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Au, Mg and Zn diffusion in GaN

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Transmission electron microscopy was used to study the defects generated in GaN heteroepitaxial layers during diffusion of Au, Zn and Mg in the temperature range 900°C – 1200°C. The diffusion annealings were carried out under N₂ pressure of 1 GPa in order to avoid decomposition of GaN. Diffusion of the metals into the GaN layers was connected with formation of voids and nanotubes along dislocation cores. Reasons and mechanisms of their formation were discussed. The penetration profiles were measured by means of SIMS. The effective diffusion coefficients and the activation energy for Au diffusion in GaN were calculated.

Keywords: diffusion, GaN heteroepitaxial layer, structural defects.

Методами просвечивающей электронной микроскопии изучали образование дефектов в гетероэпитаксиальных слоях GaN в процессе диффузии Au, Zn и Mg при температурах 900°C – 1200°C. Во избежание разложения нитрида галлия при высоких температурах диффузионный отжиг проводили в атмосфере азота под давлением 1 ГПа. Диффузия металлов в GaN сопровождалась образованием пор и нанотрубок вдоль линий дислокаций. Обсуждены причины и механизмы их образования. Методами масс-спектрометрии вторичных ионов (SIMS) измеряли профили распределения концентрации в зоне диффузии. На их основе рассчитали эффективные коэффициенты и энергии активации диффузии Au в GaN.

Ключевые слова: диффузия, гетероэпитаксиальный слой GaN, структурные дефекты.

Методами трансмісійної електронної мікроскопії досліджували створення дефектів у гетероепітаксійних шарах GaN під час дифузії Au, Zn і Mg за температур 900°C – 1200°C. Аби уникнути розпаду нітриду галія за високих температур дифузійний відпал здійснювали в атмосфері азота під тиском 1 ГПа. Дифузія металів у GaN супроводжувалася створенням пор та нанотрубок вздовж ліній дислокацій. Обговорено причини і механізми їх створення. Методами мас-спектрометрії вторинних іонів (SIMS) вимірювали профілі розподілу концентрації у зоні дифузії. На їх підставі розраховували ефективні коефіцієнти та енергії активації дифузії Au у GaN.

Ключові слова: дифузія, гетероепітаксійний шар GaN, структурні дефекти.

Introduction

GaN heteroepitaxial layers grown on Al₂O₃ substrates are widely used in blue-light optoelectronic devices. The challenge of development blue-light emitting lasers and high power optoelectronic devices requires improved control of diffusion processes taking place in GaN. Due to a large lattice misfit between the sapphire and GaN, a high density of so-called “threading dislocations” is present in the GaN. The fast diffusion along dislocation leads to deterioration of electrical contacts to GaN, thus limiting the lifetime of GaN based lasers. There are practically no quantitative data about diffusion in GaN. One of the reasons is the technical difficulty of carrying out such diffusion annealings: diffusion in GaN in conditions of thermodynamic stability at temperatures 1000°C and above must be studied under nitrogen overpressure of 1 GPa or more. On the other hand it is known that diffusion of impurities in GaAs and other III-V compounds can cause generation of voids [1]. It can therefore be expected that diffusion of metals will lead to

formation of defects in GaN as well.

The purpose of the present work was to investigate the diffusion of selected metals, such as Au, Mg and Zn, from evaporated layers into heteroepitaxial GaN layers and to characterize the microstructure after the diffusion anneals. Au was selected as one of the components for electrical contacts to GaN, and a non-reactive metal suitable for basic studies of diffusion processes. Zn and Mg diffusion is of interest since both metals are p-dopants in GaN.

1. Experiment

In the first set of the experiments thin films of Au, Zn and Mg of 20 nm thickness were deposited in vacuum of 10⁻⁷ mm Hg on the (0001) surface of 1,7 μm thickness GaN epitaxial layer grown on the sapphire substrate. Such layers produced by CREE company have block structure with average disorientation angle of about 0,1°. These layers were characterized by high density of threading dislocations 10¹⁴m⁻² (Fig.1.1).

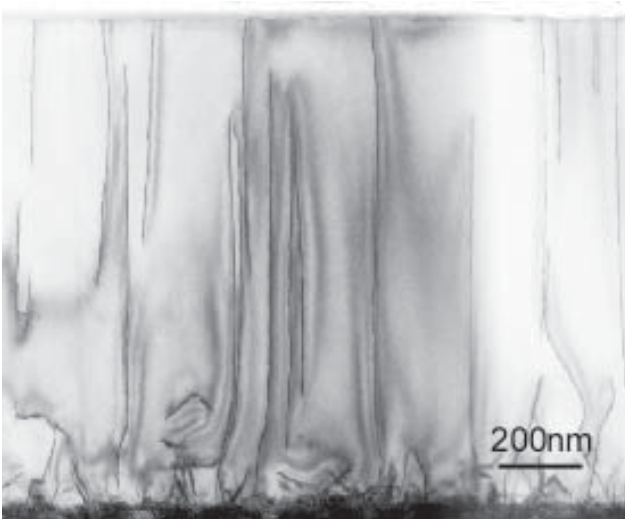


Fig.1.1. Typical TEM image of microstructure of the cross section of nonannealed GaN epitaxial layer grown on the sapphire substrate (CREE company production).

Isothermal anneals of prepared samples were done at hydrostatic N₂ pressure conditions (P_{N₂}=1 GPa) in the temperature range 900 – 1200 °C during 10 min according to procedures described in [5, 8]. The crucible with the GaN layers contained also GaN powder. The annealing procedure ensured the thermodynamic stability of the GaN layers. After anneals distributions of Au, Zn and Mg concentration in the direction normal to the (0001) atomic plate were obtained using SIMS method (Secondary Ion Mass Spectrometry).

In the second set of the experiments thin films of Au of 20 nm thickness were deposited on the (0001) surface of GaN single crystal. From the diffusion experiments with heteroepitaxial layers it was found that GaN surface shift was strongly degraded with Mg and Zn diffused into the GaN layer. It was the reason therefore to provide the diffusion experiments with Zn and Mg from gaseous phase. GaN single crystal was placed inside the crucible together with

Mg or Zn pease. Samples were anneal in the temperature range 900 – 1400 °C during 2–4 h. Concentration profiles of Au, Zn and Mg were obtained using SIMS method.

2. Experimental results and discussion

2.1. Au/GaN-monocrystal system

It wasn't found any structural changes in GaN single crystal as a result of Au diffusion in it. All substance of the gold film was penetrated into the GaN single crystal during diffusion experiment (except part of gold was evaporated). The typical penetration profiles of Au diffused into the GaN single crystal at 1 GPa nitrogen pressure are presented on Fig.2.1 a.

Considering the process as a gold diffusion in a semi-infinite solid from the instantaneous source concentration dependence Au from coordinate and time may be present as

$$C(X, t) = C(0, t) \exp\left(-\frac{X^2}{4D_b t}\right),$$

where X is the depth from the surface; D_b is the bulk diffusion coefficient of Au in GaN. From the slopes of the plots lnI vs X² (Fig. 2.1 b) values of the Au diffusion coefficients in GaN were calculated (Table I).

2.2. Au/GaN-heteroepitaxial system

Diffusion of Au into the dislocated heteroepitaxial GaN layer was accompanied by wide short crater formation (Fig. 2.2 a).

It was typical for all GaN layers covered by Au film annealed in temperature range 900 – 1200 °C. The craters are located at the places where threading dislocations emerge at the surface. In addition as it is shown on the Fig. 2.2 b, Au diffusion accompanied by voids appearing along dislocation lines. The void formation takes place in the whole temperature range but becomes more pronounced

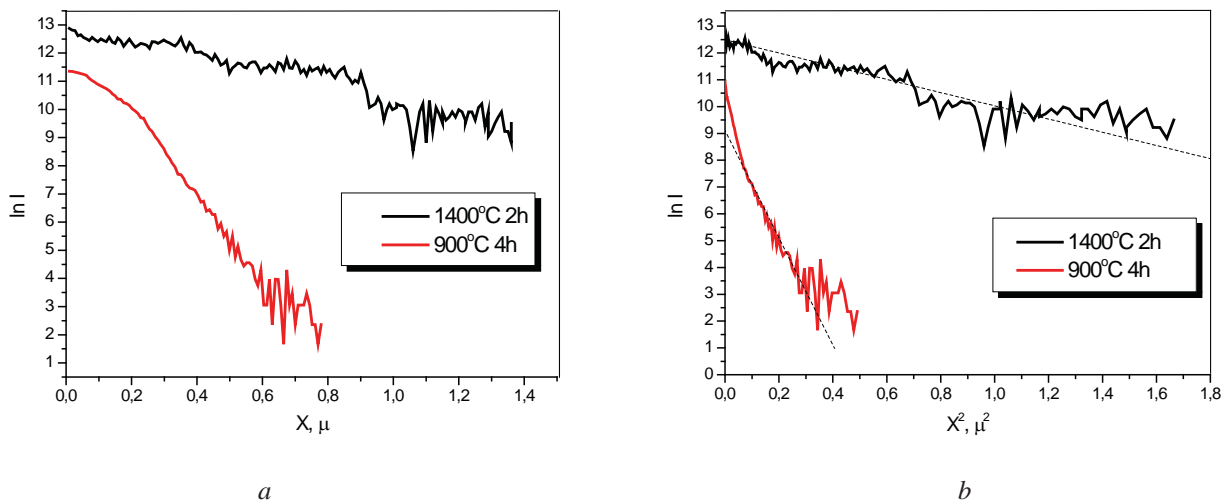


Fig. 2.1. a – The typical penetration profiles of Au diffused into the GaN single crystal at 1 GPa nitrogen pressure; b – lnI vs X² plot for Au diffusion in GaN.

Table I

| | |
|------|--------------------------------|
| T°C | $D_b, \text{m}^2\text{s}^{-1}$ |
| 900 | 5.6×10^{-19} |
| 1200 | $9.25 \cdot 10^{-18}$ |
| 1400 | 3.3×10^{-17} |

Table II

| | |
|------|--------------------------------|
| T°C | $D'a, \text{m}^3\text{s}^{-1}$ |
| 900 | $4,3 \times 10^{-22}$ |
| 1050 | $7,9 \times 10^{-22}$ |
| 1200 | $1,3 \times 10^{-20}$ |

Table III

| | | |
|------|--|--|
| T°C | $D_b^{\text{Zn}}, \text{m}^2\text{s}^{-1}$ | $D_b^{\text{Mg}}, \text{m}^2\text{s}^{-1}$ |
| 1200 | $1,6 \times 10^{-18}$ | $1,6 \times 10^{-19}$ |

at higher temperatures. The formation of small voids takes place also in the GaN bulk around of the dislocations. The SIMS penetration profiles of Au in the GaN heteroepitaxial layers are presented on the Fig. 2.3.

The estimation of the depth of the Au penetration into the GaN bulk during annealing for heteroepitaxial layer shows that diffusion of Au into the dislocated layer is realized in B regime [4]. It means that diffusion of Au along the short-circuiting paths followed by leakage, i.e., lateral diffusion into the bulk from the dislocation:

$$a < \sqrt{D_b t} < \frac{\lambda}{2},$$

where a is the dislocation core radius, λ is the average

distance between the short-circuiting paths.

In our case $\lambda \sim 100$ nm, $\sqrt{D_b t} \sim 20-30$ nm for different temperatures. Therefore the average concentration value estimated by SIMS method at the depth X from the surface is described by Suzuoka solution [2]:

$$\bar{C}(X, t) = C(0, t) \left[\exp\left(-\frac{X^2}{4D_b t}\right) + \frac{2\sqrt{D_b t}}{\lambda} (C_1 + C_2) \right],$$

where C_1 is the contribution to $\bar{C}(X)$ of diffusion along the dislocations, C_2 is the contribution to $\bar{C}(X)$ of the

volume diffusion laterally from the dislocations. If we use the Le Claire's parameter [3]

$$\beta = \frac{D'}{D_b} \frac{a}{2\sqrt{D_b t}} \quad (1)$$

where D' is the diffusion coefficient along dislocation then the value $D'a$ may be calculated from the relationship obtained in the framework of the Suzuoka solution [4]

$$-\frac{\partial \lg \bar{C}}{\partial \left(\frac{X}{\sqrt{\beta D_b t}}\right)^{5/5}} = 0,72 \beta^{0,008}$$

For fixed t and T $\sqrt{\beta D_b t} = \text{const}$ and so

$$-\frac{\partial \lg \bar{C}}{\partial X^{5/5}} = 0,72 \beta^{-0,592} (D_b t)^{-0,6} \quad (2)$$

The β value is calculated from the slope of $\lg \bar{C}$ vs $X^{5/5}$ plot. Then from (1)

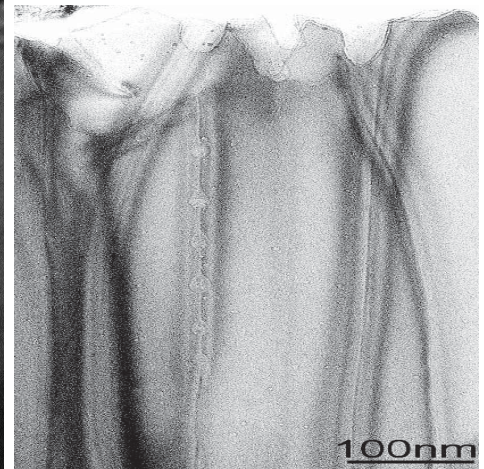
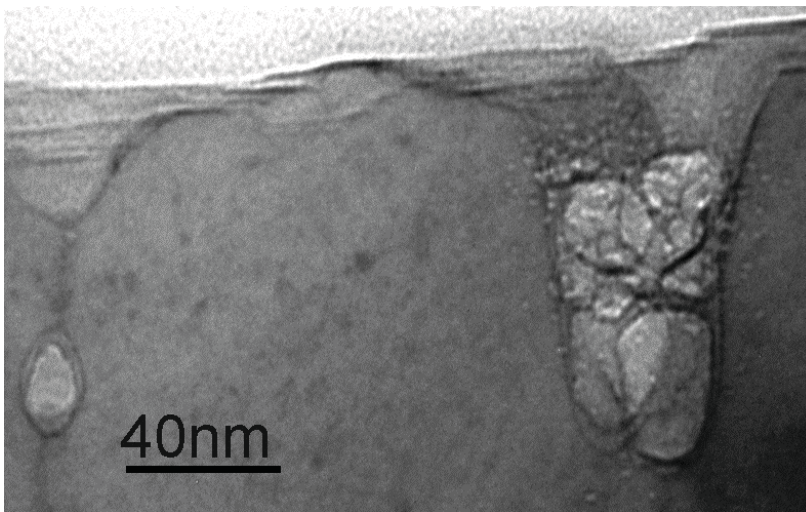


Fig. 2.2. a – Bright-field TEM image of the crater structure formed at the surface of GaN heteroepitaxial layers with deposited Au film as a result of annealing at temperatures in the range 900 – 1200°C. b – TEM bright field image of voids along dislocations.

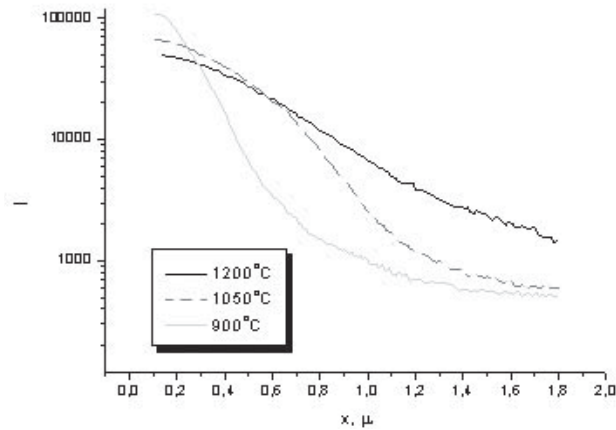


Fig. 2.3. The typical SIMS penetration profiles of Au in the GaN heteroepitaxial layers ($t = 10$ min, $P = 1$ GPa).

$$D'a = 2\beta D_b^{3/2} t^{1/2}.$$

The results of calculation of the value $D'a$ are presented on the Table II.

For understanding of structural changes taking place in heteroepitaxial GaN layers during Au diffusion it is necessary to make some assumption about mechanism of Au, Ga and N atom diffusion migration in GaN lattice.

In wurtzite-type GaN structure (Fig. 2.4 a,b) the strong electronegativity of nitrogen leads to a strong localization of the electron density around the nitrogen atoms. Nitrogen atom requires 3 electrons for completing of 2p electron shell. Gallium atom have 3 valence electrons (4s² and 4p) and 4 nearest nitrogen neighbors. So it can be assumed that the valence electrons realize the three bonds that are close to the ionic ones; and the fourth bond (in the [0001] direction) is the covalent one and can be realized by one of the 3d electrons of gallium atom and by one of the 2s electrons of nitrogen atom (Fig. 2.4 c). As a result the gallium atoms in GaN lattice have the charge of about (+3) and nitrogen atoms have the charge of about (-3).

As long as Ga and N atomic bonds in GaN lattice are closed to the ionic ones as Ga³⁺ and N³⁻ migrate in the

own sublattice. If the migration occurs by the vacancy mechanism than Au atoms diffusion may be realized in both sublattices (in supposition that Au atoms are not ionized in GaN lattice).

Generally speaking the Ga³⁺ and N³⁻ ions diffusivity must be greater than the Au atoms one because the jump frequency for example of Ga³⁺ to the V_{Ga}³⁻ vacancy is $C_V^- \Gamma_V$ and the jump frequency of Au atom to vacancy is $(C_V^- + C_V^+) C_{Au} \Gamma_V$ (Γ_V is the frequency of diffusion jumps of vacancies in crystal, C_V^- , C_V^+ – vacancy concentrations, $C_{Au} \ll 1$ is Au atoms concentration in GaN lattice).

After assumptions have done it become to be understandable the void formation effect as along dislocation lines as in the bulk. As it was above mentioned dislocation structure of GaN heteroepitaxial layer is presented by threading dislocations which are normal oriented to the surface of the layer. The diffusion flow of Au atoms along dislocations as well as in volume laterally from short circuits is accompanied by more powerful flow of the more mobile Ga³⁺ and N³⁻ from volume towards the short circuits and then along dislocations towards the GaN layer surface. The difference of this flows must be compensated by cation V_{Ga}³⁻ and anion V_N³⁺ vacancy flow from the surface along dislocations and then in volume of crystal. We have observed the display of this process as the Kirkendall effect: the voids formation along dislocation lines as well as in crystal volume near the dislocations. The edge dislocations are good absorbers of the excess vacancies but in wurtzite-type structure absorption of the vacancies by the edge dislocations leads not to their climb but to the cavity formation on it. The edge dislocation structure in wurtzite GaN is presented on the Fig. 2.5 a. The strained and ‘dangling’ bonds present in the dislocation core could permit impurities and intrinsic defects to be trapped there. The trapping of cation and anion vacancies leads to the cavity formation on the dislocation’s core as it is represented on Fig. 2.5 b–d.

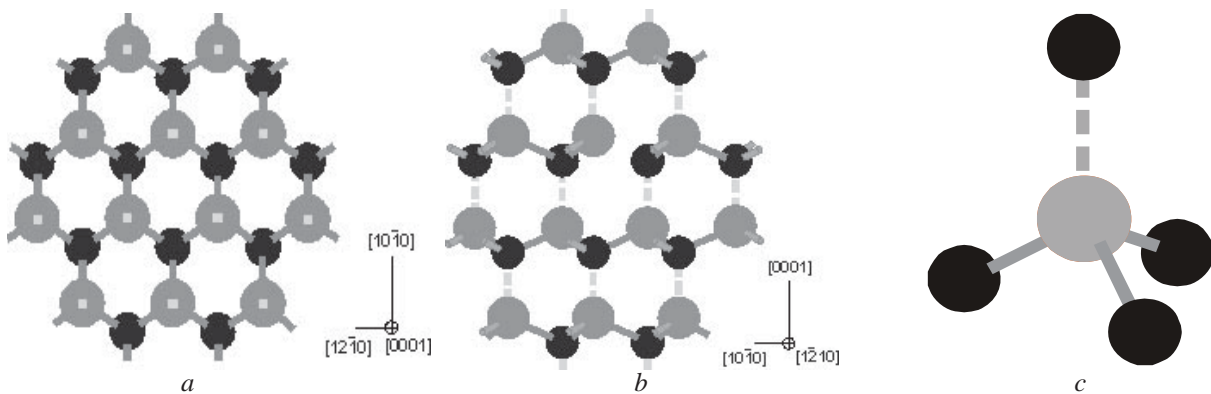


Fig. 2.4. Schematic picture of the wurtzite-type structure of GaN. The gallium and nitrogen atoms are presented as grey and black disks, respectively. The covalent bonds are presented as interrupted lines.

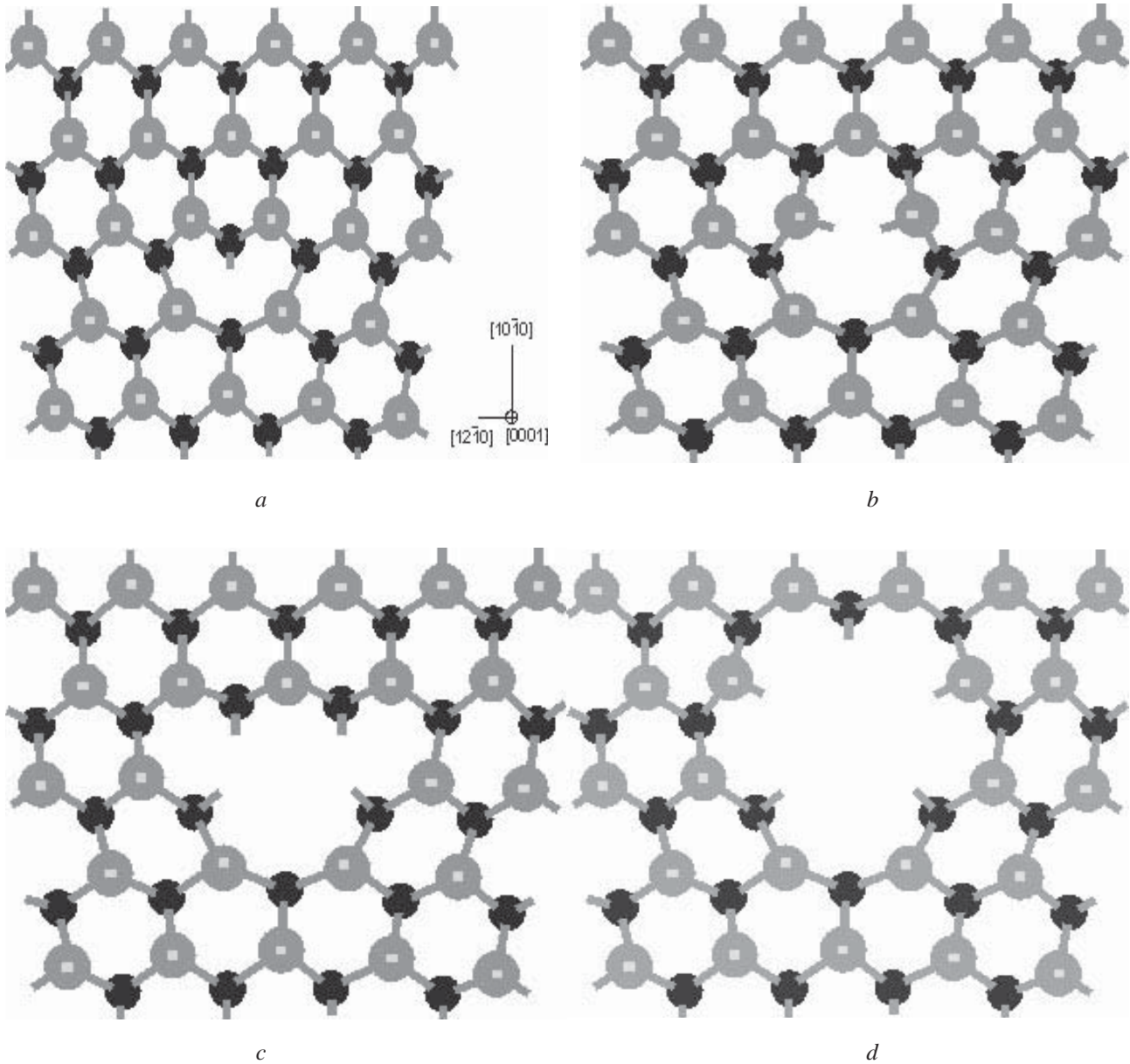


Fig. 2.5. a – The schematically presented top view (in [0001]) of the threading edge dislocation core in GaN; b,c,d – the successive stages of cavity evolution on the dislocation caused by trapping of cation and anion vacancies by the dislocation core.

Au atom moving from dislocation to the bulk is also accompanied by the vacancy flow directed from dislocation to the bulk. As the opposite charged vacancies have a tendency to form $(V_{Ga}^{3-} - V_N^{3+})$ complexes (Fig. 2.6), then the cavities in the bulk are formed from the supersaturated vacancy solution.

Formation of wide short craters located at the places where threading dislocations emerge at the surface possibly connected with weak GaN solubility in liquid Au that occurs preferably in the defect places of lattice.

2.3. Mg,Zn/GaN-single crystal system

Zn or Mg diffusion from gaseous phase in GaN may be considered as diffusion in a semi-infinite solids with

constant surface concentration. Typical penetration profiles for Zn and Mg diffusion into the GaN monocrystal are represented in Fig.2.7.

Measured concentration distribution may be approximated as erfc-function:

$$C(X) = C_0 \operatorname{erfc} \left(\frac{X}{2\sqrt{D_b t}} \right).$$

From the slope of $\operatorname{erfc}^{-1}(C/C_0)$ vs $(X/2\sqrt{t})$ plot one can obtain the bulk diffusion coefficient D_b . The calculated values of D_b are presented in Table III.

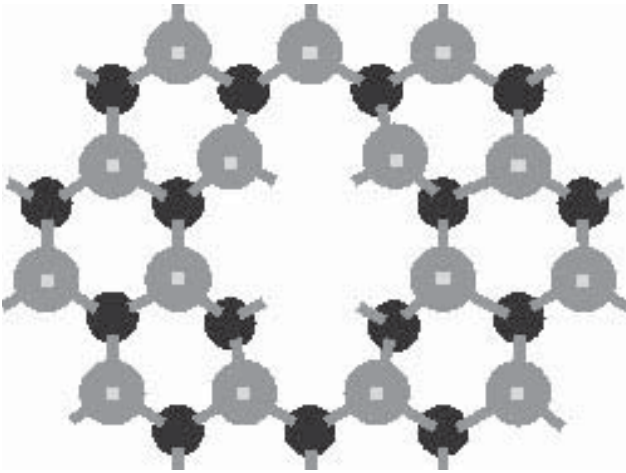


Fig.2.6. Schematic picture of the $(V_{Ga}^{3-} - V_N^{3+})$ complex in GaN.

2.4. Zn,Mg/GaN-heteroepitaxial system

The surface of GaN layers was strongly modified, and the average thickness of the GaN layer decreased by several hundred of nanometers. Fig. 2.8 shows a typical structure of GaN layers after annealing in Zn vapor. Long tubes which are filled partly by zinc are observed, with thicknesses in the range of 10 – 20 nm. Diffusion of Zn and Mg is accompanied with creation of voids along dislocation lines (Fig.2.9a) as well as at some distance from the dislocation lines. Fig. 2.9b shows a set of small V-shaped voids surrounding a larger V-shaped void. Other defects observed after Zn and Mg diffusion are nanotubes with smooth and saw-tooth-like walls (Fig. 2.10).

The GaN surface corrugations (Fig. 2.8) and decrease



Fig. 2.8. Typical structure of GaN layers after annealing in Zn vapor at temperature of 1200°C.

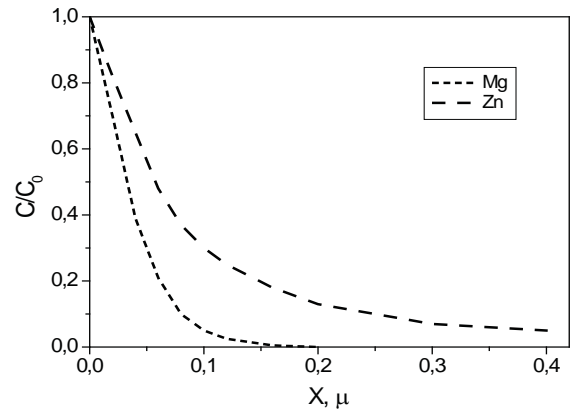


Fig.2.7. Penetration profiles for Mg and Zn diffusion into the GaN single crystal from gaseous state at 1 GPa nitrogen pressure and temperature of 1200°C;

of layer thickness indicate that GaN was destroyed near the surface at the temperature of the diffusion anneal. These surface corrugations made it impossible to estimate the diffusion coefficients.

It is generally accepted that diffusion of Zn and Mg atoms in compounds, based on the elements of groups III and V of the periodic table occurs via an interstitial-substitutional exchange mechanism [6,7], and that Zn or Mg is incorporated substitutionally on group III sublattice sites where it acts as a shallow acceptor.

Describing the structure changes during of Zn or Mg diffusion in GaN it is necessary to take into account the fact that the II-valence impurity atoms became twice ionized in GaN lattice. In this case electrons of the impurity atom ($Mg - 3s^2$, $Zn - 4s^2$) realize the ion bonds with two of the three N^{3-} anions located in (0001) plate. The covalent bond with the third anion is established. It caused p-type conductivity of GaN because electron was trapped from valence zone for creation of this bond. As the twice ionized impurity atom substitute the three time ionized Ga atom in GaN lattice then the effective impurity atom charge is about (-1) . So substitution of Ga atom by the two-valent impurity atom leads to reconstruction of the electron configuration and to displacement of the neighboring nitrogen atoms outwards with respect to the ideal lattice sites [9] (Fig. 2.11a).

In this case the impurity atom have weaker bonds in lattice in comparison with Ga atoms located near by the displaced nitrogen atoms (Fig. 2.11 b).

Thus doping of II-valent impurity in GaN must lead to the reducing of the Ga atoms diffusivity because of increasing of activation energy of Ga atom migration and of V_{Ga}^{3-} vacancy formation energy. This conclusion is in agreement with results of V_{Ga}^{3-} in GaN concentration measurements at different Mg content [10]. In [10] using positron annihilation method was found that V_{Ga}^{3-} concentration reduced down to 0 with Mg concentration

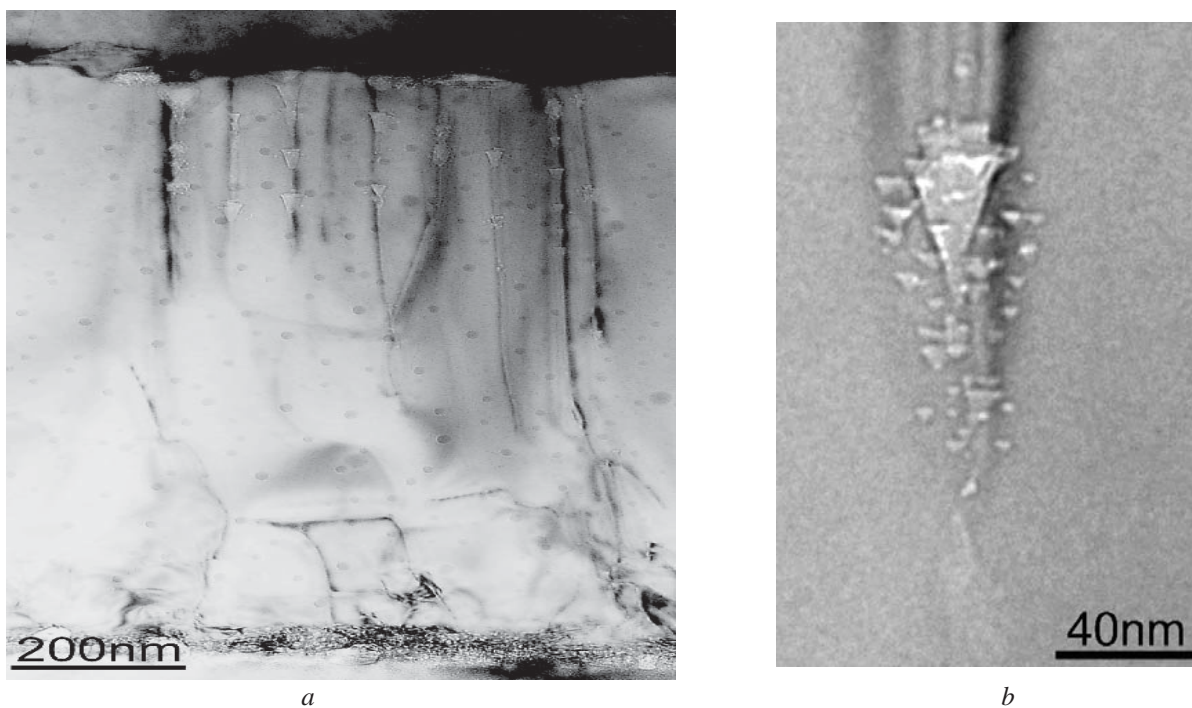


Fig. 2.9. a – voids formed along dislocation lines after annealing; b – a colony of small voids around larger V-shaped void.

increasing in GaN.

Since the activation energy of II-valent impurity atom migration $E_m^{imp} < E_m^{Ga}$ then diffusion coefficient of the impurity $D_{imp} > D_{Ga}$. So impurity atom diffusion from the surface to the volume of GaN must be accompanied by the V_{Ga}^{3-} vacancy flow directed from the volume to the surface. In this case the void formation in the GaN bulk is impossible.

The reason of nanotube and void formation can be participation of oxygen in diffusion process. There is experimental evidence that oxygen acts as a donor in bulk GaN [16] and total energy calculation show that O sits on a N site [17] where it has the effective charge of about (+1). It means that the neighboring Ga atoms replace from the ideal lattice positions as it shown on Fig. 2.12 a. As seen from Fig. 2.12 b it leads to reduce of the activation energy

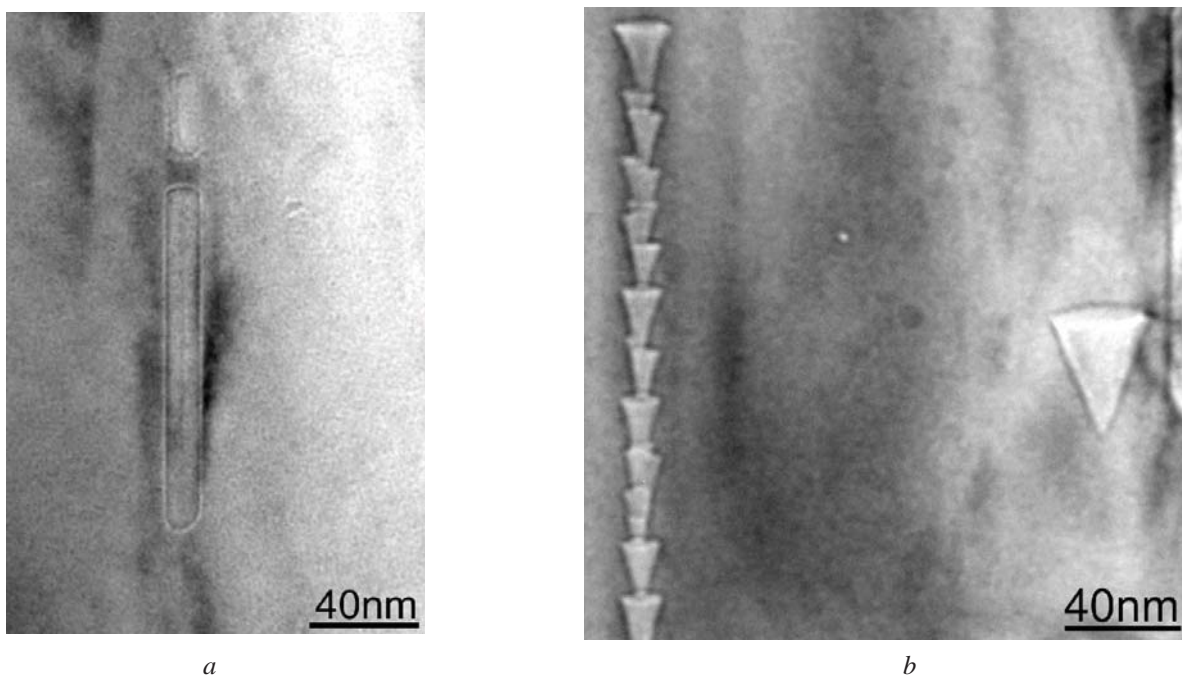


Fig. 2.10. Morphologies of nanotubes in GaN heteroepitaxial layers after Zn and Mg diffusion. a – elongated voids with smooth walls; b – nanotubes with faceted wall structure.

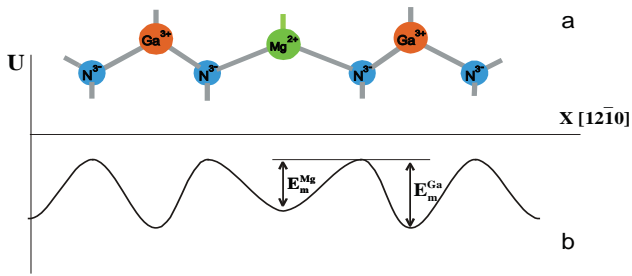


Fig. 2.11. a – The nitrogen atoms outward relaxation with respect to the regular GaN lattice sites after the two-valent impurity was incorporated substitutionally on the Ga sublattice site. Impurity Mg atom is presented as lightgray disk; b – alteration of the potential relief for the Ga sublattice sites around of the impurity. E_m^{Mg} and E_m^{Ga} are the activation energy for migration of Mg and of Ga atoms, respectively.

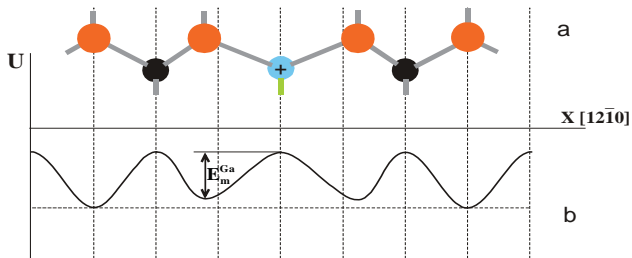


Fig. 2.12. a – The gallium atoms outward relaxation with respect to the regular GaN lattice sites after the oxygen was incorporated substitutionally on the nitrogen sublattice site. Oxygen atom is presented as disk (+); b – alteration of the potential relief for Ga sublattice sites around oxygen.

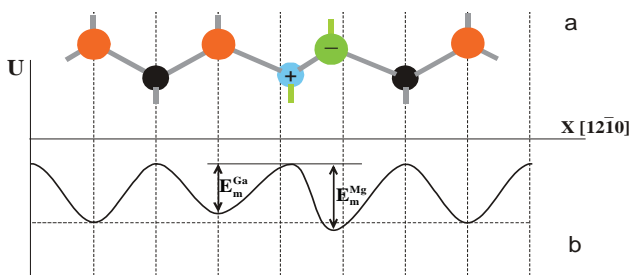


Fig. 2.13. a – The $(Mg^- - O^+)$ complex formation in GaN. O and Mg atoms are presented as (+) and (-) disks, respectively; b – alteration of potential relief for Ga sublattice sites around of $(Mg^- - O^+)$ complex.

for migration of Ga atoms as well as of the V_{Ga}^{3-} formation energy.

In the case of oxygen participation in Mg or Zn diffusion in GaN the great probability of $(Mg^- - O^+)$ or $(Zn^- - O^+)$ complexes formation is exists. From the Fig.2.13 a,b one can see that formation of such complex leads to the increasing of the activation energy for impurity atom diffusion and to the reducing of the activation energy

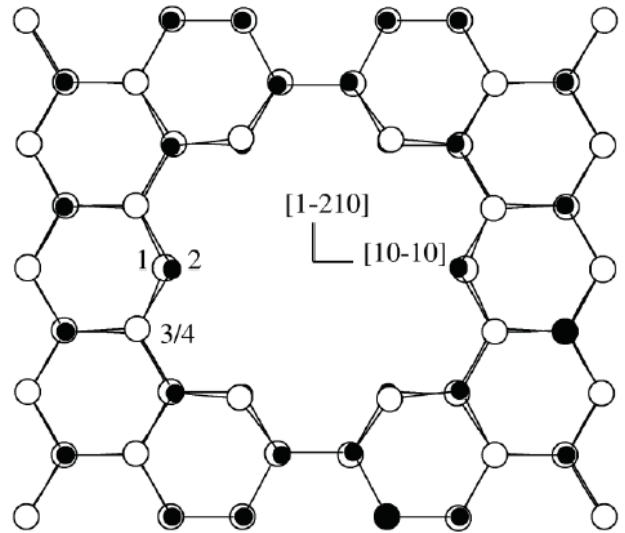


Fig. 2.14. Top view (in $[0001]$) of the relaxed core of the open-core screw dislocation. The three fold coordinated atoms 1 (Ga) and 2 (N) adopt a hybridisation similar to the (10_{-10}) surface atoms [13].

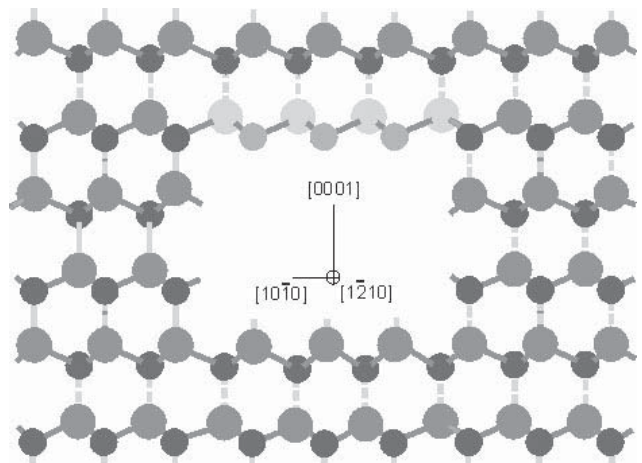


Fig. 2.15. The (000_{-1}) cavity surface in GaN passivated by MgO layer growing from supersaturated vacancy solution in presence of oxygen (light discs) and magnesium (light-grey discs) atoms.

for Ga atom diffusion.

So the direction of the preferential vacancy flow during diffusion of Zn or Mg in GaN will depend from the oxygen quantity taking part in the diffusion process. The diffusion flow of the impurity atoms may be presented as sum of the two flows:

$$J_{imp} = J_1 + J_2,$$

where J_1 is the flow of the mobile ‘free’ impurity atoms, J_2 is the flow of slow ‘impurity-oxygen’ complexes.

The nanotubes and voids formation observed in our experiments means that the preferential vacancy flow is directed from the surface to the volume of GaN. It means that $J_{imp} < J_{Ga}$, i.e. the main contribution in J_{imp} makes diffusion of the complexes¹.

¹ In our experiments we have observed the distance of the

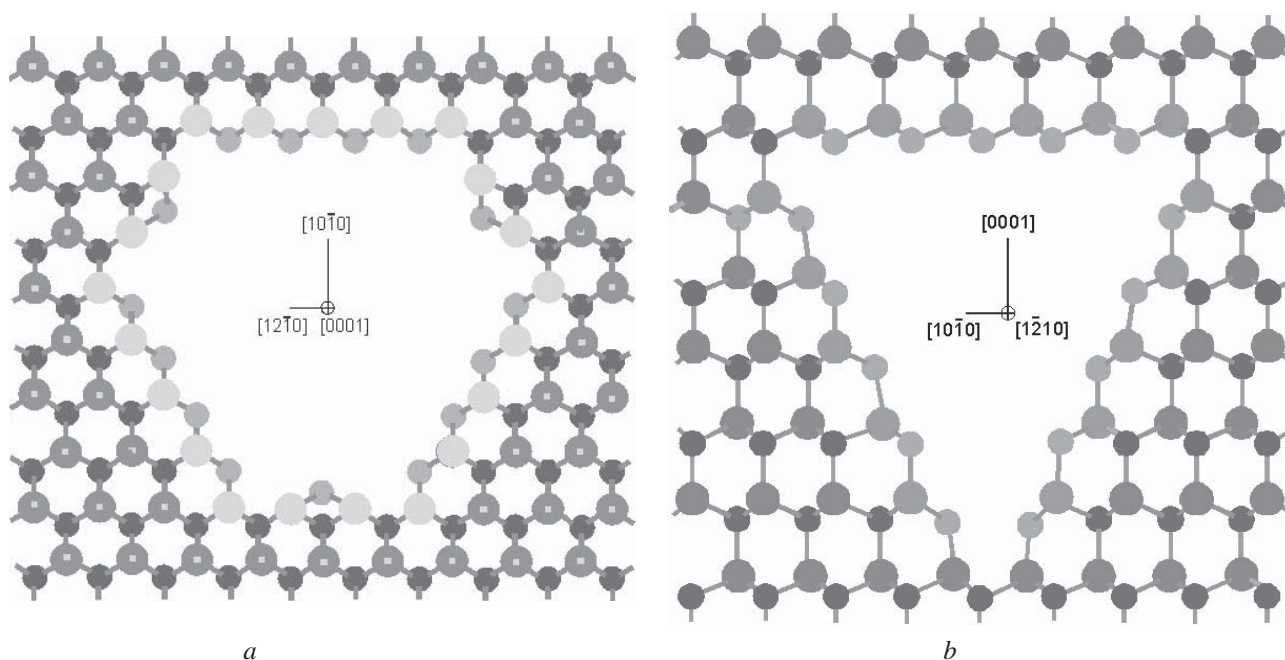


Fig. 2.16. The schematic presentation of top (a) and side view (b) of the void in GaN faceted by high density packed surfaces passivated by MgO.

Since transport of charged V_{Ga}^{3-} vacancies is limited by electroneutrality requirement it is clear that not single vacancies but neutral complexes for example $(V_{Ga}^{3-} - V_N^{3+})$ and $(V_{Ga}^{3-} - 3O_N^+)$ are move.

The directed flow of vacancies and oxygen along the dislocations can leads to the cavity formation on it. The fact that we have observed two types of nanotubes in Zn/GaN and Mg/GaN systems is connected with presence in the epitaxial grown GaN layer of two type of threading dislocations.

Threading screw dislocations in GaN lies along $[0001]$ with a full Burgers vector $b=c[0001]$. They nucleate in the early stages of growth at the sapphire interface arising from the collisions of islands during growth and threading to the surface of the crystallites [11]. At a screw dislocation there is a non-vanishing edge on the surface which favors the crystal growth. Therefore the screw dislocations are essential for the growth process and are the typical extended defects of epitaxial grown crystals.

The strong distortion in the core and thus high line energy of screw dislocation (4.88 eV/\AA [13]) makes it favorable to open the core of the dislocations and to formation of the nanpipes. The energy required to form the surface at the open-core wall is compensated by the energy gained by reducing the strain. This opening has

Zn atoms spreading in GaN greater than of the Mg atoms one. This evidently is connected with the greater bond energy of the $(Mg-O^+)$ complex in comparison with $(Zn-O^+)$ complex, so that the number of the 'bound' Mg atoms is greater than the number of Zn ones.

been observed by Liliental-Weber et al. who found some of the screw dislocations to have holes which are three atomic rows wide [12]. The theoretical calculations shows that the equilibrium diameter of the open-core is approximately 0.7 nm and the line energy of the relaxed dislocation core is 4.55 eV/\AA [13] (Fig. 2.14). A further opening gave a higher line energy because it leads to increasing of the surface energy of core walls.

Growth of GaN on sapphire by vapor phase epitaxy is often associated with the appearance of long nanpipes parallel to c-axis which have hexagonal cross sections with uniform diameters ranging from 5 to 25 nm [14]. Liliental-Weber et al. [15] have found that the density of nanpipes is increased in the presence of impurities, e.g. O, Mg, In and Si and have argued that these impurities decorate the (10_{-10}) walls of the nanpipes inhibiting overgrowth.

The internal surfaces of screw dislocations are very similar to those of the low energy (10_{-10}) surface. In [18] was found that the energy of O in N position is 0.8 eV lower at the relaxed (10_{-10}) surface. This shows that there is a tendency for O to segregate on surface.

Calculations showed that $(V_{Ga}^{3-} - 3O_N^+)$ is more stable at surface than in bulk by 2.15 eV [18]. Two O neighbours of the surface vacancy lie below the surface and each is bonded to three Ga neighbours. But the surface O is bonded to only two subsurface Ga atoms in a normal oxygen bridge site. The defect is electrically inactive with the O atoms passivating the vacancy in the same way as VH_4 in Si [18].

So oxygen has a tendency to segregate on the (10_{-10}) surface and forms stable and chemically inert $(V_{Ga}^{3-} - 3$

O_N^+) defects. These defects increase in concentration when the internal surfaces grow out. When a critical concentration of order of a monolayer is reached, further growth is prevented. This leads to nanopipes with (10_10) walls coated with GaO and supports the suggestions of Liliental-Weber et al. that nanopipes are linked to the presence of impurities [15].

Since in our experiments along with atoms of oxygen impurity atoms or its complexes with oxygen are diffused the nanotube walls adsorb the impurity atoms as well. It apparently reduces the nanotube surface energy and leads to the growth of its diameter up to the equilibrium one for present value of surface energy. This is how the nanotubes with the smooth walls appear. Au adsorption evidently weakly changes the surface energy so we didn't observe nanotubes in experiments with Au.

Pure edge dislocations in GaN lie on {10_10} planes and $\mathbf{b} = \mathbf{a} = [1\text{-}210]/3$ is their Burgers vector. They are dominant species of dislocation, occurring at extremely high densities of approximately $10^8 - 10^{11} \text{ cm}^{-2}$ in hexagonal GaN grown by MOCVD on (0001) sapphire and in analogy to screw dislocations are thought to arise from the collisions of islands during growth [19]. From a supercell calculation, in [9] was obtained a line energy of $2.19 \text{ eV}/\text{\AA}$ for the threading edge dislocation that is considerably lower than the one found for the screw dislocation with a narrow opening. This can be interpreted by noting that the edge dislocation has a smaller number of three fold coordinated atoms than the open-core screw dislocation as well as a smaller elastic strain energy. Therefore the open-core of pure edge dislocations is not observed. But being the short circuits for the impurity diffusion and the good absorbers for the excess vacancies the edge dislocation are the regions for the voids formation.

Let us consider the diffusion spreading of II-valent impurity along edge dislocation process for Mg as an example. Ionized atoms of Mg, (Mg-O^+) as well as ($\text{V}_{\text{Ga}}^{3-} - \text{V}_{\text{N}}^{3+}$) and ($\text{V}_{\text{Ga}}^{3-} - 3\text{O}_{\text{N}}^+$) complexes are moved along the dislocation from the GaN layer surface into the GaN volume. Process of Mg and O accumulation in GaN volume accompany with the process of Ga by Mg and N by O substitution. Simultaneously cavities nucleate from the supersaturated vacancy solution in the core of edge dislocations as well in crystal volume near dislocations. Since oxygen has a tendency to segregate on the surface it replaces nitrogen first of all on the cavity surface. As it moves as a complex with magnesium then the cavity surfaces become covered by MgO.

The cavity growth in wurtzite GaN in presents of oxygen occurs anisotropically because not all the crystallographic directions are equal with respect to the

oxidation process.

As is known the GaN surfaces presented by high density packed {0001} and {1010} planes have minimal energy and faceted the growing crystal. But the (0001) and (000_1) surfaces have different degrees of the chemical activity.

The gallium terminated (0001) surface presented by 3 time ionized Ga atoms which valent electrons are localized around N atoms located deeper under the surface. That is why this surface is very stable with respect to the outside chemical influence.

The nitrogen terminated (000_1) surface is presented by N atoms with complete 2p electron shell. But being in contact with atoms having lesser ionization potential than Ga atoms have the nitrogen atoms tear up the bonds with Ga and make bonds with more active donors.

That is why inside the nucleated primarily isomeric cavity (000_1) surface will oxidize first of all. It becomes so to be passivated by MgO layer and doesn't take part in further cavity growth process (Fig. 2.15).

Another surfaces of the cavity dissolve as the vacancy coming in by diffusion along dislocation core. Since part of the $\text{V}_{\text{Ga}}^{3-}$ vacancies diffuse not only as the ($\text{V}_{\text{Ga}}^{3-} - \text{V}_{\text{N}}^{3+}$) complexes but in the composition of the ($\text{V}_{\text{Ga}}^{3-} - 3\text{O}_{\text{N}}^+$) complexes than the number of $\text{V}_{\text{Ga}}^{3-}$ vacancies coming into the GaN volume exceed the number of V_{N}^{3+} ones (the $\text{C}_\text{V}^{\text{Ga}} - \text{C}_\text{V}^{\text{N}}$ difference is determined by amount of oxygen that takes part in the diffusion). That is why the process of diffusive dissolution of the high density Ga packed (0001) surface will be the fastest. It leads to the form of the faceted cavity formed on the edge dislocation as well in the GaN bulk was observed experimentally. The cavity growth process stops when all its surfaces will be passivated by oxygen. The cavity surface is covered by MgO when Mg diffuses simultaneously with O. (Fig. 2.16 a,b).

Of course the cavities nucleate and grow faster on the dislocation than in volume. Growing together they form the faceted nanotubes we have observed. The growing up small cavities formed in the bulk close to the dislocation line grow into the big cavities as seen in (Fig. 2.9).

The rare faceted voids that was observed in our experiments with Au diffusion in GaN are thought to appear as a result of the ($\text{V}_{\text{Ga}}^{3-} - 3\text{O}_{\text{N}}^+$) complexes diffusion. The diffusion mobility of this complexes is rather lower than mobility of the (Mg-O^+) or (Zn-O^+) complexes which transport oxygen during Mg or Zn diffusion in GaN.

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