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8 Atomic structure, order and disorder on high temperature reconstructed **a**-Al₂O₃(0001)

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Oxide materials are strongly represented in this anthology where in not less than five chapters, structural properties of oxide surfaces (Chapters 7, 9 and 10) are discussed or oxides play an important role as substrates for the growth of clusters and molecules (Chapters 9, 10, 12 and 13). Among the oxides, sapphire (α -Al₂O₃) is a prototype insulating crystal with innumerable applications in science, technology and industry[1]. Precise knowledge of its atomic surface structure is prerequisite for understanding and controlling processes involved in many of these applications[2]. However, despite several attempts, atomic resolution imaging on sapphire with dynamic force microscopy [3] was successfully demonstrated only years after the technique had been developed for imaging other insulating surfaces (Chapters 5 and 6). There are mainly two reasons for the inherent difficulty in atomic resolution imaging on sapphire. First, the preparation of clean and well ordered surfaces involves sophisticated surface pre-treatment and heating to high temperatures that is not readily available in many laboratories and, second, inhomogeneous charging that is frequently found on this and other insulating oxide surfaces often introduces severe instability in imaging. Therefore, atomic resolution imaging of the sapphire surface has often been considered to be the definitive test for scanning force microscopy [4] and it is the purpose of this chapter to demonstrate that dynamic force microscopy passed this test and can now be considered as a highly sensitive surface analytical technique mature enough to study any well prepared insulating surface on the atomic scale.

The (0001) sapphire surface is a fascinating example of complexity and diversity in the formation of structures on the surface of a simple binary oxide compound. Rarely any other surface has been studied so intensely over more than 30 years but kept many of its secrets so persistently and also the studies presented here raise as many questions as they answer. The surface exists in several ordered phases that can reversibly be transformed into each other by thermal treatment and oxygen exposure [5]. The 1 x 1 surface is terminated by one layer of aluminium on top of two oxygen layers [6] whereas in literature several different relaxations have been reported [7]: While measured values for the change in Al-O distance range from 50 % to 62 % [8, 9], theoretical calculations yield values between 48 % and 82 % [10, 11]. The large differences in the theoretical values is due to different methods used for calculations whereas differences in experiments were caused by different influences of surface hydroxyl groups on relaxation [6, 12].

The 1 x 1 structure is stable for temperatures up to 1270 K but is transformed to a $(\sqrt{3} \times \sqrt{3})$ R30° reconstruction at 1370 K, a $(2\sqrt{3} \times 2\sqrt{3})$ R30° at 1420 K, a $(3\sqrt{3} \times 3\sqrt{3})$ R30° reconstruction at 1520 K and finally the $(\sqrt{31} \times \sqrt{31})$ R±9° high temperature reconstruction at 1570 K [13, 5, 14, 15]. The high temperature phase has been shown to be stable up to temperatures of 1970 K and was even found to be stable upon air exposure [13, 16]. It has long been known to be oxygendeficient [14] and the $(\sqrt{31} \times \sqrt{31})$ R±9° structure with its very large unit cell has been identified by electron [13] as well as X-ray diffraction [16]. The details and topography of the atomic structure could, however, never unambiguously be determined. While a cubic arrangement of surface Al atoms was concluded from early low energy electron diffraction studies [5], results from a later very elaborate crystallographic analysis of X-ray diffraction data pointed to a hexagonal symmetry [16] and a model was developed proposing a surface structure composed of hexagonal domains with perfect hexagonal order in the centre and disorder at the domain boundaries [16,17]. Sapphire surfaces have also been intensely studied with force microscopy, however, so far imaging capabilities were limited to the nanometer scale [18, 19, 20, 21].

Here, we demonstrate that dynamic force microscopy is capable of directly evidencing the ($\sqrt{31} \times \sqrt{31}$) R9° reconstruction of α -Al₂O₃(0001) and as an unexpected result reveals a grid of protrusions representing its rhombic unit cell. By direct imaging of atomic rows and surface ions it can be confirmed that the surface is composed of domains with hexagonal atomic order in the centre and less order at the periphery. Upon dosage with water, the surface is covered with defects that are associated with hydroxyl groups and there is a tendency for cluster formation. Atomic order and disorder play an important role in the formation of these clusters that finally form a regular pattern of rings pinned by regions of maximum disorder on the reconstructed surface. This process of self-organization involves strong cluster-cluster and cluster-surface interactions and points to a strong chemical activity of disordered surface regions. Force microscopy also reveals a remarkably sharp appearance of the clusters suggesting that they are crystallites rather than irregular hydroxyl conglomerates.

The experimental techniques used for the studies reported here are basically the same as those used for atomic resolution imaging on fluorides as described in Section 6.1. For measurements on sapphire, the loop gain for the topography feedback was set to a comparably low value to obtain optimum contrast in the frequency detuning signal but at the same time also gain some information about surface topography. The high temperature reconstructed surface was prepared by a standard procedure described in the literature [22]. This procedure involved polishing, etching and cycled heating the crystal to temperatures above 1570 K in ultra-high vacuum. In Section 8.2 we describe the development of defects during exposure to the residual gas. Its composition was determined with a quadrupole mass analyser to consist mainly of water (50 %), hydrogen (30 %) and much smaller amounts of CO, CO₂ and hydrocarbons at a total pressure of $4 \cdot 10^{-8}$ Pa. For reasons outlined in Section 8.2 we anticipate that the observed effects of gas exposure are due to water and not any other of the constituents.

8.1 The clean surface

In Fig. 1 we show the surface structure shortly after preparation. The dominant feature is a rhombic grid representing the unit cell of the ($\sqrt{31} \times \sqrt{31}$) R9° reconstruction. This grid appears in both, the frequency detuning image (a) as well as the topography image (b). While the latter clearly reveals that the grid is protruding from the crystal, the frequency detuning results exhibit the details in contrast formation. There it is found that the displacement of atoms out of the surface plane is largest at the corners of the reconstruction rhombi while contrast from atomic rows in [1120] direction is best developed in their interior. Both observations are significant findings in this study and related to the question of the detailed surface structure on the atomic scale. There are two possible arrangements that have been proposed in the literature and schematic representations of both of them are shown in panels (c) and (d) of Fig. 8.1. The first proposition based upon an early low energy electron diffraction study [5] assumes that surface ions are ordered in a cubic structure that accommodates the reconstruction by the 9° rotation (panel (c)). The second model that has been developed on the basis of grazing incidence X-ray diffraction data [16] and theoretical modelling [17] is more complicated. This model proposes a transition from the well ordered bulk to



Fig. 8.1.

Frequency detuning (a) and topography (b) images [3] of the high temperature reconstructed $\alpha - Al_2O_3(0001)$ surface imaged shortly after preparation. The rhombus represents the unit cell of the $\sqrt{31} \times \sqrt{31}$ reconstructed surface that is rotated by 9° with respect to the respective direction on the 1 x 1 reconstructed surface. Lower panels are schematic representations of structure models for cubic (c) and hexagonal (d) order (and partly disorder) on the reconstructed surface taken from Refs. [5] and [16]

a partly disordered surface involving reconstruction in two surface layers of aluminium which both have a 'metallic character' [14]. The proposed structure of the topmost layer is schematically displayed in panel (d) where the main structural elements are densely packed hexagonal domains with perfect hexagonal atomic order in the centre of the domains where the lattice mismatch with respect to Al(111) amounts to 4%. The degree of order, however, decreases with distance from the centre and there is considerable disorder at the domain boundaries.

To test the surface atomic structure, higher magnification images as the one shown in Fig. 8.2(a) were taken at reduced tip-surface distance. Under these imaging conditions, the grid appears as a faint contrast only, however, atomic rows and individual surface atoms can clearly be identified. Image analysis as illustrated in the sketch Fig. 8.2(b) reveals that each side of a rhomb is intersected by ten atomic rows. This finding is perfectly compatible with the hexagonal atomic structure of the surface from Fig. 8.1(d) and excludes a cubic structure that would imply twelve intersecting atomic rows as evident from Fig. 8.1(c).

Further evidence for hexagonal atomic order follows from a direct analysis of atomic arrangements. It is found that hexagonal arrangement of atoms can directly be identified in the interior of three rhombi of Fig. 8.2(a) while it is partly suppressed by a defect in the fourth rhomb. A striking finding in this and similar images is that such hexagonal arrangements of atoms are well developed almost exclusively in the centre of the rhombi while they vanish at their sides and edges. Also this feature is well in agreement with the proposed surface structure predicting order in the centre of hexagonal surface domains and disorder at the



Fig. 8.2. (a) Magnified detail from image Fig 8.1(a) taken at reduced tip-surface distance to reveal atomic details. (b) Schematic representation of the surface indicating regions of hexagonal order in the centre of reconstruction rhombi. (c) Superposition of the hexagonal domain structure proposed in Refs. [16, 17] with reconstruction rhombi discovered by force microscopy. Surface atoms in grey shaded regions are well ordered. The image (a) as well as the schematic sketches (b) and (c) are from Ref. [3]

domain boundaries. The proposed surface domains and the rhombic structure discovered here can consistently be interpreted when superimposing both structures in a way shown in Fig. 8.2(c). According to this model, ordered regions of rhombi and hexagons coincide while the sides and specifically the corners of the rhombi intersect regions where disorder is expected. Hence, with dynamic scanning force microscopy it was not only possible to directly demonstrate a reconstruction on an insulator that is as large as that of the well known Si(111)7x7 surface [23] but also unambiguously establish hexagonal atomic order on high temperature reconstructed α -Al₂O₃(0001) and confirm propositions about partial disorder on this surface.

8.2 Defect formation upon water exposure

In this and the following section, we demonstrate that the discovered rhombic structure resulting from reconstruction may have tremendous impact on adsorption, clustering and crystallisation at the surface. After investigating the reconstructed surface, we left it exposed to the residual gas that had a pressure of $4 \cdot 10^{-8}$ Pa and was predominantly composed of water and hydrogen. Additional images were taken after dosages of $5 \cdot 10^{-4}$ Pa s and $35 \cdot 10^{-4}$ Pa s. Already in images taken after exposure to the smaller dosage, we observe a significant modification of the surface in form of defects with lateral dimensions ranging from 0.4 nm to 0.8 nm. A first high resolution result is shown in Figs. 8.3(a) and (b) while in Fig. 8.4. we display a series of consecutively taken images with larger



Fig. 8.3. Defect imaged after exposure to water at a dose of $5 \cdot 10^4$ Pa s. Defects are preferentially located in corners of reconstruction rhombi and yield contrast features in both, detuning (a) and topography (b) images that were recorded simultaneously in backward scan direction. The peculiar shape of the feature in the detuning image is explained by the schematic detuning curves shown in frame (c). Upon a transition from sapphire to hydroxide $(1 \rightarrow 2)$, the detuning drastically changes to a lower value due to the different slopes in the long range parts of the interaction curves. The opposite contrast change is observed when leaving the defect $(3 \rightarrow 4)$. There is a smooth response from the slow topography loop yielding an approach of the tip towards the surface $(2 \rightarrow 3)$ resulting in an apparent depression at the location of the defect.

frame size to demonstrate the temporal development of defect formation.

Defects appear in the detuning signal as features with a sharp change in contrast at their centre and in topography as apparent depressions. The latter observation is, however, misleading since there are good reasons to believe that defects are, in fact, protrusions. Sapphire is an extremely stable material with an activation energy for vacancy diffusion of 5.8 eV [24]. Hence, the formation of a large number of extended vacancies at room temperature due to exposure to a nonaggressive gas at low pressures is extremely unlikely. On the other hand, an interaction with water in form of hydroxylation has been reported for a variety of sapphire surfaces [25, 26, 27] and we propose that the observed defects are, in fact, the result of such hydroxylation involving water dissociation and the formation of aluminium hydroxide clusters. The appearance of the hydroxide as holes rather than protrusions is attributed to an effect of chemical contrast in force microscopy illustrated in Fig. 8.3(c) where we show schematic curves of detuning as a function of distance for the tip interacting with the metal rich sapphire surface and the chemically different hydroxide. We anticipate that for the tip-surface distance where images were taken (position 1 with detuning at pre-set value), the chemical interaction above hydroxide is much weaker than above sapphire. Consequently, the detuning drops drastically when the tip crosses from sapphire to hydroxide (position 2) and the action of the topography loop yields an approach (position 3), although, the defect is a protrusion. As the loop gain in the topography loop is small, the response is slow and there remains a strong negative detuning signal (dark contrast). After passing the hydroxide, the interaction increases suddenly (position 4) yielding a strong positive detuning signal (bright contrast).

A striking result common to all images is that defects are preferentially located in the corners of reconstruction rhombi. We attribute this to the high chemical reactivity of these sites that are those of largest atomic disorder and presumably carry a large number of low-coordinated aluminium atoms that are likely to initiate water dissociation. In fact, it has been argued that dissociation is specifically high on aluminium rich sapphire surfaces [26] and we expect that this even more applies for aluminium in disordered structures as we observe them on the high temperature reconstructed surface. Another feature illustrated in Fig. 8.4. is the high mobility of defects. In these consecutively acquired large scale frames we can follow groups of defects moving through the images due to instrumental drift along the dashed line indicated in the schematically redrawn frames to the right of the original images. While some of the defects appear to be stable, there is a considerably large number of them appearing and disappearing during the acquisition time of this series. From the corresponding damping images one knows that the tip has been perfectly stable during theses measurements and there are no indications that defects have been influenced by the scanning procedure. Hence, we conclude that there is thermally activated diffusion of defects from one corner position to another and these corners act as temporary pinning centres for defects. The presence of such diffusive motion is an important ingredient for the explanation of the re-arrangement of the surface defect structure observed upon higher dosages that is described in the following section.



Fig. 8.4. Development of defects in consecutively recorded frames (a) to (f). Some defects are stable and can be followed during their drift induced movements along the dashed line. Other defects (1, 2) appear and disappear during acquiring the series.

8.3 Self-organized formation of nanoclusters

The number of defects appearing during exposure to the residual gas increases with exposure time and after about two days one finds a stunningly regular structure of defects that is best developed in the lower half of Fig. 8.5(a). Note, that for a better visualization, the contrast in this image was inverted by image processing so that defects appear as bright features. Defects of different height (or chemical composition) are now composed into rings and these rings form a network reproducing the rhomboidal structure of the reconstructed surface. From the preferential development of defects in rhomb corners observed at lower exposures, we conclude that the rings are centred at corners. This implies that the defects are preferentially stabilised in regions of disorder and maximum protrusion what appears to be plausible since there one expects lower highest chemical activity as argued above. The ordering of almost equally sized defects into rings points to a significant interaction between defects but also to their nature as individual stable clusters that do not have a tendency to agglomerate into larger entities.

The atomic structure and chemical composition of the clusters, however, could not be determined with the force microscope and remains subject of speculation at the present stage of investigation. As discussed in the previous section, we anticipate that the aluminium rich high temperature reconstructed surface is chemically reactive and upon water exposure expected to be rapidly covered with hydroxyl groups. On the other hand, it has been proposed that hydroxyl groups have significant mobility on the surface [26] and thus they can condense into clusters at energetically favourable sites. Although, atomic resolution has not been achieved on the rough cluster covered surface, detuning images yield some structural information that is most pronounced in the upper half of Fig. 8.5(a). There, the most protruding clusters are imaged with highest contrast and they appear surprisingly sharp and regular. Therefore, we propose that they are not weakly bound hydroxide agglomerates but represent small crystallites of Al(OH)₃. In fact, there is experimental evidence for the formation of this species on alumina surfaces under high pressure conditions [27] and when hydrating the surface by rinsing with water [25]. The high reactivity expected in regions of atomic disorder on our surface could explain the observed formation of Al(OH)₃ clusters in these regions even under low pressure conditions where Gibbsite has been proposed to be the stable Al(OH)₃ structure that is well compatible with the Al₂O₃ structure [27]. The unit cell of a Gibbsite crystal shown in Fig. 8.6(b) for reference is well compatible with the size and structure of observed clusters what might indicate that they are, in fact, crystallites. The formation into rings may be facilitated by a high mobility of Al(OH)₃ clusters on the surface that has been proposed for the un-reconstructed surface, but this may equally apply to the reconstructed one [26].



Fig. 8.5.

Self-organized structure of defects (a). The tip change (\rightarrow) reveals sharp edged structures that might be Gibbsite crystallites. The unit cell of a Gibbsite crystal is shown in the magnified image (b) for comparison. For better visualisation, the contrast has been inverted in these images compared to detuning images shown in previous figures

In summary, our findings on high temperature reconstructed, water exposed α -Al₂O₃(0001) reveal a remarkable power of this surface for naturally structuring molecular clusters formed by self-organisation of the randomly offered molecules. It is the combination of effects from their stabilisation into crystallites, strong cluster-surface and cluster-cluster interactions that create at the same time an overall structure according to the surface reconstruction but an arrangement in form of clusters grouped in rings with a sub-structure having no evident relation to surface symmetry. The hydroxylation acts structurally as a stabilisation and chemically as a passivation of the reconstructed surface and readily explains the air stability of the reconstruction. It is this stability that predestines this surface to be used as a dielectric template for the creation of robust nanostructures that may be useful for various applications.

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