The growth of patterned ceramic thin films from polymer precursor solutions
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CHAPTER 4

Films of Aluminum Oxide and Doped Zinc Oxide

4.1 Introduction

In terms of composition, the most simple films that were produced in this work were oxides that consisted of only one metal or of two metals in a variable stoichiometric ratio. These materials are described first. The two materials of interest were amorphous aluminum oxide, $\text{Al}_2\text{O}_3$, and aluminum-doped zinc oxide, $\text{ZnO:Al}$, with an Al doping of approx. 2 wt%. $\text{Al}_2\text{O}_3$ has a high dielectric constant. In the corundum phase ($\alpha$-$\text{Al}_2\text{O}_3$) it is one of the hardest materials known (hardness H=9). $\text{ZnO}$ is a II-VI semiconductor with a band-gap of 3.2 eV at 300 K [36]. By substituting a fraction of the $\text{Zn}^{2+}$ ions by $\text{Al}^{3+}$ ions, which serve as electron donors, $\text{ZnO}$ is turned into a n-type semiconductor. $\text{ZnO}$ has pyroelectric and piezoelectric properties.

Both $\text{ZnO:Al}$ and $\text{Al}_2\text{O}_3$ are transparent for visible light, making them interesting for optical applications. For example, highly conductive $\text{ZnO:Al}$ is regarded as a possible substitute for indium tin oxide (ITO) as an electrode material in displays.
4.2 Aluminum Oxide

Thin films of amorphous aluminum oxide have been prepared by electron beam evaporation [39], by magnetron sputtering [40–43], by spray pyrolysis of a precursor of aluminum acetylacetonate in DMF [44], and by chemical vapor deposition [45]. Crystalline films have been obtained by ionized beam deposition (probably $\alpha$-$\text{Al}_2\text{O}_3$) [46] or by magnetron sputtering ($\gamma$-$\text{Al}_2\text{O}_3$) [43].

Amorphous $\text{Al}_2\text{O}_3$ in thin films has been found to have a dielectric constants as high as 7.7 and resistivities as high as $10^{16}$ $\Omega\cdot\text{cm}$ [40, 45]. The refractive index is in the range between 1.28 and 1.66 [39, 44].

4.2.1 Precursor Preparation

$\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$, was dissolved in DMF and PAA was added. The obtained solution was clear and of a faintly yellow color. The weight ratio $\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$: PAA was 1:1. This results in a molar ratio of $\text{Al}^{3+}$ ions to carboxylic groups of 0.1921:1 and a molar ratio of positive charges from the $\text{Al}^{3+}$ ions to carboxylic groups of 0.5763:1.

4.2.2 Film Preparation

The substrate materials for the $\text{Al}_2\text{O}_3$ films were microscope cover slips and Si wafers. They were cleaned as described in Sec. 2.4. The precursor solution was spin-cast onto the substrates at 3,000–5,000 r.p.m. and dried as described in Sec. 2.5. This yielded clear, colorless films. After calcination at 600 $^\circ\text{C}$ for 30 min (Sec. 2.7), the films showed a network of cracks (Fig. 4.1 (a)), even though the precursor films did not. An AFM scan of the film surface reveals that it is rather smooth, as is shown in Fig. 4.1 (b). On top of Fig. 4.1 a height profile of the sample is shown as taken from the AFM scan.

4.2.3 Analysis

To investigate the film composition, an $\omega$-$2\theta$ scan was taken. The diffractogram didn’t show any peaks except for a broad glass peak. This can be explained in two ways. Either the film is amorphous or, since the film thickness was approx. 70 nm, the peak intensities are too low to be detected next to the diffuse scattering radiation of the glass substrate. To answer this question,
the sample was prepared for TEM imaging by ion milling until a hole in the sample center had formed. A suitable location on the sample was chosen near the hole and diffraction images were taken in approx. two minute intervals. In the beginning, these images did not show any diffraction pattern but only the bright spot of the primary beam (Fig. 4.2 (a)). This proves that the film is amorphous. As a consequence of the continuous electron irradiation in the TEM, the film underwent a phase transition to a crystalline phase. As shown in Fig. 4.2 (a) to (d), diffraction rings developed with increasing irradiation time, which consist of individual peaks. This indicates that the number of grown crystals in the spot area is rather small. The camera of the TEM was calibrated. By measuring the diameters of the diffraction rings, the d-values (Fig. 3.5) of the lattice planes of the crystals could be calculated. This way, the phase that developed during electron irradiation was identified as either γ- or η-Al₂O₃. A distinction between these two phases was not possible by this
Figure 4.2: TEM images of an Al₂O₃ film on a microscope cover slip. (a) to (d) show how the diffraction pattern of a polycrystalline phase develops with time. (e) is identical to (d), giving the indices of the diffraction rings. After ca. 10 min, the film showed serious radiation damage in that area where the diffraction images were taken (f).
4.3 Zinc Oxide

experiment, since their lattice parameters (both are cubic) are very similar (7.911 Å and 7.914 Å, respectively, see Appendix A.4). The finding that the crystallization of Al₂O₃ took place in the vacuum of a TEM (i.e. in the absence of oxygen), is a strong indication that also the composition of the amorphous film was Al₂O₃.

It was attempted to grow α-Al₂O₃ on Si substrates at oxidation temperatures of ca. 1000 °C (rather than 600 °C). An ω-2θ scan of such a film did, however, not show any peaks except for those of the substrate.

4.3 Zinc Oxide

ZnO:Al films can be prepared by a sol-gel method from zinc acetate and aluminum chloride in 2-methoxyethanol [47] or zinc acetate and aluminum nitrate in isopropanol/ethanol [48], by rf magnetron sputtering [49–51], by spray pyrolysis of zinc acetate and aluminum chloride in a water/methanol mixture [52] or a water/isopropanol mixture [53], or by pulsed laser deposition [54]. Films of undoped ZnO have been prepared by a sol-gel process from zinc acetate in citric acid and ammonia [8] or zinc nitrate in 2-methoxyethanol [55], and by chemical vapor deposition [56].

Zinc oxide, a pyroelectric material [57], is a II-VI semiconductor [54, 58]. Its crystal structure is given in Appendix A.5. Doping ZnO with trivalent Al or In decreases the resistivity of ZnO films [52]. Al is widely used as dopant since n-type doping is easy to obtain [59]. Therefore, ZnO:Al was chosen for the preparation of thin films in this work.

4.3.1 Precursor Preparation

Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in the molar ratio 1:0.020, 1:0.017 and 1:0.012 were dissolved in DMF and PAA was added. This yielded clear, colorless solutions. From the weight ratio Zn(NO₃)₂·6H₂O:PAA of 1:1, one can calculate the molar ratio of Zn²⁺ ions to carboxylic groups as 0.2422:1 and the molar ratio of positive charges from the Zn²⁺ ions to carboxylic groups as 0.4844:1.
4.3.2 Film Preparation

Films of doped and undoped ZnO were prepared on microscope cover slips and Si wafers that were cleaned as described in Sec. 2.4. The precursor solutions were spin-cast at 3,000-5,000 r.p.m. The films were dried as described in Sec. 2.5. The dried films were heated to 600 °C in air and kept at this temperature for 30 min (Sec. 2.7). This yielded clear colorless films on the coverslips.

One can estimate the shrinkage of the film during pyrolysis in the following way: Taking a mass density of approx. 1.1 g/cm$^3$ for PAA and dividing it by the molar mass of a repeating unit, the molar density of carboxylic groups is 0.0153 mol/cm$^3$ in PAA. Taking this density also for the precursor film with complexed Zn$^{2+}$ ions, a molar ratio of 0.2422:1 for Zn$^{2+}$:carboxylic groups gives a molar density of 0.2422·0.0153 mol/cm$^3=3.6936·10^{-3}$ mol/cm$^3$ for the Zn$^{2+}$ ions in the precursor film. On the other hand, the molar density

![Figure 4.3: $\omega$-2$\theta$ scan of ZnO on a microscope cover slip. The broad peak of glass is clearly visible at low 2$\theta$ angles. Four unidentified peaks are present in addition to the ZnO peaks.](image-url)
of \( \text{Zn}^{2+} \) in crystalline \( \text{ZnO} \) is the mass density of \( \text{ZnO} \) divided by its molar mass, \( 5.675 \text{ g/cm}^3 / 81.39 \text{ g/mol} = 6.97 \cdot 10^{-2} \text{ mol/cm}^3 \), which is by a factor of 18.9 higher than in the precursor film. Therefore, theoretically, the film thickness should decrease to 5.3\% of the initial value during the high-temperature treatment.

### 4.3.3 Analysis

![Graph](image)

Figure 4.4: \( \omega-2\theta \) scan of \( \text{ZnO:Al} \) on a Si wafer. Inset: Rocking curve of the (002) reflection.

To investigate the \( \text{ZnO} \) phase, \( \omega-2\theta \) scans were taken on the Philips 2-circle-diffractometer. Fig. 4.3 shows a scan of an undoped \( \text{ZnO} \) film on a microscope cover slip. In the scanned \( \omega-2\theta \) range, all \( \text{ZnO} \) peaks are visible except for the (200) and the (201) peak, the two weakest peaks in this scan range (PDF entry \# 361451). The (002) peak has a higher intensity than the (101) peak, although the ratio should be 44:100 for a powder diffractogram. This is a strong indication for a preferential orientation of the \( \text{ZnO} \)
crystallites with the $\vec{c}$-axis normal to the film plane. While several publications do not report a preferential orientation of ZnO films [8, 52, 53], others claim a more or less strong $\vec{c}$-axis orientation of ZnO in thin films [54, 56]. In particular, films produced by a sol-gel process [47, 55] show results of $\omega$-2$\theta$ scans similar to Fig. 4.3. Fig. 4.4 shows an $\omega$-2$\theta$ scan of a ZnO:Al film on a Si wafer. Within the scanned $\omega$-2$\theta$ range all ZnO peaks and one Si peak are visible. Similar to the sample of Fig. 4.3, the intensity ratios of the (002) and (101) peaks or the (002) and (100) peaks indicate a preferential $\vec{c}$-axis orientation. The inset of Fig. 4.4 shows a rocking curve of the (002) reflection. The fact that the curve has a maximum at $\omega=16.8^\circ$ (close to 2$\theta$/2 of the (002) reflection at 2$\theta=34.38^\circ$), is another indication for a preferential $\vec{c}$-axis orientation. On the other hand, the rocking curves of the (100) and (101) reflections also show maxima at $\omega=2\theta/2$. For a film with a preferential $\vec{c}$-axis orientation, a texture scan of the (101) reflection should show a ring of higher intensity with a maximum at $\psi=58.0^\circ$ (angle between $\vec{c}^*$ and (101)). Fig. 4.5 shows a texture scan of the sample of Fig. 4.4, with $\varphi\in[0^\circ; 90^\circ]$ and $\psi\in[0^\circ; 85^\circ]$. This texture scan, however, does not show any pattern. It is therefore doubtful that the ZnO films had a preferential $\vec{c}$-axis orientation. The observation of shifted peak intensities ((002) is stronger than (101)) in the $\omega$-2$\theta$ scans could also be explained by the assumption, that for ZnO films grown from polymer solutions the peak intensities are in fact different than for powder samples. In other words, if the film was scratched off the substrate and an $\omega$-2$\theta$ scan was taken of the powder, this diffractogram would still show a stronger (002) peak.

The finding of a broad peak in the rocking curves of the (100), (002), and (101) reflections can be explained by the Bragg-Brentano geometry, which is fulfilled if $\omega=2\theta/2$ [60]. In this case the sample surface area, which is exposed
to the primary beam AND to the “view” of the detector, is maximal.

Films of Al-doped ZnO show conductance when contacted with two metal pins of a standard ohmmeter. The resistance was on the order of several MΩ for distances of several mm. This is an indication that either the doping rate or the quality of the grown crystalites is not optimal. Resistivities as low as $4 \cdot 10^{-4} \, \Omega \cdot \text{cm}$ have been reported [54] for ZnO:Al films made by pulsed laser deposition.

### 4.4 Patterned Films of Aluminum Oxide and Zinc Oxide

A major advantage of the solution deposition process applied in this work is the possibility to pattern the precursor film. In this work micromoulding was used as patterning procedure (Sec. 2.6).

Fig. 4.6 shows two patterned Al$_2$O$_3$ films on microscope cover slips, imaged by light microscopy ((a) and (b)), by SEM ((c) and (d)), and by AFM ((e) and (f)). Below the AFM images, the height profiles of the respective patterns are depicted. For this figure and Fig. 4.7, the pattern is defined by the following parameters: 1. The periodicity $a$, measured perpendicular to the line direction, or between nearest neighbour columns, respectively. 2. The width $d$ of the lines or the diameter $d$ of the columns, respectively. 3. The height $h$ of the lines or columns. Line pattern: $a=2.5 \, \mu\text{m}$, $d=500–650 \, \text{nm}$, $h=450–500 \, \text{nm}$. Column pattern: $a=1.0 \, \mu\text{m}$, $d=545(7) \, \text{nm}$, $h=195(5) \, \text{nm}$.

Fig. 4.7 shows two patterned films of ZnO:Al on microscope cover slips, imaged by light microscopy ((a) and (b)), by SEM ((c) and (d)), and by AFM ((e) and (f)). Below the AFM images, the height profiles of the respective patterns are depicted. Line pattern: $a=2.0 \, \mu\text{m}$, $d=660–700 \, \text{nm}$, $h=210(5) \, \text{nm}$. Column pattern: $a=1.0 \, \mu\text{m}$, $d=580–660 \, \text{nm}$, $h=110(7) \, \text{nm}$.
Figure 4.6: Patterned Al$_2$O$_3$ films. Details are given on page 45.
Figure 4.7: Two patterned ZnO:Al films. Details are given on page 45.
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