In-situ optical characterisation of porous alumina

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We present a new method to characterize in-situ the optical thickness of porous alumina films by the use of photoluminescence-induced Fabry-Pérot-interferences. Additionally we show, that the use of different electrolytes yields different photoluminescence pattern. A second experiment allows to determine the degree of filling of the pores by a liquid which is of importance when using the pores as templates.

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1 Introduction

Porous oxide growth on aluminium under anodic bias in various electrolytes has been studied for nearly 50 years \cite{1}. Recently, porous anodic alumina (PAA) films have been used to prepare nanostructures for a wide range of applications \cite{2}. In order to use porous alumina as template for nanowire or nanotube growth in-situ optical measurements of their thickness as well as the degree of filling are required.

Determining the refractive index and thickness of thin films from wavelength measurements only was primarily discussed by Swanepoel \cite{3}. In contrast to Swanepoel we did not measure the transmission of the alumina layer because the layer lies on a non transparent aluminium layer and we want to use a simple laser for this in-situ setup.

It has been shown, that porous alumina exhibits a photoluminescence (PL) signal \cite{4–6}. There are at least two models concerning the origin of the blue photoluminescence band formed in oxalic acid solution with its peak position centered around 470 nm \cite{4, 5}. On the one hand, Yamamoto et al. \cite{4} have reported previously that the oxalic impurity is the reason for the blue PL band. On the other hand, Du et al. \cite{5} proposed oxygen vacancies (\textit{F}\textsuperscript{+} centers) to be the origin of the blue PL emission band. Latest results by Gao et al. \cite{6} are supporting the position of Yamamoto et al., but there are still further studies necessary.

In contrast to Du et al. and Gao et al. we did measure a clear luminescence signal also from sulfuric PAA films without any heat treatment. This gives us the opportunity to compare the PL spectra of sulfuric and oxalic PAA films. Furthermore we will use the PL pattern to determine the thickness and the degree of filling by Fabry-Pérot-interferences (FPI). For determining the degree of filling of the pores we used self-organized pores anodized in sulfuric acid with a pore diameter of 25 nm.
2 Experiment

Here, we just give a brief description of how to prepare the ordered alumina membranes. For more detailed information see Refs. [7–10]. High purity (99.999%) aluminium foils were used for anodization. The substrate was degreased in acetone and cleaned in a mixed solution of HF:HNO\textsubscript{3}:H\textsubscript{2}O = 1:10:20:69. After annealing for 3 h in nitrogen atmosphere at 500 °C for recrystallization the substrate was electropolished with a solution of HClO\textsubscript{4}(60%) and C\textsubscript{2}H\textsubscript{5}OH (75:25). A two step anodizing process was used to prepare porous alumina membranes. The substrate was either anodized in 0.3 M oxalic acid (C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}) with an anodizing voltage of 40 V (sample A) or anodized in 0.3 M sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) electrolyte with an anodizing voltage of 25 V (sample B). After 48 h for the first anodization the alumina layer was removed by a solution of 0.2 M CrO\textsubscript{3} and 0.6 M H\textsubscript{3}PO\textsubscript{4} at 60 °C for at least 4 h. After that the aluminium was anodized in the range of 5 to 20 minutes for a second time. The thickness of the alumina layer was primarily determined by scanning electron microscopy (SEM) with a JEOL JSM 6300F.

For the photoluminescence measurement of the alumina membranes a helium-cadmium laser with a wavelength of 325 nm was used. The beam spot at the substrate had a diameter of 1.5 mm and the laser output was 12 mW. An off-axis parabolic mirror with a focal distance of 15 cm was used for collecting the luminescence light. The parabolic mirror was perpendicular to the sample. A 360 nm edge filter in front of the monochromator was chosen to filter the diffuse scattered laser light. The gap length at the access of the monochromator was 200 μm. The grating was blazed at 500 nm and had 150 lines per millimeter. A nitrogen cooled CCD camera was used as detector. All recorded data were corrected to the spectral sensitivity of the measurement system.

For the verification that the pores were completely filled with a liquid, water containing an ordinary, solubilized green dye was dropped on the top surface of the membrane. After waiting 10 min for a complete infiltration, the top surface of the sample was dried so that only the pores were filled. All experiments were performed at room temperature.

3 Results and discussion

Determination of the layer thickness by SEM (Fig. 1) is serving as comparison to the in-situ measurement. To calculate the thickness of the alumina layer, the PL pattern of the membranes prepared in oxalic and sulfuric acid were made. The photoluminescence spectrum of the porous alumina membrane prepared in oxalic acid is shown in Fig. 2. The peak position of the PL pattern between 430 nm and 500 nm is in agreement with literature data [4–6]. For porous alumina anodized in sulfuric acid we observed photoluminescence spectrum with much lower intensities (Fig. 3). Even if the PL intensities of sample B are much lower than of sample A the bandwidth and the shape of the spectra is quite comparable. Therefore, we believe that in contrast to Gao et al. [6] the PL emission for both the oxalic and the sulfuric PAA films has the same origin.
The appearance of the interferences can be explained with the phenomena of Fabry-Pérot-interferences. It can be assumed, that both interfaces $\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ = air are at least partly reflective. For films with the thickness $d$ and the wavelengths $\lambda_i$ of the intensity extrema are given by the Bragg equation:

$$2nd\cos \theta = m\lambda_i$$

where $m$ is the order number with integer values for maxima and half-integer values for minima. The angle of reflection $\theta$ is around zero, so it follows that $\cos \theta = 1$.

The refractive index of pure alumina is $n_{\text{Alox}} \simeq 1.65$ [11] but here alumina is porous so it is necessary to calculate the effective dielectric coefficient $\varepsilon_{\text{eff}}$. Starting point is the Maxwell-Garnett-theory, which is a good approximation for isolated inclusions [12]. If we assume that $\varepsilon_{\text{Alox}} = n_{\text{Alox}}^2$ then the effective dielectric constant reads

$$\frac{\varepsilon_{\text{eff}} - \varepsilon_{\text{Alox}}}{\varepsilon_{\text{eff}} + 2\varepsilon_{\text{Alox}}} = \frac{\varepsilon_{\text{air}} - \varepsilon_{\text{Alox}}}{\varepsilon_{\text{air}} + 2\varepsilon_{\text{Alox}}}.$$  \hfill (2)

According to Nielsch et al. the porosity $f$ of self-ordered porous alumina under optimum conditions is: $f = 0.1$ [13]. It follows with $\varepsilon_{\text{air}} = 1$ and $\varepsilon = n^2$ that the effective refractive index is $n_{\text{eff}} \simeq 1.61$. Using a solubilized dye ($n_{H_2O} = 1.33$) yields an effective refractive index of $n_{\text{eff}} \simeq 1.63$.

The order number $m$ is unknown. But it is evident, that for adjacent extrema $m$ is of the form of

$$m_i = m_0 + \frac{l_i}{2} \quad \text{with} \quad l_i = 0, 1, 2, \ldots$$

Combining Eqs. (1) and (3) yields to

$$\frac{l_i}{2} = \frac{d}{\lambda_i} - m_0.$$  \hfill (4)

Values of $l_i/2$ can be plotted as function of $2n/\lambda_i$. The rise of the linear fit determines the thickness $d$. Table 1 compares the two ways, SEM and PL-FPI respectively, for the determination of the layer thickness. Note, that extrema with lower wavelengths may be influenced by the optical filter. Determination of the thickness with the SEM is the best way if one has not to take care of not breaking the sample. The in-situ measurement and the following calculations are a very accurate tool if the layer thickness is large enough to present in a given wavelength range theoretically at least two extrema and if the luminescence is broad enough. For the wavelength range of 350 nm to 700 nm this is satisfied.
for a layer thickness greater than 400 nm. For thinner layer thicknesses the measurement errors increase significantly.

The photoluminescence intensities of pores anodized in sulfuric acid filled with solubilized green dye is shown in Fig. 4. There are weak Fabry-Pérot-interferences visible. Figure 5 displays the integrated fluorescence intensity (IFI) as function of the layer thickness. The measuring point at the origin was a sample of planar alumina, where the surface was covered at first with solubilized dye and then dried after 10 min. Thus, the covered surface can be excluded as the origin for photoluminescence and it can be affirmed that the anodizing process is the only reason for the PL band. Since the IFI increases linearly with increasing layer thickness and it is going through the origin it can be deduced, that the pores are completely filled with water containing the solubilized dye.

### 4 Conclusion and outlook

We have prepared thin PAA films with sulfuric and oxalic acid and investigated Fabry-Pérot-interferences of their intrinsic photoluminescence. These interferences enable to determine the layer thickness in-situ as long as the layer thickness is larger than 400 nm and the laser excitation intensities are around 10 mW. These parameters also allow the use of UV-laserdiodes as excitation source and thus

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<th>probes</th>
<th>layer thickness (SEM) (nm)</th>
<th>calculated layer thickness (nm)</th>
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<tr>
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<td>1220</td>
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<td>430</td>
<td>510</td>
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<td></td>
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<tr>
<td>H₂SO₄</td>
<td>1600</td>
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<td>950</td>
</tr>
<tr>
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Fig. 4 Photoluminescence spectrum of porous alumina membrane prepared with sulfuric acid. Pores are filled with solubilized green dye. Wavelength of excitation: 325 nm. The measurement was directly after infiltration of the solution. Thickness of the alumina layer (determined with SEM): (a) 430 nm; (b) 970 nm; (c) 1600 nm.

Fig. 5 Integrated intensity at different layer thicknesses. Sample prepared in sulfuric acid. Pores are filled with solubilized green dye. The measurement was directly after infiltration of the solution.
possibly a rather inexpensive quality-control testing tool. Furthermore, we showed that pores with a
diameter of 25 nm anodized in sulfuric acid can be completely filled with water.

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References