APPLICATION NOTE
Real-time monitoring of polyelectrolyte-multilayer growth onto tantalum pentoxide (Ta$_2$O$_5$) by internal reflection ellipsometry

KERSTIN OEHSE, NADJA EHRHARDT, BRIAN P. CAHILL, CHRISTIAN HOFFMANN

ABSTRACT
The consecutive deposition of layers of two polyelectrolytes, polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) onto a tantalum pentoxide substrate was measured by time-resolved ellipsometry in an internal reflection ellipsometry setup. Stepwise increase of polyelectrolyte thickness was shown by time-resolved measurement of the ellipsometric angles, delta and psi. The coated substrate was finally characterized in the dry state.

INTRODUCTION
Since 1991 when G. Decher created the layer-by-layer method of constructing polyelectrolyte multilayers on metal oxide surfaces, the process of formation of such nanocomposites has intrigued scientists from both fundamental and applicational points of view. The simple process allows a fast and stable surface modification. Since this method is based only on electrostatic interaction, polyelectrolytes can be applied on many different surfaces [1]. Therefore, they also may suit for waveguide modification such as Ta$_2$O$_5$ implemented in many highly sensitive sensors [2]. Polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) served as polyelectrolyte model compounds since they offer amino and carboxyl groups, respectively, for further surface functionalization. Optical methods, such as ellipsometry, allow a non-destructive characterization of the adsorbed layer (as a function of both space and time). Since sufficient reflectivity of the surface is a prerequisite, silicon wafers are standard substrates for this measurement technique. In this case, applying a flow cell means guiding the light beam through the sample solution. An elegant way for investigating the adsorbing organic layers on transparent substrates can be the incidence of the light beam from the backside of the surface substrate. This set-up was investigated the recent years but limited to gold surfaces utilizing the signal enhancement by excitation of surface plasmons [3]. In the present report the application of internal reflection ellipsometry for glass substrates coated with a thin Ta$_2$O$_5$ layer is demonstrated. Atomic force microscopy (AFM) visualizes the surface topology on the nanometer scale.

MATERIALS AND METHODS
Surface substrates (Oerlikon Optics, Liechtenstein) consisting of a thin layer of Ta$_2$O$_5$ (d ≈ 160 nm) on a glass slide (Schott D263) were cleaned in an aqueous solution of 1% (v/v) alkaline cuvette-cleaner (Sigma Aldrich) for 1 h at 40 °C, rinsed with ultra pure water and dried by air flow. Before coating, the substrate was activated by 1:3 (v/v) H$_2$O$_2$/NH$_3$ conc. for 30 min at boiling temperature, rinsed with ultrapure water and dried by argon flow. 1 mg/ml solutions of polyelectrolytes (polycation: polyallylamin hydrochloride, PAH, m.w. ≈ 56000 g/mol, and polyanion: polyacrylic acid, PAA, m.w. ≈ 1800 g/mol, both received from Sigma Aldrich) in ultrapure water were used at two different pH. Solution of PAA in ultrapure water was adjusted to pH = 3.5 by 1 M NaOH and 0.1 M HCl whereas using of 0.1 M NaOH and 0.1 M HCl resulted in pH = 7.5 for solution of PAH in ultrapure water [4]. For rinsing steps ultrapure water of same pH and salt concentrations as the corresponding polyelectrolyte solution was used.

A negatively charged Ta$_2$O$_5$ substrate (cleaned as mentioned above) was coated inside

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a flow cell with oppositely charged polyelectrolytes and the ellipsometric angles were simultaneously recorded at an angle of incidence (AOI) of 45° and a wavelength $\lambda = 532$ nm. 9 regions of interest (ROI) were chosen for measuring delta and psi, each ROI with a dimension of 39 x 19 pixel. Applying a 10x objective the pixel size can be calculated to 2.45 µm and a ROI of 1815 µm². Driven by a rotary lobe pump (flow rate 1 ml/min), the substrate was coated alternately with 10 bilayers of PAA and PAH, starting with the polycation. For each layer deposition step, the surface substrate was incubated for 10 min, followed by a 5 min rinsing step using water at the same pH and salt concentration as the incubation solution.

The ellipsometer (nanofil_ep3se, Accurion GmbH) was used in conventional PCSA arrangement but a glass prism fitted to the surface substrate by an index matching oil enables a perpendicular incidence into the glass medium (Fig. 1). The ellipsometric measurements in air were performed without applying internal reflection in the “normal” mode for comparison. A delta map of the coated and subsequently UV-patterned substrate in air was recorded for visualization at an AOI of 50° and: $\lambda = 532$ nm.

RESULTS
Delta and psi were obtained every 19 s according to the fastest measurement period determined by the rotation velocity of the polarizer and analyzer via 1-zone-nulling by nanofil_ep3’s kinetics add on. Instead of the ellipsometric data of all nine ROIs Fig. 3 shows the stepwise change of delta and psi of only one ROI (ROI 2) for clarity. For modelling the optical constants in table 1 were applied. Data were used as best fit values, but the refractive index of PAA contains the time of inflow (approximately 4 min), incubation without flow (10 min) and rinsing (5 min). The insemination period started with the p

| Table 1: Layer stack for modelling the time resolved measurement of delta and psi to obtain the thickness of the polyelectrolyte multilayer |
|----------|----------|----------|
| Layer stack | Refractive index $n$ | Absorption coefficient $k$ |
| glass (prism+substrate) | 1.5 | 0.02 |
| $\text{Ta}_2\text{O}_5$ (d = 161.7 nm) | 2.1 | 0.01 |
| PAA-PAH | 1.5 | 0 |
| buffer | 1.334 | 0 |

Stepwise increase of PAA-PAH multilayer thickness vs. time from 0 nm up to $(32 \pm 2)$ nm in the last layer is shown in Fig. 4. Each step shows mean values of 9 ROIs and contains the time of inflow (approximately 4 min), incubation without flow (10 min) and rinsing (5 min). The inset illustrates the linear growth of the synthetic polyelectrolyte layer [6]. Each thickness value of the PEL layer $d_{\text{PEL}}$ was calculated from 10 measured points during rinsing time. The amount of the adsorbed mass was calculated with equation (1) [7] applying $dn/dc = 0.132$ ml/mg for PAA at pH 3.5 (0.1 M NaCl) and $dn/dc = 0.156$ ml/mg for PAH at pH 7.5 (0.1 M NaCl) [8] (Fig. 5). A Box-Lucas 1 Model with the equation (2) enabled a fit of both graphs, for PAH with $a(\text{PAH}) = 1.6$ and $b(\text{PAH}) = 0.4$ and for PAA with $a(\text{PAA}) = 3.1$ and $b(\text{PAA}) = 0.2$.

The deposition of the first adsorbing layers is unstable since the electrostatic interaction with the oppositely charged polyelectrolyte in the incubation solution can remove the adsorbed layer. When a crucial amount of polyelectrolyte is attached to the surface a stable multilayer can be obtained on the $\text{Ta}_2\text{O}_5$ substrate.

$$\Gamma = \frac{dn_{\text{medium}} - n_{\text{PAA}}}{dn/dc}$$ (1)

$\Gamma$ adsorbed amount
$dn_{\text{medium}}$ refractive index of medium
$dn_{\text{PAA}}$ refractive index of PAA
$dn/dc$ absorption coefficient

Fit: Box-Lucas 1 Model
$y = a \times (1 - b^t)$ (2)

Fig. 4: Increasing layer thickness $d$ of PAA-PAH-multilayer (ML) vs. time (10-point-smoothening); inset shows linear ratio of layer thickness $d$ of PAA-PAH-ML (mean values of 10 measured points of each layer during rinsing time) vs. number of layers
For visualization the coated substrates were patterned by UV lithography (Xeradex, \(\lambda = 172\) nm, \(P = 50\) mW/cm\(^2\)). After 30 min exposure time, the substrate was rinsed with ultra pure water. A delta map of the field of view (Fig. 2) was recorded by imaging ellipsometry and converted into a thickness map (Fig. 6). The polyelectrolyte layer could be almost completely removed. Thickness values were determined in 3 ROIs by 4-zone-nulling to \((40 \pm 1)\) nm for the covered and \((4 \pm 1)\) nm for the irradiated areas. For both ROI values and map fitting the measured delta values and fit parameters were taken from Table 2.

According to the literature, the refractive index of a synthetic polyelectrolyte layer in the dry state is of higher value [9] than it was determined in liquid [5].

The same modified substrate with PAA as last adsorbed layer was investigated by AFM in air. The AFM image gives the information on a small lateral scale showing a knobbly surface with a roughness of 53.6 nm whereas the optical measurement demonstrates the homogeneity of the polyelectrolyte layer in the range of several hundreds of \(\mu\)m.

**Conclusion**

A Ta2O5 substrate was coated consecutively by two polyelectrolytes, PAA and PAH, in a flow cell and the alteration of the ellipsometric angles delta and psi was measured by in-situ ellipsometry. The linear stepwise adsorption of a multilayer can be measured in real-time and evaluated using a layer stack containing the best suited optical constants \(n\) and \(k\).

As PAA and PAH - both weak polyelectrolytes – are highly pH dependent, the observations of Grunlan et al. [11] of PAH and PAA give a hint to the alike coiled conformation at pH = 3.5 for PAA and pH = 7.5 for PAH, achieving a linear increase of layer thickness during multilayer adsorption due to approximately equal charge density. Our experiment confirms that (see inset in Fig. 4), although nearly all PAA layers exhibit thicker layers than PAH. This could be due to the larger effect of anions (PAA) than cations in coiling leading to larger thickness and to less charge density [12]. The linear plot of layer thickness against the number of layers (inset in Fig. 4) demonstrates also the quality of the optical model in Table 1.

The internal reflection set-up allows analysis of optically transparent substrates. Changes in the refractive index of the sample solution can not disturb the measurement. Conventional flow cells may suffer from unwanted changes in the refractive index due to the light beam guided through the sample medium. The application note presents the best measurement. An uncertainty lies in the application of the immersion oil where its thickness between the prism and the glass substrate is different from one experiment to the other. Therefore, the model parameters have to be developed for each single experiment. However the suitability of the model can be confirmed by reasonable assumptions of the optical parameters as they are chosen in the presented data (Tables 1 and 2).

Synthetic polyelectrolytes are relatively dense compared to natural polyelectrolytes because of their hydrophobic backbone and research shows that the refractive index of polyelectrolytes is higher in dry as in wet state because of swelling [6]. The optical thickness of the dry polyelectrolyte layer was determined to \((40 \pm 1)\) nm using \(n(\text{PAA-PAH}) = 1.55\) whereas the measurement in the flow cell resulted in \((32 \pm 2)\) nm using \(n(\text{buffer}) = 1.334\) compared to the ambient with \(n(\text{air}) = 1\), the swelling of the layer can be observed in the dry state. A lower thickness of the polyelectrolyte layer in buffer than in the dry state was determined because the incorporated water has the same refractive index as the ambient buffer and swelling can therefore not be determined.

**Table 1**

<table>
<thead>
<tr>
<th>Layer stack</th>
<th>Refractive index (n)</th>
<th>Extinction coefficient (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PAA-PAH</td>
<td>1.55 [1]</td>
<td>0.0</td>
</tr>
<tr>
<td>Ta2O5 (161.4 nm)</td>
<td>2.1</td>
<td>0.02</td>
</tr>
<tr>
<td>glass</td>
<td>1.523 [1]</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Figure 5:** Amount of adsorbed mass of PAH (rectangle) – PAA (circle) - ML vs. number of layers; mean values of 10 measured points of each thickness step during rinsing time are shown. The Box-Lucas-Fit indicates the tendency of saturation in adsorbed polyelectrolyte mass, for PAH = 1.6 ng/mm\(^2\) and for PAA = 3.1 ng/mm\(^2\).
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The ellipsometric image shows homogenous adsorption of the PAA-PAH layer. The multilayer can be patterned using UV lithography. High resolution measurement of the surface topology is given by AFM measurement. Apart from the modeling, the PAA-PAH system enables a simple and stable surface functionalization of Ta₂O₅ waveguide substrates.

Acknowledgement
We thank Helmut Bluemel from Oerlikon Optics for providing us with the Ta₂O₅ substrates.


References
[10] Data from Schott AG: n(D263 Schott-glass)