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Ultrathin $Y_2O_3(111)$ films on Pt(111) substrates

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ABSTRACT

The growth of ultrathin films of $Y_2O_3(111)$ on Pt(111) has been studied using scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), and low energy electron diffraction (LEED). The films were grown by physical vapor deposition of yttrium in a 10^{-6} Torr oxygen atmosphere. Continuous $Y_2O_3(111)$ films were obtained by post-growth annealing at 700 °C. LEED and STM indicate an ordered film with a bulk-truncated $Y_2O_3(111)$–1 × 1 structure exposed. Furthermore, despite the lattices of the substrate and the oxide film being incommensurate, the two lattices exhibit a strict in-plane orientation relationship with the $[1\bar{1}0]$ directions of the two cubic lattices aligning parallel to each other. XPS measurements suggest hydroxyls to be easily formed at the Y_2O_3 surface at room temperature even under ultra high vacuum conditions. The hydrogen desorbs from the yttria surface above ~200 °C.

1. Introduction

Thin oxide films on metal substrates are commonly used to study surface science phenomena of insulating metal oxides [1–3]. Sometimes these films resume the same structure as their bulk counterparts, for examples, oxide films of $CeO_2(111)$ [4] on Ru(0001) [5,6] and Pt(111) [7]; MgO [8,9], CoO [10,11] and FeO [12] on Ag(100); CoO(100) [13] and MnO(100) [14,15] on Pd(100); MnO(111) on Pt(111) [16]; Cr_2O_3 on Cu (111) [17]; or FeO on Ru(0001) [18] or Pt(111) [19] are bulk-like. While some other oxides form contiguous films with complex structures, such as Al_2O_3 on NiAl alloys [20] and SiO_2 [21–24], or TiO_x [25,26] on Mo (112). Some oxide films have been proven to be difficult to synthesize with a single, well-defined structure. For instance, efforts in growing well-defined ZrO_2 films on Pt(111) [27–29] or Cu(111) [30] have resulted in several structures. One reason for this may be the polymorphism of zirconia in its bulk form that may result in different competing structures in the thin film.

Generally the lower surface energy of oxides causes the wetting of metal substrates and therefore the metal substrates are usually covered at least by the first oxide monolayer. This monolayer often is quite different from the bulk-oxide structures [31–39]. The bulk-like oxide may evolve for two-layer or thicker films. This has been for example demonstrated for SnO_2/Pt(111) [40]. Pt(111) is a popular substrate for thin oxide-film growth [3] because of its high thermal stability and high resistance to oxidation. These properties of Pt ensure a sharp metal/oxide interface and no intermixing of the substrate material with the oxide film. Most oxide films with bulk structure grow in a crystallographic orientation such that the surface with the lowest energy is exposed. This means for many cubic structured oxides that the films preferentially exhibit a (111) termination. Many oxides also exhibit a strict in-plane crystallographic relationship with the substrate despite the often poor match of the lattice constants. An alignment of the oxide crystallographic structure with respect to the substrate allows obtaining single crystalline epitaxial oxide films without different grain orientations. For example, CeO_2 films grow with a (111) bulk truncation and the ceria films exhibit an in-plane alignment of the $[1\bar{1}0]$ direction parallel to the $[1\bar{1}0]$ on Pt(111) or $[11\bar{2}0]$ on Ru(0001), in other words the densely packed directions in the film and substrate are aligned.

Here, we study the growth of Y_2O_3 films on Pt(111) surfaces. Y_2O_3 condenses in the bixbyite crystal structure. Bixbyite has a body centered cubic unit cell with 80 atoms and is of space group Ia-3 symmetry. Y_2O_3 has a lattice parameter a of 10.6 Å. Bixbyite is a common crystal structure for sesquioxides, for example Dy_2O_3, In_2O_3, Pr_2O_3, La_2O_3 also exhibit this crystal structure. The bixbyite unit cell can be viewed to consist of 16 fluorite unit cells with a periodic arrangement of anion vacancies. In the bulk, each Y atom is six-fold coordinated to oxygen atoms. All oxygen atoms have a tetrahedral coordination to four Y neighbors. Therefore, similar to the fluorite structure the (111) planes are expected to be the cleavage planes, or surfaces with lowest energy. The surface unit cell of a bulk-truncated $Y_2O_3(111)$ plane is hexagonal with a surface lattice parameter of 14.9 Å.

Y_2O_3 is an excellent insulator with a wide band gap of ~6 eV. Its electronic properties, together with a good lattice match to silicon, make it a promising dielectric material for semiconductor devices [41]. Y_2O_3 is also used as a support material for transition metal catalysts in its own right [42], or as an addition to ZrO_2 to form yttria stabilized zirconia (YSZ) [43]. Adding yttria to zirconia stabilizes the cubic polymorph of zirconia. This is important in applications where structure-changes of zirconia during heat cycles would induce intolerable stresses, for example in heat barrier coatings for turbines [44]. Another extremely

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important property of YSZ is its ion conductivity which makes it a useful material for membrane materials in oxygen gas sensors and for solid oxide fuel cells. We and others have found that in YSZ yttria has the tendency to segregate to the surface [45]. Our measurements on formate oxidation on YSZ(111) samples have shown primarily dehydration reactions similar to a pure yttria surface. A pure zirconia surface, on the other hand, showed both dehydration and dehydrogenation reactions [46]. This is in agreement with an yttria segregated surface and therefore the surface chemistry of YSZ may be better described by yttria than zirconia, although the bulk concentration of yttria in YSZ is usually only around 10%. The studies presented here aim at creating a surface science model system that will enable studying surface properties of yttria. We show that thin yttria films have a bulk-like structure and the films expose the low energy (111) face. The films exhibit a crystallographic relationship with the Pt(111) substrate. Using thin films supported on a metal enabled us to perform scanning tunneling microscopy (STM) and determine the surface structure of the yttria films as the Y_2O_3(111) bulk truncation. Furthermore, X-ray photoemission spectroscopy (XPS) indicates that yttria surfaces are very easily hydroxylated.

2. Experimental methods

The experiments were performed in two separate ultra high vacuum (UHV) chambers both with a base pressure in the low ~10^{-10} Torr range. One UHV system is equipped with an Omicron variable temperature scanning tunneling microscope (STM) and low energy electron diffraction (LEED) optics and the other UHV chamber is equipped with a dual anode X-ray source and hemispherical electron analyzer for X-ray photoemission studies (XPS).

The Y_2O_3 films were prepared on a Pt(111) single crystal that was cleaned by cycles of Ar^+ ion sputtering and annealing to 1040 K and by annealing in 10^{-6} Torr O_2 at 1040 K. After this procedure a sharp (1×1) LEED pattern was obtained for the Pt (111) substrate. STM images of the clean surface show smooth terraces with straight step edges, free of impurities. Yttria was grown on the clean Pt(111) sample by reactive physical vapor deposition. Yttrium was evaporated in a water cooled e-beam evaporator. An yttrium ingot (Alfa Aesar: 99.9% excluding Ta, Ta impurity less than 1%) mounted at the end of a Mo-rod was used as the evaporating material. The yttrium was deposited in a 1×10^{-6} Torr O_2 background pressure at a rate of approximately 0.002 ML/s. The evaporation rate was estimated from the attenuation-rate of the Pt 4*f* substrate signal in XPS by assuming an exponential attenuation with film thickness and an attenuation length of 2.3 nm [47]. We define one monolayer (ML) as 3.1 Å thick yttria layer, i.e. the separation between two equivalent (111) cleavage planes of Y_2O_3. All the yttria films were grown with the substrate at room temperature and ordered films are obtained by post-growth annealing of the samples at temperatures described in the text.

All STM images were recorded in constant current mode at room temperature with electrochemically etched W tips. The large scale STM images of yttria films were acquired with bias voltages in the range of 0.3 to 0.7 V and tunneling currents of 0.1 to 1.0 nA. Atomic resolution images were obtained with a higher bias voltage of 2.2 V and tunnel currents of 0.3 nA. XPS was measured with non-monochromatized Al K_α (1486.7 eV) radiation. The spectra were recorded in normal emission with the X-ray source at 45° with respect to the sample surface.

3. Results

3.1. Surface morphology

Fig. 1 shows STM images of Y_2O_3 grown on Pt(111) substrate followed by post-annealing at different temperatures. An STM image of the clean Pt(111) substrate and its sharp LEED pattern is shown in Fig. 1(a). Fig. 1(b) shows the surface after deposition of ~1.5 monolayer (ML) yttria at room temperature (RT). RT deposition leads to uniformly distributed but disordered yttria film. No preference for any aggregation of the yttria film at step edges or other surface defects is observed. However, even for room temperature deposition the yttria film exhibits clustering with lateral cluster sizes of around 1.0 nm. Atomic-scale steps and terraces can also be identified on some of these small clusters, which indicate some crystallographic order in the film. To obtain a better order, the oxide film has been annealed to different temperatures. Fig. 1(c) shows an STM image of the Y_2O_3 film after annealing to ~500 °C. This surface exhibits meandering Y_2O_3 islands with a typical island size of 3 nm wide and ~7 nm long. All the islands have the same height with flat tops, indicating good crystallographic order. Longer annealing at this temperature does not lead to a significant coarsening of the islands. Increasing the annealing temperature to 600 °C leads to the formation of larger terraces; see Fig. 1(d). The underlying step structure of the Pt (111) substrate is clearly discerned by the height difference in the film running across the entire image. Importantly, a preferential crystallographic orientation of the island edges is now observed. The 60° symmetry of the step orientations suggests a (111) orientation of the film. Furthermore, the same orientation of the separate islands indicates that the film is not just crystalline, but that the entire film has the same orientation relative to the Pt(111) substrate, i.e. an epitaxial relationship between Y_2O_3(111) and Pt(111) exists despite the huge difference in their lattice constant. When the annealing temperature reaches 700 °C, islands coalesce further forming a contiguous film with some holes in the top layer, as shown in Fig. 1 (e). It is noteworthy that edges of the holes reveal characteristic structure, typically enclosing angles of ~120°. We observe different step heights on this surface, indicating both steps within the yttria film as well as steps from yttria to the Pt substrate. Line-scans across characteristic steps are shown in Fig. 1(e). For a (111) oriented Y_2O_3 film one may expect step heights of ~3.1 Å because of the separation between oxygen–yttrium–oxygen trilayers in the bixbyite crystal structure, as is illustrated in Fig. 1(f). However, the measured apparent height in STM is a function of the tunneling probability and therefore does not only contain information of the sample topography but also on the electronic density of states and the sample work function. Particularly, wide band gap materials with little electronic density of states within the tunneling bias range will exhibit a smaller apparent height. Holes in the yttria film exhibit an apparent depth of typical ~4.0 Å in STM measurements. Therefore this measured height indicates that the yttria film is at least two trilayers in height, i.e. a true height of 6.2 Å.

Due to difficulties in reliably measuring island heights of wide band gap materials on metal substrates with STM, ambiguities exist in the interpretation of the surface morphology. For instance, it is difficult to conclude from the STM images if the 2-dimensional (2D) Y_2O_3 islands shown in Fig. 1 are situated on top of a Y_2O_3 layer or if the Pt substrate is exposed between the islands. One approach that allows us to investigate if the surface is homogeneous or if different surfaces are exposed is to analyze the growth of additional Y_2O_3 layers. For homo-epitaxial yttria on yttria growth, which is the case on top of the 2D yttria islands, a different film morphology may be expected than if yttria is grown for example on the Pt substrate. In Fig. 2, STM images of 1.5 ML of Y_2O_3 deposited on top of a pre-formed nominal 3.0 ML Y_2O_3 film is shown. After room temperature deposition, shown in Fig. 2(a), the entire surface is covered homogeneously with a poorly ordered yttria film. No structural differences between this new yttria film can be discerned on top and in between of the 2D islands. However, subsequent annealing of the samples to 500 °C and 700 °C results in the formation of more ordered structures with clear morphological differences for different areas on the substrate. STM images of samples annealed at these temperatures are shown in Fig. 2(b) and (c). The differences in the morphology are particularly pronounced in Fig. 2(c) after annealing to 700 °C. On top of the pre-formed 2D-yttria islands it appears that the