

## Orientation of the nanocrystallites in AlN thin film determined by FTIR spectroscopy

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**Abstract.** Aluminum Nitride (AlN) films were deposited at 450°C in nitrogen ambient at a pressure of 0.1 Pa and at a laser incident fluence of  $\sim 3 \text{ J/cm}^2$  and pulse repetition rate of 40 Hz. Grazing Incidence X-ray Diffraction patterns evidenced the presence of nanocrystallites in the amorphous AlN matrix. In the FTIR spectra the characteristic Reststrahlen band of AlN crystal with a hexagonal lattice is observed but it is quite broadened ( $950\text{--}550 \text{ cm}^{-1}$ ). The angular dependence of the reflectance spectra in *p*-polarised incidence radiation demonstrates the sensitivity of the  $A_1\text{LO}$  phonon mode of the AlN nanocrystallites to their orientation toward the normal to the substrate surface. With decrease of the incidence beam angle the intensity of the  $A_1\text{LO}$  phonon mode diminishes and softening of the resonance frequency occurs.

### 1. Introduction

Aluminum nitride (AlN) films have great potential for various applications due to their excellent electronic, optical, mechanical and thermal properties, which can be tailored in a wide range. The successful fabrication of devices based on AlN thin films requires better understanding of the film properties in relation to growth condition. Various techniques are exploited for the deposition of thin AlN films, such as metal organic chemical vapor deposition (MOCVD) [1], reactive magnetron sputtering [2] and pulsed laser deposition (PLD) [3-5]. Compared to MOCVD technique, the main advantage of PLD is the ability to facilitate the growth of thin films with good crystallinity and stoichiometry at relatively low temperatures.

In our recent studies PLD of AlN films on silicon substrates were optimized by using different nitrogen pressures at a temperature of 800°C [5]. The crystallinity of the AlN structure was found to be promoted by using higher repetition rates and lower nitrogen pressures for ablation. Further our aim was to obtain AlN films with considerably good crystallinity at lower deposition temperatures starting at 450°C.



In this work we present results on the study of the structure of PLD AlN films deposited at 450°C again using high repetition rate and low nitrogen pressure. The obtained films structure was analysed by Fourier Transform Infrared (FTIR) spectroscopy. Measurements with polarised radiation give more effective results for investigations of the electromagnetic wave interactions with the phonons in the nanocrystallites, thus delivering information about the stoichiometric state of the layer. IR reflectance spectra are very informative in the spectroscopy of crystals, especially in the spectral range of the Reststrahlen band arising as a result of the TO and LO crystal phonon modes. By measuring the angular dependence of the Reststrahlen band spectra in *p*-polarised IR radiation, the orientation of nanocrystallites in polycrystalline AlN thin film was qualitatively determined. The results were supported by analysing the Grazing Incidence X-ray Diffraction (GIXRD) patterns.

## 2. Experimental details

### 2.1. Sample preparation

AlN films were synthesized on Si(100) substrates by laser ablation of a polycrystalline AlN target with a KrF\* excimer laser model COMPexPro 205 ( $\lambda = 248$  nm,  $\tau_{FWHM} \leq 25$  ns), running at a pulse repetition rate of 40 Hz. The incident laser fluence was set at  $\sim 3$  J/cm<sup>2</sup>. The laser beam was oriented with an inclination angle of 45° with respect to the target surface. The substrate-target distance was 5 cm. Before deposition, the target was cleaned by short time ablation with 1000 laser pulses. During this procedure, a shutter was placed between the target and the substrate. The target was continuously rotated at 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 pulsed laser irradiation. 15 000 subsequent laser pulses were applied resulting in a 370 nm AlN film as determined from the ellipsometric measurements.

Prior to loading the samples into the deposition chamber, the Si substrates were cleaned in diluted HF (5%) solution in order to eliminate the native oxide layer. During deposition, the substrates were heated at 450 °C using a PID-EXCEL temperature controller.

### 2.2. GIXRD patterns

The identification of crystalline phases was accomplished by 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° (2 $\theta$ ), with a step size of 0.04°, and 10 seconds per step.

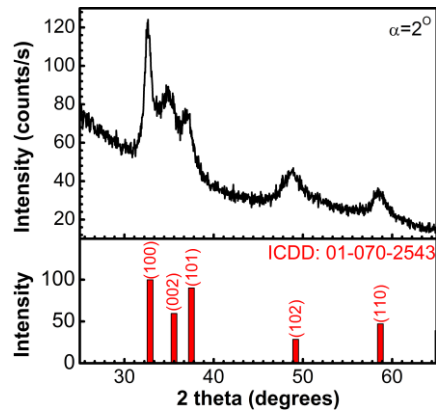
### 2.3. FTIR spectroscopy

FTIR reflectance spectra were measured using *p*-polarised incident IR radiation (electric vector *E* in the plane of incidence) at different angles: 12, 30, 45, 60 and 70 degrees. In this sense, more correct is to denote the orientation of *E* toward the normal to the film surface *z*, instead to the optical crystal axis *c* which, for every nanocrystallite, could be oriented to a random direction. The spectra were measured in the spectral region of 1200 – 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> and number of scans 64. A Bruker Vertex 70 instrument (10 000 – 30 cm<sup>-1</sup>) and a reflectance accessory Bruker A513/Q were used.

## 3. Results and discussion

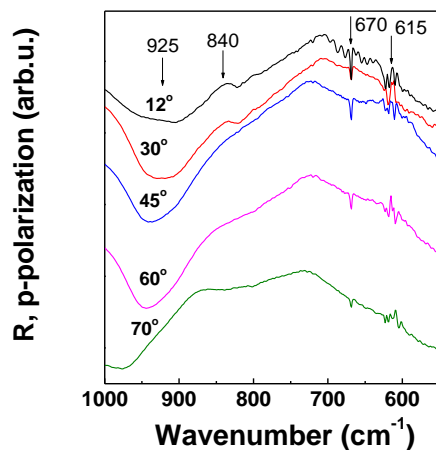
The GIXRD pattern of the AlN film deposited at 450°C is given in figure 1. The presence of well-defined but broad diffraction peaks attributed to hexagonal (wurtzite) AlN phase (ref. file ICDD: 01-070-2543, inserted at the bottom of figure 1) testified for the formation of randomly oriented AlN hexagonal crystallites in the amorphous film matrix. The amorphous AlN phase is evidenced by the broad background in the GIXRD pattern on which the 100, 002 and 101 diffraction maxima are superimposed on.

From the GIXRD results it is clearly shown that at the given deposition conditions nanocrystallites could be formed in the amorphous AlN matrix at such a low temperature as 450°C. However, the broad diffraction maxima indicate that the film structure has low crystallinity.

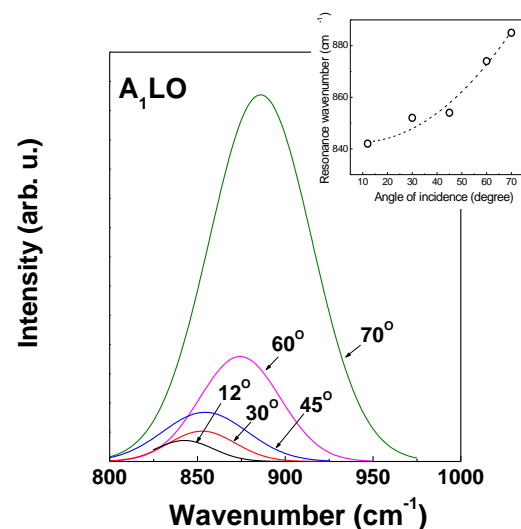


**Figure 1.** GIXRD pattern of AlN film deposited in nitrogen ambient at a pressure of 0.1 Pa and at a substrate temperature of 450°C.

FTIR reflectance spectra at different angles of incidence radiation: 12°, 30°, 45°, 60° and 70° are presented in figure 2. Despite its polycrystalline structure, the FTIR spectra of AlN thin film still exhibit the characteristic Reststrahlen band of AlN crystal with a hexagonal lattice. For hexagonal AlN, the IR active phonon vibrational modes have been determined [6-8] at ~611, ~670, ~890 and ~912 cm<sup>-1</sup>, arising from A<sub>1</sub>(TO), E<sub>1</sub>(TO), A<sub>1</sub>(LO) and E<sub>1</sub>(LO) respectively. In our measurements, the band is broadened (950-550 cm<sup>-1</sup>) with a complicated structure. For the analysis of the spectra, we used the Levenberg-Marquardt deconvolution method with four peaks. The accuracy after the procedure of the peak finding was in the order of 10<sup>-3</sup>. It turned out that the only band which changed its position with the incidence angle variation was that at 860 cm<sup>-1</sup>.



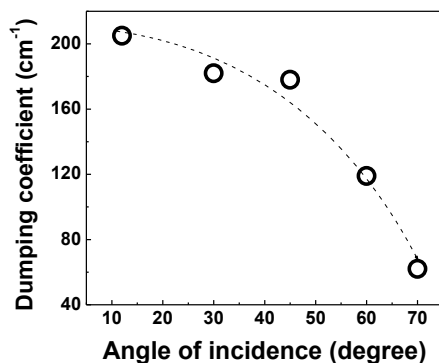
**Figure 2.** Angular dependence of the FTIR reflectance, *R*, spectra in *p*-polarised incidence radiation.



**Figure 3.** Angular dependence of the intensity of A<sub>1</sub>LO phonon mode. Insert: softening of A<sub>1</sub>LO frequency.

We assign the band around 860 cm<sup>-1</sup> to the A<sub>1</sub>LO phonon mode of the AlN nanocrystallites. The polarisation of this mode is parallel to the crystal axis *c* [9]. If there is a considerable quantity of nanocrystallites with *c* oriented close to the Si surface normal, the band intensity will show most pronounced change in *p*-polarisation, i.e. its intensity will increase with the increase of the angle of the incidence radiation: first, because the *E*||*z* component of the radiation in this geometry increases and

second, the beam optical path in the layer at large angles is maximal. The presence of crystalline AlN phase of such orientation is supported by the GIXRD analysis (see figure 1). It is seen that the corresponding peak (002) to an orientation  $c||z$  [10] is relatively intensive. The intensity increase of the band around  $860\text{ cm}^{-1}$  with increasing the angle is presented in figure 3 demonstrating qualitatively the sensitivity of the  $A_1\text{LO}$  phonon mode to the nanocrystallite lattice growth in  $z$  – direction. Moreover, the polariton resonance arising at the interaction of the  $A_1(\text{LO})$  mode with the electric vector  $\mathbf{E}$  of the IR radiation decreases in frequency with the incidence beam angle decrease (insert in figure 3). One possible explanation of this result could be that small incidence angles make the



**Figure 4.** Angular dependence of the resonance dumping coefficient,  $\gamma$ .

$p$ -polarized IR radiation sensitive also to phonon vibrations of perpendicular polarization in the  $x,y$  substrate plane which includes the nanocrystallites with oblique  $c$ -orientation close to this plane. This is equal to a force dissipation of  $\mathbf{E}$  leading to a dump of the polariton resonance oscillations in  $z$ -direction. In this case, the resonance wavenumber  $\nu$  becomes dependent on the dumping coefficient  $\gamma$  [11]:  $\nu = (\omega_0^2 - 2\gamma^2)^{1/2}$ , at  $\gamma \ll \omega_0$ ;  $\omega_0$  is the resonance polariton wavenumber of  $860\text{ cm}^{-1}$  at  $70^\circ$ . The  $\nu$ -softening with the decrease of incidence beam angle is shown in the insert of figure 3. The obtained angular dependence of the dumping coefficient  $\gamma$  is presented in figure 4. This dependence characterizes qualitatively the degree of disorientation of crystallites in the AlN film.

#### 4. Conclusions

The efficiency of FTIR reflectance spectroscopy in polarised radiation at different incidence angles for the characterisation of the PLD AlN film growth quality is demonstrated. Despite its poor crystalline structure, revealed by GIXRD, the FTIR spectra of AlN thin film still exhibit the characteristic Reststrahlen band of AlN crystal with a hexagonal lattice which, in our measurements is broadened. The sensitivity of the  $A_1\text{LO}$  phonon mode of the AlN nanocrystallites to their orientation toward the surface normal is illustrated: its intensity increases with the incidence angle increasing; softening of the resonance at the interaction of the mode with the electric vector  $\mathbf{E}$  of the IR radiation occurs by decreasing the incidence angle.

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