In situ spectrophotometry and X-ray diffraction investigations during the oxidation of copper oxide thin films

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The binary copper-oxygen contains two stable phases: cuprite (Cu₂O) and tenorite (CuO) and a metastable phase: paramelaconite (Cu₄O₃). Reactive magnetron sputtering is the unique method to synthesize the metastable copper oxide phase. When submitted to vacuum or air annealing, paramelaconite decomposes into Cu₂O or oxidizes into CuO, respectively. CuO being the stable phase at high temperature, cuprite films also oxidize into CuO during air annealing. Since these three oxides exhibit different optical transmittance [1], the spectrophotometry may be used to characterize the structure of copper oxide films. Thanks to the smart Linkam® heating cell, this study emphasis the potentialities of in-situ spectrophotometry combined with X-ray diffraction for the characterization of the structural evolution during air annealing of copper oxide films.

200-nm thick copper oxide films were deposited on glass substrates by pulsed-DC magnetron sputtering of a copper target in reactive Ar-O₂ mixtures. The composition of as-deposited films (Cu₂O, Cu₄O₃ and CuO) was controlled by the oxygen flow rate introduced in the deposition chamber. The tetragonal paramelaconite films exhibited a strong preferred orientation in the [101] direction as confirmed by pole figure. In situ XRD analyses showed that the oxidation into tenorite occured at temperature higher than 300 °C. Pole figure on oxidised film also showed a preferential orientation resulting from a crystallographic relationship between the paramelaconite and the tenorite structures. Furthermore, a growth of the oxide grain after the annealing treatment was observed by TEM analyses.

Finally, the oxidation of cuprite and paramelaconite thin films was monitored by spectrophotometry. For both oxides, a decrease of the film transmittance was observed as a function of the annealing temperature or the treatment duration, and the oxidation of cuprite/paramelaconite into tenorite was confirmed by the changes of spectra at temperature higher than 300 °C. The experimental results were fitted using the Avrami model.


Keywords
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