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Review article

In situ studies of oxide nucleation, growth, and transformation using slow electrons

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ABSTRACT

Surface processes such as metal oxidation and metal oxide growth invariably influence the physical and chemical properties of materials and determine their interaction with their surroundings and hence their functionality in many technical applications. On a fundamental level, these processes are found to be governed by a complex interplay of thermodynamic variables and kinetic constraints, resulting in a rich variety of material-specific phenomena. In this review article, we discuss recent results and insights on transition metal oxidation and rare-earth oxide growth acquired by low-energy electron microscopy and related techniques. We demonstrate that the use of *in situ* surface sensitive methods is a prerequisite to gaining a deeper understanding of the underlying concepts and the mechanisms responsible for the emerging oxide structure and morphology. Furthermore, examples will be provided on how structural and chemical modifications of the oxide films and nanostructures can be followed in real-time and analyzed in terms of local reactivity and cooperative effects relevant for heterogeneous model catalysis.

1. Introduction

Contrary to the field of semiconductor heteroepitaxy that has been firmly established in the last few decades and can well be considered mature, our understanding of oxide heteroepitaxy is still at a relatively early stage. This is particularly due to the complex, *hybrid* nature of the interface between the substrate, which generally could represent a metal, semiconductor, or insulator, and the metal oxide that is prepared on top. Owing to the large number of thermodynamically and kinetically driven effects and phenomena that have been identified in the past, no growth model has been proposed yet that incorporates all concurring mechanisms and processes in a coherent fashion. Consequently, most research efforts have been devoted to studying an increasing number of hopefully representative examples for various classes of systems to infer more general principles based on existing case studies. From this perspective, the present contribution does not aim at deducing generalized principles of oxide heteroepitaxy, but rather hopes to illustrate certain aspects of oxide nucleation and growth that have frequently been overlooked in the past, but present themselves most clearly when employing *in situ* characterization during preparation or are virtually inaccessible otherwise. In the following, we will limit the discussion to the case of binary oxide systems – it is quite obvious that the situation will become even more intricate if ternary or higher oxides are considered.

As a classical example, our understanding of Ge/Si heteroepitaxy is largely rooted in relatively straight-forward geometrical considerations as, e.g., lattice mismatch and strain accommodation, as well as thermodynamic properties, such as surface free

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energies, and kinetic limitations affecting elemental mixing and interdiffusion [1–5]. While all these aspects remain of significance in the case of hybrid oxide systems, further interfacial characteristics lead to an increased complexity. Firstly, the oxide and the substrate generally adopt different crystal structures and symmetries, typically impeding pseudomorphic growth. Secondly, in the case of multiple stable electronic configurations of the metal cation in the bulk, the surface phase diagram becomes increasingly more complex, which in turn results in an even larger geometric variability and different possibilities for strain accommodation at the expense of a changing stoichiometry and perturbed bonding configurations. Thirdly, depending on crystal orientation the exposed surface may be polar [6], driving the formation of long-range surface reconstructions for compensating the residual dipole moment and hence the reduction of the overall surface free energy [7]. Consequently, this factor is also crucial in determining the outer shape of even mesoscale or nanoscale oxide particles in isolation according to the Wulff-Kaishev theorem [8]. Fourthly, the variable chemical composition of the oxide material and the rather elevated temperatures during epitaxial growth efficiently activate interdiffusion and interfacial chemical reactions, often involving substrate oxidation, thus preventing the formation of an abrupt interface between the substrate and the oxide film. This effect may even give rise to the occurrence of novel (e.g., ternary) oxide phases, which may be stabilized as ultrathin films and which can rightfully be regarded as novel materials themselves with distinct, intriguing characteristics [9]. In this article, we will discuss recent *in situ* studies that demonstrate the intricate interplay between these thermodynamic and kinetic effects in epitaxial metal oxide growth, and we will provide examples illustrating how these effects can be used to manipulate the materials properties of the emerging oxide.

Several surface science routes exist to synthesize metal oxide films on crystalline, metallic supports under vacuum conditions, the most prominent being: (i) surface oxidation by exposure to an oxidizing gas, inducing the usually self-limiting formation of a thin oxide film [10], and (ii) deposition of a metal onto a crystalline support of a different metal in an oxidizing ambient, leading to the nucleation and growth of an oxide film whose thickness may be controlled by the amount of evaporated metal. These two processes usually result in very different sample morphologies since only the latter procedure leaves some possibility for steering the growth process by intentional lattice matching between the substrate and the metal oxide. Starting from the experimentally simpler oxidation method for a variety of transition metal surfaces, we will show the prevalence of certain principles and effects that predominantly determine the structure and morphology of the as-grown oxide films. In the second part, we will discuss *in situ* case studies that elucidate the delicate balance between thermodynamic energy considerations and kinetically driven effects in binary oxide heteroepitaxy. We will highlight how one particular experimental technique, namely Low Energy Electron Microscopy (LEEM) [11], has greatly furthered our understanding of heteroepitaxial oxide systems and will review its unique strengths for these types of studies.

2. Material and methods

2.1. Sample preparation

To be suitable for low-energy electron microscopy (LEEM) investigation, samples must be sufficiently well-ordered to produce defined diffraction peaks and flat enough such that they have atomically smooth terraces with well-separated step edges. In general, most metallic and semiconducting single crystals with sufficient electrical conductivity can be studied, and these are typically prepared by standard techniques such as inert ion sputtering and annealing to elevated temperatures. Gas treatments (e.g. H_2 or O_2) are also commonly carried out in order to remove surface oxides or residual carbon contamination prior to measurement. In order to obtain well-separated step edges and large atomically flat terraces, it is usually necessary to ensure that any miscut of the crystal prior to polishing is very small (typically $< 0.1^\circ$ from a low index face). Charging of insulating or poorly-conducting samples can cause issues performing LEEM measurements, and excessively rough samples with sharp “tips” can cause undesirable sparking during application of the microscope operating voltage (up to 20 kV).

2.2. Low-energy electron microscopy

Low-energy electron microscopy (LEEM) is a diffractive imaging technique that provides fast access to the nanoscale structure and morphology of a crystalline sample [11–19]. Its key strengths are the ability to image with high resolution (as low as 2 nm with aberration-corrected optics, although more typical resolutions are on the order of ~ 10 nm) [15,16] with video-rate acquisition (up to ~ 15 Hz) under varied sample environments. In particular, the temperature of the sample can be widely varied during imaging, generally in the range 100–1800 K, permitting the study of a range of dynamic processes. LEEM imaging can be conducted under pressures ranging from UHV (10^{-10} mbar) up to $\sim 10^{-4}$ mbar, where the short mean free paths of the electrons and the desire to maintain suitable clean surfaces are the limiting factors. This pressure range is well-suited to the study of many oxidation processes, and due to the typical geometry of the sample environment within LEEM instruments (normal incidence/emission of the electrons), it is also facile to fit metal evaporators to allow *in situ* deposition and growth of heteroepitaxial materials [12].

One of the common LEEM designs is that of the Elmitec GmbH type which utilizes a magnetic sector field. A schematic of the layout of this design is shown in Fig. 1. In this type of instrument, electrons emitted from a cathode are accelerated to the operating voltage of the microscope (typically ~ 20 kV) and after collimation via illumination optics, they pass through the magnetic sector field and the objective lens and are incident on the sample at normal incidence. The sample is held at the cathode potential offset by a bias voltage (the start voltage, typically -5 to 100 V) which corresponds to the landing energy of the probe electrons. These are reflected from the surface and pass into the objective lens, forming a real-space image of the surface within the magnetic sector field, and a surface diffraction pattern in the back focal plane of the objective. After passing through further imaging electron optics and an (optional) energy analyzer, the electrons are projected onto a phosphor screen, and the image is captured by a camera [11].