Effects of the electrolyte species on the electrochemical dissolution of polycrystalline ZnO:Al thin films

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The electrochemical anodic dissolution of sputter-deposited, aluminum-doped zinc oxide (ZnO:Al) was investigated. The dissolution proceeds mainly via a local oxygen evolution reaction and subsequent dissolution of the zinc oxide lattice. The present work focuses on the influence of the anion species in the used electrolyte. Several electrolytes (KCl, K2SO4, KNO3, KClO4) were applied. The anion species turned out to be a major factor that influenced the kinetics of the etching process. In K2SO4 solutions a strong limitation of the etching process to the close vicinity of the grain boundaries was observed. However, anodic dissolution in KCl, KNO3, and KClO4 showed an unexpected etching behavior, which lead to the formation of cavern-like structures within the ZnO:Al thin films. This was attributed to different local pH values at the ZnO:Al/electrolyte interface.

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1. Introduction

Zinc oxide is a large bandgap semiconductor that is widely used in varistors [1], gas sensors [2], light emitting diodes [3], and photovoltaic devices [4,5]. A variety of deposition techniques are utilized to produce doped zinc oxide thin films, including vapor deposition techniques such as pulsed laser deposition (PLD) [6–8], chemical vapor deposition (CVD) [9,10], and sputter deposition [11–14]. Furthermore, liquid phase deposition is feasible, e.g., the sol-gel technique [15–17], electrochemical deposition [18,19], and spray pyrolysis [20,21]. Among these deposition methods, magnetron sputter deposition is an established technique that offers the advantage of being able to produce homogeneous thin films on large areas up to several m² at moderate temperatures. Therefore, it is applicable for industrial production.

For the application of aluminum-doped zinc oxide (ZnO:Al) thin films in some optoelectronic devices, such as thin-film solar cells, a rough surface is required to provide an efficient light trapping in the absorber material. Usually, a simple chemical etching step in diluted HCl is applied to introduce a light scattering surface texture to sputter-deposited ZnO:Al thin films [22,23]. Thereby, a crater-like surface texture is achieved with a typical root mean square surface roughness of 40–150 nm. However, the actual surface texture depends strongly on both, the deposition parameters [12] and the etching conditions (etching species, concentration, temperature) [24,25].

The chemical dissolution of single crystalline ZnO is under investigation since the early 1960s [26–28] and can be understood on the basis of its wurtzite crystal structure and a dangling bond model originally developed for III–V semiconductors [29–31]. Due to the amphoteric character of ZnO it can be etched in either acidic or alkaline solutions and the conditions for thermodynamic stability are rather narrow, e.g., around pH 7–11 [32,33]. However, dissolution rates under moderate conditions are fairly low due to either slow kinetics [34] or transport limitations [35]. Fruhwirth et al. [36] and Gerischer and Sorg [34] investigated the chemical dissolution kinetics of ZnO crystals in aqueous electrolytes.

The polycrystalline nature of ZnO thin films introduces a more complex chemical dissolution behavior. In a recent review we proposed a phenomenological model for the chemical etching of ZnO thin films based on the assumption that each grain boundary has a certain inherent probability to serve as an active site for etching depending on both the compactness of the grain boundary and the etchant [24]. The anodic electrochemical dissolution discussed in the present contribution represents an extreme case within this model, being able to attack grain boundaries with high selectivity. In contrast to chemical dissolution the electrochemical dissolution is not limited by transport but by reaction kinetics [37].
Gerischer [38] and Lohmann [39] investigated the anodic dissolution of ZnO single crystals under UV illumination already in the 1960s. It was stated that anodic dissolution of ZnO is only possible under UV illumination because the process is driven by charge transfer with holes in the valence band [40,41]. Also photodissolution of magnetron-sputtered ZnO thin films was reported [42] and it was found that the etching of ZnO thin films is very sensitive to its microstructure.

However, for an electrochemical dissolution of ZnO:Al thin films in aqueous electrolytes no UV illumination is necessary for applied anodic potentials of around +2 V vs. SHE [37,43]. The anodic dissolution is supposed to proceed via two competing reactions. First one is the direct lattice decomposition (1) and second one the oxygen evolution reaction (OER, (2a)) with subsequent chemical dissolution of the crystal lattice (2b) [41,44].

\[
2\text{ZnO} \rightarrow 2\text{Zn}^{2+} + \text{O}_2 + 4\text{e}^- \\
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \\
\text{ZnO} + 2\text{H}^+ \rightarrow [\text{ZnOH}]^+ + \text{H}_2\text{O} + \text{Zn}^{2+}
\]

As reported in [43] the grain boundaries are highly preferred etch sites, whereas the grains remain relatively intact. Thus, during electrochemical dissolution, the overall film thickness persists, but grooves develop at the grain boundaries.

Even if the anion of the electrolyte does not participate in the reactions given above, a recent study [43] gives hints that the kinetics of the dissolution process depend on the anion species. Moreover, it is known in literature that the chemical nature of the electrolyte plays an important role on both the cathodic electrochemical deposition of ZnO thin films [45–50] and the dissolution of zinc or ZnO in aqueous electrolytes [51–54].

The present study aims to investigate the influence of the electrolyte on the electrochemical dissolution of polycrystalline ZnO:Al thin films in detail, in order to improve the understanding of the electrochemical anodic dissolution of ZnO thin films. Therefore, aqueous solutions of K$_2$SO$_4$, KCl, KNO$_3$, and KClO$_4$ were used as electrolytes and the effect of the anion species was investigated.

2. Experimental

Polycrystalline and approximately 900 nm thick ZnO:Al films were deposited on a cleaned (10 cm × 10 cm) glass substrate (Corning Eagle XG) using radio frequency magnetron sputtering in a vertical in-line system (VISS 300, VON ARDENNE Anlagentechnik GmbH, Dresden, Germany) from a ceramic target consisting of ZnO with 1 w/% Al$_2$O$_3$ (Cerac Inc., Milwaukee, WI, USA). The deposition was carried out at a substrate temperature of 300 °C, a discharge power density of 2 W cm$^{-2}$, and an Ar pressure of 0.1 Pa. Details about the process have been published elsewhere [55]. The films exhibit low resistivity around $2.5 \times 10^{-4}$ Ω cm and are highly transparent. The grains of the investigated material were around 100 nm in diameter oriented along the c-axis [56].

The electrolytes were prepared from ultrapure deionized water (Millipore, Schwabach, Germany) and analytical grade chemicals. Electrochemical experiments have been performed with a Gamry Reference 600 (C3, Haar, Germany) potentiostat in a conventional three-electrode setup, utilizing a Pt mesh as counter electrode and an Ag/AgCl/3 M KCl reference electrode (Deutsche Metrohm, Filderstadt, Germany) to which all given potentials are referred. The ZnO:Al-covered glass substrate was cut into 5 cm × 2.5 cm pieces. The sample was then connected as the working electrode. An area of approximately 9 cm$^2$ of the sample surface was exposed to the electrolyte. Charges are reported normalized to the geometric sample area in mC cm$^{-2}$ in order to account for small deviations in sample size. The temperature was maintained constant at 25 ± 0.5 °C during all electrochemical experiments. Anodic texturing was done either potentiostatically or galvanostatically. Aqueous solutions of K$_2$SO$_4$, KCl, KNO$_3$, and KClO$_4$ were utilized as electrolytes. After electrochemical treatment, the samples were cleaned in hot, deionized water to remove salt residues originating from the electrolyte solution.

Film thicknesses have been measured with a Dektak 3030 surface profiler (Veeco Instruments Ltd., Santa Barbara, CA, USA). Scanning electron microscopic (SEM) images have been recorded utilizing a Magellan 400 SEM (FEI Company, Hillsboro, OR, USA). A four-point probe setup RH 2030 (PhysTech GmbH, Moorsburg, Germany) was used for ex situ electrical characterization of the films under ambient conditions. Optical measurements were performed using a dual beam photospectrometer Lambda 950 by Perkin Elmer (Waltham, MA, USA).

3. Results and discussion

The cyclic voltammograms depicted in Fig. 1a are recorded with a scan rate of 10 mV/s in 0.1 M NaCl and KCl solutions, respectively. The data indicates a potential window between approximately −0.6 V up to +1.3 V vs. Ag/AgCl/3 M KCl where ZnO:Al is stable. At more cathodic potentials first a reduction to metallic zinc is observed (R$_1$) and at even higher cathodic potentials the hydrogen evolution reaction (HER) starts. In the anodic scanning direction an oxidation peak is observed (O$_1$) which corresponds to the

![Fig. 1. (a) Cyclic voltammograms in 0.1 M aqueous solutions of NaCl and KCl, respectively. The scan rate was 10 mV/s and the temperature was maintained at T=25 °C. The peaks are discussed in the text. (b) Chronoamperometric anodization of ZnO:Al thin films at a bias potential of E=2.2 V vs. Ag/AgCl/3 M KCl until a charge of Q=300 mC/cm$^2$ was exchanged at the electrode. The measurements were conducted in 0.1 M solutions of NaCl and KCl, respectively.](image-url)
stripping of electrodeposited metallic zinc. Under anodic polarization, dissolution of ZnO:Al via Eqs. (1) and (2) occurs. Both cyclic voltammograms exhibit exactly the same behavior. This suggests that the role of the cation is negligible.

Fig. 1b provides chronoamperometric data for the same samples as depicted in Fig. 1a during anodization. A constant potential of \( E = +2.2 \) V was maintained until a charge of \( Q = 280 \text{ mC cm}^{-2} \) was exchanged. The current density behavior did not differ significantly in the two electrolytes. Hence, we conclude that the cation species had no significant influence on the dissolution process. This is also observed for electrochemical deposition of ZnO [57]. However, it was found that the anodic treatments in sulfate and chloride containing electrolytes exhibit different reaction kinetics and lead to slightly different surface textures when combined with a subsequent chemical etching step [43].

Fig. 2 compares chronoamperometric current density transients of three samples anodically biased in 0.1 M aqueous solutions of \( \text{K}_2\text{SO}_4 \), KCl, KNO3, and \( \text{KClO}_4 \), respectively. The initial pH values of the solutions were determined to be 5.9, 5.6, 5.7, and 5.3 for \( \text{K}_2\text{SO}_4 \), KCl, and KNO3, and \( \text{KClO}_4 \), respectively. Though, chemical dissolution at significant rates was not observed when samples were stored in the solutions for more than 12 h. The potential was set to 2.1 V vs. Ag/AgCl|3 M KCl and the treatment was continued until the current density fell below 10 \( \mu \text{A cm}^{-2} \). Fig. 2 clearly shows differences in the dissolution behavior of the four samples, which are representative for the respective electrolyte. For all measurements the current density dropped in the beginning, which was ascribed to the formation of the electrochemical double layer, increased again to a maximum before it decreased to zero, probably due to the increased resistance of the ZnO:Al layer. However, the shape of the current density evolution in the four solutions differed in some prospects. First of all the maximum current density was decreasing from \( \text{K}_2\text{SO}_4 \) over KCl and KNO3 to \( \text{KClO}_4 \) corresponding to a decreasing dissolution rate. Consequently, the ZnO:Al layer treated in \( \text{K}_2\text{SO}_4 \) breaks down electrically much faster, resulting in a diminishing conductivity, and hence, a drop of the current density to zero. The current density declined to zero in the other electrolytes as well, but the required time increased by a factor of approximately 4, 5.5, and 9 for chloride, nitrate, and perchlorate solutions, respectively. The intermediate increase of the current density was attributed to an enlargement of the active surface area during the local corrosion of the ZnO:Al layer. The inset in Fig. 2 shows the charge per geometrical surface area that was exchanged at the ZnO:Al/electrolyte interface, which is linearly linked to the amount of altered material via Faraday’s law. This representation makes clear that in \( \text{K}_2\text{SO}_4 \) much less material was removed before the current drops. Assuming a current efficiency of approximately 90% as was shown in Ref. [57] for the case of unbuffered aqueous solutions, approximately 11%, 41%, 52%, and 56% of the initial ZnO:Al layers were dissolved in \( \text{K}_2\text{SO}_4 \), KCl, KNO3, and \( \text{KClO}_4 \), respectively.

In order to prove the hypothesis of the increasing sheet resistance being the reason for the decreasing current density, a series of eight samples for each electrolyte was treated for different times \( t \). For each sample the sheet resistance \( R_{sh} \) after etching was determined ex situ by means of a four-point probe measurement. Fig. 3 shows the evolution of \( R_{sh} \) during anodic electrochemical dissolution in the four electrolytes investigated here. As expected, \( R_{sh} \) increased much faster during etching in \( \text{K}_2\text{SO}_4 \) as compared to KCl, KNO3, and \( \text{KClO}_4 \), respectively. Note that \( R_{sh} \) is not plotted vs. the treatment time, but vs. the exchanged charge. Obviously, in \( \text{K}_2\text{SO}_4 \) less material has to be dissolved to increase \( R_{sh} \) drastically. Hence, not only the dissolution rate, which is related to the current density, was higher in the sulfate solution but also the impact of the material dissolution on the electrochemical properties of the ZnO:Al layer was higher. Thus, the resulting structures were expected to differ from one another. Especially the samples etched in \( \text{K}_2\text{SO}_4 \) were assumed to exhibit deep features that effectively inhibit a lateral current transport through the layers, resulting in the observed high sheet resistance.

Another hint for different etch structures is given by Fig. 4 which depicts spectrally resolved optical absorption data of four ZnO:Al thin films on glass. The gray solid line represents the flat as-deposited state without any surface texturing. The other data correspond to samples that were anodized in the different electrolyte solutions at \( E = 2.1 \) V. All samples were treated with a total exchanged charge of approximately \( Q = 160 \text{ mC cm}^{-2} \). Thus, assuming that the charge efficiency for anodic ZnO:Al dissolution is the same for each electrolyte, the same amount of material was dissolved for all samples. In general, in the short wavelength range, fundamental absorption due to excitation above the band gap is observed. The layers are highly transparent in the visible wavelength range, whereas the absorbance increases in the near infrared range because of free carrier absorption. Compared to the as-deposited state the absorbance of the samples treated in KCl, KNO3, and \( \text{KClO}_4 \) decreases in the infrared but only a small shift of the plasma frequency was observed. These three samples showed very similar absorption spectra. However, the sample anodized in \( \text{K}_2\text{SO}_4 \) showed a more pronounced decrease in the near infrared.
absorption, a drastic increase of the absorption above 1600 nm and a shift of the plasma frequency to higher wavelengths. It is worth noting that a similar treatment in a K$_2$SO$_4$ solution with a lower concentration of 0.06 M, exhibiting a conductance similar to the 0.1 M KCl and KNO$_3$ solutions, resulted in the same optical and electrical properties. Hence, the conductance of the solution, which is approximately twice as high for the same concentration in K$_2$SO$_4$, had no relevant impact on the dissolution process. The decrease in the plasma peak can probably be ascribed to the removal of material whereas a shift of the plasma frequency to higher wavelengths might be attributed to a lower charge carrier density (see e.g., [58–60]). The inset in Fig. 4 shows only the short wavelength range where the ZnO:Al has its bandgap energy. In the as-deposited state the degenerately doped ZnO:Al thin films exhibit a Burstein–Moss shift [61,62]. This shift was reduced during anodic dissolution in all investigated electrolytes but the effect is most distinct for the treatment in K$_2$SO$_4$, which points to a decrease in the charge carrier concentration of the ZnO:Al. This is in agreement with the shift of the plasma peak in the infrared part of the spectrum [60].

Keeping in mind that the amount of dissolved material was the same for all samples, the different absorption spectra support the thesis drawn from the chronoamperometric data that the anodic dissolution in K$_2$SO$_4$ removed more selectively the more defective and therefore more absorbing material of the layer. This material is likely to be found at the grain boundaries. This interpretation was confirmed by SEM measurements of ZnO:Al layers after anodization in K$_2$SO$_4$ and KCl, respectively. Fig. 5a and b provide images of the sample surfaces whereas, c and d show cross sections of ZnO:Al layers after anodic treatment. Comparing the surface SEM pictures in Fig. 5a and b it is obvious that anodization in KCl removes a wider region around the grain boundaries than in K$_2$SO$_4$. Nonetheless, the grain boundaries are the initiation sites of the dissolution process in both cases. In K$_2$SO$_4$ (c) the grain boundaries were removed through the whole layer after an exchanged charge of Q = 204 mC cm$^{-2}$ whereas in KCl (d) the electrochemical etching process affected only the top part of the layer, even with Q = 320 mC cm$^{-2}$. Note that in the cross section images, particularly in Fig. 5d, some artifacts from the sample preparation using focused ion beam (FIB) are apparent. Namely, the straight, vertical lines in the lower part of the layer are caused by the ion beam at points where less or less dense material was above. Consequently, the ion beam was able to penetrate deeper into the layer. Hence, surface features or less compact material at the layer surface were propagated through the layer and cause these straight lines during preparation of the cross section. It is apparent from the cross sections that the total film thickness did not change and the interior of most grains remains unattached. This is particularly true for the samples etched in K$_2$SO$_4$, where the dissolution process proceeds much faster along the grain boundaries than in KCl. Thus, in a rather short time the ZnO:Al thin film consists of individual isolated grains and the lateral resistance increases drastically. In contrast, the etching proceeds not exclusively vertical in KCl solutions but also some grains are attacked leading to a cavern-like porous structure with an intact layer underneath, which supplies lateral conductivity.

The anodic dissolution of polycrystalline ZnO:Al thin films is obviously strongly determined by the structural heterogeneity between grains and grain boundaries. Apparently, preferred conditions for anodic dissolution are located at the grain boundaries, independent of the used electrolyte species. However, after the initial dissolution event the etching progresses differently depending on the present anion. A reason for the preferred attack at grain boundaries might be a higher local defect density, which has implications for both the bending of the energy bands of the semiconductor in the space charge region near the surface and

![Fig. 4](image_url)

**Fig. 4.** Optical absorption spectra of ZnO:Al thin films on glass in the as-deposited state and after anodic treatment in aqueous solutions of K$_2$SO$_4$, KCl, KNO$_3$, and KClO$_4$. During anodization approximately 12% of the initial layer was dissolved for each sample. The inset shows a closer view of the short wavelength range close to the bandgap energy of ZnO:Al.

![Fig. 5](image_url)

**Fig. 5.** (a) and (b) depict SEM images of ZnO:Al thin film surfaces after anodic treatment in K$_2$SO$_4$ and KCl, respectively. (c) and (d) show cross section SEM images of similar ZnO:Al thin films after prolonged anodic treatment in K$_2$SO$_4$ and KCl, respectively. The cross sections were prepared by focused ion beam (FIB).
possible adsorption of ions from the solution to surface states. Apparently, the charge transfer of the band states of the ZnO:Al thin film with redox states in the aqueous electrolyte is favored in the vicinity of the grain boundaries. Moreover, the density of surface states, potentially contributing to a charge transfer between ZnO:Al and the electrolyte [63–65] is presumably elevated at the grain boundaries. More extensive studies are necessary to understand the dissolution mechanism of ZnO:Al thin films in detail.

Different surface states or band bending, however, can hardly explain the effect of the different anion species. Abd El Aal and Abd El Wanees [54] reported that sulfate ions, which are electrochemically inert under the applied potentials, act as destabilizing species for passive films on zinc electrodes. This is also confirmed by Klemm et al. [66] and was supported by higher current densities at equal bias potentials which might be related to the fact that the SO$_4^{2−}$ ions adsorb on the electrode surface and subsequently participate in the active dissolution process [47]. Adsorption of SO$_4^{2−}$ ions on the oxide film creates an electrostatic field across the film/electrolyte interface [67]. When the field reaches a certain value, the adsorbed anions are suggested to penetrate the oxide film especially at defects and promote local anodic dissolution [68]. In general, adsorption of ions on the ZnO:Al surface can establish surface dipoles which might influence the space charge region close to the semiconductor—electrolyte interface. Also formation or compensation of surface defects by adsorbed ions is conceivable. However, the polycrystalline nature of the investigated thin films makes quantitative statements about the adsorption of different species difficult.

An effect of the chemical nature of the anions on electrochemical deposition of ZnO is also observed [45]. It is found that the aspect ratio of electrodeposited nanorods is significantly lower in Cl− than in SO$_4^{2−}$ solutions. This is attributed to an even higher ability of the chloride ions to adsorb at the ZnO surface.

Furthermore, Zn$^{2+}$ ions probably form ion pairs with SO$_4^{2−}$ [69] which are assumed to decrease the activation energy for zinc dissolution and thus increase the dissolution current [51]. However, also NO$_3^−$ and Cl− containing solutions are known to enhance pitting corrosion [70,71].

Moreover, the polycrystalline structure of ZnO:Al thin films requires to take into account that the dissolution proceeds in grooves of growing depth along the grain boundaries. Thus, local saturation of the solution and as a result inhibition of dissolution might become an issue. However, this effect is not expected to be of major influence because even in solutions saturated with the zinc salt the dissolution process continues [34]. Nevertheless, a high aspect ratio between depth and width of the grooves limits transport processes and leads to a significant enrichment of dissolved zinc during etching. The complex interplay between pore formation and diffusion in the evolving porous material goes, however, beyond the scope of this paper. As reported by Gerischer and Sorg [34] the influence of the anion on the chemical dissolution rate of ZnO single crystals follows the tendency to form complexes with Zn$^{2+}$ ions and increases from NO$_3^−$ to Cl− and then SO$_4^{2−}$. Thus, the dissolution rate is probably determined by the rate at which zinc complexes diffuse away from the electrode surface [69]. This trend is in accordance with the present experiment. However, this explanation cannot account for the different structures and the higher lateral dissolution rate that was observed in Cl−, NO$_3^−$, and ClO$_4^−$ containing solutions as compared to SO$_4^{2−}$.

In fact, we suggest different pH values in the direct vicinity of the electrode to be the reason for the different evolving structures. As a result of the OER the acids corresponding to the salts are formed directly at the ZnO:Al surface according to Eqs. (3)–(6).

\[
\text{ClO}_4^- + H^+ \rightarrow \text{HClO}_4 \quad \text{pK}_A = -10[72] \\
\text{NO}_3^- + H^+ \rightarrow \text{HNO}_3 \quad \text{pK}_A = -1.4[72] \\
\text{SO}_4^{2-} + H^+ \rightarrow \text{HSO}_4^- \quad \text{pK}_A = +1.987[73] \\
\text{HSO}_4^- + H^+ \rightarrow \text{H}_2\text{SO}_4 \quad \text{pK}_A = -3[72]
\]
images have been recorded by Hans Peter Bochem (PG-8-PT, Forschungszentrum Jülich GmbH). Financial support by the Deutsche Forschungsgemeinschaft (DFG, grant PU 447/1) is gratefully acknowledged.

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