AIP Applied Physics Letters

Epitaxial oxide growth on polar (111) surfaces

J. L. Blok, X. Wan, G. Koster, D. H. A. Blank, and G. Rijnders

Citation: Appl. Phys. Lett. **99**, 151917 (2011); doi: 10.1063/1.3652701

View online: http://dx.doi.org/10.1063/1.3652701

View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v99/i15

Published by the American Institute of Physics.

Related Articles

Epitaxial growth of Fe and MgO layers on GaAs (001): Microstructure and magnetic property
J. Appl. Phys. 110, 114910 (2011)

In-situ x-ray diffraction studies on post-deposition vacuum-annealing of ultra-thin iron oxide films
J. Appl. Phys. 110, 102208 (2011)

Impact of carbon incorporation into epitaxial Gd2O3 thin films on silicon: An experimental study on electrical properties
Appl. Phys. Lett. 99, 152902 (2011)

Exploring Co2MnAl Heusler compound for anomalous Hall effect sensors
Appl. Phys. Lett. 99, 132509 (2011)

Influence of substrates on epitaxial growth of B-site-ordered perovskite La2NiMnO6 thin films
J. Appl. Phys. 110, 063913 (2011)

Additional information on Appl. Phys. Lett.

Journal Homepage: http://apl.aip.org/

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: http://apl.aip.org/authors

APPLIED PHYSICS LETTERS **99**, 151917 (2011)

Epitaxial oxide growth on polar (111) surfaces

J. L. Blok, X. Wan, G. Koster,[a] D. H. A. Blank, and G. Rijnders
Faculty of Science and Technology and MESA$^+$ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

(Received 26 July 2011; accepted 26 September 2011; published online 14 October 2011)

Obtaining atomically smooth surfaces and interfaces of perovskite oxide materials on polar (111) surfaces presents a particular challenge as these surfaces and interfaces will reconstruct. Here, the effect of the use of screening buffer layers on the epitaxial growth on such polar surfaces is investigated. Both transmission electron microscopy and *in situ* reflective high energy electron diffraction data imply that the buffer layers, $SrRuO_3$ or $LaAlO_3$, restore a near bulk-like termination at growth temperature, allowing for coherent growth of $BiFeO_3$ and $CaTiO_3$ for all deposited unit cell layers of the film material. © *2011 American Institute of Physics*. [doi:10.1063/1.3652701]

An important crystalline orientation in the perovskite system, in terms of the ability to use strain engineering and to fabricate superlattices, is the (111) direction (A schematic drawing of a (111) oriented perovskite is shown in Figure 1(a)). For example, if superlattices of perovskites are grown in the (111) orientation, it is possible to build artificial double perovskites.[1,2] Another example is work done by Xiao *et al.*,[3] which shows that it is possible to build a topological insulator by growing in the (111) direction. A lot of knowledge within the field of oxide thin films has been gained by the many heteroepitaxial systems involving cubic (001) substrates like $SrTiO_3$ in which case the surface and interface with the film perovskite structure has been well studied. From these studies, it has become clear that a good perovskite substrate surface fulfills three important criteria: (1) single termination; (2) a stable interface with air/vacuum without major reconstructions; and (3) a stable interface with the film material.

In the classic case of cubic (001) $SrTiO_3$ surfaces, the single TiO_2 surface termination can be achieved by chemical etching[4] and the stability of the $SrTiO_3$-vacuum interface poses no real problems, as the surface layer (SrO or TiO_2) bears no net charge. Only when a polar material with nominally charged layers is deposited onto neutral $SrTiO_3$ does the system have to resolve the polar discontinuity hence created, Nakagawa *et al.*[5] For the (pseudo)cubic (001) orientation of a material with nominally charged AO and BO_2 layers, criteria (1) and (2) do pose problems, such as with the rare earth scandates. It has been shown that for the latter group of materials, chemical etching can be employed. Apparently, the unavoidable reconstruction of the charged surface is not too severe, although a detailed structural analysis of the reconstructed surfaces still lacks, and Kleibeuker *et al.*[6] demonstrated that perfect epitaxy can be achieved on these treated surfaces.

For a system with the (110) orientation, criterion (3) is always met from the nominal charge point of view, see also Mukunoki *et al.*[7] However, as the surface is always charged, criteria (1) and (2) are less straightforward. Mukunoki *et al.*[7] address this issue by showing that a single terminated (110) $SrTiO_3$ surface is obtained after deposition of a very thin homoepitaxial $SrTiO_3$ layer at low oxygen pressures where the excess charge build up is compensated by oxygen vacancies.

Now for $SrTiO_3$ (111) none of the criteria are trivial: first, single terminated (111) surfaces are always polar and will reconstruct. As we will see, even though single termination can be achieved,[8,9] criterion (2) poses a problem because the inadvertent surface reconstruction prevents coherent growth of the first (few) monolayers of the film material. Such growth could lead to a multitude of morphological effects on these reconstructed surfaces, such as disrupted or intermixed interfaces and rough or three dimensional growth. Second, even when coherent growth does occur, polar discontinuous interfaces can occur, leading to a polar catastrophe. In that case, Nakagawa *et al.*[5] propose that there are two ways in which a material system prevents a polar catastrophe. One is by the intermixing of atoms between the two interfacial layers and the other is by the movement of electrons which is possible if there are multivalent atoms present.

There is an additional option: metallic screening. When materials at the interface are sufficiently conducting at deposition conditions free charge can screen and therefore stop the polar catastrophe without necessitating intermixing. Moreover, by introducing screening, the originally polar surface can also be restored to bulk termination or prevented from reconstructing, allowing for coherent growth. In this

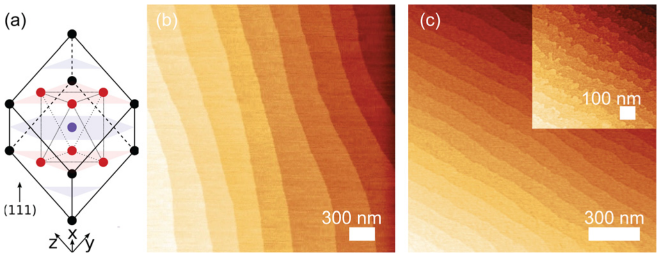

FIG. 1. (Color online) (a) A schematic drawing of a (111) oriented perovskite. (b) An AFM micrograph of a (111) oriented $SrTiO_3$ treated substrate. (c) An AFM micrograph of a chemically etched $LaAlO_3$ substrate. The inset shows an AFM micrograph of a (111) oriented $LaAlO_3$ substrate that was annealed for 1 h at a 1000 °C without any chemical treatment.

---

[a] Author to whom correspondence should be addressed. Electronic mail: g.koster@utwente.nl.

letter, to investigate the possibility of screening, we study $CaTiO_3$ and $BiFeO_3$ films grown on pseudo-cubic (111) oriented $LaAlO_3$ and $SrTiO_3$ substrates, respectively. Both systems are examples where there is an interface with materials that have differently charged layers. In the case of $SrTiO_3$ and $CaTiO_3$ they are alternating 4+ 4– layers and in the case of $LaAlO_3$ and $BiFeO_3$ they are alternating 3+ 3– layers and neither criteria is fulfilled. In both cases, problems occur during growth directly on the substrate, regardless of treatment. The possibility of growing $BiFeO_3$ coherently in the (111) orientations immediately shows why (111) oriented growth is interesting as it means $BiFeO_3$ is grown in the ferroelectric easy axis of the materials making complete switching possible.[10]

As will be shown, in the case of $BiFeO_3$ on $SrTiO_3$, this leads to 3D growth of the $BiFeO_3$ layer on $SrTiO_3$. In the case $CaTiO_3$ growth, the problem is more subtle as $CaTiO_3$ grows reasonably well on $LaAlO_3$ substrates; however, when the interface is closely studied with reflective high energy electron diffraction data (RHEED) and transmission electron microscopy (TEM), the interface unit cell layer appears to be more disordered than the subsequent unit cell layers. Here, we will investigate the possibility of screening, either by deposition of a conducting epitaxial layer or by rendering the substrate conducting. For $BiFeO_3$ often an electrode material is used, such as $SrRuO_3$; in the case of $CaTiO_3$ on $LaAlO_3$, $LaAlO_3$ becomes sufficiently conducting at high temperatures, making screening a real option. For the latter system, it turns out to be necessary to apply a few homoepitaxially grown monolayers in order to restore the room temperature reconstructed surface to an appropriate, "less" reconstructed, template at the growth temperature.

To achieve epitaxial heterostructures, smooth single terminated pseudo-cubic (111) oriented substrates are necessary. The $SrTiO_3$ substrates were treated using the method[4] Koster *et al.* describe for treating (001) oriented substrates, the results are shown in Figure 1(b). The $LaAlO_3$ substrates were first etched with 12 M NaOH followed by a rinse with 1 M NaOH. After this, they were annealed for 1 h. The resulting $LaAlO_3$ substrates can be seen in Figure 1(c). The atomic force microscope (AFM) topography images both show a smooth substrate with well ordered steps of 0.22 nm height; however, the image of the unetched substrate shows very rough step edges while the image of the treated substrate shows smooth step edges. Lateral force microscopy shows no contrast when measuring these surfaces both before and after treating the surface and are not shown.

Depositions were done with pulsed laser deposition and monitored with high pressure RHEED. The intensity of the specular spot and the RHEED diffractions patterns are used to demonstrate the type of growth. Both $BiFeO_3$ and $CaTiO_3$ were grown from sintered targets. AFM was used to show the substrates are smoothly terminated. A Philips CM300ST-FEG Twin/STEM operating at 300 kV with a resolution of 2.3 Å was used to study the crystal properties of the interfaces of our samples.

In Figure 2, the difference between growing $BiFeO_3$ directly on a (111) oriented $SrTiO_3$ substrate and growing it on the same substrate with a buffer layer of $SrRuO_3$ in between is shown. The diffraction patterns during growth show that $BiFeO_3$ immediately grows in a 3D (see Figure 2(b)) growth mode, given the square lattice transmission type pattern. However, as is shown in Figures 2(c)–2(e), when using a $SrRuO_3$ buffer layer, the $BiFeO_3$ will grow in a 2D growth mode for at least 10 nm, as judged by the 2D-nature of the diffraction pattern (streaks plus 2D spots). This differs from previous work as in those cases (e.g., Ref. 11), the $BiFeO_3$ always grows in a 3D growth mode.

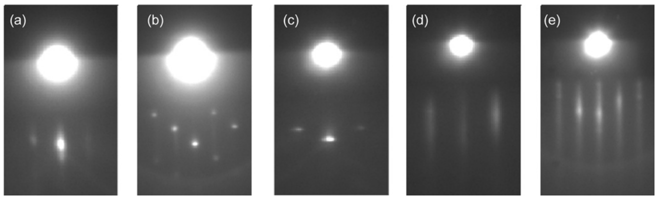

FIG. 2. (a) and (b) show the RHEED pattern before and after the $BiFeO_3$ growth without buffer layer. (c), (d), and (e) show the RHEED pattern before the buffer layer growth, after the buffer layer growth, and after the $BiFeO_3$ layer growth.

Figure 3 shows the first two oscillations during $CaTiO_3$ film growth on $LaAlO_3$ and for the growth of an $LaAlO_3$ buffer layer. This figure demonstrates two different kinds of growth: type 1, where the first maximum has a lower intensity than the second, and type 2, where the first maximum has a higher intensity than the second. The figure shows RHEED data for four samples during growth, two showing type 1 growth and two showing type 2 growth. When $CaTiO_3$ is deposited directly on the substrate, type 1 growth is achieved (blue/dark grey line). If, on the other hand, $CaTiO_3$ is grown on the buffer layer of $LaAlO_3$, both the $LaAlO_3$ and $CaTiO_3$ show type 2 growth (green/light grey and red/grey lines respectively). If the $CaTiO_3$ is grown on a buffer layer of $LaAlO_3$ that has been cooled down and heated up before the $CaTiO_3$ growth type 1, growth is again achieved (black line). TEM data of the $LaAlO_3$- $CaTiO_3$ interface shows a very different interface for the $CaTiO_3$ film with homoepitaxial buffer compared to the one without such a layer.

During a deposition run, the conductance of the $LaAlO_3$ substrate and film was measured to check whether the $LaAlO_3$ substrate or film is capable of screening the polar

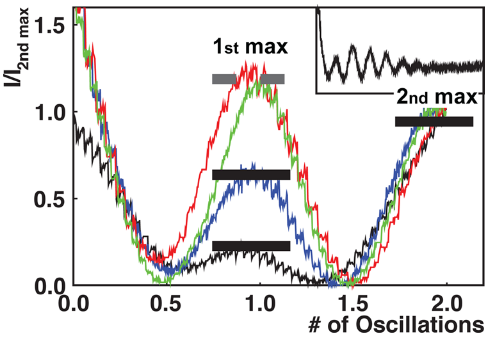

FIG. 3. (Color online) The RHEED oscillations during the first two monolayers of growth are shown for $CaTiO_3$ grown directly on (111) $LaAlO_3$ (blue/dark grey line), for the $LaAlO_3$ buffer layer grown on $LaAlO_3$ (green/light grey line), for $CaTiO_3$ grown on a $LaAlO_3$ buffer layer (red/light grey line), and for $CaTiO_3$ grown on a $LaAlO_3$ buffer layer that has been cooled down before the $CaTiO_3$ deposition (black line). The insert shows the RHEED oscillations for $CaTiO_3$ grown directly on (111) $LaAlO_3$.

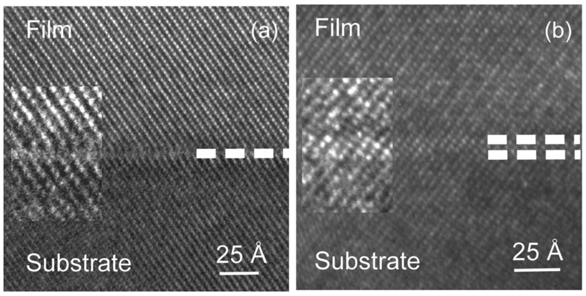

FIG. 4. TEM images of the $LaAlO_3$-$CaTiO_3$ interfaces (the (10-1) zone axis). (a) Clear dislocations at the interface between the $CaTiO_3$ and the $LaAlO_3$. (b) A coherent interface due to the presence of the buffer layer, discernible as a slightly lighter contrast for three layers indicated by the dashed lines.

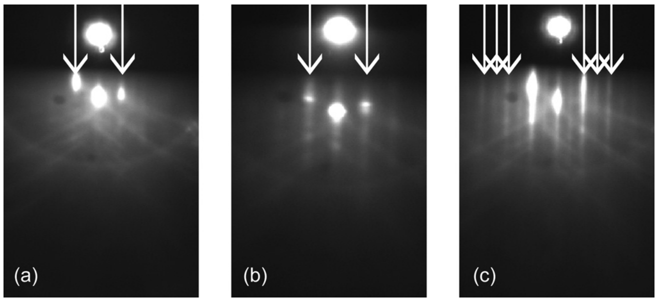

FIG. 5. (a) RHEED pattern of the $LaAlO_3$ substrate, (b) RHEED pattern after the growth of the $LaAlO_3$ buffer layer, and (c) RHEED pattern after the $LaAlO_3$ buffer layer has been cooled down. (a), (b), and (c) show the RHEED pattern for the (11-2) planes. The white arrows show the positions of the diffraction peaks.

interface. The measurement showed an onset of measurable conductance at 400 °C and a decreasing resistance down to the order of 1 MΩ as the substrate temperature increased.

The crystal structure of the $LaAlO_3$-$CaTiO_3$ interface can be seen in the TEM pictures in Figure 4 for both the $CaTiO_3$ layer that is grown directly on the substrate and the $CaTiO_3$ layer that is grown on the buffered substrate. The $CaTiO_3$ layer grown with a buffer layer shows an interface where the fringes of both the substrate materials and the film material are continuous, as opposed to the TEM image of the $CaTiO_3$ layer grown directly onto the (111) $LaAlO_3$ substrate indicating a structural reconstruction at the $LaAlO_3$-$CaTiO_3$ interface.

To check the plausibility of the removal of a surface reconstruction, we turn to Figures 5(a) and 5(b) showing the RHEED before and after the $LaAlO_3$ buffer layer growth. Here, mainly diffraction peaks are visible that belong to a bulk-like surface termination. On the other hand, turning to Figure 5(c), additional diffraction peaks point to a unit cell doubling of the surface mesh upon cooling down the $LaAlO_3$ buffer layer to room temperature, compatible with reconstruction. The appearance of a reconstructed surface is consistent with the fact that $LaAlO_3$ is highly insulating at room temperature.

In the case of $BiFeO_3$ on $SrTiO_3$, the material almost immediately grows in a 3D growth mode if it is grown directly on the $SrTiO_3$. Apparently, the wetting of the film material is severely hampered by the reconstructed polar surface. However, if it is grown with a conducting buffer layer of $SrRuO_3$, it grows in a 2D growth mode. The explanation for the coherent growth of the two (111) oriented materials on a buffer layer, which is conducting at growth temperature, can be given by the possible screening that the buffer layers provide. For the $BiFeO_3$ case with the $SrRuO_3$ buffer layer, this scenario is relatively trivial, as $SrRuO_3$ is metallic, even at the growth temperature.

For $CaTiO_3$ on $LaAlO_3$, the situation is more subtle; the RHEED intensity data during growth show that only the first monolayer grows differently from the rest of the film. This behavior is subsequently altered by using a few monolayers thick homoepitaxial buffer layer. The argument for a screening scenario in this case is that the $LaAlO_3$ buffer layer only works if it is kept at elevated temperature (700 °C) before the next layer is grown on top. When it is cooled down, the effect of growing a proper interface is negated, since $LaAlO_3$ at room temperature is a good insulator and reconstruction needs to occur. The absence of a reconstruction is corroborated by both the TEM images in Figure 4 and the RHEED images in Figure 5. It must be noted that it is possible that the conductivity of the $LaAlO_3$ is not high enough to fully screen the polarity in the $LaAlO_3$, which would require 1/2 an electron per unit cell. We propose, therefore, that a relaxation takes place, involving mostly the lighter oxygen anions, partially countering the polar build up but allowing for coherent growth of the $CaTiO_3$ from the very first unit cell layer. A thorough structural analysis of the $LaAlO_3$ surface by, for example, surface x-ray diffraction could reveal the exact nature of this relaxation.

In conclusion, the structural analysis of two polar (111) epitaxial systems before and after the introduction of a conducting buffer layer clearly shows that including the buffer layer alters the growth of the (111) perovskites. 2D growth occurs when the polar surface is sufficiently screened, avoiding a severe surface reconstruction, leading to a coherent interface.

[1] K. Ueda, H. Tabata, and T. Kawai, Science **280**, 1064 (1998).
[2] A. Roy and D. Vanderbilt, Phys. Rev. B **83**, 134116 (2011).
[3] D. Xiao, W. Zhu, Y. Ran, N. Nagaosa, and S. Okamoto, e-print arXiv cond-mat.mtrl-sci, 1106.4296v3 (2011).
[4] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank, and H. Rogalla, Appl. Phys. Lett. **73**, 2920 (1998).
[5] N. Nakagawa, H. Hwang, and D. Muller, Nature Mater. **5**, 204 (2006).
[6] J. E. Kleibeuker, G. Koster, W. Siemons, D. Dubbink, B. Kuiper, J. L. Blok, C.-H. Yang, J. Ravichandran, R. Ramesh, J. E. ten Elshof, *et al.*, Adv. Funct. Mater. 1 (2010).
[7] Y. Mukunoki, N. Nakagawa, T. Susaki, and H. Hwang, Appl. Phys. Lett. **86**, 171908 (2005).
[8] J. Chang, Y.-S. Park, and S.-K. Kim, Appl. Phys. Lett. **92**, 152910 (2008).
[9] A. Biswas, P. B. Rossen, C. H. Yang, W. Siemons, M. H. Jung, I. K. Yang, R. Ramesh, and Y. H. Jeong, Appl. Phys. Lett. **98**, 051904 (2011).
[10] J. Li, J. Wang, M. Wuttig, R. Ramesh, N. Wang, B. Ruette, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, Appl. Phys. Lett. **84**, 5261 (2004).
[11] J. Zhu, W. B. Luo, and Y. R. Li, Appl. Surf. Sci. **255**, 3466 (2008).