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SURFACE AND THIN FILMS

Sapphire Evolution of the Vicinal (0001) Sapphire Surface upon Annealing in Air

V. P. Vlasov, A. E. Muslimov, A. V. Butashin, and V. M. Kanevsky

Shubnikov Institute of Crystallography, Russian Academy of Sciences, Moscow, 117333 Russia

e-mail: amuslimov@mail.ru

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Abstract—The evolution of a terrace-step nanostructure (TSN) on the sapphire (0001) surface misoriented by an angle of 0.1° with respect to the $(10\bar{1}0)$ plane was observed by atomic force microscopy (AFM) at temperatures from 1273 to 1673 K. It was established that, with an increase in the annealing temperature to 1373 K, the step height attains 0.44 nm at a distance of 220 nm between steps; i.e., heating by 100 K doubles these parameters. In this case, the relief periodicity is retained. Rapid cooling of the substrate to 973 K leads to partial freezing of the surface structure, which makes it possible to observe the transition from one TSN to another. It was established that two steps coalescence upon annealing to 1373 K toward the $(1\bar{1}00)$ plane, which has the lowest rigidity and, consequently, the lowest atomic density. The coalescence of two steps at a specified temperature is completed at a sufficiently large distance between the steps, at which their interaction energy is negligible. Upon further annealing of the samples above 1373 K, the steps overgrow to 1 nm; however, their periodicity is broken in this case.

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INTRODUCTION

Sapphire Al_2O_3, a material having high mechanical strength, hardness, and thermal and chemical stability, is widely applied in different fields of science and technology [1]. Sapphire plates with surfaces lying in four crystallographic planes, *c* (0001), *r* $(10\bar{1}2)$, *a* $(11\bar{2}0)$, and *m* $(10\bar{1}0)$, are used as substrates for depositing various films; the *c* (0001) plane is optimal among them. External factors cause the formation of ordered steps on this plane, which often facilitate epitaxial film growth [2, 3].

The formation of a terrace-step nanostructure (TSN) on the vicinal (0001) sapphire surface is based on the shift of its equilibrium faceting by a small angle (up to 3°). The surfaces that do not correspond to the equilibrium faceting are thermodynamically unstable. Covering such surfaces by a system of steps, consisting of planes corresponding to the equilibrium faceting, leads to a decrease in their potential Ω_S. This surface structure is called the natural roughness [4, 5]. In practice, a TSN is obtained on the (0001) sapphire surface deviating from the latter by an angle of up to 1°, with subsequent annealing in air at temperatures of 1273–1800 K for 1–10 h. Annealing of the sapphire surface with a vicinal angle of 0.1° at 1273 K for 1 h leads to the formation of TSN, which is characterized by step height of $h = 0.22$ nm, corresponding to the minimum distance between oxygen layers in the sapphire crystal lattice and a distance of $d = 110$ nm between steps, depending on the vicinal angle. It should be noted that the TSN formation is often hindered by the distorting effect of different impurities, dislocations, and temperature-field inhomogeneities upon annealing.

Forming natural roughness steps arise upon annealing of crystals on thermally unstable surfaces. Despite the increase in the surface area, their growth is accompanied by a decrease in the free surface energy of the crystal. The forming steps generally consist of simple planes of singular orientations with the minimum Miller indices [6–9]. The progress in experimental study of TSNs on the sapphire surface was made using atomic force microscopy (AFM). This technique made it possible to establish the dependences of TSN on the angle of plate misorientation and the annealing temperature in air and vacuum [2]. An increase in the annealing temperature and time leads to coalescence of the initial steps with the formation of higher steps (with a height multiple of 0.22 nm) in accordance with the *zipperlike* scheme [10]. The growth of steps and, consequently, the increase in the distance between them cause surface smoothing [11]. The most likely mass-transfer processes are surface diffusion and the evaporation–condensation cycle. The final result of annealing was reported in [10, 11]; however, the time evolution of the TSN formation was not observed. In view of this, it is of interest to try to freeze the step growth.

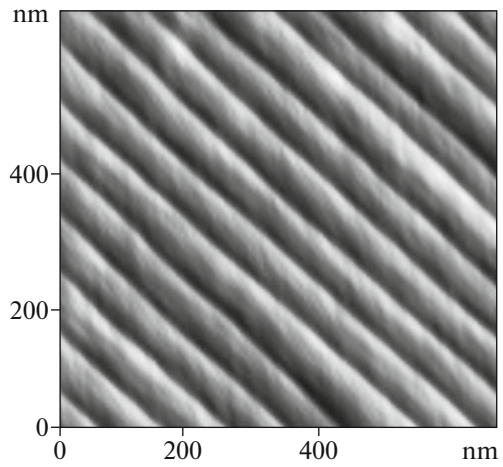

Fig. 1. AFM image of the (0001) sapphire surface after annealing in air at 1373 K for 1 h.

EXPERIMENTAL

TSNs were formed on (0001) sapphire plates subjected to one-side mechanical and chemical polishing [12]. The plate size was 5 × 10 × 0.5 mm. The vicinal angle in the $\langle 10\bar{1}0\rangle$ direction was less than 0.67°.

The plates were annealed in air in two regimes: at a fixed temperature (1273 K) for 1–6 h and for a fixed time (1 h) at temperatures in the range of 273–1673 K, with step-by-step study of the plate surface, including observation and characterization of the TSN, in a semicontact topography mode on an Ntegra Prima atomic force microscope.

Annealing at a temperature of 1273 K for 1 h resulted in the formation of steps with a height of h = 0.22 nm on the plate surface, spaced by a distance of d = 110 nm (Fig. 1).

Subsequent annealing at a fixed temperature (1273 K) for 2–6 h did not change the step parameters (h and d). However, in accordance with [10], an increase in the annealing temperature above 1273 K should lead to the formation of higher steps. In our experiments, the furnace annealing temperature was raised to 1373 K for 15 min, after which the sample was cooled. It was suggested that the transition to higher steps will be frozen in this annealing regime.

RESULTS AND DISCUSSION

A long-time (up to 6 h) annealing at a temperature of 1273 K does not change the TSN parameters. To initiate step overgrowth, it is necessary to overcome the temperature threshold of 1373 K. Upon short-time heating of sapphire from 1273 to 1373 K and rapid cooling to 973 K, areas are formed on its (0001) surface, which can be interpreted as frozen areas, where the steps grew with a simultaneous increase in the distance between them (Fig. 2).

Such areas are distributed over the surface and have different shapes (Fig. 3).

The step growth is illustrated in the figures. The steps aligned along the $[11\bar{2}0]$ direction coalesce pairwise towards the $(10\bar{1}0)$ plane.

Coalescence of steps occurs in four stages. First, triangular protrusions are formed, which are assumed

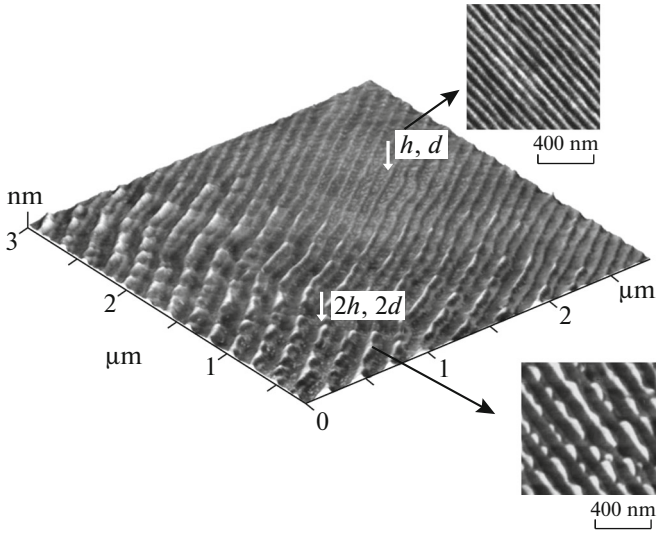

Fig. 2. AFM image of the (0001) sapphire surface after annealing at an elevated temperature (1473 K) and rapid cooling to 973 K, which shows coalescence of steps with doubling of the step height and distance between steps. The insets show the area of steps with h = 0.22 nm (top) and the area of unformed steps with h = 0.44 nm (bottom).

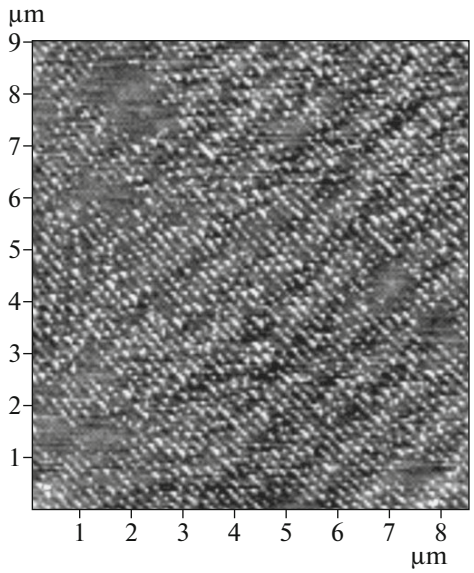

Fig. 3. AFM image of the (0001) sapphire surface, which demonstrates the distribution of areas with different shapes, where the TSN transition occurs.

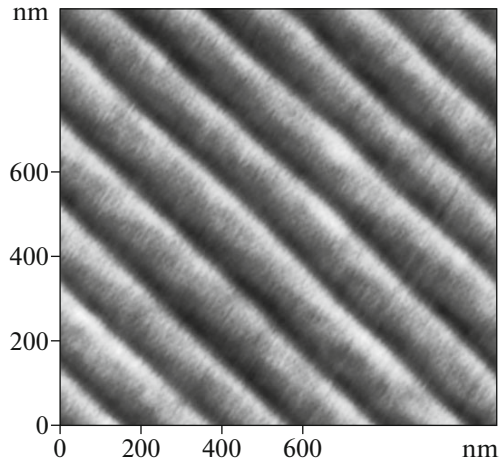

Fig. 4. AFM image of the (0001) sapphire surface after complete TSN formation upon annealing at 1473 K.

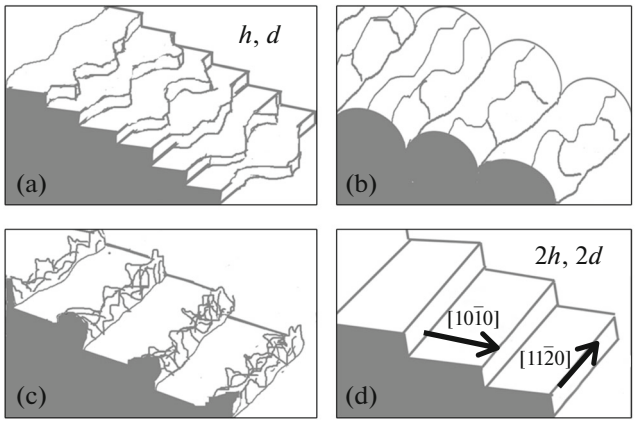

Fig. 5. Proposed scheme of step growth with an increase in the annealing temperature from 1373 to 1473 K, involving four stages: (a) formation of triangular protrusions, which are assumed to be faceted by the $(2\bar{1}\bar{1}0)$ and $(1\bar{2}10)$ planes; (b, c) intermediate stages of growth of a shapeless material mass on steps; and (d) formation of steps with h = 0.44 nm.

to be faceted by the $(2\bar{1}\bar{1}0)$ and $(1\bar{2}10)$ planes, forming an angle of 120° [13]. During annealing, the protrusions vanish and smooth steps of double height are formed, spaced by large distances (Fig. 4).

This behavior of steps upon annealing was observed in [14]. The proposed schematic of step growth is presented in Fig. 5. The second and third intermediate stages imply growth of a shapeless mass of material on the steps, which is then used to form a smooth surface. Incompletely formed steps with a height of h = 0.44 nm can be seen in the bottom inset to Fig. 2.

The formation of the surface structure is most likely related to the surface heat transfer, and the kinetics of this process is determined by surface diffusivities. Under a temperature gradient, surface atoms are affected by force F, which causes a diffusion flux directed along the surface [7]:

$$j_s = n_0 F D_s / kT,$$

where $F = F = -Q_S^* \Delta T / T$, Q_S^* is the transfer heat, ΔT is the temperature gradient, and D_s is the surface diffusivity; F may change with a change in coordinate and orientation [7]. As is known, the step face morphology is determined by rigidity of the step and surface energy of the face plane. Due to the asymmetry of the sapphire crystal structure, the step rigidity will depend on the slope direction.

Figure 6 shows in a simplified form the arrangement of atoms on the (0001) Al_2O_3 plane [13]. It can be seen that in the $(1\bar{1}00)$ plane the surface rigidity should be the lowest due to the low atomic density; therefore, one should expect a diffusive displacement of atoms in the $[1\bar{1}00]$ direction upon annealing; this effect was observed experimentally. The occurrence of triangular protrusions faceted by the $(2\bar{1}\bar{1}0)$ and $(1\bar{2}10)$ planes is explained by the high rigidity of these planes, caused by the high atomic density.

The step height increases with an increase in both the vicinal angle and annealing temperature. This phenomenon is explained by the relationship between the energy required for step coalescence and the interaction energy between steps.

The vicinal surface energy is given by the expression [15, 16]

$$f = f_o + \beta(T)|\tan\alpha|/h + \xi(T)|\tan\alpha|^3,$$

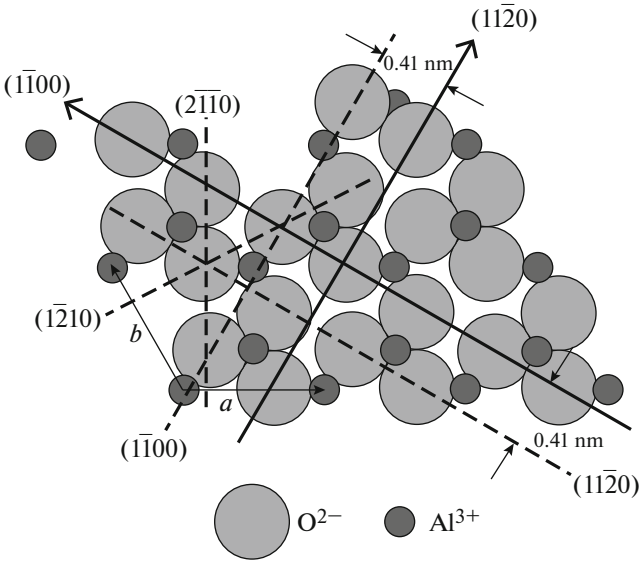

Fig. 6. Schematic diagram of atomic arrangement in the (0001) sapphire plane [13].

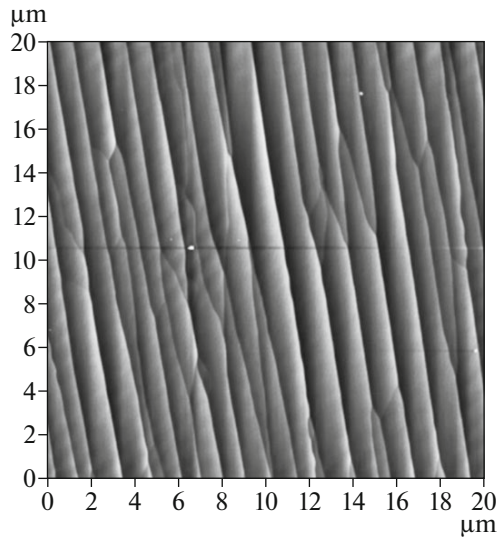

Fig. 7. AFM image of the (0001) sapphire surface after complete TSN formation upon annealing at 1673 K.

where f_o is the specific free energy of the flat part of the surface, α is the vicinal angle, h is the step height, $\beta(T)$ is the free energy of the unit length of the forming isolated step, and $\xi(T)$ is the energy per unit length due to the step interaction.

Thus, if the distance between steps is sufficiently large, the $\xi(T)$ value is negligible. An increase in temperature disturbs the balance between the coalescence energies of steps and their interaction energy, which leads to diffusive transfer of matter over the surface and coalescence of steps until this balance is recovered. This process was observed experimentally.

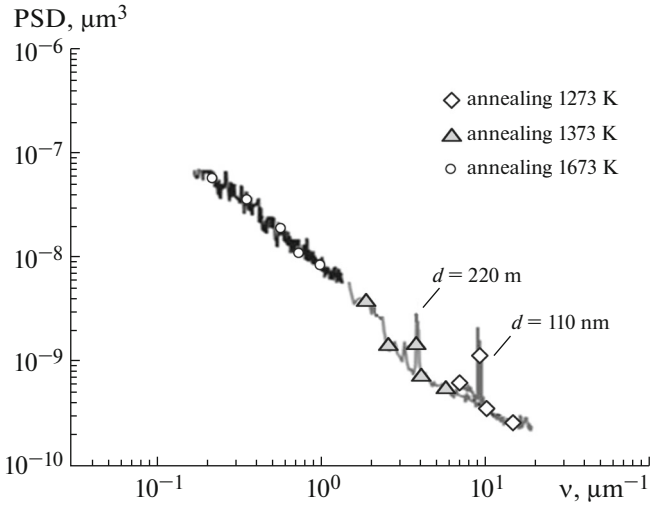

Fig. 8. PSD curves for surface roughness for three samples annealed at 1273, 1373, and 1673 K.

As the temperature increases to 1673 K, the steps significantly overgrow (Fig. 7) and the structure periodicity is broken due to the high density of Y-junction points between three steps, which are characteristic of the *zipperlike* mechanism [2]. The structure periodicity break was qualitatively estimated using the apparatus of power spectral density (PSD) function of surface roughness. For surfaces with a regular TSN, the PSD curve exhibits a peak corresponding to the nanostructure period [17]. PSD functions were plotted for the AFM images of plate surfaces annealed at 1273, 1373, and 1673 K. The spatial frequency intervals used to plot the corresponding PSD curves at three annealing temperatures were specified so as to make the spatial frequency of the peak of periodic nanostructure, derived from the AFM data, fall in it. For the samples annealed at 1273 and 1373 K, some features are observed at $d = 110$ and 220 nm, respectively (Fig. 8). For the sample annealed at 1673 K, the curve does not contain any features, which indicates the absence of a strictly periodic relief, despite the AFM predictions (Fig. 7).

CONCLUSIONS

The AFM study of the vicinal sapphire surface structure revealed the following:

(i) Annealing of the (0001) sapphire surface with a vicinal angle of 0.1° at 1273 K leads to the formation of a periodic TSN with a step height of 0.22 nm and a distance between steps of 110 nm.

(ii) An increase in the annealing temperature to 1373 K causes an increase in the step height to 0.44 nm and a distance between steps of 220 nm, with the retained TSN periodicity.

(iii) Rapid cooling of the substrate to 973 K leads to partial freezing of the surface structure, which allowed us to observe the TSN transition.

(iv) Coalescence of two steps occurs toward the $(10\bar{1}0)$ plane (equivalent to $(1\bar{1}00)$), which has the lowest atomic density, i.e., the minimum rigidity.

(v) Coalescence of steps is completed when the distance between them becomes sufficiently large and the energy of their interaction becomes negligible.

(vi) Annealing at temperatures above 1373 K leads to step overgrowth to 1 nm; however, the structure periodicity is significantly violated.

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