Romanian Reports in Physics, Vol. 66, No. 4, P. 1118–1124, 2014

ALUMINIUM NITRIDE THIN FILMS GROWN BY PLASMA ASSISTED PULSED LASER DEPOSITION*

D.-M. MARIN[1], F. STOKKER-CHEREGI[2], M. DUMITRU[2], V. ION[2], M. DINESCU[2]

[1] University of Craiova, Department of Physics, 200585 Craiova, Romania
[2] National Institute for Lasers, Plasma, and Radiation Physics (NILPRP), Department of Lasers, Str. Atomistilor nr. 409, 077125 Magurele, Romania, E-mail: stokker@nipne.ro

Received October 22, 2013

Abstract. We determine the structural, morphological and optical properties of AlN thin films grown by plasma assisted pulsed laser deposition on *c*-cut sapphire and natively oxidized Si (100) substrates. We provide insight on how substrate type and laser fluence impact the properties of the obtained films. In our study we used an Al metal target that was ablated by the first harmonic of a Nd:YAG laser (λ = 1064 nm). We discuss similarities and differences between our results, and those reported for the ablation of sintered AlN pressed powder targets.

Key words: pulsed laser deposition, III-nitrides, thin films.

1. INTRODUCTION

Aluminium nitride (AlN) is a wide direct band gap (6.2 eV at room temperature) semiconductor material [1] which has been considered for the realization of ultraviolet solid-state light sources. As such, its potential has been demonstrated both through the achievement of AlN light emitting diodes [2] or through its integration in GaN/AlGaN quantum wells [3]. More recently, owing to favourable properties such as high acoustic propagation rate and low transmission loss [4], AlN has also been proposed for the realization of surface acoustic wave (SAW) devices [5] and thin-film bulk acoustic resonators (FBARs) [6].

Growth of AlN thin films has already been reported using various techniques, including chemical vapour deposition [7], molecular beam epitaxy [8], and reactive magnetron sputtering [9]. Pulsed laser deposition (PLD) is a low-cost and environmental friendly approach to thin film growth. The laser ablated species in the plasma plume achieve high kinetic energies when they impinge onto the surface of the substrate, enhancing the mobility of the deposited adatoms. Moreover,

* Paper presented at the 16th International Conference on Plasma Physics and Applications, June 20–25, 2013, Magurele, Bucharest, Romania.

interaction with the ablated species can be enhanced by feeding the ambient gas through a radiofrequency (RF) plasma source [10], thus providing proper course for the synthesis of AlN by laser ablation of an Al metal target in highly reactive nitrogen atmosphere.

PLD has proved to be a viable alternative to other growth techniques for the synthesis of AlN [11]. However, most recent PLD studies focus on the growth of AlN thin films by ablation of sintered AlN pressed powder targets [12, 13], rather than pure Al ones. Our study is motivated by the fact that the microstructure of such films exhibit great variations with respect to growth conditions and there is no consensus or definitive conclusion regarding optimal growth conditions. Moreover, no correlation is made in these studies between the structural composition of the target and that of the obtained films. In this work we determine the structural, morphological and optical properties of AlN thin films grown by plasma assisted pulsed laser deposition on *c*-cut sapphire and natively oxidized Si (100) substrates. We aim to establish if highly oriented growth of AlN on amorphous natively oxidized Si (100) substrates can also be achieved by ablation of an Al metal target, rather than a sintered one as reported in Ref. [12].

The crystalline structure of the resulting films was investigated by means of X-ray diffraction (XRD). Atomic force microscopy (AFM) was used to analyze surface morphology. Optical properties were probed by spectral ellipsometry.

2. EXPERIMENTAL

The samples were prepared by pulsed laser ablation of an Al metal target (> 99.99% purity) in controlled reactive nitrogen atmosphere. The first harmonic of an Nd:YAG laser (λ = 1064 nm, τ = 8 ns, 10 Hz pulse repetition rate) was focused onto the target at a 45° angle of incidence. Two laser fluences were used for the preparation of the samples: 4 and 8 J/cm^2, respectively. Samples were obtained following the ablation of the Al target by 72,000 laser pulses. The ablated material was collected on *c*-cut sapphire and natively oxidized Si (100) substrates mounted on a heater, 5 cm away from the target. Substrate temperature was kept at 600°C for all samples. The entire ablation procedure was assisted by the presence of nitrogen plasma. N_2 gas (> 99.99% purity) was fed through a mass flow controller into the radiofrequency plasma generator operating at 250 W discharge power. During the deposition, the pressure in the reaction chamber was kept at a constant 5 Pa, for all samples discussed here. This pressure is within the interval of working pressures of other studies [12, 13]. The target was pre-ablated for 15 minutes in nitrogen atmosphere prior to each deposition in order to remove possible contamination with aluminium oxide.

A PANalytical X'Pert PRO MRD diffractometer was used for the XRD analysis of the resulting structures. The morphology of the samples was studied with an XE100 Park atomic force microscope. Spectral ellipsometry was performed using a VASE Ellipsometer.

3. RESULTS AND DISCUSSIONS

Figure 1 shows a typical spectral ellipsometry measurement of the amplitude component (ψ), and its theoretical fit, for an AlN thin film grown on amorphous natively oxidized Si (100) substrate, using a laser fluence of 8 J/cm^2. The inset shows the wavelength dependence of the AlN refractive index used in our model. In order to achieve a best-fit with the experimental data, our modelling of the thin film assumes a two-layer structure made of a 1.007 μm (± 0.3 nm) thick AlN layer grown on top of a 3 nm (± 0.3 nm) layer of SiO_2, i.e. the native oxide layer. A surface roughness of 9.7 nm (± 0.3 nm) was assumed in our model for the AlN layer. The experimental data was fitted using a Cauchy dispersion model [14]. Although here we discuss the optical response of one particular sample, it should be noted that all samples, both on oxidized Si (100) and sapphire substrates, exhibit very similar behaviour.

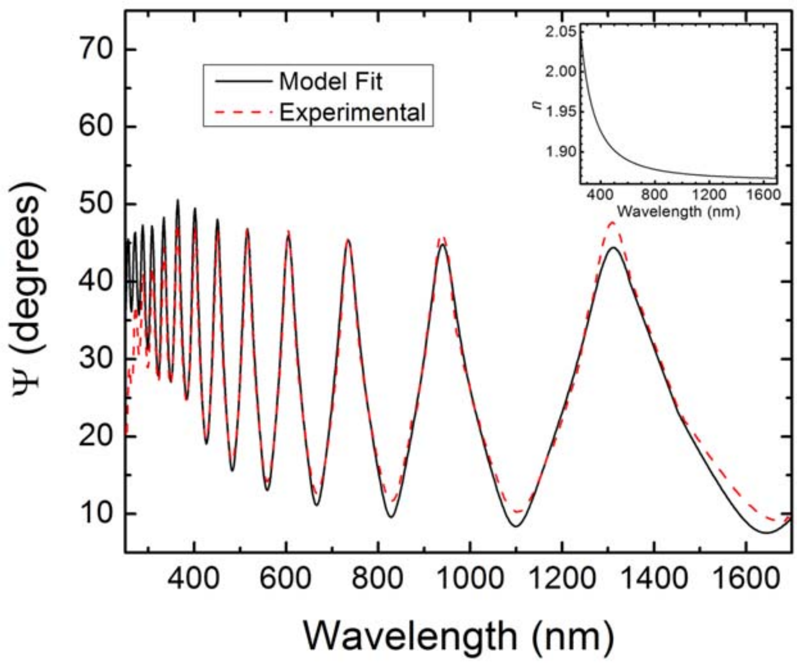

Fig. 1 – Spectral ellipsometry measurement (dashed line) and theoretical fit (continuous line) of the amplitude component (ψ) for an AlN thin grown on amorphous natively oxidized Si (100) substrate, using a laser fluence of 8 J/cm^2. The inset shows the wavelength dependence of the refractive index used in our model.

The obtained AlN thin films are highly transparent down to 350 nm. Below this wavelength a strong absorption can be noticed. Based on our ideal model, this phenomenon is normally expected to become significant only at around 200 nm.

We link the origin of this absorption to the strong scattering of light at low wavelengths on morphological defects found by AFM investigations, as discussed later in this section.

The refractive index of materials in the transparent spectral range is dependent on the atomic density, and therefore amorphous materials have a smaller refractive index than their crystalline counterparts [15]. Indeed, the derived refractive indexes for our AlN thin films are smaller than those previously reported for crystalline AlN [16], and therefore we conclude that our AlN films are amorphous, which is consistent with XRD measurements (as discussed below).

The XRD spectra, acquired in Bragg-Brentano geometry, for the samples obtained at a laser fluence of 8 J/cm^2 (Fig. 2), as well as those obtained at 4 J/cm^2 (not shown here) only reveal diffraction peaks assignable to the respective substrates, in accordance with PDF cards 01-089-9054 (Si) and 00-042-1468 (Al_2O_3), with unassigned peaks attributed to the presence of impurities. Similar findings have already been reported by other groups [13] for ambient pressures of 0.1 and 10 Pa, following the ablation of a sintered AlN target. On the other hand, this result is in stark contrast with findings reported in Ref. [12], where growth of highly oriented AlN was achieved under very similar conditions.

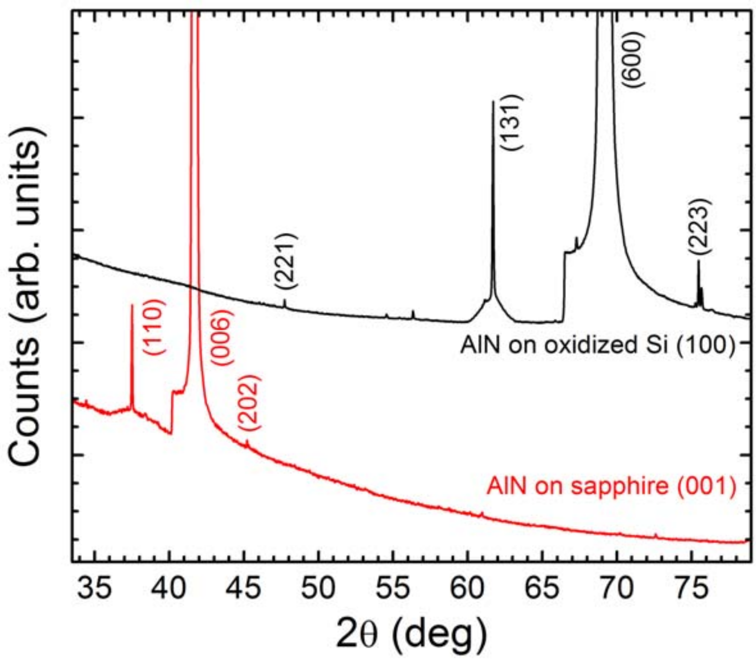

Fig. 2 – XRD spectra of the samples obtained at a laser fluence of 8 J/cm^2, on (**top**) amorphous natively oxidized Si (100) and (**bottom**) *c*-cut sapphire substrates, respectively. The spectra are shifted with respect to each other for clarity.

The XRD spectra of our samples indicate the formation of amorphous AlN on both types of substrates and for both fluences, which is consistent with our findings by spectral ellipsometry, as well as those by Ref. [13].

AFM micrographs, over areas of 40x40 μm, of AlN thin films surfaces are shown in Fig. 3. The formation of large, micron-sized droplets is revealed for both substrate types and both fluences, although in between these formations roughness values are of the order of few nanometers.

The reduction of laser fluence by a factor of two (bottom images) does not result in any particular improvement of surface morphology. At the laser fluence of 8 J/cm^2, roughness values are found to be 83 and 79 nm for samples grown on sapphire and Si (100), respectively. When a fluence of 4 J/cm^2 is used, these values change to 119 and 92 nm, respectively. Roughness values appear to be governed by the occurrence of large droplets, with sizes of the order of ~1 μm, in a given area, as no qualitative improvement of surface morphology can be observed following variation of laser fluence.

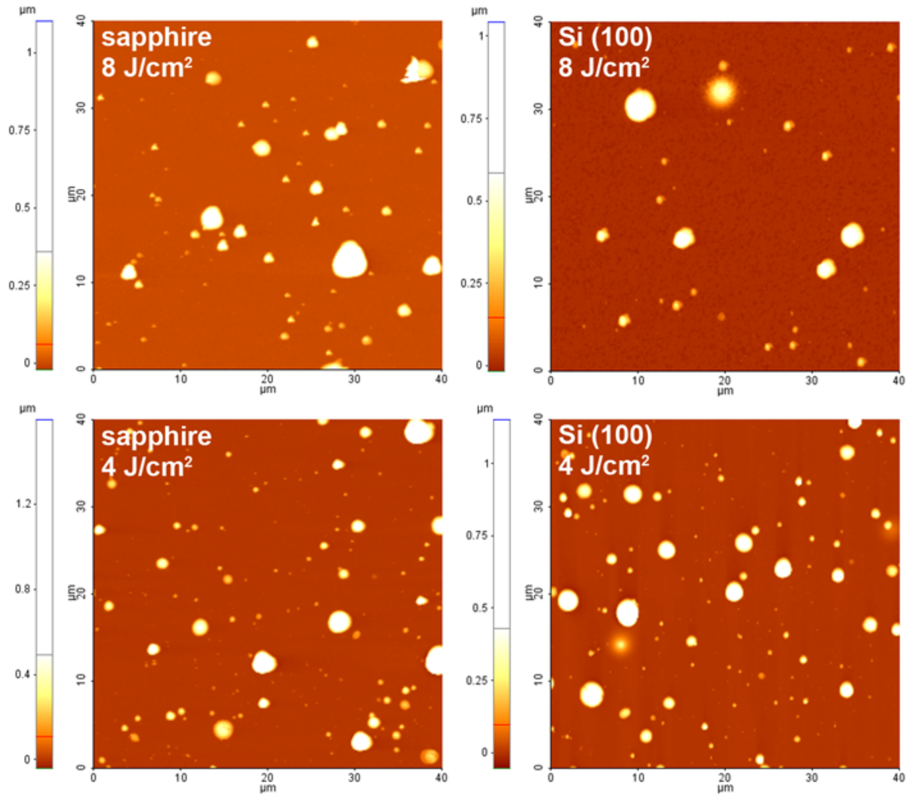

Fig. 3 – AFM micrographs over 40x40 μm areas of AlN thin films grown on *c*-cut sapphire (**left**) and amorphous natively oxidized Si (100) substrates (**right**) at fluences of 8 J/cm^2 (**top**) and 4 J/cm^2 (**bottom**), respectively.

There is a significant discrepancy between the surface roughness values found by AFM and those used for the modelling of the SE data. In order to achieve the fitting of the experimental spectra in Fig. 1, a surface roughness of several nanometers was assumed, which is consistent with roughness values of the films measured in between droplets. Our fit however was unable to account for the losses observed below 350 nm. We assume that the large morphological surface defects found by AFM act as absorption/scattering centers for ultraviolet radiation, thus explaining the deviation from the ideal optical response at low wavelengths.

4. CONCLUSIONS

AlN thin films were prepared starting from an Al metal target by plasma assisted PLD in order to provide insight on how substrate type and laser fluence impact the properties of the obtained films. Compared to previous studies on PLD growth of AlN from sintered targets, we find that our results are in agreement with those reported in Ref. [13], in the sense that at a pressure of 5 Pa we obtained amorphous AlN thin films, both on *c*-cut sapphire and amorphous natively oxidized Si (100) substrates, as supported by structural and optical characterizations. However, with our growth parameters, we were unable to reproduce the highly oriented growth reported in Ref. [12] by laser ablation of a sintered AlN target under similar experimental conditions.

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, project number PN-II-RU-TE-2011-3-0070.

REFERENCES

1. W.M. Yim, E.J. Stofko, P.J. Zanzucchi, J.I. Pankov, M. Ettenberge, S.L. Gilbert, J. Appl. Phys., **44**, 292 (1973).
2. Y. Taniyashu, M. Kasu, T. Makimoto, Nature, **441**, 325 (2006).
3. F. Stokker-Cheregi, A. Vinattieri, E. Feltin, D. Simeonov, J.-F. Carlin, R. Butté, N. Grandjean, F. Sacconi, M. Povolotskyi, A. Di Carlo, M. Gurioli, Phys. Rev., **B 79**, 245316 (2009).
4. X.H. Xu, H.S. Wu, C.J. Zhang, Z.H. Jin, Thin Solid Films, **388**, 62 (2001).
5. T. Aubert, O. Elmazria, B. Assouar, L. Bouvot, M. Oudich, Appl. Phys. Lett., **96**, 20 (2010).
6. G. Wingqvist, Surf. Coat. Tech., **205**, 5 (2010).
7. J. Dupuie, E. Gulari, J. Vac. Sci. Technol., **A 10**, 18 (1992).
8. Z. Sitar, L. Smith, R. Davis, J. Crystal Growth, **141**, 11 (1994).
9. T. Shiosaki, T. Yamamoto, T. Oda, A. Kawabata, Appl. Phys. Lett., **36**, 643 (1980).
10. F. Stokker-Cheregi, A. Nedelcea, M. Filipescu, A. Moldovan, D. Colceag, V. Ion, R. Birjega, M. Dinescu, Appl. Surf. Sci., **257**, 5312 (2011).
11. A. Kumar, H.L. Chan, J.J. Weimer, L. Sanderson, Thin Solid Films, **308–309**, 406 (1997).
12. Z.P. Wang, A. Morimoto, T. Kawae, H. Ito, K. Masugata, Phys. Lett., **A 375**, 3007 (2011).

13. A. Szekeres, Zs. Fogarassy, P. Petrik, E. Vlaikova, A. Cziraki, G. Socol, C. Ristoscu, S. Grigorescu, I.N. Mihailescu, Appl. Surf. Sci., **257**, 5370 (2011).
14. L. Nedelcu, A. Ioachim, M.I. Toacsan, M.G. Banciu, I. Pasuk, M. Buda, N. Scarisoreanu, V. Ion, M. Dinescu, Appl. Phys., **A 93**, 675 (2008).
15. Harland G. Tompkins, Eugene A. Irene (Eds.), Handbook of Ellipsometry, 0-8155-1499-9, William Andrew, Inc., 2005.
16. N. Antoine-Vincent, F. Natali, M. Mihailovic, A. Vasson, J. Leymarie, P. Disseix, D. Byrne, F. Semond, J. Massies, J. Appl. Phys., **93**, 5222 (2003).