

Interaction of nanostructured metal overlayers with oxide surfaces

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Abstract

Interactions between metals and oxides are key factors to determine the performance of metal/oxide heterojunctions, particularly in nanotechnology, where the miniaturization of devices down to the nanoregime leads to an enormous increase in the density of interfaces. One central issue of concern in engineering metal/oxide interfaces is to understand and control the interactions which consist of two fundamental aspects: (i) interfacial charge redistribution — electronic interaction, and (ii) interfacial atom transport — chemical interaction. The present paper focuses on recent advances in both electronic and atomic level understanding of the metal–oxide interactions at temperatures below 1000 °C, with special emphasis on model systems like ultrathin metal overlayers or metal nanoclusters supported on well-defined oxide surfaces. The important factors determining the metal–oxide interactions are provided. Guidelines are given in order to predict the interactions in such systems, and methods to desirably tune them are suggested.

The review starts with a brief summary of the physics and chemistry of heterophase interface contacts. Basic concepts for quantifying the electronic interaction at metal/oxide interfaces are compared to well-developed contact theories and calculation methods. The chemical interaction between metals and oxides, i.e., the interface chemical reaction, is described in terms of its thermodynamics and kinetics. We review the different chemical driving forces and the influence of kinetics on interface reactions, proposing a strong interplay between the chemical interaction and electronic interaction, which is decisive for the final interfacial reactivity. In addition, a brief review of solid–gas interface reactions (oxidation of metal surfaces and etching of semiconductor surfaces) is given, in addition to a comparison of a similar mechanism dominating in solid–solid and solid–gas interface reactions.

The main body of the paper reviews experimental and theoretical results from the literature concerning the interactions between metals and oxides (TiO₂, SrTiO₃, Al₂O₃, MgO, SiO₂, etc.). Chemical reactions, e.g., redox reactions, encapsulation reactions, and alloy formation reactions, are highlighted for metals in contact with mixed conducting oxides of TiO₂ and SrTiO₃. The dependence of the chemical interactions on the electronic structure of the contacting metal and oxide phases is demonstrated. This dependence originates from the interplay between interfacial space charge transfer and diffusion of ionic defects across interfaces. Interactions between metals and insulating oxides, such as Al₂O₃, MgO, and SiO₂, are strongly confined to the interfaces. Literature results are cited which discuss how the metal/oxide interactions vary with oxide surface properties (surface defects, surface termination, surface hydroxylation, etc.). However, on the surfaces of thin oxide films grown on conducting supports, the effect of the conducting substrates on metal–oxide interactions should be carefully considered.

In the summary, we conclude how variations in the electronic structure of the metal/oxide junctions enable one to tune the interfacial reactivity and, furthermore, control the macroscopic properties of the interfaces. This includes strong metal–support interactions (SMSI), catalytic performance, electrical, and mechanical properties.

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1. Introduction

Metal/oxide interfaces play critical roles in many applications including materials science, microelectronics, and chemical applications. Metal–oxide interactions, which consist of interfacial charge redistribution and/or mass transport upon interface formation, are important factors determining properties and performances of the heterojunctions.

For materials science, metal/oxide interfaces can be found in many technological materials, such as functional ceramics with metals, oxide dispersion-strengthened alloys, oxide coatings on metals functioning as thermal barriers or natural corrosion protection layers, etc. Fundamental problems with these systems include the adhesion strength, mechanical stability, and fracture behavior of the interfaces, which are all closely related to metal–oxide interactions [1,2]. To further understand

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