



# Oxidation of polycrystalline copper films – Pressure and temperature dependence

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## ABSTRACT

Oxidation of polycrystalline Cu films is investigated in a wide range of temperatures and O<sub>2</sub> pressures. The composition of the resulting oxide is derived from transmission and absorption spectra, analyzed with the transfer-matrix and a modified Tauc method, as well as from photoelectron spectroscopy. No Cu oxidation occurs at oxygen pressures below 1 mbar, indicative for a pressure-dependent barrier. At higher pressures, either cuprous or cupric oxide forms at oxidation temperatures below 460 K and above 500 K, respectively, while both phases coexist at intermediate temperatures. Oxide films of unknown stoichiometry, possibly Cu<sub>4</sub>O<sub>3</sub>, are revealed in the pressure range between 1 and 10 mbar. Based on these results, a formation diagram for copper oxides is developed and compared to respective phase diagrams in the literature.

## 1. Introduction

The oxides of copper represent a versatile class of semiconductors with several potential applications in microelectronics, photovoltaics, thermal- and photo-catalysis [1,2]. The vital interest in these materials arises from a number of fascinating properties. Copper oxides have a tunable band gap that ranges from 1.35 eV in cupric (CuO) to 2.15 eV in cuprous oxide (Cu<sub>2</sub>O). These values largely overlap with the solar spectrum and motivate a use as photo-active materials. Cu<sub>2</sub>O, for example, has been tested as low-cost, non-toxic absorber material for thin-film solar cells, although reported efficiencies are still poor [3,4]. The photochemical response of Cu<sub>2</sub>O has been explored in the context of water-hydrolysis and photo-degradation [5,6]. The studies revealed higher stability yet lower reactivity of the compact Cu<sub>2</sub>O(111) as compared to more open (110) and (100) surfaces [7]. From an electronic point of view, both Cu<sub>2</sub>O and CuO exhibit a pronounced *p*-type conductance behavior, being in contrast to the *n*-type nature of most other binary oxides. Copper oxides are thus promising *p*-type components in ‘all-oxide’ electronic and optoelectronic devices. The *p*-type conductance originates from a thermodynamic preference for Cu vacancies that produce hole-states in the oxide valence band [8]. Ultimate requirement for using copper oxides in advanced technologies is, however, a precise stoichiometry control, as this governs the band gap, electrical resistivity and chemical response of the material [1–5].

The oxidation of copper has been in the focus of research for quite some time. The initial thin-film stages were addressed with surface-

science techniques [9]. On Cu(111), for example, development of a native oxide has been reported that remains however below 1 nm thickness due to self-limited growth [10]. The oxidation of Cu(100), on the other hand, is governed by nucleation, growth and coalescence of individual oxide nanoparticles [11]. Oxide layers thicker than the self-terminating film can be produced either by high temperature/high pressure Cu oxidation or anodic oxidation in NaOH [12,13]. The thickness evolution hereby follows characteristic rate laws depending on temperature and O<sub>2</sub> pressure, such as logarithmic, inverse-logarithmic and various power laws [14–16]. This diversity suggests a critical dependence of the oxidation process on kinetic factors as well as on texture and crystallinity of the initial Cu samples [17].

The oxidation studies have been summarized in phase diagrams, showing the stability and coexistence regions of the different Cu-O mixtures [14,18]. At atmospheric O<sub>2</sub> pressure and moderate temperatures, CuO is the sole equilibrium phase [19]. Around 1100 K, CuO gets reduced to Cu<sub>2</sub>O and above 1350 K to metallic Cu. Remaining questions are the thermodynamic stability of Cu<sub>2</sub>O at low temperatures and the occurrence of phases with deviating stoichiometry, such as Cu<sub>4</sub>O<sub>3</sub> [20,21]. Moreover, fascinating kinetic phenomena have been identified in the context of Cu oxidation, such as the nanoscale Kirkendall effect. It arises from a strong outward diffusion of metal atoms combined with the hindered inward diffusion of oxygen and results in oxide structures with high porosity [22,23]. Also, theory largely contributed to our understanding of copper oxidation and examined for example the mechanisms of Cu-O interactions on the different Cu planes [24]. A good

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survey of the theoretical efforts can be found in a review article by Michaelides and coworkers [25].

Our work addresses the oxidation of polycrystalline Cu films, probed systematically as a function of thickness, temperature and oxygen pressure. The stoichiometry of the emerging Cu-O phases is derived from optical transmission and reflection spectra, combined with X-ray photoelectron spectroscopy (XPS). On this basis, a formation diagram for copper oxides is proposed that follows the standard phase diagram in many aspects, but shows distinct differences around the Cu/Cu<sub>2</sub>O and Cu<sub>2</sub>O/CuO phase transitions at moderate temperatures.

## 2. Experiment and simulations

Copper films of 10–55 nm thickness have been prepared by physical vapor deposition of Cu (99.9% purity) onto glass substrates at room temperature and high-vacuum conditions ( $10^{-7}$  mbar). The samples were oxidized for 60 min in a designated vacuum chamber, using high-purity oxygen at  $10^{-7}$  to  $10^{+3}$  mbar pressure and temperatures between 300 and 700 K. XPS measurements were performed *in situ* with a non-chromatized Mg-K $\alpha$  source and a hemispherical mirror analyzer (ESCALAB 200). Optical transmittance  $T(\lambda)$  and specular reflectance  $R(\lambda)$  spectra have been measured at ambient conditions with a Cary 5E spectrophotometer. From the latter, the sample absorbance  $A(\lambda)$  was calculated according to  $A(\lambda) = 1 - R(\lambda) - T(\lambda)$ .

Insights into the band gap, chemical composition and thickness of the oxidized samples have been obtained by simulating the optical spectra. For band-gap retrieval, a modified Tauc method was used,  $-q \cdot \ln(T(q))^{1/u} \propto (h \cdot c_0 \cdot q)$ , with  $T(q)$  the experimental transmittance as a function of wavenumber  $q$ ,  $h$  the Planck constant and  $c_0$  the speed of light [26]. The exponent  $u$  that accounts for the nature of the band gap was set to 3/2 (direct-forbidden) for both, Cu<sub>2</sub>O and CuO [27,28]. The band gap results from the intersection of a linear fit to  $-q \cdot \ln(T(q))^{1/u}$  and the energy axis. The film composition, on the other hand, was evaluated by comparing the experimental transmittance  $T(\lambda)$  to spectra simulated for flat and homogenous films of Cu, Cu<sub>2</sub>O, CuO or their mixtures, deposited on optically thick glass substrates [26,29]. The simulations were performed with the transfer-matrix method to account for multiple, coherent reflections and absorptions in the optical system [30]. The wavelength-dependent refraction and absorption indices ( $n, k$ ) for pure Cu, Cu<sub>2</sub>O and CuO were taken from the literature [31,32]. The sample composition was evaluated by systematically varying the sequence and thickness of the different optical layers, using the root-mean-square (rms) error to quantify the agreement with experiment. Examples for measured and simulated spectra of pristine Cu, phase-clean CuO and Cu<sub>2</sub>O samples are shown in Fig. 1. The associated rms-errors, calculated as a function of thickness and composition, are depicted as 1D and 2D false-color plots in the insets. A clear minimum in the rms-maps enabled us to safely determine composition and thickness of the optically active layers with about 5% accuracy. This sensitivity is the result of coherent reflections in thin films that control both, curve shape and maximum position in a distinct manner (Fig. 1d). Larger deviations between experiment and simulation were encountered only in the transition region of pure phases, most likely due to invalid optical constants.

## 3. Results and discussion

Fig. 2a presents a selection of copper/glass samples before and after oxidation at different temperatures. The initial Cu films are polycrystalline with 15–20 nm grain size, as probed with scanning tunneling microscopy (STM) (Fig. 2b). The changes in transparency and color of the samples upon oxidation are readily recognized by eye and form the basis for evaluating their oxidation states by UV/Vis spectroscopy. The chemical composition of the films is further explored with XPS. In section A and B of this chapter, we discuss the role of temperature and

O<sub>2</sub> pressure on Cu oxidation, while a compilation of all experimental data into a Cu-O phase diagram is presented in section C.

### 3.1. Temperature dependence of Cu oxidation

Fig. 3 presents optical transmission and absorption spectra measured for 50-nm thick Cu samples, exposed to 100 mbar O<sub>2</sub> at temperatures increasing from 400 to 630 K. Three groups of absorption and transmission curves are distinguishable, as denoted with black, blue and red colors. Comparison with Fig. 1a shows that the black spectra at the bottom of Fig. 3 belong to pristine copper. Its transmission increases up to 575 nm due to diminishing Cu *d*-band absorption, and decreases again afterwards due to the Drude response of the free electrons. The vanishing *d*-band transitions are also responsible for the sharp decrease of the absorbance between 550 and 600 nm (Fig. 3b). With decreasing film thickness, the maximum in Cu transmittance red shifts to 600 nm, because of thickness-dependent, coherent reflection and interference effects in homogenous thin films [33]. Electron confinement, on the other hand, plays no role for the *d*-band position in the examined thickness range.

The blue spectra that correspond to oxidation temperatures between 400 and 460 K show a close match with the optical response of Cu<sub>2</sub>O (Fig. 1b). Main signature of the curves is a sharp increase (decrease) in the transmittance (absorbance) at ~500 nm, reflecting the opening of the Cu<sub>2</sub>O band gap. A more accurate analysis with the Tauc method yields a gap size of 2.15 eV, in agreement with literature values for cuprous oxide (2.25 eV) [34]. The red spectra, finally, are governed by an increasing transmittance and decreasing absorbance in the wavelength range from 600 to 800 nm. The Tauc analysis gives a gap value of 1.2 eV in this case, reflecting the reduced CuO band gap.

Simulations of the experimental spectra with the transfer-matrix method provide further insights into the chemical composition of the Cu-O samples. By minimizing the rms-error between experimental and simulated curves, the nature and thickness of optically active layers, *i.e.* Cu, Cu<sub>2</sub>O and/or CuO, were determined. The accuracy of the method was checked by comparing the experimental film thickness with the sum of all layers identified in the simulations. To account for oxygen incorporation into the lattice, the thickness of initial Cu films was multiplied by 1.65 and 1.72 for Cu<sub>2</sub>O and CuO, respectively. Table 1 compiles the results for the samples shown in Fig. 3. The corrected thickness values from the fitting procedures show good agreement with the 50 nm of the Cu samples before oxidation, suggesting that the Cu amount does not change and the thickness increase indeed arises from oxygen incorporation into the lattice. Moreover, the main oxide phase identified in the simulations is always consistent with the gap value from the Tauc analysis. The sensitivity of the method can be seen when comparing spectra taken at 400 and 460 K oxidation temperature. The 550 nm transmission peak, being characteristic for cuprous oxide formed at 400 K, gets partly suppressed at 460 K. This change arises from the formation of a thin CuO layer on top of Cu<sub>2</sub>O, which modifies the interference pattern of the entire film and thus the position of the transmission maximum (Table 1).

Photo- and Augerelectron spectroscopy has been used as additional means to determine the chemical composition of oxidized Cu films (Fig. 4). Note that only the near-surface region and not the bulk sample, as in optical measurements, is probed in this case. For as-grown films, a double peak at 932.5 and 953 eV binding energy is revealed, reflecting the spin-orbit-split 2*p* states of Cu<sup>0</sup> [35]. A Cu LMM Auger line with three distinct maxima, centered at around 918 eV, confirms the metallic character of the sample. Data acquisition was hampered after oxidation due to charging effects in the partly isolating oxide films. To enable comparison with tabulated binding energies, we have corrected our data with respect to the O 1*s* binding energy that is almost identical in Cu<sub>2</sub>O and CuO (530 eV). In samples oxidized at 100 mbar O<sub>2</sub> and 400 K, the corrected Cu 2*p* hardly changes position with respect to as-grown films, which can be explained with similar Cu 2*p* binding energies in

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