MICROSTRUCTURE AND RECONSTRUCTION OF $LaAlO_3$ {100} AND {110} SURFACES

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ABSTRACT

Lathanum-aluminate ($LaAlO_3$) is one of the optimum substrates for epitaxic growth of thin oxide films. In this paper, the structures of the {100} and {110} surfaces of annealed $LaAlO_3$ are studied using reflection electron microscopy (REM). [010] and [001] steps have been observed on {100}, these are believed to be the lowest surface energy steps. The {100} surface is atomically flat, but the {110} surfaces exhibit high-density fine structures distributed on large surface terraces. These fine structures may correspond to the formation of small width (100) and (010) facets on the (110) surface. The 5×5 reconstruction is observed on {100}. No reconstruction is found on {110}.

INTRODUCTION

In epitaxic growth of high-temperature superconductor thin films, lanthanum-aluminate ($LaAlO_3$) is one of the optimum candidates for substrates. The small lattice mismatch (< 2 %) between $LaAlO_3$ and $YBa_2Cu_3O_{7-x}$ allows high quality c-axis oriented superconducting thin films to be grown on the (100) surface of the substrate. As the melting point of $LaAlO_3$ is approximately 2180 °C, the interfacial reaction can be minimized under normal growth conditions.

In general, it is believed that both the nucleation and growth of thin films are strongly affected by the structures, such as steps and dislocations, of the substrate surfaces. A direct correlation between the growth of columnar defects in $YBa_2Cu_3O_{7-x}$ and the steps on the $LaAlO_3$ substrates has been observed [1, 2]. It is anticipated that the structure of substrate surfaces has large influence on the nucleation and microstructure of the grown films. In this paper, the {100} and {110} surfaces of $LaAlO_3$ are studied with reflection electron microscopy (REM) [3, 4].

REM experiments were carried out at 300 kV and 120 kV in transmission electron microscopes (TEMs) under a vacuum of 10^{-6} to 10^{-7} torr. Bulk specimens were prepared by cutting $LaAlO_3$ single crystal sheets into samples with dimensions of about 2.5×1×0.8 mm. The {100} and {110} surfaces were mechanically polished before annealing. The polished samples were annealed at 1500 °C for 10 or 20 h in air. The crystallographic data on $LaAlO_3$ have been given by Geller and Bala [5] and Berkstresser et al. [6]. The structure is the distorted-perovskite structure with lattice constant a = b = c = 0.3788 nm and $\alpha = \beta = \gamma = 90.066°$. The structure is referred to a face-centered rhombohedral cell, in which the La^{+3} ion locates at (000), the Al^{+3} ion at (0.5 0.5 0.5), and the O^{-2} ions at the face-centers {0.5 0 0}.

Figure 1. An [001] RHEED pattern from an annealed $LaAlO_3$ (100) surface showing 5×5 surface reconstruction. The inset is the RHEED pattern.

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$LaAlO_3$ {100}

Figure 1 shows a [001] reflection high-energy electron diffraction (RHEED) pattern of the annealed $LaAlO_3$ (100) surface. Two strong superlattice reflections are observed between bulk reflections (10 0 0) and (10 $\bar{1}$ 0). The two superlattice reflections are separated by 1/5(0 $\bar{2}$ 0) and 1/5(020), respectively, from the (10 0 0) and (10 $\bar{1}$ 0) bulk reflections. On the right-hand side of (10 $\bar{1}$ 0) reflection, four equally-spaced superlattice reflections are seen. These superlattice reflections correspond to the formation of 5×5 reconstruction on the surface. $LaAlO_3$ exhibits {100} twin structures, but the twin angle is as small as 0.13°. This twin structure causes the splitting of the superlattice reflections, as seen in figure 1.

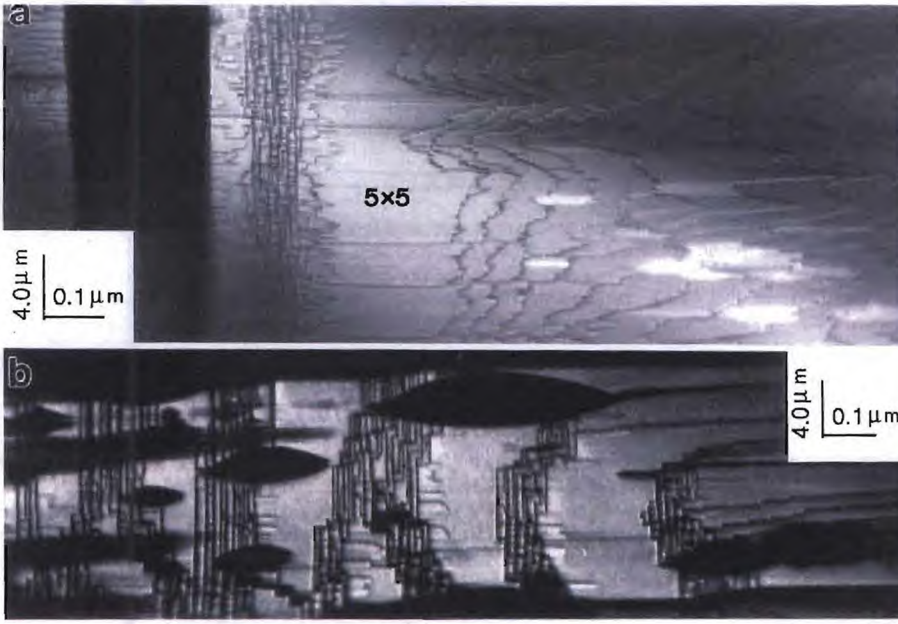

Figure 2. REM images of the $LaAlO_3$ (100) surface showing the [010] and [001] faceted steps. The images were recorded with the (10 0 0) specularly reflected beam under the diffracting condition shown in figure 1. Beam azimuth is [001].

Numerous [010] and [001] surface steps were observed on the $LaAlO_3$ (100) surfaces. Figure 2a is a REM image recorded with the (10 0 0) specularly reflected beam under the diffracting condition shown in figure 1. In the REM image, the 5×5 reconstructed area shows darker contrast due to the reduction of the (10 0 0) reflected beam intensity as the result of exciting the superlattice reflections. The unreconstructed surface areas show brighter contrast. Some of the surface areas are completely covered by the reconstructed surface layer. However, the formation of [010] and [001] steps is unaffected. The faceted steps are seen almost everywhere on the surface. The regions which show brighter and darker contrast sometime share the same terrace, and there is no step between them.

Figure 2b shows an REM image of the (100) surface entirely covered by the 5×5 reconstruction layer. Many densely distributed [001] and [010] steps are seen. The larger steps are about 2-3 unit cells in height [7]. When the specimen was annealed at 1500 °C, the surface atoms tend to move to the positions where they have the lowest energy. Our observations show that the <100> steps preserve the lowest energy in comparison to steps along any other directions on the {100} surfaces. For annealed $LaAlO_3$ (100), no dislocations were found in the flat surface areas. Dislocations have been observed only at twin boundaries [7]. Figure 3 shows two REM images of the (100) surface, exhibiting many <100> steps. The surface regions with 5×5 reconstruction show darker contrast. The dark particles seen in the image contain Si, La and Al, which are probably produced by surface impurity segregation and contamination.

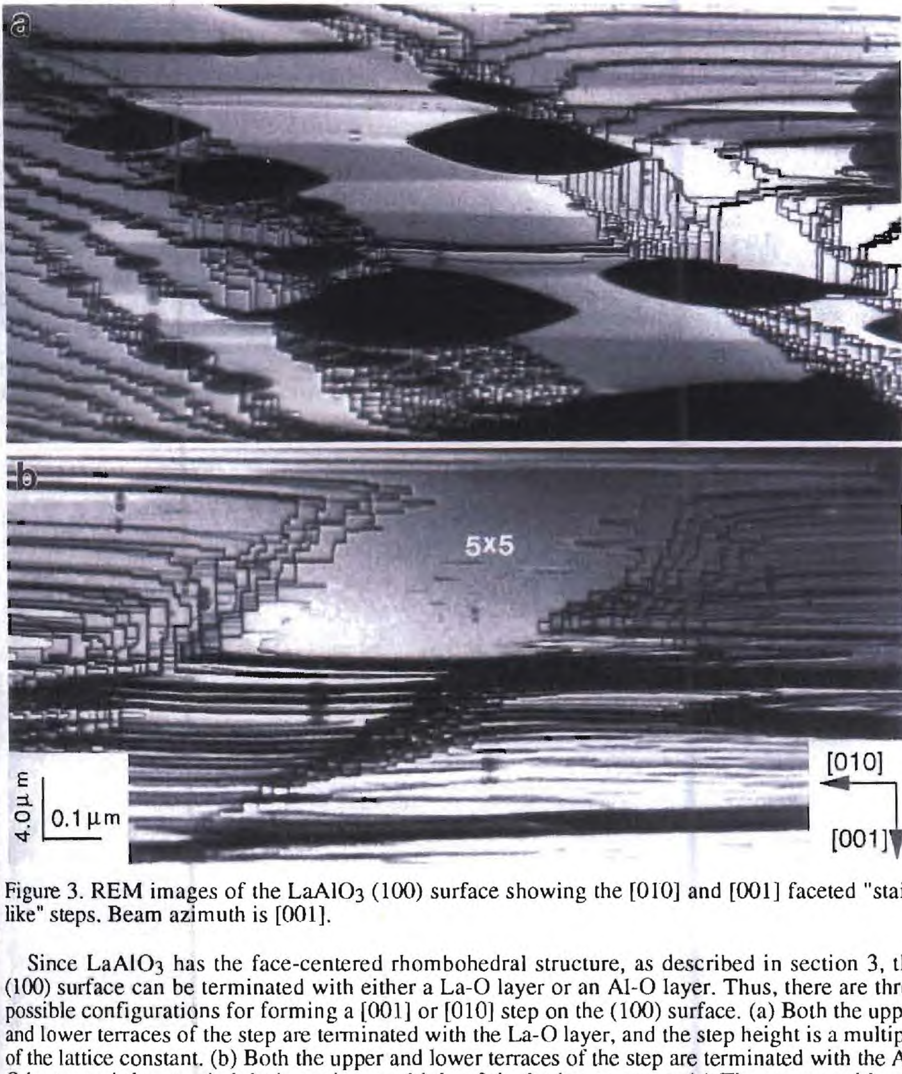

Figure 3. REM images of the $LaAlO_3$ (100) surface showing the [010] and [001] faceted "stair-like" steps. Beam azimuth is [001].

Since $LaAlO_3$ has the face-centered rhombohedral structure, as described in section 3, the (100) surface can be terminated with either a La-O layer or an Al-O layer. Thus, there are three possible configurations for forming a [001] or [010] step on the (100) surface. (a) Both the upper and lower terraces of the step are terminated with the La-O layer, and the step height is a multiple of the lattice constant. (b) Both the upper and lower terraces of the step are terminated with the Al-O layer, and the step height is again a multiple of the lattice constant. (c) The upper and lower surface terraces next to the step are terminated with the La-O layer and the Al-O layer, respectively. In configuration (c), the upper and lower terraces adjacent to the step would show different contrast because of the difference in scattering powers between La (atomic number $Z =$ 57) and Al ($Z = 13$), and the regions which show distinct difference in contrast would be separated by the surface step. However, this was not observed experimentally. The two types of contrast seen in the REM image, as shown in figure 2a for example, is due to surface reconstruction. If configurations (a) and (b) both occur, a difference in contrast should also be seen due to larger scattering power of La than that of Al, and the regions which show distinct difference in contrast must be separated by surface steps. This result has also not been observed experimentally. Therefore, the termination of the (100) surface must be produced solely by the La-O layer or the Al-O layer, but cannot be the mixture of two.

$LaAlO_3$ {110}

$LaAlO_3$ {110} surfaces were prepared under the same conditions as for {100}. Figure 4 shows a REM image of the {110} surface after annealed at 1500 °C for 10 h in air. The surface exhibits the "roof-tile" structure, showing many terraces. The length of the terrace along [001], the incident beam direction, is much larger than its width along [011] if the foreshortening effect along [001] is considered. The terrace is not atomically flat but consists of many fine step-like structures. The density of the steps is so high that each individual step cannot be resolved in the REM image. RHEED observation has not found any surface reconstruction. Figure 5 shows two REM images of the {110} surface after annealing at 1500 °C for 20 h. The widths of surface terraces have increased by a factor of approximately three in comparison to those shown in figure 4. The heights of steps between terraces are also increased by the same magnitude. Again many fine step-like structures remain on each terrace. It is apparent that the sizes of surface terraces, along both [100] and [011], increase dramatically with increasing of annealing time. The surface morphology exhibits entirely different image in comparison to that of {100}. The regions showing two distinct contrast in figure 5b is produced by the crystal rotation of 0.13° due to the presence of the {100} twin boundaries.

From the studies of the (100) surface, we have found that the <100> steps and {100} facets have the lowest surface energy. This result can be applied to interpret the morphological structure of the (110) surface. An as-polished surface is rough consisting many hills and valleys. There is a small mis-cut angle between the surface and the {110} crystallographic plane. Surface diffusion starts when the sample is annealed, leading to the formation of small terraces. REM images shown in figures 4 and 5 indicate there are many fine structures (or steps) on the (110) terraces, which may correspond to the formation of small width (100) and (010) facets on the surface, as schematically shown in figure 6a. The (100) and (010) facets are favored due to their low energy, and these facets remain on the surface even when the surface is annealed for a long time (figures 5a and 5b).

Figure 4. A REM image of the $LaAlO_3$ (110) surface, annealed at 1500 °C for 10 h in air, showing the formation of surface terraces. Beam azimuth is near [001].

The large terrace steps, as indicated by arrowheads in figure 5a, can also be (100) facets. These faces grow when atoms diffuse from the inner steps (on the (110) terrace) toward the edge of the terrace, as indicated by arrowheads in figure 6b, resulting in the growth of step height for step A. For a high index step, such as the step B in figure 6a, the atoms tend to diffuse toward steps A and C, (100) faces having the lowest surface energy, resulting in the reduction in height and width of terrace B and the increase in heights and widths of terraces A and C. This process continues until terrace B is eliminated, as shown in figure 6c. Thus, the sizes and heights of terraces A and C are increased. This is consistent with the experimental observations shown in figures 4 and 5a.

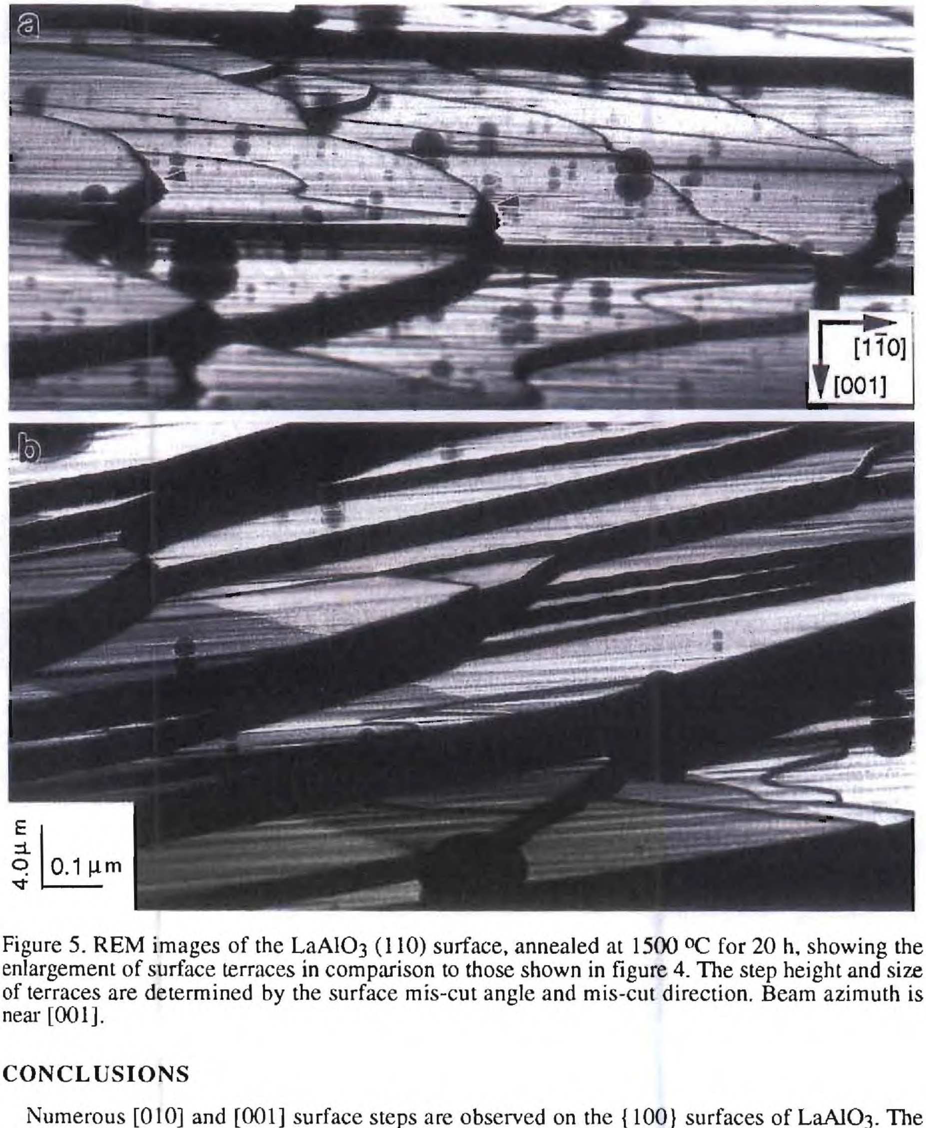

Figure 5. REM images of the $LaAlO_3$ (110) surface, annealed at 1500 °C for 20 h, showing the enlargement of surface terraces in comparison to those shown in figure 4. The step height and size of terraces are determined by the surface mis-cut angle and mis-cut direction. Beam azimuth is near [001].

CONCLUSIONS

Numerous [010] and [001] surface steps are observed on the {100} surfaces of $LaAlO_3$. The <100> steps preserve the lowest surface energy in comparison to steps along other directions on {100}. 5×5 surface reconstruction on annealed $LaAlO_3$ {100} surfaces is observed. Most of the

{100} surface areas are covered by the reconstructed layer. Surface steps may enhance the surface reconstruction but are not essential to initiate the reconstruction. $LaAlO_3$ {110} exhibits numerous high-step terraces, and each terrace is composed of atom-high steps. The size of terraces increases with increasing annealing time, but the fine step-like structure remains. The roughness of the (110) terrace is believed to be due to the formation of small (100) and (010) facets.

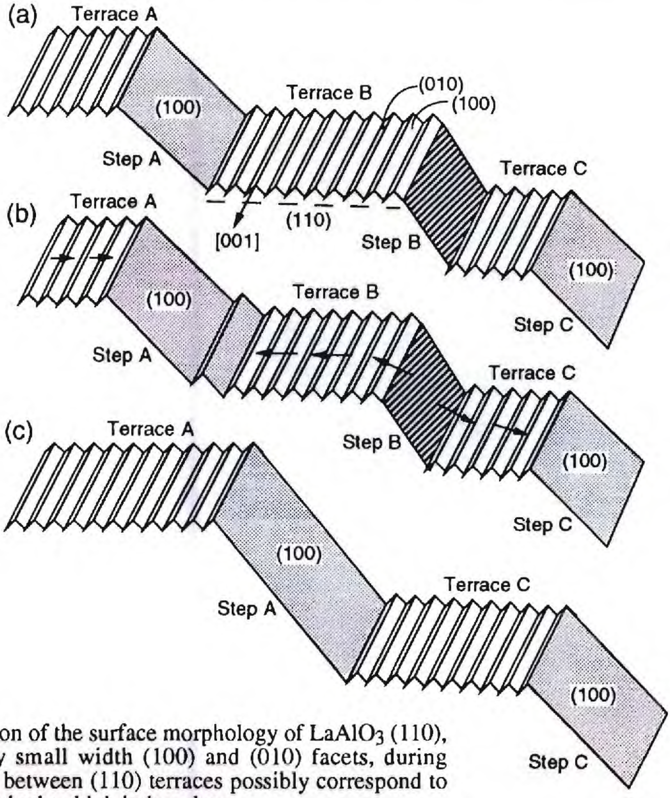

Figure 6. Evolution of the surface morphology of $LaAlO_3$ (110), formed by many small width (100) and (010) facets, during annealing. Steps between (110) terraces possibly correspond to (100) surfaces and other high index planes.

REFERENCES

1. Z.L. Wang, D.K. Christen, C.E. Klabunde, D.M. Kroeger, D.H. Lowndes and D.P. Norton, in Proc. of 52nd Annu, Meet. of Microscopy Soc. of America (San Francisco Press, 1994), G.W. Bailey and A.J. Garratt-Reed eds., pp. 790.
2. D.H. Lowndes, Z.L. Wang, D.K. Christen, C.E. Klabunde, D.M. Kroeger, and D.P. Norton, in preparation.
3. Z.L. Wang, Rep. Prog. Phys. 56, 997 (1993).
4. K. Yagi, Surf. Sci. Rep. 17, 305 (1993).
5. S. Geller and V.B. Bala, Acta Cryst. 9, 1019 (1956).
6. G.W. Berkstresser, A.J. Valentino and C.D. Brandle, J. Crystal Growth 109, 467 (1991).
7. Z.L. Wang and A.J. Shapiro, Surface Sci., submitted (1994).
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