Effect of annealing on 0001 surface (c-surface) of α-Al_2O_3

by

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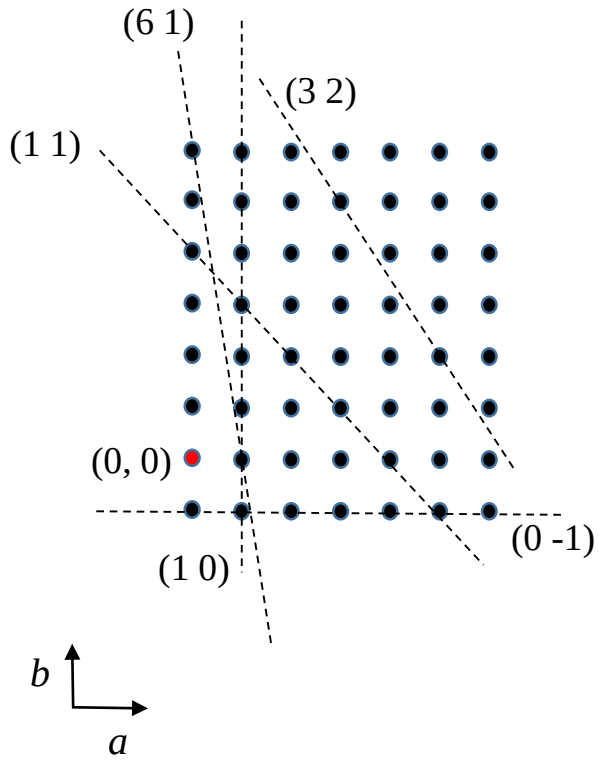
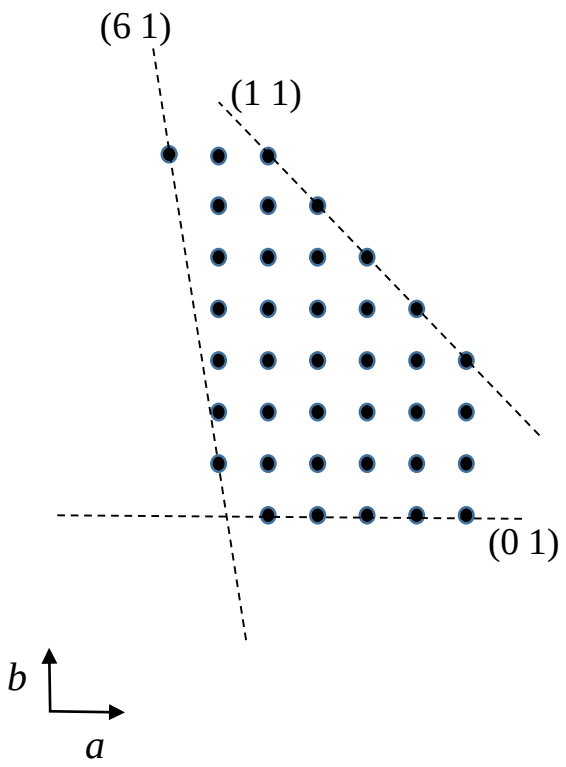
Crystal Surfaces and facets

- Planes with high Miller indices *(hkl)* have atoms lesser density of atoms compared to the planes with lower Miller indices.
- Such a surface with high Miller indices is also known as a *vicinal surface*.
- Vicinal surfaces are inclined at a very small angle to low index surfaces such as (100) i.e. they lie in the vicinity of low index surfaces and hence the name.



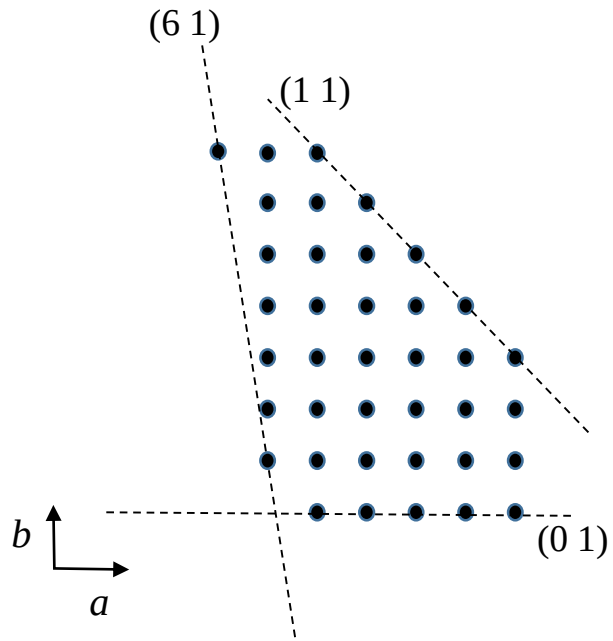
Crystal Surfaces and facets

- Shape of a crystal is determined by the kind of surface exposed during the growth process.
- Crystal growth is essentially a process of minimization of free surface energy. Surface energy depends on the number of atoms on the surface and the nature of dangling bonds.
- More the atoms on the surface, lesser the surface energy, more stable that surface is. Hence, during the growth process, surfaces with high atomic density are preferred.
- Exposed *vicinal surfaces*, during growth process, have more surface energy compared to other low index surfaces. Hence, atoms tend to deposit on vicinal surfaces at a higher rate compared to low index surfaces to minimize the total surface energy.



Crystal Surfaces and facets

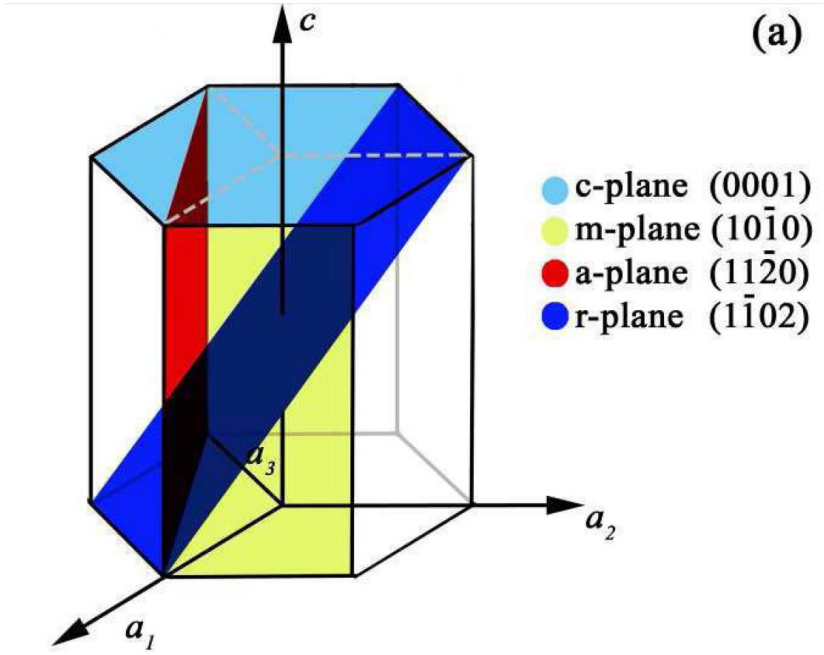
- This difference in the rate of deposition of atoms determines the direction of crystal growth, area of exposed surfaces and the shape of the crystal (which is usually different from the shape of the unit cell).
- In the figure, (6 1) is less stable than (1 1) which in turn is less stable than (0 1) surface. This will result in higher deposition rate on (6 1) surface compared to (1 1) surface. Deposition rate on (0 1) surface will be minimum.
- This means crystal will grow more rapidly leftward and eventually (6 1) surface may evolve into (1 1) surfaces.
- Thus at the end of growth process we will be left with low index surfaces (0 1), (1 1), etc.
- These surfaces are known as ***crystal facets*** and the phenomenon is known as ***crystal faceting***.

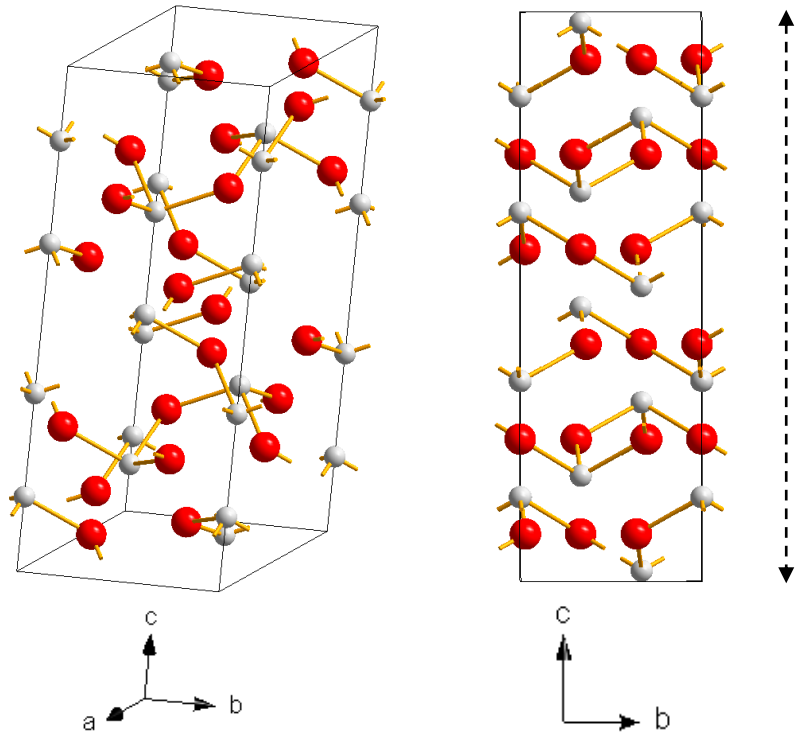


Faceting can also be induced artificially by controlling growth conditions

Hexagonal α-Al_2O_3

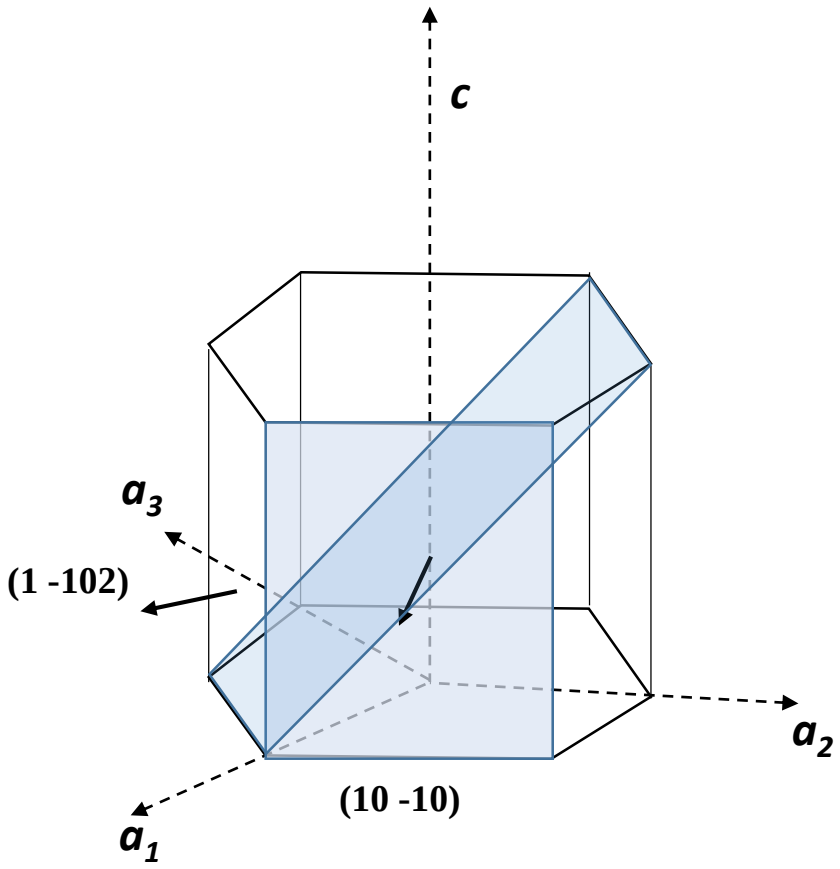
- Each unit cell is composed of six layers of oxygen separated by a double layer of aluminum.
- The distance between the two oxygen layers is ~ 0.21nm which is 1/6th of *c*.



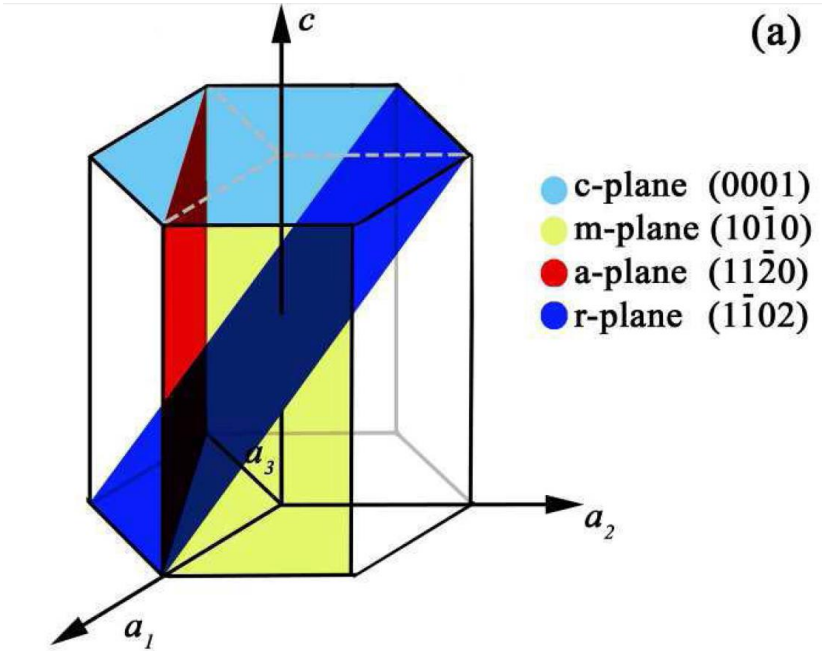


Red – Oxygen
Grey - Aluminum

Hexagonal α-Al_2O_3



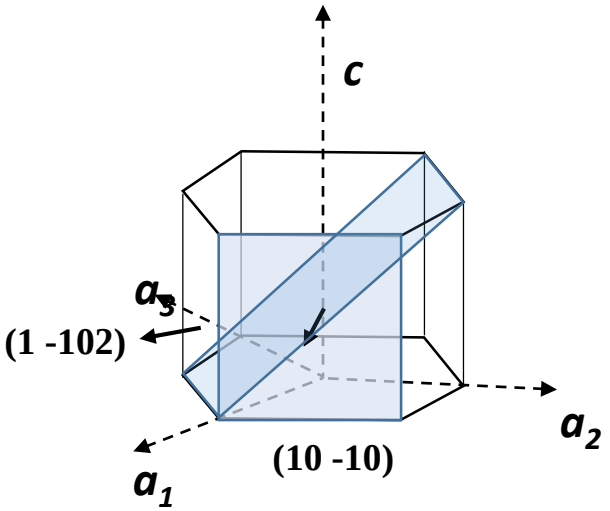
(h k i l) where h + k = - i

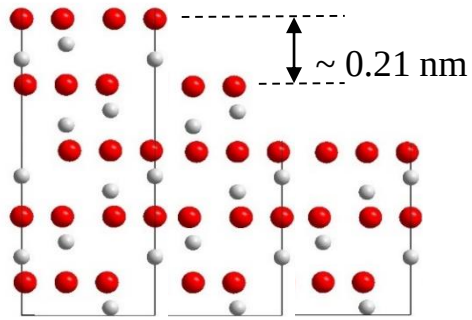


Important low index surfaces of α-Al_2O_3.

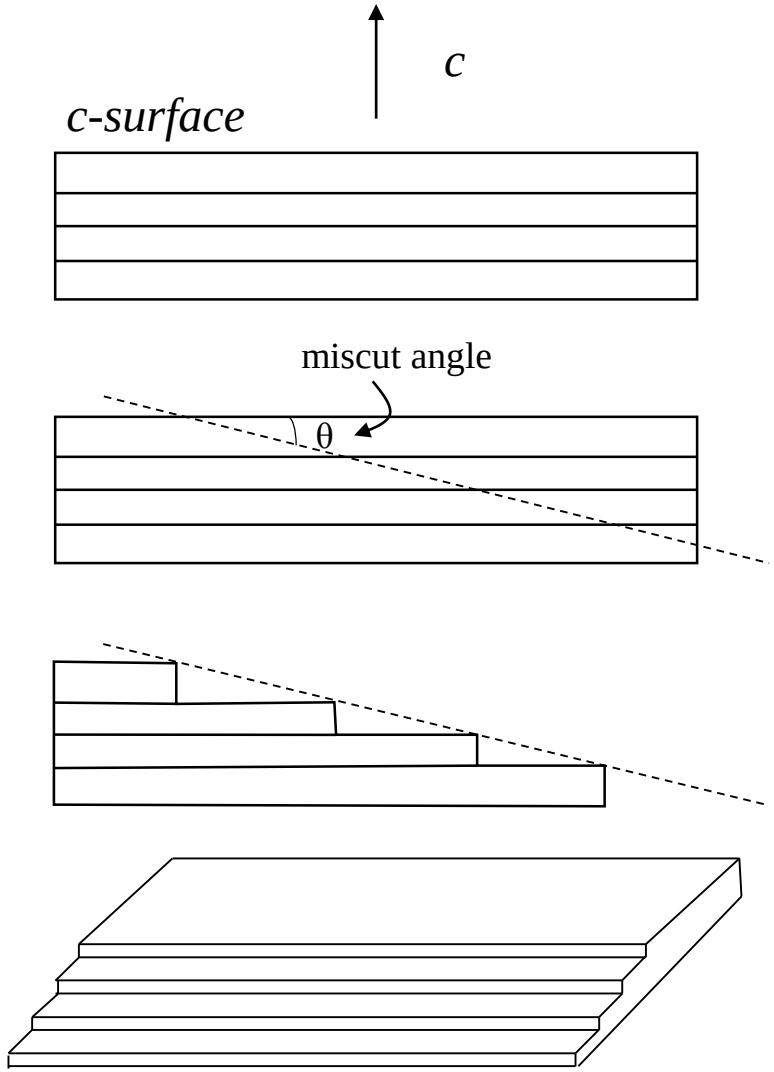
0001 surface (c-surface) of α-Al_2O_3

- Usually 0001 alumina substrates are prepared by cutting the surface at a small angle to the c-plane. This angle is known as *miscut angle*.
- The surface thus obtained is a vicinal surface and exhibits terrace-step morphology.
- In alumina, the distance between consecutive (0001) terraces is ~0.22 nm (without annealing). These terraces are separated by consecutive oxygen layers in the unit cell.
- The angle of the cut with respect to (10 -10) direction is known as *misorientation angle*.

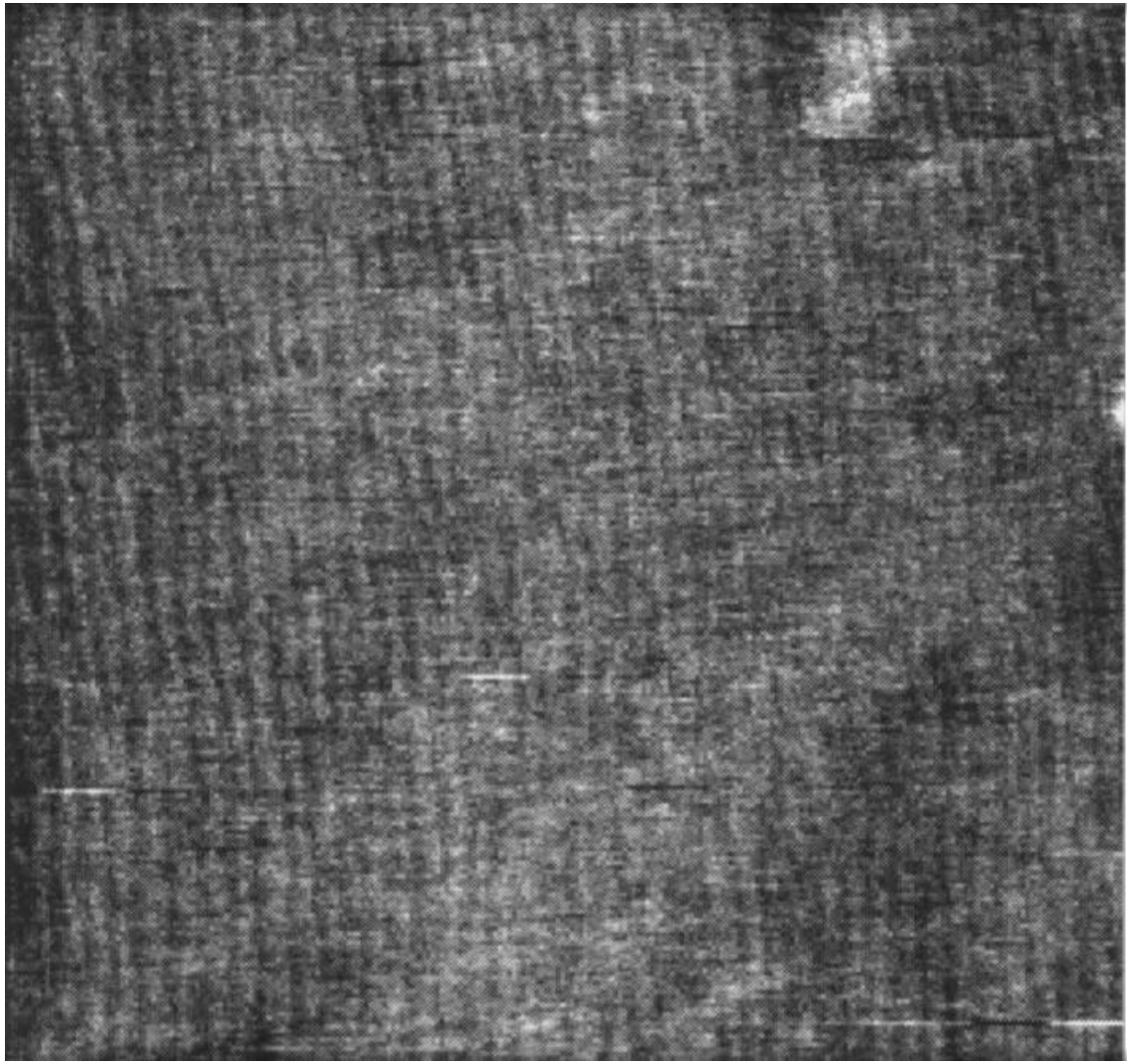




c/6 monosteps of α-alumina
(not accurate, some atoms at the junction of unit cells are not visible)



C-surface of alumina film with terrace-step morphology
(parallel lines represent consecutive oxygen layers)



1.2 X 1.2 μm^2 scan of as-received alumina 0001 substrate exhibiting monosteps [1]

Evolution of terrace-step morphology with annealing

Annealing 0001 alumina substrate above 1000^{o} C causes diffusion of atoms to minimize surface free energy which manifests in the form of significant modification in terrace-step morphology.

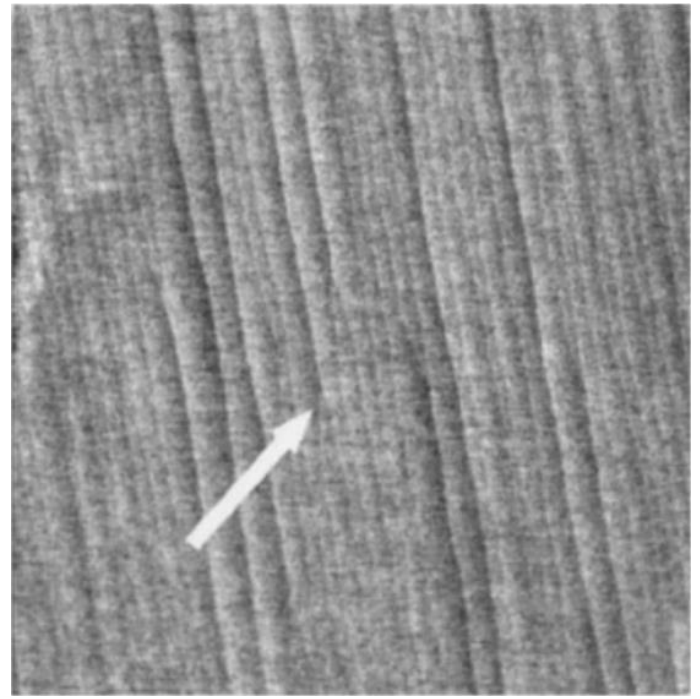
There are four distinct mechanisms to affect the diffusion of atoms:

a) Step coalescence (observed at all temperatures)
b) Step faceting (> 1200^{o} C)
c) Step bunching (> 1200^{o} C)
d) Step decomposition (> 1400^{o} C)

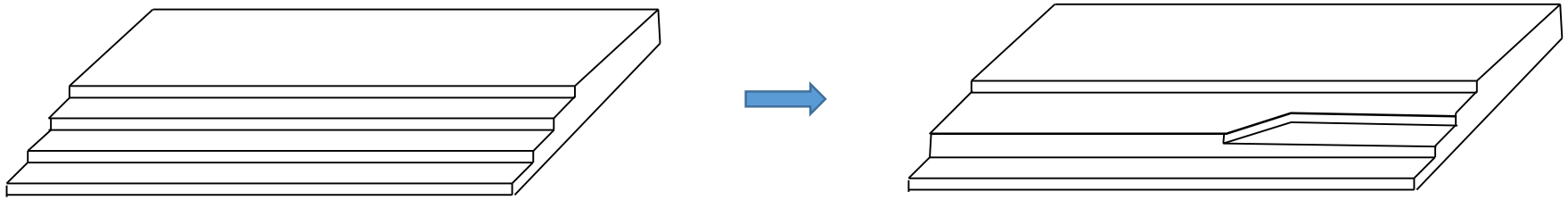
All the above processes have different activation energies which strongly depend on *miscut* and *misorientation* angles.

Step coalescence

- During step coalescence, two consecutive *c/6 monosteps* coalesce in a "*zipper-like*" fashion to give steps of a higher height.
- For temperatures < 1200^{o} C, in low miscut alumina substrates, consecutive *c/6 monosteps* combine to form *2c/6 double-steps*.
- At higher temperatures, this process leads to coalescence of double steps resulting in the formation of *multi-steps*.
- Height of the resultant step is always an integral multiple of *c/6*.
- However, for high miscuts (> 1^{o}), we may observe multi-steps below 1200^{o} C.



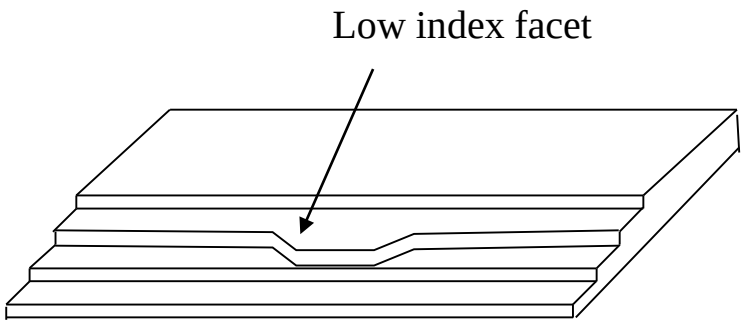
Step Coalescence at 1100^{o} C[1]



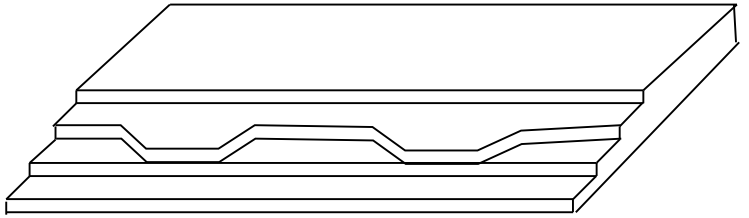
Formation of a *double-step*

Step faceting

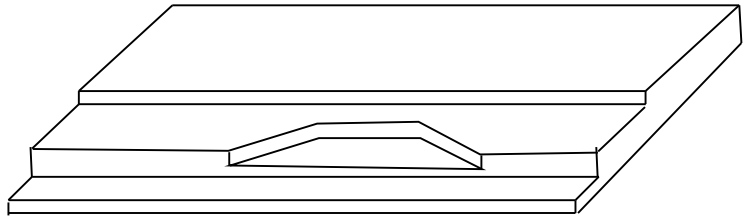
- Step faceting usually occurs at temperatures > 1200^{o} C with the exception of high miscut substrates.
- The process begins with some kind of perturbation which could be due to slight deformation in the step edge or presence of impurity, etc.
- Faceting starts with nucleation where low index surfaces (facets) first appear, followed by the growth of these facets into large domains.
- Growth of domains eventually results in merger of domains. At this stage, if the surface termination of the domains do not match or are out of phase, the domains fail to merge resulting in facets within terraces.
- Step faceting also leads to *zig-zag* form of step edges.



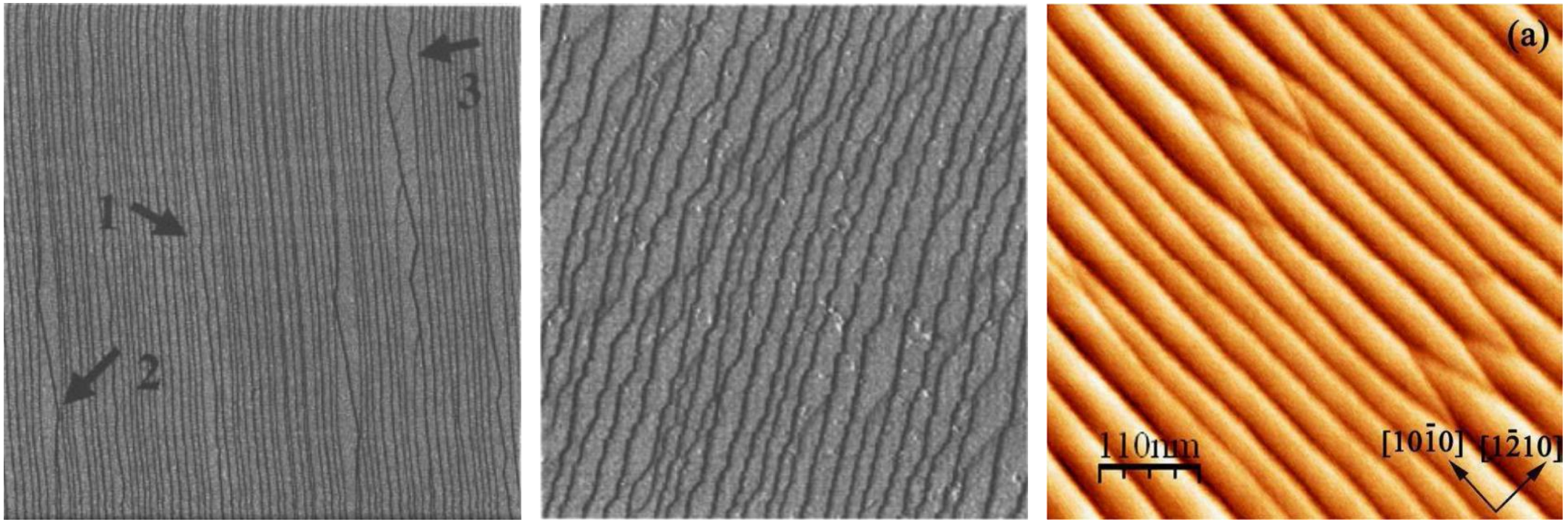
nucleation



Formation of domains



Growth of domains



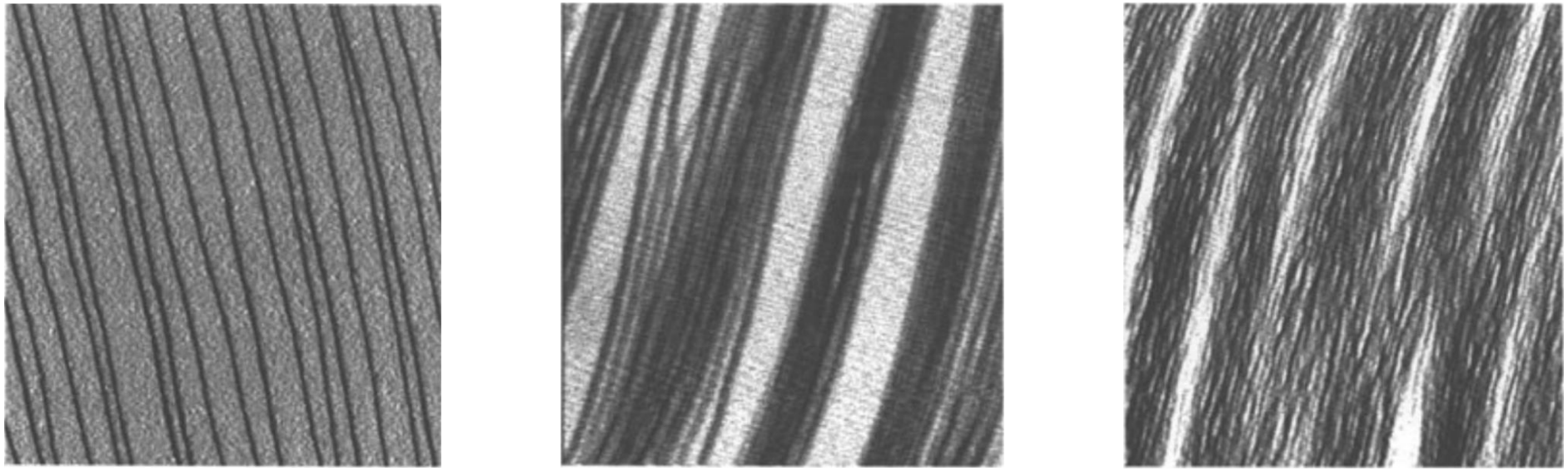
(a) (b) (c)

(a) Initiation and evolution of faceting, (b) faceted steps (1500^{o} C) [3] (c) faceted steps (1350^{o} C) [4]

Step bunching

- Like step faceting, step bunching is observed at temperatures > 1200^{o} C.

- As the name suggests, during this process the multi-steps gather in groups to form distinct bunches of steps. Each bunch give the semblance of a step and hence, each bunch is referred to as a "*macro-step*".



(a) (b) (c)

Typical AFM images showing the influence of miscut on the step bunching after 1 h of annealing in air at 1500°C (a) θ = 0.5°, (b) θ = 0.8 – 1.2°, and (c) θ = 4° [3]

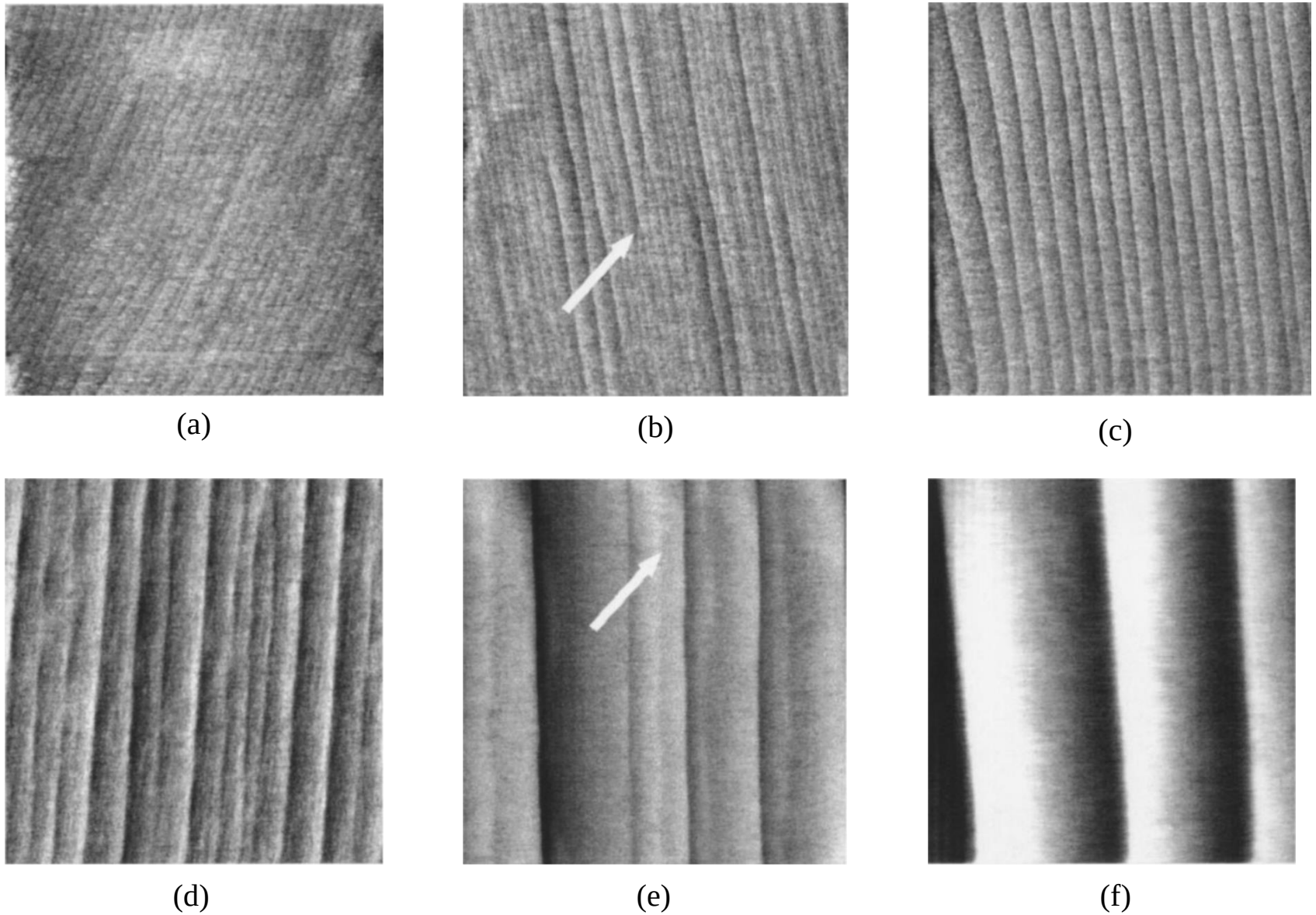
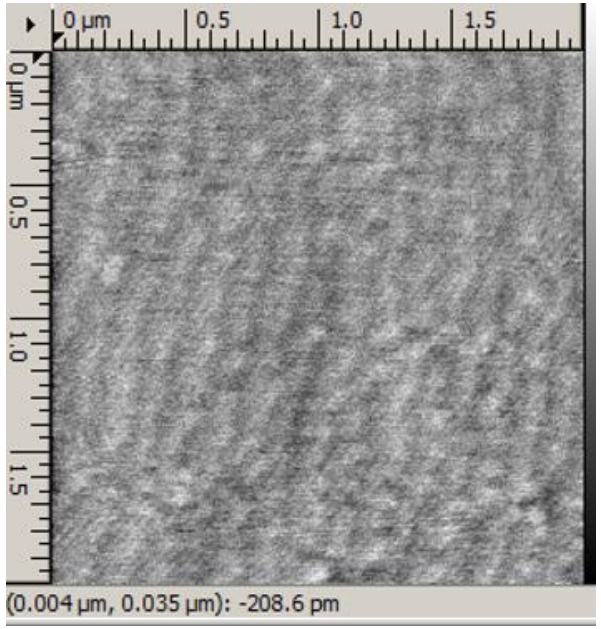


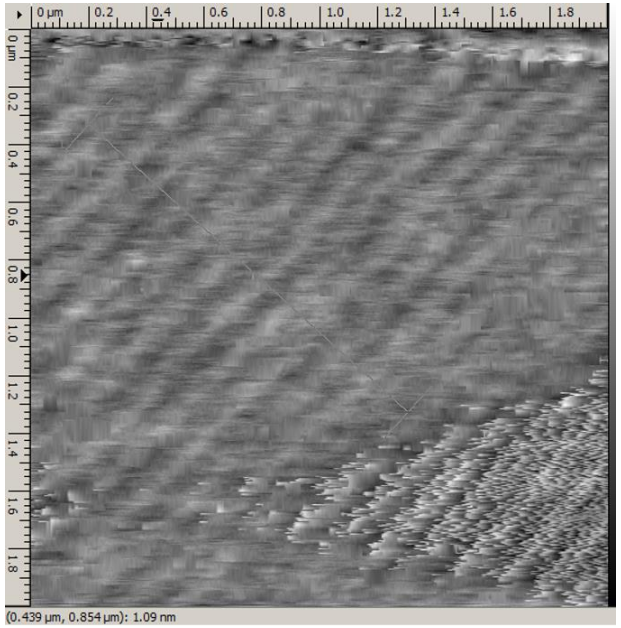
Fig. 2. α-Al_2O_3 (0001) surface morphology ($1.2 \times 1.2\ \mu m^2$) of samples annealed 1 h in air at: (a) 1000°C, (b) 1100°C, the arrow shows area of monosteps coalescence; (c) 1200°C; (d) 1300°C; (e) 1400°C, a monostep is visible (arrow); and (f) 1500°C.

Our results

2 X 2 μm^2 scans of alumina 0001 substrate

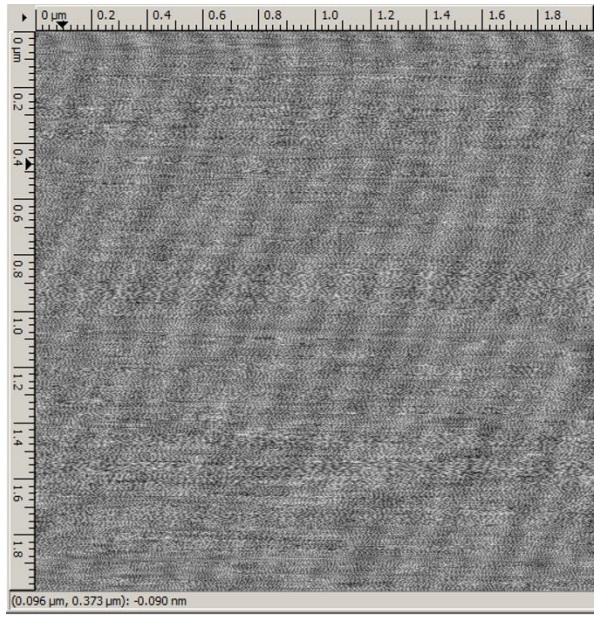
annealed at 1000 C

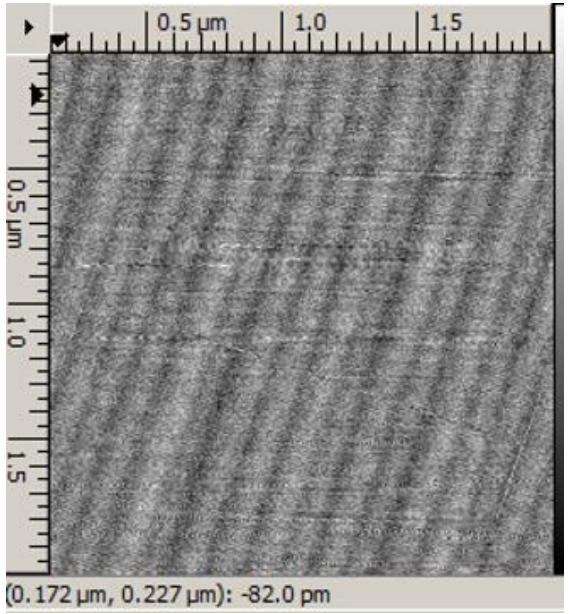




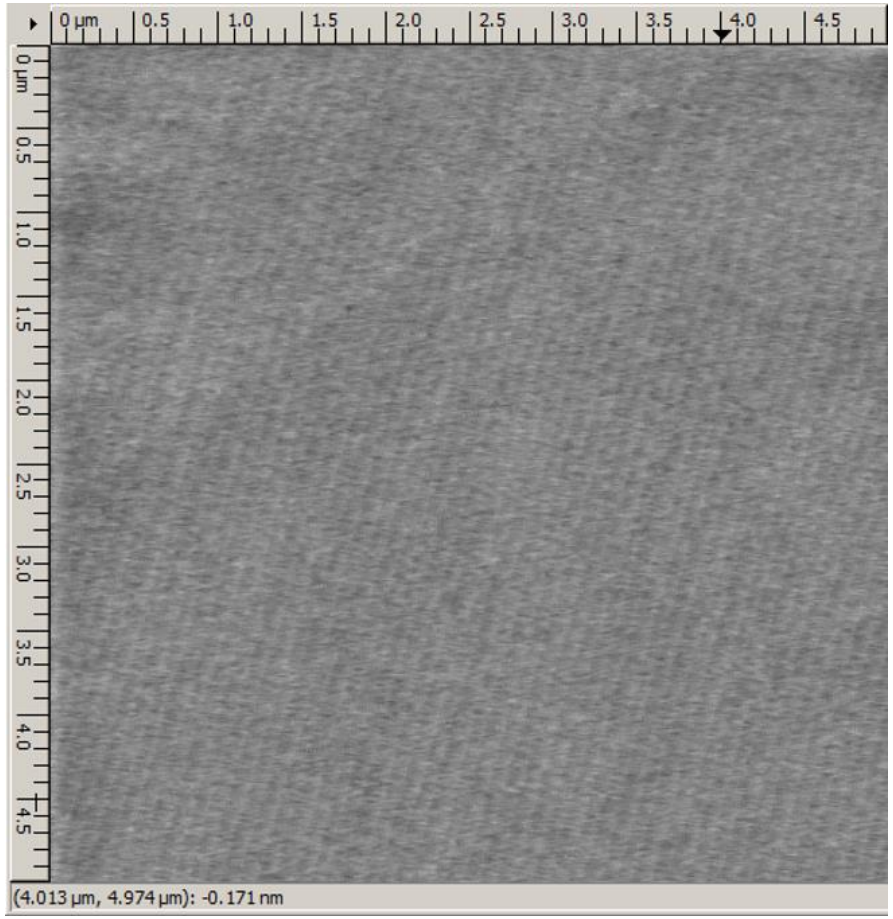
Annealed at 1100 C

Annealed at 1200 C

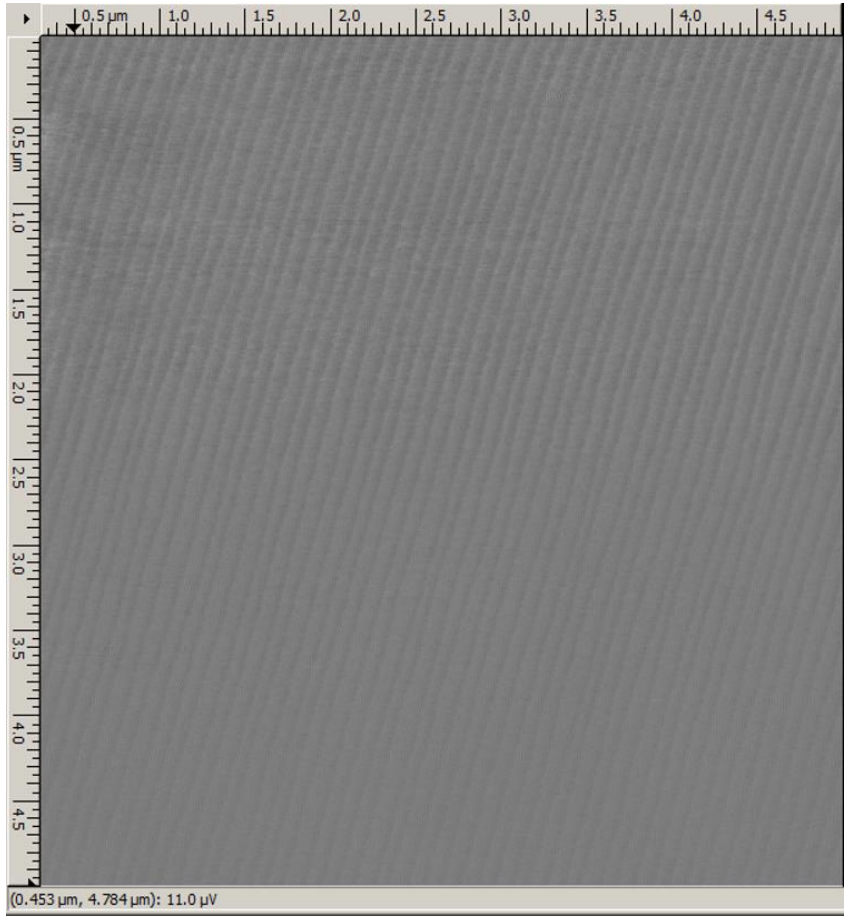




Annealed at 1300 C



Z-height profile



phase profile

5 X 5 μm^2 AFM scans of 0001 alumina annealed at 1300 C for 3 hours

References

1. *Evolution of steps on vicinal (0001) surfaces of a-alumina by* L. Pham Van, O. Kurnosikov, J. Cousty **Surface Science 411 (1998) 263–271**
2. *About anisotropy of atomic-scale height step on (0001) sapphire surface by* O. Kurnosikov1, L. Pham Van, J. Cousty **Surface Science 459 (2000) 256–264**
3. *High-temperature transformation of vicinal (0001) Al2O3-a surfaces: an AFM study* by O. Kurnosikov L. Pham Van2 and J. Cousty **Surf. Interface Anal. 29, 608–613 (2000)**
4. *Surface morphology of c-plane sapphire (α-alumina) produced by high temperature annealing* by F. Cuccureddu, S. Murphy, I.V. Shvets, M. Porcu, H.W. Zandbergen N.S. Sidorov, S.I. Bozhko **surf. sci. doi: 10.1016/j.susc.2010.04.017**