

Reactive metal–oxide interfaces: A microscopic view

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Received 10 August 2015; received in revised form 1 December 2015; accepted 2 December 2015

Abstract

Metal–oxide interfaces play a fundamental role in determining the functional properties of artificial layered heterostructures, which are at the root of present and future technological applications. Magnetic exchange and magnetoelectric coupling, spin filtering, metal passivation, catalytic activity of oxide-supported nano-particles are just few examples of physical and chemical processes arising at metal–oxide hybrid systems, readily exploited in working devices. These phenomena are strictly correlated with the chemical and structural characteristics of the metal–oxide interfacial region, making a thorough understanding of the atomistic mechanisms responsible of its formation a prerequisite in order to tailor the device properties. The steep compositional gradient established upon formation of metal–oxide heterostructures drives strong chemical interactions at the interface, making the metal–oxide boundary region a complex system to treat, both from an experimental and a theoretical point of view. However, once properly mastered, interfacial chemical interactions offer a further degree of freedom for tuning the material properties. The goal of the present review is to provide a summary of the latest achievements in the understanding of metal/oxide and oxide/metal layered systems characterized by reactive interfaces. The influence of the interface composition on the structural, electronic and magnetic properties will be highlighted. Particular emphasis will be devoted to the discussion of ultra-thin epitaxial oxides stabilized on highly oxidizable metals, which have been rarely exploited as oxide supports as compared to the much more widespread noble and quasi noble metallic substrates. In this frame, an extensive discussion is devoted to the microscopic characterization of interfaces between epitaxial metal oxides and the Fe(001) substrate, regarded from the one hand as a prototypical ferromagnetic material and from the other hand as a highly oxidizable metal.

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Keywords: Scanning tunneling microscopy and spectroscopy; X-ray photoemission spectroscopy; Molecular beam epitaxy; Metal–oxide interfaces; Oxide surfaces

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1. Introduction

Interface formation between metals and oxides are one of the most widely investigated topic in physics, chemistry and material science. The reason for this huge interest is that there is almost no technological field in which the metal–oxide interaction does not play a prominent role, including (nano) catalysis [1–3], microelectronics [4,5], magnetic storage media [6], and protective coatings against corrosion [7,8].

From a more fundamental point of view, the metal–oxide interface represents an interesting example of boundary between two materials possessing markedly different and often antithetical electronic and structural properties [9]. As a relevant case, let us mention that a few nanometer-thick (hydro)oxide skin forms at the surface of almost every metal exposed to environmental conditions [10]. The characteristics of this thin surface oxide layer and its interaction with the underlying metallic support are often key factors in determining the physical and chemical properties of metal surfaces.

The material science community has also dedicated a remarkable attention to the investigation, both theoretical and experimental, of heteroepitaxial metal–oxide systems, where, at variance from native oxides, the metal element is different from the cationic species of the oxide phase. Many physical phenomena arising in artificial metal–oxide heterostructures have been reported, spanning from magnetic instabilities [11,12], charge transfer across the metal–oxide interface [13], magnetoelectric coupling in layered multiferroic structures [14], and tunneling-induced spin filtering [15,16], just to mention a few. All these phenomena are intimately connected with the structural and chemical characteristics of the metal–oxide interfacial region. In order to control, and to some extent tuning, the functionalities of these heterostructures, it is of crucial importance to gain an in-depth understanding of the mechanisms driving the formation of metal–oxides interfaces, in terms of both thermodynamical stability and kinetic constraints imposed by the specific preparation method.

Two different classes of systems can be identified, the metal/oxide (M/O) and the oxide/metal (O/M) heterophases, sketched in Fig. 1. These two seemingly symmetric interfaces often possess different structural and chemical characteristics, mainly because different are the experimental procedures exploited for their preparation (see Section 2.1). The O/M interface is grown by depositing ultra-thin (0–10 nm thick) oxide films on metallic

substrates, exploiting the so-called reactive deposition, in which metal atoms are deposited in the presence of an oxidizing atmosphere [17]. On the other hand, the M/O interface can be obtained by depositing metallic films on well-defined oxide surfaces [18,19]. In the latter case, in order to alleviate charging problems related to the use of electron-based microscopic and spectroscopic techniques, the oxide layer of the M/O structure is often supported by a metallic substrate. Despite beyond a critical thickness the surface properties of these metal-supported ultra-thin oxide films have proven to mimic those of the corresponding bulk compounds [20,21], for few unit-cell-thick oxide films the influence of the bottom metallic substrate on the M/O properties cannot be neglected, so that the system is better described as a M/O/M layered structure.

Besides the different experimental constraints characterizing their preparation, the O/M and M/O interfaces bear also intrinsic differences, since the surface free energy of oxidic compounds is generally lower with respect to that of metallic elements (see Section 2.1). For this reason, oxide films tend to wet metallic substrates, while metals deposited on oxide surfaces are prone to clustering, or even to being encapsulated by a thin oxide layer. Such a fundamentally different growth mode observed in the early stages of formation of M/O and O/M interfaces can remarkably influence their final morphological and chemical characteristics.

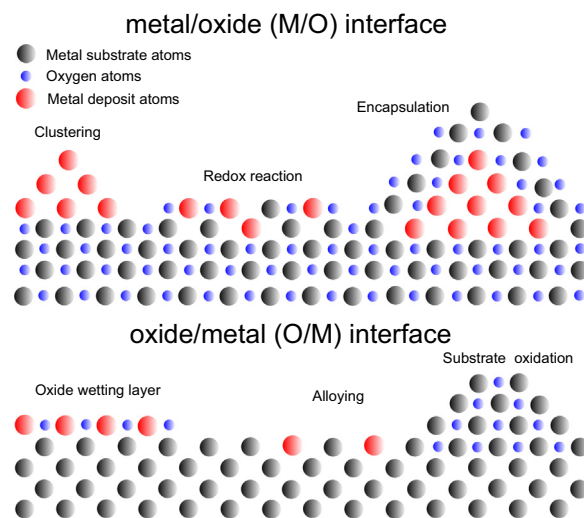


Fig. 1. Metal/oxide (M/O) and oxide/metal (O/M) interfaces. The main phenomena occurring in the early stages of interface formation are displayed.

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