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Surface morphology of c-plane sapphire (α -alumina) produced by high temperature anneal

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Abstract

A comparative study of the morphological surface evolution of c-plane (0001) α -Al₂O₃ upon annealing was investigated for non-miscut (i.e. substrates with 0° nominal miscut) and vicinal substrates. The samples were annealed in air at 1100°C for different durations of time. Although non-miscut samples do not show any step bunching at this temperature, miscut substrates show a regular and ordered stepped morphology with clearly defined terraces as revealed by Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) image analysis. The surface morphology presents a number of coalescence points, i.e. locations where two steps merge and form a multiple step. Close to the coalescence points, parallel steps change direction to different low index direction.

Keywords

Aluminum oxide; Sapphire; Step formation and bunching; Surface structure, morphology; Atomic force microscopy.

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1 Introduction

Alumina is a technologically attractive substrate with applications in electronics, optics, chemical catalysis and mechanics [1, 2, 3]. The α phase, also called ruby, corundum or sapphire, is the most thermodynamically stable. This makes α -alumina an attractive substrate for studies and understanding of metal-oxides. Sapphire has a hexagonal close-packed crystal structure and belongs to the R-3c space group with lattice constants $a = 0.476$ nm and $c = 1.299$ nm. The crystal structure along the (0001) direction is composed of an approximately hcp stacking of large oxygen anions, the separation between two oxygen planes equals 0.21 nm which corresponds to $c/6$.

Sapphire single crystals are used as substrates for deposition and the four most commonly encountered crystallographic planes are essentially: c- (0001), r- (1012), a- (11-20) and m- (10-10) (Fig.1(a)). In particular c-plane sapphire substrates are extensively used for the growth of a large range of materials, such as III-V and II-VI compounds for Light Emitting Diodes (LED) and laser diodes [4], nitrides for surface acoustic wave materials and wireless communication devices [5], and ZnO for bandgap devices [6]. Copper, palladium, silver, gold and other metals [7, 8, 9] have been deposited and studied on c-plane sapphire because the metal-alumina interface plays an important role in many materials for industrial applications such as catalysts [10], thermal barrier coatings [11] and microelectronic devices [12].

C-plane sapphire is an optimal template for growing nanowires because of its capability to provide well-ordered surface steps [13, 14, 15, 16, 17, 18, 19, 20]. The (0001) surface can have three chemically different surface terminations: an oxygen surface layer, a surface with two aluminium layers or a surface dissecting between the two aluminium layers. The latter has been predicted to have the lowest surface energy from theoretical calculations whilst the oxygen-terminated surface has the highest surface energy [21]. Several studies have been carried out in order to follow the surface evolution at high temperature. Using a dynamic scanning force microscopy technique [22] an hexagonal arrangement of atoms after surface

reconstruction was observed [23]. It has also been found that, in addition to the (1×1) termination, the (0001) surface exists in several ordered phases that can be reversibly transformed into each other by thermal treatment and oxygen exposure [24]. The high-temperature phase has been known to be oxygen-deficient [25] with a large $(\sqrt{31}\times\sqrt{31})R\pm 9$ unit cell observed by electron [26] and X-ray diffraction [27]. This superstructure has been demonstrated to promote the self-organization of clusters grown on its surface [23].

Atomic force microscopy (AFM) provides a powerful technique to study the alumina surface [13, 14, 15, 16]. Successful investigations of vicinal surfaces of alumina at the nanometre scale were also performed using high-resolution transmission microscopy (HRTEM) and reflection electron microscopy (REM) [28, 29, 30].

Annealing of (0001) α -alumina samples for several hours in air produces a terrace-and-step morphology, consisting of wide terraces (typically several hundreds of nm) separated by surface steps (typically 1-5 nm) whose height is usually a multiple of c in height ($c=1.3$ nm is the unit cell parameter of alumina along the c -axis). The surface evolution of alumina c -plane in the 1000-1500°C temperature range has been studied by several groups [13, 14, 16]. Step formation starts at temperatures above 1000°C. It has been found that annealing gives rise to steps up to ~2 nm in height. Furthermore, annealing at 1400°C for durations of between 10 min and 8 hours leads to facet nucleation and facet coarsening with a gathering of monosteps forming multiple steps [31].

Faceting enhances the complexity of the surface evolution of sapphire. Different processes can be identified during the step growth such as step coalescence, step decomposition [14], step faceting and step bunching [13, 30]. Step bunching is interesting because the gathering of steps, due to a step-to-step attractive interaction at long distances [32], allows the formation of multiple steps with considerable height. Kurnosikov *et al.* [15] showed that surface structure resulting from an anneal is defined not only by the anneal temperature and time but also by the values of miscut angle (θ) and azimuth orientation angle (φ). It is often difficult to separate

their respective influences. Step bunching is expected to be a transient phenomenon preceding the step faceting and its disappearance rate is related, among other parameters, to the miscut angle θ : the higher θ , the slower the rate of disappearance of step bunching [15]. Despite the extensive studies of alumina, very few of them correlate the surface morphology to the miscut angle.

In this paper we will compare the surface morphology of non-miscut and high miscut samples upon high temperature annealing. We focus on the step bunched structure formed as a consequence of the high miscut offset used and show that even at temperatures as low as 1100°C the use of high miscut samples makes it possible to obtain a uniform step-and-terrace surface morphology with high multiple steps.

2 Experimental

Samples of c-plane (0001) sapphire were obtained from the manufacturer (MTI corporation, Richmond, CA, USA). The samples were 10x10 mm wide and 0.5 mm thick, polished on one side. Two different kinds of substrates were used, one with no miscut and one with 3° miscut along [1-210], sketched in Fig.1(b). The alumina samples were then cleaned with isopropanol, methanol and acetone using an ultrasonic bath, and special precautions were taken to minimize exposure of the surface to any contamination from the furnace environment by annealing the samples inside an alumina crucible. They were annealed in air at 1100°C and 1350°C for different lengths of time. To maximize the temperature uniformity, the furnace ends were closed with thermal insulating bricks.

The surface structure was characterized by AFM studies performed using a SPM Solver PRO (NT-MDT, Zelenograd, Moscow, Russia) in tapping mode and ambient conditions. The topographic images were used for the measurements of the height of the steps and the width of the terraces.

TEM studies were performed in a Philips CM30-UT high resolution electron microscope (point resolution 0.17 nm). This microscope was equipped with a Schottky emitter and was operated at 300 kV.

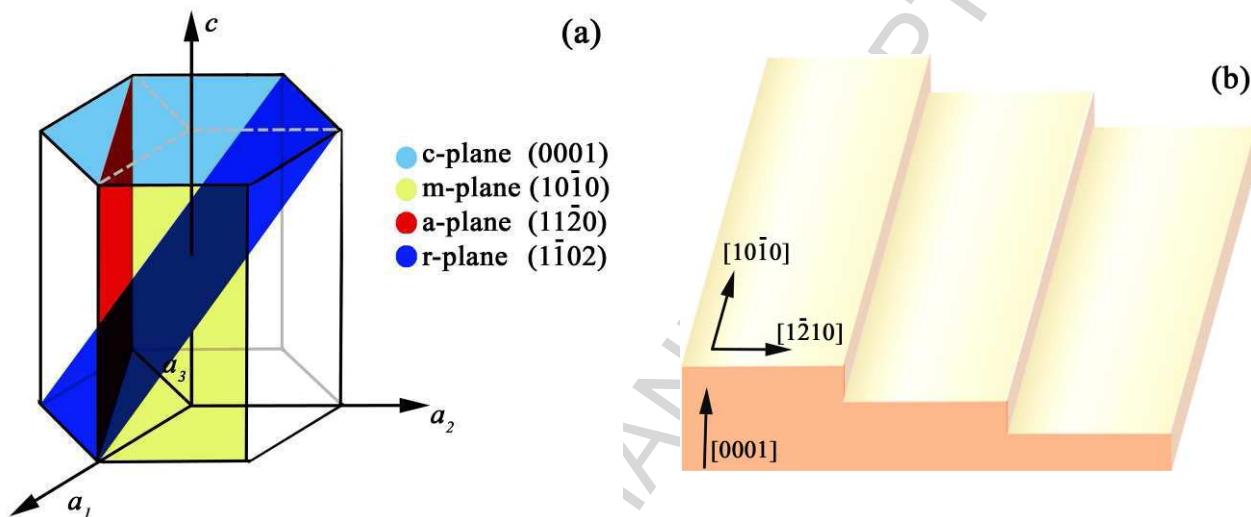


Figure 1: Sapphire crystal planes (a) and sketch of stepped vicinal c-plane sapphire (b).

3 Results and discussion

The behaviour of the alumina surface evolution is quite complex as evident from publications on the crystallographic orientation of the steps. The (0001) surface of sapphire was found to facet into a terrace-and-step morphology consisting of (0001) terraces and steps attributed to the gathering of several $c/6$ steps, where $c=1.3$ nm is the parameter of the alumina unit cell along the c -axis: the hexagonal unit cell of alumina along the c -axis comprises six layers of oxygen divided by double layers of aluminum.

3.1 Influence of annealing temperature

It has been pointed out that increasing the annealing temperature produces an increase in the average step height of c-plane sapphire surfaces [14]. Morphology of a nominally flat (0001) surface after annealing at 1100°C for 12 hours is shown in Fig.2. A regular terrace-and-step morphology is visible but the terrace edges are poorly defined. The step height mainly consists of monosteps of 0.2 nm. Further annealing does not change the average step height. At this stage the temperature is not sufficiently high for the surface atoms to rearrange and trigger the step bunching: reported step bunching manifests itself a higher temperatures [14, 15]. We confirmed this by the results in Fig.3, which shows the morphology of the same substrate annealed at 1350°C for the period of 8 hours to 20 hours. This results in a step-like structure with well defined terraces and higher steps.

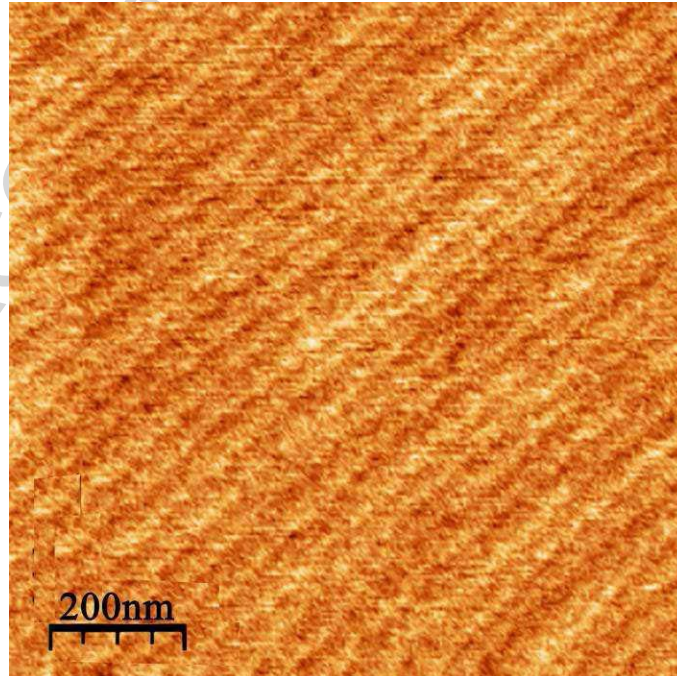


Figure 2: AFM scan of sapphire (0001) surface with nominally 0° miscut after 12 hours annealing at 1100°C.

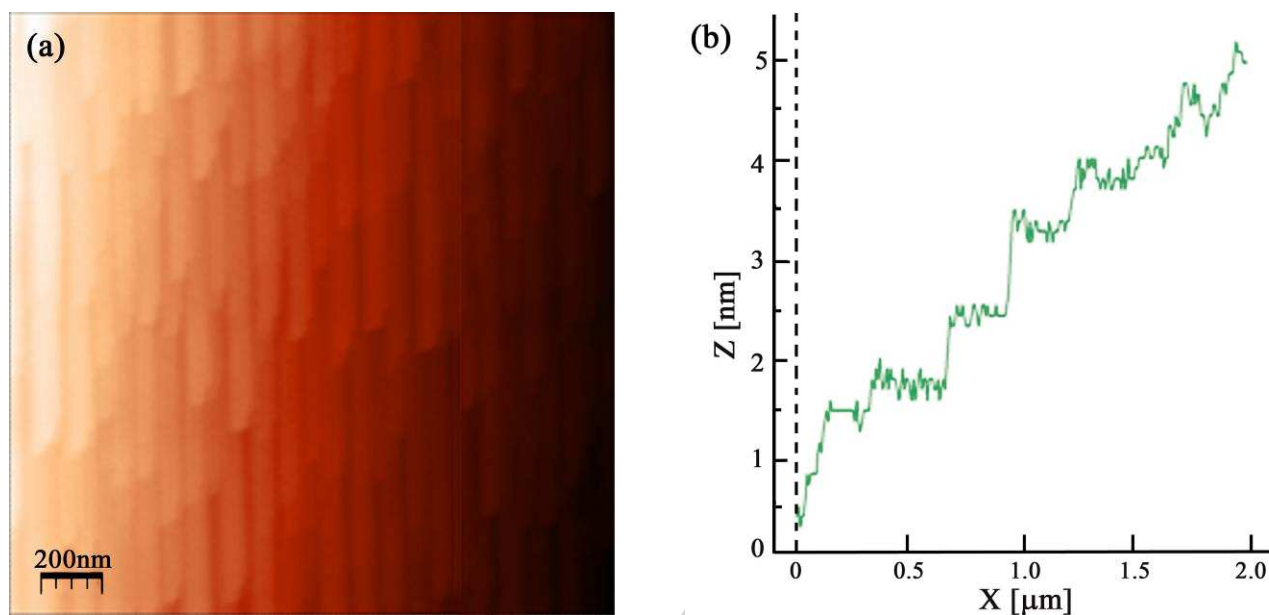


Figure 3: AFM topography scan (a) and step profile (b) of (0001) flat sapphire sample after 8 hours annealing at 1350°C in air.

The resulting terraces are about 120 nm wide with a step height which is a multiple of 0.22 nm, with a maximum height up to 2.4 nm. As can be derived from the average ratio of terrace width to step height, the surface of the studied sample is in fact miscut from the (0001) plane by some 0.15°.

Faceting of the surface resulting from formation of multiple and bunched steps is commonly observed and is being driven by the minimization of the overall surface free energy. The faceting process is thought to occur as a surface evolution through a series of distinct stages, beginning with the nucleation and growth of individual facets, formation of facet domains and coalescence of domains and single facets [31, 33, 34].

3.2 Influence of substrate miscut

A substantial change in morphology arises when the same annealing procedure is carried out on sapphire substrates with a significant miscut from (0001) plane. In

Fig.4(a) and Fig.4(b) we show two representative AFM scans for a surface with 3° miscut where the stepped structure of the substrate after 6 hours of annealing in air at 1100°C , is clearly visible. Figure 4(c) shows the profile of the stepped surface of the area presented in Fig.4(b)

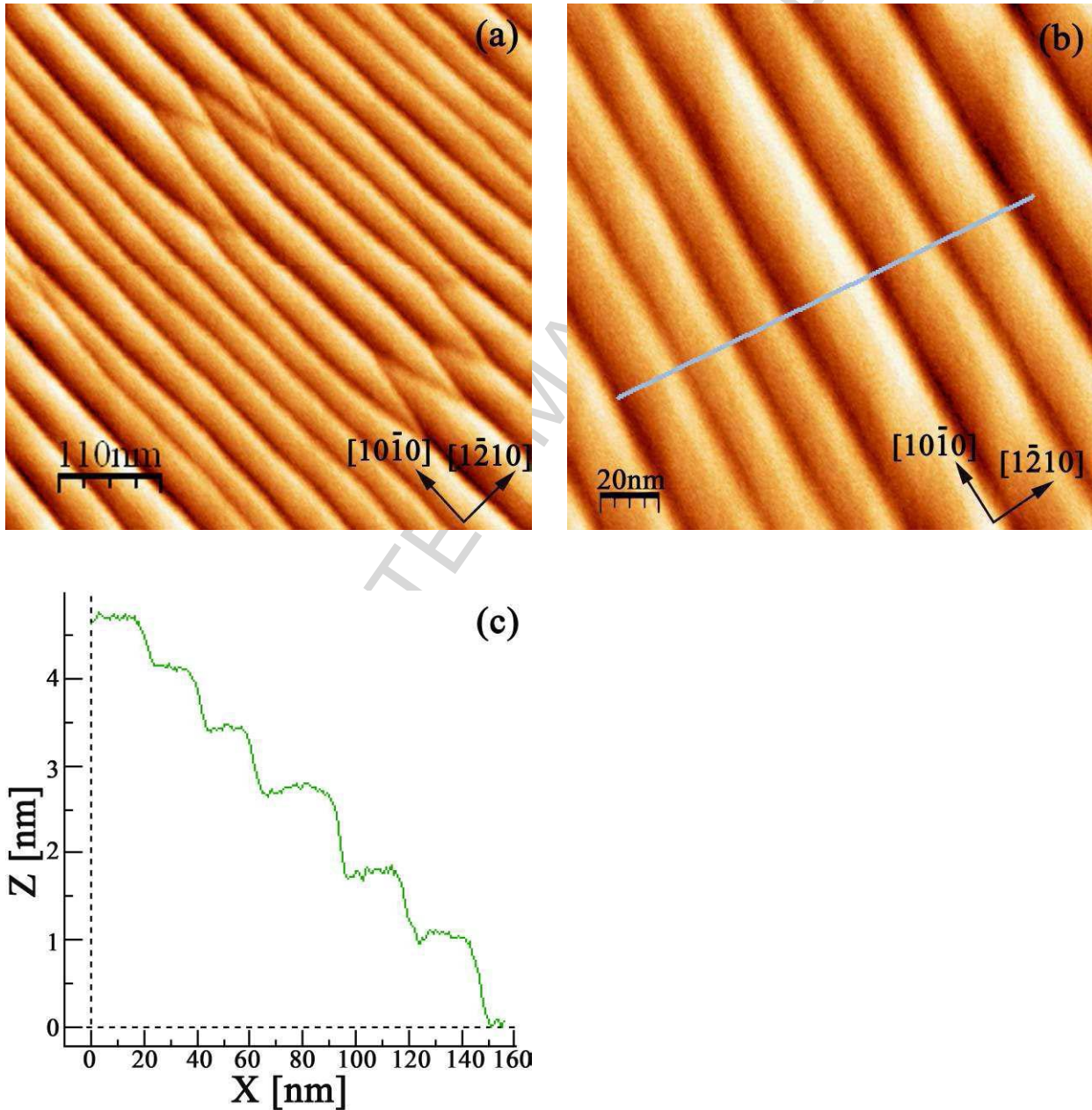


Figure 4: Morphology of a surface miscut 3° from (0001) after 6 hours annealing at 1100°C (a and b). Step profile along the line marked in Fig.4(b) corrected for plane fit (c).

The alumina (0001) surface is now completely faceted as a consequence of the advanced step bunching process. The step-and-terrace morphology extends all over the sample with high regularity. The bunched macrosteps, whose height is on average well over c , dominate. Analysis of the AFM images highlighted that step edges are straight and regularly spaced apart. They run parallel to the $[10-10]$ direction and perpendicular to the original miscut direction, $[1-210]$. The stepped structure as shown in these images is routinely repeatable. A statistical analysis of the step width distribution was carried out taking a considerable number of steps from several samples. The results are reported in Fig.5 for both 6 hours and 12 hours annealed samples. The annealing process performed for 6 hours at 1100°C produces a step and terrace morphology with an average step height of 1.5 ± 0.5 nm and an average terrace width of 44.2 ± 13.7 nm.

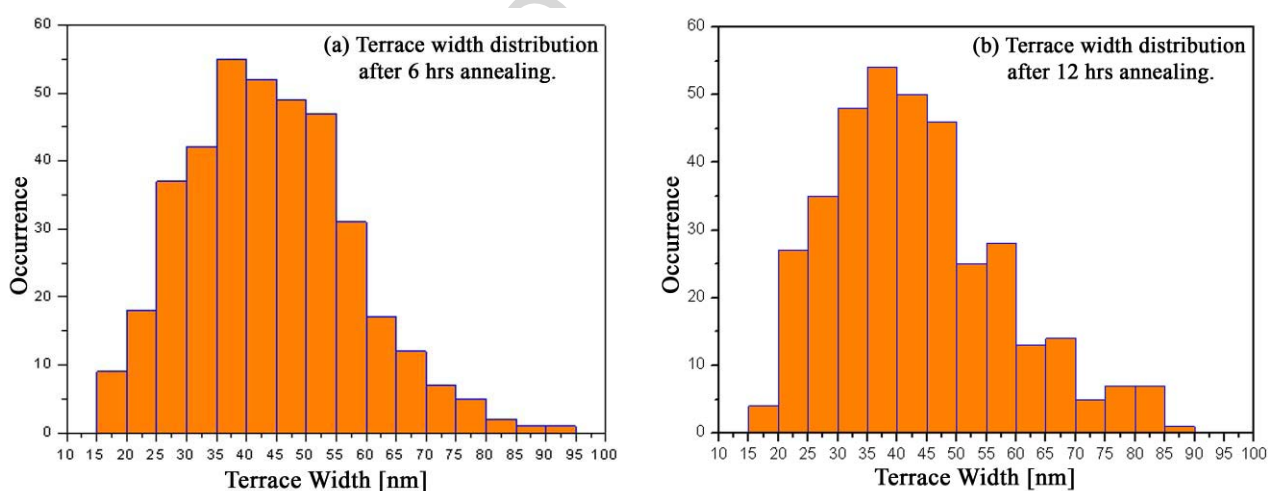


Figure 5: Terrace width distributions after (a) 6 hours and (b) 12 hours annealing at 1100°C .

According to some studies the step edges are not aligned along any low index crystallographic direction [14] while other studies showed that the annealing of c -plane sapphire produces a step-and-terrace morphology where the steps follow low index directions such as $[1-210]$ and $[10-10]$ [15, 35]. This can give rise to zigzagged steps where segments of step length alternate between these two directions. The

samples investigated in this paper were chosen to have their miscut direction along $[1-210]$ in order to facilitate formation of straight and long steps along $[10-10]$ with the least possible number of kinks. Nevertheless, as shown in Figs.6 and 7, the annealing procedure provided straight steps at times interrupted by coalescence junctions, i.e. locations where multiple steps join together forming higher steps.

In the proximity of the merging areas, parallel steps change direction generating faceting. From analysis of the AFM scans (Fig.6) the angle between the two segments of step edges at the merging point is around 150° , which corresponds to the angle between the $[1-210]$ direction and the $[1-100]$ direction. The step edges are predominantly aligned along $[1-210]$ but in the vicinity of merging steps they change direction and run along a different low index direction, $[1-100]$ (equivalent to $[10-10]$). The formation of higher steps through the coalescence of lower steps follows a "zipper-like" motion scheme (Fig.7) [14].

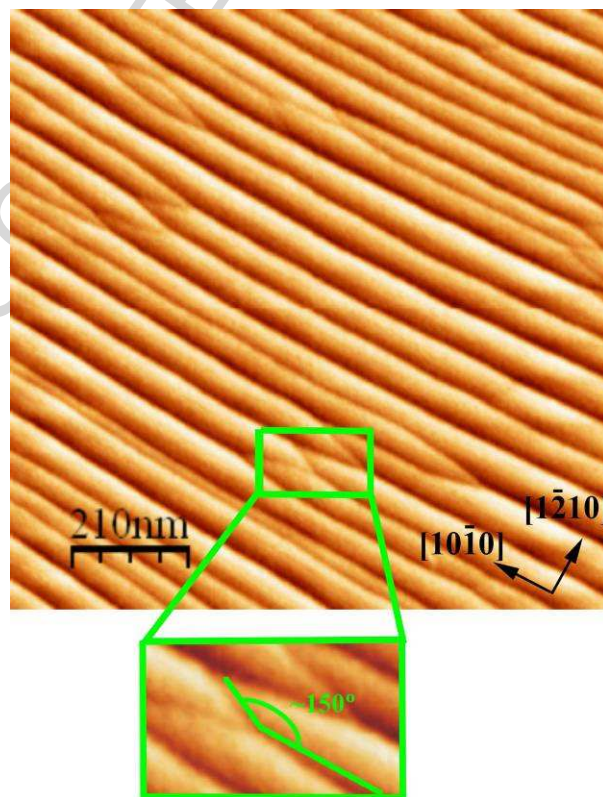


Figure 6: Step coalescence provides merging areas forming new facets. The angle between the facets corresponds to the angle between two low index directions.

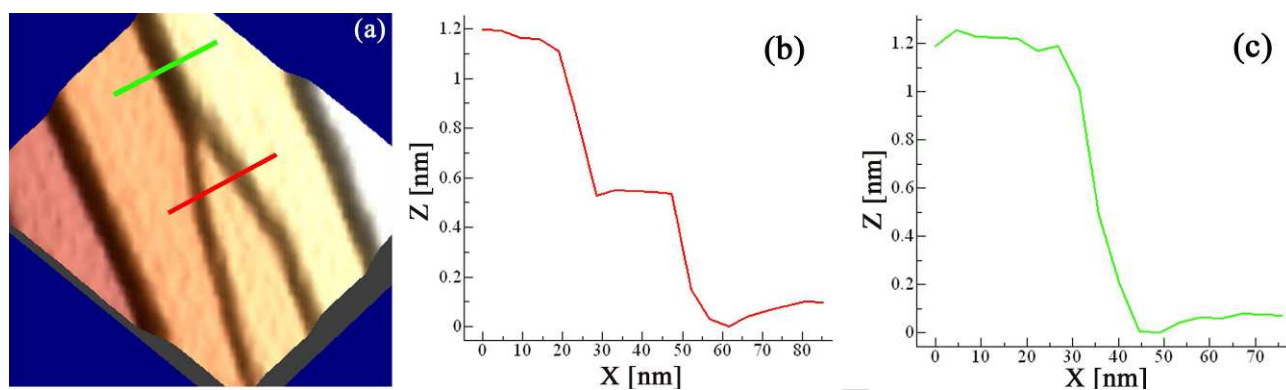


Figure 7: A 3D close view of a junction (a): the formation of multiple steps follows a "zipper-like" motion scheme where steps of smaller height join together and give rise to higher steps. Fig.7(b) and (c) show the step profile along the marked lines in (a): two steps (red line, (b)) merge "zipping" together to provide a higher multiple step (green line, (c)).

As reported earlier, the evolution of the (0001) alumina surface morphology follows several processes including step pairing, coalescence, decomposition, bunching and faceting [14, 15, 31]. The mechanism of bunching and faceting formation upon annealing was found to begin with nucleation of single facets followed by the formation of facet domains and successively by the coalescence of domains and single facets [31]. At this stage misaligned merging junctions appear on the surface: the collision of out-of-phase facet domains forms facet junctions with a misalignment of phase corners. The process continues with the coarsening of facets where the motion of facet junctions leads to a completely faceted surface, as shown in Fig.6. The presence of merging steps is then a consequence of the coarsening stage where the collision of bunched areas causes some portions of steps to deviate locally, resulting in a change in direction of the step edge to another low-index crystallographic direction. The concurring phenomena of step bunching and step faceting make the surface evolution of alumina complicated. Step faceting may start after the completion of step bunching stage or initiate as the step bunching is still ongoing. Their simultaneous manifestation is responsible for the resulting

morphology and makes it difficult to separate their respective contributions [15]. The step edge fluctuation provides a way to lower the overall surface energy during the surface evolution.

As part of the study, TEM analysis of step morphology was performed. TEM micrographs confirm the step-and-terrace structure of the samples. In Fig.8 a cross section view of the sample is shown with the α -Al₂O₃ represented by the dark area while the lighter area is the adhesive used in the preparation of the sample for the TEM analysis. The width of the terraces from the analysis of the TEM micrographs matches the results of the AFM scans. Fig.9 is a high resolution micrograph of the alumina sample viewed along [10-10] with the linear arrays of oxygen atoms in evidence. The crystal structure of alumina is clearly visible and it is possible to investigate the morphology of a single step. The micrograph shows that the macrostep is formed by the bunching of several monosteps, positioned close to each other. In this case the gathering of 10 monosteps leads to the formation of a 2 nm high macrostep. The monosteps correspond to the distance between two adjacent oxygen layers, equal to 0.2 nm.

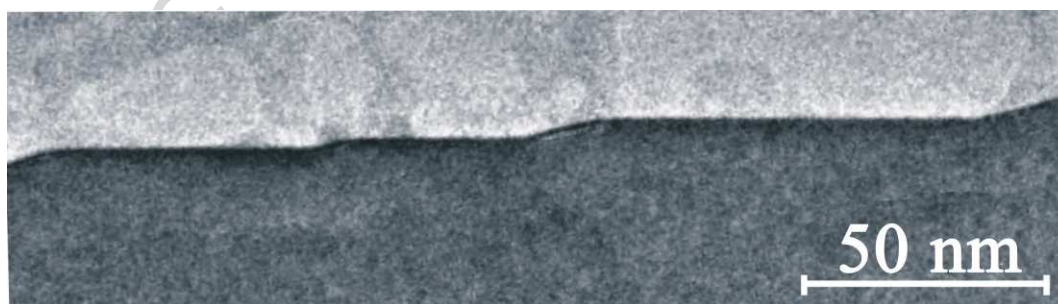


Figure 8: Low magnification micrograph of the alumina sample viewed along [10-10].

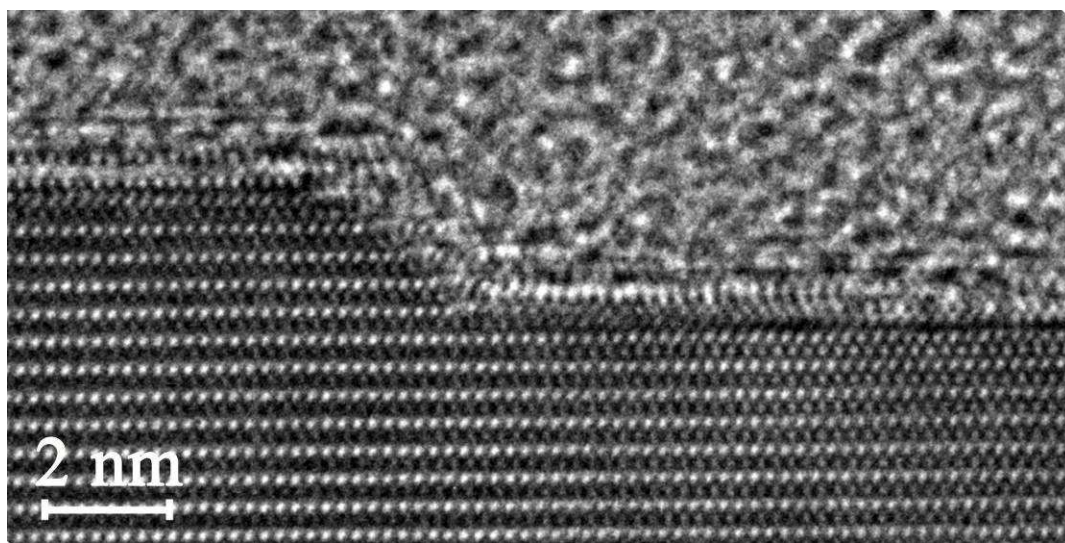


Figure 9: High resolution micrograph of the alumina sample viewed along $[10-10]$.

A considerable number of theoretical studies are available on the evolution and motion of step trains. Yet, the origins of this particular kinetic instability are still debated due to the fact that step bunching can be seen in various physical situations. The asymmetric kinetic behavior due to the Ehrlich-Schwoebel effect is a possible cause. Incorporation rates of adatoms from upper and lower terraces differ significantly and this can generate an instability of the step trains motion during step-flow growth [36, 37]. Step-step long range interaction was proposed to play an important role in step bunching. Finally, impurities can interfere with the kinetic processes and create more complex instabilities [38, 39, 40]. A model proposed by Frank in 1958 suggested that impurities on the surface can destabilize the uniform step train during the evaporation (or the crystal growth) impeding the motion of the step and reducing its velocity [39, 41]. If all the step edges had the same velocity during the surface evolution, step bunching would not occur. A difference in step edge velocities is required for bunching and this could be due to the presence of impurities. In particular, impurities seem to be a likely explanation for the dynamics of alkali metal halide surfaces where particles present on the surface act as pinning sites promoting step pile-up [42, 43]. It was reported that segregation of Ca, Mg, Ba,

Si etc. affects step and surface structure evolution of alumina samples: the presence of such impurities forces the steps to bend around them generating mesoscopic bunching [44]. The initiation of the step bunching process in alumina has been also related to high levels of K impurities while a combination of high levels of Ca and low levels of K stabilizes $c/6$ steps, preventing the bunching itself [20]. These studies show the sensitivity of alumina c -plane towards different kinds of impurities, the type of impurity atoms and its quantity can heavily affect the surface evolution. Accordingly, the annealing environment acquires marked significance as it is responsible for the adsorption of different kinds of impurities. Our results clearly suggest that the surface miscut from a low index c -plane undergoes rearrangement of atomic terraces and forms step bunching more easily than the low index surface. The rearrangement of a miscut surface takes place at a lower temperature compared to a non-miscut surface. When comparing our results with results of other publications, it should be kept in mind that other factors that are difficult to control can also influence the dynamics of step behaviour. For example, impurities in the sample as well as the adsorbates related to the annealing environment can have a significant effect [20].

3.3 Influence of annealing time

At anneal temperature of 1100°C , increasing the annealing time beyond 6 hours does not seem to produce any further substantial changes in the average step height or the average terrace width. Fig.10 shows AFM images of vicinal sapphire samples annealed in air at 1100°C for 12 hours. The samples annealed for 12 hours have an average step height of 1.8 ± 0.7 nm while the average terrace width is 43.6 ± 14.7 nm (Fig.5(b)). For practical reasons, the time of the experiment was limited by some several tens of hours. At the temperature of 1100°C , increasing the annealing time is not sufficient to provide for mass transport and facet coarsening. Changes in temperature have a more profound effect on the morphology than changes in time due

to the fact that bunching is a thermally activated process with a rate exponentially dependent on the annealing temperature.

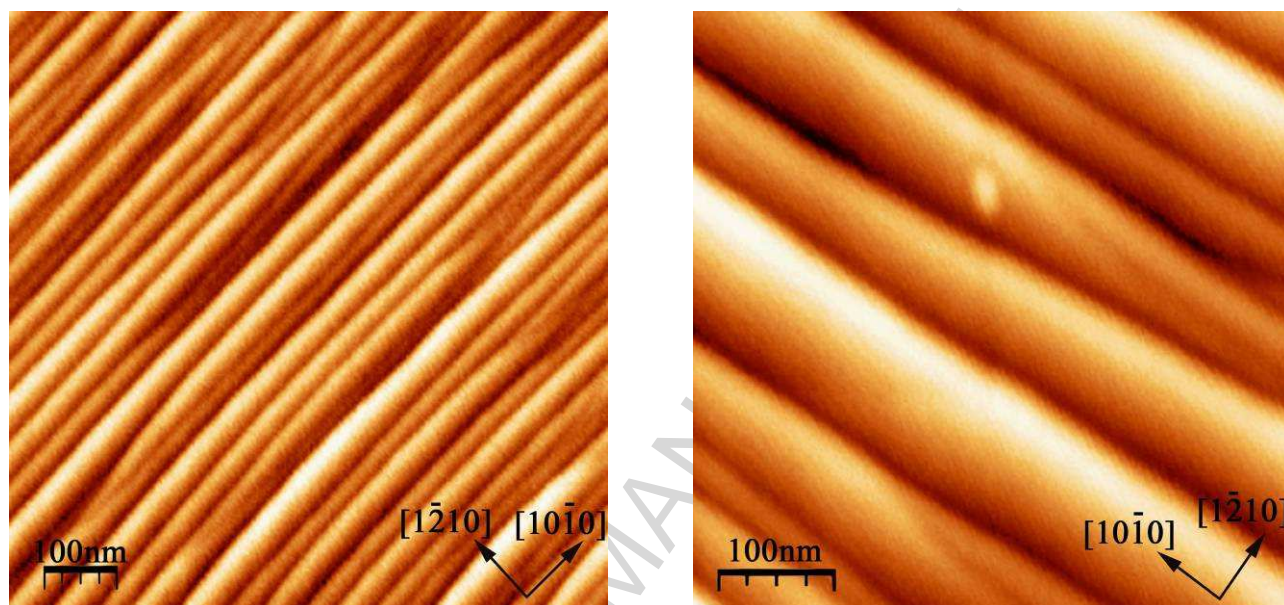


Figure 10: Surface morphology of c-plane sapphire after 12 hours annealing at 1100°C.

4 Conclusions

C-plane alumina samples with 0° nominal miscut and 3° miscut along [1-210] were annealed in air at 1100°C. The surface morphology evolution was then investigated by AFM and HR-TEM. As most of the work on alumina surfaces focuses on samples with no miscut, we show that not only temperature and time, but also the miscut angle play an important role in the surface structure evolution: for samples with a high miscut the annealing process triggers step bunching at a lower anneal temperature compared to substrates with non-miscut.

Flat samples, i.e. substrates with 0° nominal miscut, were annealed for various durations of time at 1100°C and they did not show any step bunching even after long annealing times. In this case the temperature represents the limiting factor since it is

too low for the surface atoms to rearrange. This is confirmed by annealing the same substrates at higher temperatures: in agreement with other studies, and also confirmed by our experiments, the stepped surface on non-miscut samples can be obtained by performing the annealing at higher temperatures.

However, as reported, the formation of multiple steps (of height c or higher) due to step bunching is possible on (0001) alumina only upon annealing at temperatures over 1400°C. Conversely, we demonstrate that the stepped morphology can also be obtained by annealing at relatively low temperatures (1100°C) by introducing substrates with high miscut (3°). The high miscut triggers the instability of the surface boosting the step bunching process and producing steps several nanometers high. TEM micrographs gave a closer view of the step bunching and clarify how the monosteps gather together to form a macrostep. The surface morphology appears quite uniform on the samples with steps running for several tenths of nanometers. However, the surface also clearly presents a number of coalescence points, i.e. locations where two steps merge and form a higher step. Close to the coalescence points, parallel steps change direction to align along a different low index direction. The surface morphologies shown here can be a great interest as templates for the fabrication of ordered arrays of nanowires or nanoparticles on insulating substrates for various applications [45].

Acknowledgements

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