ISSN 1063-7850, Technical Physics Letters, 2017, Vol. 43, No. 1, pp. 74–77. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © V.A. Tarala, A.S. Altakhov, M.G. Ambartsumov, V.Ya. Martens, 2017, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2017, Vol. 43, No. 1, pp. 67–73.

Growing Oriented AlN Films on Sapphire Substrates by Plasma-Enhanced Atomic Layer Deposition

V. A. Tarala*, A. S. Altakhov, M. G. Ambartsumov, and V. Ya. Martens

North Caucasus Federal University, Stavropol, 355009 Russia

**e-mail: vitaly-tarala@yandex.ru*

Received July 12, 2016

Abstract—The possibility of growing oriented AlN films on Al_2O_3 substrates at temperatures below 300°C by plasma-enhanced atomic layer deposition was examined. The samples were subjected to X-ray phase analysis and ellipsometry. It was demonstrated that the refraction index of films deposited with plasma exposures longer than 20 s was 2.03 ± 0.03. The (0002) and (0004) reflections at 2Θ angles of 35.7° and 75.9° were present in the X-ray diffraction patterns of these samples. These reflections are typical of the hexagonal AlN polytype. The full width at half maximum of the rocking curve of reflection (0002) in the best sample was 162 ± 11 arcsec.

DOI: 10.1134/S1063785017010138

Thin aluminum nitride (AlN) films have potential for use in the construction of cold cathodes [1], power devices [2], gas sensors [3], UV-light-emitting diodes, photodetectors [4], and piezoelectric RF-MEMS devices [5]. They also may be used as buffer layers in the growth of gallium nitride films [6]. Crystalline films with a controlled crystallographic orientation are required in the aforementioned applications.

Due to the lack of single-crystalline aluminum nitride substrates, AlN films are deposited onto foreign substrates (Si, SiC, or Al_2O_3), which differ from AlN in their thermal expansion coefficients and lattice constants. This induces strong internal mechanical stresses and high defect densities in synthesized layers. These stresses may be reduced by lowering the temperature of film formation.

High-quality oriented crystalline AlN films are generally grown by chemical vapor deposition (CVD) [7–9] on sapphire substrates at temperatures exceeding 840°C. The full width at half maximum (FWHM) of the rocking curve of these films is approximately 11 arcsec [9]. Films produced by magnetron sputtering (MS) [10] are deposited at a temperature of ~500°C, but have FWHM > 2°. Plasma-enhanced atomic layer deposition (PEALD) is used to grow amorphous or polycrystalline aluminum nitride films [11–16]. Literature data regarding the temperature of the onset of crystalline film growth are contradictory. For example, it was hypothesized in [12] that crystalline films may be grown only at temperatures (T) exceeding 300°C. Crystalline films were grown at $T = 250$°C in [14], and the possibility of growing such films at $T \geq 100$°C was demonstrated in [13]. Coatings with no marked orientation were deposited in all these studies. Oriented films were synthesized on sapphire substrates with a buffer GaN layer in [16], but this was done at a temperature of ~500°C. The experimental results reported in the present study suggest that it is possible to grow oriented AlN films at sapphire substrate temperatures below 300°C. The effect of the substrate temperature and the plasma exposure duration on the crystallinity of films is also discussed below.

Since heteroepitaxial AlN films with the highest degree of crystallinity are now grown on sapphire (Al_2O_3) substrates, these substrates were chosen for the present study. A PEALD TFS-200 setup (Beneq, Finland) was used to synthesize films. In all experiments, the operating frequency of the HF generator was 13.56 MHz, the power level was 200 W, and the nitrogen flow rate through the reactor chamber and the reactor was 200 and 300 sccm, respectively. After the temperature regime (210–280°C) was established, the substrate surface was treated with plasma of a gas mixture of hydrogen (80 sccm) and nitrogen (20 sccm) for 60 s. This plasma was used as the source of nitrogen in the cyclic process of film deposition. The first stage of this cycle was the introduction of trimethylaluminum (TMA), which served as the source of aluminum, into the reactor. The vapor source with TMA was thermostatted at 18°C. The duration of the TMA supply pulse was 0.05 s in all experiments. The reactor was then ventilated for $\tau_{PUR} = 30$ s in order to remove excess TMA and the products of its interaction with the substrate. After that, the substrate surface was treated with plasma of the gas mixture of hydrogen and

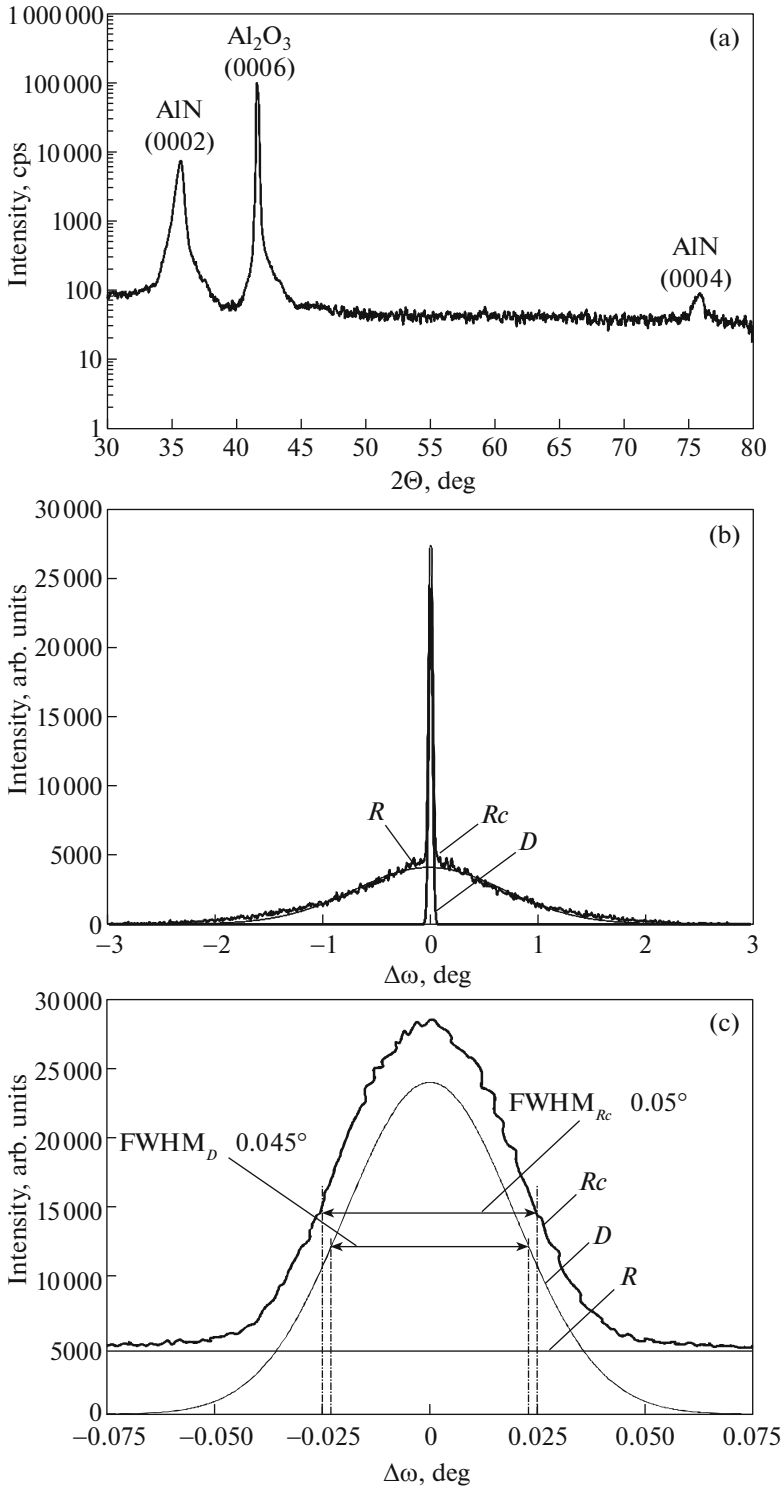

Fig. 1. Results of X-ray examination: (a) typical X-ray phase analysis curve, (b) rocking curve, and (c) enlarged view of the central part of the rocking curve.

nitrogen. The plasma exposure time (τ_{PE}) was varied from 3 to 30 s. At the final stage, the reactor was ventilated for 10 s. The number of deposition cycles was chosen so as to obtain films with a thickness of 35–40 nm.

The growth rate (GR) was estimated as the ratio of the film thickness to the number of deposition cycles. The film thickness was measured using a SE-800 (Sentech, Germany) spectroscopic ellipsometer. It was found that GR was equal to 0.100 ± 0.005 nm/cycle in

the temperature range of 210–250°C at $\tau_{PE} \leq 6$ s. When τ_{PE} was reduced to 3 s, GR went down to 0.085 ± 0.005 nm/cycle; if the substrate temperature was raised to 280°C, GR reached a value of 0.108 ± 0.005 nm/cycle. Since the lack of a dependence of GR on T suggests that the growth process is self-limited, it was hypothesized that the samples are deposited in the atomic layer deposition regime at temperatures below 250°C and are synthesized in CVD-like conditions at higher temperatures.

The examination of the dependence of refraction index n on the deposition conditions showed that n of the samples grown at τ_{PE} exceeding 6 s was as large as 2.01 ± 0.05 at a wavelength of 633 nm. The refraction index was almost independent of deposition temperature. A lightly lower value of n (1.95 ± 0.05) was measured at $\tau_{PE} = 3$ s. Since the refraction index of AlN films gets smaller at lower degrees of crystallinity, it appears probable that a plasma exposure length of 3 s is not sufficient for complete transformation of chemisorbed particles into a crystalline aluminum nitride layer.

X-ray phase analysis was performed in the range of angles 2Θ from 30° to 80° to examine the microstructure of films. An ARLX'TRA (Thermo Fisher Scientific) diffractometer fitted with a parabolic Göbel mirror and a thin-film collimator was used. These studies showed that AlN/Al_2O_3 samples grown at $\tau_{PE} = 3$ s had only the substrate-related (0006) reflections at 2Θ of approximately 41.7° in the X-ray diffraction (XRD) patterns measured in the Bragg–Brentano geometry. The lack of aluminum nitride reflections indicates that the films had an amorphous structure. Additional intense reflections with their maxima at 2Θ = 35.7° ± 0.1° (see Fig. 1a) were observed in the XRD patterns of samples synthesized at $\tau_{PE} = 6$ s. These are the reflections from planes (0002) of the hexagonal aluminum nitride polytype [7]. At $T = 250$–280°C and $\tau_{PE} \geq 20$ s, the reflections from higher-order planes (0004) emerged in the XRD patterns. This suggests that the degree of crystallinity of films increased with plasma exposure time.

It should be noted that no (0004) reflections were observed in samples deposited at a temperature of 210°C even at $\tau_{PE} = 30$ s. This implies that longer plasma exposure times are needed to increase the degree of crystallinity of films at lower synthesis temperatures. However, in our view, PEALD processes with $\tau_{PE} > 30$ s are not economically viable.

Rocking curve (*Rc*) studies were performed next. The rocking curve measured at angle 2Θ = 35.7° for one of the samples grown at $T \geq 250$°C and $\tau_{PE} \geq 10$ s is shown in Fig. 1b. Just as in [7, 17], the *Rc* shape was modeled by a sum of two Gaussian curves. Note that the narrow an intense *Rc* component (*D* curve) is associated with diffraction by the (0002) planes (see Fig. 1c), while the broad component (*R* curve) is induced by diffuse scattering, which arises in thin films due to the roughness of interfaces, the small diameter of crystallites, and the high density of dislocations. Examination of these samples showed that the full widths at half maxima of the *R* curve ($FWHM_R$) and the *D* curve ($FWHM_D$) were approximately 1.6° ± 0.4° and 0.045° ± 0.005°. The ratio of intensities of these curves (I_D/I_R) was as large as 4.5 ± 1.5. Owing to the fact that the *D* curve was more intense than the *R* curve, the full width at half maximum of *Rc* ($FWHM_{Rc}$) was comparable to $FWHM_D$ (see Fig. 1c).

When the temperature was reduced to 210°C, the I_D/I_R ratio dropped down to 0.75 ± 0.30 and the intensity of the rocking curve decreased. In addition, the value of $FWHM_{Rc}$ rose to 0.25° ± 0.05°, which indicates an increase in the density of defects and a reduction in the degree of crystallinity of films. At $\tau_{PE} = 6$ s, the value of $FWHM_R$ increased to 6.0° ± 1.5°; owing to the fact that I_D/I_R dropped to zero, $FWHM_{Rc}$ also became equal to $FWHM_R$. At even shorter exposures ($\tau_{PE} = 3$ s), amorphous samples with no reflections associated with AlN were synthesized.

To sum up, the best samples were grown at temperatures ranging from 250 to 280°C with a plasma exposure length of 20 s. These films had $I_D/I_R \approx 6$ and $FWHM_{Rc} \approx 0.045° \pm 0.003°$ (162 ± 11 arcsec). To put this in perspective, the $FWHM_{Rc}$ value of these samples is four times lower than that of an oriented AlN film ($FWHM_{Rc} = 670$ arcsec) grown by PEALD [16] on a sapphire substrate with a gallium nitride underlayer at a temperature of 500°C.

Thus, the obtained results showed that oriented crystalline aluminum nitride films may be grown at temperatures higher than 210°C by plasma-enhanced atomic layer deposition with a capacitively coupled plasma source. The degree of crystallinity of films increased with substrate temperature and plasma exposure length. In our view, the crystallinity enhancement with an increase in τ_{PE} is related to the extension of the time window in which chemisorbed particles may contribute to diffusion processes leading to the formation of larger seeds. These particles acquire the energy for diffusion in their interaction with plasma. Therefore, the adverse effects of a reduction in temperature in the PEALD process (specifically, the degradation of crystallinity of films) may be compensated for by increasing the plasma exposure length.

REFERENCES

1. A. T. Sowers et al., Appl. Phys. Lett. **71**, 2289 (1997).
2. W. Sahyoun et al., IEEE IEEE Trans. Sonics Ultrason. Freq. Control **58**, 2162 (2011).
3. P. Ivaldi et al., in *Proceedings of the Frequency Control Symposium (FCS), Newport Beach, CA, USA, June 1–4, 2010* (2010), p. 81.

4. D.-S. Tsai et al., Sci. Rep., No. 4, 2628 (2013).
5. M. Clement et al., Ultrasonics, No. 42, 403 (2004).
6. V. V. Ratnikov, D. V. Nechaev, V. N. Jmerik, and S. V. Ivanov, Tech. Phys. Lett. **42**, 419 (2016).
7. J. Blasing et al., J. Appl. Phys. **105**, 033504 (2009).
8. A. Kakanakova-Georgieva et al., J. Cryst. Growth **338**, 52 (2012).
9. Y. A. Xi et al., Appl. Phys. Lett. **89**, 103106 (2006).
10. N. Matsunami et al., Adv. Mater. Phys. Chem., No. 3, 101 (2013).
11. Y. J. Lee et al., Thin Solid Films **446**, 227 (2004).
12. M. Bosund et al., Appl. Surf. Sci. **257**, 7827 (2011).
13. M. Alevli et al., Phys. Status Solidi A **209**, 266 (2012).
14. P. Motamedi et al., J. Cryst. Growth **421**, 45 (2015).
15. M. Alevli et al., J. Vac. Sci. Technol. A **30**, 021506 (2012).
16. N. Nepal et al., Appl. Phys. Lett. **103**, 082110 (2013).
17. A. Boulle et al., J. Appl. Phys. **97**, 073503 (2005).

Translated by D. Safin