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Structural and electronic characterization of the MgO/Mo(0 0 1) interface using STM

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ABSTRACT

The nucleation and growth of ultrathin MgO films on Mo(0 0 1) have been investigated with scanning tunneling microscopy and spectroscopy. In the initial growth stage, the MgO forms rather uniform islands with rectangular shapes and defined orientation. This behavior reflects a preferential binding of the oxide O ions to the top positions in the Mo support, which can be realized only in confined areas due to the MgO/Mo lattice mismatch. At monolayer coverage, a characteristic square pattern becomes visible in the STM, indicating the formation of an MgO/Mo coincidence lattice. In the coincidence cell, the interface registry alternates between O and Mg ions being in Mo top positions. The resulting imaging contrast in the STM is dominated by a work-function modulation and not by a topographic effect, as demonstrated with STM-conductance and light-emission spectroscopy. The modulated work function in the coincidence cell is assigned to a small buckling of the oxide film with either O or Mg ions being closer to the Mo surface.

1. Introduction

Thin oxide films have attracted a lot of attention in recent years due to their importance in the materials sciences, in microelectronics and heterogeneous catalysis. Oxide films are utilized in these fields as protective coatings against corrosion, as dielectric spacer layers and electron-transparent model systems for insulating bulk oxides. Such applications heavily depend on the possibility to prepare homogeneous films without holes even if the film thickness is reduced to a few atomic layers. Only a structurally intact film guarantees the desired properties and prevents mis-operation, for instance due to pit corrosion, dielectric breakthroughs, or parasitic effects originating from the support material.

Thin oxide films on metal substrates are also ideally suited to study the fundamental properties of metal–oxide interfaces [1–3]. Their behavior depends on various structural and electronic parameters, such as the lattice mismatch between the two systems, the atomic registry at the interface and the strength of the metal–oxide adhesion. Many theoretical attempts have been made to investigate the properties of metal–oxide interfaces; however, most of these studies are restricted to idealized and defect free systems [4–6]. In particular, the role of the lattice mismatch is often neglected and support and oxide layer are artificially forced to the same lattice constant. As a consequence, crucial properties of a metal–oxide system might not be accessible to the calculations, for instance if imposed by an incommensurate relationship between ad-layer and support or by large coincidence structures. Furthermore, the numerous restructuring processes of thin-film systems to release misfit-induced lattice strain cannot be treated in a satisfactory manner. However, structural relaxation that enforces the formation of dislocations [7–9], mosaics [10,11] and 3D islands [12,13] governs not only the morphology, but also the electronic and chemical behavior of thin oxide films.

From the experimental side, even complex metal–oxide systems can be explored with surface science techniques that are sensitive to structural and electronic aspects of the interface [14,15]. Scanning tunneling microscopy (STM) plays hereby a particularly important role, as it enables a real-space investigation of interfacial properties and dominant relaxation mechanisms in thin-film systems [16–18]. The STM provides insight into the atomic morphology of an interface, but also its electronic and optical behavior can be probed via differential conductance and light-emission spectroscopy [8,19–21].

This paper discusses the structural and electronic characteristics of an ultrathin MgO film grown on a Mo(0 0 1) surface [7,22,23]. The MgO/Mo system is interesting for many aspects. Due to the high melting point of the Mo substrate, the oxide layer can be thoroughly annealed and pushed into its thermodynamically favored configuration. The large lattice mismatch of 5.4% between MgO and Mo(0 0 1) enforces complex structural relaxations, which involve the insertion of an interfacial dislocation network and the formation of screw dislocations and mosaics in the film. The thickness-dependent relaxation behavior of the MgO/Mo film has been investigated with STM and diffraction techniques before [23]. Also from an electronic point of view, the system offers a

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number of unique properties. The oxide formation induces a considerable decline of the Mo(0 0 1) work function [24,25], which in turn enables charge transfer processes from the metal into adsorbates on the oxide surface [26]. This effect has already been demonstrated for MgO/Ag(0 0 1) films [27], but is expected to be much larger on the MgO/Mo system due to a larger interfacial coupling in this case [26,28].

This paper focuses on the properties of sub-monolayer and monolayer (ML) MgO films, as their quality decisively influences the growth of thicker oxide layers. It discusses in particular the effect of the lattice mismatch on the structural and electronic properties of the MgO–Mo interface. Furthermore, regular work-function modulations on the surface of thin MgO/Mo films are identified as the origin for the distinct imaging contrast and the spectroscopic response of the system in the STM.

2. Experiment

The Mo(0 0 1) surface that is used as support for the oxide preparation is cleaned by Ar^+ sputtering, annealing in an O_2 ambience and flashing to 2300 K. This procedure is repeated until a sharp (1×1) LEED pattern without superstructure spots is obtained (Fig. 1). MgO films of up to two ML thickness are then produced by Mg deposition from a Mo crucible in 1×10^{-7} mbar O_2 at 300 K sample temperature. The deposition rate is set to 1 ML/min. After deposition, the film is annealed for 10 min in UHV at the temperatures specified in the following discussion. Averaging structural information is obtained from Low-Energy Electron Diffraction (LEED) performed with a two-grid LEED optic. Real space data is acquired with a custom-built Beetle-type STM operating at liquid nitrogen temperature (100 K). The microscope is equipped with an optical read-out that consists of two parabolic mirrors and allows detection of photons emitted during the tunnel process [29]. The photons are either collected by a CCD detector attached to a grating spectrograph or by a photo-multiplier tube that measures the integral photon yield. By these means, the wavelength distribution of the emitted light or alternatively the spatial localization of emission centers on the surface can be studied.

3. Results and discussion

3.1. Sub-monolayer MgO films

Fig. 1 presents an STM image-series of a sub-monolayer MgO film on Mo(0 0 1), being deposited at 300 K and annealed to the indicated temperatures T. The as-grown film (T = 300 K) produces featureless and diffuse STM images and shows a faint (1×1) LEED pattern, indicating its amorphous or short-range ordered structure (not shown). This behavior is maintained until the annealing temperature exceeds 700 K, when small nano-crystallites of uniform height emerge in between the amorphous patches. Their height amounts to ~2.0 Å when measured above 3.0 V sample bias, suggesting the formation of monolayer high MgO islands. With increasing temperature, the crystalline regions grow on the expense of the disordered patches that finally disappear at around 850 K. Simultaneously, the oxide film partially de-wets the substrate and the Mo(0 0 1) surface is exposed again. For T > 950 K, the MgO islands undergo an ordering process, in which they transform into uniform stripes of ~50 Å width running along the Mo[1 1 0] directions. Around 1050 K, the stripes coalesce into large irregularly shaped oxide patches, most likely due to Ostwald ripening. Furthermore, the MgO starts desorbing from the surface and larger regions of bare Mo(0 0 1) become visible. Above 1100 K, the oxide film has finally disappeared and only small randomly-shaped islands remain visible. It should be noted that the MgO desorption temperature sensitively depends on the initial oxide coverage and sub-monolayer structures evaporate at considerably lower values than thick films [30].

The ordering process of the MgO film observed by STM is also revealed with LEED. A LEED pattern with sharp Mo(1×1) reflexes surrounded by four [1 1 0]-oriented satellites shows up only for annealing temperatures above 700 K (Fig. 1, right inset). The absence of a genuine MgO-induced superstructure hereby indicates that the primitive cells of oxide and support coincide and the MgO exposes a (0 0 1) surface as well. Furthermore, the MgO[1 0 0] direction needs to align with the Mo[1 1 0], as only in this configuration the lattice parameters are comparable [23]. The satellites have a fixed, energy-independent separation from

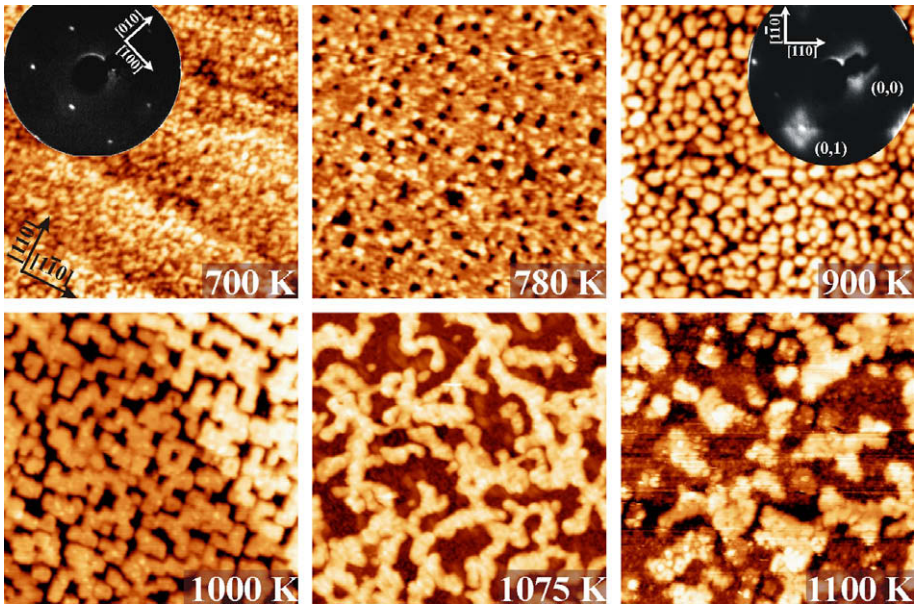

Fig. 1. STM series of a sub-monolayer MgO/Mo(0 0 1) film deposited at 300 K and annealed to the indicated maximum temperatures for 10 min (U_s = 2.5–3.5 V, 100×100 nm^2). The left and right insets show LEED patterns of the bare Mo support (120 eV) and the MgO film after annealing to 900 K (55 eV), respectively. The four satellites around the MgO reflexes indicate the mosaicity of the oxide film.