Morphological and Kinetic Insights into Cu$_2$O–CuO Oxidation

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The conversion of Cu$_2$O to CuO thin films is probed in situ with UV–vis transmission spectroscopy at various thermodynamic conditions. The obtained spectral series are simulated with different CuO/Cu$_2$O growth models, using the transfer-matrix method and Bruggeman’s mean-field approach to account for Cu residuals in the oxide matrix. The analysis reveals that Cu$_2$O oxidation proceeds via a flat and homogeneous reaction front, in contrast to polycrystalline copper that preferentially oxidizes along the grain boundaries. The conclusion is supported by the measured activation energy for Cu$_2$O oxidation, which is compatible with Cu diffusion via the bulk oxide and not via line defects. The kinetics of CuO growth is found to follow logarithmic and exponential rate laws at low and high temperature, respectively. While the logarithmic regime is governed by CuO nucleation within the Cu$_2$O phase, the exponential dependence results from self-heating of the sample in the exothermic reaction. In both cases, traces of unreacted copper are detected in the oxide matrix, giving rise to a characteristic tail in the transmission response.

1. Introduction

The formation of inorganic oxides is in the focus of research already for several decades.[1–3] The reasons for this unbroken interest are obvious. Corrosion of metals causes enormous economic damage every year and reliable corrosion protection is, therefore, a formidable task for modern societies. Conversely, inorganic oxides are of economic interest by themselves, for instance, as catalysts in chemistry, dielectric spacers in microelectronics, absorber materials in photovoltaics, or as surface finishing.[4] Several fundamental theories, backed by even more experimental studies, have been developed over the years to describe the principles of metal oxidation. The most common ones are the diffusion-based Tammann model,[5,6] the Wagner theory combining diffusion and electric field effects,[7] and the Cabrera-Mott scheme that accounts for electron tunneling as initial step in an oxidation process.[8] The level of understanding is less advanced when it comes to oxide interconversions, that is, processes in which cations of an inorganic material switch oxidation state in response to an altered oxygen chemical potential. While deeper oxidation is desirable in some cases, e.g., from Cu$_2$O to CuO given the perfect photovoltaic bandgap of the latter,[9] oxide reduction shall be avoided in others, for example, to protect the metal–insulator transition in VO$_2$.[10] In addition, reducible oxides with low switching barriers between high and low oxidation states, such as ceria, are of high economic relevance and play a crucial role as oxygen buffers in heterogeneous catalysis.[11,12] Therefore, a mechanistic understanding, as already reached for the oxidation of metals, is also desirable for oxide interconversions.

Many oxidation theories developed for metals can, however, not be transferred to oxides. This is evident for the widely used Cabrera-Mott scheme, which treats electron tunneling from the Fermi level of a metal through an emerging oxide film as driving force for an oxidation.[8] The presence of a bandgap and the lack of free electrons render this model inappropriate for the description of oxide conversions. Conversely, other approaches, as based on Fick’s diffusion or ion transport in electric fields, retain their validity also in the case of oxides.[7] So far, no universal theory has been developed to analyze deeper oxidation of oxide materials. Instead, many competing approaches are available to satisfy an even larger number of experimental observations that deal with stoichiometry changes in oxides.[4]

This sometimes unsatisfying situation shall be sketched for the example of Cu$_2$O–CuO conversion, providing an introduction to the scientific topic of this study. Formally, the reaction increases the Cu oxidation state from +1 to +2 and doubles the number of O anions in the unit cell (from 4Cu/2O in a 78 Å$^3$ cell to 4Cu/4O in an 81 Å$^3$ cell).[9] Simultaneously, the structural building blocks change from linear O–Cu–O units in Cu$_2$O to square-planar CuO$_4$ groups in CuO. Insights into the thermodynamics of Cu$_2$O–CuO oxidation came mainly from surface-science experiments, using X-ray photoelectron spectroscopy (XPS) to monitor phase changes as a function of O$_2$ pressure and temperature.[12,13] In contrast, the kinetics of CuO formation was monitored via microgravimetry, ellipsometry, and Rutherford backscattering, in combination with electron microscopy and different marker techniques to produce snapshots of the oxide morphology. The experiments unraveled two CuO
growth regimes, following either a parabolic \( d \sim \sqrt{t} \) or logarithmic law \( d \sim \ln(1 + t/t_0) \). While logarithmic laws were mostly found at the onset of oxidation, the parabolic behavior prevailed as the reaction continued and films became thicker. Parabolic laws are typically connected with diffusion-controlled oxidation schemes, in which Cu hops via cationic vacancies in the CuO lattice toward the reaction zone. In contrast, logarithmic laws have been associated with the formation of CuO nuclei in the Cu2O host, or Cu diffusion along grain boundaries.

Alternatively, the development of space-charge layers and inhibited O2 activation at the oxide surface have been suggested as reasons for a logarithmic time dependence of oxidation. Also, reported activation energies for Cu2O–CuO conversion deviate substantially from study to study, possibly due to differences in purity and granularity of the raw material and different oxidation conditions. A general theory that captures the variety of oxidation experiments is neither available for Cu2O nor for other inorganic oxides.

In this work, our recently developed method to follow oxidation reactions in situ via optical transmission spectroscopy has been applied to the reaction from Cu2O to CuO. The technique exploits distinct changes in the dielectric properties of the materials upon oxidation and translates them into oxide growth curves by means of appropriate models. Our analysis reveals that Cu2O–CuO conversion occurs along a planar and homogeneous reaction front, in contrast to Cu oxidation where grain boundaries serve as primary oxidation pathways.

### 2. Results and Discussion

#### 2.1. Analysis of the Transmission Spectra

Figure 2 shows three spectral series, acquired during Cu2O–CuO oxidation at 100 mbar O2 and the indicated temperatures. The spectra are color-coded, running from blue (initial curve) to red (after the given reaction time) in equal time steps. While the blue curves are similar in all three series, proving the identical Cu2O starting point of the reaction, the final states (red/black curves) differ in panel (a) with respect to panel (b) and (c). Apparently, only an incomplete CuO layer develops at 540 K (Figure 2a), whereas the oxidation finishes within 608 and 91 s at 600 K (panel b) and 660 K (panel c), respectively. After a fast initial period, the reaction slows down in time, as deduced from the decreasing spacing of adjacent curves and the closeness of red and black spectra, the latter taken 2300 s after reaction onset. The raw data reveal that the Cu2O–CuO conversion proceeds faster at high temperature, as expected for an activated process.

To start our analysis, optical bandgaps were retrieved from the transmission spectra by means of the Tauc method. For this purpose, the experimental transmittance as a function of wavelength \( T(q) \) is fitted to: \[ \frac{h \cdot c_0 \cdot q}{\alpha} \propto (\ln(T(q)))^{1/\alpha} \]

where \( h \) is the Planck constant, \( c_0 \) is the speed of light, and \( u = 3/2 \) is the exponent for direct-forbidden optical transitions. The gap size...

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**Figure 1.** a) Three-layer model with percolated Cu2O chains in the central layer, being successfully used to describe Cu oxidation as discussed in ref. [20]. b) Corresponding TEM image showing the granular Cu film with an amorphous Cu2O layer on the top (scale bar 20 nm). No TEM data could be acquired for the Cu2O–CuO oxidation step given the insulating nature of the sample. c) Three-layer CuO/Cu2O/Cu2O model used to model Cu2O oxidation in this study.

**Figure 2.** Spectral series acquired during Cu2O–CuO oxidation at 100 mbar O2 pressure and a) 540 K, b) 600 K and c) 660 K oxidation temperature. The spectra are color-coded and proceed from blue to red in the given times and finally to black after 2300 s.
is given by the intercept of a linear fit to \([-q \cdot \ln (T(q))]^{2/3}\) and the energy axis. The obtained values of 2.1 and 1.1 eV at the beginning and end of the spectral series are in good agreement with the reported bandgaps for \(\text{Cu}_2\text{O}\) and \(\text{CuO}\), respectively, demonstrating a rather complete oxide conversion (Figure 3).[9] In between the two extremes, the gap size evolves gradually as the \(\text{CuO}\) fraction in the sample increases at the expense of the \(\text{Cu}_2\text{O}\) phase.

To analyze the time dependence of oxide growth, the optical transmission curves were fitted to different \(\text{CuO}/\text{Cu}_2\text{O}\) model structures, using tabulated \(\text{Cu}\), \(\text{Cu}_2\text{O}\), and \(\text{CuO}\) bulk dielectric functions as input parameters.[23,24] The simulations were based on the transfer-matrix method that accounts for multiple, coherent transmission and reflection paths in a multilayer system deposited on optically thick glass.[25,26] Different sample geometries were tested and iteratively optimized to reduce the rms error between experiment and theory and to approach the real film morphology upon oxidation. For this purpose, the films were modeled with two or three layers, each one comprising either pristine \(\text{Cu}_2\text{O}\), pristine \(\text{CuO}\), or mixtures of one oxide phase and spherical \(\text{Cu}\) particles (Figure 1c,d). The spatial distribution and mutual coupling between the inclusions were approximated with the Maxwell–Garnett and Bruggeman theory for isolated plasmonic particles and percolated particle chains, respectively.[27,28] While the Maxwell–Garnett approach turned out to be unable to reproduce the experimental data, indicating that no isolated particles evolved during oxidation, the Bruggeman theory allowed us to simulate the optical data with high accuracy. The fitting procedure provided information on the thickness of active layers and the amount of \(\text{Cu}\) inclusions at any time of the experiment.

We have started the evaluation of our transmission data with a simple \(\text{CuO}/\text{Cu}_2\text{O}\) two-layer model without metal inclusions. Such an approach would be successful if \(\text{Cu}_2\text{O}\) oxidation proceeds via a planar reaction front that moves through the film. To visualize the level of agreement, arbitrarily selected transmission curves taken at three points in time and two temperatures are compared with their corresponding best fits (Figure 4). The overall match is good at short wavelengths, e.g., below 750 nm at 660 K oxidation temperature, but gets worse as wavelength increases. Moreover, the agreement is better at higher oxidation temperature, as also revealed from the root mean square (rms) errors of the fits across the spectral series (Figure 4d). In fact, the error seems largest in the wavelength region of the oxide bandgaps, with the measured transmission being systematically lower. This discrepancy points to effective scattering/absorption centers located in the gap region of the oxides, a phenomenon that is often empirically treated with an Urbach tail.[29]

An Urbach tail causes the transmittance to increase only gradually when moving into the gap region of a dielectric material and is typically modeled with an exponentially decaying \(k\)-part (absorptive) of the complex refractive index. To test whether an Urbach tail would reduce the rms error of our simulations, we have extrapolated the \(k\)-part of the \(\text{CuO}\) refractive index with such an exponential decay into the gap region (Figure 5a, green curve). The new refractive index indeed improves the fitting of the experimental data over the entire wavelength range, as demonstrated for the last curve of the 660 K series in Figure 5b and with the reduced rms error in Figure 4d (open circle). This success provides indirect evidence for the presence of absorptive centers in the \(\text{CuO}\) gap region, yet without insight into their nature.

Following the concept of Urbach tail, we have refined our structure model for the \(\text{Cu}_2\text{O}–\text{CuO}\) conversion by adding a third layer that holds the anticipated absorptive centers. As sample preparation was conducted with high-purity materials at ultra-high-vacuum conditions, we propose that unreacted copper might be responsible for the tail. The extra layer, thus, contains \(\text{Cu}\) inclusions either in a \(\text{Cu}_2\text{O}\) or \(\text{CuO}\) matrix and locates at the bottom of the sample close to the glass interface (Figure 1c,d). Several \(\text{Cu}\) arrangements have been tested, among which the percolated \(\text{Cu}\) spheres of the Bruggeman model yield the best match with the experiment, as shown in Figure 6. In the upper panels (a–c), the \(\text{Cu}_2\text{O}–\text{Cu}\) mixed layer lies below the regular \(\text{CuO}/\text{Cu}_2\text{O}\) sequence of the two-layer model. The corresponding simulations perfectly reproduce the experimental data at the reaction
onset, when CuO only forms in the upper half of the sample and does not interfere with Cu residuals at the interface. The agreement deteriorates as the oxidation continues and the reaction front reaches the buried particles. At this point, a two-layer sequence composed of a CuO top and a CuOCu interface layer yields better results (Figure 6d–f). The same trend is reflected in the rms errors, plotted for the oxidation course in Figure 6g. While the CuO/CuOCu model performs better in the second half of the reaction, the CuO/Cu2O/Cu2OCu three-layer model gives lower errors at the beginning. However, both models are clearly superior to a plain CuO/Cu2O double layer without Cu inclusions.

Summarizing the first results, the Cu2O–CuO conversion is best accounted for by a flat reaction front that steadily moves through the oxide film. The reduced transmission in the oxide gap region is ascribed to unreacted copper near the glass interface that might be insusceptible to oxidation due to a favorable crystal structure exposing unreactive Cu(111) facets. The Cu2O–CuO conversion seems to follow a different mechanism than the oxidation of polycrystalline copper described in our earlier work. There, a two-layer model, mimicking a flat metal-oxide interface, was found to be unsuitable to fit the experimental data and a network of percolated Cu and Cu2O chains was required for simulation. Apparently, diffusion processes along...
grain boundaries are decisive for copper oxidation, whereas a planar reaction front seems sufficient to model the Cu₂O–CuO conversion in this work. More evidence for this conclusion is provided in the following paragraph.

2.2. Time Dependence of CuO Growth

Based on the two- and three-layer models discussed previously, an automated fitting routine was developed for the spectral series, delivering the nominal CuO thickness and the amount of residual Cu in the sample at any point in time. The resulting CuO growth curves for experiments performed at 100 mbar O₂, 80 nm initial Cu₂O thickness, and the indicated temperatures are shown in Figure 7a. As expected, the Cu₂O–CuO conversion proceeds slowly and remains incomplete at low temperature, but accelerates as the temperature increases. For example, while only 10% of the Cu₂O layer converts to CuO within 1500 s at 480 K, the oxidation finishes in ≈100 s at 660 K. The Cu₂O oxidation thereby proceeds at high rates at the onset of reaction and slows down as more and more Cu₂O gets consumed. By linearizing the growth curves between 20–60 nm (660 K), 9–48 nm (600 K), 7–13 nm (540 K), and 3–5 nm (480 K), a rate constant kᵣ is determined and plotted in an Arrhenius-type diagram in Figure 7b. A linear fit to the data yields an activation energy of (79 ± 17) kJ mol⁻¹. Moreover, the amount of unreacted copper, associated to the long-wavelength tail in the optical data, was found to decrease from 18% to 5%, 3%, and finally 1% as the oxidation temperature increased from 480 to 540, 600, and 660 K, respectively (Figure 7c). The gradual disappearance of metallic copper demonstrates the increasing oxidative power at higher temperature, i.e., the increasing oxygen chemical potential.

To gain a mechanistic understanding of CuO formation, the initial oxidation period has been fitted to common rate laws predicted by different oxidation models.[2,5,7,8] Later stages of the reaction were omitted as the limited availability of Cu₂O and not the reaction kinetics controlled the growth behavior. The following dependencies have been tested: logarithmic \( d(t) \approx \ln(1 + t/t₀) \), power \( d(t) \approx (1 + t/t₀)^{1/p} \) with \( p = 2 \) and \( 3 \) for parabolic and cubic laws, and exponential \( d(t) \approx \exp(1 + t/t₀) \). A logarithmic behavior was found for the low-temperature growth of CuO, but changed to a linear and an exponential regime at 600 and 660 K oxidation temperature, respectively (Figure 7d–g). These findings will be compared with classical oxidation models in the final part of our article.

2.3. Mechanism of CuO Growth

Our in situ optical view onto Cu₂O–CuO oxidation has produced two main results. The first one is the flat and homogeneous reaction front that can be satisfactorily described with a two-layer model when Cu residuals at the backside of the sample are accounted for. A flat CuO/Cu₂O interface is in sharp contrast to the spatially inhomogeneous reaction front found for copper oxidation, where grain boundaries in the polycrystalline film serve as oxidation channels (Figure 1a).\(^{[20]}\) Apparently, grain-boundary diffusion is less important for the Cu₂O–CuO conversion described here, for the following reasons. The oxidation of both, Cu and Cu₂O, are governed by an outward diffusion of copper and not by an inward flux of oxygen, as concluded from tracer experiments and the observation of the Kirkendall effect.\(^{[16,31,32]}\) The Cu species are transported either via grain boundaries or Cu vacancies in the bulk material, resulting in two distinct activation energies of about 40 and 100 kJ mol⁻¹, respectively.\(^{[20,33–35]}\)
Earlier Cu$_2$O–CuO oxidation studies revealed activation energies of 106 and 114 kJ mol$^{-1}$ for reactions conducted at 100 mbar O$_2$ and 700 and 1000 K temperature, respectively. Only in a single work on highly crystalline samples, a reduced activation energy of 38 kJ mol$^{-1}$ was reported that would be compatible with grain-boundary diffusion. The activation energy of 80 kJ mol$^{-1}$ measured here also lies in the range of bulk-diffusion processes. The negligible role of domain boundaries points to a nano-crystalline or even amorphous nature of our Cu$_2$O films, an assumption that is supported by cross-sectional transmission electron microscopy (TEM) images taken during the Cu–Cu$_2$O oxidation step (Figure 1b). Although the granular character of the metal is clearly resolved, the Cu$_2$O top layer seems featureless and without discernable domain structure. The development of amorphous Cu$_2$O is expected from the low oxidation temperature of 420 K, which ensures the development of phase-clean Cu$_2$O without CuO inclusions, but is too low to trigger crystallization of the film.

The second outcome of our study is an oxidation rate that follows a logarithmic law below 600 K but changes to an exponential behavior above this temperature. Various temperature courses have been reported for the Cu$_2$O–CuO conversion in the literature. While logarithmic laws were preferentially found at the onset of Cu$_2$O oxidation, the behavior changed to parabolic or even cubic dependencies in the course of the reaction. Parabolic rate laws are consistently assigned to diffusion-mediated oxidation schemes, whereas some ambiguity exists in the interpretation of the logarithmic laws. A common explanation is the blocking model of Davies et al., which assumes successive closure of low-energy diffusion paths in the Cu$_2$O host due to compressive strain exerted by the spatially expanded CuO phase. Other models consider the activated formation of CuO nuclei in the Cu$_2$O matrix as the reason for logarithmic growth. Also, the development of space-charge layers across the reaction front, quantum-mechanical tunneling of electrons, or reduced dissociation rates of O$_2$ molecules were discussed in the context of logarithmic rate laws. We favor an interpretation based on the CuO nucleation model because our Cu$_2$O films lack specific low-energy diffusion channels and are unsuscetible to electron tunneling and enhanced oxygen adsorption right from the beginning. However, a final explanation for the logarithmic CuO growth curves at low temperature cannot be given in this study.

Beyond a critical temperature of 600 K, the CuO thickness increases exponentially in time, at least in the first half of the reaction (Figure 7g). Such an accelerated growth was also observed in Cu-oxidation studies performed at high temperature and O$_2$ pressure, i.e., high oxidation yields. The exponential dependence was explained with self-heating of the sample in the exothermic reaction, resulting in a gradual temperature rise and an increased reaction rate. A similar scenario is proposed for the high-temperature Cu$_2$O oxidation also in this study. The Cu$_2$O–CuO conversion is an exothermic process and releases 146 kJ mol$^{-1}$ thermal energy. For a 80 nm thick Cu$_2$O film on 10 x 10 mm$^2$ glass (0.3 μmol), the process generates 0.05 J of heat and leads to a temperature increase of 2080 K, as calculated with a Cu$_2$O heat capacity of 70 J mol$^{-1}$ K$^{-1}$. Even if a substantial portion of the heat is dissipated via thermal transport through the glass or radiation cooling, self-heating of the sample seems a plausible cause for the observed exponential growth. A similar behavior is not detected at low temperature, where the Cu$_2$O–CuO turnover and thus the exothermic heat release...
per time is insufficient to compensate for dissipative losses, and the reaction temperature stays constant. The Cu$_2$O oxidation at 600 K is a special case, where the logarithmical deceleration of the reaction due to hindered mass diffusion and the exponential increase due to self-heating balance out to yield a linear CuO growth curve (Figure 7f). Independent of the initial regime, the growth curves flatten out toward the end of the reaction when most of the Cu$_2$O precursor is consumed (Figure 7a). The proposed mechanism of self-heating is not easily confirmed in our study, as the reactive Cu$_2$O volume is negligibly small and does not lead to a measurable temperature increase in the sample holder. A validation might be possible in future by replacing the glass support with a sapphire holder of high thermal conductance, which drains the heat from the reaction zone and prevents self-heating of the oxide films.

3. Conclusions

Optical transmission spectroscopy has been exploited for monitoring the Cu$_2$O–CuO interconversion at various thermodynamic conditions. The reaction proceeds along a uniform and planar reaction front and not along grain boundaries, as observed previously for copper oxidation. This is in line with the derived activation energy of $\approx 80$ kJ mol$^{-1}$, being compatible with Cu diffusion through a bulk material. At low temperature, the oxidation follows a logarithmic rate law that might be governed by the formation of CuO nuclei in the Cu$_2$O host. At higher temperature, the growth develops an exponential time dependence, being assigned to self-heating of the sample during the exothermic reaction. Our experiments have demonstrated that optical spectroscopy can be applied as powerful in situ technique to follow oxidation processes with high temporal resolution. It, therefore, seems to be an interesting alternative to classical approaches, such as microgravimetry and ellipsometry, to unravel oxidation principles.

4. Experimental Section

The experiments were performed in an ultrahigh-vacuum setup ($p = 1 \times 10^{-9}$ mbar), composed of a preparation chamber with heating and sputtering stages, a copper effusion cell and an electron diffraction system, as well as a high-pressure oxidation chamber. The latter could be filled with 1 bar of oxygen (99.9995%) and heated at temperatures of up to 800 K. A collimated light beam from a halogen lamp passed the chamber at the sample position and enabled in situ optical transmission spectroscopy in the wavelength range of 400–1000 nm. Typically, 5,000 spectra were acquired in each experimental run, which allowed us to follow oxidation processes with high temporal resolution. Prior to data analysis, the spectra were corrected for the transfer function of the optical setup, including the bare glass substrate. The Cu$_2$O samples for oxidation were produced via room temperature deposition of 50 nm Cu$_2$O, CuO, morphology, oxidation kinetics, oxide conversion

Keywords

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