

In-situ Photoemission of Cu Oxidation and Reduction at Elevated Pressure

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The reaction between copper and oxygen has many implications ranging from solid state reaction dynamics over electromigration in semiconductor devices to heterogeneous catalysis.

The reactivity is described in several interlinked processes. Chemisorption of oxygen on the bare metal is followed by surface reconstruction and sub-surface compound formation. Then follows oxidation of the metal to Cu I oxide, to complex intermediate sub-oxides and finally to Cu II oxide. Although Cu oxides are thermodynamically stable under standard conditions they tend to loose oxygen at low chemical potential and to occur in kinetically-controlled mixtures of sub-oxides. The presence of water complicates the issue further as many oxo-hydroxide defective and stoichiometric forms also exist.

The reaction kinetics is controlled by the tendency to nanostructure initially bulk crystals both during oxidation and reduction. The control variable is the defect structure of the bulk crystal given in defects and in the strain of the lattice. The defects also determine the reactivity of Cu and its oxides towards reduction and oxidation.

In this complicated situation it is essential to use in-situ analytical methods and to observe the dependence of the findings on the chemical potential of the reaction atmosphere. Conflicting results about intermediates and reaction sequences find their explanation in insufficient control of the reaction details: Cu can oxidize or be reduced in many different ways that even may co-exist on large crystal.

The presentation focuses on in-situ high pressure studies of redox processes on surfaces using high-pressure XPS and NEXAFS as observation tools. It also relates the findings to bulk methods such as thermoanalysis and X-ray diffraction. The presentation highlights the critical role of strain and sub-surface compound formation, two phenomena very hard to detect in ex-situ studies, in understanding the reaction dynamics.