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INVESTIGATION OF ZnO LAYERS TREATED BY RBQE METHOD

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ABSTRACT. We investigated new quasiepitaxial ZnO layers treated by RBQE method. To state that in the process of the formation of new ZnO layers neither extraction of sulfur from the basic ZnS crystal nor inclusion in basic crystal of activated oxygen existed in the gas phase occur, the implantation of ZnO samples by S^+ ions has been carried out. In PL spectra of ZnO ($\rho \approx 10^9$ to 10^{10} Ωcm) samples obtained by implantation of S^+ ions (T = 300-350°C; in O_2) λ = 390 nm (λ = 385 nm, λ = 400 nm); λ = 440 nm; λ = 460 nm and λ = 505 nm peaks were observed. In our opinion, these peaks correspond to (V_{Zn}^{-}-V_O^{++}); V_O^{++}; AX^+; V_{Zn}^{-}; V_O^{+}, respectively. In PL spectrum of implanted ZnO layers the peak related to sulfur has been observed. Thus, the obtained ZnO serves as a protective layer.

The control of electrical and optical properties of wideband semiconductors is very problematic because of strong compensation and self-compensation caused by residual impurities and point defects. For this reason the inversion of conductivity type is problematic [1,2].

The ZnO, ZnS are very interesting materials among the wideband semiconductors [3]. The ZnO quasiepitaxial layers are obtained on the base of ZnS by RBQE method [4,5]. Quasiepitaxial layers are formed by metal component that because of diffusion comes out of the volume of basic crystal onto the surface and oxygen singlet radicals from gas phase. In our case the RBQE method enables us to obtain single crystalline layers of ZnO on the basic crystal of ZnS but generally it might be used for other binary compounds. To state that in the process of the formation of new ZnO layer neither extraction of sulfur from the basic ZnS crystal nor inclusion in basic crystal of activated oxygen existed in the gas phase occur the implantation of ZnO samples by S^+ ions has been carried out.

By means of RBQE method the single crystal layers of ZnO were grown on the basic ZnS crystal, the *n*-type ZnS samples with $\rho=10^2$ Ωcm grown by gas phase epitaxy were used as initial basic crystals. To obtain, new single crystal layers of ZnO the treatment was carried out in the atmosphere of activated oxygen obtained by RF-discharge of 40-80 Wt. The treatment temperature was 300-900ºC and duration was 45 min-6 hours. We have studied electrical and optical properties of the basic crystals and new quasiepitaxial layers.

The *n*-type ZnO ($\rho \approx 10^2$ Ωcm) samples were implanted by S^+ ions ($E = 150$ keV) with $D = 10^{14}$-10^{16} cm^{-2} doses. The density of ion current was $J = 0.3$ to $2\mu A/cm^2$. The subsequent heat treatment of implanted samples was carried out within the temperature interval of 300-500°C in molecular oxygen atmosphere. Duration of treatment was 4-8 hours.

PL spectra of the obtained ZnO layers were studied. We measured PL of ZnO/ZnS quasiepitaxial layers grown at various temperatures 350ºC-850ºC. The PL spectra of ZnO quasiepitaxial layers grown at different temperatures are given in Fig.1.

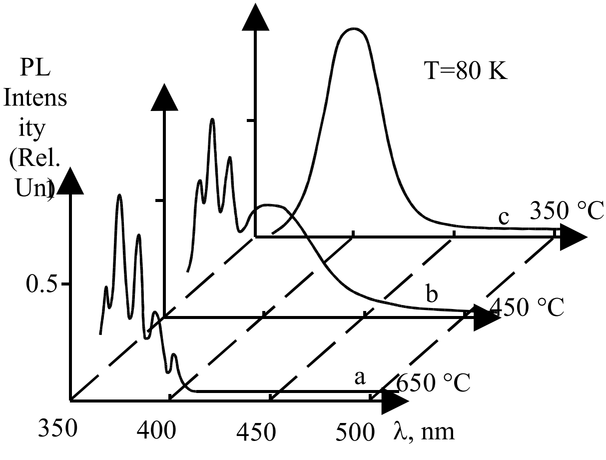

Fig.1. PL spectra of ZnO quasiepitaxial layers grown at different temperatures

At T = 650ºC stoichiometric layers of ZnO ($\rho \geq 10^{13}$ Ωcm) were obtained. In the PL spectrum exciton part was observed ($\lambda = 367$ nm - A exciton, $\lambda = 371$ nm – bound exciton; $\lambda = 374$ nm; $\lambda = 383.4$ nm; $\lambda = 392$ nm and $\lambda = 401$ nm - phonon replicas of A exciton), visible part was completely vanished. During the treatment at T = 450ºC a weak hole conductivity ($\rho = 10^5$-10^6 Ωcm) was observed. In the PL spectrum the exciton emission is partially covered by the emission band with maximum at $\lambda = 390$ nm. Subsequent lowering of temperature growth leads to increase of the intrinsic defect hole conductivity. At T = 350ºC p-type ZnO layers with resistivity $\rho = 10^2$ Ωcm were obtained. In the PL spectrum of this crystal $\lambda = 390$ nm band completely covers the exciton part. With temperature decrease the quantity of uncontrollable impurities also decreases and the degree of monocrystallinity of the built up layers increases.

The band, connected with sulfur, was not observed in PL spectra of ZnO quasiepitaxial layers. Thus, there is no diffusion of sulfur in building layers of ZnO during the RBQE.

After removing the quasiepitaxial ZnO layers the basic ZnS crystal was studied. In the PL spectrum pikes connected with oxygen do not take place. As to oxygen implantation in ZnS basic crystal, in our opinion this process does not develop or its intensity is so low that in PL spectrum of ZnS the peak related with oxygen has not been observed.

When ZnO was implanted with S+ ions (J = 0.3 to 0.5 μA/cm^2) *n*-type ZnO samples were obtained with high resistivity $\rho \approx 10^9$-10^{10} Ωcm (in by heat treatment in O_2 at T = 300 to 350°C). *n*- type ZnO samples with low resistivity ($\rho \approx 10^3$ to 5×10^3 Ωcm) were obtained by heat treatment at T > 350°C in the atmosphere of O_2. When ion current density was J ≥ 2 μA/cm^2, *n*- type ZnO samples were obtained with resistivity $\rho \approx 10^3$ to 2×10^3 Ωcm. When ZnO crystal was implanted at the density of ion current more than J = 2 μA/cm^2 *n*- type samples of $\rho \approx 10^3$-2×10^3 Ωcm resistivity were obtained. This is caused by self-annealing of radiation defects in the process of implantation.

The temperature of heat treatment T = 300 to 350°C was found to be enough for stimulation of diffusion in the crystal after ion implantation. The obtaining of *n*-type ZnO samples with $\rho \approx 10^9$ to 10^{10} Ωcm corresponds to the establishment of equilibrium between the crystal and molecular oxygen atmosphere at this temperature. The PL spectra of implanted ZnO samples were investigated. In PL spectra of ZnO ($\rho \approx 10^9$ to 10^{10} Ωcm) samples obtained by implantation of S^+ ions (T = 300-350°C; in O_2) λ = 390 nm (λ = 385 nm, λ = 400 nm); λ = 440 nm; λ = 460 nm and λ = 505 nm peaks were observed (Fig.2). In our opinion, these peaks correspond to (V_{Zn}^--V_O^{++}); V_O^{++}; AX^+;V_{Zn}^-; V_O^+ , respectively.

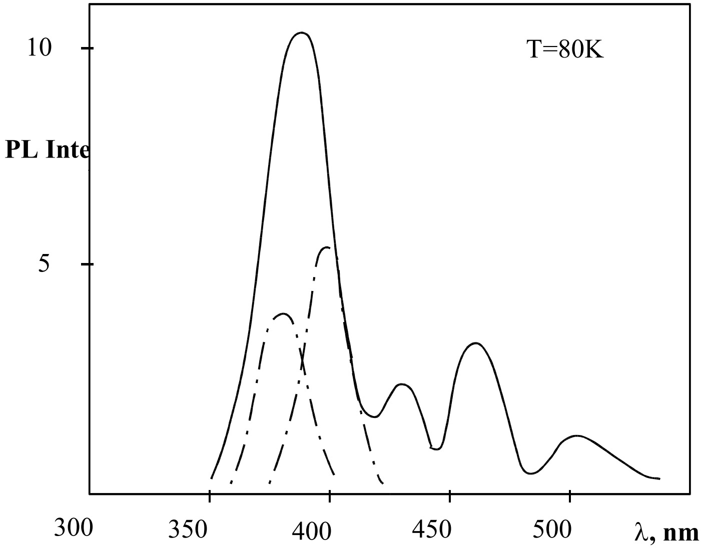

Fig.2. PL spectra of implanted ZnO by S^+ ions

In order to identify defects responsible for the bands observed in the PL spectra we consider the mechanisms of defects creation in ZnO. As it was mentioned *n*-type ZnO was taken as an initial basic crystal. It is obvious that the quality of donor type defects such as V_O, V_O^+ and Zn_i should be high in it. Creation of zinc vacancy is high in the area where defect already exists, in particular near to V_O^+. In the PL spectrum λ = 460 nm line might be connected with V_{Zn}^-. The low intensity of this line may be explained with the low electron capture cross-section. The λ = 390 nm line is characterized with wide half width and it changes the shape according to the excitation conditions. It indicates, that the line does not have the elementary structure. We disintegrated the line and we received two elementary peaks with maxima at λ = 385 nm and λ = 400 nm wavelength. Proceeding from local electro-neutrality the recharging of one charged oxygen vacancies V_O^+ into double charged ones V_O^{++} must occur. The latter has a wide capture cross-section, and consequent peak growth must be observed in the PL spectrum. Indeed, the growth of λ = 400 nm line and the reduction of λ = 505 nm line define this process. Radiation of λ = 400 nm line is connected with electron transition from the conductivity band to the V_O^{++} center. Radiation of λ = 505 nm line is connected with transition of electron from conductivity band to V_O^+ level. The growth of V_{Zn}^- and V_O^{++} must stimulate formation of their complex (V_{Zn}^--V_O^{++}). The λ = 385 nm line in PL spectrum is connected with transition to this center from the conductivity band.

We think that the implantation of sulfur in ZnO samples causes the formation of AX^+ centers. This is proved by the existence of λ = 440 nm peak in PL spectrum. The peak λ = 440 nm registered in PL spectrum is connected with the formation of AX^+ complex defect center initiated by interstitial sulfur. The mechanism of formation of complex defect initiated by impurity center at implantation of sulfur in ZnO can be presented as follows: when sulfur occupies the interstitial site AX^+ center should be formed in case of S_i relaxation [6,7]. First S_i captures the valence electron (from valence band) causing the formation of anion-cation O-Zn pairs, and as a result S_i releases 2e into conduction band and sulfur is charged positively. Thus, sulfur implanted in ZnO acts as a donor. We think that the obtained AX^+ complex defect first captures a free hole and then a free electron from the valence band resulting in the formation of center bound exciton.

In PL spectrum of ZnO implanted by S^+, a band with maximum on $\lambda = 440$nm has been observed additionally; the case was not observed in PL spectrum of ZnO obtained on ZnS base. Thus, there is no diffusion of sulfur in new layers of ZnO during the RBQE.

An important feature of RBQE method is the fact, that on the one hand the obtained ZnO is a protective layer for ZnS, i.e. it can inhibit S and allows to extract Zn only. As a result the conductivity type inversion in surface layers is possible. On the other hand, at fixed oxygen concentration control of concentration of Zn extraction from ZnS by temperature change is possible, which enables electrical and optical properties of new layers to vary in wider range. The obtained semiconductive ZnO layer not only inhibits S in ZnS, but prevents inclusion of oxygen occurring in gas phase in ZnS. Thus, it has been shown that it is possible by the RBQE method to achieve the conductivity type inversion with the aid of semiconductor ZnO protective layer. Thus, the obtained ZnO serves as a protective layer.

In that way, we can conclude that when obtaining ZnO layers on ZnS base by RBQE neither sulfur atoms diffusion in the obtained layers nor oxygen atom implantation in the basic crystal takes place. This points out higher effectiveness of RBQE method.

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