Optical properties of multilayered Alq$_3$/α-NPD structures investigated with spectroscopic ellipsometry

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Alternating layers consisting of tris(8-quinolinolato) aluminium (Alq$_3$) and N,N-Di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (α-NPD) were prepared by organic molecular beam deposition (OMBD) in high vacuum (HV) on hydrogen passivated (111) oriented silicon. The Si(111) substrates were kept at room temperature and the deposition rate was monitored by a quartz microbalance. The typical thickness of the individual layers is in the range of 1-10 nm. The samples were studied by spectroscopic ellipsometry in the range from 0.73 to 5 eV. The evaluation of the ellipsometry measurements shows good agreement between the experimental and simulated data, assuming sharp interfaces and using the optical constants of the single layers. However, small deviations exist in the range where Alq$_3$ and α-NPD have absorption peaks indicating an electronic interaction at the interfaces.

1 Introduction

In recent years multilayered organic structures have attracted considerable attention [1]. Compared to bulk materials multilayered heterostructures can have unusual optical and physical properties which open new possibilities for optoelectronic devices, including organic light emitting diodes (OLEDs) and solar cells. Multilayer OLEDs showed a marked increase in efficiency of light emission compared to single heterostructures [2, 3]. Also the observation of exciton confinement by Forrest [4, 5] in organic multilayers attracted interest [6–9]. In contrast to inorganic materials, organic multilayers, however, are less studied and the electronic interaction at the interface in organic/organic heterostructures is not well understood.

This work deals with the preparation and investigation of organic multilayers consisting of 16 alternating layers of Alq$_3$ and α-NPD. α-NPD is a hole transporting material while Alq$_3$ is an electron transporter commonly used as active medium in commercial OLEDs. Their molecular structure is shown in Figs. 1 and 2. These materials form optically isotropic layers with low surface roughness [10, 11]. As investigation technique we employed spectroscopic ellipsometry which is a very sensitive and non-destructive tool for optical characterisation of single layers and complex multilayer structures [12].

2 Experimental

The organic multilayers consisting of 8 periods of Alq$_3$ and α-NPD were grown by OMBD in high vacuum (HV-8×10$^{-7}$ mbar) on hydrogen passivated Si(111). The substrate was kept at room temperature during deposition. The source materials Alq$_3$ and α-NPD with 99.9% purity were supplied by Sensient-
Syntec. The substrates were degreased with isopropanol and de-ionized water before etching in 40% HF for 2 min. After passivation the substrates were immediately transferred into the deposition chamber. In order to obtain the dielectric functions of the materials several films with different thickness in the range of 30 nm to 120 nm were prepared as single layers. The thickness of the films was controlled by a quartz crystal microbalance positioned in the vicinity of the samples. The change in resonant frequency is proportional to the film thickness. The deposition rate was kept constant at approximately 0.5 nm/min. After calibrating the quartz microbalance system, multilayered structures with different thickness were grown on the Si(111) substrates. The thickness of the individual Alq\textsubscript{3} and \(\alpha\)-NPD layers in the stack was kept constant.

Ellipsometric measurements were carried out using a variable spectroscopic ellipsometer (VASE, A.Woollam Co., Inc.). Ellipsometry measures the change in polarisation state of light after reflection or transmission of a sample. The ellipsometric measurements are usually expressed in terms of the polarisation angle, \(\Psi\), and the phase delay, \(\Delta\).

\[
\tan \Psi \epsilon^{i\Delta} = \rho = \frac{r_p}{r_s},
\]

where \(r_p\) and \(r_s\) are the complex Fresnel reflection coefficients for p- and s-polarised light. A detailed description of the ellipsometry principles and theory can be found in Refs. [13, 14].

The spectra were recorded at different angles of incidence (65°, 70°, 75°) in the range of 0.73-5 eV with a 0.02 eV step in order to determine the thickness and the dielectric function. Before evaluation of the organic films the passivated Si(111) substrate was measured. The determined dielectric function of the substrate was used in the model simulation for describing the response of the single organic layers and the multilayers.

### 3 Results

#### 3.1 Dielectric functions

The optical constants of single layers of Alq\textsubscript{3} and a-NPD were determined from ellipsometry as shown in Figs. 1 and 2. A very good agreement between simulated and experimental data was achieved using an isotropic model for the organic layers. The transparent range (0.73-2 eV) was used to determine the thickness and the surface roughness of the layers using a Cauchy model [14]. The surface roughness of films up to 30 nm was less than 1 nm. This shows that these materials can form layers with sharp interfaces and are well suited for preparation of multilayers. For a first approximation the dielectric function was determined by a point-to-point fit. In this fitting procedure \(\varepsilon_1\) and \(\varepsilon_2\) were determined at every wavelength. In a mathematical based model Gauss functions were used in order to simulate the shape of \(\varepsilon_2\) obtained by the point-to-point fit. To the imaginary part of the dielectric function a Kramers-Kronig transformation was applied to obtain the real part of the dielectric function. The thickness was kept fixed during the fit. The obtained dielectric functions are in very good agreement with the corresponding refractive index and extinction coefficient values described in Refs. [10, 11] where the samples were prepared by organic vapour phase deposition (OVPD). As can be seen there are big differences between Alq\textsubscript{3} and \(\alpha\)-NPD in the line shape in the absorbing range (\(E > 2.5\) eV).
3.2 Multilayer structure

The ellipsometry spectra of the multilayered structure were simulated using the WVASE Software [8] taking into account the previously determined optical constants of Alq₃ and α-NPD. The thickness for all Alq₃ (α-NPD) layers was considered to be the same in the stack. In the numerical fit the free parameters were the thickness of the Alq₃ and α-NPD layers. The difference between the experimental points and the generated values is evaluated through the values of the mean square error (MSE):

$$\text{MSE} = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left[ \left( \frac{\psi_{\text{mod}} - \psi_{\text{exp}}}{\sigma_{\psi_{i,\text{exp}}}} \right)^2 + \left( \frac{\Delta_{\text{mod}} - \Delta_{\text{exp}}}{\sigma_{\Delta_{i,\text{exp}}}} \right)^2 \right]},$$

where N is the number of the experimental points, M is the number of fit parameters and σ is the standard deviation for each point. The results of the thickness determination for the multi-layered structures are shown in Table 1. The expected values for the thickness are based on the quartz microbalance calibration. The differences between the expected values and the measured values are relatively small. Considering the fact that the model consists of 16 layers the MSE values are also low. This indicates a very good agreement between experimental data and the simulation.
Table 1  Thickness of Alq₃ and α-NPD in multilayers determined by ellipsometry.

<table>
<thead>
<tr>
<th>Alq₃</th>
<th>α-NPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>dₑₓ</td>
<td>dₑₓ</td>
</tr>
<tr>
<td>10±0.1</td>
<td>9.90±0.05</td>
</tr>
<tr>
<td>8±0.1</td>
<td>8.16±0.04</td>
</tr>
<tr>
<td>6±0.1</td>
<td>6.78±0.03</td>
</tr>
<tr>
<td>4±0.1</td>
<td>3.17±0.03</td>
</tr>
<tr>
<td>2±0.1</td>
<td>2.19±0.01</td>
</tr>
<tr>
<td>1±0.1</td>
<td>1.24±0.02</td>
</tr>
</tbody>
</table>

Even the multilayer with 1 nm nominal layer thickness can be described with sharp interfaces. These results confirm that we have high quality multilayered structures with constant thickness of the individual layers and a very low interface roughness.

Figure 3 shows the effective dielectric function of the multilayers with nominal individual layer thickness in the range from 1 nm to 10 nm. The effective dielectric function is calculated from the ellipsometry results as if the sample would be an isotropic bulk [15]:

$$\langle \varepsilon \rangle = \sin^2 \Phi_0 + \sin^2 \Phi_0 \tan^2 \Phi_0 \left[ \frac{1-\rho^2}{1+\rho^2} \right]$$

where $\Phi$ is the angle of incidence.

**Fig. 3** Experimental effective dielectric function of multilayers with layer thickness in the range 1-10 nm (for 65° angle of incidence).

As can be seen the optical response varies a lot by changing the thickness of the layers. It shows that the effective dielectric function of the system is influenced by the optical properties of the individual layers and by optical interferences. The optical response can be tuned within a large range by changing the thickness of the individual layers and the number of periods.

In Fig. 4 the differences between experimental and simulated data are presented. In the transparent range of Alq₃ and α-NPD up to 2.3 eV the deviations are negligible. Differences appear in the absorbing range of the materials. It seems that the starting point of the low energy deviations is shifting towards higher energies with decreasing layer thickness. However, the deviations centred at 4.6 eV seem to have no thickness dependent shift.
This is also the energy range where Alq$_3$ has its strong absorption peak. Considering the fact that in the effective $\varepsilon_2$ the energy positions of features are strongly thickness dependent the deviation at 4.6 eV indicates a small change in the optical properties of Alq$_3$. This is probably due to the electronic interaction between Alq$_3$ and $\alpha$-NPD at the interfaces. The deviations in this energy range can be simulated using slightly modified optical constants for Alq$_3$ in the multilayer. However, this is only a qualitative evaluation. It is difficult to get a more quantitative prediction because there are a lot of parameters which have to be considered. Further experiments and theoretical calculation are needed for a clearer assignment of the deviations.

Fig. 4 Differences between experimental and generated effective $\varepsilon_2$ (65° angle of incidence).

4 Summary

Investigations on optical properties of multilayers consisting of 16 alternating layers of Alq$_3$ and $\alpha$-NPD with different layer thickness were presented. The materials form isotropic layers with very sharp interfaces. In order to describe the experimental data a model using optical properties of single layers of Alq$_3$ and $\alpha$-NPD was used to determine the thickness of the layers. Furthermore, the validity of the model was studied. The differences between the experimental and simulated data in the absorbing range of the materials indicate electronic interface effects. Ellipsometry thus is a powerful tool in evaluating multilayered organic structures.

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References