
THE INFLUENCE OF ANNEALING IN THE ATMOSPHERE OF ATOMIC OXYGEN ON THE PHOTOLUMINESCENCE OF ZnO LAYERS IMPLANTED BY As AND N

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It is shown that the implantation of films of Zn oxide by acceptor admixtures of arsenic and nitrogen with the subsequent annealing in the atmosphere of atomic oxygen leads to a change in the spectra of photoluminescence (PL). The PL spectra reveal the bands with maxima at 3.33 and 3.29 eV which are caused by the implantation of As and N, respectively.

1. Introduction

Zinc oxide is widely applied in optoelectronics due to the high electron conductivity and optical transparency. Alloyed with donor admixtures (Al and Ga), it is traditionally used as a transparent contact that has high radiative, chemical, and thermal resistance. However, of special interest is the application of ZnO as a base material to create the structures used in lasers and diodes and emitting in the blue and ultraviolet spectral regions.

Among wide-gap semiconductor compounds A^2B^6 , ZnO possessing a forbidden gap width of 3.437 eV at 2 K [1] is very similar to GaN ($E_g \approx 3.5$ eV) by its optical and electrophysical properties. The main advantage of ZnO consists in the great binding energy of an exciton (60 meV), which allows one to derive the efficient exciton luminescence at room temperature.

To develop optical devices on the base of ZnO, it is necessary to possess high-quality materials of both the n - and p -types of conductivity. There appeared a number of reports on the growing of ZnO of the n -type with the use of elements of group III such as Al, Ga, and In [2, 3]. However, the derivation of a material of the p -type is a complicated technological problem even now [4]. This is related to that undoped films of ZnO derived by any method have the n -type of conductivity at the expense of a great number of intrinsic defects-donors like interstitial zinc, Zn_i , or oxygen vacancies, V_O [5].

The possibility to derive ZnSe with the n -type of conductivity was demonstrated for the first time in [6] by means of the alloying by N radicals during the growing by the methods of MBE and MOCVD [7, 8]. This allowed

one to first derive ZnSe-based blue and blue-green high-quality laser diodes [9, 10].

The authors of work [11] synthesized high-quality ZnO films by the MBE method with the use of nitrogen radicals. Though the concentration of N was about $1 \times 10^{19} \text{ cm}^{-3}$ by the data of the SIMS analysis, no change in the type of conductivity was observed. In authors' opinion, this is related to the creation of deep traps on the basis of N-involved defects. Recent years, there appeared the communications [12, 13] on the derivation of epitaxial ZnO films of the p -type which were alloyed by elements of group V (N, As) with a concentration of holes $\sim 10^{19} \text{ cm}^{-3}$. The alloying with N was realized [12] in the process of growing of ZnO films by means of the addition of N_2O and the simultaneous use of Ga as a coactivator. The application of molecular nitrogen N_2 did not induce the hole conductivity. The authors noted that the activation of the p -type of conductivity occurred only at the expense of an increase in the solubility of N due to the introduction of a donor admixture. However, the twofold alloying leads to a sharp decrease in the current carrier mobility up to $0.05 \text{ cm}^2/(\text{V}\cdot\text{s})$. In our opinion, the use of N_2O and Ga gives the positive effect due to, first of all, the introduction of excessive oxygen in a film. The point is in that the deficiency of oxygen in ZnO induces the appearance of intrinsic defects of the donor type (interstitial Zn and vacancies of oxygen) which compensate the acceptors conditioned by N.

In work [13], the layers of ZnO of the p -type were derived on a substrate of GaAs of the n -type. The authors noticed that ZnO of the p -type appeared as a result of the thermal diffusion of components of the substrate into the ZnO film at an annealing temperature of 723 K. According to the data of measurements of the Hall effect, the concentration of holes reaches $10^{18} \div 10^{19} \text{ cm}^{-3}$ with the mobility of carriers $\sim 0.1 - 10 \text{ cm}^2/(\text{V}\cdot\text{s})$, respectively. By the authors' assertion, As is a more promising acceptor for ZnO as compared to N, because

their attempts to derive ZnO of the p -type with the use of N were unsuccessful.

We mention the appearance of the first communications on the derivation of p - n junctions on the base of ZnO alloyed by donor and acceptor admixtures [14, 15]. Only a single work [16] has reported on the derivation of LEDs by using a ZnO-based homo- p - n junction. However, the derived diodes manifested a weak electroluminescence in the wavelength range 400–900 nm, whereas undoped ZnO films revealed the intense ultraviolet photoluminescence in the region of bound excitons at a wavelength of 370 nm. In the authors' opinion, such a wide region of electroluminescence can be caused by intrinsic and admixture defects being present in the LED structure. Thus, it is necessary to activate an alloying admixture in such a way that it would cause the necessary value and type of conductivity and not decrease the luminescence intensity.

The purpose of the present work is to study the influence of the annealing in the atmosphere of oxygen radicals (atoms) on the luminescent properties of ZnO films alloyed with As and N. The use of oxygen radicals [17, 18] gives the maximum possible effective pressure of oxygen above a film and allows one to change the stoichiometry of a material to the side of the excess of oxygen by decreasing the concentration of intrinsic defects of the donor type.

2. Experimental Procedure

Here, we study PL of ZnO:As⁺ and ZnO:N⁺ films. The initial ZnO films alloyed with Ga were derived from the gaseous phase on the substrate of amorphous SiO₂ at a temperature of 620 K. The thickness of the films was measured with a microscope MII-4. According to the data on the Hall effect, the layers have the n -type of conductivity with a concentration of carriers equal to $2 \times 10^{17} \text{ cm}^{-3}$ and a mobility of $120 \text{ cm}^2/(\text{V}\cdot\text{s})$ at room temperature.

The admixture of As and N was introduced by means of the ion implantation by doses in the range $1 \times 10^{19} - 5 \times 10^{21} \text{ cm}^{-3}$. The energy of implanted ions was 100–200 keV. The distribution of the admixture in the implanted layer was controlled by the SIMS analysis. The type of conductivity of the implanted layers was determined by the sign of thermo-EMF.

With the purpose to eliminate radiation-induced defects, to recover a crystal structure, and to control both the composition of intrinsic defects and the deviation of a stoichiometry to the side of the excess of oxygen, we carried out the post-implantation annealing.

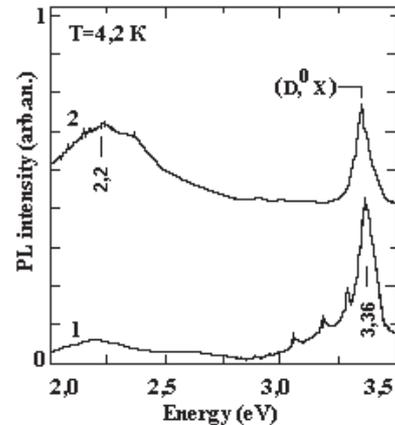


Fig. 1. PL spectra of initial ZnO:Ga films (1) and those implanted by As⁺ ([As]= $1 \times 10^{19} \text{ cm}^{-3}$) (2) and annealed in the atmosphere of molecular oxygen at 773 K

ZnO:As⁺ and ZnO:N⁺ films were annealed for 30 min in the atmosphere of oxygen radicals (atoms) in the temperature interval 570–1270 K. Under equilibrium conditions of the annealing, the partial pressure of atomic oxygen is defined by the reaction $\text{O}_2 = 2\text{O} + D$, $K_D = P_{\text{O}}^2/P_{\text{O}_2}$, where D is the dissociation energy of a molecule of oxygen. Since this energy is equal to 5.16 eV, the partial pressure of atomic oxygen, $P_{\text{O}} = K_D^{1/2} \exp(-D/2kT) P_{\text{O}_2}^{1/2}$, was low at the used annealing temperatures. In our work, the pressure of atomic oxygen was increased due to the dissociation of oxygen molecules by a HF-discharge. Upon the dissociation of 0.01% of oxygen molecules at the pressure $P_{\text{O}_2} = 1 \text{ Pa}$, the pressure of atomic oxygen was $P_{\text{O}} = 0.01 \text{ Pa}$. Such a pressure of atomic oxygen can be reached at the expense of the thermal dissociation of molecular oxygen at 1000 K and the pressure $P_{\text{O}_2} = P_{\text{O}}^2/K_D \approx 10^{11} \text{ Pa}$.

Atomic oxygen was derived in a HF-discharge of 200 W in power at a pressure of molecular oxygen equal to 0.1–10 Pa. The ion component of the oxygen plasma was separated by a magnetic field so that only atomic oxygen or radicals reached the film surface. The concentration of atomic oxygen near the ZnO film surface was $10^{16} - 10^{17} \text{ cm}^{-3}$. The PL spectra of the films were studied at liquid-helium temperatures. An N-based pulse ILGI-503 laser was used as an exciting source.

3. Experimental Results

In Fig. 1, we present the spectrum of initial ZnO:Ga films. The spectrum contains the intense 3.36-eV peak and phonon recurrences with maxima at 3.29, 3.21, and

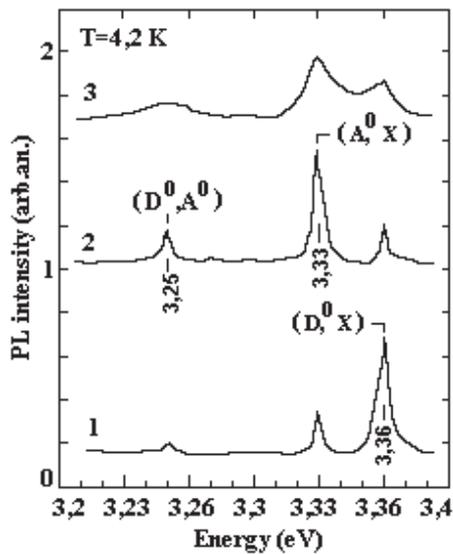


Fig. 2. PL spectra of ZnO:As⁺ films annealed in the atmosphere of oxygen radicals at 673 K. The implantation doses are $1 \cdot 10^{19}$ (1), $3 \cdot 10^{20}$ (2), and $5 \cdot 10^{21}$ cm⁻³ (3)

3.14 eV. The optical phonon energy was ≈ 72 meV. In the visible region, we observe a wide band with a maximum at 2.2 eV. The 3.36-eV peak is related to the annihilation of excitons localized at neutral donors.

The dependence of the PL spectra of implanted ZnO:As⁺ and ZnO:N⁺ layers which were annealed at 673 K on the implantation dose is presented in Figs. 2 and 3, respectively. At a dose of $1 \cdot 10^{19}$ cm⁻³, the peaks at 3.33 and 3.25 eV appear in the PL spectrum of ZnO:As⁺ films (Fig. 2, curve 1). The intensity of the 3.33- and 3.25-eV peaks increases with the implantation dose (Fig. 2, curve 2). With increase in the dose up to $5 \cdot 10^{21}$ cm⁻³, we observe a decrease in the intensity of PL of the 3.33-eV band.

In the PL spectra of ZnO:N⁺ layers, there appear new bands in the blue spectral region at 3.07, 3.14, and 3.22 eV and the ultraviolet emission peak at 3.29 eV which are due to excitons probably bound on acceptors (Fig. 3, curve 1). The dependence of the intensity of the PL bands on the implantation dose is similar to that for ZnO:As⁺ films.

It is interesting to trace the influence of the annealing temperature on PL of implanted layers. In Fig. 4, we show the dependence of the PL spectra of ZnO:As⁺ layers on the annealing temperature in the interval 673–1273 K. The layers were implanted with a dose of $3 \cdot 10^{20}$ cm⁻³. In the temperature interval 673–873 K, the annealing led to an increase in the intensity of the

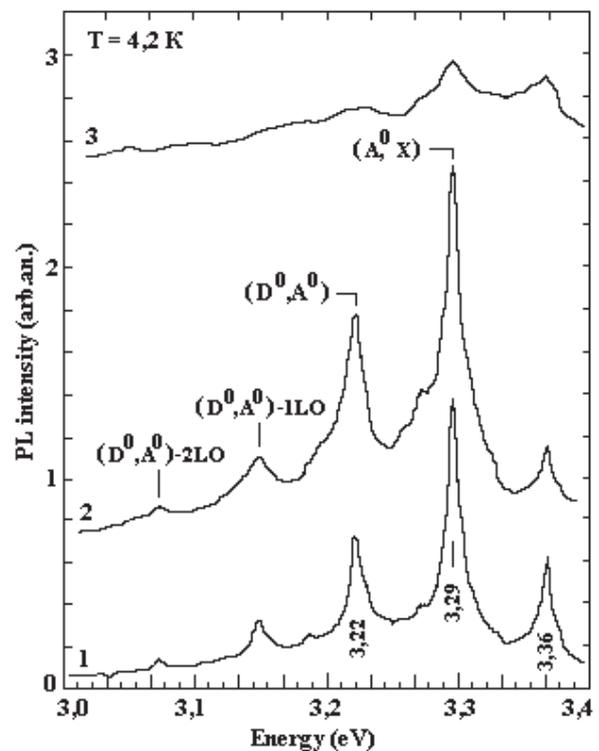


Fig. 3. The same as in Fig. 2 for ZnO:N⁺ films

3.33-eV line (curves 1, 2). With increase in temperature above 973 K, the intensity of the 3.33-eV peak decreases.

In the PL spectra of ZnO:N⁺ layers implanted by a dose of $5 \cdot 10^{20}$ cm⁻³, we observe the decrease in the intensity of blue bands with increase in the annealing temperature of films from 673 to 1273 K. The intensity of the 3.29-eV peak grows with the annealing temperature up to 900 K. At $T_{\text{anneal}} > 1070$ K, the intensity of the 3.29-eV peak decreases sharply. The maximum implantation dose of $5 \cdot 10^{21}$ cm⁻³ (Figs. 2, 3) leads to a weak luminescence of films for all annealing temperatures.

As compared to the initial ZnO films (Fig. 1), the presence of additional peaks in the region of excitons bound on acceptors with the maxima at 3.33 eV (Fig. 2) and 3.29 eV (Fig. 3) in the spectra of all ZnO films implanted by As and N, respectively, is obvious. It is worth noting that the annealing in the atmosphere of molecular oxygen does not lead to the appearance of the additional bands of PL in the spectra of implanted ZnO films (Fig. 1, curve 2). In correspondence with the sign of thermo-EMF, the implanted layers of ZnO annealed in the atmosphere of atomic oxygen in the temperature range 673–900 K have the *p*-type of conductivity.

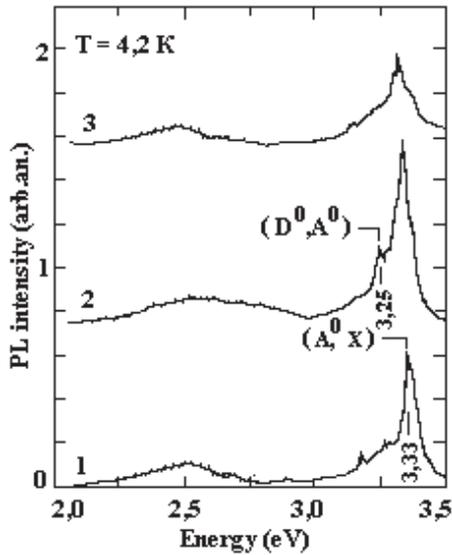


Fig. 4. PL spectra ZnO:As⁺ films implanted by a dose of $3 \times 10^{20} \text{ cm}^{-3}$ after the annealing in the atmosphere of oxygen radicals at temperatures 673 (1), 873 (2), and 1173 K (3)

4. Discussion of the Results

The experimental results presented above allow us to relate the peaks at 3.33 and 3.29 eV to the recombination of excitons on the acceptor (A°, X), i.e. the admixture of arsenic, As_O , and nitrogen, N_O , localized in the sublattice of oxygen. These peaks are present only in the PL spectra of alloyed ZnO:As⁺ and ZnO:N⁺ films, respectively. By studying ZnO:N⁺ films at 80 K, the authors of work [19] observed a band with a maximum at 3.27 eV which is related, in the authors' opinion, to the recombination of excitons localized at acceptors N_O .

In compounds A^2B^6 , an exciton bound to a neutral acceptor can be represented in the form of a hydrogen molecule under condition $m_h^* \gg m_e^*$ (upper energy limit) or a hydrogen ion (H^-) for $m_h^* \leq m_e^*$ (lower energy limit) [20]. Then the binding energy of an exciton and a neutral acceptor lies in the scope $0.055E_A < E_e^A < 0.33E_A$, where $E_A = \frac{13.6m_h^*}{m_0\epsilon_0^2}$ eV is the ionization energy of a neutral acceptor. By using the effective mass of a hole $m_h^* = 0.73m_0$ and the low-frequency permittivity $\epsilon_0 = 8.75$ [21], we get that the emission of the exciton bound to a neutral acceptor belongs to the region $3.28 \text{ eV} < \lambda_e^A < 3.36 \text{ eV}$.

The above-presented calculations demonstrate that the bands of bound excitons lie in the scope of expected positions of the line of excitons bound to neutral acceptors. The theoretical estimation of the ionization energy of a neutral acceptor gives the value $\approx 130 \text{ meV}$.

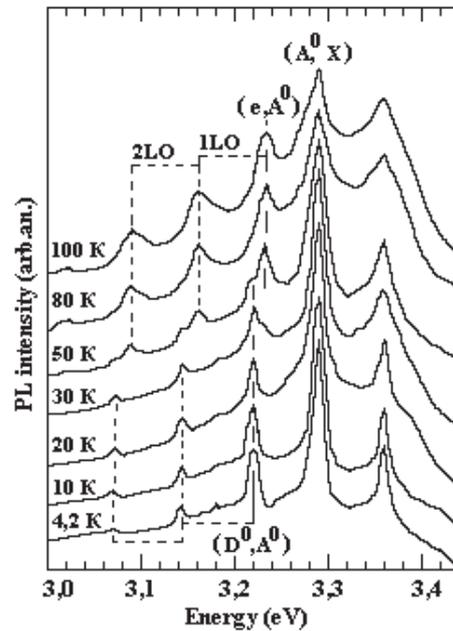


Fig. 5. Temperature dependence of the 3.22-eV PL band for ZnO:N⁺ films

The peaks attain the maximum intensity at $T_{\text{anneal}} \approx 900 \text{ K}$.

It is obvious that, at low annealing temperatures, some atoms of the admixture act as substitutional defects, and some ones do as interstitial defects. An increase in the annealing temperature leads to the efficient recovery of a crystal lattice and to the efficient introduction of admixture atoms into the sublattice of oxygen.

An increase in the implantation dose induces a decrease in the intensity of the observed bands. It is probable that, at high doses of the implantation, a great number of intrinsic defects which are radiationless centers of recombination is formed. An increase in the annealing temperature to 1270 K leads to the evaporation of an alloying admixture [22] and, as a consequence, to a decrease of the intensity of the peaks at 3.33 and 3.29 eV, respectively.

The band observed at low temperatures with a maximum at 3.22 eV (3.25 eV) in the PL spectra of ZnO:N⁺ (ZnO:As⁺) films is related to the recombination of carriers on donor-acceptor pairs (DAP) (D^0, A^0) (Fig. 5). With increase in the temperature of a specimen, the intensity of the 3.22-eV band decreases, and the peak position shifts to the short-wave spectral region. A similar dependence on temperature is typical of the DAP-transitions which are transformed into the free

electron—acceptor transitions, (e, A^0) , at temperatures higher than 80 K, when shallow donors belonging to the composition of a pair are thermally ionized. By using the position of the 3.22-eV peak, we may calculate the ionization energy of a neutral acceptor. The DAP-transition energy $E_{h\nu} = E_g - (E_A + E_D) + \frac{e^2}{\epsilon r}$, where E_g is the forbidden zone width, E_A and E_D are the ionization energies of an acceptor and a donor, respectively, and $e^2/(\epsilon r)$ is the Coulomb term taking the donor-acceptor interaction into account. In view of the fact that $E_D \approx 50$ meV and taking $\frac{e^2}{\epsilon r} \approx 10$ eV [23], we get $E_A \approx 170$ meV. This value is close to that calculated in [24]. It is probable that nitrogen localized in the sublattice of oxygen or a more complicated complex including nitrogen is responsible for the level with $E_A \approx 170$ meV. For the 3.25-eV band (ZnO:As^+), $E_A \approx 138$ meV. The activation of the p -type of conductivity is observed only in the case of the annealing in the atmosphere of oxygen radicals (atoms).

5. Conclusion

We have studied the influence of the annealing in the atmosphere of oxygen radicals on the PL properties of ZnO layers implanted with ions of As and N. It is established that the PL bands with maxima at 3.33 and 3.29 eV related to the recombination of excitons on acceptor states of As_O and N_O , respectively, arise only under conditions of the annealing in the atmosphere of oxygen radicals. The PL bands at 3.25 and 3.22 eV are conditioned by the DAP-transitions in ZnO films implanted by As and N, respectively. The energy levels of acceptor centers are $E_A \approx 138$ meV for As and $E_A \approx 170$ meV for N. As a donor with $E_D \approx 30 \div 50$ meV, the admixture of Ga_Zn or the vacancy V_O can be considered.

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ВПЛИВ ВІДПАЛУ В АТМОСФЕРІ АТОМАРНОГО КИСНЮ НА ФОТОЛЮМІНЕСЦЕНЦІЮ ШАРІВ ZnO , ІМПЛАНТОВАНИХ МИШ'ЯКОМ ТА АЗОТОМ

I.V. Rogozin

Резюме

Показано, що імплантація плівок оксиду цинку акцепторними домішками миш'яку і азоту з наступним відпалом в атмосфері атомарного кисню приводить до зміни спектрів фотолюмінесценції (ФЛ). В спектрах ФЛ спостерігаються смуги з максимумами 3,33 і 3,29 eV, зумовлені імплантацією миш'яку і азоту відповідно.