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Atomistic details of oxide surfaces and surface oxidation: the example of copper and its oxides

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Abstract

The oxidation and corrosion of metals are fundamental problems in materials science and technology that have been studied using a large variety of experimental and computational techniques. Here we review some of the recent studies that have led to significant advances in our atomic-level understanding of copper oxide, one of the most studied and best understood metal oxides. We show that a good atomistic understanding of the physical characteristics of cuprous (Cu_2O) and cupric (CuO) oxide and of some key processes of their formation has been obtained. Indeed, the growth of the oxide has been shown to be epitaxial with the surface and to proceed, in most cases, through the formation of oxide nano-islands which, with continuous oxygen exposure, grow and eventually coalesce. We also show how electronic structure calculations have become increasingly useful in helping to characterise the structures and energetics of various Cu oxide surfaces. However a number of challenges remain. For example, it is not clear under which conditions the oxidation of copper in air at room temperature (known as native oxidation) leads to the formation of a cuprous oxide film only, or also of a cupric overlayer. Moreover, the atomistic details of the nucleation of the oxide islands are still unknown. We close our review with a brief perspective on future work and discuss how recent advances in experimental techniques, bringing greater temporal and spatial resolution, along with improvements in the accuracy, realism and timescales achievable with computational approaches make it possible for these questions to be answered in the near future.

Contents

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1. Introduction

Copper is a material which has accompanied human prehistory and history, and it is still highly relevant today. Cold working of copper has been performed for at least 10,000 years and smelting of copper ore for around 7000 years [1]. Its use as a construction material, *e.g.* in piping, can be dated back to ancient Egypt, and its importance in this field has not diminished nowadays. In the modern world it has acquired further uses, for example in electrical systems and electronic devices.

Within this long history, the properties of copper have been extensively studied and exploited, however much is still unknown about this important metal. In particular, the oxidation and corrosion of copper, which impacts its performance in industrial and technological applications, is still not completely understood.

Copper is found to readily oxidise at room temperature [2–4], and the presence of an oxide layer, however thin, can compromise its uses in technology. As an example, copper could be an environmentally friendly and low-cost substitute for the (currently used) tin-lead or (promising) gold- and silver-based solder alloys in electronic packaging, if there was a way to prevent its oxidation [5]. Moreover, copper canisters are used for nuclear waste disposal, and understanding the oxidation and corrosion of copper in anaerobic conditions is thus of critical importance [6]. On the other hand, the existence of stable copper oxides at room temperature, with a ~ 2.0 eV band gap, makes them interesting for catalytic [7], gas sensing [8], optoelectronic and solar technologies [9,10]. Thus, there currently is a two-fold interest in understanding copper oxides: from the one hand, to mitigate against technological failure, and on the other hand, to exploit their potential industrial applications.

Copper is also considered a model system to understand the formation of metal oxides in general. The atomistic details of the oxidation process tend to be system-specific, with some metals showing uniform oxide growth (*e.g.* Ref. [11]), and others complex temperature-dependent phenomena such as surface roughening (*e.g.* Ref. [12]) and island formation (*e.g.* Refs. [13,14]). However, the copper oxidation process is one of the most studied with a large number of experimental and computational methods, and one of the better understood. Therefore, a detailed understanding of copper oxidation, of the techniques used to study it and of the challenges which are still open is invaluable when considering the oxidation process on any other system.

In this review, we discuss the status of knowledge of copper oxidation from the atomistic point of view, which we believe is of key importance if we want to learn how to prevent or manipulate copper oxidation. We cannot hope to provide a complete review of all the work done on this subject since the beginning of the last century [15–17]. We are therefore going to focus on recent surface science, spectroscopy and atomistic computational work which has been performed to understand the properties of copper oxides and their formation, and on the open challenges that can be addressed using these techniques.

First, a brief overview on the experimental and computational techniques which have been used for the study of oxide structures and oxidation kinetics is given (Section 2), in order to clarify some of the terminology used throughout the review. The structural and electronic characteristics of the bulk oxides and their surfaces are then presented (Section 3). We subsequently look at the interaction of clean copper surfaces with oxygen and the initial stages of controlled oxidation (Section 4) as well as long-term oxidation (Section 5). Finally, in Section 6, conclusions and perspectives are given.

We hope that it will be clear from the following that tremendous progress has been made in understanding the atomistic details of copper oxides and their formation under different conditions. However, equally important gaps in our understanding remain, especially in terms of the formation kinetics and the structure of the resulting oxide surfaces.

2. Experimental and computational techniques

An enormous number of experimental [18–21] and computational techniques are available to investigate the physical and chemical characteristics of solids, surfaces and surface kinetic processes. Many of them have been used over the years to *e.g.*, understand oxide structures, characterise oxide surfaces, understand the oxidation kinetics and investigate bulk properties of the oxides. For clarity, in this section we provide a brief introduction to the most relevant techniques which have been used on copper oxide and which are going to be mentioned in the following sections, with an emphasis on strengths and weaknesses of each approach.

In early studies of oxidation, thermogravimetric analysis (TGA), where changes in physical and chemical properties of materials are measured as a function of time, was widely used to study the onset of oxidation by recording the mass gain of a sample under oxygen exposure. Whilst useful in providing a