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In-situ growth monitoring by spectroscopy ellipsometry of MOCVD cubic-GaN(001)

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Abstract

In-situ and on-line spectroscopic ellipsometry has been carried out during the metal–organic chemical vapor deposition of cubic GaN on GaN/GaAs(001) templates fabricated via molecular beam epitaxy. The optical response at growth temperature and the different growth stages have been monitored and the real and imaginary part of the pseudo-dielectric function has been computed by means of the two-phase (ambient-bulk substrate) model. Kinetic ellipsometry measurements acquired, respectively, under and above the energy gap of the deposited material are discussed.

Keywords: Ellipsometry; Metalorganic chemical vapor deposition; Cubic GaN; On-line monitoring

1. Introduction

III-nitride compounds, AlN, GaN, InN and their alloys (InGaN, InAlN and AlGaN) exist in two phases: the hexagonal wurtzite and the cubic zinc-blende. The two crystalline structures of these compounds have direct energy gaps whose minimum and maximum values at room temperatures, given for the binary compounds InN and AlN, are, respectively, ~0.7 eV and 6.2 eV for the hexagonal phase and 1.7 eV and 4.9 eV for the cubic. Such properties make the III-nitrides strong candidates for the fabrication of optoelectronic devices working in the wavelengths range from near-infrared to ultraviolet, for instance full color displays, high density information storage, laser printers and light detectors. Furthermore, the high mechanical and thermal stability, the good thermal conductivity and high break-down voltage of the III-nitrides make this materials suitable for high temperature and high power applications, e.g. field effect transistors and heterojunction bipolar transistor working at high frequency and temperature.

The cubic phase (*c*-phase) of the III-nitrides, due to its higher crystallographic symmetry in comparison with the hexagonal phase, brings attractive advantages like easy cleavage and higher mobility, which could favorably influence the fabrication process and the performance of, for example, diode, lasers. Despite the mentioned benefits, up to date, little work has been done on cubic III-nitrides. Due to its metastable nature, the quality of the *c*-GaN layers is poorer than that of the hexagonal one. For this reason, further development of cubic GaN growth method is highly necessary. The growth by molecular beam epitaxy (MBE) of *c*-GaN directly on cubic substrates like, e.g. GaAs has been already reported [1], but the use of *c*-GaN(001)/GaAs(001) templates grown by MBE as substrate for the subsequent deposition of cubic GaN(001) by metalorganic chemical vapor deposition (MOCVD) is a novel approach which allows the nucleation of *c*-GaN(001) in a more efficient manner. Electron based techniques, as reflection high energy electron diffraction cannot be used for in-situ monitoring and characterization of the deposition of epitaxial layers at the higher pressure at which the MOCVD is carried out. Instead, optical methods like spectroscopy ellipsometry (SE) have been successfully employed for such purpose during the growth of III–V and II–VI compounds by MOCVD [2,3]. In this work we report on the use of SE for the on-line monitoring of the MOCVD of *c*-GaN on MBE-grown GaN/GaAs templates and the in-situ char-

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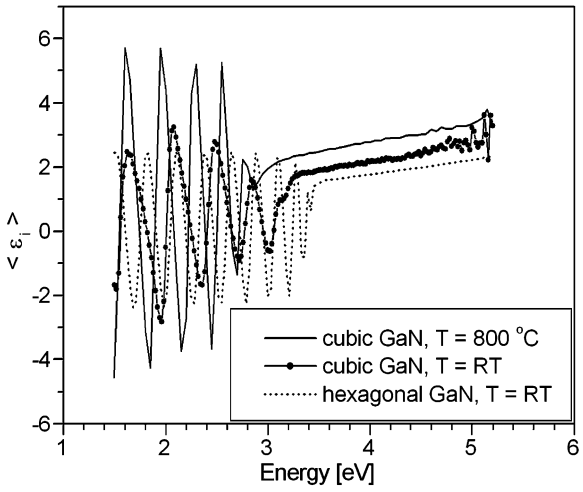

Fig. 1. Ellipsometric spectra of the pseudo-dielectric function for cubic GaN at room temperature and 800 °C. The spectrum of hexagonal GaN at room temperature is given for comparison.

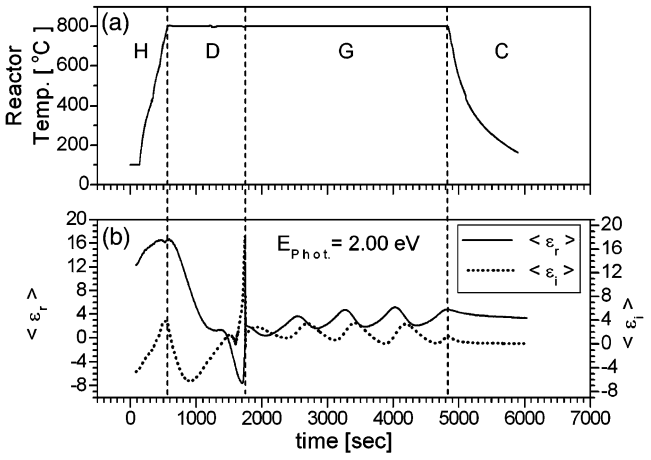

Fig. 2. (a) Substrate temperature vs. time. (b) SE of cubic GaN MOCVD at 2.0 eV: real and imaginary part vs. time.

acterization of the obtained layers. A comparison between on-line monitoring of the MOCVD growth by SE at photon energies below and above the energy gap of the *c*-GaN is presented. The crystalline quality of the layers has been investigated by means of ex-situ X-ray diffraction and compared with values reported in literature.

2. Experimental procedure

Cubic GaN(001)layers, 400 and 650 nm thick, grown on GaAs(001) wafers by MBE at the University of Paderborn Germany [4] were used as substrates in the present work. The subsequent growth stages have been carried out in an Aixtron 200RF horizontal tube MOCVD reactor. Trimethylgallium (TMGa) and ammonia (NH_3) were used as precursors for Ga and N, respectively. H_2 was used as carrier gas. Fluxes of TMGa between 8.8 and 35.3 μmol/min and of NH_3 equal to 0.005 mol/min or 0.022 mol/min, respectively, were set for the deposition of the layers, while the substrate temperature was either 780 or 800 °C. For the given fluxes and substrate temperatures the minimum and maximum growth rates were 8.0 nm/min and 19.5 nm/min, respectively. The reactor pressure was equal to 200 mbar for the whole set of growths.

A preheating at 780 or 800 °C, whose duration varied along the set of growths, was carried out previous deposition in order to desorb the oxide layer at the surface of the GaN(001)/GaAs(001) templates.

An Isa Jobin Yvon phase modulated ellipsometer has been attached to our MOCVD reactor for the in-situ monitoring of the growth of cubic GaN(001) layers. The polarizer of the ellipsometer was placed in a way that the angle of incidence was equal to 69.8°. Measurements of the ellipsometric angles Ψ and Δ were carried out in two modes: a kinetic mode where their temporal evolution was recorded at a fixed photon energy as the growth proceeded and a spectroscopic mode where their dependence on the photon energy was obtained. For the kinetic mode the photon energies were chosen to be either 2.0 eV or 3.5 eV in order to monitor the growth, respectively, under and above the energy gap of *c*-GaN at the growth temperature. For the spectroscopic mode the photon energy ranged from 1.5 to 5.5 eV. The real and imaginary part of the pseudo-dielectric function of the material was computed by means of the two phase model (ambient-bulk substrate) [5].

Ex-situ high resolution X-ray diffraction measurements, in the $\omega/2\theta$ and ω (rocking curve) scan modes, were carried out in a Philips MPD1880/HRX-ray diffractometer in order to evaluate the crystalline quality of the grown layers.

3. Results and discussion

Since we have faced a lack of published data on the optical constants of *c*-GaN at higher temperature, our first task was to analyze the optical behavior of *c*-GaN at growth temperature. The energy gap of *c*-GaN has been found to be approximately 2.85 eV at 800 °C as shown by the solid line plotted in Fig. 1. Furthermore, the full circle-solid line and the dotted line give, for comparison, the spectra of cubic and hexagonal GaN at room temperature, respectively. The obtained energy gaps of 3.2 and 3.4 eV are in agreement with the values reported in literature [6]. The spectra of Fig. 1 are dominated by the interference fringes for photon energies lower than the energy gap while for photon energies higher than the energy gap the light is strongly absorbed by the topmost layers of the GaN and the interference fringes vanish.

Fig. 2 shows an example of on-line kinetic measurement, acquired during deposition of a cubic GaN layer in our MOCVD reactor, of (a) the temperature of the sample holder and of (b) the real and imaginary part of the pseudo-dielectric function. The vertical dashed lines mark the different stages of the growth. The deposition starts with the stage heating (H), where the temperature of the MBE cubic-GaN/GaAs template was risen up from its room value to 800 °C. The next step is the desorption (D), where the template is kept at 800 °C for some minutes under H_2 atmosphere in order to outgas and get a smooth surface for the subsequent deposition of the *c*-GaN layer. In this case, the desorption was as long as 20 min. The successive step is the deposition (G) of *c*-GaN at a growth temperature of 800 °C and a flux equal to 8.8 μmol/min for TMGa and 0.02 mol/min for NH_3. The stage cooling (C) corresponds to the end of the growth where the fluxes of TMGa and H_2 are interrupted and the substrate cooled down.

For the ellipsometric measurement, shown in Fig. 2b a photon energy of 2.0 eV was chosen in order to be well below the energy gap of *c*-GaN at 800 °C. In this way damping, due to absorption of the light, is avoided and the interference fringes, which give information on the time evolution of the thickness and the state of the surface for the different stages of growth, are visible. During heating (H), the real and imaginary part of the pseudo-dielectric function increases due to the change of the optical constants. The desorption step (D), as we can see in the kinetic measurement, produces the onset of interference fringes: hint that a fraction of the MBE *c*-GaN layer is desorbed. A small perturbation of the interference fringes generated by fluctuations of the H_2 flux can be observed in the figure at approximately 1200 and 1600 s. The fact that in the early steps of the deposition (G), the amplitude of the oscillations is smaller in comparison with the one recorded at the desorption stage is related to an increase of the surface roughness. As the growth proceeds the amplitude of these oscillations shows a slow increase getting a maximum at 3.5 cycles, which indicates a progressive smoothing of the surface. After that, the amplitude of the oscillation slightly decreases, suggesting a deterioration of the surface.

A further example of in-situ monitoring by ellipsometry of the deposition of *c*-GaN by MOCVD on the MBE *c*-GaN/GaAs template is shown in Fig. 3. In this case, the temperature was 780 °C during both desorption and growth. The flux of NH_3 was 0.005 mol/min for the whole deposition. The flux of the TMGa source was set to 8.8 μmol/min and 17.7 μmol/min for steps G(i) and G(ii), respectively, reported in Fig. 3a. The deposition proceeds following a similar sequence of stages as those described in Fig. 2: heating (H), desorption (D), growth (G) and cooling (C). In this case, the

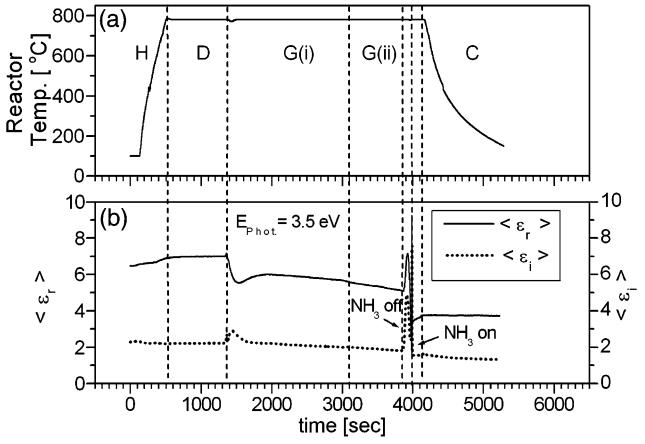

Fig. 3. (a) Substrate temperature vs. time. (b) SE of cubic GaN MOCVD at 3.5 eV: real and imaginary part vs. time.

photon energy was chosen to be 3.5 eV, which is above the energy gap of the cubic and hexagonal GaN at growth temperature. For such photon energy the sensitivity of ellipsometry to the surface of the sample increases as the light interacts just with a region close to the topmost surface, due to the strong absorption of photons with energy greater than the energy gap. Atomic force microscopy (AFM) measurement on the MBE grown *c*-GaN(001)/GaAs(001) template, used in this work as substrate, show a root mean square roughness of approximately 20 nm. With the onset of the MOCVD process, the real and imaginary part of the pseudo-dielectric function decreases and increases, respectively. Preliminary simulations of the response of the pseudo-dielectric function as the growth evolves were carried out. The results suggest that the observed evolution of the optical constants values correspond to an increased roughness of the surface as confirmed by AFM measurements, which at this stage gave a root mean square roughness of approximately 30 nm. Before the growth is ended the flux of NH_3 is shortly interrupted. As it is show in the figure the surface of the sample is hardly affected by the lack of NH_3.

Fig. 4 gives the full width at half maximum (FWHM) of the X-ray rocking curve for the (002) diffraction vs. thickness for *c*-GaN layers. The open squares correspond to the *c*-GaN layers grown by MBE on GaAs substrate. The full squares denote the *c*-GaN layers grown by MOCVD on the MBE-GaN/GaAs templates. The dashed lines mark the range of FWHM for *c*-GaN reported in the literature [1,7]. The FWHM of the rocking curve of our samples shows the expected decrease as the thickness of the layer increases. In addition, its values are within the region between the two dashed lines, therefore we can infer that the quality of our MOCVD cubic-GaN layers are of comparable quality with those reported in literature.

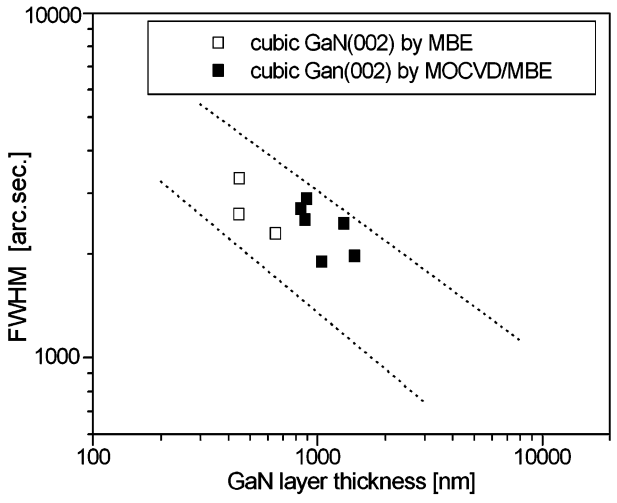

Fig. 4. FWHM of the X-ray rocking curve for the symmetric (002) diffraction from cubic GaN.

4. Conclusions

In the present work we have shown that the growth of cubic GaN by MOCVD on MBE grown cubic-GaN/GaAs templates is feasible. The single stages of the MOCVD growth of *c*-GaN have been in-situ monitored by kinetic ellipsometry at photon energies under and above the energy gap. Thus, it was possible to know in real time the temporal evolution of the thickness and surface state of the cubic GaN layers during the deposition. In that way, a feedback, which relates the growth parameters with the state of the layer, have been implemented. The crystalline quality of the deposited layer was of comparable quality with those reported in literature. In a previous work, we demonstrated the on-line composition determination of ternary hexagonal GaN-based compounds via SE [8]. The next step will be to extend the investigation to ternary *c*-GaN-based alloys, in the perspective of developing a close-loop control of MOCVD growth of cubic GaN via spectroscopic ellipsometry.

References

[1] H. Okumura, K. Ohta, G. Feuillet, K. Balakrishnan, S. Chichibu, H. Hamaguchi, P.S. Yoshida, J. Cryst. Growth 178 (1997) 113.
[2] D. Aspnes, W.E. Quinn, S. Gregory, Appl. Phys. Lett. 56 (1990) 2569.
[3] A. Bonanni, D. Stifter, A. Montaigne-Ramil, K. Schmidegg, K. Hingerl, H. Sitter, J. Cryst. Growth 248 (2003) 211.
[4] D. Schikora, M. Hankeln, D.J. As, K. Lischka, T. Litz, A. Waag, T. Buhrow, F. Henneberger, Phys. Rev. B 54 (1996) R8381.
[5] D.E. Aspnes, in: B.O. Seraphin (Ed.), Optical properties of solids. New Developments, North Holland Publishing Company, 1976, Chapter 15.
[6] O. Ambacher, J. Phys. D: Appl. Phys. 31 (1998) 2653.
[7] Z.Q. Li, H. Chen, H.F. Liu, J.H. Li, L. Wan, S. Liu, Q. Huang, J.M. Zhou, J. Cryst. Growth 208 (2000) 786.
[8] A. Bonanni, K. Schmidegg, A. Montaigne-Ramil, H. Sitter, K. Hingerl, D. Stifter, J. Vac. Sci. Technol. B 21 (4) (2003) 1.