1. Introduction

Aluminum (Al) appears to be a drosophila system when it comes to the scientific exploration of oxidation processes on metal surfaces. The unbroken interest that lasts already for several decades lies on practical economic as well as fundamental scientific grounds. Al oxidation follows a self-passivating scheme and spontaneously terminates at \( \approx 2 \) nm oxide thickness almost independent of the reaction pressure and temperature. Aluminum is therefore a common admixture to metallic compounds to establish corrosion protection at ambient conditions. In this respect, the oxidation of Al-containing metal alloys has been investigated in detail, with special focus on W–Al, Ti–Al and Ni–Al systems. The self-passivating oxide grown on NiAl(110) takes hereby a special role as its structure, composition, and electronic properties were studied down to atomic length scales with various surface-science techniques.

Aluminum oxidation has also been identified as a prototype reaction that proceeds according to the Cabrera–Mott scheme. The starting point is the build-up of an electric field across the emerging oxide film, stimulated by spontaneous electron tunneling from the metal/oxide interface to the oxide surface. The tunneling electrons attach to adsorbed O\(_2\) molecules and promote their dissociation to oxygen anions. The electric field now drives the diffusion of cations from the metal/oxide interface and anions from the surface toward the reaction zone. In the case of Al, mass transport during oxidation is governed by the outward diffusion of Al\(^{3+}\) ions, whereby the enhanced Al mobility may lead to the formation of hollow structures, according to the Kirkendall effect. With increasing oxide thickness, the efficiency of the charge transfer diminishes, partly because of the finite tunneling length of electrons, and partly because of the decreasing potential gradient between metal/oxide interface and oxide surface. As a result, Cabrera–Mott oxidation terminates spontaneously at a few nanometer oxide thickness. For Al, the critical thickness value was determined to \( \approx 2 \) nm at low-temperature conditions, in full agreement with the predictions of Cabrera and Mott. Thicker films only develop at oxidation temperatures above 550 K, when the reaction switches to the Wagner scheme, controlled by the drift motion of cations and anions along potential gradients in the emerging oxide layer.

The decisive role of field-driven mass transport in the Cabrera–Mott mechanism has been impressively demonstrated with experiments performed in presence of an external electric field. For this purpose, preoxidized Al(111) was bombarded with low-energy electrons to induce charging effects, that is, a surface electric field, which indeed sustained the oxidation reaction beyond the expected Cabrera–Mott thickness. The build-up of an electric field could even be separated in time from the \( O_2 \) exposure, proving that the electron bombardment not only stimulates \( O_2 \) dissociation but is indeed a requirement for the mass transport during oxidation. Accompanying theoretical studies on Al oxidation revealed that both the diminishing electric field and the reduced \( O_2 \) binding strength to the dielectric surface terminate the oxidation process. With the suspended charge...
transfer through the oxide layer, the formation of peroxy- or super-
peroxo-oxygen species comes to an end, while neutral O$_2$ molecules
are unable to adsorb. The self-passivation of aluminum and other
metals is thus inherently connected with the efficiency of charge
transfer from the metal/oxide interface to the oxide surface.[11,12]
Al oxidation in the ultrathin limit is typically explored with
X-ray photoelectron spectroscopy, probing the rise of the Al$^{3+}$
2p and O 1s peak intensities upon oxidation.[14,15,19] The approach
is however limited to relatively low oxygen chemical potentials,
given the sensitivity of the method to high-pressure backgrounds.
In this work, we use an entirely optical scheme to probe oxidation
processes in situ with high temporal resolution. The method is
based on changes of the optical transmittance of metal films upon
oxidation and neither restricted to low pressures nor tempera-
tures. It was recently utilized to analyze the oxidation behavior
of copper at O$_2$ pressures between 10$^{-3}$ and 100 mbar and temper-
atures between 400 and 700 K.[21] The experiments revealed that
the Cabrera–Mott mechanism is decisive only in early stages of the
reaction, whereas Cu mass transport along grain boundaries
becomes relevant later in the process.[22] Also, the Cu$_2$O to
CuO phase transition at 550 K renders the oxidation behavior dif-
ferent from the one expected for simple metals.[23] We exploit our
experience on Cu oxidation to investigate the passivation reaction
of Al and its pressure and temperature dependence in this work.
Our optical analysis reveals a two-step oxidation scheme, with an
initial fast step that proceeds up to $\approx$2 nm oxide thickness and a
subsequent slow one that leads to further oxide thickening and
depends on pressure and temperature.

2. Results and Discussion

2.1. Analysis of the Transmission Data

Figure 1 shows transmission spectra of differently thick Al metal
films deposited prior to oxidation. The optical response at short
wavelengths is governed by the Drude behavior of free electrons
with $\approx$15 eV plasma frequency.[24] At longer wavelengths, the
transmission increases again and runs through a shallow maxi-
mum at 850–900 nm, related to Al interband transitions at the W
and $\Sigma$ points of the Brillouin zone.[23] The wavelength-
specific transmittance as a function of film thickness follows the
Lambert–Beer law (Figure 1c). If reflections at surface and
interface are neglected, an absorption coefficient of $\alpha =$ 0.15 nm$^{-1}$ is derived, in good agreement with tabulated data.[26] To retrieve the Al oxidation characteristic, a reliable sim-
ulation of the measured transmission traces is essential, as dis-
cussed in detail in Section 2.2. For pure metal films, the
transmission response was calculated with Al slabs of variable
thickness and bulk dielectric properties.[24] The results poorly
matched the experimental data and overestimated the transmis-
sion at short wavelengths (Figure 1a). To improve the fit, a dielec-
tric function measured explicitly for thin Al films was used,[27] yet
without solving the discrepancy to experiment. The agreement
could be significantly improved by introducing a finite roughness
to the Al layer that mimics its polycrystalline texture. For this
purpose, spherical Al islands with $\approx$7 nm radius and a midposi-
tion located 3 nm below the surface were placed on top of the
slab. The best fit to an experiment performed with a 7 nm Al film
is shown by the long-dashed curve in Figure 1a. To confirm that
pronounced surface roughness is indeed responsible for the optical
behavior, the morphology of as-grown Al films on glass was
recorded with scanning tunneling microscopy (STM). The STM
topography in Figure 1b clearly reveals the granular nature of the
films, as reflected by 5 nm rms roughness. The pronounced film
granularity is caused by the weak Al–glass adhesion, giving rise
to 3D Vollmer–Weber growth, and the high mobility of hot Al atoms arriving on the surface.[28] The granular morphol-
ogy also affects the oxidation behavior of the Al films, as
discussed later.

Figure 1. a) Optical transmission spectra of differently thick Al metal
films, and corresponding best fits using bulk (grey solid line) and thin-film dielectric
functions (black dashed line).[27] Reliable fitting needs to account for the film granularity via truncated Al ellipsoids placed on the surface (long-dashed curve). b) STM topographic image of a 15 nm thick Al film on glass ($600 \times 600$ nm$^2$, $U_g = 1.5$ V, $I = 1$ nA). c) Transmission at 850 nm of differently thick Al films plotted on a logarithmic scale. A linear fit to the data reveals the Al absorption coefficient $\alpha$. 

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Figure 2 shows two series of transmission spectra, recorded during the oxidation of Al films at a) 400 K, 10 mbar O₂ and b) 600 K, 100 mbar O₂. The spectra are color coded and display the evolution of the transmission response during vacuum annealing (gray) and oxidation (red–blue). The dashed and solid black lines on top represent the sample state at the end of the oxidation step and after oxygen cool-down, respectively. The inset in (a) shows the difference of the transmission curves (2) and (1) from the series in (b).

The relevant quantity to be evaluated is therefore the transmitted intensity during oxidation as it reflects the continuous conversion of Al metal into transparent alumina with 8 eV bandgap. In the two experiments of Figure 2, the transmitted intensity remains constant during the initial warm-up, but quickly increases after first O₂ contact, as seen by the large spacing of the red spectra. In the course of the reaction, adjacent curves crowd together, and the blue and yellow lines cannot be separated anymore. This bunching indicates a decreasing speed of oxidation. Minor spectral changes become visible after the oxidation step during O₂ cool-down, when an additional peak appears at 820 nm (Figure 2a, inset). This modification is reversible and the peak vanishes again upon heating the sample in vacuum. Without going into detail, we assign the new feature to absorptive elements in the growing alumina film. Good candidates are O vacancies or color centers that produce discrete optical transitions inside the oxide bandgap. No assignment to a specific defect type can be made as the transition wavelength depends on charge state and local environment of the vacancy in a presumably amorphous oxide layer.[30] The oxygen deficiency is removed during O₂ cool-down, causing the absorption band to disappear, but reappears upon vacuum annealing in agreement with the observations.

2.2. Retrieval of the Aluminum Oxidation Kinetics

To extract information on the time-dependent oxide growth, the optical transmission series were fitted to Al/Al₂O₃ slabs on optically thick glass, using tabulated dielectric functions for bulk Al and Al₂O₃.[24] The simulations were based on the transfer-matrix method that accounts for multiple coherent transmission and reflection paths in a multilayer optical system.[21,31,32] Two sample geometries have been tested for their ability to reproduce the experimental data, an Al/Al₂O₃ bilayer and a trilayer system with Al at the bottom, mixed Al/Al₂O₃ at the interface, and Al₂O₃ on top. The optical response of the interface layer was described by the Maxwell Garnett and Bruggeman approach, accounting for isolated plasmonic particles and percolated particle chains embedded in a homogenous optical medium, respectively.[33,34] Insertion of an interfacial layer was found to be crucial to
describe oxidation reactions in Cu films as it mimics preferential oxidation along grain boundaries in the material. In the case of aluminum, however, an Al/Al2O3 bilayer model turned out to be sufficient to reproduce the experimental data, suggesting the development of planar reaction fronts. In fact, the presence of a metal/oxide interface layer hardly affected the fitting results, as the wide-gap alumina adds no signature to the transmission spectra. Having set the oxidation model to an Al/Al2O3 bilayer geometry, all optical series were fitted with one set of parameters using an automatized search routine that minimizes the rms error between experiment and simulation. The fitting procedure translates the observed transmission rise into the oxidation of metallic Al to transparent alumina, whereby other Al losses, for example, via evaporation, are discarded at our experimental conditions. As no information on stoichiometry and crystallinity of the alumina film is available, we report the reduction of the Al layer thickness in the following.

A compilation of our Al oxidation experiments, performed at various temperatures and O2 pressures, is presented in Figure 3. All thickness curves were set to identical start values to remove tiny modulations in the Al coverage. The Al thickness remains constant in the initial heating step, but sharply drops once oxygen is supplied and the reaction gets ignited. Two regimes can be distinguished in the course of the reaction. The first one is characterized by high oxidation rates, accounts for more than 75% of the total metal/oxide conversion and lasts for about 100 s. The subsequent regime exhibits considerably lower rates and continues until the end of the experiment, yet with diminishing speed. To find a mathematical description of the oxidation behavior, we have fitted the changes in Al layer thickness to common rate laws reported in the literature. A direct and an inverse logarithmic law were considered for the initial fast regime, according to ΔAl(t) = A – B · ln(t) and ΔAl(t)^−1 = A – B · ln(t), respectively, the latter in accordance with the Cabrera–Mott theory. For the slow regime, a power-law dependence ΔAl(t) = A – B · t^α was tested, whereby α = 0.5 would be in line with Wagner’s oxidation model. The fast oxidation process could indeed be reproduced with both logarithmic laws, with the direct one yielding slightly better results (Figure 3b, inset). The slow regime, on the other hand, was fitted to a power law with exponent α = 0.1, much smaller than in Wagner’s theory. Although best fits are shown only for the 500 K oxidation trace, similar results have been obtained for all other experimental runs. Apparently, the Al oxidation follows a similar mechanism over the entire pressure and temperature range explored here.

To make the oxidation behavior at different temperatures and pressures comparable, we linearized the growth curves in the fast and slow regime. The derived slopes reflect the oxide growth rates k in nm s⁻¹ and have been plotted for different oxidation parameters in Figure 4. The temperature-dependent data are plotted in an Arrhenius format to extract the activation barrier for Al oxidation. The k values revealed for the fast process fall approximately on a straight line, corresponding to a single activation energy of E_{act} = (6 ± 2) kJ mol⁻¹. For the slow regime, a larger slope is found in the Arrhenius plot and the derived energy increases to E_{act} = (12 ± 2) kJ mol⁻¹. As no Arrhenius behavior is expected for the pressure dependence of oxidation, these data are plotted in a k–p diagram and fitted to a power law. The deduced exponent amounts to 0.3 for the fast oxidation regime, but lies below 0.1 for the slow one, suggesting an almost pressure-independent rate. Panels (c) and (d) of Figure 4 finally show the total decrease of the Al layer thickness during oxidation.

Figure 3. a) Decrease of the Al layer thickness due to oxidation at different temperatures and 10 mbar O2 pressure. b) Similar data but for different O2 pressures and a fixed temperature of 600 K. The inset shows a fit of the 500 K/10 mbar oxidation curve to a direct (brown) and inverse (orange) logarithmic time dependence as well as to a power law (blue). While the first two laws are applied to the fast oxidation regime before 200 s, the latter describes the subsequent, slow process.
The latter is the anticipated behavior for Cabrera–Mott oxidation, as identified in many earlier Al oxidation studies.\(^{10–15}\) It makes a number of predictions that can be tested for the actual experimental results.

First, Cabrera–Mott oxidation that relies on field-driven transport of cations and/or anions to the reaction zone intrinsically leads to self-limited oxide growth.\(^{1,8}\) The reason is the finite tunneling length of electrons from the metal/oxide interface to the oxide surface.\(^{20}\) Typical tunneling lengths of electrons in wide-gap insulators are of the order of 1–2 nm, and alumina films grown by spontaneous Al oxidation are indeed always in this range.\(^{10,14,18,37}\) Our data reveal corresponding film thicknesses only at oxidation temperatures below 450 K, whereas high-temperature, high-pressure conditions enable the oxide to thicken above 2 nm (Figure 4). In fact, the deduced oxide thickness exhibits a pronounced temperature dependence, which seems in contrast with a solely field-driven mechanism.\(^{37}\) However, also the Cabrera–Mott model predicts a temperature-dependent oxidation rate according to:

\[
\frac{d\Delta d}{dt} \approx \exp\left(\frac{-U + qaE_0\Delta d}{k_B T}\right),
\]

with \(U\) the rate-limiting diffusion barrier, \(E_0\) the electric field across the oxide layer, \(q\) the cationic charge, and \(a\) the typical hopping distance in the oxide.\(^{13}\) This can be used to calculate a maximum oxide thickness \(\Delta d_{\text{max}}\) to be obtained in a Cabrera–Mott-type process. For this purpose, the growth rate is set to a small value, typically 1 monolayer per 10\(^5\) s, and the electric field is expressed with help of the oxide thickness. The derived inverse relationship between thickness and temperature, \(\Delta d_{\text{max}} \approx T^{-1}\),

Figure 4. Rates of the initial fast and the subsequent slow oxidation process shown a) logarithmically as a function of inverse temperature and b) linearly as a function of pressure. While lines in (a) are Arrhenius-type fits, those in (b) serve as guides to the eye. c) Changes of the Al-layer thickness in the total (black symbols) and fast oxidation process (red symbols) for different temperatures. d) Similar data for different O\(_2\) pressures and 600 K temperature. The inset in (d) demonstrates the linear relationship between oxidized Al layer thickness and inverse temperature, as discussed in the text.

for all temperatures and pressures used in this study. Apparently, the metal/oxide conversion increases continuously with temperature, whereby nearly 75% of the turnover occurs in the fast process. Conversely, two regimes are revealed for the pressure dependence. While the converted Al layer thickness increases up to 100 mbar O\(_2\) pressure, it saturates above this value. Again, most of the metal/oxide conversion takes place in the initial fast oxidation step.

### 2.3. Discussion

The aforementioned experiments provide in situ oxidation traces for polycrystalline Al slabs measured in a wide range of pressures and temperatures and over extended time intervals. None of the oxidation curves could be described with a single rate law, that is, a logarithmic, inverse-logarithmic, or parabolic time dependence. A reliable mathematical description was possible only if the oxidation process was divided into an initial fast and a subsequent slow regime, to be fitted separately.\(^{15,36}\) The boundary between both regimes was set, somewhat arbitrarily, to the end of the fast decay of the Al-layer thickness at around 100 s. As fast and slow process continuously pass over into each other; no precise transition point is discernible, which however has no effect on the following discussion. The initial, fast oxidation regime is reliably fitted to both direct and inverse logarithmic time dependencies (Figure 3). The latter is the anticipated behavior for...
can now be fitted to height values measured at the end of the fast oxidation step (Figure 4d, inset). Despite the good match, we abstain from reading off further quantities from the fit, such as the diffusion barrier, because of the large structural uncertainties of the growing oxide film. The temperature dependence of the oxide thickness confirms however that Cabrera–Mott oxidation is a thermally activated and not only a field-driven process, in agreement with the intrinsic nature of diffusive mass transport. The finite temperature in our experiments also explains why a direct logarithmic time dependence describes the data better than the inverse logarithmic law of Cabrera and Mott that is valid only at low temperature (Figure 3b).[8]

The pressure dependence of the fast oxidation step can be derived from changes in the rate constant \( k \) and the Al layer thickness \( \Delta Al \) with \( O_2 \) pressure (Figure 4b,d). Whereas both the rate constant and the oxidized Al height monotonously increase with pressure below 100 mbar \( O_2 \), they saturate above this threshold. The finding is compatible again with the Cabrera–Mott model, where the field gradient between oxide surface and metal/oxide interface largely drives the reaction. The surface electric field is hereby controlled by the coverage of \( O_2 \) adsorbates, which in turn depends on the gas-phase pressure according to Langmuir’s adsorption theory.[37] In thermal equilibrium, the surface coverage rises almost linearly in the limit of low pressures, but flattens off and becomes constant as the pressure rises. This behavior reflects the gradual filling of the available oxygen adsorption sites until saturation coverage is reached. The saturation pressure, in turn, depends on the surface temperature, with an increasing desorption yield or, equivalently, a lower sticking coefficient of adsorbates revealed at high temperature.[39] In Al oxidation studies performed at 300 K, a saturation pressure of \( \approx 1 \) mbar was determined,[3,37] a value that rises to 100 mbar at the 600 K used in the experiment of Figure 4b. Beyond this value, the oxidation rate and converted Al layer thickness become nearly pressure-independent, as the saturation coverage of oxygen is reached.

The fast and presumably Cabrera–Mott-type oxidation step is followed by a slower regime that proceeds for extended time periods and shows no self-termination. One characteristic of this second process is a much steeper temperature dependence that gives \( (12 \pm 2) \) kJ mol\(^{-1}\) activation energy in an Arrhenius fit, almost twice as large as for the fast regime. The higher activation energy is responsible for a reduced metal/oxide conversion rate, and most of the oxide growth indeed happens in the initial, fast step (Figure 4c). However, it makes the second regime also more relevant for high-temperature oxidation, when the activation barrier is easily overcome. Indeed, the Al fraction converted in the fast with respect to the total process becomes smaller as the temperature rises, until almost 30% of oxide growth occurs in the second regime at 700 K (Figure 4c). Conversely, the slow regime exhibits almost no pressure dependence and proceeds with similar rates throughout the entire \( O_2 \) pressure range. This insensitivity excludes a Cabrera–Mott-type process, in which the coverage of adsorbed anions controls the efficiency of field-driven diffusion and thus of the entire reaction. A pressure-independent rate, as observed in the slow regime, rather points to thermally activated diffusion as a prerequisite for Al oxidation. This is supported by the constant difference in converted Al layer thickness at the end of the fast regime with respect to the total reaction for all \( O_2 \) pressures (Figure 4d). Finally, the slow oxidation regime exhibits a weak, power-law dependence on time, in contrast to the logarithmic behavior revealed for the fast process (Figure 2b).

The succession of two oxidation regimes has been reported earlier for aluminum,[15,36] but also for other metals such as copper.[12] Whereas the fast regime is consistently assigned to the Cabrera–Mott mechanism, especially at low oxidation temperature, the nature of the slow process is still under debate. Its activation barrier is twice as large as for the fast regime, where atoms diffuse due to a combination of electric-field and thermal effects,[18,19] but much lower than for atom diffusion in bulk oxides.[17,39] Several concepts have been proposed to solve this discrepancy. Amorphous oxides, as typically formed during Al oxidation,[11,15] exhibit a large number of low-coordinated lattice sites that facilitate atom hopping in response to a concentration gradient. The result is a temperature-dependent transport scheme through the emerging oxide layer, as conceptually described in the early oxidation models of Bedford, Tammann, and Wagner.[16,40,41] Especially at high temperatures, partial crystallization of the oxide may take place, resulting in nano- or microgranular films.[31,42] Material transport in this case is substantially promoted by grain boundary diffusion and numerous oxidation experiments have been explained with this concept.[35,39,43] Typical activation barriers for boundary diffusion are of the order of 20–40 kJ mol\(^{-1}\) and exceed the value extracted for the slow regime here.[44,45] Independent of the exact mechanism, either defect- or boundary-mediated diffusion, thermally activated motion of Al species through a poorly ordered oxide layer seems decisive for Al oxidation in the second, slow regime. The underlying theoretical concept is based on Fick’s diffusion that predicts a power-law dependence of the transport rate on time with an exponent \( \alpha \) of 0.5.[1,16,41] At special conditions, also cubic laws were found with \( \alpha = 0.3 \), still larger than the \( \alpha = 0.1 \) derived here.[45] To solve this discrepancy, insights into structural properties of the emerging alumina films are required in the future. The main property of the slow oxidation step is, however, its nonpassivating character, which enables oxide thickening beyond 2 nm. As the process gets activated only above 450 K, it is not in conflict with the common perception of self-limited Al oxidation at room temperature.

3. Conclusion

An in situ optical approach has been used to monitor the oxidation of aluminum as a function of temperature and oxygen pressure. The reaction was found to proceed according to an initial fast and a subsequent slow regime. The fast oxidation process hereby follows the Cabrera–Mott mechanism, and shows moderate temperature, yet pronounced pressure dependence up to 100 mbar \( O_2 \). It self-terminates at 1–2 nm oxide thickness. The subsequent slow regime, on the other hand, shows steeply increasing oxidation rates at high temperature, but little pressure dependence. It is tentatively assigned to thermally activated Al diffusion through a highly defective oxide toward the surface, where oxidation takes place. The maximum oxide thickness exceeds 2.5 nm at 700 K oxidation temperature and 100 mbar \( O_2 \) pressure. The transition between the slow and fast regime
demonstrates the breakdown of Cabrera–Mott oxidation at elevated temperature and large oxide thickness.

4. Experimental Section

The experiments were performed in an ultrahigh-vacuum system \((p = 1 \times 10^{-5} \text{ mbar})\) that comprises a preparation chamber equipped with an Al effusion cell, mass spectrometer, and sample heating stage as well as a high-pressure oxidation cell.\(^{21,22}\) The latter enables in situ oxidation experiments performed at \(O_2\) pressures of up to 1 bar (purity 99.9995%) and 300–800 K temperature, realized with encapsulated halogen lamps of 100 W heating power. To monitor the progress of the reaction, the optical transmission was thereby monitored not only in the 60 min of oxidation, but also during initial vacuum annealing and oxygen cool-down after the reaction. The samples were prepared by room-temperature deposition of 5–20 nm Al (purity 99.999%) onto sonicated and acetone-cleaned cover glasses. The layer thickness was detected with a quartz microbalance and verified later by fitting the transmission intensity to the Lambert–Beer law of absorption. Immediately after deposition, the samples were transferred to the high-pressure cell and heated to the designated temperature. The actual oxidation was ignited by setting up the desired \(O_2\) pressure within 3 s. To analyze the surface morphology of as-deposited Al films, the samples could be explored ex situ with a table-top scanning tunneling microscope.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data available on request due to privacy/ethical restrictions.

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