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APSUSC-31574; No. of Pages 8

ARTICLE IN PRESS

Applied Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Multi-stage pulsed laser deposition of aluminum nitride at different temperatures

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ARTICLE INFO

Article history:
Received 20 June 2015
Received in revised form 14 October 2015
Accepted 15 October 2015
Available online xxx

Keywords:
Aluminum nitride
Multi-stage deposition
Seed layer
Different temperatures
Pulsed laser deposition

ABSTRACT

We report on multi-stage pulsed laser deposition of aluminum nitride (AlN) on Si (1 0 0) wafers, at different temperatures. The first stage of deposition was carried out at 800 °C, the optimum temperature for AlN crystallization. In the second stage, the deposition was conducted at lower temperatures (room temperature, 350 °C or 450 °C), in ambient Nitrogen, at 0.1 Pa. The synthesized structures were analyzed by grazing incidence X-ray diffraction (GIXRD), transmission electron microscopy (TEM), atomic force microscopy and spectroscopic ellipsometry (SE). GIXRD measurements indicated that the two-stage deposited AlN samples exhibited a randomly oriented wurtzite structure with nanosized crystallites. The peaks were shifted to larger angles, indicative for smaller inter-planar distances. Remarkably, TEM images demonstrated that the high-temperature AlN "seed" layers (800 °C) promoted the growth of poly-crystalline AlN structures at lower deposition temperatures. When increasing the deposition temperature, the surface roughness of the samples exhibited values in the range of 0.4–2.3 nm. SE analyses showed structures which yield band gap values within the range of 4.0–5.7 eV. A correlation between the results of single- and multi-stage AlN depositions was observed.

1. Introduction

Aluminum nitride (AlN) is one of the III–V compound semiconductors with a band gap energy of ~6.2 eV for hexagonal wurtzite structure [1,2] and ~5.4 eV for metastable cubic zinc-blende AlN structure [3,4]. It has excellent electronic, mechanical, chemical and thermal properties [5–7], which can be easily tailored according to its applications, including light-emitting devices such as laser diodes and light emitting diodes, as well as high-power electronics [5,7,8].

High quality AlN films have been synthesized by different deposition techniques, such as molecular beam epitaxy [9,10], radio-frequency reactive magnetron sputtering (MS) [11,12], and pulsed direct current reactive MS [13,14], plasma enhanced atomic layer deposition [15,16], metal organic chemical vapor deposition [17,18], and pulsed laser deposition (PLD) [19,20]. One important advantage of PLD technique is the ability to preserve the stoichiometry of the target in the deposited thin films [21]. Moreover, PLD ensures an excellent adherence of the deposited material to substrate, a growth rate controlled with a high accuracy degree (10^{-2}–10^{-1} nm/pulse), the absence of contamination, and deposition with great versatility of multi-layers and doped films [21,22].

In previous studies, we optimized the pulsed laser deposition of AlN films on Si wafers by using different Nitrogen (N_2) pressures [23–25] at high temperatures. In the present work we explore and report on the multi-stage PLD of AlN, by applying subsequent deposition stages (at 800 °C and room temperature (RT), 350 or 450 °C, respectively), aimed to obtain crystalline films even at low deposition temperatures.

2. Materials and methods

2.1. PLD experiment

PLD experiment has been performed inside a stainless steel Ultra High Vacuum reaction chamber using a KrF* excimer laser source (λ = 248 nm, $\tau_{FWHM} \le 25$ ns), running at a repetition rate of 40 Hz.

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http://dx.doi.org/10.1016/j.apsusc.2015.10.093
0169-4332/

Please cite this article in press as: L. Duta, et al., Multi-stage pulsed laser deposition of aluminum nitride at different temperatures, Appl. Surf. Sci. (2015), http://dx.doi.org/10.1016/j.apsusc.2015.10.093

Table 1
Substrate temperatures used for the single- and multi-stage PLD depositions and the corresponding sample codes.

Single-stage deposition		Multi-stage deposition	
Sample code	$T_{substrate}$ (°C)	Sample code	$T_{substrate}$ (°C)
AlN1	RT	AlN5	800/RT
AlN2	350	AlN6	800/350
AlN3	450	AlN7	800/450
AlN4	800	AlN8	RT/800/450

The laser beam was directed under an angle of 45° with respect to the target surface.

Polycrystalline AlN pellets from Plasmaterials (2.5 cm diameter × 0.6 cm thickness) were used as targets for the experiment. Commercial Si (1 0 0) wafers were used as deposition substrates and were placed parallel to the targets, at 5 cm separation distance. The laser fluence onto the target surface was set at ~3 J/cm^2 (with a corresponding laser spot size of ~12 mm^2).

Before deposition, the targets were submitted to a "cleaning" process with 1000 laser pulses. During this procedure, a shutter was interposed between the target and the substrate. This way, the potential remnant impurities and defects on the target surface, are removed. The targets were continuously rotated with 0.4 Hz and translated along two orthogonal axes to avoid the formation of deep craters in order to ensure a uniform deposition during the multi-pulse laser irradiation. Prior to the introduction into the deposition chamber, the Si wafers were immersed for 10 min in Hydrofluoric acid (5%) solution in order to eliminate the native oxide layer.

First, batches of samples have been prepared by employing a single-stage deposition process, with the substrates heated and maintained at different constant temperatures (RT, 350, 450, or 800 °C, respectively) using a PID-EXCEL temperature controller.

Next, batches of two-layered samples have been synthesized by a multi-stage deposition process carried out at different substrate temperatures. These two-layered structures had as the first "seed" layer (in contact with the Si substrate) the AlN film deposited at 800 °C. The subsequent stages were conducted at reduced temperatures: RT, 350 or 450 °C, respectively.

Before each experiment, the reaction chamber was evacuated using a high vacuum system down to a residual pressure of 10^{-5} Pa, while the substrate was heated up to 800 °C and maintained at this temperature for 60 min in order to remove the native oxide from Si surface. The dynamic ambient gas pressure during the thin film growth was kept at 0.1 Pa by feeding high-purity N_2 into the chamber with the aid of a calibrated gas inlet. An MKS 4000 controller was used for the measurement of the gas pressure.

For the synthesis of each layer, 15,000 subsequent laser pulses were applied. Table 1 collects the substrate temperatures used for the single- and multi-stage depositions and introduces the sample codes which will be further used in the whole text.

2.2. Characterization of deposited structures

(a) The identification of crystalline phases was carried out by grazing incidence X-ray diffraction (GIXRD) using a *Bruker D8 Advance* diffractometer, in parallel beam setting, equipped with Cu target X-ray tube. The incidence angle was set at 2°, and the scattered intensity was scanned in the range of 25–65° (2θ), with a step size of 0.04°, and 15 s per step.

(b) The transmission electron microscopy (TEM) analyses were performed with a *Philips CM 20* microscope, working at 200 keV accelerating voltage. The cross-section TEM samples were prepared by ion beam thinning. The high resolution TEM (HRTEM) measurements were done on a *JEOL* microscope, working at 300 keV accelerating voltage.

(c) The surface morphology of the deposited films was studied by atomic force microscopy (AFM), using a *XE-100* apparatus from Park Systems. The surface scanning was performed in the non-contact mode. Sharp tips (PPP-NCHR type from Nanosensors^{TM}), having 125 μm in length, 30 μm width and a radius of curvature of <8 nm, were employed for measurements. The spring constant was of 42 N/m and the resonance frequency of ~330 kHz, respectively. The topographical AFM images were scanned over areas of 4 × 4 μm^2. The images were processed with the XEI Image Processing Program (v.1.8.0), developed by Park Systems for display purpose and the root mean square roughness (R_{RMS}) evaluation.

(d) The spectroscopic ellipsometry (SE) measurement was carried out on a *VASE-Woollam* apparatus, in the spectral range of 193–1700 nm, at three angles of light incidence: 60, 65, and 70°, respectively. For the ellipsometric data simulation, Cauchy and General Oscillator models were applied. The thickness of the films, the values of refractive index (n), extinction coefficient (k), and the band gap energy (E_{og}) were determined with an accuracy of ±0.2 nm, ±0.005, and ±0.05 eV, respectively.

3. Results and discussion

All deposited structures were adherent to Si substrates as proved by "finger" and "scotch" tests. This is in consensus with other studies from the literature that report on the good mechanical behavior of AlN films in terms of hardness, elastic modulus, pull-out and scratch adherence, or wear [26–28].

3.1. Grazing incidence X-ray diffraction

The GIXRD patterns of the PLD single- and multi-stage deposited films are comparatively given in Fig. 1. For the single-stage AlN film deposited at RT, the GIXRD pattern (not shown here) showed an amorphous structure. The GIXRD patterns (Fig. 1a) of the single-stage samples deposited at 350 °C and 450 °C temperatures (AlN2 and AlN3 samples, respectively) displayed broad diffraction maxima, indicative of the low crystallinity of these films. The GIXRD patterns of AlN4 (Fig. 1a) and AlN5 (Fig. 1b) samples are very similar pointing that the diffraction maxima prevalently originate from the 800 °C "seed" AlN layer. Nanocrystallites could be formed in the RT deposited layer, but they are either in low amount or have small sizes, and thus their contribution to the GIXRD pattern is almost insignificant.

In the case of multi-stage depositions (Fig. 1b), the presence of diffraction lines, attributed to hexagonal (wurtzite) AlN phase (ICDD: 01-070-2543), as well-defined maxima testified for the formation of randomly oriented AlN hexagonal crystalline structures. The most intense peaks are placed at $2\theta \approx 32.6°$, $2\theta \approx 35.4°$, $2\theta \approx 37.3°$, $2\theta \approx 49.1°$, and $2\theta \approx 58.5°$ and correspond to the AlN 100, 002, 101, 102 and 110 reflections, respectively. The consistent peak shift (of $2\theta \approx 0.1$–$0.2°$) toward lower angles, with respect to the position of lines of the reference ICDD: 01-070-2543 file, point to the increase of interplanar distances in the case of AlN PLD films.

Thus, the GIXRD results prove the AlN films crystallization in hexagonal phase.

3.2. Transmission electron microscopy

TEM studies were performed on samples prepared by multi-stage PLD deposition. The layers deposited onto the 800 °C "seed" layer (AlN5–AlN8 samples) had a columnar-type structure with hexagonal AlN phase crystallites. This is in good accordance with the GIXRD results presented in the previous section. This can be better seen in the bright field TEM images and the selected area electron diffraction (SAED) patterns given in Figs. 2–5. One can