Nitridation of GaAs Surface by Low Energy Ion Implantation with In Situ Control of Chemical Composition

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1. Introduction

Nitridation of GaAs by low energy N$_{2}^+$ ion beams is an effective way for passivation and isolation of GaAs based structures (DeLouise, 1992, 1993; Pan et al., 1998; Hecht et al., 2001; Li et al., 2001; Kumar et al., 2009). The research activity in the field of ion induced GaAs nitridation accompanied by annealing for crystal structure restoration has been stimulated recently by the problem of perfect crystalline GaN film growth on GaAs substrate with using the implanted GaN layer as a buffer (Majlinger et al., 2008, 2009; Kumar et al., 2009). Low energy N$_{2}^+$ ion implantation enabled fabrication of GaN nanolayers even for device applications (Meškinis et al., 2004). Obvious advantages of the low energy implantation as a method for nitride nanolayer fabrication are relative simplicity, compatibility with other high vacuum techniques and possibility to control elemental and chemical composition of the nanolayer in situ by means of different kinds of electron spectroscopy. Qualitative chemical analysis of the implanted layers resulted in the conclusion that they are pure GaN films (DeLouise, 1992, 1993; Pan et al., 1998; Meškinis et al., 2004; Kumar et al., 2009) or the films mainly consisting of GaN (Hecht et al., 2001; Majlinger et al., 2008, 2009). Using x-ray photoelectron spectroscopy (XPS) with synchrotron radiation (SR) made it possible to reveal an essential contribution of the phase of dilute GaAsN alloy in addition to GaN (Majlinger et al., 2008, 2009; Mikoushkin et al., 2009) and to perform quantitative chemical analysis of the implanted layer with the help of the high resolution mode of this method (Mikoushkin et al., 2009). Efficient creation of the phase of GaAsN alloy has also been observed when GaAs was bombarded with a mixture of N$_2^+$ and Ar$^+$ ions (Gordeev et al., 2003; Mikoushkin et al., 2008).

The unique property of dilute GaAs$_{1-x}$N$_x$ alloy is that the band gap $E_g$ sharply decreases with enhancement of the nitrogen concentration $x$ even in the range of low concentrations $x$ (Bi & Tu, 1997; Sik et al., 2001). The band gap becomes as narrow as $E_g \sim 1$ eV already at $x \sim 0.03$, which should be compared with $E_g \sim 1.44$ eV at $x = 0$. This makes dilute GaAs$_{1-x}$N$_x$ alloy to be one of the most promising materials for infrared applications (Henini, 2005). Unfortunately, higher nitrogen concentrations $x > 0.03$ in alloys are difficult to achieve by means of basic growth technologies (Henini, 2005). There have been only a few reports published since 1997 about more concentrated GaAsN alloys (Bi & Tu, 1997; Toivonen et al., 2000; Moody et al., 2002; Veal et al., 2004). The physical restriction in fabricating alloys with higher nitrogen concentrations may be in their instability at growth temperatures typically...
exceeding 550÷650°C (Mikoushkin et al., 2008). This instability results in decay of the alloy into thermodynamically more stable chemical phases: GaAsN → GaN and GaAs. Therefore the problem arises whether it is possible to fabricate nanofilms of GaAs$_{1-x}$N$_x$ alloys with higher nitrogen concentrations $x > 0.03$ at low temperatures by low energy implantation of GaAs. Based on the research done, the answer will be shown below to be positive. The implantation technique will be shown to enable fabrication of dilute GaAs$_{1-x}$N$_x$ alloys with nitrogen concentration $x \sim 0.09$ and, correspondingly, with the narrow band gap. The problem was solved with in situ control of chemical composition by high resolution XPS with synchrotron radiation and, surprisingly, by ordinary Auger Electron Spectroscopy (AES).

2. Nitridation of GaAs with high resolution synchrotron radiation based XPS diagnostics of chemical composition

Introduction. The classic research of De Louise seems to be the first study devoted to GaAs nitridation by low-energy N$_2^+$ ion implantation (DeLouise, 1992, 1993). It was performed under XPS control which is known to be one of the most powerful methods for elemental and chemical analysis (Briggs & Seah, 1983). Using this method with MgKα x-ray source the author showed that the implantation results in fabrication of nitrogen rich layers characterized by nitrogen concentration ranging from [N] \sim 15 at.\% at energy $E_i = 3.0$ keV up to [N] \sim 30 at.\% at energies $E_i = 0.5 \div 1.2$ keV. Creation of GaN layer was revealed by the analysis of Ga3d photoemission spectra. As a result of nitrogen implantation, the author observed a chemical shift of Ga3d photoelectron line due to additional contribution at higher binding energy which was attributed to the GaN phase. Analogous line shifts were observed later by other authors who came to similar conclusion about formation of GaN nanolayer on the GaAs surface in the implantation process. The only fact slightly disturbed the suggested interpretation: the photoemission signal contained contribution of GaAs besides the GaN. Presence of GaAs line in Ga3d spectrum was explained by the contribution of GaAs substrate which was possible to observe because the mean free path of Ga3d photoelectrons generated by MgKα/AlKα x-rays exceeded the thickness of nitrided layer. Therefore the GaAs signal was explained by the substrate contribution.

The geometry of the experiment described below according to Ref. (Mikoushkin et al., 2009) was made different. XPS chemical analysis of nitride film fabricated by implantation of N$_2^+$ ions with the energy $E_i = 1.5$ keV was performed at different experimental conditions compared to previous studies, namely at the conditions when the mean free path $\lambda$ of photoelectrons generated by low energy synchrotron radiation is less than the thickness of the nitrided layer. Therefore photoelectrons of only nitrided layer were detected. Nevertheless contribution of a phase being chemically similar to the GaAs was observed apart from the phase of GaN. This contribution proved to be comparable with the content of the main phase. High energy resolution of the method made possible to show that the revealed phase is GaAs$_{1-x}$N$_x$ alloy and that the layer fabricated by implantation of nitrogen consists of the wide band gap matrix of GaN with the narrow band gap clusters of GaAs$_{1-x}$N$_x$ ($x \sim 0.05 \div 0.10$) alloy, which can be considered as a quantum dot system.

Experimental details. The experiment was carried out at the BESSY II storage ring in Berlin using monochromatic synchrotron radiation of the German-Russian beamline equipped with the plane-grating monochromator (PGM) and photoelectron spectrometer with hemispherical analyzer VG CLAM-4 (Fedoseenko et al., 2003). The total energy resolution of
the method was better than 300 meV. Control of the elemental and chemical composition of sample was performed by measuring in situ core-level photoemission spectra: Ga3d, As3d, N1s. The photon energy scale of the monochromator was calibrated using Au 4f_{7/2} line of gold (E_B = 84.0 eV).

Commercial GaAs (100) n-type (n ~ 10^{18} cm^{-3}) wafer was taken as a sample. It was implanted at room temperature under high vacuum conditions by nitrogen ions N_2^+ of low energy E_i = 1500 eV in the preparation chamber of the electron spectrometer. The incidence angle was normal to the surface. The dose of the implanted ions Q ~ 3*10^{16} cm^{-3} was close to the dose sufficient for saturation of the nitrogen concentration in the near-surface area (DeLouise, 1992). The surface of the sample was preliminary cleaned by Ar^+ ions with the energy E_i = 1500 eV which was high enough to prevent considerable enrichment of the surface by the atoms of gallium. As a result of cleaning, the layer of native oxide and contaminations was completely removed from the surface, which was checked by measuring the O1s and C1s spectra. The thickness of the nitrided layer or the projected range of nitrogen ions was estimated by SRIM code (Ziegler et al., 1985) to be about d ~ 2.5 nm. The peculiarity of the conducted experiment was in relationship of the thicknesses of the nitrided layer and the near surface layer controlled by XPS which is determined by the mean free path of detected photoelectrons \lambda ~ 0.5 \pm 1.0 nm. The last one was made less than the thickness of nitrided layer by diminishing the photoelectron kinetic energy down to E_e ~ 100 \div 126 eV using x-rays of low energies: h\nu = 150 eV for measurement of Ga3d and As3d lines and h\nu = 500 eV for N1s line. Therefore photoelectrons of only nitrided layer were registered.

**Analysis of photoelectron spectra.** The total concentration of the implanted nitrogen is one of the most important characteristics of the nitrided layer. It was estimated by the analysis of the N1s and Ga3d line intensities. To neglect the energy dependence of the spectrometer transmission, kinetic energies of these photoelectrons were made close to each other (E_e ~ 100 \div 126 eV). Mean free paths of these photoelectrons characterised the analysed layer proved to be equal at this condition too. Comparison of the intensities normalized to the corresponding photoemission cross sections \sigma(N1s, h\nu = 500 eV) and \sigma(Ga3d, h\nu = 150 eV) (Henke et al., 1993) gave the content of nitrogen [N] ~ 25 at.%. This value proved to be close to the values obtained in Ref. (DeLouise, 1992; Li et al., 2001). The embedded nitrogen can create different chemical compounds with matrix atoms besides GaN.

When colliding with the surface, molecular nitrogen ions dissociate, and chemically active atoms penetrate into the substrate to a projected range of about several nanometers before they completely lose their kinetic energy. At the end of this process, the nitrogen atoms can react with the matrix, substituting arsenic and resulting in formation of the following chemical phases: GaN, GaAsN, GaAs, As and AsN. High energy resolution SR-based XPS method enabled development of quantitative diagnostics of chemical composition for the nitrided layer with determining the concentrations of mentioned chemical phases. To solve this problem, photoelectron spectra of As3d, Ga3d and N1s measured for exceptionally nitrided layer without any substrate contribution should be considered. These spectra are shown in Fig. 1, 2 and 3.

Photoelectron spectrum of arsenic represented in Fig.1 confirms the qualitative model of nitrogen ion interaction with matrix, describing partial replacement of arsenic by nitrogen.
As3d spectrum on implanted GaAs surface (Fig. 1b) shows some contribution of a phase of elementary arsenic As0. The spectrum confirms absence of AsN phase earlier reported for the layers nitrided by low energy implantation (DeLouise, 1992; Hecht et al., 2001; Li et al., 2001; Kumar et al., 2009). Finally, As3d spectra give new important information that the major part of arsenic remains in the nitrided layer and practically saves line position and corresponding chemical state. This fact implies creation of dilute alloy GaAsN with low nitrogen concentration which does not essentially influence the chemical state of arsenic atoms. This assumption was confirmed by the spectra of Ga3d and N1s.

![As3d spectrum](image)

**Fig. 1.** As3d photoemission spectrum of GaAs (a) and GaAs implanted by nitrogen ions with energy $E_i = 1500$ eV (b). The last one is decomposed into different contributions.

Implanted nitrogen atoms substitute arsenic and create chemical bonds with gallium, which is seen in the Ga3d photoemission spectra shown in Fig. 2. Curve 1 corresponds to Ga3d line of atomically clean surface of GaAs prepared by Ar+ ion etching. Curve 2 is the spectrum of the surface implanted by nitrogen ions. Implantation shifts Ga3d spectrum to higher binding energies. Decomposition of the spectrum of the implanted surface into Gaussian contributions shows that the phase of GaN is dominating one, but a contribution of the substance being chemically similar to GaAs is observed in the nitrided layer too. This contribution is comparable with the content of the main phase. Before it will be shown that this phase is definitely the phase of GaAs$_{1-x}$N$_x$ alloy, some remarks about Ga3d and As3d spectra should be made.
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Fig. 2. Ga3d photoemission spectrum of GaAs (1) and GaAs implanted by nitrogen ions with energy $E_i = 1500$ eV (2). The last one is decomposed into different contributions.

Important characteristics of the gallium chemical state, the binding energies of Ga3d core electron, were obtained: $E_B$(Ga3d) = 19.4 eV and 19.8 eV for GaAs and GaN, correspondingly. These values proved to be in the frame of published data, though by 0.5 eV and 0.3 eV larger than those reported in Ref. (DeLouise, 1992; Li et al., 2001). A reason of this discrepancy may be in different positions of the Fermi level in samples being differently treated. The spectrum of implanted sample shows also a small contribution of gallium oxide Ga$_2$O$_3$. Origin of this contribution was in presence of residual oxygen in the gas system of the ion source which was not desirable and planned. But this small contamination not only did not essentially affect the spectra but it also was used for the additional analysis of the As3d photoemission spectrum (Fig. 1). This spectrum shows absence of As$_2$O$_3$ with binding energy $E_B = 44.5 \pm 46$ eV (Briggs & Seah, 1983) despite the presence of residual oxygen in vacuum system, which illustrates higher resistivity of arsenic to oxidation and nitridation compared to gallium. Therefore the absence of AsN seems to be natural because of lower electronegativity of nitrogen. Stability of the As3d lines against nitridation mentioned above evidences also no influence of the embedded atoms and defects to the Fermi level position.

The phase GaAs observed in Ga and As spectra of nitrided layer was assumed to be GaAs$_{1-x}$N$_x$ (x << 1) dilute alloy which is chemically similar to the GaAs because of low nitrogen concentration x, and therefore it cannot be identified because of extremely small chemical shift of the corresponding lines. But this task was solved in N1s spectrum and the assumption was unambiguously confirmed. Fig. 3 shows N1s photoemission spectrum of the implanted sample (curve 1) with prominent line of the GaN phase. The binding energy of N1s core electron in GaN $E_B$(N1s) = 396.7 eV is in agreement with the previously published data. It coincides with that obtained in Ref. (DeLouise, 1992) and is less by 0.3 eV than the value given in Ref. (Zhu et al., 1992; Li et al., 2001). High total energy resolution of the beamline used and the endstation enabled revealing some asymmetry of N1s photoemission line related to additional contribution at higher binding energy where the line of GaAsN was expected. Indeed, the binding energy N1s in alloy Ga-As-N should be between the energies in N-Ga and N-O compounds. The asymmetry becomes stronger after
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bombardment of the film by Ar$^+$ ions (curve 2, Fig.3a), which was shown in our former works to enhance the contribution of the phase of GaAs$_{1-x}$N$_x$ alloy in nitrided layer due to mixing and homogenization of the material favoring to alloy creation (Gordeev et al., 2003; Mikoushkin et al., 2008). The difference of the spectra 2 and 1 (curve 3) shows growth of the discussed contribution at $E_B$(N1s) = 397.3 eV as a result of Ar$^+$ ion bombardment of the film. Therefore, the conclusion was made that essential contribution of the phase of narrow band gap GaAs$_{1-x}$N$_x$ alloy was revealed in the film besides the dominating phase of the wide band gap GaN.

Fig. 3. N1s photoemission spectrum of GaAs implanted by nitrogen ions (curve 1, a) and its decomposition (b), spectrum of the implanted layer followed by Ar$^+$ ion bombardment (curve 2, a) and their difference (curve 3, a). The energy of implanting N$_2^+$ and bombarding Ar$^+$ ions is $E_i = 1500$ eV. The photon energy $h\nu = 501.3$ eV.

Fig. 3b demonstrates decomposition of the N1s spectrum of the nitrided layer corresponding to curve 1 in Fig.2a into contributions of different chemical phases. The decomposition gave the N1s binding energy $E_B$(N1s) = 397.5 eV in GaAs$_{1-x}$N$_x$ alloy which turned out to be very close to the data of XPS measurements (~397.3 ÷ 397.8 and 397.6 eV) of single-phase dilute alloys GaAs$_{1-x}$N$_x$ with $x = 0.04$ and $x = 0.01$ grown by MBE in Ref. (Spruytte at al., 2001; Veal at al., 2004), correspondingly. Advantage of the present measurements is that the difference (0.8 eV) with the energy of GaN was obtained in one experiment and in one sample. The obtained information is necessary for diagnostics of the GaAs nitrides which is complicated by small energy difference of these chemical states and large spread in the binding energies published for GaN and other nitrides by different
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authors. Comparison of the binding energies obtained in this work for alloy in as prepared nitride layer (397.5 eV) and in the layer with lower nitrogen concentration after bombardment by Ar$^+$ ions (397.3 eV) points out to some natural dependence of the GaAs$_{1-x}$N$_x$ alloy binding energy on the nitrogen content: the higher content $x$, the lower energy $E_B(N1s)$.

Decomposition of the N1s line gave also the portion of nitrogen in alloy $\sim 10\%$ in the conducted experiment, which provides at list 30 at.% of the alloy contribution. Taking into account the total concentration of nitrogen [N] $\sim 25$ at.%, and the ratio of GaN and GaAs$_{1-x}$N$_x$ phases ($\sim 0.6/0.4$), which follows from the decomposition of Ga3d spectrum (Fig.2), the content of nitrogen in alloy GaAs$_{1-x}$N$_x$ was estimated to be $x \sim 0.10$. This value is high enough to decrease the band gap of the alloy below the value $\Delta = 1$ eV (Bi & Tu, 1997; Sik at al., 2001).

Fig. 4. Scheme of the nanostructure GaAsN/GaN formed on the GaAs surface as a result of implantation of low energy nitrogen ions N$_2^+$.

The revealed phase of GaAs$_{1-x}$N$_x$ alloy is generated on the atomic level due to segregation of atomic complexes into clusters. The characteristic size of the clusters cannot be more than the thickness of the nitrided layer. Thus we came to the conclusion that the fabricated nitrided nanofilm being a system of the narrow band gap clusters of GaAs$_{1-x}$N$_x$ ($x \sim 0.10$) alloy in the wide band gap matrix of GaN is characterized by the main attribute of a quantum dot system. Fig. 4 shows a scheme of the nitrided layer formed on the GaAs surface by implantation with low energy nitrogen ions N$_2^+$. The film thickness shown corresponds here to the length of nitrogen depth profile calculated by SRIM codes which is essentially longer than the SRIM projected range (see below). The implanted layer contains comparable contributions of two phases and represents a quantum dot like nanostructure GaAsN/GaN rather than an entire GaN film assumed in many former publications.

Conclusions. As a result of the conducted research, in situ chemical composition diagnostics of the GaAs nitrides has been developed using high resolution synchrotron radiation based photoelectron spectroscopy. Chemical phases of GaN, GaAsN and GaAs were distinguished by electron spectroscopy for the first time. Core level binding energies in GaAs$_{1-x}$N$_x$ ($E_B = 397.5$ eV) and in GaN ($E_B = 396.7$ eV) and their difference ($\Delta E_B = 0.8$ eV) were measured in one experiment with high accuracy. The model of chemical composition and atomic structure of the nitrided layers fabricated by implantation with low energy N$_2^+$ ions into GaAs surface has been essentially improved. We revealed that the nitride nanolayer is not an entire GaN layer. It
consists of the narrow band gap clusters of GaAs\textsubscript{1-x}N\textsubscript{x} (x ~ 0.10) alloy in the wide band gap matrix of GaN, which makes the nanofilm similar to a quantum dot system.

3. Auger diagnostics of chemical composition of GaAs nitride nanolayers

Introduction. The research described above showed that low energy ion implantation makes it possible to fabricate nitrided layers with large contribution of the phase of dilute alloy GaAs\textsubscript{1-x}N\textsubscript{x} (x ~ 0.10). Moreover, this alloy is characterized by high concentration x of nitrogen and by the narrow band gap desirable for infrared optoelectronic applications. High nitrogen concentration in alloy seems to be a result of specificity of implantation technology allowing fabrication at room temperature, which prevents the alloy decay. The aim of the next step of research was to increase the contribution of GaAsN alloy in the nitrided layer. To solve this problem, some measures were undertaken. For example, initial enrichment of the substrate surface by gallium and the total nitrogen concentration in implanted layer was reduced by some increasing the energies of etching and implanting ions.

Unfortunately synchrotron radiation based diagnostic methods are not easily available for routine experiments. Therefore, diagnostics of the GaAs nitrides on the basis of ordinary Auger Electron Spectroscopy (AES) was planned to be developed. The drawback of AES for chemical analysis is large natural width (against chemical shifts) and complicated shape of Auger lines. Fortunately, considerable relaxation shifts of Auger lines in nitride compounds make it possible to distinguish them from each other (Aksenov et al., 1998, 1999; Mikoushkin et al., 2008). Energies of Auger transitions in nitride compounds were determined in the conducted experiments and quantitative Auger diagnostics of chemical composition of nitrided nanolayers was developed (Mikoushkin, 2011).

Experimental details. The experiments were carried out in an electron spectrometer LHS-11 (Leybold AG) equipped with a hemispherical energy analyzer, in which the residual vacuum in the analytical chamber was P < 2 \times 10\textsuperscript{-10} Torr. The native oxide removing, sample surface cleaning and nitrogen ion implantation were performed in a technological chamber (P ~ 2 \times 10\textsuperscript{-9} Torr) equipped with a Penning type ion gun IQP-10/63 (Leybold AG) generating a beam with the diameter exceeding the sample target size. The object under study was the epitaxial film of GaAs (100) analogous to that grown in Ref. (Gordeev, 2003). The film was grown at Ioffe Institute at substrate temperature of 580 °C to a thickness of 100 nm on semi-insulating GaAs (100) substrate using Intevac Gen II MBE system (Zhukov, 2001). The crystalline structure was controlled by conventional High Energy Electron Diffraction system. The procedure of the surface cleaning with Ar\textsuperscript{+} ions is known to unify the surface layer of GaAs and to result in formation of reproducible properties of the layer, characterized by amorphous structure and essential enrichment by gallium atoms. The energy of Ar\textsuperscript{+} ions E\textsubscript{i} = 2500 eV was taken to be high enough to prevent large enrichment of the surface by gallium and to eliminate conditions for efficient creation of GaN phase during nitridation. Then the film was implanted at room temperature by N\textsubscript{2}\textsuperscript{+} ions at normal incidence, with the dose of implanted ions Q ~ 10\textsuperscript{17} cm\textsuperscript{-2} sufficient for saturation of the near-surface layer with nitrogen (DeLouise, 1992). All the operations were controlled by measuring the Auger spectra of the main elements, GaLMM, AsLMM, NKV, and those of possible impurities, OKV, CKV. The Auger spectra were recorded relative to the Fermi level in the mode of constant relative energy resolution (AE/E = const). This mode enabled us to use the known coefficients for the “peak-to-peak” line intensities to obtain element composition of the material (Davis at al., 1976). Positions of GaLMM and AsLMM Auger
lines ($E_A = 1066.3$ and $1224.7$ eV, correspondingly) of the GaAs surface prepared coincided with those known for surfaces prepared by chemical etching and crystal cleavage (1066.2 and 1224.5 - 1225.0 eV, respectively) (Briggs & Seah, 1983) indicating negligible surface charging under the diagnostic beam. The energy of the implanted ions $E_i = 2500$ eV was taken also somewhat higher than typical energies used in former low energy implantation experiments. It provided relatively large thickness of the nitrided layer which was estimated by SRIM code as the projected range of nitrogen ions $d \sim 3.6$ nm (Ziegler et al., 1985). Thus, the mean free path of the detected electrons $\lambda \sim 1.5$ nm was markedly less than the thickness of the nitrided layer, and the experiment was performed under the conditions when the electrons ejected by only nitrided layer were collected without any contribution from the GaAs substrate. The choice of the relatively high energy of the implanted ions ($E_i = 2500$ eV) resulted also in twofold reduction of the total nitrogen concentration in the nitrided layer as compared to the maximum concentration achieved at energies below 1000 eV. The lack of nitrogen prevents creation of GaN and decay of GaAsN, which was assumed to help domination of GaAsN alloy in the nitrided layer aimed at in the research. A special experiment was performed by Electron Energy Loss Spectroscopy to confirm the information about chemical composition of the film by the analysis of plasmon spectra.

**Analysis of Auger spectra.** Formation of GaN in nitrided layers was confirmed in the previous studies of low energy implantation of nitrogen into GaAs by the chemical shift of Ga3d photoelectron line and the corresponding change of the Ga3d binding energy $\Delta E_{BE} = 0.7\pm0.4$ eV (e.g. Li et al., 2001; Mikoushkin at al., 2009). Fig. 5 shows a significantly larger shift $\Delta E_A = 3.5$ eV of GaLMM Auger line resulting from $N_2^+$ ion bombardment. This Auger line shift is caused by the large change in the extra-atomic relaxation energy related to the change in the response of the whole electron system to creation of a vacancy in core level. Therefore the shift $\Delta E_A = 2.4$ eV of the AsLMM Auger spectrum represented in Fig. 6 is of the same order despite the restricted involvement of arsenic into the creation of new chemical bonds accompanied by the insignificant chemical shift of photoelectron As3d line (Li at al., 2001; Kumar at al., 2009; Mikoushkin at al., 2009).

![Fig. 5. GaLMM Auger spectra of GaAs (right curve) and GaAs implanted by nitrogen ions with energy $E_i = 2500$ eV (left curve). The last one is decomposed into different contributions (dotted curves). The linear background is subtracted. The electron energy is measured relative to the Fermi level.](www.intechopen.com)
Fig. 6. AsLMM Auger spectra of GaAs (right curve) and GaAs implanted by nitrogen ions with energy $E_i = 2500$ eV (left curve). The last one is mainly described by one contribution (dotted curve). Energy positions of Auger lines in AsN, As$_2$O$_3$ and As were taken in Ref. (Aksenov et al., 1999; Briggs & Seah, 1983).

Analysis of GaLMM and AsLMM spectra was performed by means of their decomposition into contributions corresponding to the chemical phases which should be expected in the nitrided layer: GaN, GaAsN, GaAs, AsN, As. Auger spectra of these contributions were approximated by the spectra of GaAs (elementary spectra) centered at the known energy positions or in the range of the values published in literature. Thus the shape and width of the elementary spectra were kept constant, whereas their relative intensity and energy position were varied for better agreement of the model with the experimental spectra. The assumption about the independence of the shape and width of the spectra from the chemical state seems to be reasonable since these Auger transitions involve only core levels. Fig. 6 shows that AsLMM Auger spectrum of nitrided layer is mainly described by one line without essential contributions of GaAs, As and AsN phases. As was mentioned in previous part, absence of AsN was also reported in several studies of nitrided layers fabricated by low energy implantation (DeLouise, 1992; Hecht et al., 2001; Li et al., 2001; Kumar et al., 2009). Therefore the chemical state of arsenic at $E_A = 1222.6$ eV shown in Fig. 6 should be assigned to GaAsN. This conclusion can be made irrespective of the information about the position of the Auger line in AsN given in Ref. (Aksenov et al., 1998, 1999) and of the previous results cited. Indeed, AsN cannot be a dominant state of arsenic because the concentration of As atoms in the layer studied exceeds that of nitrogen atoms and exceeds manifold the concentration of nitrogen atoms unbound with Ga. Since the main state is not GaAs, it should be attributed to GaAsN (Mikoushkin, 2011).

GaLMM spectrum also does not show any presence of GaAs, but it cannot be described by one line (Fig. 5). Decomposition of the spectrum shows additional contribution at lower kinetic energy $E_A = 1060.5$ eV besides the main line at $E_A = 1062.8$ eV. These lines were attributed to GaN and GaAsN phases, respectively, as the energy of Auger transition in GaN should be less than that in GaAsN because of larger core level chemical shift. The same sequence of Auger energies in these compounds follows from Ref. (Aksenov et al., 1998,
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1999): $E_A\text{(GaN)} = 1062.7 \text{ eV}$ and $E_A\text{(GaAsN)} = 1063.0 \div 1065.5 \text{ eV}$, though these values differ from the values obtained in this work. Thus, analysis of $GaLMM$ and $AsLMM$ Auger-spectra of the nitrided layer showed minor contributions of GaAs, As and AsN phases, confirmed formation of two nitrides observed earlier in Ref. (Majlinger et al., 2008, 2009; Mikoushkin et al., 2009) and revealed domination of the phase of GaAsN alloy in the layer studied.

![Fig. 7](https://www.intechopen.com)

Fig. 7. a). $N_{KVV}$ Auger spectra of GaAs implanted by nitrogen ions with energy $E_i = 2500 \text{ eV}$ (1) and bombarded by $Ar^+$ ions with energy $E_i = 2500 \text{ eV}$ and increasing doses (2, 3, 4). b). $N_{KVV}$ Auger-spectrum of implanted GaAs (1) decomposed into different contributions (dotted lines). The linear background is subtracted.

GaN and GaAsN phases were identified unambiguously in $N_{KVV}$ spectra. Fig 7a shows $N_{KVV}$ Auger spectrum of GaAs after implantation (1). The spectrum demonstrates doublet structure in the region of the maximum which becomes even more reliably pronounced upon double differentiation and is indicative of the presence of two intense lines in the central part of each spectrum and two less intense components in the high energy wing. This shape is repeated in other $N_{KVV}$ spectra (2 - 4) measured in the course of etching the layer by $Ar^+$ ions. $N_{KVV}$ Auger spectra of nitrides are known to consist of two peaks of different intensity: the main and satellite ones (e.g., Aksenov et al., 1999). Therefore the experimental spectrum was modeled by two double peak elementary spectra with the main lines centered close to the above mentioned peculiarities in the central region of the experimental spectrum. The shape and width of the elementary spectrum were fixed again, while the intensity and position were varied. Fig. 7b gives an example of the spectrum decomposition, from which it can be seen that the sum of the elementary spectra (dotted curve) well describes the experimental spectrum (thick solid curve). Analysis of $N_{KVV}$
experimental spectrum shows two contributions with main peak positions at $E_A = 379.8 \pm 0.2$ and $382.8 \pm 0.2$ eV. The first one coincides with the NKVV Auger energy of GaN and the second one turns up in the interval of Auger energies $E_A = 381.5 \pm 383$ eV of disordered GaAsN phase generated in plasma nitridation of GaAs surface (Aksenov et al., 1998, 1999). Fig. 7b shows that the major part of nitrogen atoms is contained in GaN phase, which is in agreement with the results of the former studies of low energy ion nitridation of GaAs surface. The conducted analysis enabled us to determine the energies of NKVV Auger-transitions in GaN and GaAsN in one experiment with one sample, with the accuracy sufficient for reliable identification of these phases without referring to synchrotron radiation facilities.

Relative intensities of the elementary spectra in the decomposed NKVV spectrum give distribution of nitrogen atoms in GaN and GaAsN phases: $[N]_{\text{GaN}} = 0.7$ and $[N]_{\text{GaAsN}} = 0.3$. The concentration of chemically bound nitrogen atoms in the implanted layer was estimated to be $[N] \sim 12 \text{ at.\%}$. Hence, the concentrations of GaN and GaAsN are: $[\text{GaN}] \sim 12 \times 0.7 + 2 = 17 \text{ at.\%}$ and $[\text{GaAs}_{1-x}\text{N}_x] \sim 83 \text{ at.\%}$, which is in qualitative agreement with the result of the less accurate decomposition of the GaLM spectrum represented in Fig.5: 25/75 at.\%. The content of nitrogen in alloy is $[N]_{\text{GaAsN}} \sim 12 \times 0.3 = 3.6 \text{ at.\%}$, hence $x \sim 0.09$. Thus, a nanofilm consisting mainly of dilute alloy $\text{GaAs}_{1-x}\text{N}_x$ with high concentration of nitrogen $x \sim 0.09$ was fabricated by low energy ion implantation.

**Analysis of EELS spectra.** A critical point in quantitative characterization of the chemical composition of the nitrided layer is the reliability of the conclusion made above about the negligible contribution of GaAs chemical phase. In contrast to the present study, an intensive signal of GaAs in photoelectron spectra was detected in former works, though it was explained by the contribution of GaAs substrate due to comparability of the mean free path of the photoelectrons with the thickness of nitrided layer. Experimental conditions of this work exclude the contribution of the substrate. But the phase of GaAs can be formed due to the low stability of alloy with high nitrogen concentration against external impacts such as ion bombardment: $\text{GaAs}_{1-x}\text{N}_x \rightarrow (1-x)\text{GaAs} + x\text{GaN}$ (Mikoushkin et al., 2008). Decay of alloy also enhances the content of the more stable chemical phase of GaN characterized by lower Gibbs energy. On the other hand, the fact of low GaAs concentration is the evidence of the reverse process of alloy creation. This process can be induced by secondary ion cascades generated by implanted ions. Ion cascades induce mixing atoms of the material, input of energy into the system and formation of the GaAsN phase. To confirm the possible role of ion cascades in forming nitride layer by low energy implantation, minor contribution of GaAs and other results of the conducted chemical analysis, an additional experiment with using Electron Energy Loss Spectroscopy (EELS) was performed. Fig. 8 shows EELS spectra of GaAs before and after implantation. The main peak of the spectra corresponds to the bulk plasmon. The plasmon energy of the implanted layer $\hbar\omega = 17.8$ eV proved to be between the plasmon energies $\hbar\omega = 15.5$ eV and $\hbar\omega = 19.5$ eV (Sánchez et al, 2004) of GaAs and GaN, respectively. Decomposition of the implanted layer spectrum was done using GaAs spectrum as the elementary one for all constituents. The small contribution of transitions from Ga3d core level into unoccupied states revealed in GaN in Ref. (Sánchez et al, 2004) was added for better agreement of calculated and experimental spectra. The relative intensity of elementary spectrum in the decomposition is proportional to the corresponding fraction of the chemical phase. Fig. 8 shows contributions of GaAsN (main contribution), GaN (minor contribution) and GaAs (marginal contribution). Thus the
conclusion about the domination of the GaAsN alloy in the implanted layer has been confirmed by the data of EELS experiment.

![EELS spectra of GaAs (left curve) and GaAs implanted by nitrogen ions with energy $E_i = 2500$ eV (right curve). The last one is decomposed into different contributions (dotted lines). The background of multiply scattered electrons is subtracted.](image)

Conclusions. Thus, analysis of N$KVV$ Auger spectrum of nitrided layer fabricated by low energy implantation revealed well resolved features associated with two compounds, GaN and GaAsN, characterized by small difference in core level chemical shifts. This made it possible to determine the energies of Auger transitions in these compounds in one experiment, with the accuracy being sufficient for reliable separation of corresponding contributions into experimental Auger line. Decomposition of N$KVV$ Auger spectrum showed that GaN phase contains the major part of nitrogen atoms (~70%), which qualitatively agrees with former studies of implanted layers by XPS and is the evidence of reliability of the conducted Auger analysis. The experimental conditions, which ensured that the detected electrons did not contain signal of GaAs substrate, made it possible to determine the overall chemical composition of the nitrided layer. It proved to be a nanofilm with the thickness of about 4 nm, consisting mainly of dilute alloy $\text{GaAs}_{1-x}\text{N}_x$ with high concentration of nitrogen $x \sim 0.09$. High nitrogen concentration $x$ implies formation of the narrow band gap ($E_g < 1$ eV) of the material. Domination of the nitrogen rich $\text{GaAs}_{1-x}\text{N}_x$ alloy in the nitrided layer was assumed to be provided by secondary ion cascades generated by implanted ions. The obtained results were confirmed by the analysis of EELS spectra of the nitrided layer. Thus it has been shown that the low energy implantation technique is a promising way for fabricating dilute $\text{GaAs}_{1-x}\text{N}_x$ alloys with high nitrogen concentration.

4. Formation of $\text{GaAs}_x\text{N}_{1-x}$ nanolayer on GaAs by manipulations with $\text{N}_2^+$ and $\text{Ar}^+$ ion beams

Introduction. The nitridation by low energy implantation of the epitaxial GaAs film described in previous section enabled obtaining the nitrided layer containing of about 80
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at.% of dilute alloy GaAs\(_{1-x+N_x}\) with high nitrogen concentration \(x \sim 0.09\). Surprisingly, the ordinary Auger electron spectroscopy proved to be an efficient tool for \textit{in situ} diagnostics of chemical composition of GaAs nitrides. These two important results favored development of the implantation technology for fabrication of entire nanofilms or the nanofilms mainly consisting of dilute alloy GaAs\(_{1-x+N_x}\). The research devoted to this development resulted in enhancement of the GaAs\(_{1-x+N_x}\) alloy content up to 98 at.% due to chemical effect of “inert” Ar\(^+\) ion beam on nitride nanolayers (Mikoushkin, 2010). This effect is caused in particular by the material homogenization due to intermixing of chemical phases by ion cascades efficiently generated by heavy argon ions. As a result of the nitrided layer modification, the major part of nitrogen goes from GaN to GaAs\(_{1-x+N_x}\).

\textbf{Experimental details.} The research was a continuation of the experiments described in previous section. Bombarding the sample surface with Ar\(^+\) ions was performed directly in the analytical chamber using a scanning beam of the ionization type ion gun IQE-12/38 (Leybold AG). The ion energy was \(E_i = 2500\) eV. The concentration of nitrogen in the implanted layer was \([N] \sim 12\) at.% and decreased to \([N] \sim 2.5\) at.% upon the bombardment with argon ions. The task of determining the chemical state of nitrogen in the implanted nitride layer was solved by the method of AES described above.

\textit{Analysis of depth profiles of the film chemical composition.} Determining the thickness of fabricated nanofilms is of particular importance in their characterization. Rough estimation of the thickness considered as the projected range of ions was made by SRIM code (Ziegler at al., 1985). It is \(d \sim 3.6\) nm for the nitrogen N\(_{2+}\) ions with energy \(E_i = 2500\) eV. More accurate determination of the nitrided nanofilm thickness was made in this research by TRIM code calculations (Ziegler at al., 1985) of the dependence for the nitrogen concentration on the distance to the surface, or the nitrogen depth concentration profile. This depth profile normalized to the irradiating flux is shown in Fig. 9. The figure shows that real thickness of the implanted layer essentially exceeds the projected range \(d \sim 3.6\) nm. The layer thickness considered as the full width at half maximum of the profile proved to be twice as much as the projected range: \(h \sim 8.5\) nm.

Fig. 9 also shows the analogous depth profile for argon implanted into GaAs with energy \(E_i = 2500\) eV which was calculated with the assumption that argon did not sputter the layer. Comparison of the profiles for argon and nitrogen results in conclusion important for the described experiment devoted to modification of the nitrided layer by Ar\(^+\) ion bombardment: Ar\(^+\) ions mix all atoms of the nitrided layer throughout the whole thickness. For further analysis of the modification process, one should take into account two processes induced by ion bombardment: (i) spattering the upper layer, and (ii) hammering atoms into deeper layers. These processes result in gradual diminishing the nitrogen concentration in the layer with retaining its thickness.

To analyse the chemical composition of the layer under modification, Auger spectra should be considered again. Some of the NKVV Auger electron spectra measured in this study were shown in Fig. 7a. Curve 1 corresponds to the spectrum of as prepared nitride layer. Curves 2 – 4 were obtained after the bombardment of the nitride layer by Ar\(^+\) ions for 3, 7, and 12 min, respectively. A quantitative analysis of the revealed nitride phases was carried out by the spectra decomposition described above. The ratios of areas under the elementary spectra correspond to the content of nitrogen atoms in the revealed nitride phases. Decomposition
of the as prepared nitride film showed that only about 70% of nitrogen atoms enter into the GaN phase and about 30% of nitrogen is contained in the GaAsN phase.

As can be seen from Fig. 7a (curves 2 – 4), the bombardment of the nitride layer by Ar$^+$ ions leads to a redistribution of the intensities of the main nitride components, which is related to an increase in the fraction of the GaAsN phase. Fig. 10 shows plots of the relative content of nitrogen in the GaN and GaAsN phases versus duration of the sample bombardment by Ar$^+$ ions. In addition to the scale of irradiation duration, Fig. 10 also presents the scale of evaluated depth of the sputtered (etched-off) layer. This scale was calibrated to the TRIM calculated profile assuming that a decrease by half in the concentration of nitrogen in the...

Fig. 9. Depth concentration profiles for nitrogen and argon implanted into GaAs with energy $E_i = 2500$ eV which were calculated by TRIM code (Ziegler at al., 1985).

Fig. 10. Plots of the relative content of nitrogen in the GaN and GaAs$_{1-x}$N$_x$ phases versus duration of the sample bombardment by Ar$^+$ ions.
nitride layer approximately corresponded to the average depth \( h \) of nitrogen ion penetration. The data in Fig. 10 demonstrate the chemical effect of an argon ion beam on the nitride layer, which leads to a gradual disappearance of the GaN phase and a growth of the GaAsN phase. As a result of this treatment, the distribution of nitrogen between the two phases changes to the opposite.

Quantitative elemental and chemical composition of the nitrided layer and its variation in \( \text{Ar}^+ \) bombardment were determined in our experiment. Fig. 11 shows dose-dependencies of the Ga and As concentrations as well as the content of the main chemical phases GaN and GaAsN. Concentration of nitrogen is a difference between Ga and As concentrations. One can see that the initial nitrided layer contains \( \sim 83 \) at.\% of GaAsN alloy. But the treatment of the layer by \( \text{Ar}^+ \) ion beam enhances this contribution above \( 98 \) at.\%. The nitrogen content in \( \text{GaAs}_{1-x}\text{N}_x \) alloy proved to be relatively high ranging from \( x \sim 0.09 \) to \( x \sim 0.04 \) in the course of \( \text{Ar}^+ \) bombardment.

The observed effect of the argon induced alloy formation can be explained by the intermixing of chemical phases (clusters of substances with different compositions) by ion cascades that are effectively generated by the heavy argon ions (Gordeev et al., 2003; Mikoushkin et al., 2008). In addition to the indicated chemical phases, this cascade process involves (i) residual (substituted) arsenic atoms not sputtered during the implantation and (ii) GaAs phase, the fraction of which increases as the nitride layer is sputtered by the argon ion beam and atoms of the GaAs substrate are involved in the process:

\[
\text{GaN} + \text{GaAsN} + \text{As} + \text{GaAs} \rightarrow \text{GaAsN}. \tag{1}
\]

The resulting solid solution is characterized by a greater relative content \( x \) of nitrogen and, hence, becomes unstable and exhibits partial decomposition (Mikoushkin et al., 2008):

\[
\text{GaAs}_{1-x}\text{N}_x \rightarrow x \text{GaN} + (1-x) \text{GaAs} \tag{2}
\]

The dynamic equilibrium of the processes (1) and (2) results in the distribution of nitrogen between the two nitride phases presented in Fig. 10. As the material is sputtered and the

![Graph showing concentration vs. sputtered depth and concentration vs. bombarding time](image-url)
nitrogen concentration [N] in the nitride layer decreases, the nitrogen concentration in GaAs$_{1-x}$N$_x$ alloy drops, this solution becomes stable, and its relative fraction increases.

**Conclusions.** Using the procedure of *in situ* Auger control, it has been established that only about 70% of nitrogen atoms of the nitrided layer prepared by implantation of N$_2^+$ ions with energy $E_i = 2500$ eV into an epitaxial layer of GaAs(100) is contained in the GaN phase. The remaining 30% enter into a GaAsN solid solution. It is established that the bombardment by accelerated argon ions produces a chemical effect on the nitride layer, which is related to a cascade mixing of the material. As a result, the nitrogen distribution between these competing phases changes to the opposite and the phase of GaAsN alloy becomes completely predominating. Finally, the 8 nm thick nitrided film consisting as far as 98 at.% of GaAs$_{1-x}$N$_x$ alloy with relatively high nitrogen concentration $x \sim 0.04$ has been fabricated by low energy implantation technique.

5. Conclusion

*In situ* quantitative chemical composition diagnostics of the nitrided nanolayers has been developed using high resolution synchrotron radiation based photoelectron spectroscopy and ordinary Auger electron spectroscopy. Chemical phases of GaN, GaAsN and GaAs were distinguished for the first time in nitrided layers formed on the GaAs surface by N$_2^+$ low energy ion implantation. Core level binding and Auger energies for these phases were measured in one experiment with high accuracy which made possible the developed diagnostics of the GaAs nitrides. We revealed that 5 nm thick nitride nanolayer created at high vacuum conditions by implantation of N$_2^+$ ions with energies below $E_i = 1500$ eV into GaAs(100) surface at room temperature is not an entire GaN layer. It consists of the narrow band gap clusters of GaAs$_{1-x}$N$_x$ alloy with high nitrogen concentration $x \sim 0.10$ in the wide band gap matrix of GaN. This system has a sign of a system of quantum dots. The implantation of N$_2^+$ ions at an energy of $E_i = 2500$ eV into an epitaxial layer of GaAs(100) was shown to form a nitride layer with a thickness of about 8 nm. Auger diagnostics for quantitative chemical analysis of the nitrided layers has been developed using the values of NKVV Auger energies in GaN and GaAsN chemical phases measured in one experiment, with the accuracy being sufficient for separating their contributions into the experimental spectrum. Using this diagnostics, it has been established that 70% of nitrogen atoms in the nitrided layer is contained in the GaN phase. The remaining 30% enter into a GaAs$_{1-x}$N$_x$ ($x \sim 0.09$) alloy. Nevertheless the alloy proved to be a dominant phase (> 80 at %) with inclusions of GaN clusters. It was established that the bombardment by accelerated argon ions produces a chemical effect which is related to a cascade mixing of the material. As a result of the nitride layer modification the distribution between these competing phases changes to the opposite and the domination of GaAs$_{1-x}$N$_x$ alloy becomes absolute (> 98 at %). Thus, the possibility of fabrication of the narrow band gap GaAs$_{1-x}$N$_x$ dilute alloy nanofilms with high nitrogen concentration $x$ was demonstrated with the help of low energy ion implantation.

6. Acknowledgment

The research was supported by the Russian Foundation for Basic Research (RFBR № 08-08-12230-ofi), by the Ministry of education and science of Russia (Contract No P2431) and by the German- Russian Laboratory at BESSY II.
7. References


Ion implantation presents a continuously evolving technology. While the benefits of ion implantation are well recognized for many commercial endeavors, there have been recent developments in this field. Improvements in equipment, understanding of beam-solid interactions, applications to new materials, improved characterization techniques, and more recent developments to use implantation for nanostructure formation point to new directions for ion implantation and are presented in this book.

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