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Structure and thermal stability of fully oxidized TiO_2/Pt(111) polymorphs

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ABSTRACT

We present a thorough investigation of TiO_2 films of different thicknesses grown on Pt(111) surface by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED). When the thickness is below 10 monolayers (ML) the film, growing on top of a wetting monolayer, has the structure of a TiO_2(B) polymorph, related to the *rect′*-TiO_2 reported in the ultrathin regime. The film is characterized by islands with a high defect density and with grain boundaries where the lattice is shifted between two adjacent islands. Thermal treatment in oxidizing conditions reduces the number of surface defects without modifying the average island size. Above 10 ML, a different rutile-like oxide structure appears, labelled as *quasi*-(1×2) according to the LEED pattern. STM shows a quite rough and granular morphology, which is largely improved by thermal treatment, resulting in ordered islands covering more than 75% of the film. STM reveals, on the ordered islands, the incommensurate (1×2) surface unit cell, as well as a new (7×1) periodicity that does not find a counterpart in the LEED pattern. Beyond 20 ML coverage a higher grade of surface roughness and defectivity is observed, which can be improved only after very long thermal treatment. This gives rise to ordered patches covering an area of about 45%, and with the same surface structure observed at lower coverage. The (7×1) periodicity is not compatible considering previous models of bulk oxide surfaces, suggesting that a stress-mediated mechanism could play a role, during the growth of each island, in defining the observed periodical corrugation.

1. Introduction

Titania (TiO_2) is one of the most relevant strategic materials in many technologically important areas, like heterogeneous catalysis [1–3], photo-assisted oxidation [4], optical [5,6] and photovoltaic devices [7]. Nano-dimensional TiO_2, such as ultrathin supported films [8–10], nanosheets, nanorods and nanoparticles [3], showed surface mediated structural and chemical properties different from those of the most common bulk polymorphs (rutile, anatase and brookite) [8,11]. For instance, the reactivity towards water dissociation is related to the oxide surface termination and to the density of defects [12,13], and therefore a detailed knowledge of the surface properties of the nanodimensional TiO_2 phases is crucial to exploit the full potential of these nanostructures.

In this framework, our research group strongly focused on the growth of reduced and fully oxidized ultrathin oxide layers on Pt(111) surface, and their structural, morphological and chemical peculiarities have been accurately investigated with a full set of surface science techniques [8,14–21]. Even if the reduced films are really interesting for their peculiar structures and chemical properties [8], their effective use out of the vacuum is vanished by their reactivity toward oxygen [17]. The fully oxidized ultrathin films are more interesting for applications: in this case, rather unusual polymorphs have been observed in the ultrathin regime (i.e. lepidocrocite-like and TiO_2 (B) [19]). As bridging system between bulk oxide surfaces and ultrathin films, stoichiometric thin films (up to few tens of layers thick) have recently been studied to verify the behaviour with respect to water dissociation [22]. However, no precise information on the surface structure and morphology of such films has been reported yet.

In this paper we present a thorough investigation of such TiO_2/Pt(111) films of different thicknesses. At low coverage TiO_2(B) films with the (001) termination are obtained (previously named as *rect′*-TiO_2 [8] when dealing with ultrathin films), while at higher coverage a TiO_2 rutile-like film is observed with a new surface periodicity. The structure and the thermal stability of the films are discussed through scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) data.

2. Materials and methods

Pt(111) was cleaned by repeated cycles of 1 keV Ar ion sputtering and UHV annealing up to 970 K with 1 K/s cool down rate, until no C, O, or residual Ti contamination was detected by XPS. Ti was evaporated by a joule-heated filament of high purity (4 N) Ti on Pt(111) substrate at room temperature, in an oxygen-rich environment (O_2 pressure = $5\cdot10^{-6}$ mbar) (for details see ref [22]). The reference monolayer (ML) is defined as the Ti amount needed to build a (001)-anatase TiO_2

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bilayer sheet, with 0.24 nm plane spacing. Evaporation rate of 0.4 ML/min was estimated through the growth of an ultrathin reduced TiO_x film in UHV based on LEED and STM data: at around 1 ML there is a sharp phase transition from *z′*-TiO_x phase to *w′*-TiO_x (see [8]) on the whole sample surface, ensuring also low Ti coverage gradient. Moreover, the nominal coverage was compared with the film thickness measured by STM using the large pits observed in the film extending down to the first wetting layer.

All the annealing treatments were performed in an oxygen pressure of 5×10^{-6} mbar, with heating and cooling rates of 1 K/s and with a final constant temperature treatment of 20 min at 873 K. We define the as-grown film as the result of a Ti deposition at RT in oxygen-rich environment (O_2 pressure $=5\cdot10^{-6}$ mbar) followed by a single annealing at 873 K in the same oxidizing conditions.

STM, LEED and XPS where performed in a UHV multiscan lab from Omicron. STM images were acquired in constant current mode with Pt/Ir tips cleaned by electron bombardment. Base pressure in both preparation and analysis chambers is lower than 1×10^{-10} mbar.

3. Results

STM morphologies of the oxide layers were obtained at different θ coverage. We first discuss the results for θ<10 ML, confirming the behaviour already observed for the ultrathin films, i.e. the presence of the TiO_2(B) polymorph with the (001) termination, previously labelled as *rect′*-TiO_2. We then present data for coverage θ>10 ML, when a new TiO_2 structure is obtained, named *quasi*-(1×2) film according to its LEED pattern [22].

3.1. θ<10 ML: TiO_2(B) films

The LEED and STM data corresponding to a coverage θ=5 ML, but representative of the θ≤10 ML coverage regime, are presented in Figs. 1 and 2. The LEED of the as-grown film (Fig. 1a) shows the Pt(111)-related (1×1) spots with an inner set of clear rings, which can be attributed to different azimuthal orientations of the oxide islands, with some background, indicating partial disorder at the surface. In fact, the STM images of the as-grown films indicate an overall system morphology characterised by highly irregular islands and large pits. At large scale (Fig. 1c) many relatively small neighbouring islands (nominal average diameter<40 nm), separated by wiggling boundary walls form the top layer. A large number of holes inside the islands indicates a large defectivity, in line with the high background of the LEED pattern. Moreover, the large pits (black areas) with very irregular borders are extending down to the substrate surface. Due to the weak interaction of the Pt(111) metal substrate with the oxygen layer at the interface [23,24], a Vollmer-Weber-like growth of TiO_2 islands is expected, with a weak epitaxial orientation with respect to the Pt(111) substrate. The STM data at low coverage (see ref. [22]) suggest an initial Stransky–Krastanov growth mode. However, the present data are more compatible with a layer by layer growth mode, suggesting that a transition in the growth mode is taking place for θ>4 ML.

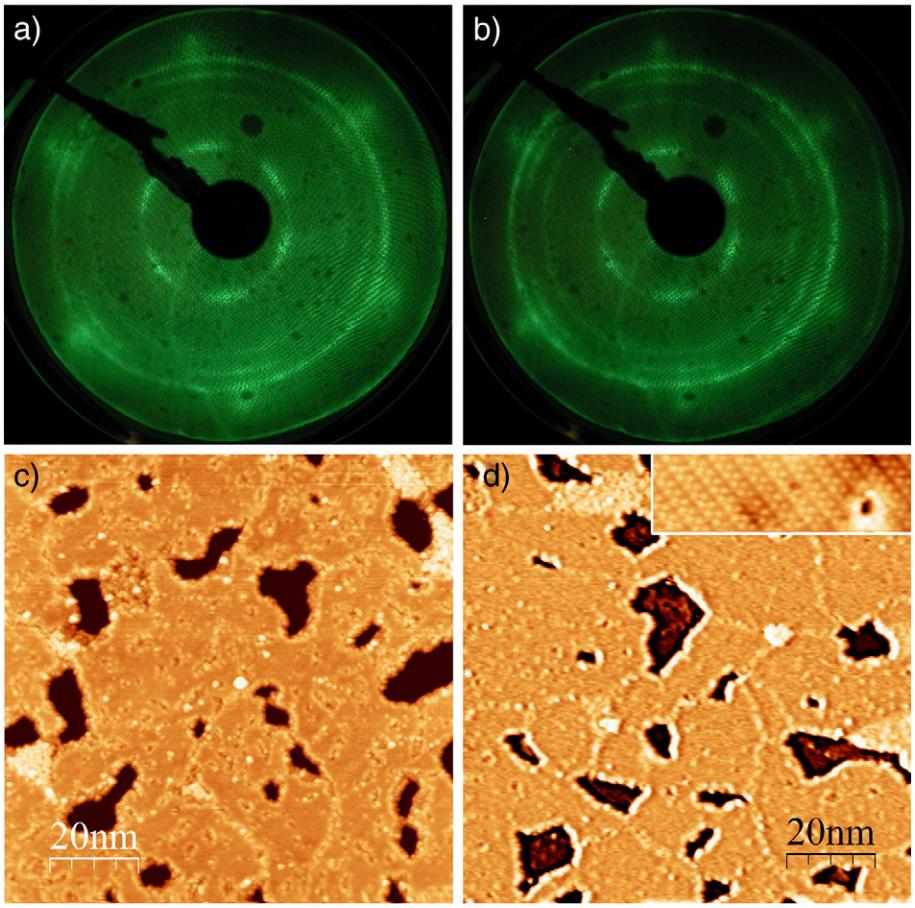

Fig. 1. a) LEED pattern ($E_P=55$ eV) of as-grown TiO_2/Pt(111) film at θ=5 ML showing the *rect′*-TiO_2 symmetry [19]. b) LEED pattern ($E_P=55$ eV) of the same system after annealing in oxygen, no relevant modifications observed. c) 100×100 nm^2 STM frame (V=+1.6 V, I=0.2 nA) of as-grown film corresponding to a). d) 100×100 nm^2 STM frame of annealed film. The 7.5×2.5 nm^2 high resolution inset (V=+1.6 V I=0.84 nA) shows the persistence of some defects in the film surface.