allows studying optical characteristics of the material (transmission, reflection and photoluminescence spectrum) directly on the Ni–ZnSe samples. The Ni contacts form high potential barriers, $\varphi_0$, to ZnSe ($\varphi_0 = 1.2-2.0$ eV) [2]. This fact is particularly important for exploitation of the structures at high temperatures.

The photoluminescence was excited by the 337 nm nitrogen laser. Emission spectra, $N_\omega$, were measured using a setup which incorporated a grating monochromator and standard synchronous detection circuit. Spectra were recorded automatically, with taken into account the nonlinearity of the optical components in the measuring system, and were plotted as the number of incident photons per energy range unit, $N_\omega$, against photon energy, $\hbar\omega$. For measurements of the transmission, $T_\omega$, reflection, $R'_\omega$, and photosensitivity spectra halogen and deuterium lamp with a "smooth" spectrum were used. Diagram of the system and the measurement procedure of ordinary and differential optical spectra is described in detail in previous paper [5].

## 3. Results and discussion

Normalized to the maximum intensity of the luminescence spectrum of Ni–ZnSe junctions made on mirror-like ZnSe surfaces (type 1) exhibit a dominant exctitonic peak in the vicinity of the ZnSe energy gap and a weak band

with a maximum $\approx 2.1$ eV assigned to defects, as shown in Fig. 1. The shape of the spectrum does not depend on the Ni deposit on the sample surface — it is the same when measured with the Ni rectifying contact and without it on the mirror-like surface of ZnSe. This confirms that the Ni layer is homogeneous and transparent.

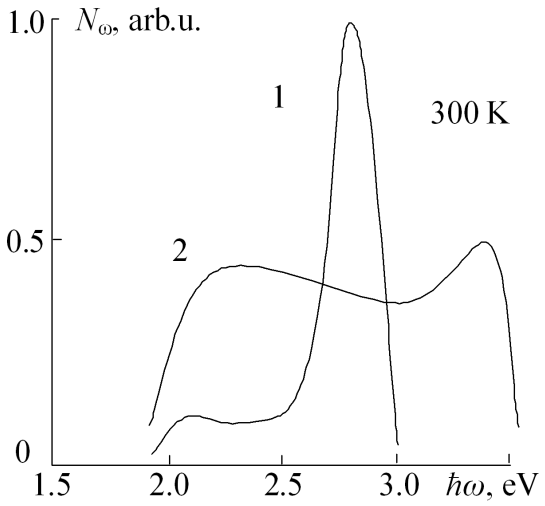


Fig. 1. Typical photoluminescence spectra contacts of Ni–ZnSe with mirror (1) and matt (2) surface substrates.

When one prepares ZnSe substrates in such a way that the surface becomes matt (type 2) the photoluminescence spectra change significantly, which is wide and without singularity, curve 2 in Fig. 1. The experimentally observed decrease in the intensity of the radiation is taken into account by multiplying the normalized to the maximum of the curve 2 by a factor, which is determined by the ratio of ordinates $N_\omega/N_{\omega 1}$ at $\hbar\omega \approx 2.7$ eV for samples with a matt and mirror surfaces, respectively, under the same conditions of measurement. The strong photoluminescence (PL) peak at 2.7 eV disappears. Most characteristic peculiarity of this spectrum is, however, the appearance of luminescence with energies $\hbar\omega$ significantly higher than the band gap of zinc selenide ($E_g \approx 2.7$ eV at 300 K [2]). We note that the high energy PL emission cannot originate from a chemical species formed by the chemical treatment on the ZnSe surface in the process of surface preparation, for example from ZnO. This is confirmed by differential optical reflectance spectra, $R'_\omega$ shown in Fig. 2. Reflectance of samples having the different surfaces (mirror-like and matt) show very similar profiles with the peak positions which coincide with the energy gap of zinc selenide. We note that the peak of $R'_\omega$ for heterolayers ZnO synthesized on ZnSe substrates are close to $\hbar\omega \approx 3.3$ eV [6].

Thus, the luminescence at photon energy $\hbar\omega > E_g$ must originate from other objects. The most probable explanation assumes formation of low-dimensional quantum structures on the type 2 ZnSe surfaces. The quantum structures are formed in result of the chemical preparation procedure leading to the matt surface. This assumption is confirmed by atomic force microscopy (AFM) study. The AFM images reveal on the ZnSe matt surface the presence of grains with lateral dimensions in the range of 30–300 nm [5]. The nanograins has the shape of pyramids and most probably the short-wave emission (including the wide peak at 3.4 eV) originates from the tops of these pyramid. The absence of pronounced peculiarities at $\hbar\omega > E_g$ in $N_\omega$ spectra is probably due to size dispersion of the nanograins. Let us note that the pyramids of larger size have relatively little influence on the spectral distribution of low-energy radiation, but cause a significant change in the transmission, Fig. 3a.

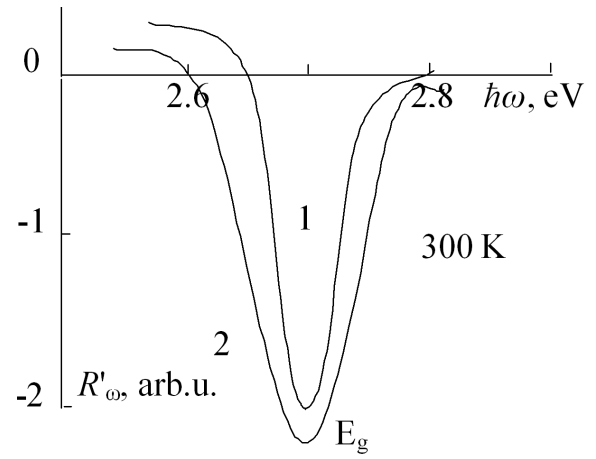


Fig. 2. Typical differential reflection spectra with mirror (1) and matt (2) surface.

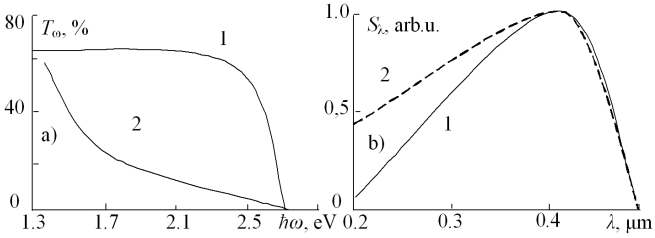


Fig. 3. (a) Typical transmission spectra and (b) the spectral response of the samples with mirror (1) and matt (2) surfaces, measured at temperature $T = 300$ K.

The absolute value of optical transmission, $T_\omega$, shown in Fig. 3a, sharply decreases at $\hbar\omega < E_g$ for type 2 structures. The effect is due to an increase of the optical scattering processes on the large nanograins. It is interesting to note, however, that the high energy edge of transmission $T_\omega$ for both types of samples intercept on the abscissa at the energy gap of ZnSe, which provides additional evidence that no other chemical species is formed on the ZnSe surface in result of the chemical procedure.

The surface modification of the ZnSe substrate observed by optical measurements influences other phys-

ical properties of the material and of ZnSe structures covered by rectifying contacts. We note that the height of the potential barrier of Ni–ZnSe junction increases by 20–30% for type 2 structures (with matt ZnSe surface) in comparison to the structures made on mirror-like ZnSe surfaces. This causes an increase in adequate circuit voltage $V_{oc}$, as well as decreases the dark current structures of type 2 as compared to type 1. Moreover, the first of them, due to a more developed surface generates stronger short-circuit current $I_{sc}$ at the same diodes area and illumination power.

In the case of type 2 Ni–ZnSe structures one can expect enhanced photosensitivity in the high energies as compared to type 1 structures. This is because, as in the case of $n$-CdTe, one expects that the presence of quantum structures on the surface decreases the surface recombination rate by the factor of two [4]. This effect was observed by the increase of monochromatic sensitivity, $S_\lambda$, in the high-energy spectral range. A similar effect is observed in the case of contacts Ni–ZnSe junctions shown in Fig. 3b, in which curves 1 and 2 are normalized. It can be seen that the modification of the substrate causes a significant increase in $S_\lambda$ at short wavelengths and does not affect the profile of the spectral curves at $\lambda \geq 0.4\ \mu$m. However, the absolute value of the monochromatic sensitivity at the maximum near $\lambda \approx 0.4\ \mu$m is about 0.12 A/W and 0.08 A/W for the diodes type 2 and 1, respectively. This is a consequence of increasing the effective area of the photosensitivity of the matt surface compared with a mirror.

## 4. Conclusion

Thus, these results indicate the possibility of obtaining of quantum structures on the surface of ZnSe substrates by treating them in the etchant $H_2SO_4$:$H_2O_2$ = 3:1. This is confirmed by AFM topography, as well as the presence in the photoluminescence spectra of photons with energies much greater than the band gap of zinc selenide. Rectifying contacts Ni–ZnSe based on these modified substrates have large values of the open circuit voltage and short-circuit current, and higher shortwave photosensitivity compared to similar contacts created on substrates with a smooth surface.

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