Ellipsometric characterization of AlN films synthesized by Pulsed-Laser-Deposition

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Abstract. AlN films were synthesized on Si(100) by pulsed laser deposition at 800°C and different incident laser fluences in vacuum and in nitrogen at 0.1 Pa. Two KrF* (λ = 248 nm) excimer laser sources were used generating pulses of 7.4 and 25 ns duration, respectively. The incident laser intensity on target was kept constant in all experiments within (3-4)x108 W/cm2. The films were studied by ellipsometry (SE) in the spectral range λ = 190÷900 nm and the optical parameters, such as refractive index, high frequency dielectric constant and single oscillator energies were estimated. The analysis of the SE results revealed that the films, deposited with short laser pulses and low laser fluence (3.7 J/cm2) were characterized with refractive index values higher than 2 and an optical band gap energy value of ~ 5 eV, suggesting that their structure was polycrystalline with cubic crystallites. With longer laser pulses and large fluence the refractive index values decreased and the values of the energetic parameters increased suggesting that the films, deposited in vacuum were polycrystalline with hexagonal phase, while those, deposited in nitrogen at 0.1 Pa were amorphous.

1. Introduction
Aluminium nitride thin films are promising for various technological applications, such as electroacoustic and optical devices, protective coatings and insulating layers. It has been established that preferential orientation of polycrystalline AlN films affects and often improves the properties of practical use such as piezoelectricity [1] or hardness [2,3].

AlN generally crystallizes in either hexagonal wurtzite (h-AlN) structure or cubic zinc-blende (c-AlN) polytype, which is reported theoretically as metastable phase [4]. On the other hand, because of its higher crystallographic symmetry, cubic AlN is expected to have several advantages for device applications, such as lower carrier scattering and higher doping efficiency. Since the growth of cubic AlN is quite difficult due to its metastable nature, the quality of cubic nitrides has been inferior to that of hexagonal ones. Theoretical investigations of the thermal conductivity of AlN have shown that the
energy difference between two kinds of phase structure of AlN is so small that both hexagonal and cubic phases are able to coexist in a realistic material [5]. Still, relevant data on the formation of each of the crystalline phases of AlN have been scant. Because of that, the properties of AlN have been extensively studied in the last decade, both theoretically and experimentally. The main accent has been placed on development of new deposition techniques and optimization of the growth conditions of AlN films. One of the most efficient and versatile techniques is pulsed laser deposition (PLD) possessing many advantages like the ability to grow thin films with good crystallinity and stoichiometry at low temperatures. There is still 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 synthesis is an important task in all application areas of AlN films.

Our research deals with pulsed laser deposited AlN films, with a focus on their structure and optical and electrical properties. The recent investigations revealed that the structure of the growing AlN films strongly depends on the laser fluence. Thus, at low fluences (2.7-3.7 J/cm²) the films were polycrystalline with 30-60 nm sized predominantly cubic crystallites [6-8]. When increasing the laser fluence to 10 J/cm², the prevalent crystalline phase turned from cubic to hexagonal [9]. The nitrogen pressure in the gas ambient during deposition played a decisive role in the crystallization process.

Here we present results of spectroscopic ellipsometric (SE) studies of the effect of deposition conditions on the growth of PLD AlN films and on their optical properties. The dependence of the films structure on the laser fluence and nitrogen content in the vacuum chamber during deposition is discussed.

2. Experimental details
AlN films were synthesized by pulsed laser deposition on crystalline Si substrates. Prior to deposition, the chamber was evacuated to 10⁻⁴ Pa and the substrates were heated up to 800°C, a temperature at which the native SiO₂ covering the wafers is known to decompose. The target consisting of polycrystalline AlN with 99% purity was rotated with 0.3 Hz to avoid piercing and to ensure a clean surface during multi-pulse laser irradiation. Two pulsed KrF* excimer laser sources (λ = 248 nm) were used for the ablation of the targets. The first one, model M-1701, generated pulses of 7.4 ns, while the second, a COMPEXPro 205, delivered pulses of 25 ns duration. 20,000 subsequent pulses were applied for the synthesis of each structure. The films were synthesized on substrates kept at a temperature of 800°C during deposition. Two different deposition regimes were applied: (i) laser pulse duration of 7.4 ns, repetition rate of 2 Hz, target-substrate distance of 4 cm, incident laser fluence of 3.7 J/cm², and (ii) laser pulse duration of 25 ns, repetition rate of 3 Hz, target-substrate distance of 5 cm, incident laser fluence of 10 J/cm². Accordingly, the laser intensity on the target was in all cases similar, within the narrow range of (3 – 4) x 10⁸ W/cm². This way we could independently study the effects of laser pulse duration and incident laser fluence.

The AlN films synthesis was carried out in vacuum (5x10⁻⁴ or 10⁻⁴ Pa) or in nitrogen at dynamic pressures of 0.1 Pa.

Depending on deposition conditions, the film thickness in the first set was in the range of 600-800 nm, while for the second set of experimental conditions the film thickness was in the range of 400-600 nm. There was a tendency for the thickness to decrease with nitrogen addition.

The ellipsometric measurements were carried out either on a Rudolph 436 ellipsometer covering the wavelength range from 300 to 820 nm or on a Woollam ellipsometer in the wavelength region of 190-900 nm. The angle of light incidence was 50°. Based on our [10] and other observations [11] that the PLD AlN films are transparent in the spectral range under consideration, the determination of the optical constants were performed using the Cauchy’s equation in the wide spectral range of 400-900 nm. Below 400 nm some light scattering due to surface roughness can arise and, therefore the optical constants were inferred by solving the inverse problem of ellipsometry in this spectral region.
3. Results and discussion

The spectral dependences of the refractive index \( n \) of the studied AlN films are presented in figure 1. In a wide wavelength region of visible light all the \( n \) values are within 2-2.2, being characteristic for polycrystalline AlN material [12], as the larger the \( n \) value the higher the order of crystallinity.

The shape of the curve for the films, deposited at 3.73/cm² laser fluence differs from that for films, deposited at more than twice higher laser fluence, suggesting different film structure. For low laser fluence, the refractive index values are very close, which is inherent for similar film structure. Contrary to that, films deposited at high laser fluence (10 J/cm²) have different refractive index values being evidence that film structures should differ from each other. The index data of AlN film, deposited at high laser fluence and in small amount of nitrogen at a dynamic pressure of 0.1 Pa, shows \( n \) values below 2 in almost the whole spectral region studied. Such spectral dependence is characteristic for amorphous AlN material [12].

![Figure 1. Dispersion curves of the refractive index of AlN films deposited at different laser fluence and in different gas ambient.](image)

The extinction coefficients for all the films remained below the value 0.02 even when approaching the near ultraviolet region, showing that the PLD AlN films are transparent in the studied spectral range. This makes it impossible to calculate the optical band gap energy \( E_{og} \) values. However, we could estimate how much the optical bandgap should be and what the influence of deposition conditions on its value is. For this purpose we analysed the refractive index dispersion curves using the concept of the single oscillator [13] and applying two approaches.

The first approach considers a single oscillator at wavelength \( \lambda_0 \). It includes the high frequency region, where the dielectric constant \( \varepsilon_i \) can be calculated using the simple classical dispersion equation \( (n_i^2 - 1)/(n_0^2 - 1) = 1 - (\lambda_0/\lambda)^2 \), where \( n_0 \) is the refractive index of an empty lattice at infinite wavelength and it gives the high frequency dielectric constant \( \varepsilon_\infty = n_0^2 \). These values were deduced from the plots of \( 1/(n^2 - 1) \) versus \( 1/\lambda^2 \), presented in figure 2, from the linear constants of the resulting straightline equation \( y = a - bx \) (\( a = 1/(n_0^2 - 1) \) and \( b = \lambda_0^2/(n_0^2 - 1) \)). The wavelength \( \lambda_0 \) is related to the energy at which direct interband electron transitions take place (\( \lambda_0 = hc/E_0 \)). The calculated quantities are summarized in Table 1.

In the second approach the refractive index data were analyzed below the interband absorption edge using the single-effective-oscillator equation \( n^2 - 1 = E_0 E_d/(E_0^2 - E_d^2) \) [13]. \( E_0 \) is the oscillator energy and it represents the average band gap being a distance between the “centers of gravity” of the valence and conduction bands. \( E_d \) is the dispersion energy of a single oscillator, it is a measure of the intensity of the inter-band optical transition and does not depend significantly on the band gap. These energetic
parameters were determined from the intercept and slope resulting from the extrapolation of the curves in figure 3, which represents the plots of $1/(n^2-1)$ versus $E^2$. The values of $E_0$ and $E_d$ are also given in Table 1. The values of $n_0$ and $E_0$, obtained by the two approaches are in good coincidence.

![Figure 2](image1.png)  
**Figure 2.** Plots of $1/(n^2-1)$ against $\lambda^{-2}$ for AlN films deposited at different laser fluences and in different gas ambient.

![Figure 3](image2.png)  
**Figure 3.** Plots of $1/(n^2-1)$ against $E^2$ for AlN films deposited at different laser fluences and in different gas ambient.

| Table 1. Optical constants and structure of PLD AlN films in dependence on deposition conditions. |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|
| Deposition condition (at constant laser intensity (3-4)x10^8 W/cm^2 and number of pulses 20,000) | Pulse duration | Laser fluence | Repetition frequency | Gas pressure |
|-----------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                   | 7.4 ns          | 3.7 J/cm²       | 2 Hz            | Vacuum (5x10⁻⁴ Pa) |
|                                   |                 | 10 J/cm²        |                 | Nitrogen (0.1 Pa) |
|                                   |                 |                 |                 | Vacuum (10⁻⁴ Pa) |
|                                   |                 |                 |                 | Nitrogen (0.1 Pa) |
| Optical constants                 |                 |                 |                 |                 |
| $n_0$                             | 1.91            | 1.98            | 2.1             | 1.88            |
| $\varepsilon_{\infty} = n_0^2$   | 3.65            | 3.92            | 4.41            | 3.53            |
| $\lambda_0$                       | 253.4 nm        | 240 nm          | 148 nm          | 135             |
| $E_0 = \hbar c/\lambda_0$         | 4.89 eV         | 5.17 eV         | 8.38 eV         | 9.18            |
| $n^2 - 1 = E_0 E_d / (E_{\infty} E')$ |                 |                 |                 |                 |
| $n_0$                             | 1.91            | 1.98            | 2.1             | 1.88            |
| $E_0$                             | 4.88 eV         | 5.16 eV         | 8.37 eV         | 9.2 eV          |
| $E_d$                             | 13.01 eV        | 15.06 eV        | 26.9 eV         | 23.17           |
| Film structure                    | Cubic AlN phase | Hexagonal AlN phase | Amorphous AlN phase |
|                                  | Polycrystalline AlN |

The oscillator energy $E_0$ is empirically related to the lowest direct band gap energy $E_{\text{og}}$ as $E_0 \approx 1.5E_{\text{g}}$ [13], where $E_{\text{g}}$ is an optical threshold energy level at which electron transitions begin and cause absorption to appear in the film. The optical band gap energy $E_{\text{og}}$ is expected to be higher than $E_{\text{g}}$, as the relation between $E_{\text{g}}$, $E_0$ and $E_{\text{og}}$ is $E_{\text{g}} < E_0 < E_{\text{og}}$ [13].
According to the limitation $E_0 < E_{\text{og}}$, for the AlN films, deposited at lower laser fluence, the real bandgap energy value is higher than 4.8 eV. For cubic AlN structure, bandgap values of 5.1 eV [14] and 4.5-6 eV [15] for direct electron transitions and, $E_{\text{og}} \sim 3.5$ eV for indirect electron transitions [16] are reported. Based on this and on the obtained refractive index values, a conclusion can be made about the film structure, namely that PLD AlN films, deposited at these conditions are polycrystalline with cubic phase crystallites. This conclusion was recently confirmed by the XRD studies on these films [6,9].

In the case of PLD deposition with longer laser pulses and high fluence (Table 1), the gas ambient obviously played more decisive role in the crystallization process. From the refractive index data analysis one can conclude that the AlN films, deposited in vacuum are polycrystalline, while the films grown in nitrogen ambient at 0.1 Pa have an amorphous structure. Since the refractive index of cubic AlN is somewhat larger than that of hexagonal modifications when approaching the absorption edge [12, 14] this suggests that in the PLD AlN films deposited in vacuum the crystallites are grown in hexagonal phase. This can be an explanation for the larger values of the energetic parameters registered for these films. Our XRD studies on PLD AlN films, deposited in vacuum at similar conditions and with high laser fluence of 8.6 J/cm², have revealed that films had a prevalent hexagonal polycrystalline structure [9].

4. Conclusions
The analysis of the SE results revealed that by varying the pulsed laser deposition conditions the optical parameters of the PLD AlN films changed to parameters characteristic for either cubic or hexagonal polycrystalline AlN. The PLD AlN films, deposited with short laser pulses and low fluence, are polycrystalline with cubic phase crystallites. In the case of PLD deposition with longer laser pulses and high fluence the PLD AlN films structure has a stronger dependence on the amount of nitrogen during the synthesis, as AlN films deposited in nitrogen at a dynamic pressure of 0.1 Pa grow in amorphous phase.

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