Equilibrium faceting formation in vicinal Al_2O_3 (0001) surface caused by annealing

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Abstract

We report on a heat-induced transformation of the surface of α-alumina (0001) crystals which have a off-cut in the $[1\bar{2}10]$ direction. Annealing the crystal causes the surface to transform into a regular array of (0001) and $(1\bar{2}16)$ facets. The resultant faceted morphology represents the equilibrium state of the system. It is demonstrated that the average terrace periodicity is determined by the annealing temperature. Possible causes for the surface rearrangement are also discussed. The method could be used for producing templates with controlled periodicity for growth of nanostructure arrays.

1. Introduction

The preparation of metal oxide surfaces of high quality is of fundamental importance for optical and electronic devices. In particular, α-Al_2O_3 (sapphire) possesses properties which make it a very promising material. Different stable orientations were recently identified for sapphire, either from first principle calculation [1, 2] or through experiment [3, 4, 5, 6]. Their surface free energy per unit area were obtained and the Wulff construction for the single crystal derived. However, discrepancies between the various results are still present. The surface evolution towards its equilibrium crystal shape appears as a rather complex phenomenon where thermodynamic arguments, adatom mobility and the presence of contaminants [7, 8] can interplay in the resulting equilibrium morphology. Furthermore, the introduction of possible off-cuts from an high symmetry orientation complicate even more the picture.

Among the stable surface orientations, the c-plane Al_2O_3 (0001) surface is so far the most widely studied and most commonly used surface. These templates have recently attracted additional interest as they offer the possibility of reconstructing their surfaces into a hill and valley structure [9]. It was demonstrated

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that annealing of the (0001) surface can produce periodic step-and-terrace arrangements with a step height $h \sim 1.2\,\mathrm{nm}$ [10]. The step rearrangements of c-plane α-Al_2O_3 have been previously investigated as a function of parameters such as annealing temperature [10, 11, 12, 13], time [9, 13, 11, 14], atmospheric environment [12], pressure [15], off-cut angle [13, 16] and orientation [13]. If the surface is off-cut along the $[1\bar{2}10]$ direction, the resulting vicinal surface before annealing appears covered by steps running along the $[10\bar{1}0]$ direction. If c is the length of the unit cell along the [0001] direction, each step presents a height of $c/6 = 0.22\,\mathrm{nm}$, corresponding to the distance between two consecutive oxygen layers along the [0001] direction. It is now generally believed that upon annealing at temperatures of $\sim$1100°C in atmosphere, the monoatomic steps gather forming double height steps[10] and, if the temperature increases, the steps increase further in height in multiples of $2c/6$. Never the less, no clear picture of the reconstruction mechanisms have been proposed for the (0001) surface. As sapphire is interesting for its strong anisotropy in the diffusion coefficients and the relatively slow diffusion rate (the reconstructive process takes place on a timescale on the order of hours), the system also appears to be a perfect candidate to clarify doubts and open questions for surface instabilities of metal oxides in general, such as $SrTiO_3$ [17] and MgO [18].

In this report, we developed a comprehensive study of the annealing effects on Al_2O_3 (0001) off-cut along the $[1\bar{2}10]$ direction, by varying the annealing temperature and off-cut angle. The aim of the study is two-fold. First, it will be demonstrated that the morphology of the surface can be tuned even in the sub-100 nm range. In particular, the periodicity can be modified by changing the annealing temperature while different step heights can be obtained by changing the initial off-cut angle. The possibility of engineering the Al_2O_3 (0001) surface is hence shown. Second, we demonstrate that the mechanism behind the surface rearrangement is related to faceting and the possible origins responsible for the surface evolution are discussed.

2. Experimental

C-plane single crystal single-side polished Al_2O_3 substrates (MTI, USA) were prepared using three different nominal off-cuts $\theta = 2°$, 3° and 6° along the $[1\bar{2}10]$ direction. The quality of the substrates was checked by X-ray diffraction, which confirmed the (0001) surface orientation and the absence of any long range disorders like mosaicity. Each sample off-cut was within 0.1° of the nominal value as confirmed by XRD. Several pieces were cut from each substrate, cleaned in HCl and washed in deionised water. In order to remove any contamination, solvent treatment with methanol, acetone and high grade propanol-2-ol was finally performed in an ultrasonic bath. After the cleaning procedure the templates were checked with Atomic Force Microscopy (AFM) which showed atomically flat surfaces without any impurities detectable by AFM. The samples were then placed in a high purity alumina crucible (99.7% pure) and put in an alumina tube furnace with the same nominal purity. All samples were annealed in air. To provide homogeneous heating, the tube was closed at both

ends by alumina bricks. Samples were loaded into the furnace at 1000° C and annealed for 24 hours at temperatures T between 1300° C and 1450°C. A heating and a cooling rate of 10° C/min was used to reach the required annealing temperature. As the diffusion rate of the surface adatoms increases exponentially with the temperature, such a fast cooling rate ensures that the observed morphology after annealing corresponds to the equilibrium state of the surface at the annealing temperature.

We characterized the samples with both an AFM in tapping mode and a transmission electron microscope (TEM). The AFM is an Asylum Research MFP-3D instrument. Si tips with Al backside coating were used with nominal resonance frequency of 250 kHz and a tip radius of $\leq$10 nm. The setup was previously calibrated using a known reference sample. For each sample annealed at least 4 different areas were scanned and the results averaged over more than 150 points. A FEI Titan TEM operating at 300 kV was used to obtain an out-of-plane cross section of the surface. The sections for the TEM analysis were prepared in a Carl Zeiss Auriga CrossBeam focused ion beam scanning electron microscope (FIB-SEM). A 10 nm Au/Pd layer was deposited by sputtering in order to protect the surface lamellae. Subsequently, the *in situ* lift-out technique was used to remove a section of the sample and affix it to a TEM grid. The sample was then polished to $\sim$100 nm thickness with 30 keV gallium ions. In order to reduce surface damage and amorphisation, the sample was finally polished with 5 keV gallium ions. The substrate was aligned to the $[10\bar{1}0]$ zone axis for imaging. All the images used here were acquired in bright-field mode.

The elemental composition analysis was carried out in order to address the issue of surface contamination. Sample's composition was investigated by X-ray photoelectron spectroscopy (XPS) using an Omicron Multiprobe XP system (Mg X-ray source and E125 Analyser). An Omicron CN 10 charge neutraliser was used in order to compensate for sample charging. Obtained spectra were analysed with the CasaXPS software.

3. Results and discussion

During the experiment, the temperature dependency was studied using identical 6° off-cut samples at temperatures of 1300° C, 1350° C, 1400° C and 1450° C and the role of the off-cut was analysed at 1400°C. The results are presented in Table 1.

The surface appears remarkably uniform after annealing and Figure 1 shows the typical resulting morphology. Parallel steps run along the $[10\bar{1}0]$ direction and cover the whole surface in an almost periodical fashion. The rearrangement of the surface preserves the overall surface orientation, as confirmed with both XRD and AFM. The average period $< l >$ increases with the temperature T. This behaviour may be explained, accordingly with previous studies [10], by considering the surface rearrangement as a thermally activated diffusion process, by assuming an equivalence between surface periodicity and average displacement of adatoms. In this case, the periodicity is proportional to an effective diffusion constant $D = D_0 \exp(-E_{ac}/k_B T)$, with E_{ac} being the activation energy and k_B

Off-cut angle	2°	3°	6°			
T ($°C$)	1400	1400	1300	1350	1400	1450
$< l >$ (nm)	132 ± 25	129 ± 28	77 ± 21	79 ± 22	132 ± 15	197 ± 58
$< h >$ (nm)	4.8 ±1.7	5.7 ±1.6	7.6 ± 1.7	7.7 ± 2.0	11.5 ± 3.1	20.8 ± 4.6

Table 1: Average periodicity $< l >$ and step height $< h >$ with the related standard deviation as a function of annealing temperature and off-cut angle. The terrace width increases with the annealing temperature. If the same periodicity is obtained for different off-cut angles, different step heights are produced.

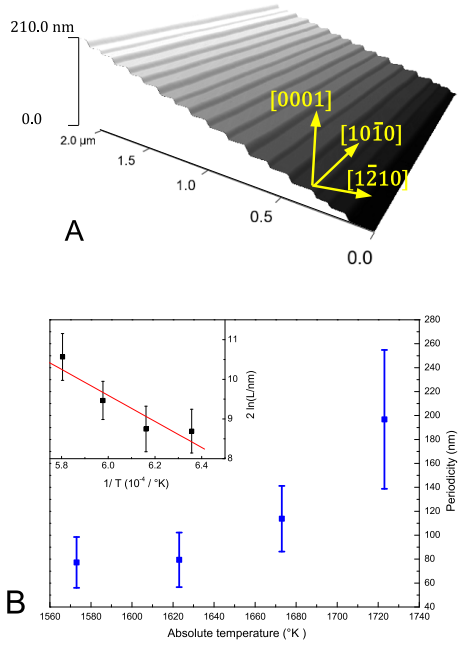

Figure 1: Faceting formation after annealing of $Al_2O_3(0001)$ at high temperature. (A) 2×2 μm^2 AFM image after first-order subtraction. The surface is off-cut 6° along the [1$\bar{2}$10] direction. After annealing in atmosphere at 1350° C for 24 hours, the surface appears remarkably uniform and nearly periodic facets can be observed. The crystallographic orientations are also indicated. (B) Temperature dependence of the period as a function of the annealing temperature. A monotonous increase of the periodicty with the temperature is observed. The Arrhenius plot of period is shown in the inset.

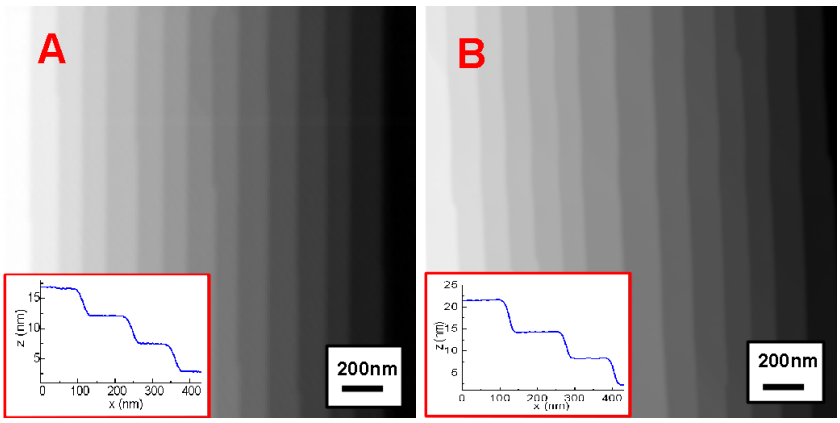

Figure 2: 2×2 μm^2 AFM images of $Al_2O_3(0001)$ off-cut 2° (A) and 3° (B) along the $[1\bar{2}10]$ direction. The surfaces were annealed at 1400°C for 24 hours. A typical AFM section can be observed in the inset.

the Boltzman constant. As the annealing time is the same for each sample, the periodicity is then expected to increase exponentially with the rise in annealing temperature. The Arrhenius plot in the inset of Figure 1 might confirm this trend and suggests an activation energy $E_{ac} = 2.8 \pm 0.8$ eV. However, the large errors in the associated data, the few data points available and the disclosure from the exact linear behaviour renders difficult to surely attribute this as the leading phenomenon for the step rearrangement. However, the value obtained is consistent, within the experimental error, with the one 2 eV of nominally flat sapphire [10] even if a large off-cut was used in the present measurements. This simple argument appears hence to be insufficient to completely explain the measured temperature dependency.

Substrates with different off-cut angles produce similar results (see Figure 2 (A) and (B)). For a given periodicity, changes in the initial off-cut angle result in steps with different heights. Surfaces with comparable periodicity were analysed, and the step height appeared smaller for smaller off-cut, preserving the overall surface orientation. The periodicity can thus be varied, for a given off-cut angle, by changing the annealing temperature and the step height can be tuned by varying the initial sample off-cut. A full tuning of the parameters characterising the morphology of the stepped surface, periodicity and step height, can hence be obtained. Furthermore, the mechanism behind the rearrangement of the surface appears to be common for all samples. This is suggested by Figure 3, where the probability $P(l)$ of observing two steps separated by a distance l is plotted with respect to the relative period $l/ < l >$. It is evident that the distribution does not remarkably depend on either the annealing temperature or the off-cut angle.

The crystalline structure of the faceted surface was measured using high resolution TEM. The analysis has been performed for different periodicities for the 6° samples. All steps appear inclined at the same angle $\theta^* = 42°$ with respect to

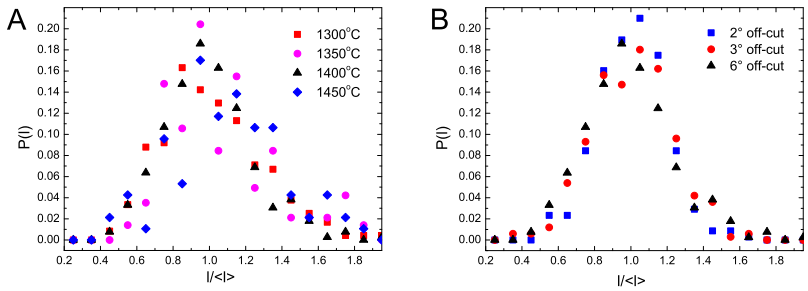

Figure 3: Normalised distribution of the period as a function of $l/ < l >$ for different annealing temperatures (A) and substrate off-cut (B) for an annealing temperature of 1400° C. The curves follow the same Gaussian distribution.

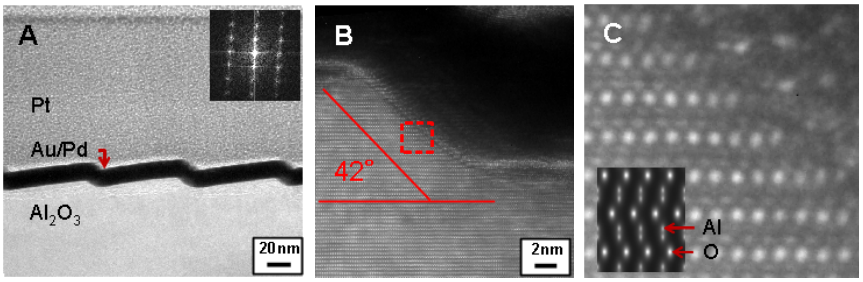

Figure 4: TEM section of a sample with a 6° off-cut and annealed at 1350° C for 24 hours. An Au/Pd protecting layer has been sputtered on the surface before the section preparation in order to protect the surface. (A) Low magnification of the surface, obtained after alignment of the crystal axis with the TEM optical axes (see FFT inset). (B) High magnification image, the crystal structure can be clearly observed. The step inclination of 42° with respect to the $[1\bar{2}10]$ is shown, corresponding to a surface orientation of $(1\bar{2}16)$. (C) Magnified view of the outlined area in (B). In the inset a java electron microscope simulation shows the expected Al and O positions using the tabulated crystal structure of Al_2O_3.

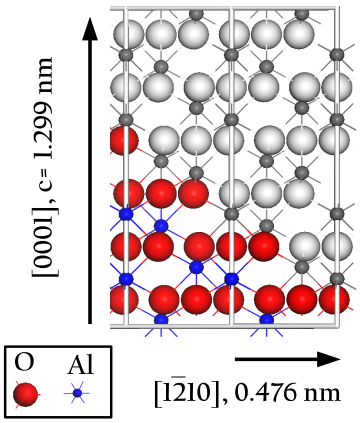

Figure 5: Section of the Al_2O_3 unit cell along the [1$\bar{2}$10] direction. The coloured atoms are present along the step edge.

the [1$\bar{2}$10] direction shown in Figure 4 (B). Such an inclination corresponds to the (1$\bar{2}$16) orientation. This angle appears independent of the step height and it is also in accordance with previous TEM results obtained for different off-cut samples [16]. Being also independent of the step height, the result suggests that surface transformation process is driven by a faceting mechanism, the two facets being the (0001) plane of the terrace and the (1$\bar{2}$16) plane of the steps. Analysis of the highly magnified image suggests the steps are most likely oxygen terminated and each monoatomic step is separated by two consecutive oxygen atoms along the off-cut direction (Figure 4 (C)). However, a conclusive determination of the exact surface termination would require an aberration corrected high resolution TEM. The possible atomistic composition of the unrelaxed surface can be observed by cutting the Al_2O_3 unit cell along the step direction (see Fig. 5) and terminating the surface with oxygen atoms. The (1$\bar{2}$16) orientation observed here was never observed before as a stable orientation or its energy calculated by first principle calculations [2]. No information on the step energy is then available in literature. It would be interesting to calculate from first principles the surface energy of the different possible terminations and compare the structures with the current experiment.

The faceting formation is confirmed again by the presence of bowtie merging defects on the surface as shown in Figure 6 (A). Different defects are outlined and the merging points never appear isolated (see Figure 6 (B)). This is a consequence of coarsening process of the facet domains: when different faceted areas grow and overlap, the observed junctions are produced [19].

Thermodynamic arguments can be used as a basis for understanding the faceting phenomenon as we noted that the surface morphology has reached thermodynamic equilibrium in our experiments. The calculated diffusion constant [13] of adatoms on the surface of Al_2O_3 is $10^{-8}\,cm^2s^{-1}$ at 1500°C. This means that the surface reaches equilibrium over a distance of 10 μm at annealing

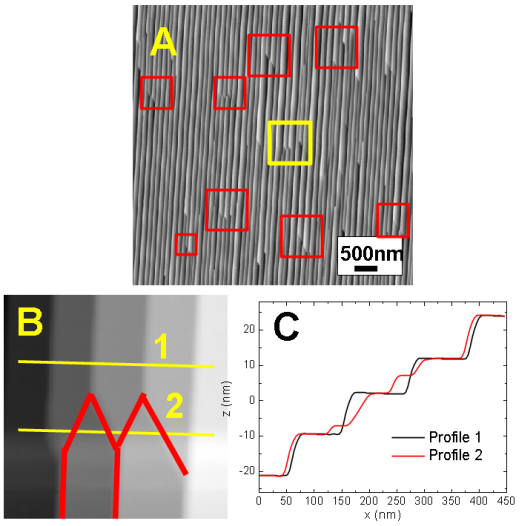

Figure 6: (A) Surface of a 6° off-cut sample after annealing at 1400 °C. Defects, highlighted by red squares can be identified and were attributed to coarsening of faceted domains [9]. (B) A magnification of the yellow area. (C) Section along lines 1 and 2 of (B).

durations of the order of 1 hour, which is much smaller than the 24 hour long annealing cycles used in this study. To independently confirm this point, two samples were annealed at 1400°C for 24 hours and 72 hours and no change in the periodicity was observed. Thus the surface reached the equilibrium condition, in line with previous reports [14, 16]. The resulting temperature dependency of the terrace width and step height can be related to minima of the surface free energy of the system.

The temperature dependency of the equilibrium surface morphology could be explained following thermodynamic arguments introduced by Marchenko [20]. However, further refinement of his theory based on the free energy of the surface cannot fully explain our results. In his approach, the constraint of the conservation of the average surface orientation of a vicinal surface implies the coexistence of alternating facets. At the intersections between different facets the strains are unbalanced and generate elastic forces propagating into the bulk. These forces can be represented by long-range elastic attractive monopoles having a logarithmic dependency on the inter-step distance. It was found that these structures exhibit an optimum period, corresponding to the minimum of the surface free energy of the system. If the dipolar and higher term interactions are truncated, the optimum period is

$$< l >= \frac{\pi e a^*}{\sin(\pi \frac{\theta}{\theta^*})} \tag{1}$$

where e is the Neper number and θ and θ^* are the off-cut and the angle between the facets repectively. The length a^* depends on the elastic properties of the

material via the relation

$$a^* = a \exp[\pi Y \eta/(1-\nu^2)\tau^2]. \quad (2)$$

In Eq. (2) Y is the Young modulus, ν the Poisson ratio, η is the step energy per unit length, τ is the surface tensor at the edge and finally a is a cut-off length of the order of the atomic dimensions. The exponential increase in the resulting periodicity can then be driven within this framework by a decrease in the surface tensor τ. Nevertheless, the dependency on the off-cut angle θ predicted by Eq. (1) is not verified. In the experiments, the same fixed value of $\theta^* = 42°$ at all the off-cut angles was observed (compare Fig. 4 B with Cuccureddu *et al* [16]). At the same time, for different off-cuts, different values of the sine term in the denominator of Eq. (1) are expected and therefore different values of $< l >$. From Table 1, however, the surfaces manifest the same period of the faceted structure at all values of the off-cut angle (compare data for 2°, 3°, 6° samples at 1400°C). This is in striking contrast with the results previously reported for other materials [21]. An even more refined model [22] following the theory proposed by Marchenko is unable to correctly reproduce the behaviour observed in the current experiment and new theory may be required to explain these results. Disagreement between theory and experiment could arise from inhomogeneity in the material or by different step surface terminations. It has already been pointed out that adjacent steps have different terminations [13] and different step energies can then be *a priori* expected, modifying the analytical form of the optimum period of Eq. (1).

The peculiar behaviour shown by our measurements can be finally attributed to the substrate quality as the existence of contaminants could possibly interfere with the kinetic processes involved, creating more complex instabilities. It was reported that common segregation of contaminants such as Ca, Mg, Ba, Si can affect the step and surface structure evolution of sapphire samples, generating mesoscopic steps [8]. XPS measurements were conducted in order to address this issue and results are shown in Figure 7. Black and red lines correspond to spectra of a 6° off-cut substrate measured before and after annealing at 1400°C respectively. The XPS analysis revealed that initially carbon accounts for the bulk of surface impurities (at 27%). Also minute quantity of Ca (0.5%) was found prior to annealing. Carbon concentration significantly reduced as a result of annealing (12.4%), while concentration of Ca increased (1.2%). Also, Si (at 3.7%) and Mg (at 0.1%) impurities appeared on the surface as a result of annealing and either migrating from the bulk or present in the annealing atmosphere due to their presence in the furnace alumina tube. Previous reports suggest also Ca as the principal cause of surface stabilization of the Al_2O_3 basal plane [23] and the presence of such impurities could explain the unusual $(1\bar{2}16)$ step orientation measured by TEM. Because of the adsorption of such impurities, some facets may then disappear while others may become more stable.

The faceting formation of the Al_2O_3 (0001) surfaces remains rather unclear and is a complex phenomenon which could be attributed to an interplay among the possible effects discussed above. Deeper investigations of the phenomenon

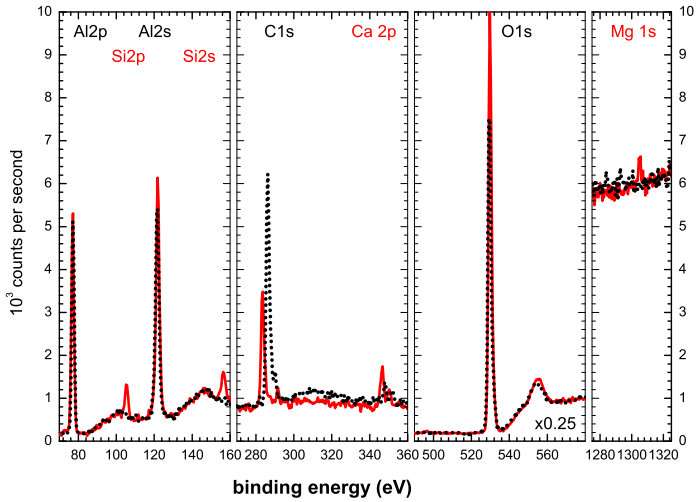

Figure 7: XPS spectra of a 6° off-cut substrate before (black line) and after (red line) annealing. The annealing appears to leave traces of Ca, Si and Mg on the surface which can affect the final morphology of the system.

is required to describe the evolution of the surfaces. However, the possibility of tuning the morphological parameters and an atomistic view of the surface rearrangement has been introduced in this manuscript. Our results should further enable the use of c-plane Al_2O_3 also as a nanostructured template for large scale self-assembled depositions [24, 25, 26, 27].

4. Conclusions

The morphology of off-cut c-plane α-Al_2O_3 was investigated by annealing at temperatures 1300°-1500° C. The procedure followed to produce stepped templates was described and the formation of a step and terrace structure is attributed to faceting formation. The surface breaks into the (0001) terraces and the $(1\bar{2}16)$ facets. The obtained surfaces were thermodynamically stable and did not further evolve by increasing the annealing time. The possibility of changing both periodicity and step height was demonstrated by modifying the annealing temperature and substrate off-cut angle. The average terrace periodicity increases exponentially with increasing anneal time while the step height increases with larger off-cut angles. These substrates could be utilised as tunable textured templates for the growth of nanostructures. Various mechanisms that could be responsible for the regular faceting arrangement have been discussed. However, none of these can fully explain the observed behaviour. Deeper investigation in the causes of the surface rearrangements are required to explain the resulting surface morphology.

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