Impact of Granularity on the Oxidation Kinetics of Copper

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Polycrystalline copper films with mean grain sizes varying by three orders of magnitude are prepared to correlate morphology and oxidation kinetics of metals. The films are oxidized to cuprous oxide at well-defined pressure and temperature conditions, monitoring the progress of the reaction by in situ optical transmission spectroscopy. The oxidation kinetics is retrieved by fitting the optical data to a three-layer Cu$_2$O/Cu$_2$O–Cu/Cu model with the central layer accounting for the inhomogeneity of the oxidation front due to grain boundaries. The analysis reveals the highest oxidation rates for Cu films with finest granularity, demonstrating the decisive role of grain boundaries for Cu mass transport during oxidation. Moreover, reaction rates are found to differ by one order of magnitude for oxidation along the grain boundaries and into the crystalline Cu grains. In fact, slow oxidation into the Cu crystallites is responsible for an incomplete metal-oxide conversion in the case of coarse-granular films. The experiments demonstrate the direct interplay between morphology and oxidation kinetics for metals.

1. Introduction

The oxidation of metals is a topic of huge economic and scientific relevance. One reason is the enormous financial damage due to corrosion every year, the other reflects the large efforts to fabricate tailor-made oxide materials for applications in heterogeneous catalysis, microelectronics, and optics. Over the years, numerous theoretical concepts have been developed to describe the time, temperature, and pressure dependence of oxide growth. Most of them provide an empirical and macroscopic view of oxidation, reducing the process to a few mechanistic steps.[1,2] Prominent examples are the Wagner theory that treats metal oxidation in the framework of ion diffusion in local electric fields and the Cabrera–Mott approach where electron tunneling across an emerging oxide layer is the pivotal step.[3,4] The microscopic aspects of metal oxidation, in contrast, are hardly accounted for in the classical models. In particular, the role of morphological peculiarities, such as defects, impurities, and grain boundaries, is often neglected.

This simplification stands in sharp contrast to experimental observations. Especially, low-temperature oxidation rates are often higher than those predicted by the classical theories, a gap that reduces at elevated temperatures.[5] To get an impression of the discrepancy, activation energies for oxidation reactions shall be compared, the latter providing a measure for diffusive mass transport in the sample. Experimental values, as extracted from Arrhenius analyses, are typically three times lower than the calculated diffusion barriers for crystalline solids. More specifically, while the activation energy for low-temperature Cu oxidation was measured to be 30–40 kJ mol$^{-1}$ by means of thermogravimetry, ellipsometry, or optical spectroscopy,[6–9] the associated diffusion barrier in crystalline Cu$_2$O was calculated to be 100 kJ mol$^{-1}$ with different theoretical models.[10,11] Experimental and theoretical activation barriers only converge beyond 1000 K oxidation temperature.[6,12]

The discrepancy can be solved when the mass transport along grain boundaries is considered.[13–15] In fact, activation energies for Cu diffusion along Cu$_2$O boundaries have been calculated to be 40 kJ mol$^{-1}$, in good agreement with the experimental data.[7,16] The pivotal role of boundary diffusion for metal oxidation was verified for other metals as well. An early example concerns the oxidation of Ni, where diffusion processes have been monitored by means of tracer methods.[13,17] Derived diffusion coefficients were found to be three orders of magnitude higher for grain boundaries than the bulk NiO lattice. Similar trends were obtained for Fe oxidation that requires an activation energy of $\approx 190$ kJ mol$^{-1}$ at 700 K,[18] whereas calculated barriers for Fe and O diffusion of 450 and 480 kJ mol$^{-1}$, respectively, are much higher.[19] The concept of grain boundary diffusion was also used to rationalize the low-temperature oxidation of Cr to Cr$_2$O$_3$ and Al to Al$_2$O$_3$.[20,21] Si oxidation to SiO$_2$ represents an interesting exception, as boundary-controlled processes seem irrelevant here probably due to the amorphous nature of the oxide film.[14] Density functional theory (DFT) calculations were carried out to gain a mechanistic understanding of the enhanced diffusivity along boundary defects.[22] Mainly the open packing of atoms and the large number of vacancies were found to promote boundary diffusion, whereas the locally modified electronic structure plays only a minor role. Although the relevance of grain boundaries for metal oxidation is generally accepted nowadays, the experimental basis of this important concept is still weak.

In this work, we have explored the impact of granularity and surface roughness on the experimental oxidation rate of copper. For this purpose, copper thin films with different morphologies...
have been prepared, either by copper deposition at elevated temperatures or exposing the layers to various post-annealing steps. The resulting morphology in terms of grain density and surface roughness was probed with scanning tunneling microscopy (STM). The actual oxidation was conducted in a high-pressure cell at defined pressure and temperature conditions and monitored in situ by ultraviolet (UV)–visible (vis) transmission spectroscopy. Our study provides a clear and quantitative correlation between sample morphology and oxidation characteristic, with finer granularity promoting faster reactions. This result underlines the unique role of boundary diffusion for mass transport in an oxidation process.

2. Results and Discussion

To explore the interplay between film morphology and oxidation kinetics, we produced five sets of copper thin films on glass, each one with a unique granularity. The nominal film thickness was set to 50 nm in all cases by means of a quartz microbalance. The smallest grain sizes were achieved by room-temperature Cu deposition (sample A), whereas a moderate ripening effect could be initiated by postannealing the samples to 600 and 700 K for 60 min (samples B and C). Coarse-granular films were produced by Cu deposition onto glass substrates preheated to 600 and 700 K (samples D and E). Sample preparation at even higher temperatures did not result in flat and homogeneous Cu films, and their oxidation behavior could not be compared with the ones of the low-temperature samples.

To monitor the time evolution of Cu to Cu2O conversion, optical transmission spectra were recorded during the oxidation procedure. The spectra were fitted with a user-programmed software to appropriate three-layer models of the sample, composed of a homogenous Cu2O top, a Cu bottom, and a Cu2O–Cu mixed layer in between (Figure 1).[23] The interfacial layer accounts for an inhomogeneous metal-oxide reaction front and mimics an oxidation process that proceeds along grain boundaries of the material.[24] The boundaries were modeled with the Bruggeman mean-field approach,[25] either as percolated Cu2O chains in copper or Cu percolations in Cu2O at the beginning and end of the reaction, respectively. A simplified Cu2O/Cu two-layer model did not allow for successful data fitting, demonstrating the spatially inhomogeneous nature of the reaction front. Also, CuO inclusions in the different layers did not improve the fitting accuracy, in line with an oxidation temperature of 420 K, being too low for Cu2O to CuO conversion. More details of the fitting procedure are given in the Supporting Information.

2.1. Film Morphology

Figure 1 shows a selection of STM topographic images for as-grown, postannealed, and preheated Cu thin films. For the as-grown sample (A), the grain structure is well reflected in an array of protrusions separated by dark boundaries. Statistical analysis of several measurements revealed a grain density of \((6 \pm 2) \times 10^{10} \text{ cm}^{-2}\), which goes along with a surface roughness of \(\approx 3.5 \text{ nm}\). Postannealing to 600 and 700 K (samples B and C) hardly changed these values, apart from a moderate decrease in the grain density and a small flattening effect. Apparently, ripening processes are not effective for compact Cu layers at the given temperature.[26] Drastic morphological changes were observed, however, after Cu deposition onto preheated samples (D and E). The respective STM data displayed large Cu grains.
with several 100 nm diameter, being separated by trenches that are most pronounced at 600 K deposition temperature (Figure 1c,d). Accordingly, the grain density decreased to $(2 \pm 0.5) \times 10^7$ and $(1.5 \pm 0.5) \times 10^6 \text{cm}^{-2}$ for 600 and 700 K deposition temperatures, respectively. Moreover, a 3–4-time larger surface roughness was detected, as individual crystallites protruded from the surface by several nanometers. High-temperature Cu deposition seems thus to be suited to alter the film morphology, probably because large grains form right at the beginning and no postorganization of the crystallites is required in subsequent annealing steps. The impact of film morphology on the oxidation kinetics of copper will be discussed in the following paragraph.

2.2. Optical Data

Optical transmission spectra of the bare Cu films, produced by the aforementioned preparation schemes, are shown in Figure 2. Although the nominal film thicknesses are identical in all three cases, the spectral shape varies considerably, indicative of pronounced morphological differences. Spectra of as-grown (A) and postannealed films (B and C) are perfectly simulated with a homogenous 50 nm-thick Cu slab on glass. The characteristic spectral shape hereby results from the Drude behavior of the Cu free electrons that interferes with the d-band absorption below 600 nm. Conversely, the data of preheated samples have to be treated with a refined geometry to account for enhanced surface roughness. The best match to the experiment is revealed with a Maxwell–Garnett approach that models the optical response of spheroidal metal particles in a dielectric host (Supporting Information). The surface roughness is well reproduced by a mixture of 90% Cu in form of oblate particles and 10% vacuum. The remaining deviations at long wavelengths are explained with the size distribution of Cu grains that have not been considered in our fitting procedure.

The evolution of the optical transmittance during Cu oxidation is shown by three spectral series in Figure 3. The blue curves hereby reflect the optical response of the initial Cu films, as discussed earlier. As the oxidation proceeds (color change from blue to red), the long-wavelength transmittance continuously increases, whereas the maximum redshifts and flattens out. At the end of the series (black curves), the characteristic signature of a dielectric material is developed with high transmittance in the gap region and a more or less steep decline at 600 nm. A Tauc analysis of the spectral shape reveals a mean gap size of 2 eV, in good agreement with the bandgap of cuprous oxide (Supporting Information). Although the general evolution of the transmittance follows a similar behavior for the differently prepared samples, a closer inspection reveals a number of deviations. The first one concerns the absolute sample transmittance after oxidation. While the as-grown films (A) reach 40% transmittance above 700 nm wavelength, this value decreases to 25% and 20% for postannealed (B and C) and preheated samples (D and E), respectively. For the latter, not even the high-wavelength plateau, typical for dielectric materials, has developed, and the overall spectral shape still resembles the one of metallic copper. Nonetheless, the oxidation process has

![Figure 2](Image)

**Figure 2.** Optical transmission spectra and respective best fits of a) as-grown, b) post-annealed, and c) preheated Cu films of $\approx 50 \text{nm}$ thickness. While a regular Cu slab is sufficient to model the data in (a,b), the pronounced film roughness has to be accounted for in (c).

![Figure 3](Image)

**Figure 3.** Spectral series acquired during oxidation of a) as-grown, b) postannealed, and c) preheated Cu samples at 420 K and 100 mbar O$_2$ pressure. The spectra are color coded and proceed from blue to red in the indicated periods of time. The endpoint of each reaction is represented by a black curve, acquired 2400 s after the reaction onset.
reached a quasi-equilibrium state in all cases, as deduced from the bunching of cyan, yellow, and red curves in the panels (b) and (c) and the relatively small change from red to black lines, the latter being measured 30 min later. Apparently, a thorough Cu–Cu$_2$O conversion is only achieved for as-grown films at the given conditions (420 K, 100 mbar O$_2$), whereas the reaction remains incomplete for postannealed and preheated Cu films.

To analyze the oxidation kinetics in more detail, each spectrum of an experimental run has been fitted to the Cu$_2$O/Cu$_2$O–Cu/Cu three-layer model shown in Figure 1f. It should be noted once more that the mixed layer in the center of the slab has been introduced to describe oxidation along the grain boundaries of the film, as discussed in our earlier work.[24] To visualize the level of agreement between experiment and simulation, two arbitrarily selected spectra from each series in Figure 3a–c are shown together with their best fits in Figure 4a–c. The agreement is compelling, suggesting that our model geometry is able to mimic the morphological changes in the sample during oxidation. A general assessment of the fit quality is shown in Figure 4d and depicts the root-mean square (RMS) error between experiment and simulation in the course of the reaction. Total errors are small and typically one order of magnitude lower than the best fits obtained with a Cu$_2$O/Cu two-layer model. Larger deviations only occur for postannealed films, where they arise from undulations in the transmittance at long wavelengths (Figure 4b, lower panel). A possible reason is the excitation of plasmons in isolated Cu grains surrounded by Cu$_2$O, a scenario that is not adequately treated in the Bruggeman approach.[25] The initial error in simulations of the preheated Cu films relates to the larger surface roughness of these samples, which is not accounted for in our automatized fitting routines to reduce the number of free parameters.

The fitting of the optical data now provides morphological insights into the Cu samples during oxidation, for example,

![Figure 4](image-url)

**Figure 4.** Experimental transmission curves and corresponding best fits at two points in time during the oxidation of a) as-grown, b) postannealed, and c) preheated Cu samples. d) Evolution of the RMS error between experiment and best fits during oxidation. All spectra have been simulated with the three-layer model shown in Figure 1f.

![Figure 5](image-url)

**Figure 5.** a) Cu$_2$O growth curves for the five Cu samples (A–E), as derived from spectral fitting of the transmission curves shown in Figure 3. Averaged oxidation rates of the samples A–E, determined from the slopes of the Cu$_2$O growth curves in the time interval between b) 100 and 200 s and c) three later periods of time.
on the thickness of the Cu₂O top layer and the Cu₂O/Cu ratio in the mixed layer. Figure 5a shows the Cu₂O growth in the samples explored in this study, whereby the total thickness comprises the oxide contributions in top and mixed layers. Evidently, the initial oxidation rate is similar in all five samples, in other words; the first 20 nm of Cu₂O forms equally fast in as-grown, post-annealed, and preheated Cu films. In the as-grown films, oxidation continues with a comparable speed up to a 45 nm nominal oxide thickness, beyond which the reaction slows down and finally levels out at 2000 s. The final oxide thickness of 75 nm corresponds to a complete Cu to Cu₂O conversion, which explains the high transmittance of sample A in Figure 3a. The oxidation behavior of sample B, postannealed for 1 h at 600 K, is similar to the one of the as-grown film. Again the oxidation rate sharply decreases after the formation of nominally 45 nm Cu₂O; however, the final oxide thickness saturates already at 58 nm or 75% Cu conversion. In contrast, only 43 and 38 nm nominal oxide thickness is reached for 700 K postannealed and preheated copper samples, corresponding to 57% and 50% metal conversion, respectively. The high amount of unreacted copper, especially in the last two samples, rationalizes the strong metallic signature in their transmission spectra (Figure 3c).

To analyze the different oxidation courses in more detail, we take a closer look on the Cu₂O growth rates in different time intervals of the reaction. For this purpose, segments of the growth curves have been linearized, and the respective slopes are plotted in Figure 5b,c. In the initial reaction stage between 100 and 200 s, the slopes are generally largest, yet decrease from 0.27 in sample A to 0.16 nm s⁻¹ in sample E. In the next interval (500–1000 s), only the as-grown films (A) maintain an appreciable speed of oxidation of 0.02 nm s⁻¹, whereas all other rates drop below 0.01 nm s⁻¹. A similar picture arises for the third interval (1000–1500 s), only that the absolute rates decrease even further. In the last period from 1500 to 2000 s, all growth rates have dropped below 0.005 nm s⁻¹, indicating that the reactions have essentially stopped in all five samples.

2.3. Correlation between Oxidation Kinetics and Film Morphology

The final section of our work aims at developing an oxidation model for Cu films of different morphologies on the basis of the experimental data. The emphasis lies on the grain boundaries, the abundance of which varies by two orders of magnitude between as-grown (10¹⁰ cm⁻²) and preheated Cu films (10⁶ cm⁻²). We start our discussion with the reaction onset, i.e., the first 200 s after exposing the samples to O₂. In this regime, high oxidation rates are revealed independent of the film morphology, suggesting that neither the grain boundaries, nor the surface roughness are important for the process. The observation is compatible with a Cabrera–Mott-type mechanism, in which electron tunneling from the metal-oxide interface through the emerging oxide film is responsible for activating and dissociating the incoming O₂ molecules. The emerging ions then propagate through the oxide layer, following the electric field, and react to an oxide precursor. The tunneling process is independent of film morphology, explaining the similar reaction rates for all five samples. It exclusively relies on the wave function overlap between the Cu interface and the ad-oxygen and therefore self-terminates if the oxide thickness reaches 3–5 nm. At this stage, the Cabrera–Mott scheme breaks down and is replaced by more long-range oxidation mechanisms that depend on the sample morphology.

The rate-limiting step in all subsequent oxidation schemes is the diffusive transport of either O species into or Cu species out of the sample. In the case of Cu oxidation, the latter process prevails, as proven by tracer experiments and the observation of the reverse Kirkendal effect. The most successful oxidation model in the limit of thick films is the Wagner theory, which assumes ion diffusion due to local charge imbalances as the decisive step. This links the speed of oxidation directly to the diffusion of Cu cations and brings the sample morphology into play. Ion diffusion in crystalline solids is governed by site exchange processes between vacancies and regular lattice sites and typically requires large activation energies. In the case of Cu, hopping barriers of about 100 kJ mol⁻¹ have been predicted by theory. Such barrier heights were indeed found in high-temperature oxidation experiments, where lattice diffusion of copper is the main process. Low-temperature Cu oxidation, in contrast, is governed by reduced activation energies of ≤40 kJ mol⁻¹, being assigned to Cu transport along grain boundaries. Boundary diffusion is promoted by the structural disorder between two crystalline regions of the sample and relies on a reduced packing density of atoms and a higher concentration of vacancies and defects. These microscopic peculiarities explain enhanced diffusion along grain boundaries as compared with crystalline areas.

In search for an analytic relationship between morphology and oxidation kinetics, the reaction rates in the first time interval from Figure 5b were plotted against the grain density in the different Cu samples (Figure 6a). The correlation is obvious; high oxidation rates are found for as-grown and postannealed films with small Cu grain sizes, whereas preheated films made of large crystallites exhibit much lower rates. Even a direct proportionality is revealed when the oxidation rate is plotted against the square root of the grain density, a procedure that may be rationalized as follows. Enhanced mass transport is expected along the entire perimeter of the N copper grains in the surface, scaling with \( d_{peri} \approx N \cdot \pi \cdot r_{Grain} \). The grain radius, in turn, connects to the grain density via \( \rho_{Grain} = \frac{1}{N} \cdot \frac{1}{r_{Grain}} = \frac{N}{A} \) with A as the sample area. By combining both equations, a square root relation between perimeter length and grain density is found and the oxidation rate scales with \( d_{peri} \approx \sqrt{\rho_{Grain}} \approx k \). Although the statistical basis of our study is small, a corresponding plot seems to support this relation. Our reasoning is supported by the activation energy for Cu oxidation, as derived from the temperature-dependent reaction rates discussed in our earlier work. The deduced barrier height of 35 kJ mol⁻¹ is in good agreement with grain boundary diffusion yet much lower than for bulk diffusion. A particular role of grain boundaries was also suggested from transmission electron microscopy data that successfully visualized the preferred copper oxidation along boundary defects. Finally, we have tested a possible interplay between measured oxidation rates and surface roughness of the five different Cu samples; however, could not reveal a convincing relationship (Figure 6c).
Also in later intervals, the oxidation rates of the five explored Cu samples feature different time behaviors (Figure 5c). All growth curves display a distinct kink after \( \approx 200 \text{ s} \) \( \text{O}_2 \) contact time; however, the realized oxide thickness at the kink position deviates substantially. For as-grown and mildly postannealed films, the kink position emerges after the consumption of approximately two-thirds of the initial copper metal. At this point, the fast-moving reaction front along the grain boundaries reaches the backside of the Cu film, and the supply of fresh metal for oxidation declines markedly. In other words, the discontinuity arises as the boundary oxidation is replaced by a reaction that moves into the crystalline grains (Figure 7). This assignment bears two interesting aspects. First, from the different slopes before and after the kink position, the ratio between boundary- and grain-oxidation rates can be approximated. While a ratio of around 10 is found for as-grown films, it reaches more than 50 for the postannealed ones. As absolute grain densities are similar in both cases, the large deviation may give a hint on structural differences between the boundary defects. While rough and disordered boundaries with low diffusion coefficients are expected for as-grown films, the boundaries may straighten up and increase their transport capacity for postannealed samples. Consequently, the speed of oxidation decreases more drastically when switching from a boundary to an in-grain regime in the latter case. Second, the kink position provides insight into the mean width of the boundary-mediated oxidation channels. Considering the definition of the perimeter length from above, it can be approximated to 18 nm for as-grown films at the kink position. The mean radius of the initial Cu grains has reduced from \( \approx 25 \text{ nm} \) to \( \approx 17 \text{ nm} \) at this stage, i.e., only one-third of the metal volume is left when the oxidation switches to the slower in-grain regime. Nonetheless, the reaction completes in the remaining 2000 s of the experiment, and a final Cu to Cu\(_2\)O conversion of 95% is reached.

A similar scenario, yet with different numbers, can be developed for the preheated films with a grain density that is two orders of magnitude lower than for the as-grown ones. Here, the oxidation front reaches the backside of the sample, already at 20 nm nominal oxide thickness, which corresponds to 25% metal conversion. The reason is the lower weight of grain boundaries in the oxidation process, being only partly compensated by an increased width of the oxidized channels (\( \approx 80 \text{ nm} \)).

At the kink position, the initial grain radius is reduced from \( \approx 460 \) to 420 nm, i.e., compact metal cores are left when the oxidation regime produces a kink in the oxide growth curves. While reaction rates are sufficiently fast to complete the oxidation of fine-granular films, almost 50% of the copper remains unreacted in films with larger Cu crystallites.

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**Figure 6.** Dependence of the initial Cu oxidation rate from Figure 5b on a) the mean grain density of Cu films, b) its square root as a measure of the perimeter length of Cu grains, and c) the surface roughness. The \( k \approx \sqrt{\rho_{\text{Grain}}} \) plot shows the best correlation.

**Figure 7.** Sketch of the oxidation mechanism of coarse and fine-granular Cu films. After rapid formation of a surface oxide according to the Cabrera–Mott scheme, the oxidation front proceeds along grain boundaries in the sample. The transition to a much slower grain oxidation regime produces a kink in the oxide growth curves. While reaction rates are sufficiently fast to complete the oxidation of fine-granular films, almost 50% of the copper remains unreacted in films with larger Cu crystallites.
oxidation switches from the fast to the slow regime (Figure 7). As a result, the total oxide thickness only reaches 38 nm at the end of the reaction and 50% of the copper remains metallic. The unreacted metal locates in the center of the original Cu grains, an interpretation that is supported by the spectral simulations. At the endpoint of the reaction, the best fit with a three-layer model is obtained with a 50 nm-thick mixed layer composed of 50% metal and 50% oxide, capped by a 20 nm-thick surface Cu₂O film. In contrast, modeling of the as-grown films yields a 20 nm-thick interface layer with just 2% metal inclusions being capped by a 55 nm-thick Cu₂O layer. The bottom Cu layer at the glass interface has dissolved in both cases. The oxidation of the preheated Cu films with their large grains has essentially terminated after 2500 s contact time with oxygen. A thorough oxidation process was monitored in situ by means of optical transmission spectroscopy in a wavelength range of 400–1000 nm. For maximum temperatures of 800 and 1500 K, respectively. The oxidation rate was rationalized by the interplay of a fast boundary-assisted oxidation process and a slow in-grain oxidation regime, implying that the copper is chemically inert at room temperature and only roughness and granularity of the films but not the true atomic configuration was in the focus of the measurements. Further details of the setup can be found in the literature.[24]

The copper films used in this study were deposited onto sonicated and acetone-cleaned cover glasses. The nominal film thickness was set to 50 nm, as determined with a quartz microbalance, and verified with optical transmission data. To start the actual oxidation reaction, the samples were transferred to the high-pressure cell, heated to 420 K, and exposed to 100 mbar O₂ to ignite oxidation. Simultaneously, spectral acquisition was started to follow the reaction progress with 1 s temporal resolution. At the employed conditions, the reaction typically lasted for 2400 s and produced more than 2000 transmission spectra per experimental run. Shorter (longer) oxidation times were realized by increasing (decreasing) the oxidation temperature or increasing (lowering) the O₂ pressure, as discussed in previous studies.[23,24] Spectral fitting was accomplished with a user-programmed software based on the transfer-matrix method that accounts for multiple coherent transmission and reflection paths between the optically active layers and the glass support.[35,36] The material properties of Cu and Cu₂O entered the calculations via their tabulated dielectric functions.[37,38] The optically inhomogeneous Cu₂O–Cu mixed layer in the center of the slab was modeled with Bruggeman’s mean-field approach (Supporting Information). The fitting procedure generated information on the thickness of the three layers as well as the Cu₂O/Cu ratio in the mixed layer at any time of the reaction. It thus enabled us to monitor the progress of oxide formation with a high temporal resolution. The quality of the fit was evaluated with the RMS error between the experimental curves and their best fits.

3. Conclusions

In situ optical transmission spectroscopy has been used to probe the oxidation characteristics of copper films with different morphologies. A clear correlation was found between the granularity of oxide films, the time-dependent oxidation rates, and the metal-to-oxide conversion at the end of the reaction. As-grown Cu films characterized by small grains and a large number of boundaries exhibit the highest oxidation rates and thoroughly oxidize to Cu₂O. Conversely, highly crystalline films prepared by Cu deposition onto preheated samples can be oxidized only to 50% under the thermodynamic conditions of the experiment. The observed oxidation kinetics has been qualitatively rationalized by the interplay of a fast boundary-assisted and a slow in-grain oxidation regime, implying that fine-granular copper films can be oxidized more effectively than their coarse-crystalline counterparts. Our results emphasize the unique potential of optical spectroscopy to follow the reaction processes in situ and develop mechanistic models for metal oxidation.

4. Experimental Section

The experiments were performed in an ultrahigh vacuum chamber (p ≈ 10⁻⁹ mbar), containing a copper effusion cell and two heating stages for maximum temperatures of 800 and 1500 K, respectively. The oxidation reactions were conducted in an attached high-pressure cell that was filled with 10⁻⁵–10⁻⁷ mbar oxygen (99.9995%) and heated to 300–800 K. The oxidation process was monitored in situ by means of optical transmission spectroscopy in a wavelength range of 400–1000 nm. For this purpose, white light from a halogen lamp was focused onto the sample and the transmitted intensity was detected with a Peltier-cooled, single-line charge-coupled device detector. Morphological characterization of the samples was realized with an STM located in a second vacuum chamber and thus required a sample transport through air. However, no deterioration of the experimental results was expected in this case, as copper is chemically inert at room temperature and only roughness and granularity of the films but not the true atomic configuration was in the focus of the measurements. Further details of the setup can be found in the literature.[24]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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