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Gallium oxide buffer layers for gallium nitride epitaxy

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Gallium nitride (GaN) is very attractive semiconductor material because of its unique properties. The serious matter is a lack of easy access to bulk crystals of GaN. Synthesized crystals are precious and rather small. For these reasons almost all device manufacturers and researchers apply alternative substrates for gallium nitride devices epitaxy and it causes that the technology is intricate. Alternative substrates need buffer layers – their technology is usually complex and expensive. We have proposed a simple method to avoid large costs: applying gallium oxide – monoclinic β-Ga_2O_3, as the buffer layer, which has structural properties quite good matched to GaN. As the substrates made from single crystal gallium oxide are still hardly available on the market, we have used hydride vapour phase epitaxy (HVPE) GaN epilayers as a starting material. It can be GaN layer under good quality – middle or low. The oxidation process converts top GaN to β-Ga_2O_3 layer which can release or absorb the strain. Applying such structure in another, second, epitaxy of GaN allows to obtain good quality epitaxial structures using HVPE technique.

Keywords: hydride vapour phase epitaxy, gallium nitride, gallium oxide, thermal oxidation, buffer layer.

1. Introduction

Monoclinic β-Ga_2O_3 is the only variety of gallium oxide Ga_2O_3 which is stable in high temperature and remains stable after cooling. It is a very promising electronic material for numerous applications [*e.g.*, 1–3]. Structural parameters of this oxide are very similar to the gallium nitrides ones. The lattice mismatch has a minimum of 2.6% for the in-plane epitaxial relation $\langle 011\rangle_{Ga2O3} \parallel \langle 10\bar{1}0\rangle_{GaN}$ [4].

It is worth to utilize considerable similarity in the structure and lattice parameters of gallium nitride and gallium oxide to obtain good quality epitaxial GaN structures. In order to benefit from this likeness, it is necessary to rebuild oxide surface by

nitridation. In this process part of oxygen atoms are replaced by nitrogen atoms. In the HVPE (hydride vapour phase epitaxy) system it can be done by using ammonia gas as a nitridation agent.

2. Experiment

In the experiments we have used GaN epitaxial layers, which were grown in conventional, open HVPE system on sapphire substrates: three-temperature zone furnace and horizontal quartz reactor [5]. Nitrogen (6N) was used as the carrier gas. GaCl was formed by the reaction of gaseous HCl (6N) and liquid Ga (6N) at 920 °C. HCl was diluted by nitrogen. NH_3 (7N) was used as the source gas. Total gas flow was about 4500 ml/min. The temperature in growth zone was kept at 1060 °C.

The sample preparation was performed in two steps: (1) oxidation of the GaN layers and (2) nitridation of oxidized samples and re-epitaxy. In order to choose the optimal method in terms of structural properties and surface smoothness, oxide layers were fabricated on the top of GaN epitaxial structures by thermal oxidation in three ways: (1) wet oxidation in nitrogen and water vapour, (2) wet oxidation in nitrogen, water vapour and oxygen (mixed oxidation) and (3) dry oxidation in nitrogen and oxygen. The thermal oxidation system was described in [6, 7] and is shown in Fig. 1. It was a three-zone resistant furnace with a saturator and gas manifold (nitrogen and oxygen). All pipes and a quartz tubular reactor were purged with nitrogen. N_2 was bubbled in hot (97 °C) deionized water in a saturator and carried water vapours to the reactor.

Reaction kinetics of thermal wet oxidation and reaction results depend on several parameters: the temperature of the reaction zone (a), the water source temperature (water bubbler) (b), the flow of a main carrying gas (c), the flow of the carrying gas through the water bubbler (d), the time of the reaction (e) and the kind of carrier gas (f). Parameters from (a) to (e) were studied in [5] – in all processes only nitrogen N_2 (6N) and water steam from deionized water (from the bubbler) were used. In those

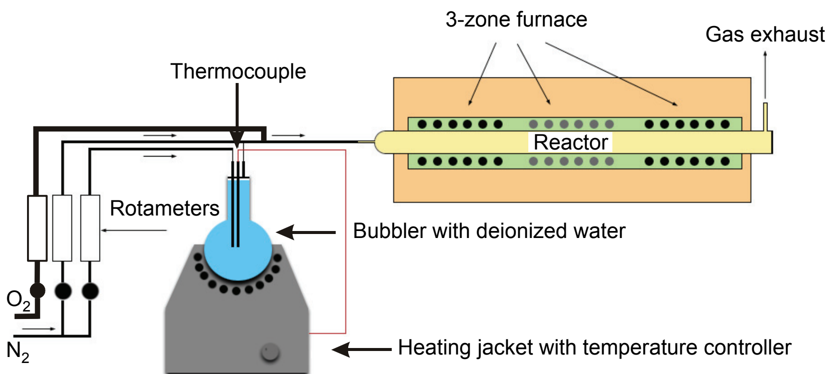

Fig. 1. Scheme of a thermal oxidation system used in the experiments.

investigations oxygen was added as a second oxidation agent. The type of oxidation methods, as well as conditions of nitridation, *i.e.*, process time, temperature and ammonia flux were studied.

In the second stage, the oxidized structures were put into a quartz reactor in ambience of nitrogen. Then atmosphere was changed – ammonia gas was switched to the reactor, after that a boat with the sample was transferred to the right temperature zone for the nitridation. The temperature was set in the range from 850 to 950 °C. Time of nitridation was changed from 15 to 120 minutes. The ammonia flow was varied from 400 to 1000 ml/min. On the restructured surface, gallium nitride was grown at typical epitaxial conditions [8].

3. Results and discussion

X-ray diffraction and microRaman measurements were used to determine the quality of the fabricated structures. Rocking curves measurements allowed to determine the relation between good oxidation process and nitridation conditions. Examined structures were measured after oxidation as well as after nitridation/re-epitaxy processes.

Samples G50 and G80 were similar: both were grown on sapphire substrates in HVPE system. The thickness of GaN layer was amounted to 5.2 and 3.3 μm, respectively. Conditions of the oxidation process for samples G50 and G80 were different (Table 1). The temperature of nitridation processes for those samples was the same – 925 °C. Oxidation temperature applied for sample G50 was a bit too high – the surface was slightly damaged. After nitridation the fabricated epilayers had thicknesses of 12 and 13 μm, for G50 and G80, respectively.

T a b l e 1. Conditions of samples preparation.

Sample	Oxidation process	Temperature of oxidation	Time of oxidation	Time of nitridation	Flux of ammonia
G50	Mixed	1000 °C	60 min	15 min	400 ml/min
G80	Dry	925 °C	180 min	15 min	800 ml/min

The X-ray spectra were measured using Philips X-ray diffractometer XRD–HRD with the parallel beam optics and CuKα1 radiation of $\lambda = 1.540597$ Å. For measured samples θ–2θ scans were performed.

On both presented samples (G50 – Fig. 2 and G80 – Fig. 3), after thermal oxidation, polycrystalline structure on the surface was observed. After nitridation and re-epitaxy on G80 sample (Fig. 3**b**), the improvement of structural quality of GaN layer was evident – considerable decrease in asymmetrical reflections intensity of the GaN layer, such as (100). Strong GaN (002) and (004) reflections and extinction of asymmetrical reflections indicated the preferred orientation of the investigated GaN layer.

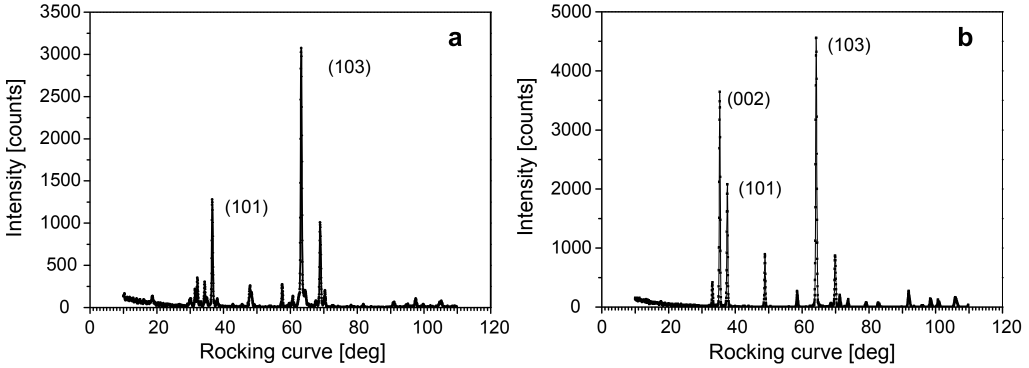

Fig. 2. X-ray rocking curves of sample G50 after oxidation (**a**) and after nitridation and re-epitaxy (**b**).

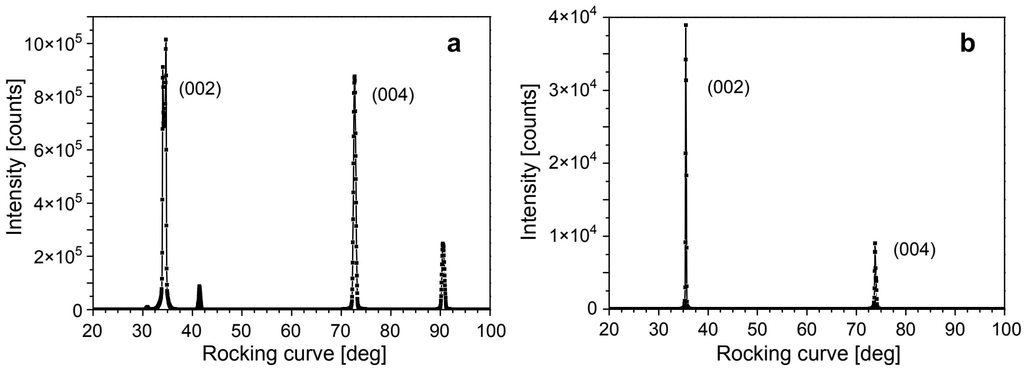

Fig. 3. X-ray rocking curves of sample G80 after oxidation (**a**) and after nitridation and re-epitaxy (**b**).

The lattice parameter of GaN material (and also for any other material) can be calculated using Bragg's equation and the position of the reflections forms measured diffraction pattern where Bragg's equation is given by:

$$2d\sin(\theta) = n\lambda$$

(where $\frac{1}{d^2} = \frac{4}{3}\frac{hh+hk+kk}{a^2} + \frac{ll}{c^2}$ and λ is the wavelength of X-ray radiation) or using the position of reflections on reciprocal space maps. In this particular situation we used first approach.

The strain parameter in this situation is understood as:

$$\varepsilon = \frac{c - c_0}{c_0} \times 100\%$$

where c – the lattice parameter calculated from the measured sample, c_0 – the lattice parameter of bulk GaN.

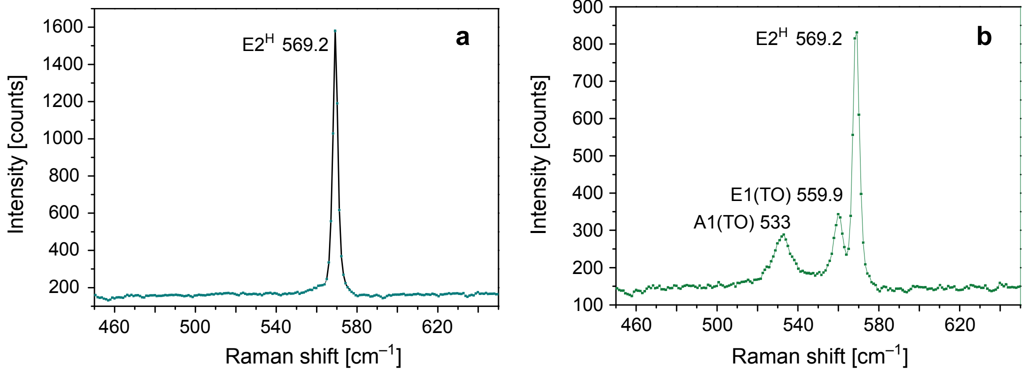

Fig. 4. Raman scattering spectra of GaN layer: excitation laser beam parallel to *c*-axis (growth direction) – focus on the surface (**a**), excitation laser beam perpendicular to *c*-axis – measurements from the edge, 10 μm from the oxide buffer (**b**).

Calculated lattice parameters of GaN layer of the G80 sample were as follows: after thermal oxidation – 5.1893 Å and strain – 0.083%, after nitridation and re-epitaxy – 5.0863 Å and strain – $\varepsilon_c = -2.25\%$. The strain of the measured layer was increased in association with matching the layer to the surface, and transition of the polycrystalline structure to the single crystalline. For G80 sample the value of the FWHM parameter of (002) reflection was equal to 543 arcsec. It is a typical value for GaN layers obtained by HVPE method.

Appropriate parameters of growth conditions of G80 sample allow to obtain a single crystalline structure of the GaN layer – only symmetrical reflections (002) and (004) were visible on θ–2θ scans (Fig. 3**b**) – it contrasted with G50 sample where polycrystalline structure of the GaN layer was observed (Fig. 2**b**).

MicroRaman measurements were made from the surface and from the cross-section. We have used microRaman system, produced by Horiba–Dilor–Yvon Spex with He-Ne laser, and the wavelength of 633 nm in back-scattering geometry at room temperature. The diameter of laser spot was 1.0 μm. It is worth noting that the position of E2(high) phonon mode is the same in both configurations (see Fig. 4): parallel (normal to the layers surface – called $z(xx)\bar{z}$) or perpendicular (normal to the edge – called $x(zy)\bar{x}$) to the growth direction (*c*-axis).

According to HARIMA [9], the position of E2(high) mode for the bulk (unstrained) GaN is 567.6 cm^{-1}. Measured values (Fig. 5) were equal and amounted to 569.2 cm^{-1}. In order to quantify the dependence of the phonon frequency shift on the strain, KISIELOWSKI *et al.* [10] employed Raman scattering, photoluminescence and X-ray diffraction on GaN thin films. They derived a consistent description of their experiments within the linear and isotropic elastic theory using a Poisson ratio of $\nu = 0.23$ and a Young modulus of $E = 290$ GPa – they applied the equations $\varepsilon_a = E - (1 - \nu)\sigma_a$ and $\varepsilon_c = -2E - \nu\sigma_a$. KISIELOWSKI *et al.* [10] found that the strain of 1 GPa triggers the phonon's mode shift of about 4.2 cm^{-1}. In our sample, the set phonon shift close to 1.6 cm^{-1} corresponds to the stress of $\sigma_a = 380$ MPa. The calculated biaxial strains

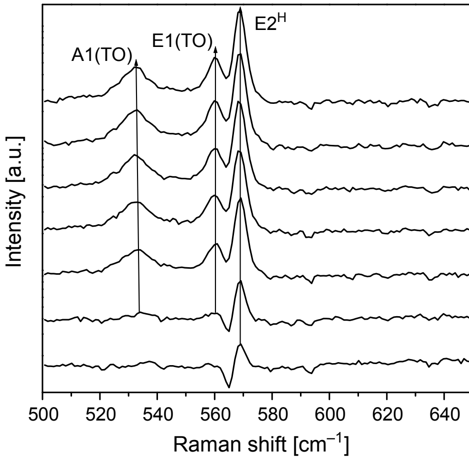

Fig. 5. Raman spectra observed from the edge.

are equal: $\varepsilon_a = 1\times10^{-3}$ and $\varepsilon_c = 6\times10^{-4}$. In our calculations the shifts of the E2(high) mode position (the difference between Harima's data and the data from Fig. 5) were taken into account. All observed emission lines A1(TO), E1(TO) and E2(high) phonons show the blue shift from the values for bulk GaN [10] but there are small values – for A1(TO) and E1(TO) they amount to ~1 cm^{-1} only.

Cross-section mapping was made for G80 sample (measurements with an excitation laser beam perpendicular to *c*-axis – signals come from the edge). One can observe that the position of E2(high) phonon mode is the same – without a shift along the layer – from the buffer layer to the surface of GaN epilayer (Fig. 5). The intensity of E2(high) signals rise with the moving of the measurements point in the epilayers from the buffer to the surface.

4. Conclusions

We have determined the proper type of HVPE GaN oxidation method. It was the mixed ($N_2 + O_2 + H_2O$) method. The conditions of nitridation process of gallium oxide buffer layers, that means: time, temperature and ammonia flux, were studied. The flux of ammonia gas and the temperature had a crucial influence on the parameters of the nitridated layer. Relatively long times (*e.g.*, 120 minutes), high temperatures but a small amount of ammonia gave poor results.

Monoclinic gallium oxide β-Ga_2O_3 seems to be a candidate for a good buffer layer, but its wide application in the nitrides technology requires further studies. We used HVPE GaN epilayers grown on sapphire which had below average morphology and crystal quality. The starting gallium nitride layers were not thick (as for HVPE layers) – several micrometers only. The finally obtained, in this study, GaN layer on the sam-

ple G80 had a thickness of about 16 μm in total (the first and the second epilayers) and revealed the FWHM equal to 576 arcsec. The Raman measurements provided also information about the stress (σ_a = 380 MPa) and strains ($\varepsilon_a = 1\times10^{-3}$ and $\varepsilon_c = 6\times10^{-4}$) levels in the GaN crystal.

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References

[1] BABAN C., TOYODA Y., OGITA M., *Oxygen sensing at high temperatures using Ga_2O_3 films*, Thin Solid Films **484**(1–2), 2005, pp. 369–373.

[2] JING ZHANG, KOSEL T.H., HALL D.C., FAY P., *Fabrication and performance of 0.25-μm gate length depletion-mode GaAs-channel MOSFETs with self-aligned InAlP native oxide gate dielectric*, IEEE Electron Device Letters **29**(2), 2008, pp. 143–145.

[3] YE P.D., *Main determinants for III–V metal-oxide-semiconductor field-effect transistors (invited)*, Journal of Vacuum Science and Technology A **26**(4), 2008, pp. 697–704.

[4] VÍLLORA E.G., SHIMAMURA K., KITAMURA K., AOKI K., UJIIE T., *Epitaxial relationship between wurtzite GaN and β-Ga_2O_3*, Applied Physics Letters **90**(23), 2007, article 234102.

[5] KORBUTOWICZ R., KOZŁOWSKI J., DUMISZEWSKA E., SERAFIŃCZUK J., *X-ray characterization of thick GaN layers grown by HVPE*, Crystal Research and Technology **40**(4–5), 2005, pp. 503–508.

[6] KORBUTOWICZ R., PRAŻMOWSKA J., WĄGROWSKI Z., SZYSZKA A., TŁACZAŁA M., *Wet thermal oxidation for GaAs, GaN and Metal/GaN device applications*, [In] *The Seventh International Conference on Advanced Semiconductor Devices and Microsystems, ASDAM 2008: Conference Proceedings, Smolenice, Slovakia, October 12–16, 2008*, [Eds.] S. Hascik, J. Osvald, IEEE, Piscataway, NJ, 2008, pp. 163–166.

[7] KORBUTOWICZ R., PRAŻMOWSKA J., *Wet thermal oxidation of GaAs and GaN*, [In] *Semiconductor technologies*, [Ed.] J. Grym, In-Teh, Vukovar, 2010, Chap. 6.

[8] KORBUTOWICZ R., DUMISZEWSKA E., PRAŻMOWSKA J., *Thick GaN layers on sapphire with various buffer layers*, Crystal Research and Technology **42**(12), 2007, pp. 1297–1301.

[9] HARIMA H., *Properties of GaN and related compounds studied by means of Raman scattering*, Journal of Physics: Condensed Matter **14**(38), 2002, p. R967.

[10] KISIELOWSKI C., KRÜGER J., RUVIMOV S., SUSKI T., AGER J.W., III, JONES E., LILIENTAL-WEBER Z., RUBIN M., WEBER E.R., BREMSER M.D., DAVIS R.F., *Strain-related phenomena in GaN thin films*, Physical Review B **54**(24), 1996, pp. 17745–17753.

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