Appl. Phys. A 80, 551–555 (2005)
DOI: 10.1007/s00339-004-2973-7

Applied Physics A
Materials Science & Processing

C. HIMCINSCHI[1,✉]
N. MEYER[2]
S. HARTMANN[3]
M. GERSDORFF[2]
M. FRIEDRICH[1]
H.-H. JOHANNES[3]
W. KOWALSKY[3]
M. SCHWAMBERA[2]
G. STRAUCH[2]
M. HEUKEN[2]
D.R.T. ZAHN[1]

Spectroscopic ellipsometric characterization of organic films obtained via organic vapor phase deposition

[1] Halbleiterphysik, Technische Universität Chemnitz, Reichenhainerstr. 70, 09107 Chemnitz, Germany
[2] AIXTRON AG, Kackertstr. 15–17, 52072 Aachen, Germany
[3] Institut für Hochfrequenztechnik, Technische Universität Braunschweig, Schleinitzstr. 22, 38106 Braunschweig, Germany

Received: 28 November 2003/Accepted: 18 June 2004
Published online: 11 August 2004 •

ABSTRACT Thin films of *Tris*(8-hydroxyquinoline)-aluminum(III) (Alq_3) and N,N′-Di-[(1-naphthyl)-N,N′-diphenyl]-(1,1′-biphenyl)-4,4′-diamine (α-NPD) were deposited on large-area silicon substrates by means of the recently developed organic vapor phase deposition (OVPD) method. Variable-angle spectroscopic ellipsometry was used to measure the optical constants of OVPD Alq_3 and α-NPD layers in the 0.8–5 eV energy range. The absorption onset which defines the lower limit of the optical band gap was found to be at ∼ 2.65 eV and ∼ 2.9 eV for Alq_3 and α-NPD, respectively. Additionally, the thicknesses of the layers as well as the thickness profiles of the organic thin films were determined along the 8″ diameter of the wafers. The thickness analysis revealed large-area uniform deposition of the films.

PACS 78.20.Ci; 81.70.Fy; 81.15.-z

1 Introduction

Organic light-emitting devices (OLEDs) have become attractive due to their potential use in various lighting applications including flat-panel displays. *Tris*-(8-hydroxyquinoline)-aluminum(III) (Alq_3) and N,N′-Di-[(1-naphthyl)-N,N′-diphenyl]-(1,1′-biphenyl)-4,4′-diamine (α-NPD) are among the most commonly used electron-transport and hole-transport materials in OLEDs [1–5], respectively. The molecular structures of Alq_3 and α-NPD are shown in Fig. 1. The recently developed organic vapor phase deposition (OVPD) process [6, 7] is well suited for thin film deposition of such materials on large-area substrates. The principle of OVPD combined with the close-coupled showerhead enables the efficient and reproducible deposition on large substrate sizes [8]. The precise control of nitrogen carrier gas by standard mass-flow controllers, the steady-state process temperature, and the process pressure are key parameters for industrial mass production.

The accurate determination of the organic layer thicknesses and the thickness uniformity across the whole substrate is of paramount importance for display applications. Spectroscopic ellipsometry is a non-destructive very adequate method for the measurement of the thicknesses of the organic layers. Moreover, ellipsometry allows the determination of the optical constants of the organic materials and their knowledge contributes to the understanding and optimization of the organic-based devices.

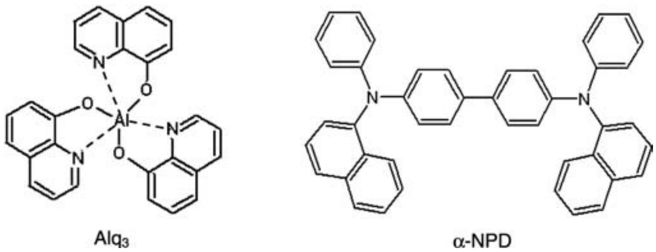


FIGURE 1 Molecular structures of Alq_3 and α-NPD

In this paper we report the employment of spectroscopic ellipsometry for thickness profiling of Alq_3 and α-NPD layers deposited by OVPD on 8″ Si substrates. The optical constants of Alq_3 and α-NPD were determined in the spectral range of 0.8–5 eV using a multi-sample analysis procedure. To our knowledge, this is the first report of the optical constants of OVPD-grown organic thin films.

2 Experimental

Single layers of Alq_3 and α-NPD were deposited by the OVPD process on 8″ Si wafers covered with 100 nm thermally grown oxide. In order to deposit an organic film by means of OVPD, the organic material has to be thermally evaporated from a container and diluted in an inert carrier gas, e.g. nitrogen, which will transport it towards the substrate cooled to ∼ 5 °C. The Alq_3 and α-NPD container temperatures were 292.1 °C and 274.1 °C, respectively, while the reactor walls were heated to 300 °C to prevent condensation. The total flow of the nitrogen carrier gas was set to 1000 sccm and the source flows for Alq_3 and α-NPD to 20 sccm and 30 sccm, respectively. The reactor pressure was kept at 0.9 mbar. After venting the reactor with nitrogen, the samples where transferred into a manual handler where they were sealed in plastic bags under nitrogen atmosphere. The

✉ Fax: +49-371/5313-060,
E-mail: c.himcinschi@physik.tu-chemnitz.de

Sample	Substance	sccm	Mean thickness / nm	Minimum thickness / nm	Maximum thickness / nm	Standard deviation / nm	Standard deviation / %
a1	Alq_3	20	63.2	62.5	64.3	0.47	0.7
a2	Alq_3	20	156.7	155.5	157.2	0.5	0.3
n1	α-NPD	30	33.7	33.5	34.1	0.15	0.4
n2	α-NPD	30	107.2	106.4	109.4	0.92	0.9

TABLE 1 Alq_3 and α-NPD sample descriptions and thicknesses as determined from ellipsometry

samples were kept in this condition for 2–3 days until they were measured in air by ellipsometry.

The samples investigated in this study (see Table 1) are labeled a1 and a2 (Alq_3) and n1 and n2 (α-NPD). The deposition times for the samples a1 and n1 were the same, while they were two and three times larger, respectively, for the samples a2 and n2.

The ellipsometric measurements were performed using a variable-angle spectroscopic ellipsometer (VASE, Woollam Co.) in the spectral range from 0.8 eV to 5 eV with a step in energy of 0.02 eV. The ellipsometric spectra were recorded at angles of incidence near the Brewster angle of Si, namely 65°, 70°, and 75°. For curve fitting of ellipsometric spectra the WVASE32 program was employed.

3 Results and discussion

Spectroscopic ellipsometry is an optical technique which measures the changes of the polarization state of a polarized light beam after reflection from the sample under study. These changes are measured as the ellipsometric parameters Ψ and Δ, which are related to the ratio of the effective reflection coefficients $\langle r_p \rangle$ and $\langle r_s \rangle$ for p- and s-polarized light:

$$\varrho = \frac{\langle r_p \rangle}{\langle r_s \rangle} = \tan(\Psi)\exp(\mathrm{i}\Delta), \quad (1)$$

where ϱ is the complex reflectance ratio. $\langle r_p \rangle$ and $\langle r_s \rangle$ are functions of the complex refractive indices of the film and substrate and of their thicknesses. In order to extract useful information about a sample (thicknesses and optical constants of the layers) the experimental data are compared with the data generated using a model which describes the structure of the sample and its optical response.

One straightforward and very important model for understanding how the values of the thickness or optical constants can be computed is the three-phase model consisting of ambient–film–substrate. In the calculation of Ψ and Δ ellipsometric spectra the propagation of light through the multilayered structures is completely described by the complex refractive index $\tilde{n} = n + \mathrm{i}k$ and the thickness t of each layer. This model considers that propagation of light in a layer is governed by linear equations and the continuity of the tangential electric field across an interface between two isotropic media can be written as a 2×2 matrix. Following this approach, the effective reflection coefficients $\langle r_p \rangle$ and $\langle r_s \rangle$ can be determined from the Fresnel coefficients of transmission and reflection at each interface. Analytic algebraic expressions can be written for predicting Ψ and Δ as functions of optical constants and layer thickness. The algebra for calculating Ψ and Δ will not be presented here, but can be found in standard references [9].

The next step is to compare the actual measured Ψ and Δ values with the predictions of the model based on Fresnel equations, assuming values of the optical constants and thicknesses. The unknown parameters in the model are adjusted in order to get the best match between the model and the experimental data using a Marquardt–Levenberg algorithm. The fit algorithm minimizes the mean-square error (MSE) value, which quantifies the differences between the experimental and predicted data [10]:

$$\mathrm{MSE} = \sqrt{\frac{1}{2N-M} \times \sum_{i=1}^{N} \left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}} \right)^2 - \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}} \right)^2 \right]}, \quad (2)$$

where N is the number of measured Ψ and Δ pairs, M is the number of fit parameters, and $\sigma_\Psi^{\mathrm{exp}}$ and $\sigma_\Delta^{\mathrm{exp}}$ are the standard deviations of the experimental data points.

For a given sample there are three unknown parameters: thickness t, refractive index n, and extinction coefficient k, which have to be determined from only two ellipsometric parameters Ψ and Δ. By performing measurements at several angles of incidence, more sets of Ψ and Δ data are available and the problem can be solved numerically. The problem can be further simplified by analyzing first the data in the spectral region where the film is transparent ($k = 0$). In this spectral region the optical response of the transparent films can be described by a Cauchy dispersion relation for the refractive index: $n(\lambda) = a_n + b_n/\lambda^2$, where the Cauchy parameters a_n and b_n are constants and λ is the wavelength. In this case the determination of optical constants and thickness simplifies because only three fit parameters, which are constant, namely the thickness t and the Cauchy parameters a_n and b_n, have to be calculated from all the sets of (Ψ, Δ) pairs measured at different wavelengths or angles of incidence. The Alq_3 and α-NPD films were found to be transparent in the spectral range of 0.8–2.5 eV. Keeping the thickness determined by means of the Cauchy model fixed, the Ψ and Δ spectra can be fitted in order to determine the optical constants in the whole spectral range (0.8–5 eV).

A second approach is to use multi-sample analysis [11]. In this fitting procedure the ellipsometric spectra from several samples with different thicknesses are analyzed simultaneously assuming that the samples have the same optical constants. In this paper both approaches, Cauchy and multi-sample analysis, are combined in order to increase the confidence in the results.

The thickness of the SiO_2 layer which covers the Si substrate was found to be 101 nm from the ellipsometric spectra of a reference Si/SiO_2 substrate. The optical constants for Si and SiO_2 used in the fitting procedure were taken from the literature [12].

Ellipsometric spectra were measured at 21 different points along one diameter of the Alq_3 and α-NPD OVPD samples. The data from different positions on one sample were analyzed simultaneously using the Cauchy model. In this way the film thicknesses at different points of the sample were determined and a thickness profile along a diameter of the 8″ wafer was obtained. In Fig. 2 the thickness profiles for the samples a1 and n2 are plotted. A 'U'-like shape can be observed with higher thicknesses towards the wafer edges. This phenomenon is known as the 'edge effect' and originates from the distortion of the flow profile induced by the 8″ wafer [6]. The carrier gas forms a nitrogen boundary layer directly above the substrate where the transport of the organic molecules is driven only by diffusion, and hence the organic molecules in this boundary layer condense due to the temperature gradient. At the edges of the wafer the nitrogen boundary layer is thinner and consequently the deposited organic film is thicker. However, it should be noted that the layer thickness is extremely homogeneous, with a maximum of 0.35% standard deviation excluding 2.0 cm from the edges.

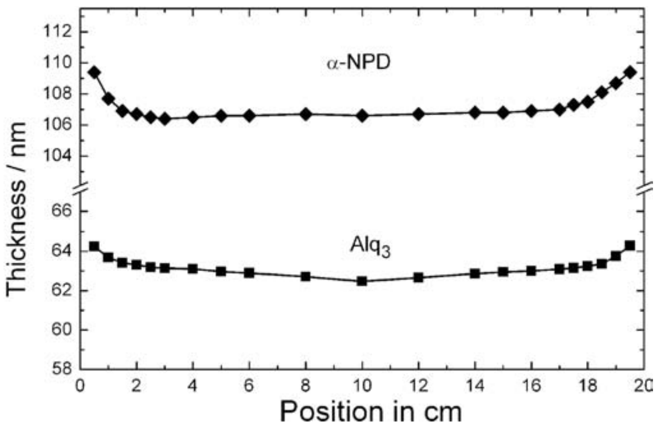


FIGURE 2 Alq_3 and α-NPD thickness profiles along the 8″ wafer diameter for the samples a1 and n2

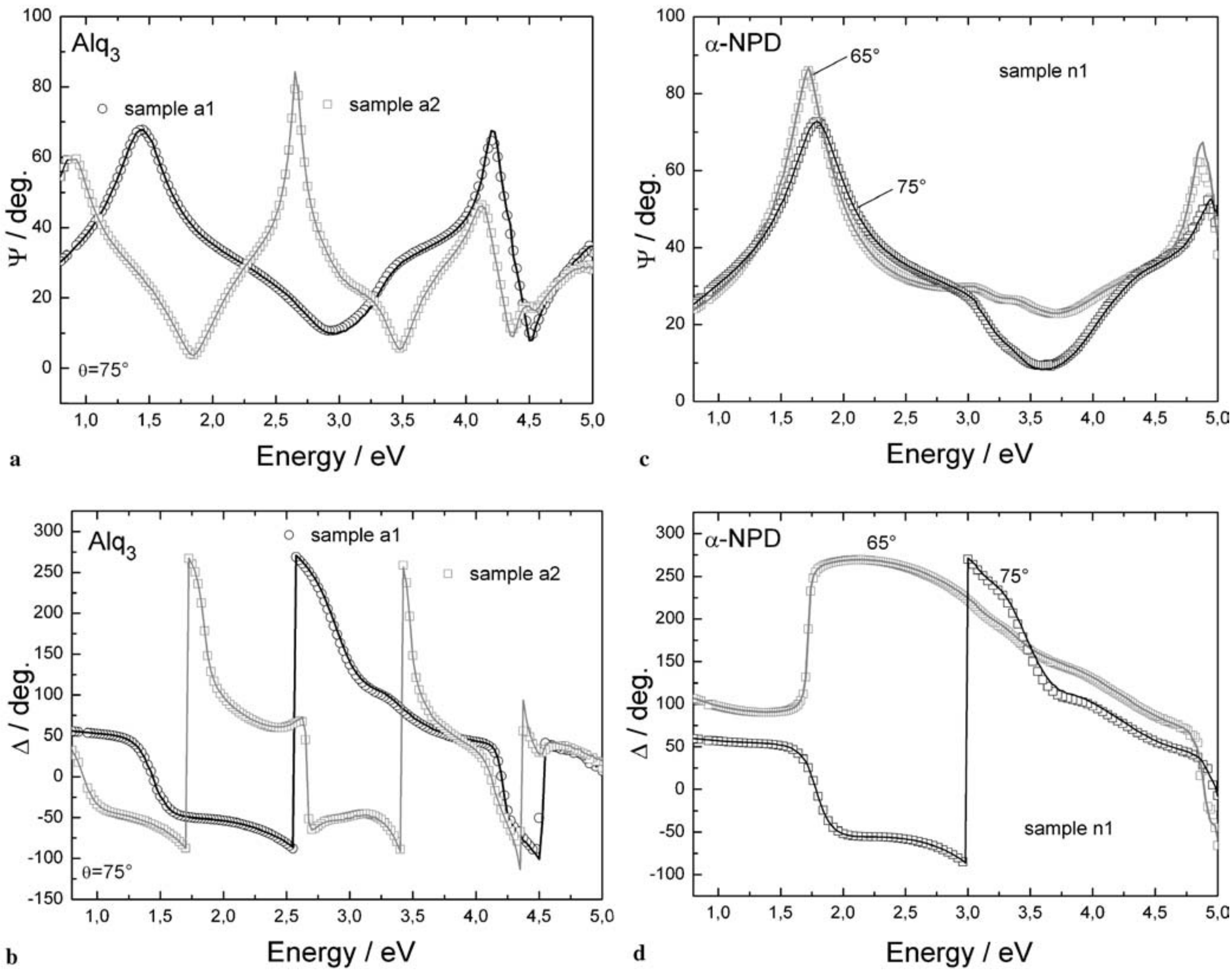


FIGURE 3 *Ψ* and Δ ellipsometric spectra (for 75° incidence angle) for Alq_3 samples a1 and a2 ((**a**) and (**b**)). The *symbols* indicate the experimental points and the *lines* represent the point-by-point fits. **c** and **d** show the experimental and fitted *Ψ* and Δ ellipsometric spectra for the α-NPD sample n1 for 65° and 75° incidence angles

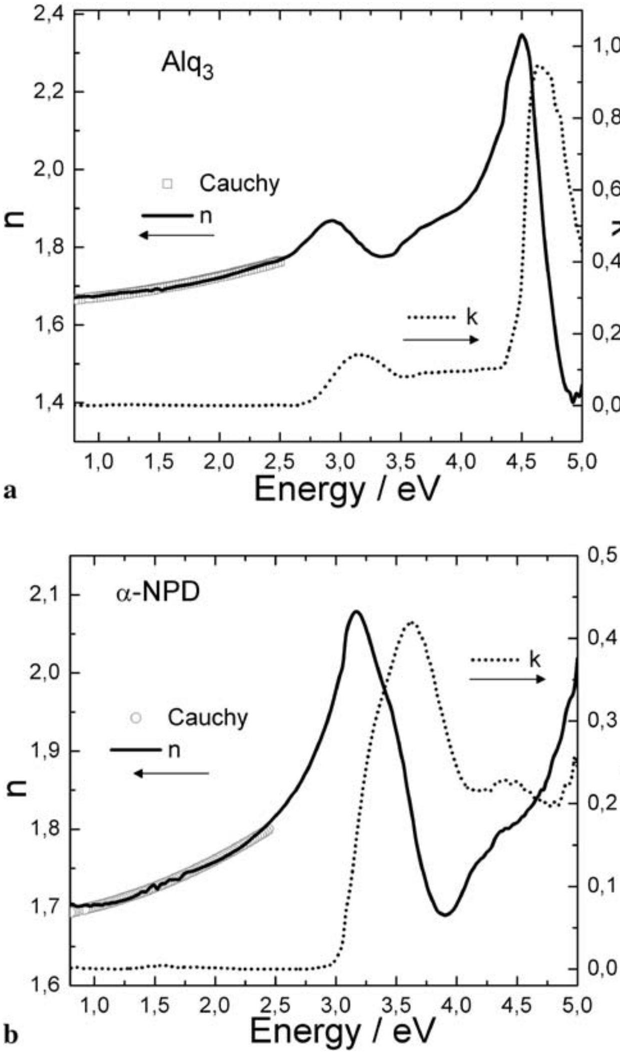
In Table 1 the values for the mean, minimum, and maximum thicknesses obtained by means of the Cauchy model for all four samples are provided. The standard deviation of the thickness considering the measurements of 21 points on each sample was found to be below 1 nm, representing only 0.3%–0.9% standard deviation in all cases.

In a next step the film thicknesses obtained from the Cauchy model fitting were kept fixed and point-by-point fits were performed in order to determine the optical constants of the Alq_3 and α-NPD OVPD films in the entire spectral range. In a point-by-point fit there are no constraints on the functional form imposed on the optical constants. During the point-by-point fit the ellipsometric spectra of the points in the center of the a1 and a2 samples were fitted at once in a multi-sample analysis manner. The same procedure was applied for the α-NPD films (samples n1 and n2).

In Fig. 3 the ellipsometric spectra for Alq_3 and α-NPD samples are shown by symbols and the corresponding point-by-point fits by lines. For clarity, the Ψ and Δ spectra for the Alq_3 a1 and a2 samples are shown in Fig. 3a and b only for an angle of incidence of 75°. The differences between the spectra for a1 and a2 samples are due to the different thicknesses of the Alq_3 films (63.2 nm and 156.7 nm, respectively). On the other hand, the angle of incidence also affects the Ψ and Δ spectra, as can be seen in Fig. 3c and d for the example of the n1 sample of α-NPD. It should be pointed out that an excellent agreement between the experimental and fitted data was obtained in the whole spectral range for all three angles of incidence and for all four samples. This proves the reliability of the thickness determined using the Cauchy dispersion relation for the refractive index.

The dispersion of the optical constants for Alq_3 obtained as a result of simultaneously point-by-point fitting the middle-point spectra of the samples a1 and a2 is shown in Fig. 4a by lines. The refractive index resulting from the initial Cauchy fit in the 0.8–2.5 eV energy range where k was assumed to be 0 is depicted by symbols. As can be observed, there is a very good agreement between the optical constants determined from Cauchy and point-by-point fits.

The onset of absorption defined by the minimum energy value where k is not 0 was found to be at $\sim$ 2.65 eV. This represents the lower limit of the optical gap and is in good agreement with previously reported values of 2.61 eV and 2.7 eV [13, 14]. The shape of the structures in the refractive index and extinction coefficient spectra around 2.9 eV and 3.15 eV, respectively, is in very good agreement with the data by Masenelli et al. [13] for thermally evaporated Alq_3 films. Those data, however, were restricted to the energy range of 2.2–3.4 eV. A good agreement between the optical constants of the OVPD Alq_3 films with those of thermally evaporated Alq_3 was also observed in a larger energy range [15, 16]. However, the amplitude of k at 4.7 eV is slightly higher for the OVPD films in this study compared with the data by Celii et al. [15]. The peaks at 3.15 eV and 4.7 eV in the dispersion of the extinction coefficient were also observed in the Alq_3 absorption spectra by Aziz and Narasimhan [17]. The optical constants reported by Djurisic et al. [16] show a very broad and less resolved absorption feature at 3.2 eV. The non-zero extinction coefficient obtained below 2.5 eV was attributed to surface roughness or chemical degradation of their films deposited on transparent substrates (glass). Moreover, compared with the previous ellipsometric studies of Alq_3 films [13, 15, 16], we extend the range where the optical constants were determined towards the near infrared up to 0.8 eV (1550 nm).



a
b

FIGURE 4 Refractive index n and extinction coefficient k derived from the ellipsometric spectra for Alq_3 (**a**) and α-NPD (**b**). *Symbols* indicate the refractive indices obtained from the initial Cauchy fits

In the present study no degradation of the optical constants due to hydrolysis of Alq_3 after exposure to atmosphere (even for one month) was found, in contrast to the reports by Djurisic et al. [16] and Higginson et al. [18]. This fact can be attributed to the different deposition procedure used, reflecting a better stability of the OVPD films.

In Fig. 4b the optical constants for α-NPD OVPD films derived from simultaneously fitting of the ellipsometric spectra from the points in the center of the samples n1 and n2 are shown by lines. The values of the refractive index determined from the initial Cauchy fit are shown by symbols. The absorption onset occurs at 2.9 eV with the extinction coefficient being dominated by a feature at 3.6 eV with a maximum magnitude of 0.42 and by a shoulder at 4.4 eV. To our knowledge, the only attempt to determine the optical constants of α-NPD was in the spectral range of 1.24–4.96 eV [19]. In that study the dielectric constant shows only one peak at 3.58 eV. However, considering the large energy steps (~ 0.25 eV) used for the ellipsometric measurements above 3.5 eV, it is very likely that the weak structure at 4.4 eV was not resolved. Moreover, the absorption spectra of OVPD α-NPD films on glass substrates (not shown here) clearly indicate that one oscillator is not enough to describe the optical constants.

We have also employed a fitting procedure based on the oscillator model. The minimum number of oscillators required to obtain a good fit of the experimental data were 5 and 4 for Alq_3 and α-NPD, respectively. It should be noted that phenomenological models (such as an oscillator model) often give ambiguous solutions due to the strong correlation between the oscillator parameters. Therefore, it is more likely that a point-by-point fitting provides more reliable material-related optical properties [16]. However, the good agreement found between the optical constants obtained with point-by-point and oscillator models indicates the Kramer–Kronig consistency of the point-by-point optical constants.

4 Summary

Thin Alq_3 and α-NPD films were deposited on 8″ Si substrates by organic vapor phase deposition. The thickness analysis by variable-angle spectroscopic ellipsometry revealed very uniform films with minor 'edge effects' originating from the distortion of the flow profile in the vicinity of the wafer edges. However, even including these effects, the standard deviation of the thickness considering 21 points along one sample diameter is below 1 nm in all cases.

The refractive index and extinction coefficient of Alq_3 and α-NPD were determined from ellipsometry in the spectral range from 0.8 eV to 5 eV. These optical constants were derived using a multi-sample analysis approach that employs simultaneous point-by-point fitting of ellipsometric spectra recorded for samples with different thicknesses of the organic layer.

The optical constants of Alq_3 and α-NPD are significantly different at energies above 3 eV. This provides the possibility to determine e.g. the doping level in the case that one material is doped with the other or to determine individual thicknesses in superstructures formed by alternating Alq_3 and α-NPD layers.

ACKNOWLEDGEMENTS The authors gratefully acknowledge the BMBF Project No. 01BD153 'Innovatives Abscheideverfahren (OVPD) für die Herstellung organischer Schichtstrukturen' for financial support.

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