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Thickness-dependent optical properties of aluminum nitride films for mid-infrared wavelengths

Leonid Yu. Beliaev,^{1, a)} Evgeniy Shkondin,² Andrei V. Lavrinenko,^{1, b)} and Osamu Takayama¹

¹⁾DTU Fotonik – Department of Photonics Engineering, Technical University of Denmark, Ørstedes Plads 343, DK-2800 Kgs. Lyngby, Denmark

²⁾DTU Nanolab - National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Ørstedes Plads 347, DK-2800 Kgs. Lyngby, Denmark

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We present a comparative study of optical properties of aluminum nitride (AlN) thin films with different thicknesses. The films with thicknesses ranging from 66 nm to 303 nm were deposited by reactive sputtering and plasma enhanced atomic layer deposition (PEALD). Permittivity was extracted from an ellipsometry and Fourier-transform infrared (FTIR) spectroscopy reflection measurements. Our particular focus is on the influence of the deposition method and film thickness on the AlN dielectric function. Here we show that both PEALD-deposited and sputtered AlN films exhibit a monotonic dependence of negative permittivity on their thickness for vast mid-IR wavelengths including the Reststrahlen band around $11.5 - 15 \mu\text{m}$ ($\sim 870 - 667 \text{ cm}^{-1}$). By structural analysis it was shown that PEALD-deposited layers contain a lower amount of oxygen and have smoother surfaces than deposited by the sputtering technique. On the other hand, sputtered films have higher densities and crystallinity, which results in the higher background permittivity (ϵ_∞). In FTIR spectra of the PEALD-deposited layers, two specific features are observed which can be explained by higher concentration of nitrogen due to nitrogen-rich plasma in the ALD process. Such peculiarities of the optical properties of AlN films should be taken into account in potential applications of this material for metamaterials and nanostructured systems.

I. INTRODUCTION

Currently, mid-infrared (IR) photonics that operate in the wavelength region of $2.0 - 20.0 \mu\text{m}$ ($5000 - 500 \text{ cm}^{-1}$) has attracted great interests due to the large number of the possible applications, such as chemical and biological sensing,¹⁻³ optical free-space communications,⁴ invisible-fence alarm systems,⁵ passive radiative cooling,^{6,7} light detection and ranging (LIDAR) systems^{8,9} and so on. Up to present, a wide variety of materials has been studied for mid-IR wavelengths, such as transparent dielectrics¹, metals, doped semiconductors,^{10,11} phononic materials.¹²

Among various mid-IR materials, one of a particular interest is aluminum nitride (AlN). Its optical properties vary from transparent dielectric to phononic material with its permittivity changing from positive to negative in the mid-IR wavelength around $11 \mu\text{m}$ ($\sim 909 \text{ cm}^{-1}$).¹³ AlN is a III-V semiconductor with a wide direct band gap of 6.2 eV, good thermal conductivity, mechanical strength, decomposition temperature and chemical inertness.¹⁴ Due to those properties AlN has been used for a wide variety of applications in microelectronic and optoelectronic devices,¹⁵ such as light emitting diodes (LED),¹⁶ resonators,¹⁷ microwave filters,¹⁸ dye-sensitized solar cells,¹⁹ and so forth. AlN is transparent from visible to mid-IR wavelengths and can be considered as a low-loss material up to $10 \mu\text{m}$ ^{20,21} ($\sim 1000 \text{ cm}^{-1}$).²² Above $11 \mu\text{m}$ ($\sim 909 \text{ cm}^{-1}$) to $15 \mu\text{m}$ ($\sim 667 \text{ cm}^{-1}$), AlN exhibits negative permittivity due to its phonon resonance in the region called the Reststrahlen band, which can be exploited for mid-IR photonics in order to manipulate infrared light.¹² Another

interesting optical property of AlN within the wavelength region is the epsilon-near-zero (ENZ) regime²³ near the longitudinal optical (LO) phonon frequency, where the permittivity of AlN becomes close to zero. The real part of the constant vanishes around $11.3 \mu\text{m}$ ($\sim 885 \text{ cm}^{-1}$), while the imaginary part is relatively small.^{12,13,24-27} Recently, various ENZ materials have drawn attention due to intriguing optical effects associated with vanishing permittivity²⁸ and studied for sensing,²⁹ enhanced fluorescence emission,³⁰ enhanced transmission through subwavelength apertures,³¹ strong subwavelength field enhancement,³² and engineering the frequency response of optical antennas.³³⁻³⁵

There are various methods of AlN thin films deposition including carbothermal nitridation of Al_2O_3 and subsequent sintering,^{36,37} metalorganic chemical vapor deposition,³⁸ molecular beam epitaxy (MBE),³⁹ sputtering,^{13,40} and atomic layer deposition (ALD).⁴¹ ALD is a well-known technique that allows to obtain high-quality films with precise thickness control.⁴² ALD deposition has been successfully applied for the fabrication of different high aspect ratio nanostructures with various materials, such as Al_2O_3 , TiO_2 ,⁴³ Al-doped ZnO trenches,⁴⁴⁻⁴⁶ pillars,⁴⁷ and tubes,⁴⁸ TiN trenches⁴⁹ and tubes,⁵⁰ multi-compound coaxial tubes.⁵¹ However, conventional thermal ALD requires temperatures higher than 400°C that above the trimethylaluminum (TMA) decomposition temperature. This typically leads to higher carbon and hydrogen presence in the deposited films and lower quality of the coatings. The use of plasma enhanced atomic layer deposition (PEALD) allows much better quality, since it enables the deposition at lower temperatures.^{52,53} However, optical properties and ENZ behaviour for mid-IR wavelengths have been mainly studied for AlN deposited by sputtering films^{13,24-26} or MBE.²⁷ In addition, there are very few studies whose optical properties were retrieved for films of different

^{a)}Electronic mail: leobe@dtu.dk

^{b)}Electronic mail: alav@fotonik.dtu.dk

thicknesses.^{52,54} However, this was performed mainly by ellipsometry and is limited by the near-infrared wavelengths. Extension of such analysis for longer wavelengths, up to mid-IR wavelengths where its permittivity turns from positive to negative into Reststrahlen band, is urgently required due to the advent of mid-IR absorption sensing.

Hence, in this paper we report on the mid-IR optical properties of AlN deposited by PEALD with NH_3 and N_2 plasma, and reactive sputtering. The AlN film thickness measured independently by spectroscopic ellipsometry and X-ray reflectivity (XRR) ranges from 66 nm to 303 nm. Optical characterization of the films was carried out using an ellipsometer and Fourier-transform infrared (FTIR) spectrometer covering the vast wavelength interval from 210 nm to $20.0\ \mu\text{m}$ ($\sim 47619 - 500\ \text{cm}^{-1}$). From the reflectance data we extracted a dielectric function of each film and revealed that there is a monotonic film thickness dependence on AlN's real part of permittivity for broad mid-IR wavelengths beyond $2.0\ \mu\text{m}$ ($\sim 5,000\ \text{cm}^{-1}$) including the Reststrahlen band by PEALD while sputtered AlN films show saturation of such dependence. In addition, structural properties of the coatings were characterized by (XRR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) in order to understand how certain composite **properties** affect dielectric function.

II. ALN FILM DEPOSITION

We fabricated two sets of AlN thin film samples by different techniques. The first set of samples was made by PEALD using NH_3 -based plasma. Thicknesses of samples as given by ellipsometry and XRR are: 66, 103, 128, 203, and 298 nm. The second set was created by reactive sputtering aiming thicknesses as close as possible to those of the first set. We ended with thicknesses 66, 98, 131, 170, 202, and 303 nm. Additionally to test plasma dependence of PEALD samples we fabricated a sample with thickness of 98 nm by N_2 -plasma enhanced ALD. All films were deposited on $350\ \mu\text{m}$ thick double-side polished Si (100) substrates.

A. PEALD deposition

The PEALD deposition was carried out in a commercial hot-wall reactor (R200 Advanced, Picosun) equipped with the remote plasma source. To prevent oxidation and presence of moisture, the tool has a load-lock used for delivering the substrates into the reactor chamber. The precursors used for AlN deposition were TMA supplied by Stream Chemicals and either NH_3 or N_2 enhanced by plasma. The deposition temperature was set at $350\ ^\circ\text{C}$ and plasma power to 3000 W for all of the PEALD runs. The recipe used in this work is presented in Table I. The deposition rate is measured to be 0.137 and 0.056 nm/cycle for NH_3 and N_2 processes, respectively.

TABLE I. Recipe for the PEALD deposition.

Sample thickness (nm)	Number of cycles	Precursor	Carrier gas flow (sccm)	Pulse time (s)	Purge (s)
66	568	TMA	100	0.1	8.0
		NH_3	150	5.0	30.0
103	852	TMA	100	0.1	8.0
		NH_3	150	5.0	30.0
128	1136	TMA	100	0.1	8.0
		NH_3	150	5.0	30.0
203	1704	TMA	100	0.1	8.0
		NH_3	150	5.0	30.0
298	2272	TMA	100	0.1	8.0
		NH_3	150	5.0	30.0
98	1750	TMA	100	0.1	8.0
		N_2	150	20.0	30.0

B. Sputtering deposition

The reactive sputtering deposition was carried out in a commercial sputter system (CMS-18 from Kurt J. Lesker Company). To prevent or reduce moisture and other impurities the tool has a load-lock used for delivering the substrates into the process chamber. During the deposition, the substrates were heated and kept at $400\ ^\circ\text{C}$. The deposition consisted of two stages. First, pre-sputtering of Cr with the closed substrate shutter was performed for 3 minutes in order to bind the remained water vapour and lower the base pressure inside the chamber. Second, the AlN sputtering itself was proceeded. The recipe used in this work are presented in Table II. The deposition rate is measured to be 0.06 nm/s.

TABLE II. Recipe for the reactive sputtering deposition.

Sample thickness (nm)	Deposition time (s)	Gas	Pressure (mTorr)	Target	Power (W)
67	990	50% N_2 in Ar	1	Al	300
98	1500	50% N_2 in Ar	1	Al	300
131	2180	50% N_2 in Ar	1	Al	300
170	3200	50% N_2 in Ar	1	Al	300
202	3600	50% N_2 in Ar	1	Al	300
303	5000	50% N_2 in Ar	1	Al	300

III. STRUCTURAL CHARACTERIZATION

A. Elemental analysis by XPS

The chemical composition of the films was investigated by X-ray photoelectron spectroscopy using an instrument (K-Alpha by Thermofisher Scientific) equipped with the Al K_{α} X-ray source with photon energy 1486.6 eV. The full XPS survey spectra and high resolution scans of Al $-2p$, N $-1s$, C $-1s$, and O $-1s$ signals were analysed. It shows (see Table III) that the films made by ALD tend to have more preferable stoichiometry (an Al/N ratio close to 1) and less impuri-

ties compared to sputtered films. Oxygen contamination with concentration more than 11% is observed in all films. This phenomena has been reported previously.⁵² This occurs as a result of the high reactivity of aluminum and oxygen, which origin includes leaks, wall outgassing, insufficient chamber passivation, and the traces that enter through the load-lock. Minor carbon impurities, less than 1 at.% was observed in all prepared samples, except the film prepared by PEALD using pure N₂ plasma. In this particular case, the carbon concentration was very pronounced (8.3 at.%) most probably appeared due to insufficient reaction of N₂ plasma species with TMA.

TABLE III. XPS results for both PEALD and reactive sputtering AlN film samples.

Sample thickness (nm)	Al (at.%)	N (at.%)	O (at.%)	C (at.%)	Al/N
PEALD NH ₃					
66	47.5	40.8	11.6	0.1	1.17
103	48.1	40.6	11.2	0.2	1.18
128	47.8	41.1	11.0	0.1	1.16
203	47.7	41.0	11.2	0.1	1.16
298	47.6	41.1	11.2	0.1	1.16
PEALD N ₂					
98	41.7	36.3	13.5	8.3	1.15
Sputtering					
67	48.6	39.0	11.5	0.7	1.25
98	47.7	35.9	15.4	0.6	1.33
131	48.6	37.4	13.2	0.6	1.30
170	46.6	37.3	15.0	1.0	1.25
202	48.3	36.1	14.9	0.6	1.34
303	46.5	31.1	20.9	1.1	1.49

B. XRR analysis

X-ray reflectivity measurements were performed with a Rigaku SmartLab 3kW diffractometer equipped with Cu K α X-ray source. The incoming beam was of small divergence and adequately monochromated by carefully selecting the optical scheme - a parabolic multilayer mirror, Ge(220) double-bounce monochromator and slits. Density, thickness, and surface roughness were obtained by fitting the measured XRR data to a theoretical model using Rigaku XRD Smartlab reflectivity analysis software. The implemented model contains the silicon substrate, native silicon oxide layer, and deposited AlN film with a thin surface layer of lower density to compensate for moisture and oxidation effect. XRR results reveal that the sputtered AlN films have significantly higher densities (supplementary material at [URL will be inserted by AIP Publishing]) compared to ALD films. The measured density of about 3.2 g/cm³ is the same as reported for the fully crystalline AlN.⁵³ On the contrary, the ALD samples have density values close to values reported for amorphous or polycrystalline ALD-deposited AlN films (2.5–2.8 g/cm³).^{52,55,56} Analysis of the roughness showed that ALD films were smoother compared to sputtered films. The slightly higher average roughness of the sputtered films could be at-

tributed to the more precise, self-limiting deposition protocol of ALD. Also, for both ALD and sputtered films the average roughness increases a bit with the thickness. These results are in a good agreement with reported in literature.^{52,53} In addition, the roughness and thickness of thin films were independently estimated by AFM and ellipsometry measurements, respectively.

C. XRD analysis

FIG. 1. XRD θ - 2θ measurements of samples made by (a) reactive sputtering and (c) PEALD (NH₃/N₂), respectively. Black line is the reference measurements from Si substrate without film; The average crystallite size estimated by Scherrer equation samples made by (b) reactive sputtering and (d) PEALD (NH₃/N₂), respectively.

To gain further information on the structural properties of the AlN thin films, X-ray diffraction measurements were performed using the same equipment as in the case of XRR. θ - 2θ scans were acquired in a parallel beam geometry implementing a parabolic multilayer mirror and using the incident and receiving slits of 0.5 mm and a set of Soller slits of 5° to minimize the beam divergence. The scan was conducted at the 20 – 90° angle range of 2θ . For both ALD and sputtered films, the peaks around 36° and 38° were observed, which attributed to the (002) and (101) crystalline AlN orientation, respectively.^{53,54,57,58} Since the peak at 36° is more pronounced compared to 38° for all the deposited films, the growth favors the (002) orientation instead of the (101). For the sputtered films both peaks are more pronounced due to higher crystallinity level of the structure, which is in agreement with the XRR measurements. The Lorentzian fit through the measured peaks allowed estimating the average grain size by the Scherrer equation^{59,60}:

$$D = \frac{K\lambda}{\beta \cos(\theta)}. \quad (1)$$

Here, K is the Scherrer factor, λ is the wavelength of Cu K α

radiation, θ is a Bragg angle and β is the full-width at half-maximum (FWHM) of the observed peak with instrumental correction (0.13°). The results presented in Fig. 1 demonstrate a monotonically increasing nonlinear dependence of the average crystallite size D with the film thickness. Hence, increasing the thickness leads to the growth of the crystallinity of the thin films, which is indicated by rising and narrowing of the diffraction peak. Furthermore, it is obvious that the grain size of a sputtered layer is higher in comparison with the ALD sample (for PEALD distinct peaks appear only from 200 nm thickness). The average grain size was also independently estimated by AFM measurements.

D. AFM analysis

The accuracy of surface roughness evaluated by XRR analysis was additionally verified by atomic force microscopy (AFM Dimension Icon-PT by Bruker AXS) operated in the tapping mode. The root-mean-square (RMS) surface roughness was determined for each film as shown in supplementary material at [URL will be inserted by AIP Publishing]. Supporting the XRR analysis, it was observed that roughness of the samples increases with the thickness. The AFM images of the AlN film of 100 nm thickness made by both PEALD (with NH_3 and N_2 plasma) and reactive sputtering are shown in Fig. 2. See supplementary material at [URL will be inserted by AIP Publishing] for images with other thicknesses. Moreover, the grain size estimation was performed using the watershed algorithm implemented in the NanoScope Analysis 1.7 software, where only separated grains were considered due to their statistical significance. As for the XRD analysis, an increase in the grain size with the film thickness was observed.

FIG. 2. AFM images (1 μm scale) of samples made by (a) reactive sputtering, (b) PEALD with N_2 - and (c) NH_3 -plasmas, respectively.

IV. OPTICAL CHARACTERIZATION

A. Spectroscopic ellipsometry for visible and near-infrared wavelengths

The film thickness and permittivity of the AlN film samples were measured using an ellipsometer (VASE by J. A. Woolam Co). The measurements were performed in a spectral range of 210 – 1690 nm ($\sim 47619 - 5917 \text{ cm}^{-1}$). Ψ and Δ

ellipsometry parameters were measured at three angles of incidence (55° , 60° and 65°) and the corresponding experimental dielectric constants were extracted by the Cauchy-Urbach model.^{61–64} Fitted example, all obtained coefficients and the real and imaginary parts of dielectric functions (ϵ_1 and ϵ_2), are presented in supplementary materials [URL will be inserted by AIP Publishing]. From the data, we can observe that the background permittivity (ϵ_∞) increases with the growing thickness. Moreover, the value for the films made by reactive sputtering is higher than those made by PEALD. According to the XRR and XRD data, sputtered films have higher densities and higher crystallinity in comparison with ALD films. The improvement of crystallinity leads to increasing of ϵ_∞ and therefore overall dielectric constants as well.

B. FTIR measurement for mid-infrared wavelengths and fitting

FIG. 3. FTIR experimental and fitted reflection for sputtered AlN films with various thicknesses.

Free-space reflection measurements in the mid-infrared range were conducted by the FTIR spectrometer (VERTEX 70, Bruker).^{44,47,65} A series of measurements were performed with the unpolarized incident light in the wavelength range of $\lambda = 2.0 - 20.0 \mu\text{m}$ ($5000 - 500 \text{ cm}^{-1}$) with resolution of 4 cm^{-1} . The measured reflectance spectra in supplementary material at [URL will be inserted by AIP Publishing] are the average of five different points on each sample and each measurement is the average of 32 scans. All measurements were performed at the incidence angle of 12° . Each reflectance spectrum was normalized by that from an aluminum mirror. **As an example, we show the measured reflection spectra and fitted reflection of sputtered AlN films in Fig. 3.**

The FTIR reflectance spectra of the samples exhibit various vibrational modes, which can be classified according to their origin as AlN, Si/SiO_2 and carbonaceous/aqueous ones. The peaks around $4.23 (\sim 2364 \text{ cm}^{-1})$ and $14.95 \mu\text{m} (\sim 669 \text{ cm}^{-1})$ presented in most of samples can be assigned

FIG. 4. Real (a,b) and imaginary (c,d) permittivity of AlN films deposited by PEALD NH_3 , N_2 plasmas and reactive sputtering, respectively.

to CO_2 absorption due to the deviating CO_2 levels in the atmosphere.⁶⁶ In some cases, the pronounced peak at $14.95 \mu\text{m}$ of CO_2 is present in reflection spectra. Therefore, we did not fit simulated reflectance for this particular peak in retrieving the permittivities of AlN films. The features around $2.7 \mu\text{m}$ ($\sim 3704 \text{ cm}^{-1}$) and very broad in the $5.2 - 7.9 \mu\text{m}$ ($\sim 1923 - 1266 \text{ cm}^{-1}$) range are attributed to water absorption. Moreover, in the second broad band can be also contributions from the asymmetric and symmetric bending modes, respectively, of methyl, methyne, and methylene groups, which are common impurities in thin films deposited with TMA-based processes.^{52,67}

The relatively strong features around $16.5 \mu\text{m}$ ($\sim 606 \text{ cm}^{-1}$) and less intense around 10.3 ($\sim 971 \text{ cm}^{-1}$) and $11 \mu\text{m}$ ($\sim 909 \text{ cm}^{-1}$) are assigned to the Si modes.^{68,69} The band around $12 \mu\text{m}$ ($\sim 833 \text{ cm}^{-1}$) is assigned to the Si—N bond, which is possibly created due to the diffusion of Si atoms into the AlN matrix.⁷⁰ The other feature observed around $13.5 \mu\text{m}$ ($\sim 741 \text{ cm}^{-1}$) arise from the native oxides of the substrates.^{54,71} In addition, it is possible that longitudinal optical (LO) phonon mode¹² of Al-N and stretching Al-O mode contribute to the features around 13.5 and $11.3 \mu\text{m}$ ($\sim 885 \text{ cm}^{-1}$), respectively. However, it is hard to distinguish those from the Si and SiO_2 modes.^{72,73}

The band around $15 \mu\text{m}$ ($\sim 667 \text{ cm}^{-1}$) observed for all sam-

ples could be assigned to the transverse optical (TO) phonon mode of Al-N. In addition, in the data obtained for PEALD with NH_3 plasma two new resonances are clearly seen around 3.2 ($\sim 3125 \text{ cm}^{-1}$) and $4.7 \mu\text{m}$ ($\sim 2128 \text{ cm}^{-1}$). The band at $3.2 \mu\text{m}$ is attributed to NH stretching in Al-NH_2 ^{14,55} and the band at $4.7 \mu\text{m}$ is assigned to Al— N_2 bonding.¹⁴ The feature at $4.7 \mu\text{m}$ is also seen for PEALD with N_2 plasma, whereas for the sputtered samples these low-wavelength resonances are absent.

C. Optical properties/permittivities

The measured FTIR reflection and fitted reflection spectra by using the RefFit software^{44,74,75} are shown in Fig. 3 and supplementary material at [URL will be inserted by AIP Publishing]. The entire procedure of permittivity retrieval is given in supplementary material at [URL will be inserted by AIP Publishing]. First, we retrieved the permittivity of a $350 \mu\text{m}$ double side polished Si substrate from the free-space reflection. The permittivity of Si substrate was found by fitting the simulated reflection spectra to the measured reflection, assuming that the permittivity of Si follows the Lorentz model with seven Lorentzian terms (supplementary material at [URL will be inserted by AIP Publishing]). The Si substrate's permit-

TABLE IV. Fitted Lorentz parameters of AlN films.

Sample thickness (nm)	ϵ_∞	ω_{TO} cm ⁻¹	γ_1 cm ⁻¹	ω_2 cm ⁻¹	γ_2 cm ⁻¹	ω_3 cm ⁻¹	γ_3 cm ⁻¹	ω_{LO} ¹² cm ⁻¹
PEALD NH ₃								
66	3.68	649	31.7	2077	119	3204	332	885
103	3.70	649	28.7	2077	119	3204	332	885
128	3.75	649	27.4	2077	119	3204	332	885
203	3.82	649	25.5	2077	119	3204	332	885
298	3.83	649	23.4	2077	119	3204	332	885
PEALD N ₂								
98	3.61	649	30.7	2077	90.3	-	-	885
Sputtering								
67	4.29	649	30.9	-	-	-	-	885
98	4.38	649	27.2	-	-	-	-	885
131	4.52	649	25.6	-	-	-	-	885
170	4.62	649	23.3	-	-	-	-	885
202	4.68	649	21.4	-	-	-	-	885
303	4.76	649	19.7	-	-	-	-	885

tivity was used for the rest of permittivity retrieval process of AlN films.

Then, we measured reflection spectra from AlN film deposited on Si substrate, which was used to fit the simulated reflection by the transfer matrix method. Hereby we assume that the permittivity of AlN film follows the Lorentz model, we vary the parameters of the model and simulate reflection spectra so that the simulated reflection spectra “fit” the measured reflection spectra, giving us the set of parameters to obtain the film permittivities. The fitted results for all samples can be found in the Table IV. Hereby we note that the error bars are a few percent in the overall spectrum so is the fitted reflection curves (Fig. 3). Therefore, we estimate the overall error of fitted permittivities to be similar values. The frequency-dependent real and imaginary part of permittivity for the AlN film samples were modeled using an isotropic permittivity:^{12,25,27,33,76–79}

$$\epsilon(\omega) = \epsilon_\infty \left(1 + \frac{\omega_{LO}^2 - \omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\omega\gamma_1} + \sum_{i=2}^3 \frac{\omega^2 - \omega_i^2}{\omega_i^2 - \omega^2 - i\omega\gamma_i} \right), \quad (2)$$

where ϵ_∞ is the high-frequency permittivity, ω_{LO} and ω_{TO} are TO and LO phonon frequencies, and γ is the scattering rate, respectively. Parameters γ , ω_{LO} and ω_{TO} were taken from FTIR fitting made by RefFit software^{80,81} and ϵ_∞ from ellipsometry measurements.

D. Structural and optical properties

Figure 4 shows the retrieved real and imaginary parts of complex permittivity. **The zero-crossing wavelength for ϵ_1 is around 11.25 μm ($\sim 888 \text{ cm}^{-1}$) and slightly red-shifted with the increase of the thickness for the both sputtered and PEALD-deposited films with NH₃ and N₂ plasma, respectively.** That point is associated with the LO phonon fre-

quency for the undamped system.⁸² In the concordance with the ellipsometry data that shows an increase of ϵ_∞ with growing of the sample thickness, the peak intensity of the real part of permittivity around 15.0 μm also rises with the growing sample thickness, as shown in Fig. 5(a). From the figure, we can observe that the change in negative permittivity peak becomes larger as the film thickness increases for the both sputtered and PEALD-deposited films. This trend swaps from monotonic increase to decrease below 11.2 μm ($\sim 893 \text{ cm}^{-1}$) and also above 16.1 μm ($\sim 621 \text{ cm}^{-1}$). For the imaginary part at the same wavelength as shown in Fig. 5(b), we also see the trend where growing sample thickness reduces the value of imaginary part of permittivity. This is due to the fact that the scattering constant γ , obtained from fitting, decreases with increasing film thickness that results in more crystallinity of the layers according to the XRD and AFM analysis. The more crystalline is the layer, the less is the scattering constant. In addition, this trend is also shown by decrease of the imaginary part of permittivity, associated with losses.

FIG. 5. The dependence of the change in (a) the real and (b) imaginary part of peak permittivity around 15.1 μm in wavelength with increasing film thickness deposited by PEALD with NH₃ and sputtering.

V. CONCLUSION

In summary, we have investigated structural and optical properties of AlN films with different thicknesses ranging from 66 nm to 303 nm fabricated by PEALD with NH₃ and N₂ plasma, as well as by reactive sputtering. These films are characterized by ellipsometry, FTIR, XRR, XRD, XPS and AFM to conduct elemental analysis and compare composite and optical properties and their influence on dielectric functions of AlN on mid-IR wavelengths. The PEALD-deposited films are less contaminated with oxygen and have smoother surfaces in comparison with the sputtered films. According to the XRR, XRD and AFM data, the sputtered films, in contrary, have higher densities and higher crystallinity than the ALD films. The increase of the film crystallinity leads to the growth in permittivities, which is shown as the rise of ϵ_∞ value and intensity of permittivity peak due to decrease of the scattering constant. Moreover, higher concentration of N obtained in the PEALD films results in higher probability of creation of Al–NH₂ and Al–N₂ bonding. The corresponding peaks are spotted in the FTIR spectra. **We observe a distinct almost monotonic dependence of the dielectric func-**

tion of the films on their thickness for both sputtered and PEALD-deposited AlN films. This trend was observed for wide mid-IR wavelengths beyond $2.0\ \mu\text{m}$ ($\sim 5,000\ \text{cm}^{-1}$) that we characterized including the Reststrahlen band from $11.5 - 15\ \mu\text{m}$ ($\sim 870 - 667\ \text{cm}^{-1}$). The slope of such dependence is defined by the fabrication routine, and in our case is higher for sputtered samples. This fact as well as process-dependent films parameters must be taken into account while designing nanostructured elements with phononic and ENZ features for mid-infrared photonics.

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DATA AVAILABILITY

The data that support the findings of this study are available within the article and its supplementary material. The data are also available from the corresponding author upon reasonable request.

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