

Influence of AlN Buffer Layer Deposition Temperature on Properties of GaN HVPE Layers

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Gallium nitride layers were deposited on AlN and double layer (AlN/AlGaN) buffers grown at various temperatures on Al₂O₃. Stress in layers was evaluated based on the Raman scattering and photoluminescence measurements. The obtained values were less than 1 GPa.

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1. Introduction

Recently gallium nitride appeared to be promising material for application in optoelectronics and electronics. Because of the lack of GaN native crystals alternative substrates are commonly applied. All of them exhibit thermal and lattice mismatch compared to GaN which causes defects generation and strain in deposited layers. Various buffer layers can be applied to minimize the stress which is especially undesirable in optoelectronic devices because it modulates the properties of active layer. The paper presents results of investigation of aluminium buffer layers temperature of deposition influence on the strain in subsequent high temperature GaN layer. Hydride vapor phase epitaxy (HVPE) was applied because it offers the unique possibility to obtain high growth rates and thus, thick layers, which are candidates for free-standing substrates after further delamination.

2. Experimental details

High-temperature gallium nitride (HT-GaN) layers were deposited by HVPE on (0001) oriented sapphire substrates with low temperature aluminum nitride (LT-AlN) buffers. The LT-AlNs were deposited at 500, 600, 700 °C (denoted as sample 500, 600 and 700, respectively) by metalorganic vapor phase epitaxy (MOVPE) technique. Double buffer layer composed of LT-AlN deposited at 600 °C and followed by Al_xGa_{1-x}N grown at 960 °C (denoted as 600/960) was also investigated.

Before loading into the MOVPE reactor, the substrates were chemically cleaned. Deposition of buffers was preceded by pre-heating of sapphire substrates at 1120 °C (H₂ atmosphere, 10 min) and nitridated in NH₃:H₂ solution at graded temperature from pre-heating temperature to the temperature of buffer growth. Additionally, aluminium nitride intermediate layer was heated for 10 min at graded temperature from 600 to 960 °C in NH₃:H₂ solution.

After buffer layers deposition samples were chemically cleaned and heated in HVPE chamber in NH₃:N₂(1:10) solution for 10 min at 1050 °C. More details are included in [1]. Temperature of HT-GaN layer growth was 1050 °C and their thicknesses were to 50 μm.

The Raman scattering spectra as well as photoluminescence (PL) were measured at room temperature. For the Raman measurements 632.8 nm line of He-Ne laser with beam diameter of about 1 μm and its power density of 60 kW/cm² was used. Measurements were performed in $x(z, y)\underline{x}$ and $z(x, x)\underline{z}$ geometries where z direction is along c -axis and x as well as y perpendicular to the c -axis. As a pump beam for PL investigation xenon lamp line of 280 nm with full width at half maximum (FWHM) of about 10 nm and the density of excitation power of 1 mW/cm², was used. The PL spectra were not normalized to xenon lamp spectra.

3. Results and discussion

Morphologies of LT-AlN buffers were similar. Diameter of grains and their heights estimated by atomic force microscopy measurements (not shown) were 10 nm and 30 nm, respectively. The HT-GaN samples were single

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crystalline as revealed X-ray diffraction measurements (not shown), described earlier [2].

As expected, $E2^H$ and $E1(TO)$ modes were observed in the Raman scattering spectra in $z(x,x)z$ geometry. Absence of $A1(LO)$ modes for almost all samples was possibly caused by high concentration of intrinsic free electrons [3] which could arise from N vacancies — point defects. This mode occurred only for sample 700, see Fig. 1. Intensities ratios of $E2^H$ and $A1(LO)$ modes were similar for measurements made in other points (with step of $2 \mu\text{m}$) of sample surface (gray and light gray lines) which indicated on uniform concentration of carriers within the layer.

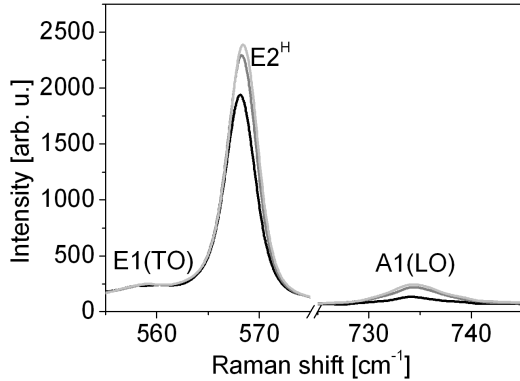


Fig. 1. Raman scattering spectra measured in several points of sample surface (geometry $z(x,x)z$).

The Raman cross-sectional spectra measured in $x(z,y)x$ geometry are depicted in Fig. 2. For all samples $E2^H$, $A1(TO)$ and $E1(TO)$ modes were observed. The $E1(LO)$ modes expected at about 745 cm^{-1} were present only for sample 600 (not shown). The aluminium content in double buffer layer was estimated to be below 10% based on $A1(TO)$ mode shift of sample 600/960 which revealed GaN-like two-mode behaviour.

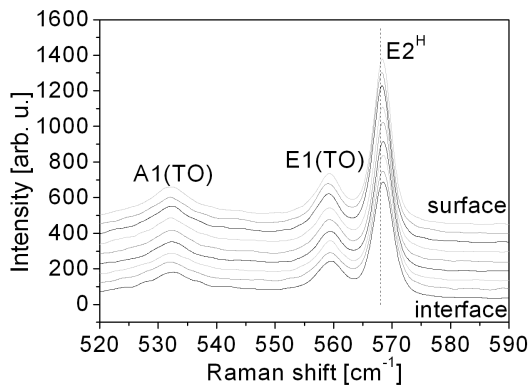


Fig. 2. Raman scattering spectra measured from the substrate to the surface (geometry $z(x,x)z$).

The FWHM of $E2^H$ mode could be an indicator of the degree of the distortion in a layer [4]. Although $E2^H$

mode FWHM is also sensitive to the strain, additionally, the extension of the peak is asymmetrical [3]. Nevertheless values of FWHM (sample 500 — 2.7 cm^{-1} , sample 600 — 3.7 cm^{-1} , sample 700 — 3.33 cm^{-1} , sample 600/960 — 3.83 cm^{-1}) confirmed earlier conclusions derived from XRD measurements, described elsewhere [2]. Both samples which consisted of LT-AlN deposited at 600°C exhibited poor quality.

Blue shift of $E2^H$ mode of $x(z,y)x$ spectra indicated on stress occurrence in all layers. Red shift observed in measurements from substrate to the surface arose from the stress vanishing. The shift of mentioned $E2^H$ mode as well as PL spectra band-to-band peak enabled biaxial stress evaluation near the surface and interface after Kozawa et al. [5], Fig. 3.

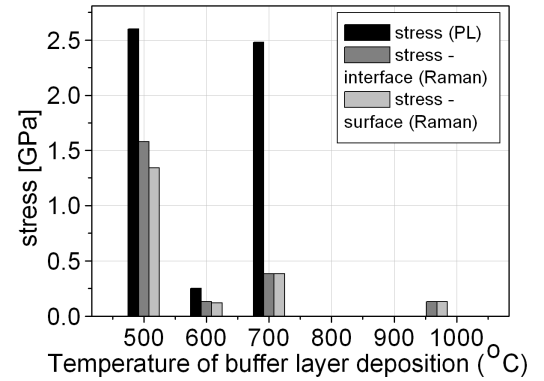


Fig. 3. Stress of gallium nitride layers deposited on template substrates.

Stress values obtained for samples 500 and 700 confirmed conclusions from PL spectra measurements; stress in these samples had the largest value. Comparable values of stress near the surface and interface were observed for samples 600 and 600/960. For calculation, bulk material Raman shift mode was assumed to be 568 cm^{-1} after Kim et al. [6]. Considering biaxial stress condition, Poisson ratio of $\nu = 0.23$ and a Young modulus of $E = 290 \text{ GPa}$ [7], also ε_c strain along the c -direction was estimated. The values were as follows: 22.8×10^{-4} (sample 500), 1.9×10^{-4} (sample 600), 6.0×10^{-4} (sample 700), 2.0×10^{-4} (sample 600/960). Following formula after Wang et al. [8] theoretical value of strain was calculated to be 21.1×10^{-4} which is in good agreement with that occurring in the layer of sample 500 (after assumption of $\Delta\alpha = 2.05 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $\Delta T = 1030^\circ\text{C}$, valid for HVPE technique process conditions). Values of strain corresponded well with that obtained for thick films of GaN presented by Wang et al. [8].

4. Conclusions

Gallium nitride layers deposited by HVPE technology on buffered (0001) sapphire substrates with buffers were investigated. As buffer layers LT-AlN films deposited by MOVPE technology at temperatures of $500, 600, 700^\circ\text{C}$

and double AlN/Al_{0.1}Ga_{0.9}N layers deposited at 600 and 960 °C were applied. The Raman scattering E₂^H mode blue shift confirmed occurrence of stress in the layers. The largest value of stress occurred within the layer deposited at 500 °C. Sample deposited at 600 °C as well as double layer buffer exhibited smaller stress which with connection with revealed earlier poor crystalline quality could lead to the conclusion that those layers were relaxed. Measurements of the Raman shift from the substrate to the surface showed red shift of E₂^H mode which proved stress vanishing. Additionally absence of A₁(LO) mode of the Raman scattering spectra indicated on high concentration of intrinsic carriers in HT-GaN layers, excluding the layer grown on AlN layer deposited at the highest temperature.

Acknowledgments

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