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Growth dynamics of pulsed-laser-deposited AlN films♣

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Films of AlN with different thicknesses are synthesized by pulsed laser deposition in a nitrogen gas ambient. The study of the structure and surface morphology is focused on the different mechanisms governing the film growth. Film crystalline properties, growth rate, lattice mismatch induces strain and strain relaxation process is considered. The films start growing in a 2D mode, resulting in a smooth surface and a predominantly amorphous structure with a small amount of crystalline AlN. The change in the surface energy with the number of laser pulses applied is the reason for the formation of a 3D structure and 3D island growth at the later stages, resulting in a rough surface and a dense polycrystalline film structure with a cubic phase. These conclusions conform to results from structural and optical analyses.

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1. Introduction

Aluminium nitride (AlN) presents excellent electronic, mechanical, chemical and thermal properties, and it is a promising substrate material for emerging wide-bandgap electronic and opto-electronic devices based on the III-nitride system (AlN, GaN, InN) and their alloys (AlGaN, InGaN). For many of these applications, including blue and UV LEDs, solid state lasers, solar-blind UV detectors, high power and high frequency devices, high qualities of the films and substrate and low dislocation densities are critical for the device performance.

AlN films and buffer layers can be grown via pulsed laser deposition (PLD) [1-3]. This method can lead to improved film qualities, but there is no straightforward theoretical or experimental model of the processes during deposition and the resulting film properties. Hence, the characterization of film growth and the mechanisms governing the film surface morphology could be very useful.

In this paper we present the results of a study of the growth dynamics of pulsed-laser-deposited AlN films by examining the film structure, IR response and surface morphology of the synthesized films grown to different film thicknesses at different nitrogen gas pressures during deposition. The influence of these technological conditions on the surface roughness is considered and the different growth mechanisms governing the depositions are speculated upon.

2. Experimental details

Films of AlN with different thicknesses were synthesized by pulsed laser deposition (PLD) on Si substrates. The UV KrF* laser source was operating at λ = 248 nm, pulse duration = 7 ns and repetition rate = 2 Hz. The polycrystalline AlN target was rotated during ablation to avoid piercing, as its distance from the Si substrate was 4 cm. The radiation energy fluence on the target was set to 3.7 J/cm^2. Prior to deposition, the substrates were heated to 800°C while the residual pressure in the chamber was kept at 10^{-5} Pa for 60 minutes in order to remove the native oxide. During deposition, the temperature was kept at 800ºC, providing good conditions for the growth of crystalline AlN [1].

The deposition of AlN films was carried out in vacuum or in a N_2 ambient at dynamic pressures of 0.1 or 10 Pa. Deposition was stopped after 3000, 8000, 15000 or 20000 laser pulses, and the samples were cooled to room temperature at a rate of ~5°C/min or ~25°C/min. The thickness of the AlN films was from 100 nm to 1 μm depending on the number of laser pulses applied and with a tendency to decrease with increasing N_2 pressure.

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The surface morphology was studied by recording atomic force microscopic (AFM) images on an NT-MDT (Russia) Solver scanning probe microscope and a non-commercial AFM microscope. Surface scanning was performed in a semi-contact mode to avoid altering the sample in subtle ways. Information on the crystalline structure was obtained by large-angle (2Θ = 0-90°) XRD measurements using Philips X'Pert equipment. Fourier Transform Infrared (FTIR) reflectance spectra were measured on a Shimadzu IRPrestige-21 spectrometer in the range 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. X-ray diffraction analysis

Detailed analysis of the measured XRD spectra has been presented elsewhere [4]. In summary, we demonstrated strong dependence of the polycrystalline film texture on the nitrogen pressure during deposition and a prevalence of the cubic phase. A similar structure has been reported in Ref. [3] for PLD AlN films deposited at 630°C in 20 Pa N_2. Fig. 1 shows the XRD spectra recorded for AlN films deposited at a N_2 pressure of 0.1 Pa, up to different thicknesses. As seen, intense Bragg peaks characterizing the cubic phase of AlN can be observed only in thick films (Fig. 1b), when the amount of AlN material is sufficient for X-ray measurement. Nevertheless, in the XRD spectrum of a thin film (Fig. 1a) some small peaks at the same positions appear, pointing to rudimental crystallization in a possibly still amorphous AlN matrix. The crystallites grew mostly in the {111} direction. The corresponding lattice constant of these film structures is a=0.4045 nm (ASTM 46-1200) [5].

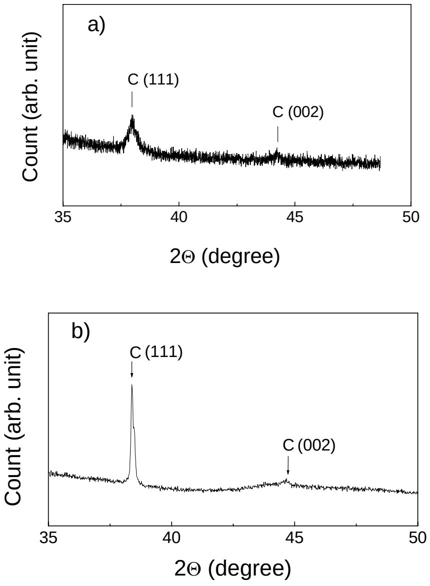


Fig. 1. XRD spectra of ~300 nm (a) and ~1400 nm (b) AlN films synthesized at a pressure of 0.1 Pa.

With increasing N_2 pressure, the ratio of (111) to (001) oriented crystallites gradually changes [4]. At a pressure of 10 Pa, the XRD pattern (Fig. 2) reveals a strong (001) texture. The cubic crystallites grow preferably in the {001} instead of the {111} direction. The effect of a gradual change in the texture with the nitrogen pressure was observed by Okamoto et al. [2], where hexagonal AlN films with different orientations were grown by PLD on sapphire, by varying the nitrogen gas pressure.

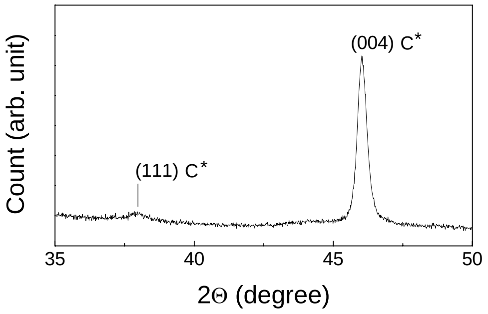


Fig. 2. XRD spectrum of a ~900 nm thick AlN film synthesized in nitrogen at a pressure of 10 Pa.

The Bragg peak broadening in the XRD spectra is an evidence for the formation of small sized crystallites. The size of the crystallites was estimated from the peak broadening using the Sherrer formula and assuming a spherical shape of the crystallites [6]. In general, the crystallite sizes are in the nanoscale range. For the 0.1 Pa case, the average size calculated from the dominant C(111) peaks is around 54 nm, while from the dominant C(001) peaks for the 10 Pa case it is 39 nm. The latter results in a smoother film surface for the higher pressure syntheses, as is revealed from the AFM image analysis given below.

3.2. FTIR reflectance spectra analysis

In Fig. 3, the FTIR reflectance spectra of the AlN films, deposited up to different thicknesses atN_2 pressures of 0.1 Pa and 10 Pa, are presented.

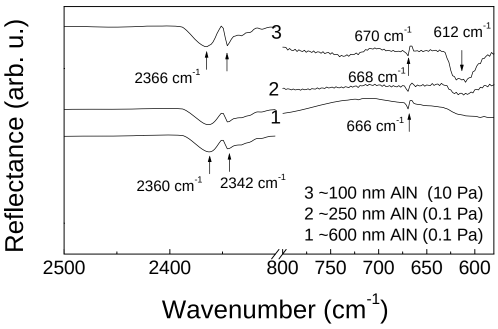
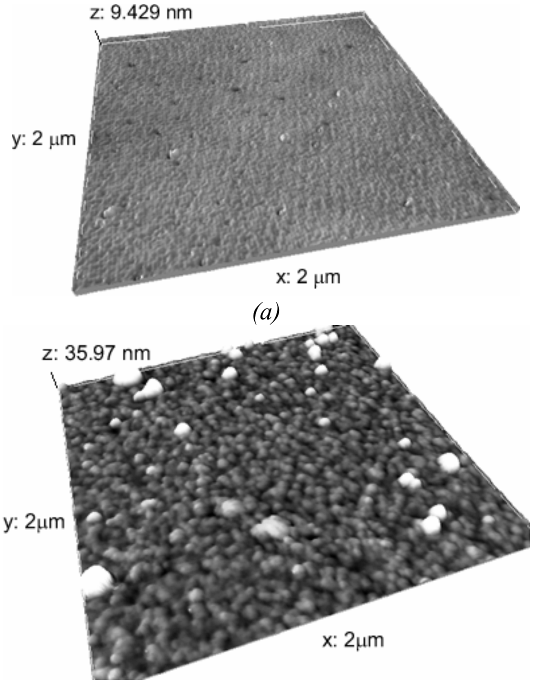


Fig. 3. FTIR reflectance spectra of AlN films deposited at N_2 pressures of 0.1 and 10 Pa.

The observed characteristic band in the 2360-2342 cm^{-1} range is related to vibrational excitations of polycrystalline AlN [7]. Here, this band splits into two separate ones with positions of 2362 and 2344 cm^{-1} for AlN films deposited at 0.1 Pa. For AlN films deposited at 10 Pa, they are centered at 2366 and 2344 cm^{-1} (Fig. 3). They may originate from the cubic AlN polycrystalline structure of these films. Other characteristic bands, occurring at ~ 612 and 670 cm^{-1} are attributed to the A_1(TO) and E_1(TO) vibration modes of Al-N, respectively [8,9]. It is interesting to note that the A_1(TO) phonon mode can be observed only in the spectra of thin films, as with increasing film thickness the intensity of the 612 cm^{-1} band is vanishing. Apparently, during deposition the initial amorphous structure of the AlN film converts gradually to a fully polycrystalline one, as proved by the XRD data. The E_1(TO) mode shift towards lower wave numbers with increasing film thickness is an inference for stress relaxation in the growing films.

3.3. Surface morphology

The structural transformations are well reflected in the alteration of the surface morphology of the AlN films. The nano-sized crystallites on AlN film surface are well visualized by AFM imaging. In Fig. 4, AFM images of the AlN films grown at a N_2 pressure of 10 Pa are presented. Fig. 4a shows the surface morphology of a 100 nm AlN film, deposited with 3000 laser pulses, while Fig. 4b represents the surface of a ~ 900 nm thick film deposited with 20000 laser pulses.



(a)

(b)

Fig. 4. AFM 3D images from a 2x2 µm^2 surface area for films deposited at 10 Pa N_2 pressure with 3000 (a) and 20 000 (b) laser pulses.

It is well seen from Fig. 4 that the thin film has a smooth surface. By increasing the number of laser pulses, i.e. the deposition time, the surface roughness increases and AlN crystallites become visible. The average roughness, S_a, is about 0.23 nm in the case of the thin film and increases to 1.42 nm when the pulses reached 20000.

The root-mean square roughnesses, S_q, are 0.31 nm and 2.81 nm for the thin and thick films, respectively. The vertical amplitude, S_y, denoted in the AFM images (Fig. 4) increased from 9.4 nm to 36 nm with the deposition time.

By decreasing the nitrogen pressure, a gradual increase of the surface roughness is detected, which can be caused by the increasing size of the crystallites that have emerged from the surface. This is demonstrated in Fig. 5, where a 3-dimensional image, taken from a scanning area of 2x2 µm^2, of a 0.1 Pa AlN film surface is presented.

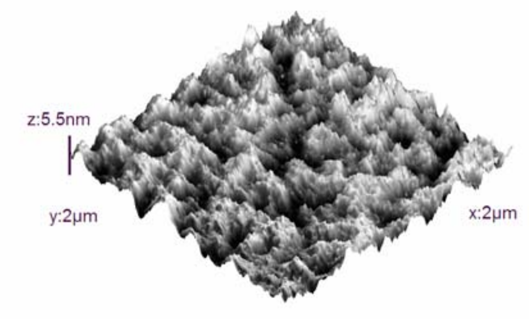


Fig. 5. An AFM 3D image from a 2x2 µm^2 surface area for films deposited at 0.1 Pa N_2 pressure with 20000 laser pulses.

Thus, we can speculate that at the beginning of film growth the films are deposited in a 2D mode which transforms into 3D island growth after some number of laser pulses. The smooth surface of the thin AlN films is evidence for 2D growth, during which the lattice strain, caused by the lattice mismatching between Si and AlN, increases. Thus, the surface energy also increases and, at certain critical thickness less strained 3D structures begin to form and strain relaxation starts. This suggestion is supported by the FTIR data analysis (Fig. 3). The strain is reduced by generation of misfit dislocations. The growth rate is relatively low, for 10 Pa N_2 pressure it is 0.4 Å/pulse (one monolayer is deposited with about 10 pulses), and the temperature is high, meaning enhanced residence time of adatoms and a large diffusion coefficient, so that the adatoms can find and sit at their proper energetically favourable lattice sites [10].

The average growth rate is relatively constant for the whole deposition process. Thus, it is not a change in kinetics which determines the different growth mechanism in the beginning, as in the case of [10], where the surface roughness and crystal quality are improved for the low-growth-rate case. In our case, the initial growth increases the strain from the interface mismatch, then the growth mechanism changes and ultimately leads to the formation of a polycrystalline AlN structure.

4. Conclusions

Pulsed laser deposition of AlN films onto Si(111) substrates results initially in 2D film growth, reflected in the films' predominantly amorphous structure with internal strains and smooth surface. As the deposition proceeds, the film growth mechanism transforms into 3D crystalline growth, leading to relaxation of interface induced stresses and the formation of polycrystalline cubic AlN material with a rough surface. An increase in nitrogen pressure leads to a change in film texture, different crystallite orientations and smaller sized crystallites, and thus, it results in reduced film roughness.

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