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Photoluminescence and electrophysical properties of *p*-type ZnO layers implanted with V Group elements

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Ion implantation of arsenic and nitrogen into zinc oxide film (As and N being acceptor impurities in ZnO) has been shown to result in formation of the hole conductivity only if the film is annealed in the presence of oxygen radicals. The ion implantation and subsequent anneal influence not only the electric properties but also the photoluminescence spectra of $ZnO:Ga:As^+$ ($ZnO:Ga:N^+$) layers. The luminescence bands due to As and N introduction appear in the UV and visible spectral regions.

Показано, что ионная имплантация мышьяка (азота) в пленку оксида цинка (As и N как акцепторная примесь в ZnO) может приводить к формированию дырочного типа проводимости только в случае отжига в атмосфере радикалов кислорода. Ионная имплантация и последующий отжиг влияют не только на электрические свойства слоев $ZnO:Ga:As^+$ ($ZnO:Ga:N^+$), но и на их спектры фотолюминесценции. Полосы люминесценции, которые вызваны внедрением As и N, наблюдаются в ультрафиолетовой и видимой областях спектра.

Zinc oxide is among the most popular semiconductor materials and is used in devices operated in surface acoustic waves, integral optic elements, gas sensors, and solar converters. Of a special interest is the ZnO application as a material for lasers and diode structures emitting in blue and UV spectral regions. Among the wide-band A^2B^6 semiconductors, ZnO having the band gap width 3.437 eV at 2 K [1] is very similar to GaN ($E_g \approx 3.5$ eV) in its optical and electrophysical properties. The main ZnO advantage over GaN consists in the high exciton binding energy (60 meV) that provides an efficient exciton luminescence at room temperature. Both *n*- and *p*-type conductance ZnO materials are necessary to develop optical devices. However, it is difficult today to provide the *p*-conductive material [2] because the impurity-free ZnO films prepared by any method show the *n*-type conductance due to the great number of intrinsic donor defects, such as zinc interstitials (Zn_i) or oxygen vacancies (V_O) [3].

High-quality single-crystalline ZnO films have been synthesized using the MBE method with N radicals acting as the *p*-type impurity [4]. Although the N concentration (as measured by SIMS) is about 10^{19} cm^{-3}, no changes in the conductance type were observed. In the opinion of the authors, this is associated with formation of deep traps based on defects bound to nitrogen. The *p*-type ZnO films doped with V Group elements (N, As) with hole concentration about 10^{19} cm^{-3} were obtained [5, 6]. The film X-ray diffraction pattern show an intense narrow ZnO (0002) peak evidencing a high crystal perfection and strong film orientation along the *c* axis. The films were doped

with nitrogen in the course of growing by addition of N_2O and simultaneous usage of Ga as a co-dopant. The authors note that the *p*-type activation is due only to the fact that introduction of the donor impurity favors the increased solubility of nitrogen. The double doping, however, causes a sharp drop of the current carrier mobility down to 0.05 $cm^2/(V{\cdot}s)$. In [6], the *p*-type ZnO films have been obtained on *n*-type GaAs substrate. The *p*-type ZnO is formed due to thermal diffusion of the substrate components into the ZnO film at the annealing temperature of 723 K. The hole concentration, as determined from the Hall effect measurements, attains 10^{18} to 10^{19} cm^{-3} at the carrier mobility of about 0.1 to 10 $cm^2/(V{\cdot}s)$, respectively. The authors contend that As is a more prospective dopant in ZnO than N, since their attempts to obtain the *p*-type ZnO using N were unsuccessful. There are some reports to *p–n* transitions obtained using zinc oxide doped with donor and acceptor impurities [7, 8]. The work [9] is the only one that reports an emitting homo-*p–n* transition based on ZnO. The diodes prepared, however, showed a weak electroluminescence in the wavelength range of 400 to 900 nm, while undoped ZnO films show an intense photoluminescence in the bound exciton region at 370 nm. The wide electroluminescence region, as the authors suppose, may be due to intrinsic and extrinsic defects in the *p–n* transition region. The purpose of this work is to study the effect of annealing in oxygen radical atmosphere on As- and N-doped ZnO films. The use of oxygen radicals [10, 11] provides the highest possible effective oxygen pressure over the film and makes it possible to shift the material stoichiometry towards oxygen excess, thus reducing the concentration of intrinsic donor defects.

The photoluminescence (PL) and electrophysical properties of $ZnO{:}Ga{:}N^+$ and $ZnO{:}Ga{:}As^+$ films were examined in this work. The initial Ga-doped ZnO films were prepared by the MOCVD on the amorphous SiO_2 substrate at 620 K. The film thickness as measured using a MII-4 microscope was 0.5 to 1 μm. The X-ray diffraction was measured using a DRON-2 instrument in Cu K_α emission. The diffraction pattern evidence the ZnO (0002) orientation without any reflections characteristic of other orientations. As determined using the Hall effect, the layers possess the *n*-type conductivity at the carrier concentration of 10^{17} cm^{-3} and mobility of 120 $cm^2/(V{\cdot}s)$ at room temperature. The As(N) impurity was introduced by ion implantation at $1{\cdot}10^{19}$ to $5{\cdot}10^{21}$ cm^{-3} doses. The implanted ion energy was 100 to 200 keV. The impurity distribution in the implanted layer was controlled by the SIMS method. The conductivity type of the implanted layers was determined by the Hall method. The conductivity was measured using four-probe technique. For the *n*-type layers, aluminum contacts were used while for the *p*-type ones, gold. The contacts were deposited in a VUP-5 unit. To eliminate the radiation-induced defects, to control the intrinsic defect composition, and to shift the stoichiometry towards oxygen excess, the $ZnO{:}Ga{:}N^+$ and $ZnO{:}Ga{:}As^+$ films were annealed for 30 min in oxygen radical atmosphere within the temperature range of 573 to 1273 K. The PL spectra of the films were examined at helium temperatures using a nitrogen pulse laser ILGI-503 as the excitation source. The oxygen radicals were produced in a HF discharge of 40 W power under molecular oxygen pressure of 0.1 to 10 Pa. The ion component was separated out of oxygen plasma using a magnetic field so that only oxygen radicals attained the film surface. The oxygen radical flow near the substrate surface was 10^{16} to 10^{17} $cm^{-2}{\cdot}s^{-1}$.

Fig. 1 presents the spectrum of initial ZnO:Ga films. An intense peak at 3.36 eV is observed in the spectrum as well as phonon repetitions peaked at 3.29, 3.21, and 3.14 eV. The optical phonon energy is about 72 meV. In the visible region, there is a wide band peaked at 2.28 eV. The 3.36 eV peak is ascribed to annihilation of excitons localized at neutral donors. The dependence of spectra for implanted $ZnO{:}Ga{:}As^+$ and $ZnO{:}Ga{:}N^+$ layers annealed at 773 K on the implanting dose is shown in Figs. 1 and 2, respectively. As to $ZnO{:}Ga{:}As^+$ films, 3.33 and 3.25 eV peaks appear at the dose of $1{\cdot}10^{19}$ cm^{-3} dose (Fig. 1c). The intensity of those peaks increases with the implanting dose. As the dose rises up to $5{\cdot}10^{21}$ cm^{-3}, the 3.33 eV PL band intensity drops. In PL spectra of $ZnO{:}Ga{:}N^+$ layers, new bands appear in the blue region at 3.07, 3.14, and 3.22 eV as well as an UV emission peak at 3.29 eV ascribed to exciton possibly localized at an acceptor (Fig. 2a). The PL band intensity dependence on the implanting dose is similar to that observed for $ZnO{:}Ga{:}As^+$ films.

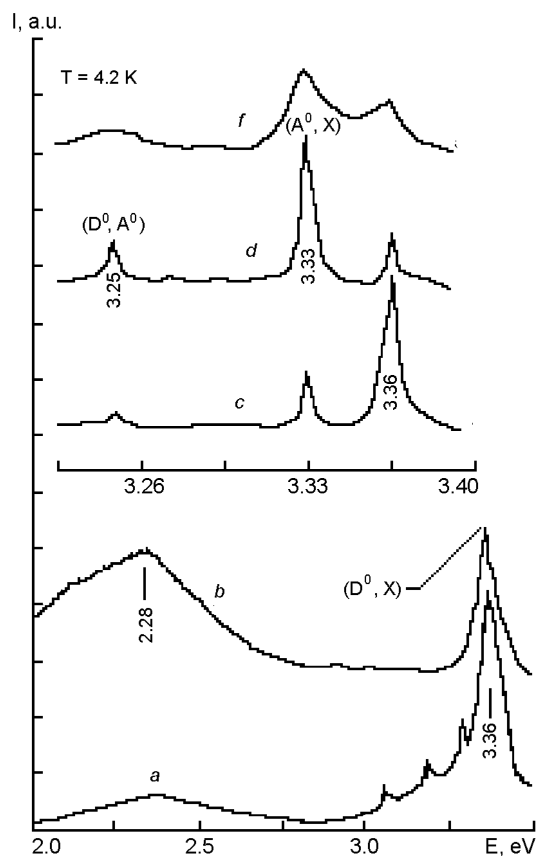

Fig. 1. PL spectra of initial ZnO:Ga films (a); those implanted with As+ (10^{19} cm^{-3} dose) and annealed in molecular oxygen at 773 K (b); those implanted with As^+ and annealed in oxygen radicals at 773 K, the implantation doses (cm^{-3}): $1\cdot10^{19}$ (c), $3\cdot10^{20}$ (d), $5\cdot10^{21}$ (f).

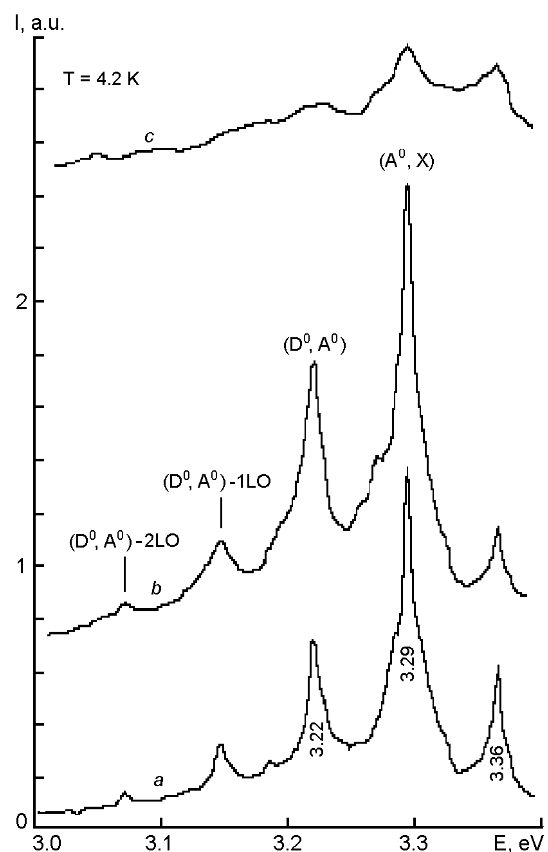

Fig. 2. PL spectra of $ZnO:Ga:N^+$ films annealed in oxygen radicals at 773 K, the implantation doses (cm^{-3}): $1\cdot10^{19}$ (a), $3\cdot10^{20}$ (b), $5\cdot10^{21}$ (c).

As compared to the initial ZnO films (Fig. 1a), additional peaks in the region of acceptor-bound excitons at 3.33 eV (Fig. 1c) and 3.29 eV (Fig. 2a) are seen in the spectra of all the As and N implanted ZnO films. It is to note that the annealing under molecular oxygen atmosphere does not cause any additional PL bands in the implanted ZnO film spectra (Fig. 1b). The experimental results presented above allow us to ascribe the 3.33 and 3.29 eV peaks to the exciton recombination at the (A^0,X) acceptor impurity (As_O and N_O) localized in the oxygen sublattice. Those peaks are present only in the PL spectra of doped films $ZnO:Ga:As^+$ and $ZnO:Ga:N^+$, respectively. In $ZnO:N^+$ films, a band peaked at 3.27 eV was observed [12] that is associated with recombination of excitons localized at accepting nitrogen atoms substituting for oxygen.

Theoretically estimated ionization energy of neutral acceptor $E_A = 13.6m_h^*/m_0\varepsilon_0^2$ (where the effective hole mass $m_h^* = 0.73m_0$ and low-frequency dielectric constant $\varepsilon_0 = 8.75$ [12]) is about 130 meV. The ionization energy of the acceptor center, as determined basing on temperature dependence of intensity for the 3.33 and 3.29 eV PL bands, is about 132 meV and 158 meV for As_O and N_O, respectively. The maximum intensity of those peaks is attained at annealing temperature of about 900 K. At low annealing temperatures, the impurities act obviously as the substitution defects and as inclusion ones. The elevation of annealing temperature results in an efficient reconstitution of the crystal lattice and introduction of the impurity atoms into the oxygen sublattice. The implantation dose increase results in reduced intensity of the observed spectral bands. This evidences formation of numerous intrinsic defects (being non-radiative recombination centers) at high implantation doses. The band peaked at 3.22 eV (3.25 eV) observed at low temperatures in PL spectra of $ZnO:Ga:N^+$ ($ZnO:Ga:As^+$) films

Table. Resistivity and conductivity type of ZnO:Ga:As$^+$ (ZnO:Ga:N$^+$) films annealed in oxygen radicals as a function of annealing temperature

Sample	Implantation dose, cm^{-3}	Annealing temperature, K				
		673	773	873	973	1073
		Resistivity, Ω·cm				
ZnO:Ga:As$^+$	$1\cdot10^{19}$	$4.5\cdot10^3$ (*n*)	$7.4\cdot10^2$ (*p*)	120 (*p*)	$5.2\cdot10^4$ (*n*)	$2\cdot10^6$ (*n*)
	$3\cdot10^{20}$	$5\cdot10^3$ (*p*)	70 (*p*)	37 (*p*)	$3\cdot10^4$ (*n*)	$4.3\cdot10^5$ (*n*)
	$5\cdot10^{21}$	$1.3\cdot10^3$ (*p*)	42 (*p*)	20 (*p*)	$4.8\cdot10^3$ (*n*)	$1.5\cdot10^5$ (*n*)
ZnO:Ga:N$^+$	$1\cdot10^{19}$	$7\cdot10^3$ (*n*)	$1\cdot10^3$ (*p*)?	320 (*p*)	$3.5\cdot10^4$ (*n*)	$6\cdot10^5$ (*n*)
	$3\cdot10^{20}$	$2.2\cdot10^3$ (*n*)	65 (*p*)	43 (*p*)	$2.1\cdot10^4$ (*n*)	$2\cdot10^6$ (*n*)
	$5\cdot10^{21}$	$3\cdot10^3$ (p)?	83 (*p*)	30 (*p*)	$3.3\cdot10^3$ (*p*)?	$7\cdot10^5$ (*n*)
ZnO:Ga:N$^+$	$1\cdot10^{20}$	$3.2\cdot10^4$ (*n*)	$2.8\cdot10^5$ (*n*)	$1\cdot10^6$ (*n*)	∞	∞

Note: The ZnO:Ga:N$^+$ sample ($D = 1\cdot10^{20}$ cm^{-3}) has been annealed in molecular oxygen.

is related to recombination of carriers at donor-acceptor couples (DAC) (D^0,A^0), see Figs. 1c, 2a. The temperature dependence of the 3.22 eV (3.25 eV) band shows its dropping intensity and the peak shift towards shorter wavelengths. Such a temperature dependence is typical of DAC transitions that are transformed into the free acceptor-electron (e, A^0) ones at temperatures exceeding 80 K when the small donors included into the couple are thermally ionized [14].

The dependence of ZnO:Ga:As$^+$ (ZnO:Ga:N$^+$) film electric conductivity on the annealing conditions is presented in the Table. The specific resistance of the films is observed to drop when the annealing is done in the 673 to 873 K interval. The resistivity reduction is due to changes in the intrinsic and impurity defect composition of the implanted layers. No conductivity type inversion is observed when the annealing is done at 673 K. In this case, it is just the deep donor levels V_O that are the main centers compensating the *p*-type impurity. This is confirmed by the green band peaked at 2.3 eV in the PL spectra, that band being related to oxygen vacancies fored as F^+ centers [15]. It is seen from the Table that the implanted layers annealed in 773 to 873 K temperature range show the *p*-type conductivity, the resistivity amounting 20 Ω·cm.

It is to note that in our experiments, the implanted layer resistivity is much lower than in [12]. At low annealing temperatures, a higher resistivity is observed that can be explained by the fact that the temperature is insufficient to provide the diffusion of intrinsic and extrinsic defects. In 773 to 873 K temperature range, the resistivity is 20 to 40 Ω ·cm. According to [16], the Ga impurity favors the N solubility, the latter increasing sharply at Ga concentrations 10^{20} cm^{-3} or higher. Nitrogen oxide was used as the *p*-type impurity. It is to note that the *p*-type conductivity is observed only if N_2O is activated by a HF discharge. Unlike the results from [3, 5, 16], in our opinion, the use of nitrogen oxide and gallium provides the positive effect, in first turn, due to introduction of excess oxygen (being a component of N_2O plasma) into the film. This hinders the formation of intrinsic donor defects compensating the acceptors caused by oxygen.

Fig. 3 presents the SIMS profile of the impurity distribution for *p*–ZnO:Ga:N$^+$ films. The SIMS data confirm the supposed enrichment of ZnO films in oxygen during the annealing. The O:Zn ratio is 1.06:1. These data agree well with results [17] where the annealing of ZnO films in air has been found to favor the film enrichment in oxygen, as determined by X-ray photoelectron spectroscopy. The authors believe that the excess oxygen is in free state, i.e., as interstitial oxygen. The annealing temperature elevation above 900 K results in an increased resistivity. This means an increased concentration of intrinsic donor defects that compensate the acceptors. It has been shown [11] that there is a critical temperature for A^2B^6 compound annealing in chalcogene vapors, the exceeding thereof doing not result in hole conductivity. The critical temperature for ZnO in oxygen radical flow of 10^{16} cm^{-2}·s^{-1} is estimated theoretically to be of 850 K [18], that agrees well with the experiment. At temperatures

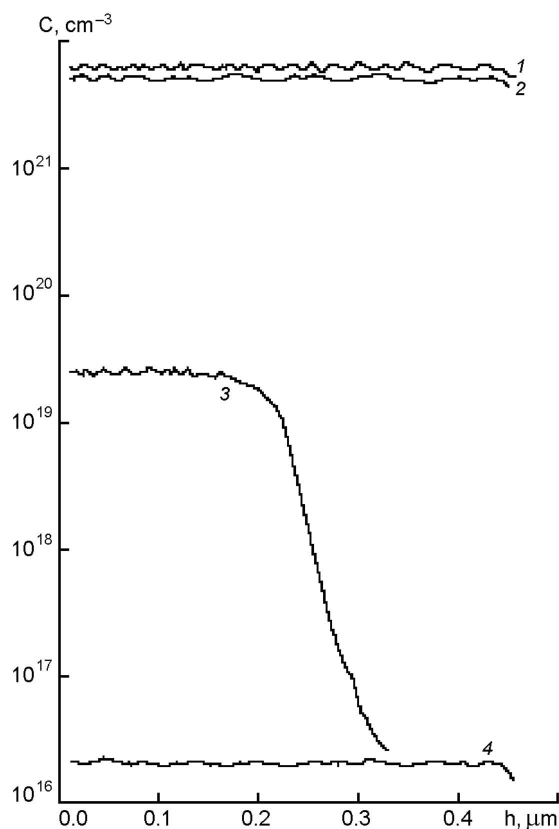

Fig. 3. SIMS profile of nitrogen impurity distribution in $ZnO:Ga:N^+$ films implanted at $2\cdot10^{20}$ dose and annealed in oxygen radicals at 773 K (*1* $-O_{18}$, *2* – Zn_{64}, *3* – N_{14}, *4* – Ga_{69}).

exceeding 1000 K, the dopant is observed to be evaporated [19]. At a further elevation of annealing temperature up to 973 K, the resistivity increases up to $10^4\ \Omega\cdot$cm. The annealing in molecular oxygen atmosphere does not result in the conductivity type inversion, independent of the As (N) impurity concentration. It has been shown in [11] that the use of chalcogene radical atmosphere at the annealing increases the effective pressure of the atomic chalcogene by more than 5 decimal orders. This results in the conductivity type inversion in $ZnO:Ga:As^+$ ($ZnO:Ga:N^+$) films. The *p*-type ZnO films annealed at 873 K show the lowest resistivity. The films doped with As (N) at $5\cdot10^{21}$ cm^{-3} concentration have the carrier concentration of $3.1\cdot10^{21}$ cm^{-3} ($1.3\cdot10^{21}$ cm^{-3}) and mobility of 2 cm^2/(V·s) (1.1 cm^2/(V·s)), respectively. The further elevation of the annealing temperature in oxygen radical atmosphere results in increasing resistivity and *n*-type conductivity.

Thus, we have studied the effect of annealing in oxygen radical atmosphere on PL and electrical properties of ZnO layers implanted with As and N ions. The PL bands peaked at 3.33 and 3.29 eV are due to exciton recombination at As_O and N_O acceptor centers, respectively. The energy levels of the acceptor centers are 130 meV for arsenic and 150 meV for nitrogen. ZnO layers of *p*-type have been obtained when annealed at 773 to 873 K. The acceptor impurity is activated only if being annealed in oxygen radical atmosphere.

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Фотолюмінесцентні та електрофізичні властивості шарів ZnO *p*-типу імплантованих елементами V групи

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Показано, що іонна імплантація миш'яку (азоту) у плівку оксиду цинку (As і N як акцепторна домішка у ZnO) може приводити до формування діркового типу провідності тільки у випадку відпалу в атмосфері радикалів кисню. Іонна імплантація і наступний відпал впливають не тільки на електричні властивості шарів $ZnO:Ga:As^+$ ($ZnO:Ga:N^+$), але й на їхні спектри фотолюмінесценції. Смуги люмінесценції, що викликані впровадженням As і N, спостерігаються в ультрафіолетовій і видимій областях спектра.