Anodic oxidation of thin aluminum and tantalum films was performed in an electrochemical droplet cell. Thicknesses from 2 up to 8 nm were employed on 10 nm thick aluminum and tantalum films. Under ultrahigh vacuum conditions the conductivity of the remaining metal film is monitored as function of time. Equally prepared oxide films were accomplished in metal-insulator-metal capacitors, which were used to monitor the capacitance as a function of time. The combination of the two experimental setups shows clearly, that small losses in the capacitance of aluminum oxide capacitors are due to slight thickening of the oxide even under vacuum conditions. Up to one monolayer of the base aluminum electrode can be oxidized during 107 s. Modeling in terms of migration of either oxygen anion interstitials or metal cation migration points preferably to the latter one. Tantalum oxide films of the same thickness show a much larger stability indicating either a lower content of mobile ions or a higher activation barrier for ionization and migration.

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Anodic oxidation is an intensively studied field in electrochemistry. Since the early days of so-called wet diodes (based on aluminum or copper oxide1-4) the technical application of thin oxide films always pushed and motivated a continuous research in this field. Today a well-founded parameter set as pH value and anion type allows potentiostatic oxidation to be a highly suitable method for the production of nonporous insulating compact oxides.3-6

Additionally, properties such as high breakdown field strength and scalability in thickness open a wide field of applications for electrochemical oxidation procedures also concerning transition metal oxides such as Ti, Zr, Hf, Nb, and Ta.5,7

Anodic oxidation is accomplished at positive potentials. This means an increase of the intrinsic electric field at a metal-oxide interface6,9 (metal-oxide interface positively charged, oxide-electrolyte interface negatively charged). The growth process is based on the conduction of ionic species supplied by the electrolyte and the electrode. Oxygen and metal ions driven by the electric field at the metal-electrolyte interface contribute to the observed current during the oxidation process. A simultaneous migration of metal cations and oxygen anions seems to be surprising at first glance since the bigger ion radius of O2- (rO2- = 132 pm, rA13+ = 57 pm) should hinder the migration of O2- anions. But defect sites in amorphous oxides also provide effective transport channels for anions.10,11

Wang and Hebert performed a comprehensive modern theoretical work considering the metal ion as well as the oxygen ion transport during anodic oxidation through amorphous oxide films.12 They derived a model describing conduction as migration of defect clusters that are created by an inward displacement of oxygen ions around an oxygen vacancy. The calculations gave transport numbers for cations and anions for Al, Nb, and Ta.13

Oxygen vacancies also seem to play an important role in oxides formed by gas phase oxidation. Recently vacancies were found to be a reason for instabilities in aluminum oxide tunnel barriers.14,15

The field driven ionic transport in the course of oxide growth can also be investigated in ultrahigh vacuum (UHV) conditions. Yates, Popova and co-workers14,16 applied field strengths of E = 1.4 \times 109 V/m to a 7 Å thick oxide film. Subsequent dosing of oxygen induced a thickness increase up to 11 Å. During this additional oxide growth the initial electric field was inevitably reduced and a saturation value of the oxide thickness was reached. A maximum value of the field strength, which remains in the oxide films, is predictable. This value Eresidual is at least smaller than 1.4 \times 7/11 \times 109 V/m = 0.9 \times 109 V/m. It means that further oxide growth induced by an electric field E will certainly happen under UHV conditions with E > Eresidual when an oxygen supply is provided.

In anodic oxides a similar estimation can be done. The field strength E in an oxide film has to overwhelm the formation field strength Eform for further anodic oxide growth. In an acetate buffer Eform is 0.6 \times 109 V/m.17

The values of Eresidual and Eform are quite similar. Thus, a pronounced enhancement of ionic transport due to incorporated electrolyte species does not seem to exist in anodic oxides produced in acetate buffers. (This may be different for experiments using other electrolytes.18)

Field induced ionic transport through amorphous oxides can be understood as a hopping of ionic species between defect sites separated by a distance s. Thereby Eresidual \cdot s and Eform \cdot s can be understood as lower limits for the activation energies of ionic transport which enables further oxide growth. Provided that s is similar in both types of oxides, ionic transport seems to have nearly the same activation energy Eρ. Assuming s as the half of the lattice constant (s = 0.35 nm), one would evaluate a minimum activation energy Eρ \approx 0.3 eV.

Different values of activation energies are found for thermally activated diffusion as self-diffusion of oxygen in aluminum and tantalum oxide that are well investigated in bulk crystals. Values of Eρ \approx 2-8 eV are found in the temperature range 1100-1400 K.10,11

But the processes on an atomic level may be quite different in this temperature range.

In the present work we want to raise the question whether the existence of mobile charge carriers and the remaining field strength Eresidual lead to diffusion processes of ions, which are influenceable by an electric field E. In thin oxide films diffusion to the oxide interfaces would increase the film thickness and may remarkably change the properties of electronic devices containing thin oxide films. Thereby a better understanding of electric field activated diffusion in thin films would help to overcome some problems in electrochemical device manufacturing.

An established tool for monitoring small changes in oxide films is the investigation of resistivity changes in metal-metal oxide-metal tunnel junctions.13,19-21 In these works the tunnel resistivity, which probes the electron transport normal to the oxide interfaces, is monitored. Since the tunnel probability is proportional to \exp(-\sqrt{2}φg) and \exp(-d) (φg, height of tunnel barrier, d, oxide thickness) it is a very sensitive tool to detect even small changes in the oxide film. Additionally these samples allow the modification of the field across the oxide by an applied tunnel voltage. Konkin and Adler found a strong field dependence of the long term resistivity change in such devices. An applied positive tunnel voltage (Al ground electrode
positive, Pb top electrode negative), which increases the intrinsic field in the oxide, was found to raise the tunnel resistivity of the samples during a period of several tens of hours. A negative voltage that diminishes the intrinsic field was found to keep the junctions in a stable state. The results were interpreted in terms of an ionization and subsequent migration of aluminum atoms into the oxide layer. These results would support the above-mentioned migration of mobile ions. However, the observed resistivity increase can be discussed in terms of changes in the barrier height or in the oxide thickness as well. So the results of these experiments cannot be discussed unambiguously.

Therewith we set up a new line of experiments to detect small deviations from the equilibrium state of the oxide at room temperature. Smooth metal films \((d = 10 \text{ nm})\) were electrochemically oxidized, so that only 2 nm of the metal remained. A resistivity measurement of the remaining metal probes the lateral electronic conductivity (see Fig. 2). Changes in the oxide may influence the resistivity of the remaining metal by two processes:

1. Crystallization of the oxide would cause significant mechanical stress leading to a tearing of the underlying metal film. Abrupt changes of the resistivity can be expected in this case. At room temperatures this is not very likely since crystallization of alumina is observed at \(T > 400 \text{ K}\).\(^{22,23}\) For \(\text{Ta}_2\text{O}_5\) even higher temperatures \((T = 600 \text{ K})\) are needed.\(^{24}\)

2. Migration of mobile ions in the oxide film into the metal or dissolution of metal atoms into the oxide would lead to a continuous oxidation of the remaining metal. A continuous increase of the metal’s resistivity up to an unmeasurable infinitely high value might be detected then.

Thus, smooth resistivity changes detected as function of time are supposed to be due to ion migration.

An advantage of the method is that the results are not influenced by the barrier height at the metal-oxide interface. Thereby, the experiment is only sensitive to changes in the remaining metal. Furthermore, we combine these results with capacitance data of metal-oxide-metal systems, which probe the conduction processes normal to the oxide interface.

The present work applies the two mentioned experimental methods to different chemical systems:

1. Ta–TaO\(_x\) since it is one of the most spread metal-insulator systems in capacitive devices (e.g., Ref. 25-27).

2. Al–AlO\(_x\) since new aspects as spin selection rules found for the adsorption of oxygen on aluminum\(^{28}\) and the abstraction of oxygen atoms during adsorption\(^{29}\) seem to shed new light on this intensively investigated metal-oxide system (e.g., Ref. 30-33).

**Experimental**

The aluminum films were evaporated on isopropanol cleaned microscope glass slides from a thermal source containing a tungsten basket in a high vacuum chamber. Evaporation was done at room temperature. Tantalum films were prepared under the same conditions by an electron beam evaporator. Small evaporation rates of 0.01 nm/s were chosen to ensure a homogeneous film thickness and small roughness <1.5 nm.

It should be mentioned that the film homogeneity depends on the evaporation conditions. In Fig. 1 two atomic force microscope (AFM) line scans of aluminum films (15 nm nominal thickness) are shown for evaporation rates of 0.5 and 0.01 nm/s. While the latter one shows a roughness of only 1.5 nm, a much higher roughness of 5 nm can be seen for higher evaporation rates. These samples also have a much lower conductivity (reduced by a factor of 20) compared with the smooth aluminum films, albeit the nominal thickness is the same.

Two different types of setups are used in the current work.

1. For the resistivity measurements the metal films of 10 nm thickness were used, which were anodically oxidized up to an oxide thickness of 8 nm. The 3 mm wide and 20 nm long metal samples were covered with the oxide which embraces the whole width of the metal film on a length of 5 mm, see upper half of Fig. 2.

2. For the capacitance measurements the metal films of 30 nm thickness were anodically oxidized (on the whole width of the metal film and on a length of 8 mm) up to an oxide thickness of 2 nm. After the transfer to the UHV chamber a 15 nm thick silver film was deposited on the connected potentiostat.
The oxidation of the metal films for both types of samples was performed in an electrolytic droplet cell as described in Ref. 34 and 35 using an acetate buffer electrolyte which minimizes parallel corrosion processes during oxidation.59 The aluminum films were kept under nitrogen atmosphere during the transport from the vacuum chamber to the droplet cell to avoid contamination with an air formed oxide.

Resistance measurements started immediately, whereas capacitance measurements could be started only after 10 h when a sufficient vacuum level (p = 2 × 10⁻⁸ mbar) was reached for the evaporation of the metal top electrode. A Keithley multirange ohmmeter was used to measure the resistivity in dc mode.

For the capacitance measurements the silver top electrode was taken as ground and the bias voltage was applied to the aluminum or tantalum back electrode. Hence, a positive bias voltage means an increase of the remaining field strength E_{\text{residual}}, whereas a negative bias weakens it. Capacitance measurements were always performed at 0 V bias by monitoring the charging current when a saw tooth voltage of 0.1 V with dU/dt = 0.02 V/s was applied. Experiments dealing with the temporal changes of the capacitance under applied bias voltage always show values taken at 0 V. The bias voltage was interrupted for the measurement period.

Oxide thickness were confirmed ex situ by time of flight-secondary ion mass spectroscopy and X-ray photoelectron spectroscopy sputter-profile measurements.

**Results**

*Electrochemical oxidation.*—A typical oxidation cyclovoltammogram (further called cv) of a freshly evaporated aluminum film is shown in the upper view graph of Fig. 3. Starting with a cathodic current density j = 20 μA cm⁻² at E_{SCE} = −1.1 V the current increases up to a plateau current density I_{pl} = 1.3 μA cm⁻². In the cathodic sweep the current rapidly drops to zero.

The cv changes when the sample is exposed for 2 h to dry oxygen atmosphere instead of a transport under nitrogen atmosphere [p(O₂) = 10⁵ Pa], see middle view graph. The cathodic current density at E_{SCE} = −1.1 V vanishes, the current remains at low values (<10 μA cm⁻²) up to a potential of E_{SCE} = −0.4 V. Then the current increases and shows a pronounced overshoot. The overshoot is followed by a plateau current, which has the same value as in the previous experiment. The current overshoot is usually explained by the sequence of two processes:

1. At first emission of O₂⁻ and Al³⁺ ions starts from the oxide-electrolyte and metal-oxide interfaces, respectively.
2. Subsequently the charge carriers meet the opposite interface, further oxide growth starts and the current settles down to I_{pl} again.15,39

The retarded onset of the plateau current density (ΔE ≈ 0.8 V) of the gas phase oxidized sample compared to the freshly prepared sample can thus be taken as a measure for the thickness of the gas phase oxide layer, d_{gpo}. It would correspond to d_{gpo} = 0.8 V · E_{form} = 1.4 nm (E_{form} = 1.6 V/m⁰.₄₀). This value differs from that one found previously for polished wires (d_{gpo} = 2.5 nm).40 We think that this difference might be due to the higher defect density of polished wires. A value of 2.5 nm could also be reproduced for metal films, which were evaporated with a higher rate of 0.1 nm/s. These samples had a higher roughness (5 nm) than the ones evaporated with 0.01 nm/s (1 nm) as determined by AFM measurements. The results show that the final thickness of gas phase oxide layers decreases with decreasing defect density of the aluminum surface. For single crystals even smaller values of 0.4 nm were found.41

The potential of the current overshoot can also be taken as a tool to study inhomogeneous oxide structures. An inhomogeneous structure was produced in the following manner: Half of the metal film was transported under nitrogen atmosphere and oxidized under the droplet cell by a cv with E_{final} = +3.0 V. Drop cell positioned in the center of the film as shown in the inset. Middle view graph: Cyclovoltammogram of an aluminum film exposed for 1 h to ambient conditions. Bottom view graph: Droplet positioned on the intersection of anodically oxidized (E_{final} = 3.0 V) and ambient gas phase oxidized aluminum film (see inset). Cyclovoltammogram taken up to E_{final} = 3.5 V.

![Figure 3](image-url)
Capacitance measurements.— In Fig. 4 capacitances of aluminum-aluminum oxide-silver samples are shown for different bias voltages. The traces show a pronounced dependence on the bias voltage. A negative bias voltage of $U_T = -1\, \text{V}$ leaves the capacitance of the sample in a long term stable state. Zero volt bias voltage leads to a permanent loss of capacitance over the whole time scale. A saturation value does not appear even for $t > 10^5\, \text{s}$. A positive bias $U_T = +1\, \text{V}$, on the other hand, leads to a quite fast saturation for $t > 6 \times 10^4\, \text{s}$.

The observed capacitance losses with positive and zero bias voltages are irreversible and cannot be nullified by a negative $U_T$. Considering the dipole layers at the two oxide interfaces one can easily imagine a field induced exchange processes between the two interfaces. However, this process should be reversible. The nonreversibility points more to either a permanent decrease of the dielectric permittivity $\varepsilon_r$ or to a slight thickness change of the oxide. Considering $\varepsilon_r$ as unchanged during the experiment, one can evaluate a maximum value of the thickness change $\delta(t)$ simply by

$$C(t) = \varepsilon_0 \cdot \varepsilon_r \frac{A}{d_0 + \delta(t)}$$

The thickness change $\delta(t)$ is evaluated from the measurements shown in Fig. 4 and plotted in Fig. 5.

A maximum thickness change of 6 Å is calculated which corresponds to around two monolayers (lattice constant of the oxygen fcc-lattice in $\gamma$ alumina is 2.8 Å$^{42}$).

However, a clear assignment of the capacitance changes to a thickness increase cannot be done on the basis of the data presented here. The data could also be explained by a reduction of $\varepsilon_r$ by 40%.

Corresponding experiments with tantalum-tantalum oxide devices show only constant capacitance values. The results also do not depend on the bias voltage up to $\pm 1\, \text{V}$ and are therefore not shown here.

Resistivity measurements.— In Fig. 6 the resistivities $R$ of 4- and 2 nm thick metal films (aluminum and tantalum) are plotted vs time.

For 4 nm thick tantalum $R$ remains constant at $R = 2500\, \Omega$ from $t = 0\, \text{s}$ to $t = 1.8 \times 10^5\, \text{s}$, whereas $R$ for 4 nm thick aluminum shows a noticeable increase from 730 to 815 $\Omega$ on the same time scale, see upper view graph of Fig. 6. A saturation value of 820 $\Omega$ is reached for $t > 3 \times 10^5\, \text{s}$ (not shown in Fig. 6).

The different behavior of aluminum and tantalum is even more pronounced for 2 nm thick metal films. The tantalum film then
shows a slight increase of the resistivity from 15.4 to 15.8 kΩ, see inset in lower view graph. The aluminum film shows a permanent increase of the resistivity. The rate $dR/dt$ increases again at $t = 1.2 \times 10^{3}$ s. At $t = 1.8 \times 10^{3}$ s $R$ reaches a value of $4 \times 10^{3}$ Ω which is the detection limit of our measurement system. Similar observations could be reproduced for several aluminum samples but a comparable resistivity increase for tantalum samples could never be found.

It should be mentioned that 2 nm thick tantalum films lose their conductivity completely when the thickness of the oxide top layer is increased by 0.4 nm. Hence, tantalum films with thicknesses below 1.5 nm seem to be insulators. So we can exclude thickness changes in the range of several 0.1 nm for the explanation of the resistivity changes for tantalum shown in the lower view graph of Fig. 6.

One can conclude that the resistivity experiments point to a thickness increase of the anodic oxide in the case of aluminum after the end of potentiostatic oxidation. One could thus argue about the observed temporal behavior of the capacitances in aluminum oxide capacitors also in terms of thickness changes. This is done in the next section.

 capacitate and resistivity measurements concordantly point to a stable metal-oxide interface for tantalum-tantalum oxide systems.

**Discussion**

The experiments shown above point to small thickness changes after potentiostatic oxide formation of the aluminum oxide (see Fig. 5). It could be explained by either a migration of aluminum atoms into the oxide or by oxygen ions penetrating the aluminum film. Both processes would be enhanced by an applied positive bias voltage and agree with our experimental results. Keeping in mind the big difference in melting points for Al and Ta $^{43}$ [$T_{\text{melt}}(\text{Al}) = 933$ K, $T_{\text{melt}}(\text{Ta}) = 3290$ K] one can easily imagine that migration of Ta atoms into the oxide appears at a much lower rate than the parent process for Al.

A migration of oxygen ions to the oxide surface might also occur. It can be detected by the oxidation of adjacent metal layers (see upper view graph of Fig. 8). The oxidation of evaporated copper films (up to 1 monolayer copper oxide) was found on polycrystalline aluminum oxide $^{44}$ as well as on Al$_2$O$_3$$(0001)$ single crystal surfaces $^{45}$ both prepared in ultrahigh-vacuum. Albeit the migration of oxygen ions into the silver is not supported by a positive bias, one could speculate that the small capacitance loss, which appears even at a negative bias voltage (see zoom in Fig. 5), might be due to that process.

This observation might also be due to a more or less instantaneous chemical reaction of the metal with the surface layer of the oxide. Hydroxide layers can be found on anodic oxide surfaces $^{46,47}$. They may provide reactants for an oxidation reaction of the top metal $^{48}$ by 2 OH$^-$ + M$^{\text{top}}$ → H$_2$ + 2 O$^{2-}$ + M$^{\text{top}}_{\text{aq}}$. This reaction was found to be important for Cr, Fe, Co, Ni, but less significant for the noble metals $^{49}$.

Since our resistivity measurements show clearly that the main processes occur at the bottom interface, our results will be discussed in the frame of the two following processes (both occurring at the aluminum-oxide interface):

1. Al-atom migration into the oxide.
2. Excess oxygen migration from the oxide into the Al layer.

At first a simple macroscopic description is analyzed. Then two more detailed models considering the above-mentioned processes are discussed.

**Macroscopic description.**—The initial oxide thickness at $t = 0$ s after oxide formation is $d_0$. During the thickness increase $[d(t) \neq 0]$ the field strength $E_{\text{oxide}}$ in the layer (initial value $E_{\text{residual}}$)

$$\text{Resistivity change of a } \approx 4 \text{ nm thick aluminum film (evaporated with 0.5 nm/s) as function of time after anodic oxidation of a 6 nm thick top layer aluminum oxide.}$$

![Figure 7: Resistivity change of a 4 nm thick aluminum film](image7)

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decreases \( \propto 1/d \). From a simple point of view one can assume a proportionality between the instantaneous field strength \( E_{\text{residual}} \cdot d \omega \) and the growth rate \( d(t) \), thus giving

\[
\frac{d(t)}{d(t)} = A \cdot E_{\text{residual}} \cdot \frac{d_0}{d(t)} [2]
\]

\( A \) is a proportionality constant \( ([A] = [m^2/(V \text{ s})]) \). To get a value of \( A \) we interpret the resistivity measurements in Fig. 6 in the following way:

The oxide thickness after formation was 8 nm \( (d_0 = d(0) s = 8 \text{ nm}) \). \( E \) at \( t = 0 \) s is taken to be \( E_{\text{residual}} \): The remaining aluminum lost its resistivity completely at \( t_{\text{end}} = 1.5 \times 10^5 \text{ s} \). Thus we set \( d(t_{\text{end}}) = 10 \text{ nm} \).

The solution of Eq. 2 is

\[
d(t) = \sqrt{2} \cdot A \cdot E_{\text{residual}} \cdot d_0 \cdot t + d_0^2 [3]
\]

leading to \( A = 2.5 \times 10^5 \text{ m}^2/(V \text{ s}) \). Equation 3 delivers the well known parabolic law. But saturation values as found in the experiments do not match with Eq. 3. Hence, one has to look for different models.

Microscopic description: Migration of oxygen ions.— The hopping of ions in amorphous oxides can be treated as transport between two local potential minima (see lower view graph of Fig. 8).

We consider a system where a nonstoichiometric ion can hop between two lattice sites with an activation energy \( E_a \). Due to the remaining field strength in the oxide one has to consider a hop along an asymmetric potential scheme. The uphill transition rate against the field strength \( E_{\text{oxide}} \) may then be written as

\[
k_1 = \nu \cdot e^{-E_a/2k_BT} \cdot d_{\text{oxide}}(t) [4]
\]

Downhill the electric field strength the transition rate is

\[
k_1 = \nu \cdot d_{\text{oxide}}(t) [5]
\]

The downhill density \( n_d \) will populate and the uphill density \( n_u \) depopulate according to first order rate equations

\[
\begin{align*}
    n_u &= k_1(t)n_d - k_1(t)n_u \\
    n_d &= k_1(t)n_d - k_1(t)n_u
\end{align*} [6]
\]

The initial conditions for the ion densities at \( t = 0 \) s directly after oxide formation are named \( n_u^n \) and \( n_d^n \). For the solution of the differential equation system including the differentiation of forward and backward reactions one can get \( n_u(t) - n_u(t) \) as

\[
n_u(t) - n_u(t) = \frac{1}{k_1(t) + k_1}(k_1(t) \cdot n_u^n - n_u^n - n_u^n)
\]

\[
-2 \cdot e^{-|E_a|/2k_BT} (k_1(t) \cdot n_u^n - k_1(t) \cdot n_u^n)
\]

\[
+ k_1(t) \cdot (n_u^n + n_u^n) [7]
\]

Multiplying the above term with the oxide thickness \( d_{\text{oxide}} \) gives the number of ions \( N_{\text{oxide}} \) which leave the oxide per unit area. As a simple approximation we take \( 3/5 \cdot N_{\text{oxide}} \) to be oxygen ions which migrate into the aluminum film. Each oxygen ion may reduce 2/3 Al ions. The number of Al atoms per m² in one (111) layer \( N_{\text{Al}} \) can be estimated to be

\[
N_{\text{Al}} = a_{\text{Al}} \cdot \sqrt{3} \cdot \rho(\text{Al}) \cdot \frac{M_{\text{mol}}(\text{Al})}{M_{\text{Al}}(\text{Al})} [8]
\]

with \( \rho(\text{Al}) \): density, \( M_{\text{mol}}(\text{Al}) \): molar weight, \( a(\text{Al}) \): lattice constant of the Al.

The number of oxidized aluminum layers \( \ell \) is then

\[
\ell(t) = \frac{2}{5} \cdot d_0 \cdot \frac{n_u(t) - n_u(t)}{\rho(\text{Al}) \cdot \sqrt{3} \cdot \frac{M_{\text{mol}}(\text{Al})}{M_{\text{Al}}(\text{Al})}} [9]
\]

where \( d_0 \) denotes the thickness of the oxide layer at \( t = 0 \) s. Since \( k_1(t) \) and \( k_1(t) \) are functions of time and thereby depend on the oxide thickness, the equation system 4-9 cannot be solved analytically. The equations are thereby iteratively solved on a time mesh with \( t = 0.1 \text{ s} \) resolution. Densities of mobile ions \( n_u = n_u^n = 0.5 \cdot 3/5 \cdot \rho(\text{Al}) \) were used according to Möhring, who determined the amount of mobile species by modeling the current overshoot in the cv of anodic oxidation. In Eq. 4 and 5 the hopping distance \( d \) is taken to be half of the oxides lattice constant \( a (a = 2.8 \times 10^{-10} \text{ m})^{1/2} (d = 1.4 \times 10^{-10} \text{ m}) \). The attempt frequency \( \nu \) can be taken from the phonon frequency of the oxide. Characteristic phonon frequencies found by electron energy loss spectroscopy in nonstoichiometric oxide films are found at 400 and 960 cm⁻¹ corresponding to around 10¹² s⁻¹ for \( \nu ^{\text{ac}} \).

Plots of \( \ell(t) \) are exemplified for three different values of the activation energy \( E_a \) (see lower view graph of Fig. 9). A saturation value (further called \( \ell_s \)) of \( \ell_s \approx 4 \text{ Å} \) is calculated. The activation energy determines the time dependence until the saturation value is reached. The experimental limitations (start and end of data recording \( t > 10 \text{ s}, t < 3 \)
Table I. Capacitance changes $\Delta C$ of samples with different initial oxide thickness $d_0$ measured at $U_T = 0$ V; $\ell_\nu$ is evaluated by Eq. 1 with a constant $e_\nu$.

<table>
<thead>
<tr>
<th>$d_0$ (nm)</th>
<th>$\Delta C$ ($\mu$F cm$^{-2}$)</th>
<th>$\ell_\nu$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.7</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>0.31</td>
<td>4</td>
</tr>
<tr>
<td>3.9</td>
<td>0.19</td>
<td>3</td>
</tr>
<tr>
<td>4.8</td>
<td>0.13</td>
<td>4</td>
</tr>
</tbody>
</table>

$\times 10^5$ s) restrict the comparison with the theoretical model to activation energies $0.9 \text{ eV} < E_a < 1.2 \text{ eV}$. The corresponding depletion of mobile charge carriers in the oxide is shown in the upper view graph of Fig. 9.

The calculated values for $E_a$ from 1.0 to 1.2 eV are somewhat lower than the values of the activation energy for oxygen self-diffusion ($\approx 2.2 \text{ eV}$) in polycrystalline alumina.

Albeit the maximum value of the thickness increase at $t = \infty$ is quite near to the experimentally found value of 6 Å, one has to discuss several shortcomings of the model:

1. The maximum thickness increase $\ell_\nu$ scales linearly with the initial oxide thickness $d_0$ [see Eq. 9]. This cannot be confirmed by capacitance measurements. The evaluation of the capacitance changes $\Delta C$ for samples with different initial oxide thicknesses $d_0$ is listed in Table I. An evaluation with Eq. 1 leads to more or less constant thickness changes $\ell_\nu$. This is not consistent with Eq. 9.

2. The evaluated maximum values of $\ell_\nu$ in Fig. 5 can only be explained by reasonable values of $\delta$, $E_{\text{oxide}}$, and $E_a$ when a quite high amount of mobile species of $n_\nu^0 = n_\nu^0 = 0.5 \cdot 3/5 \cdot p_{\text{Al}_2\text{O}_3}$ is assumed.

Therefore a different approach has to be considered.

Aluminum vacancies are likely to be found on $\gamma$-alumina interfaces. In our case an aluminum-deficient amorphous oxide could induce an ionization of aluminum atoms and a subsequent migration of cations into the oxide film. This would lead to a consumption of the aluminum layer lying below the oxide and a slight oxide growth.

Microscopic description: Aluminum cation migration.—An ionization of aluminum atoms and a subsequent migration of aluminum cations could depend both on the electric field strength applied to the sample. The electric field resident in the oxide film will influence the first layers of the aluminum film since the screening length in the metal film is of the order of the lattice constant. A field dependent “melting” or “viscous flow” of monolayer metal atoms and subsequent solution into the oxide is thus conceivable.

The formulation of field dependent transition rates is equivalent to that one presented in Eq. 4, 5, and 7. As $n_\nu(t = 0 \text{ s})$ we take the areal density of aluminum atoms in one monolayer $N_{\text{Al}}$ as $n_\nu^0 = 4.2 \times 10^{19}$ atoms m$^{-2}$. The state $n_\nu^0$ is taken to be the $\text{Al}^{3+}$ ion state in the aluminum-oxide interface which is assumed to be empty at $t = 0$. The jump distance $[\delta(E) \text{ in Eq. 4 and 5}]$ from the metal substrate into empty interstitial sites in the interface is taken to be $\delta = 1.2 \text{ Å}$. The areal density of oxygen interstitials and subsequent oxidation of the bottom metal contains several deficiencies (high amount of several 10% for concentration of mobile species, proportionality to initial oxide thickness). But, activation energies $E_a$ in the range from 0.9 to 1.2 eV were found to coincide with the temporal evolution of the capacitance as well as the resistivity measurements. Additionally, the calculated proportionality of the oxide growth after the end of potentiostatic oxidation to the initial oxide thickness is not in concordance with the experiments.

This discrepancy might be caused by an inhomogeneous potential distribution. Especially at the interfaces the potential drop might be more pronounced than in the bulk of the oxide.

Conclusion

Recapitulating, we can state that field strength dependent migration processes modify the properties of anodic oxides even in ultra-high vacuum after the end of potentiostatic oxidation. However, these effects are much more significant for aluminum than for tantalum. This big difference is surprising since the electrochemical properties (cyclovoltammogram, migration of both ion types during growth, film formation factor) are quite similar. After the end of potentiostatic oxidation both oxides will contain mobile cation and anion species. These results cause the necessity to discuss aging processes in terms of both anion and cation migration.

A simple macroscopic description gives a parabolic law, which does not explain the observed saturation values for the thickness increase.

Figure 10. Upper view graph: Calculated depletion of one monolayer aluminum in contact with amorphous oxide (jump distance $\delta = 1.4 \text{ Å}$) plotted for different tunnel voltages across a 2.4 nm thick oxide layer. Activation energy $E_a = 0.9 \text{ eV}$. Lower view graph: Same calculation as above with $E_a = 1.1 \text{ eV}$. Calculations performed for $T = 300 \text{ K}$.
A microscopic description concerning the migration of metal cations into the oxide is in accordance with the experimental data for the same activation energies as in the anion migration model. The cation migration can be justified by metal vacancies at the metal-oxide interface (in the case of aluminum oxide) and is thus independent of the oxide thickness.

The simplest argument for the difference between tantalum and aluminum found in the experiments may be due to the difference in the melting points of the metals. For aluminum atoms one could speculate about a lower activation energy for a hopping process from the metal into the oxide compared to tantalum.

Moreover, one difference might be the absence of tantalum vacancies at the tantalum-oxide interface. This would hinder the diffusion of further metal atoms into the oxide.

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