Investigation of MOVPE-grown GaN layers doped with As atoms

A. F. Tsatsul'nikov, B. Ya. Ber, A. P. Kartashova, Yu. A. Kudryavtsev, N. N. Ledentsov, V. V. Lundin, M. V. Maksimov, A. V. Sakharov, A. S. Usikov, and Zh. I. Alfërov

A. F. Ioffe Physicotechnical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia

A. Hoffmann

Technische Universität Berlin, D-10623 Berlin, Germany

Conditions are investigated for the injection of arsenic into gallium nitride layers grown by metal-organic vapor-phase epitaxy. It is shown that the deposition of GaAs on a GaN surface relieves stresses in the GaN layer. The high-temperature overgrowth of a thin GaAs layer by a GaN layer causes As atoms to diffuse into the GaN, produces a thick, homogeneously doped GaN:As region, and creates a bright band in the photoluminescence spectrum with a maximum at ~ 2.5 eV. © *1999 American Institute of Physics.* [S1063-7826(99)00707-3]

Considerable attention has recently been given to the fabrication of light-emitting devices that operate in the visible and ultraviolet regions of the spectrum. This interest is largely attributable to the sweeping potential of such devices for applications in color television and in memory units. The greatest progress was in the use of structures based on the system InGaN–GaN, which permits the radiation energy to be varied within the range $\hbar\omega = 1.96 - 3.5$ eV. This system has provided the basis for the construction of light-emitting diodes operating from the green to the UV region of the spectrum. However, the fabrication of green-emitting lasers requires a higher content of InN (more than 35 mole %) in the active zone of InGaN. But then the excessive mismatch of the lattice parameters with GaN creates difficulties in the growth of such layers, leads to deterioration of the structural and, hence, optical characteristics of the active zone of In-GaN, and results in degradation of the device characteristics. These obstacles necessitate the use of alternative methods for solving the problem of extending the optical range of GaN-based devices.

One way to solve the problem is by the monitoring and regulation of self-organization processes in constrained systems. For In-containing systems these effects produce local regions of elevated In content and can be used to achieve major modifications of their optical properties. The formation of InGaAs quantum dots with diameters ~ 100 Å, which are capable of shifting the photoluminescence line to a wavelength $\lambda \approx 1.3$ μm, has been demonstrated in a conventional InGaAs-AlGaAs system; the same shift has been impossible to achieve using InGaAs-based quantum wells.[1] Numerous studies of InGaN quantum wells have shown that their optical properties are governed by recombination processes in local regions of elevated In content.[2] For the system InAlN-GaN this kind of phase separation has made it possible to generate optical radiation in the red region of the spectrum.[3]

In addition to InGaN-GaN, the constrained GaAsN-GaN system has received attention in recent studies.[4] It is characterized by a greater mismatch of the lattice parameters

($\sim 25\%$ between GaAs and GaN) than in InGaN-GaN ($\sim 12\%$ between InN and GaN). However, theoretical calculations show that the decrease in the width of the band gap with the introduction of GaAs (~ 150 meV for 1% GaAs) greatly exceeds the analogous value for InN (~ 25 meV for 1% InN). Consequently, even slight additives of GaAs can significantly lower the energy of the optical transition. It has also been shown that the introduction of As improves the transport and optical characteristics of GaN layers.[5]

Here we report an investigation of the injection of As into GaN epilayers grown by metal-organic vapor-phase epitaxy (MOVPE) (organometallic compound hydride epitaxy). We intend to show that the deposition of GaAs on the surface of a GaN layer and its subsequent removal lead to stress relief and partial relaxation of the GaN layer. The deposition of a thin GaAs layer between GaN layers results in the formation of local GaN:As regions due to the emergence of a new band in the photoluminescence spectra, its maximum occurring at an energy $\hbar\omega \approx 2.5$ eV.

The GaN:As samples were grown on (0001)-oriented sapphire α-Al$_2$O$_3$ substrates in a horizontal reactor with inductive heating and a reduced pressure of 200 mbar. The vapor carrier was hydrogen or argon, the source of the group III element was trimethyl gallium (TMG), and the nitrogen source was ammonia. Tertiary butylarsine (TBA) or a 10% mixture of arsine (AsH$_3$) with hydrogen provided the source of arsenic. The resulting structures were investigated by secondary ion mass spectroscopy (SIMS) and photoluminescence, which was excited by an He-Cd laser with a pump power density of 25 W/cm^2 and was controlled by a cooled photoelectric multiplier. The surface morphology and the thickness of the layers were investigated by means of a scanning electron microscope.

The MOVPE preparation of GaAsN solid solutions has the distinctive feature that the growth of GaAs and the growth of GaN take place under different conditions. Typical growth temperatures for GaAs are $T_s = 600 - 750$ °C for a ratio of group III to group V components in the vapor phase
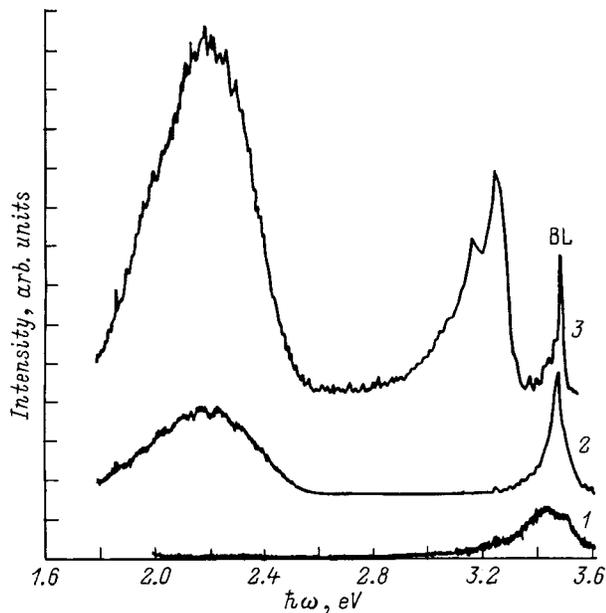
FIG. 1. Photoluminescence spectra of GaN layers grown in a TBA flux at various temperatures: (*1*) $T_s = 800\,°C$; (*2*) 840 °C; (*3*) 1040 °C. Measurement temperature $T = 77$ K.
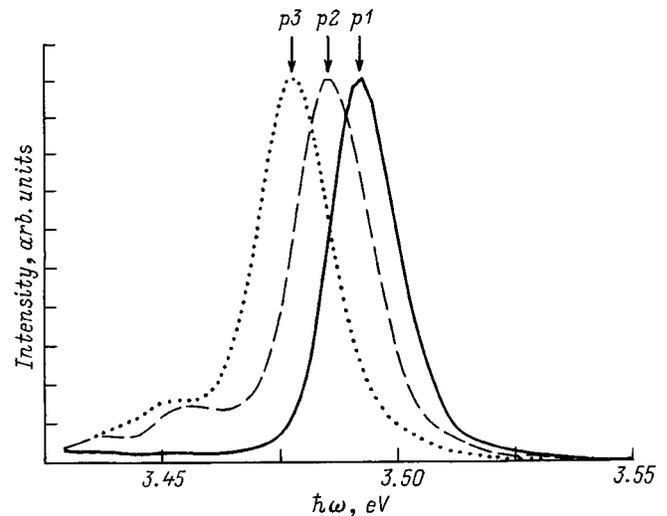

FIG. 2. Photoluminescence spectra of a GaN layer after etching of the GaAs layer from its surface. The spectra are recorded at different points of the sample surface with different effective thicknesses of the deposited GaAs. Measurement temperature $T = 77$ K.

equal to 30–100, as opposed to the analogous parameters for the preparation of high-quality GaN epilayers: $T_s = 1030 - 1080\,°C$ at a III-V ratio of 2000–5000 (Ref. 6). In the initial stage of our project, therefore, we began the investigation of the injection of As into GaN by growing GaN layers at various growth temperatures in a TBA flux of $(1.5 - 15) \times 10^{-4}$ mole/min. The procedure entailed, first, the growth of a virgin (not intentionally doped) GaN layer of thickness 2.5–3 μm on a sapphire substrate[7] and then the additional injection of TBA into the reactor. Figure 1 shows the photoluminescence spectra of these samples. It is evident from the figure that lowering the temperature under the stated conditions does not significantly alter the edge photoluminescence intensity (BL), whereas the defect-induced blue line with a maximum at $\hbar\omega = 3.25$ eV vanishes from the photoluminescence spectrum. Consequently, the optical properties of the GaN layers do not suffer any appreciable degradation. On the other hand, the emergence of new photoluminescence lines due to the injection of As atoms is not observed. No changes were observed in the photoluminescence spectra of samples grown at lower TBA fluxes.

This result can be explained as follows. The growth of the GaAs layer (instead of a GaN + As layer) on a GaN layer with the injection of an ammonia flux into the reactor has shown that the growth rate of GaAs at identical growth temperatures ($T_s = 800\,°C$) and TMG fluxes is almost an order of magnitude higher than the growth rate of GaN. This means that the thermal decomposition of TBA produces a quantity of reactable arsenic or its compounds in the vapor phase far in excess of the quantity of reactable nitrogen generated by the decomposition of ammonia. Processes of interaction in the vapor phase between the components of group V elements involving TMG probably results in the formation of stable polymer products, which lower the growth rate and obstruct the injection of As.

In the next stage of our investigations we used a 10% mixture of arsine with hydrogen as the arsenic source. The use of AsH_3 was conducive to more controlled growth of GaAs layers on GaN. Initially a GaAs layer of thickness ~ 0.6 μm was grown on a GaN surface. The GaAs layer had a polycrystalline structure owing to the large mismatch of the lattice parameters of GaAs and GaN. The thickness of the GaAs layer differed in different parts of the sample. After etching of the GaAs in an etchant $H_2SO_4{:}H_2O_2{:}H_2O = 5{:}1{:}1$ we investigated the photoluminescence of the GaN at different points of the structure surface ($p1$, $p2$, $p3$) characterized by different thicknesses of the initially deposited GaAs layer (Fig. 2). The effective thickness of the GaAs layer decreased from point $p3$ to point $p1$. Clearly, the deposition and subsequent etching of the GaAs significantly reduced the photoluminescence line on the long-wavelength side, the position of the $p3$ band essentially coinciding with the position of the free-exciton photoluminescence line in the unconstrained GaN. The total photoluminescence intensity scarcely changed in this case. Consequently, the deposition of GaAs leads to partial relaxation of the GaN epilayer. The effective thickness of the GaN relaxation layer is not smaller than the thickness at which the He-Cd laser beam is absorbed: $d \simeq 0.3$ μm.

Since the growth of GaN + As layers simultaneously in ammonia and arsine fluxes also failed to yield the expected results, we employed a different technique for the injection of As into GaN, based on the formation of thin GaAs layers in a GaN host. For this purpose we grew samples in which thin GaAs layers (30 nm and 60 nm) deposited on the GaN surface at 730 °C were overgrown by a GaN layer of thickness ~ 50 nm at 1030 °C. It is important to note that at the indicated growth temperatures the GaN is thermally unstable in a hydrogen ambient without an ammonia flux.[8] The GaAs layer and the subsequent GaN layer were therefore grown in
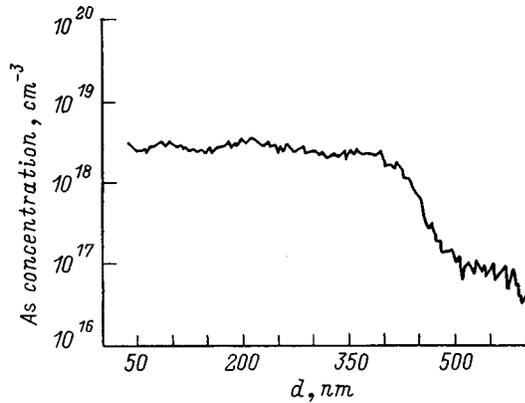
FIG. 3. SIMS profile of a structure with an intermediate GaAs layer of thickness 60 nm in GaN.
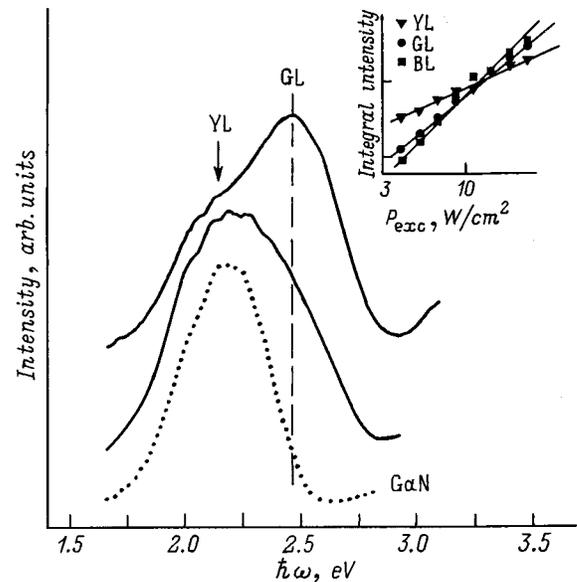

FIG. 4. Photoluminescence spectra of GaN layers with different thicknesses of the deposited GaAs layer. Inset: dependence of the total intensities of the lines YL, GL, and BL on the intensity of the exciting light beam P_{exc}. Measurement temperature $T = 77$ K.

an argon ambient. Figure 3 shows the SIMS profile of such a sample with a GaAs layer of thickness 60 nm. It is evident that a GaN:As layer of thickness $\sim$400 nm with an average density of As atoms $\sim 3 \times 10^{18}$ cm^{-3} is formed instead of a thin GaAs layer in the given structure. We can therefore conclude that the diffusion of As atoms either during deposition of the GaAs layer or during high-temperature overgrowth resulted in the formation of a thick As-doped GaN layer. Figure 4 shows the photoluminescence spectra of the investigated structure in the interval $\hbar\omega = 1.5 - 3$ eV. The spectra of these structures acquire a new line (GL) with a maximum at $\sim$2.45 eV (Ref. 9), whose intensity increases as the effective thickness of the deposited GaAs layer increases. It must be noted that this line does not occur in the photoluminescence spectra of samples grown at a low temperature (Fig. 1) and is therefore specifically attributable to the injection of As rather than to defects formed as a result of the low growth temperature. The dependence of the total GL intensity on the pump power density P_{exc} is described by the relation $I_{GL} \sim P_{exc}^{1.7}$ (see the inset in Fig. 4), which is typical for impurity-induced photoluminescense (line intensity YL $I_{YL} \sim P_{exc}$) and closely resembles the behavior of the photoluminescence edge (BL edge intensity, $I_{BL} \sim P_{exc}^{2}$). We can therefore assume that the GL is attributable to recombination processes in local GaN:As regions.

We have thus investigated the conditions for the injection of As into GaN layers during MOVPE growth. We have shown that the deposition of GaAs on a GaN surface reduces

stresses and leads to partial relaxation of the GaN surface layer. The subsequent overgrowth of the thin GaAs layer by a GaN layer at high temperature produces local GaN:As regions due to the emergence of a new band in the photoluminescence spectrum with a maximum at $\sim$2.5 eV.

[1] D. L. Huffaker, G. Park, Z. Zou, O. B. Shchekin, and D. G. Deppe, Appl. Phys. Lett. **73**, 2564 (1998).

[2] Y. Narukawa, Y. Kawakami, M. Funato, S. Fujita, S. Fujita, and S. Nakamura, Appl. Phys. Lett. **70**, 981 (1997).

[3] S. Yamaguchi, M. Kariya, S. Nitta, T. Takeuchi, C. Wetzel, H. Amano, and I. Akasaki, Appl. Phys. Lett. **73**, 830 (1998).

[4] L. Bellaiche, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **70**, 3558 (1997).

[5] L. J. Guido, P. Mitev, M. Gherasimova, and B. Gaffey, Appl. Phys. Lett. **72**, 2005 (1998).

[6] R. D. Dupuis, J. Cryst. Growth **178**, 56 (1997).

[7] W. V. Lundin, A. S. Usikov, and U. I. Ushakov, M. V. Stepanov, B. V. Pushnyi, N. M. Shmidt, V. Tret'yakov, M. V. Maximov, and A. V. Sakharov, in *Seventh European Conference on Metal-Organic Vapour Phase Epitaxy and Related Growth Techniques, EW MOVPE VII, Workshop Booklet* (Berlin, 1997), F10.

[8] J. C. Zolper, M. H. Crawford, J. Howard, J. Ramer, and S. D. Hersee, Appl. Phys. Lett. **68**, 200 (1996).

[9] X. Li, S. Kim, E. E. Reuter, S. G. Bishop, and J. J. Coleman, Appl. Phys. Lett. **72**, 1990 (1998).

Translated by James S. Wood