Reactive Magnetron Sputtering Technology for Receiving III Nitrides

Zurab Kushitashvili[1*], Amiran Bibilashvili [2,3], Nugzar Dolidze[4], Givi Skhiladze[5], Revaz Guliaevi[6]

[1)] LEPL Institute of Micro and Nanoelectronics, Chavchavadze ave.13, 0179 Tbilisi, Georgia; email: zurab.kushitashvili@micronano.ge; https://orcid.org/0000-0001-7140-3438

[2)] Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland;

[3)] Institute of Geological Sciences, Polish Academy of Sciences, Twarda 51/55, 00-818 Warszawa, Poland;

[4)] LEPL Institute of Micro and Nanoelectronics, Chavchavadze ave.13, 0179 Tbilisi, Georgia;

[5)] LEPL Institute of Micro and Nanoelectronics, Chavchavadze ave.13, 0179 Tbilisi, Georgia;

[6)] LEPL Institute of Micro and Nanoelectronics, Chavchavadze ave.13, 0179 Tbilisi, Georgia;

http://doi.org/10.29227/IM-2024-01-78

Submission date: *11.2.2023* | Review date: *8.3.2023*

Abstract

In the present work is studied synthesis of galium nitride (GaN) and aluminum nitride (AlN) by DC Reactive Magnetron Sputtering technology. As a sputtering target was used high purity (99.9999%) Gallium and Aluminum materials and as a reagent gas was used high purity (99.9999%) Nitrogen. Magnetron sputtering system with strong magnets (1450 mT) allows to make plasma at a low preasure 3×10^{-2} Pa and deposition process was carried out at high vacuum conditions. Deposited layers of GaN and AlN on the sappire substrate was analysed by X-ray diffraction (XRD) and revealed the crystalline nature highly oriented with the (0002) for both nitrides. For chemical composition was measured X-ray Photoelectron Spectroscopy (XPS) and it was found out the ratios of Ga:N and Al:N to be 1.07 and 1.04 respectively. For surface analysis was made Scanning Electron Microscopy (SEM). Optic transmission spectra showed band gaps to be 3.43 eV and 6.13 eV for GaN and AlN respectively.

Keywords: reactive magnetron sputtering, scanning electron microscopy, the x-ray diffraction, nitrides

Introduction

In the recent years, the III nitride (GaN, AlN) materials have attracted a lot of attention due to their potential for high-power, high-frequency, high electron mobility, wide energy bandgap and high temperature applications [1-5]. For formation III nitride semiconductor materials have been proposed many technologies such as atomic layer deposition (ALD), molecular beam epitaxy (MBE), metalo organic chemical vapor deposition (MOCVD) and others. Some of them are high temperature tecnologies, others require expensive technological equipment and laboratory enviroments and so on. All this circumstances effect on the price of the fabricated material and devices based on it.

In the present work, we have studied Reactive Magnetron Sputtering technology [6] for synthesis of GaN and AlN. The main essence of this technology is to use pure gallium (Ga) for a sputtering target instead of GaN target (usually used in the deposition systems) [7-10] and updated magnetron sputtering system with strong magnetic field, which allows currying out the process of sputtering in a high vacuum. Moreover, gas inlet system is set up so that gas line enters directly inside magnetron and creates local pressure, which is higher than in outside space of the vacuum chamber. Because of this, the stream of the nitrogen molecules is directed from the magnetron toward outside space and prevents entering some unwanted impurities from chamber and other side of the vacuum system to the plasma area. Thus, as a result we get high purity GaN and AlN deposited layers.

Experimental

In the experiment was used 2 inch sapphire wafers 400µm thickness and surface orientation (0006). Prior to the experiment substrate surface was chemically cleaned using standard techniques. Rotary and turbo pump combination was used to get the desired vacuum. The base pressure of the system was less than 1.3 × 10-4 Pa. Sputtering target was made by 50mm diameter Ga and Al materials. The distance between the target and sapphire substrates was kept at 70mm and the substrate temperature during the deposition was 6000C. In the vacuum system was entered pure nitrogen (6N) by high precision needle valve. At a base voltage about 400 V was applied to the cathode and was formed the nitrogen plasma with plasma current 100mA. All depositions were carried out at a total pressure of 3 × 10-2 Pa. Received layers thicknesses were 0.8µm and 0.6µm for GaN and AlN respectively.

After deposition, final structures were a) Al2O3 + GaN; b) Al2O3 + AlN; c) Al2O3 + AlN + GaN. These structures were investigated by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM) and Optic Transmission Spectra Analysis.

Results and Discussion

X-Ray Diffraction

Figure 1 shows XRD patterns for structures Al2O3 + GaN (a line), Al2O3 + AlN (b line) and Al2O3 + AlN + GaN (c line).

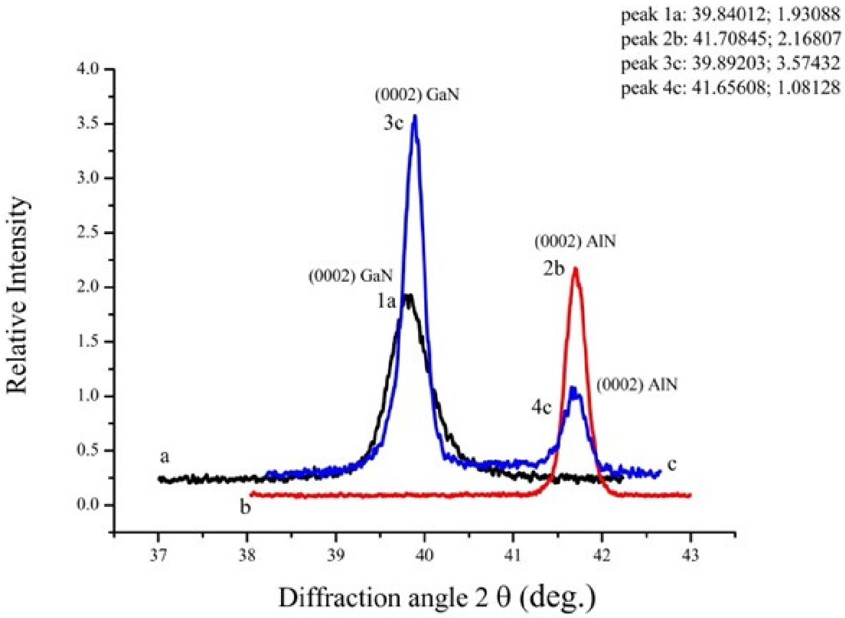


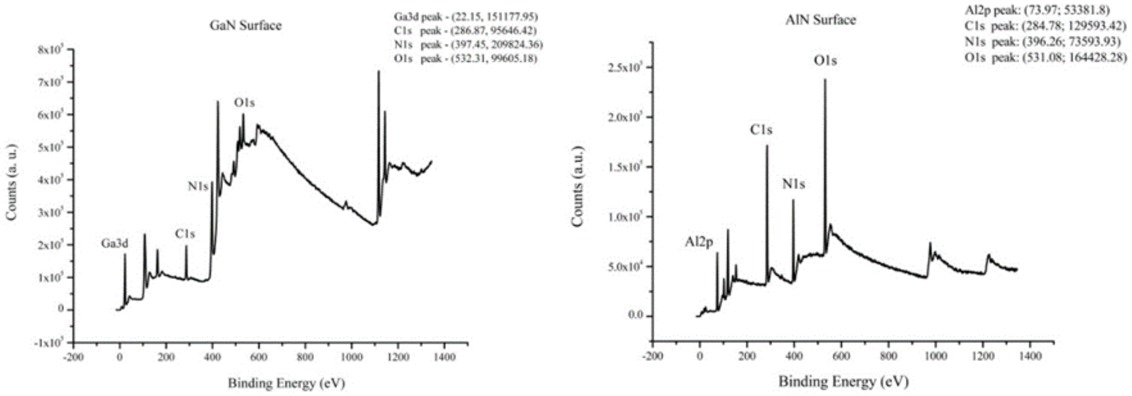
Fig. 1. XRD graphs of GaN and AlN

The X-ray diffraction measurements were carried out on the conventional X-ray diffractometer „DRON-4-07" in the following modes: acceleration voltage – 19 kV, current – 15 mA, radiation source CoKα_1 with wavelength λ = 1.7889 Å, diffractometer recording speed 2 deg/min. The crystalline quality of the nitrides was evaluated using symmetric x-ray scans. The Y axis scale corresponds to relative intensity (1000 imp/s to be 5 units). The GaN (0002) 1a peak is clearly seen at 39.84^0 and full width half maximum (FWHM) is 2000 s, while GaN (0002) 3c peak is seen at 39.89^0 and FWHM is 878s. The reason is that, 1a peak corresponds to the deposition of GaN on sapphire and it is known lattice mismatch between GaN and sapphire is 16% [11]. Such a large mismatch induces stresses in the first few layers of GaN grown on sapphire and XRD peak is small and wide.

In the case 3c peak GaN is grown on the AlN buffer layer. AlN has a good match to GaN but a bad match to sapphire [11]. Thin layer of AlN on sapphire helps the crystal quality of subsequently grown GaN and 3c peak is higher and sharper, than 1a peak. The 2b and 4c peaks correspond to the AlN grown on sapphire. The 4c peak has a FWHM 966 s and 2b has a FWHM 960 s and diffraction angles are 41.70^0 and 41.66^0 respectively.

X-Ray Photoelectron Spectroscopy – XPS

For the chemical analysis of the GaN and AlN layers, XPS was carried out using monochromatic high-performance XPS spectrometer with a monochromatic Al Kα x-ray source (hυ = 1486.71 eV). XPS acquisition parameters are: total acquisition time is 2 min 16.1 s, source type Al Kα, spot size 400 µm, lens mode- standard, analyser mode CAE : pass energy 200.0 eV, energy step size 1.000 eV, etch time = 150.008 s



(a) (b)

Fig. 2. a) XPS survey scan of GaN, b) XPS survey scan of AlN.

Figure 2 show the survey scan of XPS spectra for the GaN and AlN layers, where all the peaks of Ga, N, Al, C and O can be seen. The Ga2d peak and Al2p corresponds to the binding energies 22.15 eV and 73.97 eV, other peaks attributed to C1s, N1s, O1s and data from XPS reports are shown in Table 1 and Table 2. As shown from the Table 1, the ratio Ga:N is 1.07 which is in good accordance with chemical formula of GaN. From Table 2 seems the ratio Al:N to be 1.04.

Tab. 1. XPS reports and elemental analysis of GaN layer received by Magnetron Sputtering

Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) KE^0.6	At. %	PP Height CPS	PP Hgt (N)	PP At. %
Ga3d	22.15	151177.95	3.33	572845	6655.63	29.65	167400.08	194.49	33.35
N1s	397.45	209824.36	4.38	950740	7952.77	35.42	215756.4	180.48	30.95
C1s	286.87	95646.42	3.09	362694	5153.16	22.95	104710.71	148.77	25.51
O1s	532.31	99605.18	3.85	483381	2689.01	11.98	106819.69	59.42	10.19

Tab. 2. XPS reports and elemental analysis of AlN layer received by Magnetron Sputtering

Name	Peak BE	Height CPS	FWHM eV	Area (P) CPS.eV	Area (N) KE^0.6	At. %	PP Height CPS	PP Hgt (N)	PP At. %
O1s	531.08	164428.28	3.31	599895	3334.59	12.82	177148.2	98.47	11.39
C1s	284.78	129593.42	2.89	462734	6567.66	35.82	140531.2	199.46	34.09
Al2p	73.97	53381.8	2.92	169954	4076.85	25.46	58825.76	141.11	27.79
N1s	396.26	73593.93	2.93	243361	2034.33	25.90	82210.28	68.72	26.73

SEM Analysis

Figure 3 indicates the cross-section SEM image of GaN. It is clearly observed the interface between sapphire and GaN. The thickness of GaN is about 0.8μm.

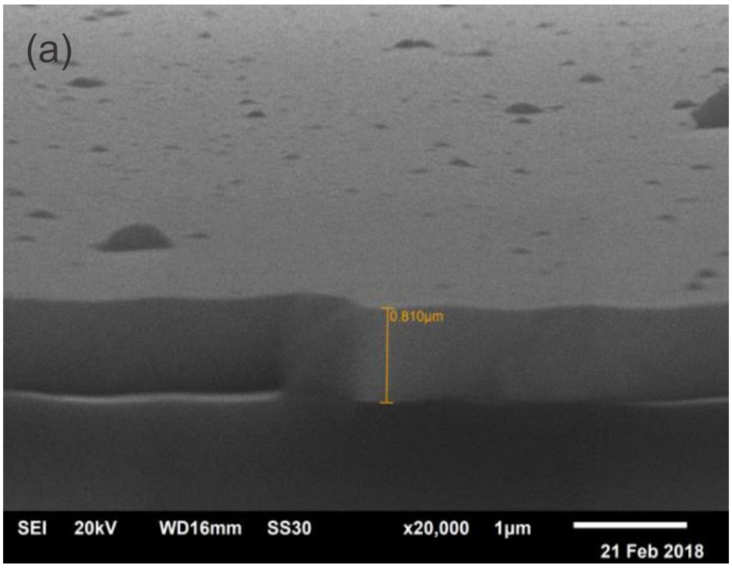
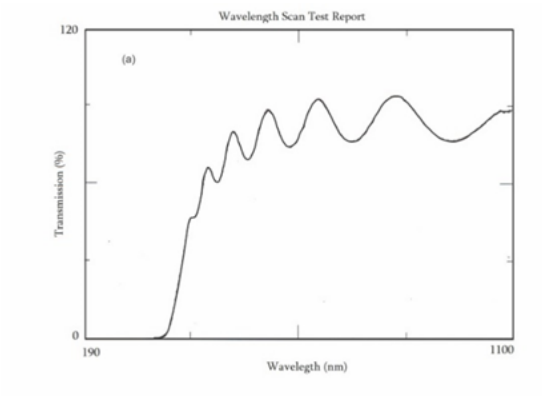


Fig. 3. SEM cross-section image of GaN

Transmission Spectrum

For study optic properties of GaN and AlN materials received by reactive magnetron sputtering were analysed by UV/VIS 2800 transmission spectra analyser. Figure 4 shows transmission spectra both materials in the range 190-1100 nm wavelength. From the data of transmission spectra seems that for GaN transmittance starts at 361 nm and for AlN starts at 202 nm. Intensive transmittance (~90%) happens at 540nm and 410nm. for GaN and AlN respectively. Calculated band gaps at these wavelengths are 3.43 eV and 6.13 eV for GaN and AlN respectively, which are in good accordance with their theoretical values of band gaps.



a)

b)

Fig. 4. a) Transmission spectra of GaN, b) Transmission spectra of AlN

Conclusion

We have studied the reactive magnetron sputtering technic for receiving III nitrides. In the updated magnetron sputtering system with strong magnetic field and with Ga and Al targets were deposited thin layers of GaN and AlN on the sapphire wafers. Was have analysed X-ray diffraction and revealed the crystalline nature highly oriented with the (0002) for both nitrides. For chemical composition was measured X-ray Photoelectron Spectroscopy and it was found out the ratios of Ga:N and Al:N to be 1.07 and 1.04 respectively. Scanning Electron Microscopy showed morphology and thickness of GaN. Optic transmission spectra showed band gaps to be 3.43 eV and 6.13 eV for GaN and AlN respectively. As a result from this research we can assume that magnetron sputtering technology is suitable for growing wide band gap materials such as GaN and AlN. In the process of growing GaN it is possible to dope it from alternative magnetron sputtering system and make p-n junction, quantum wells, high efficiency solar cells using InGaN/GaN heterojunction and other optoelectronic devices.

Acknowledgments

The work is implemented under the #YS-21-488 project of Shota Rustaveli National Science Foundation of Georgia.

References

1. N.-Q. Zhang, S. Keller, G. Parish, S. Heikman, S. P. DenBaars, U. K. Mishra, "High breakdown GaN HEMTs with overlapping gate structure", IEEE Electron Device Lett., vol. 21, pp. 421-423, Sept. 2000, doi: 10.1109/55.863096
2. L. F. Eastman, K. Chu, J. Smart, J. R. Shealy, "GaN materials for high-power microwave amplifiers", Mater. Res. Soc. Symp. Proc., vol. 512, pp. 3-7, 1998. doi: 10.1143/APEX.5.066503
3. S.T. Sheppard, K. Doverspike, W.L. Pribble, S.T. Allen, J.W. Palmour, L.T. Kehias, and T.J. Jenkins, ''High-power microwave GaN/AlGaN HEMTs on semi-insulating silicon carbide substrates'', IEEE Electron Device Lett., vol. 20, pp. 161-163, April 1999, doi: 10.1109/55.753753.
4. U. K. Mishra, P. Parikh, and Y. F. Wu, "AlGaN/GaN HEMTs—an overview of device operation and applications," Proc. IEEE, vol. 90, no. 6, pp. 1022–1031, Jun. 2002, doi: 10.1109/LED.2005.861027
5. Y. F. Wu, A. Saxler, M. Moore, R. P. Smith, S. Sheppard, P. M. Chavarkar, T. Wisleder, U. K. Mishra, and P. Parikh, "30-W/mm GaN HEMTs by field plate optimization," IEEE Electron Device Lett., vol. 25, no. 3, pp. 117–119, Mar. 2004, doi: 10.1109/LED.2003.822667.
6. H. Akinaga, S. Németh, J. De Boeck, L. Nistor, H. Bender, and G. Borghs, '' Growth and characterization of low-temperature grown GaN with high Fe doping'', Appl. Phys. Lett. 77, pp. 4377-4380, Octo. 2000, doi: 10.1063/1.1335547
7. H. Ofuchi and M. Oshima, "Fluorescence x-ray absorption fine structure study on local structures around Fe atoms heavily doped in GaN by low-temperature molecular-beam epitaxy", AIP Appl. Phys. Lett. 78, pp. 2470 (2001); doi: 10.1063/1.1368184
8. N. Theodoropoulou and A. F. Hebard, "Characterization of high dose Fe implantation into p-GaN", AIP Appl. Phys. Lett. 79, pp. 3452 (2001), doi: 10.1063/1.1420406
9. Shinji Yudate, Ryo Sasaki, Takashi Kataoka, Sho Shirakata, "Growth condition dependence of photoluminescence of Eu-doped GaN films prepared by radio frequency magnetron sputtering", ELSEVIER B.V, Optical Materials 28, pp. 742-745, 2006, doi: 10.1016/j.optmat.2005.09.013.
10. C.W. Zou, M.L. Yin, M. Li, L.P. Guo, "GaN films deposited by middle-frequency magnetron sputtering", ELSEVIER B.V, Applied Surface Science, 253, pp. 9077-9080, Sept. 2007, doi: 10.1016/j.apsusc.2007.05.037.
11. William A. Melton, Jasques I. Pankove, "GaN growth on sapphire", ELSEVIER B.V, Journal of Crystal Growth vol. 178, pp. 168-173, June 1997, doi: 10.1016/S0022-0248(97)00082-1.