Characterisation of high-temperature annealing effects on $\alpha$—$\text{Al}_2\text{O}_3$ (0001) substrates

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Characterisation of high-temperature annealing effects on \( \alpha - Al_2O_3(0001) \) substrates

BingCui Qi, B. Agnarsson, K. Jonsson, S. Olafsson and H.P. Gislason
Science Institute, University of Iceland, Dunhagi 3, IS-107, Reykjavik, Iceland
E-mail: bing@raunvis.hi.is

Abstract. High temperature annealing in air has been applied as an effective ex-situ surface treatment for the \( \alpha - Al_2O_3(0001) \) substrates used in molecular beam epitaxy (MBE) growth of III-nitrides. The method is based on the criterion that atomically smooth surface of terrace-and-step like structure, which is considered to be crucial in obtaining a high quality epilayer, could be produced upon high temperature annealing. The annealed surface was mostly studied by atomic force microscopy (AFM) imaging. In this work, the effects of high temperature annealing on the surface morphology, crystalline quality, optical quality and surface reconstruction behaviour of \( \alpha - Al_2O_3(0001) \) substrates were fully studied using AFM, triple-axis high resolution X-ray diffraction (THRXRD), spectroscopic ellipsometry (SE) and in-situ reflection high-energy electron diffraction (RHEED). A new strategy, \( H_2 \) thermal cleaning at 1100°C followed by \( O_2 \) annealing at 1300°C was proposed as an efficient surface treatment for \( \alpha - Al_2O_3 (0001) \) substrates for MBE growth.

1. Introduction

Atomically smooth surface with terrace-and-step like structures of \( \alpha - Al_2O_3(0001) \) substrates has been considered crucial in MBE growth to achieve high quality epilayers [1, 2, 3]. Furthermore, the surface steps of the substrate could also serve as potential templates for epitaxial growth of nanostructures [4]. It is generally accepted that high temperature annealing is an effective method to achieve atomically flat surface of \( \alpha - Al_2O_3(0001) \) substrates. The annealed surface morphology strongly depends on the annealing conditions and the crystallographic orientation of the substrate [5]. Annealing of the (0001) surface results in a terrace-and-step structure, while annealing of the (10\( \overline{1} \)0) surface results in a hill-and-valley structure [6, 7]. Terrace-and-step morphology is attained via faceting [6, 8]. Straight and zigzag steps can be formed depending on the inclination direction of the vicinal surface toward the \( \alpha \)-axis [11\( \overline{2} \)0] or the \( m \)-axis [1\( \overline{1} \)00] [1]. It begins with the formation of multiple-step domains separated by terrace-and-step structures with single c/6-high steps. The steps preferably exist in pairs; then merge together to form facet domains of multiple c/6 steps in height. The facet domains coalesce with increasing annealing time [2, 5]. Local or global coalescence of multiple steps was observed depending on annealing temperatures. Finally the coalescence domains re-evolved into thermodynamically-stable, faceted terrace-and-step morphology [5].

The objects of our work are to compare the annealing surface morphology in air and \( O_2 \) and to comprehensively characterise the annealing effects on the surface morphology, the crystalline quality and surface reconstruction behaviour of \( \alpha - Al_2O_3(0001) \) substrates using AFM, THRXRD, SE and RHEED.
2. Experimental

$\alpha$–$\text{Al}_2\text{O}_3$(0001) substrates (from CrysTec), 10×10×0.5 mm, polished on one side, RMS < 0.5 nm, with nominal miscut < 0.3° towards [11¯20] were used in this study. Annealing was conducted in high purity alumina tube ($\text{Al}_2\text{O}_3 \geq 99.5\%$) furnace at 1300°C, with the substrate enclosed in a re-crystallised alumina tube, in air or $\text{O}_2$ (5.0 N purity) environment respectively. When $\text{O}_2$ was used, the substrate was firstly thermally cleaned with $\text{H}_2$ (5.0 N purity) at 1100°C for one hour followed by $\text{N}_2$ (5.0 N purity) purging for about half an hour before supplying $\text{O}_2$ gas.

AFM analysis was performed with XE-100 multi-mode AFM system (PSIA Inc.) in air, in contact mode using Si probe (NANOSENSORS). RHEED images were obtained in a VG-Semicon V80H MBE system with 15 keV incident beam energy and incidence angle < 3°. SE analysis was performed with PhE-102 Spectroscopic Ellipsometer. THRXD analysis was carried out with PANalytical X’Pert PRO Extended MRD system. High resolution reciprocal space map (RSM) of symmetric reflection of a [0 0 6] plane and asymmetric reflections of [1 1 12], [1 1 9] and [2 0 10] planes were collected. For symmetric reflection, 90° rotation in $\Phi$ was applied; for asymmetric reflections, 60° or 120° rotation in $\Phi$ was performed. Lattice parameters and full width at half maximum (FWHM) values were deduced from RSM using the PANalytical Epitaxy program. The normalised data based on different $\Phi$ positions for a fixed reflection plane was used to compare the changes in crystalline quality of the $\alpha$–$\text{Al}_2\text{O}_3$(0001) substrates before and after annealing.

3. Results and discussion

3.1. AFM analysis

AFM images of $\alpha$–$\text{Al}_2\text{O}_3$(0001) annealed at 1300°C in air or $\text{O}_2$ for different time periods are shown in Figure 1. It can be seen that the annealing time had a great influence on the surface morphology of $\alpha$–$\text{Al}_2\text{O}_3$(0001). The step-terrace structure was hardly visible after 3 hours annealing in air. After increasing the annealing time to 6 hours, a few large parallel terraces of 2-3 step heights with uniform single steps distributed between the large terraces became visible. Compared to annealing in air, the step-terrace structure of the surface developed faster when annealed in $\text{O}_2$, which became visible after 3 hours of annealing in $\text{O}_2$. Increasing the annealing time to 6 hours in $\text{O}_2$, the steps became highly corrugated due to strong faceting.

The results from annealing longer than 6 hours show that similar surface morphology was achieved for the surface annealed in air for 20 hours and the surface annealed in $\text{O}_2$ for 11 hours. Well-defined, sharp hexagonal- edged steps and the wider terraces of strongly-faceted step edges with multiple heights became the dominating features of the surface morphology. Pairing of single-height steps into wider faceted terraces of multiple-heights was occasionally observed.

In summary, AFM analysis shows that the surface morphology evolution process of $\alpha$–$\text{Al}_2\text{O}_3$(0001) substrate upon high temperature annealing in air was thermodynamically and kinetically different from that in $\text{O}_2$. While the terrace-step structure and terrace faceting developed faster by annealing in $\text{O}_2$ than in air, similar surface morphology were achieved both in air and in $\text{O}_2$ with longer annealing time.

3.2. RHEED images

The RHEED images of $\alpha$–$\text{Al}_2\text{O}_3$(0001) surfaces before and after annealing are given in Figure 2. Results in Figure 2 show that twin spots/double short streaks were commonly observed after high-temperature annealing. A complex pseudo high-order surface reconstruction seems to be induced by high temperature surface annealing. The reconstructed pattern was found thermodynamically stable in ultra-high vacuum (UHV). The presence of twin spots/double short streaks in the RHEED pattern suggests that the surface edge faceting of the substrate was enhanced by high temperature annealing[9]. However accurate information on the surface reconstruction patterns needs to be obtained by low energy electron diffraction (LEED)[10].
Figure 1. AFM images of $\alpha$-$\text{Al}_2\text{O}_3(0001)$ annealed at 1300°C for different time, magnification: (a,d,g,j,h,k) $1 \times 1 \mu m^2$; (b,e,i,l) $3 \times 3 \mu m^2$; (c,f) $5 \times 5 \mu m^2$. 
3.3. Spectroscopic ellipsometry (SE) analysis

Full-depth optical quality changes of \( \alpha-Al_2O_3(0001) \) substrates due to annealing were probed with SE spectra in the wavelength range of 250-900 nm (1.38-4.96 eV) at four incidence angles of 55°, 60°, 75° and 80°, corresponding to below, close, near and above the Brewster angle of \( \alpha-Al_2O_3(0001) \) substrate. The typical SE spectra of \( \psi \) at incidence angle of 55° and 75° were chosen to show in Figure 3. It can be seen that no obvious shift of peak positions corresponding to the absorption band-gap energy of \( \alpha-Al_2O_3(0001) \) substrate was detected before and after annealing.

![SE spectra](image)

**Figure 3.** SE spectra of \( \psi \) of \( \alpha-Al_2O_3(0001) \) substrates annealed at 1300°C, before annealing in air (---), after 4.5 h annealing in air (▽), before annealing in \( O_2 \) (…), after 6 h annealing in \( O_2 \) (+), at incidence angle of (a) 55° and (b) 75° respectively.

3.4. THRXRD analysis

THRXRD RSM measurements of symmetric [0006] reflections and asymmetric [1112] reflections of \( \alpha-Al_2O_3(0001) \) before and after annealing are summarised in Tables 1 and 2.

The results show that the change in lattice parameters of the \( \alpha-Al_2O_3(0001) \) substrate upon annealing was within 10 times the statistical measurement error and the drift of lattice parameters due to thermal influence from the ambient. This is in the order of \( 6 \times 10^{-6} \). The changes in the out-of-plane tilt were within 100 times the statistical measurement error. The data suggests that annealing might also change the crystalline size and crystalline quality of the \( \alpha-Al_2O_3(0001) \) substrate. The quality of the crystal plane orientation generally improved after annealing. However, more accurate surface crystal lattice measurement and qualification methods should be used to finalize the effects of annealing on \( \alpha-Al_2O_3(0001) \) substrate crystallinity.
Table 1. Standard deviation of the lattice parameters calculated from THRXRD RSM data.

| [h k l] | Ambient | Annealing | \( \sigma_d(\text{Å}) \) | \( \sigma_{FWHM}(\Omega/\Theta)(\%) \) | \( \sigma_{FWHM}(\Omega)(\%) \) |
|--------|---------|-----------|-----------------|------------------|------------------|
| 0 0 6  | in air  | before    | 4.47 \times 10^{-6} | 1.78 \times 10^{-4} | 1.40 \times 10^{-4} |
|        |         | after     | 1.58 \times 10^{-5} | 1.19 \times 10^{-4} | 2.59 \times 10^{-4} |
|        | in O\(_2\) | before    | 2.45 \times 10^{-5} | 1.59 \times 10^{-4} | 1.59 \times 10^{-4} |
|        |         | after     | 1.67 \times 10^{-5} | 1.02 \times 10^{-4} | 7.85 \times 10^{-5} |
| 1 1 2  | in air  | before    | 5.83 \times 10^{-6} | 2.90 \times 10^{-4} | 6.50 \times 10^{-5} |
|        |         | after     | 5.35 \times 10^{-6} | 5.51 \times 10^{-4} | 3.82 \times 10^{-4} |
|        | in O\(_2\) | before    | 4.98 \times 10^{-6} | 5.49 \times 10^{-4} | 1.40 \times 10^{-4} |
|        |         | after     | 4.23 \times 10^{-6} | 6.15 \times 10^{-4} | 7.34 \times 10^{-4} |

Table 2. Relative changes of the lattice parameters calculated from THRXRD RSM data.

| [h k l] | Ambient | \( d(\text{Å})(\%) \) | FWHM(\(\Omega/2\Theta\))(\%) | FWHM(\(\Omega\))(\%) |
|--------|---------|-----------------|------------------|------------------|
| 0 0 6  | in air  | 5.95 \times 10^{-3} | 3.25 | 7.82 | -0.78 |
|        | in O\(_2\) | 5.36 \times 10^{-3} | -7.44 | -1.82 | 6.00 |
| 1 1 2  | in air  | 1.57 \times 10^{-3} | -1.18 | -7.44 | -6.05 |
|        | in O\(_2\) | 2.04 \times 10^{-3} | -1.18 | -0.82 | -6.05 |

4. Conclusion

AFM analysis shows that the development of surface morphology of \( \alpha – Al_2O_3(0001) \) substrate induced by annealing in air and in \( O_2\) was different. Thermal cleaning in \( H_2\) followed by annealing in \( O_2\) was thermodynamically and kinetically efficient to produce terrace-step like surface structure. Well-defined hexagonal-edged facets of single and multiple atomic-step heights were formed after annealing longer than 6 hours. THRXRD analysis suggests that the crystalline quality and lattice parameters could be affected by high-temperature annealing. The lattice plane spacing generally expanded and the quality of crystal plane orientation was improved after annealing. The SE analysis shows no obvious shift of absorption peak positions above and the near band-gap energy of the \( \alpha – Al_2O_3(0001) \) substrate after annealing.

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