In situ oxidation studies of Cu thin films: Growth kinetics and oxide phase evolution

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ABSTRACT

A comprehensive understanding of the oxidation of Cu thin films in the low-temperature regime is of fundamental interest and particularly relevant for applications in the fields of micro- and nanoelectronics, sensors, catalysis, and solar cells. The current study reports on the oxidation kinetics of PVD grown Cu thin films (20–150 nm thick) and the oxide phase evolution from Cu₂O to CuO upon thermal oxidation in the temperature range of 100–450 °C. XRD investigations in the laboratory and at the synchrotron show that the oxide phase formation critically depends on the oxidation conditions such as temperature and oxygen partial pressure. The real-time synchrotron XRD measurements reveal that the formation of the CuO phase only starts after complete oxidation of the Cu films to Cu₂O films. *In situ* resistance measurements were performed to follow the oxide growth rate of Cu₂O on Cu films in the temperature range of 100–300 °C in air and in 10 mbar *p*O₂. It is found that the oxidation kinetics of Cu films to Cu₂O films follows the linear rate law, which is attributed to surface reaction controlled oxidation. The oxygen dissociation rate at the gas–solid interface is the rate-limiting process. A dramatic decrease in the linear oxidation rate is observed at low oxygen partial pressures. The fundamental differences between the oxidation rate-limiting processes of Cu as compared to other transition metal films are discussed.

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I. INTRODUCTION

Cu is one of the most commonly used metals for interconnections in micro- and nanoelectronic devices, sensing components, and power electronics owing to its high electrical and thermal conductivity. One major drawback of using Cu interconnections and interlayers for device integration is that Cu is easily oxidized, even at low temperatures, e.g., below 200 °C.¹ With the recent advancements in novel wide bandgap technologies (e.g., those based on SiC), typical device packaging and operation temperatures shift to temperatures below 250 °C.^{2–4} In such cases, the use of Cu films for device integration can become limited by its poor oxidation resistance during long-term operations at slightly elevated temperatures. Therefore, it is necessary to understand the oxidation kinetics of Cu layers in the low-temperature regime, e.g., below 300 °C. So far, most of the oxidation kinetics studies for Cu have been performed for thick Cu films or bulk Cu metal at temperatures above 350 °C.^{5–7} The few reported studies on the low-temperature oxidation kinetics of Cu thin films generally have been performed at a single temperature

(or narrow temperature range) and/or at a single (or undefined) oxygen partial pressure (*p*O₂) (see Table I). For most of these low-temperature oxidation studies, the Cu surface was covered with a native oxide at the onset of oxidation, as indicated by the respective column in Table I. Such native oxide films are spontaneously formed upon air exposure and acts as an initial diffusion barrier for continued oxidation at room temperature.^{8,9} Experimental studies on the initial stages of oxidation of bare (without a native oxide film) metal surfaces typically requires *in situ* deposition, oxidation, and analysis of pure metal thin films in a ultrahigh vacuum (UHV) system.¹⁰ Alternatively, the native oxide on the metal surface can be elaborately removed by alternating cycles of ion-sputtering and subsequent high-temperature annealing under UHV conditions prior to *in situ* oxidation. However, the initial oxidation rate on bare metal surfaces is extremely fast due to the electric-field assisted diffusion of the ions through the oxide film under influence of the so-called Mott field.^{8,9} Hence, the initial stages oxidation studies on bare metal surface are typically performed at

TABLE I. Summary of literature studies on the oxidation kinetics of thin Cu films. The studies have been mostly performed on polycrystalline Cu films as grown by different deposition techniques, e.g., thermal evaporation,¹² magnetron sputtering,¹³ and e-beam evaporation.¹⁴ Most studies on the oxidation kinetics were performed with a native oxide on the metal surface prior to oxidation.

Cu film thickness (nm)	Oxidation conditions			Oxidation kinetics	Activation energy (eV)	Reference
	Native oxide	T (°C)	Atmosphere			
50–60	Yes	85–135	31 Pa O ₂	Linear	0.66	15
20	Yes	120–150	Air	Parabolic	0.55	14
35	Yes	125	Air	Linear	...	12
<14	Yes	140	Air	Cabrera–Mott	...	16
>16–25	Yes	140	Air	Parabolic	...	16
<100	Yes	180–260	Air	Parabolic	0.57	17
35	Yes	175–250	Air	Power law	0.35	13
500	Yes	175–400	Dry air	Linear for $T < 250$ °C, Parabolic for $T > 250$ °C	0.31	18
300	Yes	250	Air		1.04	19
50	No	105	0.1–12 Pa O ₂	Linear	...	20
30	No	187	Undefined	Parabolic	...	21
50–60	No	85–135	Undefined	Linear	0.66	22

relatively low oxygen partial pressures (p_{O_2}), e.g., below 1 Pa (0.01 mbar).¹⁰ In practice, the spontaneous formation of a native oxide film on the Cu surface can hardly be prevented.

A comprehensive study on the thermal oxidation of polycrystalline Cu thin films with a native oxide at low temperatures ($T < 300$ °C) and for different partial oxygen pressures (from atmospheric conditions to low oxygen partial pressures) and for different Cu film thicknesses (in the submicrometer range), which is of particular technological interest, e.g., for Cu-based microelectronic packaging technologies, is still missing. Hence, the underlying oxidation mechanisms for Cu thin films in the low-temperature regime are still not well understood and still under debate.¹¹

While the rapid oxidation of Cu metal film limits its use in certain applications, other technologies require the oxidized forms of Cu, such as electronics,²³ catalysis,²⁴ sensors,²⁵ optoelectronics,²⁶ and solar cells.^{27,28} Cu forms two stable semiconducting oxides upon oxidation: cuprous oxide (Cu_2O , for simplicity written as Cu_2O in the text) and cupric oxide (Cu_{1-y}O , for simplicity written as CuO in the text), where “ y ” denotes the oxide nonstoichiometry.^{29–31} The formation sequence of the oxide phases (Cu_2O and CuO) upon oxidation of Cu metal films at low temperatures, sometimes referred to as double layer formation,⁵ is rarely studied^{1,10} and still not fully clear. This twofold interest for the application of Cu thin films in metallic and in oxidized forms for modern technologies makes the fundamental understanding of Cu thin film oxidation essential.

Previous studies on the oxidation kinetics of Cu performed above 350 °C report that the oxidation kinetics typically follows the parabolic rate law with Cu_2O as the predominant oxide phase.⁵ On the contrary, different growth laws, such as the cubic rate law,³² the parabolic rate law,^{17,19} the inverse logarithmic law,³² and the linear rate law^{15,20,32} have been reported for the oxidation of Cu films below 300 °C. The different growth laws for the oxidation kinetics of Cu films, as reported in the literature, are summarized in Table I. It follows that, even for the same temperature and film thickness ranges, different oxide growth laws were reported. These

contradictions on the oxidation kinetics of Cu thin films at low temperatures can be attributed to the fact that the oxide growth rate depends on various parameters, including the oxidation temperature (T), the oxygen partial pressure (p_{O_2}), and also on the thickness, morphology, grain size, and texture of the Cu film and of the growing oxide film (as formed by short-circuit diffusion of anions or cations along oxide grain boundaries).^{5,11}

This study provides comprehensive and fundamental understanding on the thermal oxidation of polycrystalline Cu films with a native oxide as a function of temperature (100–450 °C), oxygen partial pressure (in air and in 1 vol. % O₂/Ar) and the Cu film thickness (from 20 nm to 150 nm). To this end, the oxidation kinetics of the Cu films, pertaining to the initial growth of Cu_2O , and the subsequent phase evolution from Cu_2O to CuO , were investigated by combining *in situ* XRD and *in situ* resistance measurements. The experimental findings are discussed in terms of: (i) the sequence of oxide phase formation, (ii) the oxidation kinetics as a function of the oxidation conditions, which includes identification of the rate-limiting oxidation step (e.g., surface-controlled or diffusion-controlled), and (iii) the fundamental differences in the rate-determining processes for the oxidation of Cu films as compared to other transition metals and to perovskites.

Oxide growth laws for thin films: The oxidation kinetics of metal films is described by different models.³³ Corresponding model descriptions relevant to the current study (the oxidation of Cu thin films with a native oxide) are briefly described in the following. For the oxidation of metal surfaces with a native oxide film at elevated temperatures, surface-charge-induced electrical fields can generally be neglected;^{8,9} the oxidation kinetics of a metal film is then controlled by either the diffusion of ionic and electronic species through the growing oxide film (Wagner theory) or by surface reactions at the gas–solid interface. Diffusion-controlled growth assumes the formation and growth of dense oxide films on the metal surface by ambipolar diffusion of species (i.e., cations, anions, and their vacancies, as well as electrons and holes) through the oxide layer under influence of the chemical potential gradients [see Fig. 1(a)].^{34–37}

FIG. 1. The schematic profiles of the chemical potential of Cu (μ_{Cu}) and of O (μ_{O}) across the Cu_2O layer, as grown by the oxidation of Cu films, for the specific cases of (a) chemical-diffusion-controlled oxidation and (b) surface reaction controlled oxidation.^{35,46} Reproduced and modified with permission from Unutulmazsoy *et al.*, Phys. Chem. Chem. Phys. **19**, 9045–9052 (2017). Copyright 2015 Author(s), licensed under a Creative Commons Attribution 3.0 Unported (CC BY) 3.0 license.

In this case, the ionic and electronic fluxes will both strongly depend on the defect chemistry and the electronic structure of the growing oxide film. For example, cation vacancies are the prevailing defects in Cu_2O that create electron holes.^{38–40} The cation vacancies in Cu_2O are reported to be either neutral^{38,41} or also singly ionized.⁴² The defect chemistry of CuO is less studied than that of Cu_2O ; doubly ionized cation vacancies are reported to be the prevailing defects.^{43–45} During Cu oxidation, the Cu cations diffuse outward through the growing Cu_2O layer⁴⁴ (inward diffusion of oxygen ions is much slower³⁸). The respective ion flux under influence of the chemical potential gradient across the oxide layer is directly related to the growing oxide thickness, X , and the integration of the ion flux then results in the parabolic rate law,

$$X^2 = k_p \times t, \quad (1)$$

where k_p is the parabolic rate constant, and t is the oxidation time.

If the oxidation reaction is surface controlled, relative homogeneous distribution of the oxygen and the defect concentrations through the growing oxide film causes a chemical potential step at the gas–oxide phase interface, which acts as a driving force for further oxidation since the variation in oxygen concentration (δc_{O}) deviates from the equilibrium value [Fig. 1(b)]. Since δc_{O} remains constant until the entire metallic layer is consumed by oxidation, resulting in a constant flux of ions ($j_{\text{O}} = -j_{\text{Cu}} = -k\delta c_{\text{O}}$), which yields a linear oxide growth rate,

$$X = k \times t, \quad (2)$$

where k is the surface reaction rate constant.

II. EXPERIMENTAL METHODS

Cu thin films with thicknesses of 20, 50, and 150 nm were deposited on $10 \times 10 \text{ mm}^2$ sapphire substrates (single crystalline $\alpha\text{-Al}_2\text{O}_3\text{—C}(0001)$, CrysTec) by DC magnetron sputtering in an ultrahigh vacuum chamber (UHV, base pressure $<1 \times 10^{-8}$ mbar)

from a pure Cu target (99.99%) at room temperature. The sapphire substrates were ultrasonically cleaned in acetone and ethanol prior to deposition. In addition, an RF-plasma cleaning was performed inside the UHV chamber. Ag electrodes ($\sim 800 \text{ nm}$ thick) for *in situ* resistance measurements were deposited by a sputter coater (LEICA EM ACE200) on the sides of the Cu films using a shadow mask [see the inset in Fig. 7(a)].

2-theta (2θ) diffraction and x-ray reflectivity (XRR) patterns of as-deposited and oxidized films were measured using a Bruker D8 Discover x-ray diffractometer, operated in Bragg–Brentano geometry. The XRD diffraction patterns were obtained in the 2θ range of $20^\circ\text{--}90^\circ$ with a step size of 0.02° using Cu $K\alpha_{1-2}$ radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV and 40 mA). In addition, pole figures of the Cu{111} family of planes were recorded to determine the texture of the as-deposited Cu films. The topography of the metallic and oxidized Cu films was investigated by atomic force microscopy in tapping mode (AFM, VEECO E-Scope). High-resolution scanning electron microscopy (SEM, Hitachi S-4800) was used to analyze the surface morphology and the average grain size of the metal and the oxidized Cu films (in-plane). A cross section of the partially oxidized Cu film and an electron transparent cross-sectional lamella of the fully oxidized Cu film were prepared by focused ion beam (FIB) milling under the vision of scanning electron microscopy (SEM) using an FEI Helios Nanolab Dual Beam. Before the ion milling, protective Pt layers were predeposited on the surface by electron beam and ion beam, respectively. The lamella was analyzed by scanning transmission electron microscope (STEM; JEOL JEM 2200 field emission transmission electron microscopy operated at 200 kV). X-ray photoelectron spectroscopy (XPS, Physical Electronics Quantum 2000) was used to determine surface oxide phases on the metallic films and the oxidized films.

Real-time high-temperature synchrotron XRD measurements during oxidation of the thin Cu films were carried out at the material science beamline (MS-X04SA) at the Swiss Light Source (SLS) in Paul Scherrer Institute (PSI), Villigen, Switzerland. The MS-X04SA beamline is designed to provide x-rays in the energy range of 5–40 keV for real-time analysis. The experiments were carried out on the powder diffraction branch using a photon energy of 25 keV ($\lambda = 0.49396 \text{ \AA}$) in transmission mode with a two-dimensional detector (PILATUS, DECTRIS). A detailed description of the beamline setup and the detector is given elsewhere.⁴⁷ The beamline setup was equipped with a custom-designed compact furnace for *in situ* heating (IRELEC) during the XRD measurements, specially adapted for transmission diffraction measurements (beam size: $0.8 \times 3 \text{ mm}^2$). The furnace was operated in vacuum (base pressure of $\sim 10^{-5}$ mbar). The temperature is regulated through an Eurotherm 3208 temperature controller. The samples were heated up to the desired temperatures with 5 K/min heating rate in vacuum ($\sim 4 \times 10^{-5}$ mbar); when the temperature was constant, the vacuum pump was turned off resulting in a slow back-fill of the chamber with air up to ~ 5 mbar. Because of these experimental limitations of the custom-designed furnace system, oxidation measurements could only be performed in the 1–5 mbar pressure range. Successive diffraction patterns were recorded in the 2θ range of $0^\circ\text{--}30^\circ$ with a time interval of 60 s.

In addition, oxidation experiments were carried out in the laboratory for *in situ* resistance measurements of the films. The Cu

FIG. 2. (a) Cu {111} pole figure of a 150 nm thick film in the as-deposited state. (b) XRD diffraction patterns of the Cu films with different thicknesses. (c) Average grain size in the as-deposited Cu thin films (out-of-plane) as a function of the film thickness, as derived by the Scherrer equation.^{48,49} The film thicknesses of 20, 50, and 150 nm are nominal thicknesses; the uncertainty is on the order of $\pm 10\%$.

thin films were heated up in a tube furnace (*Nabertherm* equipped with a *Eurotherm* temperature controller) to the desired oxidation temperature with a heating rate of 10 K/min in Ar atmosphere ($>99.9999\%$ with a constant flow rate <200 ml/min). The temperature was controlled by a Pt-100 thermocouple, which was positioned close to the sample. The Ar flow was interrupted when temperature is stabilized (within $\pm 5^\circ\text{C}$), and then air was flushed into the furnace while starting the *in situ* resistance measurements. The resistance changes of the Cu films during oxidation were measured laterally across the samples by a two-point DC measurement (*Keithley 2410*). Additional *in situ* resistance measurements were performed in a 1 vol.% O_2 /Ar gas mixture at a constant flow rate (<200 ml/min). The resistance measurements during oxidation were performed at a constant temperature in the range of 100°C – 300°C for Cu film thicknesses of 20, 50, and 150 nm. The oxide thicknesses were calculated from the resistance of the remaining metallic part of the films while accounting for the molar volume difference between the metal and the oxide.

III. RESULTS AND DISCUSSION

A. Structural characterization of as-deposited Cu thin films

The texture of the as-deposited 150 nm thick Cu film is presented in Fig. 2(a), which shows the pole figure of the Cu{111} family of planes. The presence of multiple rings in the pole figure indicates the polycrystallinity of the Cu film with a preferred growth along the [111] direction, as evidenced by six intense poles. In addition, these six poles indicate an in-plane coherency between the as-deposited Cu film and the (0001) surface plane of the $\alpha\text{-Al}_2\text{O}_3$ substrate which has sixfold symmetry. Besides Cu grains with a preferential Cu [111] orientation, (200) reflections from Cu grains were also observed [see Fig. 2(b)]. The average Cu grain size (out-of-plane) was determined from the measured diffraction patterns by using the Scherrer formula^{48,49} [see Fig. 2(c)]. The average

grain size of the Cu metal films increases with increasing thickness up to a threshold value of 50–60 nm. For 150 nm thick films, the grain size saturates at ~ 60 nm, which is slightly higher than one-third of the film thickness, while for 20 nm and for 50 nm thick films, the average grain size approximately coincides with the film thickness. Even for Cu films with a thickness of 300 nm, the average grain size saturates at around 60 nm [see Fig. 2(c)].

The average grain size of roughly 50–60 nm, as observed at the surface of the 150 nm thick Cu film by SEM and AFM (see Fig. 3) coincides with the corresponding average Cu grain size indicated by XRD (see Fig. 2). Notably, the average surface roughness of the Cu thin films (measured by AFM) is below 2 nm for the studied Cu film thickness range of 20–150 nm, which also indicates that even the thinnest studied film, 20 nm, is a continuous metallic film. As evidenced by AFM and XRR, all the as-deposited Cu films in this study (i.e., 20, 50, and 150 nm thick) are dense and have a smooth surface with an average surface roughness of less than 2 nm in a $5 \times 5 \mu\text{m}^2$ area (see Fig. S2 in the supplementary material for the XRR results).

FIG. 3. (a) SEM and (b) AFM images of the surface of the as-deposited Cu film with a thickness of 150 nm.

B. Structural characterization of the Cu films during and after oxidation

The real-time HT-XRD investigations during oxidation at the synchrotron give a detailed picture of the oxide phase evolution by time, since it is possible to measure the 2θ range of 0° – 30° in less than 60 s (see Fig. 4). The oxide phase evolution was studied by HT-XRD for the oxidation of 150 nm thick Cu film at 450°C in a total pressure range of 1–5 mbar in air. As reflected by the representative HT-XRD diffractograms for selected oxidation times in the range of 0–80 min in Fig. 4(a), the Cu_2O peak becomes dominant after 25 min, while the Cu peak intensity has decreased due to the consumption of the Cu layer by the growing oxide.

The reflections from the remaining Cu layer have completely disappeared after 45 min of oxidation and then only Cu_2O reflections remain [Fig. 4(a)]. The HT-XRD study thus clearly indicates that the oxidation of a 150 nm thick Cu film at 450°C starts with the formation and growth of Cu_2O ,

Only after complete oxidation of the Cu film into Cu_2O , as reflected in Fig. 4(a) after 45 min of oxidation and more clearly in Fig. 4(b) by the intensity decrease of the Cu_2O reflection, the phase transformation from Cu_2O to CuO is initiated,

If the oxidation temperature is high enough, prolonged oxidation can result in the full transformation of the Cu_2O layer into a single phase of CuO as is the case for the experimental conditions

pertaining to Fig. 4(b). A similar measurement, performed for a 50 nm thick Cu film at 400°C , confirms that the phase transformation from Cu_2O to CuO only proceeds after complete oxidation of the Cu film into Cu_2O .

Figure 4(b) not only displays the oxide phase formation sequence, but also gives a rough indication of the oxidation kinetics of Cu to Cu_2O and of Cu_2O to CuO . The linear decrease of the normalized integrated area of Cu during the first 45 min of oxidation is accompanied by a linear increase of the normalized integrated area of Cu_2O [blue region in the Fig. 4(b)], which suggests that the oxidation process follows the linear rate law, as discussed in greater detail in Sec. III C [see Fig. 7(b)]. The oxidation kinetics of Cu_2O to CuO , as reflected by the respective normalized integrated area in Fig. 4(b) (red region), clearly differs from the linear growth law and seems to be controlled by a parabolic rate law (diffusion controlled), which will be addressed in more detail in a follow-up study.

The corresponding sequence of phase formation upon oxidation of the Cu thin films is shown in Fig. 5, which is also mentioned in the literature.¹ The cross-sectional SEM image of a partially oxidized Cu film after 20 min of oxidation in air at 240°C [see Fig. 5(b)] shows that the Cu_2O phase grows layer-by-layer on top of the Cu film. Since Cu diffusion in Cu_2O is much faster than O diffusion, e.g., more than one order of magnitude at 1000°C ,^{38,44} the reaction front for Cu_2O formation is the metal–gas interface. Figure 5(c) shows images of an as-deposited Cu thin film as well as of fully oxidized single-phase Cu_2O (oxidized at 275°C for 2 h) and CuO layers (oxidized at 400°C for 30 min). The optical differences between Cu_2O (transparent) and CuO (opaque) phases (on a transparent sapphire substrate) are clearly visible to the eye, reflecting

FIG. 4. (a) Selection of representative real-time HT-XRD diffractograms for oxidation times in the range of 0–80 min, as recorded during the oxidation of a 150 nm thick Cu film at 450°C in the 1–5 mbar pressure range of air. Only the most intense peak positions are highlighted. Some additional broader peaks, which are not labeled, arise from the sample holder. (b) Normalized integrated area of the respective peaks for Cu, Cu_2O , and CuO based on the left HT-XRD diffractograms as a function of oxidation time, evidencing that the Cu_2O phase transforms into CuO only after full oxidation of the Cu film.

FIG. 5. (a) Sketch of successive stages of oxidation of Cu films, first forming Cu₂O and then transforming into CuO. (b) Cross-sectional SEM image by FIB of a partially oxidized Cu film (150 nm) into Cu₂O (oxidized at 240 °C for 20 min in air), representing the second stage of oxidation. (c) Cu thin films before and after oxidation. Distinct optical differences between Cu₂O (transparent; oxidized for 2 h at 275 °C) and CuO (dark opaque; oxidized for 30 min at 400 °C) layers are visible to the eye.

the different oxidation treatments in air. As confirmed by additional XRD measurements, a single-phase of Cu₂O is still present after prolonged oxidation (e.g., 2 h) in air at temperatures below 300 °C; the CuO phase is only formed toward higher temperatures $T \geq 300$ °C.

However, due to the low surface-sensitivity of the HT-XRD measurements in the transmission mode, it cannot be ruled out that the outer surface of the evolving Cu₂O film (up to a depth of few nanometers) in contact with the oxidizing atmosphere is actually a mixture of Cu₂O and CuO. XPS analysis (with a typical probing depth of several nm) of the as-deposited Cu thin film with a native oxide layer indeed indicates the presence of both oxide phases (Cu₂O and CuO) at the outer surface of the thin films with a typical thickness below 3 nm (see Fig. S1 in the [supplementary material](#)).

The kinetics of the phase transformation from Cu₂O to CuO is strongly dependent on the oxidation conditions, such as the oxidation temperature, the oxidation time, and the oxygen partial pressure. For short oxidation times, low oxidation temperatures (e.g., $T < 300$ °C) and/or low partial oxygen pressures, a full transformation of the Cu₂O layer into CuO is kinetically hindered. This opens experimental pathways for the exclusive formation of Cu₂O layers by tailoring the oxidation conditions, as demonstrated in Fig. 6 for the thermal oxidation of a 50 nm thick Cu film (for less than 10 min at 240 °C).

Additional XRD grain size analysis (by the Scherrer formula) of the oxidized Cu films for various film thicknesses and oxidation temperatures indicates that the average Cu₂O grain size is in the range of 8–12 nm, which is in good agreement with the STEM

analysis in Fig. 6(b). Figure 6(b) shows a cross-sectional STEM image of the Cu film after full oxidation to Cu₂O: The dashed red circles indicate individual oxide grains, while the blue square indicates a typical Moiré pattern due to overlapping of specific crystal planes of the oxide grains along the primary electron beam direction in the ~80 nm thick TEM lamella. The features in Fig. 6(b) indicate an average grain size in the oxide film of ~10 nm, which is much smaller than the film thickness. This implies that the average grain size of the developing Cu₂O layer is independent of the initial metallic film thickness [or grain size; see Fig. 2(c)] and also of the oxidation temperature between 100 °C and 300 °C. A literature study on the oxidation of Ni thin films⁴⁶ also reported a smaller grain size for the growing oxide film compared to the initial metallic film. While the average grain size of a 150 nm thick polycrystalline Ni film (as grown by e-beam evaporation) is around 100 nm, the resulting grain size of the growing oxide film is in the range of 10–30 nm.⁴⁶ The smaller grain size for the growing oxide layer suggests a considerable contribution of grain-boundary diffusion to the effective diffusion coefficient during the oxidation process.

C. Oxidation kinetics by *in situ* resistance measurements

The layer-by-layer growth of Cu₂O on the Cu film is shown in Fig. 5(b), which gives the possibility to follow the oxidation kinetics of the metal films (with a native oxide on the surface) by *in situ* resistance monitoring of the remaining metallic film using in-plane resistance measurements.

FIG. 6. (a) XRD diffraction patterns of a 50 nm thick Cu film before and after complete oxidation at 240 °C. (b) STEM image of an oxidized Cu film into Cu_2O at 240 °C for less than 10 min. The red circles and blue squares indicate the nanocrystalline domains and Moiré patterns in the oxide, respectively. The same Cu_2O sample is used for the XRD analysis in (a) and for the STEM analysis in (b).

Figure 7(a) shows the *in situ* resistance measurement of the 50 nm Cu film at 200 °C in air upon oxidation. The resulting oxide layer growth curve (growing oxide film thickness, X , as a function of time, t), as given in Fig. 7(b), is calculated from the measured resistance values of the remaining metallic Cu film. The figure indicates that the oxidation of Cu follows a linear rate law [see Eq. (2)], as attributed to the rate-limiting dissociation of oxygen at the oxide-gas surface. Figure 7(c) shows a logarithmic plot of X vs t , which confirms that the oxidation of Cu film is surface reaction controlled since the slope is close to 1. If the oxidation rate constant of Cu is diffusion controlled [parabolic rate law, see Eq. (1)], the slope of the $\log X$ vs $\log t$ graph would yield a value close to 0.5.

The *in situ* resistance measurements of 20, 50, and 150 nm thick Cu thin films during oxidation at temperatures in the range of 100–300 °C in air indicate linear oxidation kinetics for all the samples and thus a surface reaction controlled oxidation process as presented in Fig. 7 is a representative case. An Arrhenius plot for oxidation kinetics measurements of the Cu films at different temperatures and for various film thicknesses is presented in Fig. 8(a). It follows that the activation energies (E_a) of the Cu oxidation process in air are in the range of 0.5–0.7 eV, roughly independent of Cu film thickness. The activation energy values in the current study are in good agreement with those reported in the literature as summarized in Table I. The activation energy for the

FIG. 7. (a) Resistance measurement of a 50 nm thick Cu film during oxidation at 200 °C in air. The inset shows a typical sample geometry ($10 \times 10 \text{ mm}^2$) with the contact electrodes (width of $\sim 1 \text{ mm}$). (b) Calculated oxide thickness, X , as a function of time, t , and (c) logarithmic scaling of X vs t .

FIG. 8. Arrhenius plot for the oxidation of (a) 20, 50, and 150 nm thick Cu films in air and (b) 50 nm thick Cu films in air ($p\text{O}_2 = 210 \text{ mbar}$) and in 1 vol. % O_2 ($p\text{O}_2 = 10 \text{ mbar}$).

oxidation of the 150 nm thick Cu film has a relatively large error bar, which might be attributed to the recrystallization of the Cu metal in the temperature range of the measurements,⁵⁰ which may strongly affect the oxidation kinetics. When the oxidation of a metal film is controlled by a surface reaction like in the case of Cu films in this study, the surface reaction rate constant (k) can be easily modified by changing the experimental conditions. For example, while high $p\text{O}_2$, UV light illumination, or using O_3 atmosphere is expected to increase the oxidation rate constant, a lower $p\text{O}_2$ is expected to decrease the oxidation rate constant of surface reaction limited processes. To reveal the strong $p\text{O}_2$ dependence of the oxidation kinetics of Cu thin films, the oxidation rate constants of 50 nm Cu films in air ($p\text{O}_2 = 210 \text{ mbar}$) and in 1 vol. % O_2/Ar ($p\text{O}_2 = 10 \text{ mbar}$) are compared in Fig. 8(b). Since the oxidation of Cu films is surface reaction controlled, a dramatic decrease in the oxidation rate constant of Cu films occurs at lower $p\text{O}_2$. Interestingly, the lowering of the $p\text{O}_2$ not only results in a dramatic decrease in the oxidation rate, but also results in a lower activation energy, $E_a = 0.34 \pm 0.02 \text{ eV}$ [Fig. 8(b)].

It may be expected that the oxidation at a lower $p\text{O}_2$ results in a higher O-vacancy concentration at the outer surface of the growing cation deficient Cu_2O layer,³⁸ resulting in a lower activation barrier for dissociative O_2 chemisorption according to Density functional theory (DFT) predictions.^{51,52} Indeed, the experimentally determined activation energies in the range of $E_a = 0.3\text{--}0.7 \text{ eV}$ are in good agreement with reported activation energies for the dissociative chemisorption of O_2 molecules in literature (as calculated by DFT),^{51,52} e.g., $E_{\text{chem}} = 0.2\text{--}0.8 \text{ eV}$ for dissociative chemisorption on defective Cu_2O (111) surfaces. In general, O_2 molecules have an increased activation barrier for dissociative chemisorption on metal oxide surfaces in comparison with pure metal surfaces; typically,

(sub)surface vacancies are needed to lower the kinetic barriers for oxygen adsorption.⁵² As demonstrated by DFT calculations in Ref. 52, oxygen vacancies on the Cu_2O (111) surface exhibit a strong catalytic activity for O_2 dissociation in comparison with the O_2 dissociation on the defect-free Cu_2O surface.

Notably, the activation energies reported in this study are also very similar to activation energies (0.42–0.54 eV) for the oxidation of thick Cu sheets at temperatures in the range between 350 and 500 $^{\circ}\text{C}$, where grain-boundary diffusion in Cu_2O is dominant and the oxidation follows the parabolic rate law.⁵ The activation energies reported in the current study are also comparable to reported activation energies for the parabolic rate law for thin film oxidation (see Table I). This suggests that a reliable identification of the rate-limiting steps for the thermal oxidation process of a metal or alloy requires a comprehensive experimental data set of the oxidation kinetics as a function of both temperature and partial oxygen pressure. In addition, for a valid assessment of the oxidation kinetics, it should be verified that a single oxide phase develops during the oxidation process.

D. Cu diffusion in Cu_2O as compared to cation diffusion in other binary oxides and perovskites

It has been shown that the oxidation of metal films, such as Cr, Al, Ti, Co, and Ni, typically obeys the parabolic rate law, even for very thin films (e.g., 10 nm thick), indicating a chemical-diffusion-controlled oxidation.^{46,53} Moreover, it has been shown for the oxidation of Ti and Ni thin films that a dramatic change of $p\text{O}_2$ does not significantly affect the parabolic rate constant.⁴⁶ On the contrary, the oxidation of Cu thin films below 300 $^{\circ}\text{C}$ follows the linear rate law, indicative for a surface-controlled oxidation process. Even for the

50 nm thick films, a dramatic decrease of the (linear) oxidation rate is observed when lowering the $p\text{O}_2$ [Fig. 8(b)]. The main reason for the distinct difference in the oxidation kinetics of Cu thin films is the much faster diffusion coefficient of Cu in the Cu_2O as compared to cation diffusion coefficient in other transition metal oxide films. For the oxidation of metal thin films in the nanoscale, the chemical potential gradients through the growing oxide film can be large. Such large chemical potential gradients across the developing oxide layer in combination with a high self-diffusion coefficient of ionic species in the oxide can lead to ionic fluxes that are fast enough to compete with the oxygen dissociation rate at the oxide surface, the slower process being the rate-limiting step. It follows that the oxidation kinetics of metal thin films can change from diffusion controlled to surface reaction controlled below a certain critical metal film thickness. The transition between a diffusion-controlled reaction and a surface-controlled reaction is given by $k \cdot l_c \approx D$, where k is the surface exchange coefficient, l_c the critical sample thickness, and D the (tracer or self) diffusion coefficient.⁵⁴

As illustrated in Fig. 9, the tracer diffusion coefficient of Cu in Cu_2O ^{39,55} is of the same order as the relatively fast tracer diffusion coefficients of O in mixed conducting perovskites like Fe-doped SrTiO_3 ⁵⁶ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$,⁵⁷ which is very high compared to cation diffusion coefficients in other transition metal oxides, e.g., NiO .⁴⁶ The cation and oxygen diffusivities in the oxides of other transition metals like Ni, Cr, Co, Al, and Ti are typically much lower compared to the ionic diffusivities in Cu_2O and in mixed conducting oxides. For example, as depicted in Fig. 9, the diffusion coefficient of Cu in Cu_2O (and O in mixed perovskites) is several orders of magnitude higher than Ni diffusion in NiO .⁴⁶ Consequently, the oxidation of metal films of Ni, Cr, Co, Al, and Ti is typically

diffusion controlled, even for relatively small film thicknesses, e.g., 10 nm.^{46,53} Hence, the corresponding critical sample thickness, l_c , is expected to be lower than 10 nm for the oxidation of metal films of Ni, Cr, Co, Al, and Ti. On the contrary, for Cu thin films, the value of l_c is expected to be much thicker: 1–100 μm like in the perovskites.⁵⁴ In summary, the diffusion of Cu in Cu_2O is so fast that the surface reaction can become the rate controlling step for the oxidation of Cu thin films. Possibly, as a result of the fast cation diffusivity, the average oxide grain size of the developing Cu_2O overlayer is relatively small as compared to, e.g., NiO layers formed on Ni thin films.⁴⁶ Fast diffusion along the oxide grain boundaries can further enhance the effective ionic diffusion coefficients during the oxidation process.

IV. CONCLUSIONS

The oxidation kinetics of Cu thin films in the temperature range of 100–300 °C for film thicknesses between 20 and 150 nm was investigated and found to follow a linear rate law, which indicates that the oxidation process is surface reaction controlled. It is postulated that the rate controlling step is the oxygen dissociation at the oxide–gas interface. Consequently, a dramatic decrease in the oxidation rate constant of Cu films occurs at low partial oxygen pressures (10 mbar $p\text{O}_2$). The oxidation of thin films of other transition metals, like Ni, Cr, Co, Al, and Ti, typically exhibit a parabolic growth rate for similar oxidation conditions, characteristic for a chemical-diffusion-controlled oxidation process. The different oxidation kinetics for Cu thin films can be attributed to the very fast diffusion of Cu cations in the Cu_2O lattice (and along oxide grain boundaries); the cation and anion diffusivities in other binary oxides are generally much slower. The fast cation diffusivity may also rationalize the relatively small grain size of the developing Cu_2O layer. This suggests that further investigations are necessary for a detailed understanding of the microstructure effects on the oxidation kinetics of Cu films. As evidenced by *in situ* HT-XRD, the CuO phase only starts to form after complete oxidation of metallic Cu film into Cu_2O phase. The present study provides guidelines to synthesize single-phase Cu_2O or CuO thin films on a substrate with a very simple technique, thermal oxidation of Cu films, which could be used for applications in different fields, e.g., electronics, sensors, catalysis, and solar cells.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for XPS analysis and for XRR analysis of metallic Cu films.

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There are no conflicts of interest to declare.

FIG. 9. Tracer diffusion coefficient of cations in NiO ,⁴⁶ Cu_2O ,^{39,55} and of oxygen in Fe-doped SrTiO_3 ⁵⁶ and in $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$.⁵⁷ Reproduced and enriched with permission from Unutulmazsoy *et al.*, APL Mater. 5(4), 042302 (2017). Copyright 2017 AIP Publishing LLC, licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).

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