VIS/IR spectroscopy of thin AlN films grown by pulsed laser deposition at 400°C and 800°C and various N₂ pressures

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Abstract. The optical properties of pulsed-laser-deposited (PLD) AlN films on silicon are reported in the wide visible and infrared spectral range from 5x10⁴ cm⁻¹ to 350 cm⁻¹. The films were deposited at 400 °C or 800 °C and in vacuum or nitrogen gas ambient at pressures from 0.1 Pa to 10 Pa. The optical constants of the films were determined by modelling the spectroscopic ellipsometry data recorded in both the visible and infrared spectral ranges. The PLD AlN films deposited in vacuum have a bandgap energy of 6.2 eV in a good agreement with the crystalline AlN material, while an effective bandgap narrowing was observed for films deposited in N₂ ambient. This effect was most pronounced in films deposited at 400 °C, where the optical absorption below the fundamental edge was the largest due to a larger degree of disorder in the films. Fourier transform infrared spectroscopy was used to identify AlN phonon modes and stress in the films. The shift and broadening of the E₁(TO) peak towards the higher wave numbers indicates that an increased compressive stress is developed in the deposited films as the nitrogen pressure is increased.

1. Introduction

Aluminum nitride (AlN) films have great potential for various applications due to their excellent electronic, optical and thermal properties, which can be tailored by varying the deposition methods and the technological conditions. AlN and other thin III-nitride films are finding applications in high-power and high-frequency devices, high-power switches and blue and ultraviolet light-emitting devices and photo-detectors. The successful fabrication of devices based on thin AlN films requires a better understanding of the optical and electronic properties as related to the growth condition. Various techniques are employed for the deposition of thin AlN films, such as metal organic chemical vapor deposition (MOCVD) [1], reactive magnetron sputtering [2,3] and PLD [4-8]. Compared to MOCVD, PLD has the main advantage of ensuring the growth of thin films with good crystallinity and stoichiometry at relatively low temperatures.

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AIN with a stable wurtzite structure has a direct bandgap of 6.2 eV [9,11]. Cases where the AlN
bandgap has been determined to be considerably below 6.2 eV have been attributed to oxygen
contamination. The index of refraction reported in the visible spectrum is ranging from 1.99 to 2.25
depending on the AlN crystallinity. The phonon structure of AlN has also been subject to several
studies, where the LO and TO modes have been reported at about 905 cm\(^{-1}\) and 667 cm\(^{-1}\), respectively,
while the E\(_2\) mode has been observed at 665 cm\(^{-1}\) [9].

In our recent studies, PLD AlN films on silicon were optimized by using different nitrogen
pressures [5,6] at relatively high temperatures. The crystalline structure of the AlN was found to be
promoted by using higher repetition rates for the ablation and deposition at lower nitrogen pressures.
In this study, the focus is on the optical properties of the optimized PLD films by complementary
VIS/IR ellipsometry and Fourier transform infrared spectroscopy (FTIR). The optical constants and
vibrational spectra are related to the film structure and deposition conditions.

2. Experimental details
AlN films were deposited on (100)Si substrates by laser ablation of a polycrystalline AlN target by a
248-nm COMPEXPro 205 pulsed KrF* excimer laser source. The incident laser fluence was 4 J/cm\(^2\)
with a pulse duration of 25 ns and a pulse repetition rate of 40 Hz. The substrate-target distance was
5 cm. The Si substrate was heated to either 800°C or 400°C. The depositions at 800°C were carried
out in a vacuum ambient at 10\(^{-5}\) Pa residual pressure or in nitrogen gas with a dynamic pressure of
0.1 Pa and 10 Pa. For deposition at 400°C the nitrogen pressure was 0.1 Pa. The target was rotated at
0.3 Hz to avoid piercing and to ensure a clean surface during the multi-pulse laser irradiation. A
shutter was placed between the target and the substrate during the first 1000 laser pulses. Thus, the
impurities and defects still present on the target surface after cleaning could be collected and removed
before reaching the deposition area. For the synthesis of each structure, 20 000 consecutive laser
pulses were applied which resulted in different film thicknesses (from 500 nm to 700 nm) depending
on the nitrogen pressure and the laser pulse repetition rate.

The optical response of the AlN films was measured in the wide spectral region from 190 nm to
28 µm by UV/visible and infrared spectroscopic ellipsometry (VIS/IR SE) and Fourier transform
infrared (FTIR) transmission/absorption measurements. The VIS SE measurements were performed
using a Woollam VASE rotating compensator ellipsometer at multiple angles of incidence (Φ = 55°,
60°, 65°, 70°, 75°). Ellipsometric data in the IR range 400 – 4000 cm\(^{-1}\) were recorded with 16 cm\(^{-1}\)
spectral resolution at angles of incidence Φ = 60° and Φ = 70°. The FTIR spectroscopic measurements
were carried on a Shimadzu FTIR-8400s spectrometer in absorption mode. The spectra were collected
over the range of 7.8×10\(^3\) to 350 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

3. Results
The optical constants of the AlN films were obtained by modelling the measured ellipsometric
parameters Ψ and Δ. For the case of a multilayered structure consisting of the substrate, the film and a
surface roughness layer, a parameterized optical model was exploited to extract the complex refractive
index of interest from the measured dispersion of Ψ and Δ. The parameters in the model were the AlN
film thickness \(d\), the surface roughness layer thickness \(d_r\), the AlN optical response \((n, k)\) and the
established Si optical response. Using an effective medium approximation, the surface roughness layer
was modelled as commonly assumed as containing 50% air and 50% AlN material. The optical
constants of the AlN films were properly modelled using the Cauchy equation combined with an
Urbach absorption tail. For illustration of the optical model fitting accuracy, the Ψ and Δ spectra
measured at Φ = 60° and the corresponding model-generated ones are presented in figure 1 for an AlN
film deposited at 800°C and 0.1 Pa nitrogen gas ambient.

In figure 2, the refractive index and extinction coefficient of AlN films deposited at different
ambient pressures and temperatures are presented in the region of normal dispersion from 180 to
1200 nm. The index of refraction, \(n\), of PLD AlN films is 2.0-2.1 for wavelengths between 550 and
1200 nm, increasing to about 2.8 at 180 nm. The high-frequency dielectric constant \(\varepsilon_{\infty}\) was calculated
Figure 1. Experimental and model ellipsometric data of the AlN/Si structure deposited at 800°C and 0.1 Pa N$_2$ pressure; model data is given from the best fitting. The experimental data is recorded for an angle of incidence of 60° in the spectral range from 190 to 1680 nm. The mean-square error value of the fit is 31, which implies good approximation in the case of thick films. The fringes are induced by the finite film thickness of 672 nm. The surface roughness layer obtained in the model is 2.92 nm, in a very good agreement with the AFM data, where the root-mean-square roughness parameter is estimated at 2.6 nm.

Figure 2. Optical response of AlN films deposited at different ambient pressures and temperatures in the region of normal dispersion from 180 to 1200 nm.

from the long-wavelength refractive index using the dispersion theory: 
\[ \varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega) = [n(\omega)+ik(\omega)]^2 \]
yielding \( \varepsilon_{\text{re}} = n^2 \) for long wavelengths. The \( \varepsilon_{\text{re}} \) values for different deposition conditions are presented in table 1 and are close to the high-frequency dielectric constant of AlN \( \varepsilon_{\text{re}} = 4.84 \) reported by Collins at al. [10]. The AlN films are mostly transparent in the 400 – 900 nm spectral range with absorption registered below 400 nm (figure 2). The refractive index values were higher for the films deposited at low N$_2$ pressure and in a vacuum ambient due to the optimized crystallization under these conditions. Using a low substrate temperature and increased nitrogen pressure led to deterioration of the film’s crystalline quality, so that the effective refractive index decreased. Our previous structural investigations [6] did also show that the crystallization is promoted at lower pressures, confirming our present results.

The extinction coefficient \( k \) at 400 – 1000 nm is almost zero when nitrogen ambient is used during deposition and becomes about 0.1 for AlN films synthesized in vacuum. Using the extinction coefficient, \( k \), we determined the optical absorption of the films, \( \alpha = 4\pi k/\lambda \). The width of the optical bandgap \( E_g \) is estimated from the Tauc plot (figure 2, inset) represented as \( (\alpha E)^2 \) vs. \( E \) (photon energy) for direct bandgap materials. The linear part in the Tauc plot indicates the onset in the absorption due to
the bandgap transitions and, when extrapolated, the optical band gap of the material was approximated (e.g. figure 2, inset). The bandgap energies of the AlN films deposited at different ambient pressures are presented in figure 3. Single crystalline AlN has a direct bandgap transition width of 6.2 eV [9,11]. The PLD AlN films deposited in vacuum have a bandgap energy of 6.2 eV in a good agreement with the crystalline AlN material. The slightly lower bandgap energy for other films deposited at 800°C and N₂ ambient is due to optical absorption below the fundamental edge, or the so-called Urbach tail. This effect is explained by the exponential distribution of the density of localized states in the tails of the allowed bands due to disorder and defects in the crystalline structure. One can observe the characteristic exponential absorption edge of Urbach tails resulting in linear approximation of \( \ln(\alpha) \) vs. photon energy, as illustrated in figure 3, inset, for AlN films deposited at 800°C and 0.1 Pa N₂. The narrowing of the bandgap due to this effect is most clearly observable in the AlN films deposited at 400°C, where \( E_g \sim 4.1 \text{ eV} \) is considerably lower (figure 3). This is consistent with the fact that a lower temperature deposition of AlN favors the formation of crystalline defects with energy levels extending deep in the AlN bandgap thus reducing the effective forbidden gap.

The optical response of the AlN films was extended to the infrared range using IR ellipsometry. The ellipsometric parameters \( \Psi \) and \( \Delta \) were measured in the range 2.5 – 25 \( \mu \text{m} \). The optical model included the AlN layer thickness, roughness and transitions that were modelled using TOLO and Gauss oscillators. The fit of the experimental data with the optical model yielded a very low mean-square error MSE \( \sim 8-11 \). The dispersion features appearing in the spectra can be analyzed in the dispersion of the imaginary, \( \varepsilon_2(\omega) \), part of the dielectric function of PLD AlN films derived from the spectroscopic ellipsometry. The \( \varepsilon_2(\omega) \) dispersion showed a pronounced feature in the photon wavenumber range 400 – 800 cm\(^{-1}\) arising from absorption due to phonon modes in the AlN films (figure 4). The phonon band is centered at about 650 cm\(^{-1}\) for most of the films and is shifted to the lower wavenumbers (~610 cm\(^{-1}\)) for the AlN deposited in vacuum. This is consistent with the findings that vacuum laser deposition results in a slightly different stoichiometry of AlN films [12].

**Table 1.** High-frequency dielectric constant \( \varepsilon_{\infty} \) of PLD AlN films, synthesized at different nitrogen ambient pressures.

| \( \text{N}_2 \) pressure | \( \varepsilon_{\infty} \) |
|--------------------------|-----------------|
| vacuum                  | 4.34            |
| 0.1 Pa                   | 4.49 (4.35 for 400°C) |
| 10 Pa                    | 4.08            |

**Figure 3.** Optical band gap of AlN films deposited at different ambient pressures and temperatures as estimated from the absorption onset.

**Figure 4.** IR dispersion of the imaginary part \( \varepsilon_2(\omega) \) of the complex dielectric function of AlN films deposited at different ambient pressures and temperatures.
The dispersions of $\varepsilon_2(\omega)$ shown in figure 4 are the result of the modelling; thus they lack details on the separate phonon modes contributing to the absorption. To have details on the phonon modes in this region, Fourier transform infrared spectroscopy was performed providing a better spectral resolution (figure 5). The broad absorption band appearing in the modelled $\varepsilon_2(\omega)$ dispersion was registered in the FTIR in the region 750 – 550 cm$^{-1}$ with a distinct peak at about 686 cm$^{-1}$ arising from the E$_1$(TO) phonon mode of AlN. The shift and broadening of the E$_1$(TO) peak towards the higher wavenumber indicates that an increased compressive stress is developed in the deposited films as the nitrogen pressure is increased. The peak observed at about 620 cm$^{-1}$ originates from the vibrational modes in the Si substrate. Additional modes were observed at 669 cm$^{-1}$ and 706 cm$^{-1}$ for the films deposited at 800°C and at low pressure ambient (vacuum and 0.1 Pa N$_2$).

4. Conclusions

Optical constants of PLD AlN films on Si are reported in a wide region from the visible to the IR spectra ($5 \times 10^4$ cm$^{-1}$ to 350 cm$^{-1}$) as measured by spectroscopic ellipsometry and FTIR spectroscopy. The effects of the nitrogen pressure and the deposition temperature are related to the band gap width and the optical constants dispersion. The vibrational spectra analysis shows the presence of the characteristic AlN E$_1$(TO) phonon mode. AlN films deposited at 0.1 Pa N$_2$ pressure and a higher temperature have the widest band gap and exhibit a small broadening in the dispersions due to crystalline disorder.

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