Nucleation of a Complex Oxide during Epitaxial Film Growth: $SmBa_2Cu_3O_y$ on $SrTiO_3$

V. C. Matijasevic,* B. Ilge, B. Stäuble-Pümpin, G. Rietveld, F. Tuinstra, and J. E. Mooij
Applied Physics and DIMES, Delft University of Technology, 2628 CJ Delft, The Netherlands

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Film growth of a complex oxide is investigated during nucleation on a substrate surface. Using atomic force microscopy we have imaged subunit cell coverage of $SmBa_2Cu_3O_7$ deposited by reactive molecular beam epitaxy on a (100) $SrTiO_3$ substrate. After a threshold deposition, c-axis islands are observed to nucleate predominantly along the surface steps. The heights of the nucleation islands are examined and a consistent layer stacking model is proposed. Cation stoichiometry of the nucleation islands is inferred to be dependent on the substrate surface and different from the bulk. [S0031-9007(96)00404-8]

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Long range Coulomb interactions between charged elements of a crystal are important in film growth of ionic materials. In view of the difficulty of forming a complete microscopic model for growth of complicated ionic materials such as complex oxides, it is interesting to examine first empirically how film growth proceeds. A particular example is the class of layered cuprates known as high-temperature superconductors. In this Letter we present high-resolution atomic force microscopy (AFM) images of less than one unit cell thick cuprate films. These snapshots of the initial deposition reveal the structure of the growth islands which nucleate on the substrate surface. Based on additional cross-sectional electron microscopy and photoemission data, we also present a model for the layer stacking in the nucleation islands.

The most commonly studied cuprates today are $YBa_2Cu_3O_7$ (YBCO) and its isostructural variants (*R*BCO) in which a rare earth atom replaces yttrium. Monitoring of *in situ* reflection high-energy electron diffraction during film deposition has suggested that growth of the YBCO structure proceeds in a unit-cell-by-unit-cell manner [1]. This can also be inferred from observation of unit-cell high steps by scanning tunneling microscopy (STM) of YBCO films [2,3]. Although much scanning probe microscopy work on cuprate films has been reported recently, nucleation has not yet been described [4].

Our cuprate films are grown with a reactive molecular beam epitaxy (MBE) system adapted for growth of oxides. Independently shuttered elemental sources are used with an ozone beam as an oxidizing agent [5]. $SmBa_2Cu_3O_7$ (SBCO) is grown by codepositing Sm, Ba, and Cu. The deposition rates are adjusted to the cation ratio of 1:2:3 prior to deposition. Such films have been grown in our system and characterized extensively [5,6]. Our deposition technique is distinguished by a relatively large surface mobility, due to a high temperature and a low pressure during growth. Typically, our films which are thicker than 15 unit cells (uc) have sharp superconducting transitions at 93 K and critical currents above 10^6 A/cm^2 at 77 K. For the films presented here, the total rate of deposition was 0.03 nm/s and the substrate temperature was 800 °C. One film had an additional 0.5 monolayer (ML) of BaO deposited. We performed all AFM scans within 1 h from the moment of sample exposure to air.

Our $SrTiO_3$(100)-oriented substrates have a miscut (vicinal) angle of the surface normal way from [100] of less than 1° [7]. A Nanoscope III AFM system [8] in tapping mode is used to obtain images of the surfaces. Vicinal steps on the substrates can be observed by AFM if the substrates were previously heated. Figure 1 shows an AFM image of a typical $SrTiO_3$(100) surface. It can be seen that our AFM can resolve unit-cell-high steps. The height of

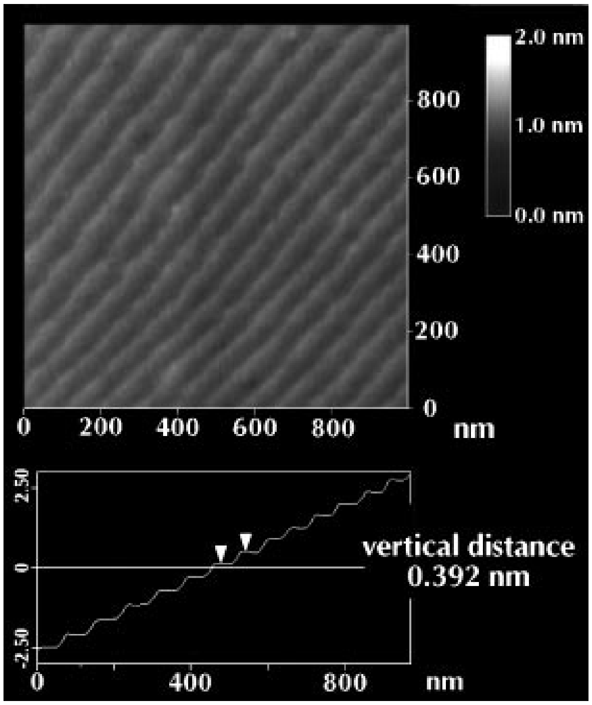

FIG. 1. An AFM micrograph of a (100) $SrTiO_3$ substrate after annealing in an ozone beam at 750 °C in the MBE system. The height information of this picture has been plane fit so that the average is level. Steps reflect the miscut of the substrate surface away from the (100) plane. In this case the miscut angle is 0.27°. A line section is shown on the bottom.

the steps as determined by AFM is 0.39(1) nm, in accord with the $SrTiO_3$ lattice parameter of 0.390 nm.

Figure 2 shows AFM pictures of three different samples obtained after deposition of 0.33, 0.75, and 1.0 uc SBCO on (100) $SrTiO_3$ substrates with a vicinal angle of 0.35°. The film in Fig. 2(b) had an extra 0.5 ML BaO deposited prior to SBCO. The film with a deposited 0.33 uc, Fig. 2(a), shows barely any surface structure. The mean roughness is 0.1 nm. Outlines of substrate steps and a corresponding height modulation can be distinguished in certain areas. Films with 0.75 and 1.0 uc SBCO deposited, however, show much more structure. One can distinguish several different types of growth islands. The linearly percolating islands (shown in orange) have a height of 1–2 nm and a separation of approximately 70 nm. Taller islands (5–10 nm high, shown in blue gray) are also seen. In this Letter we will discuss only the details of the 1–2 nm islands. They represent most of the coverage in Figs. 2(b) and 2(c).

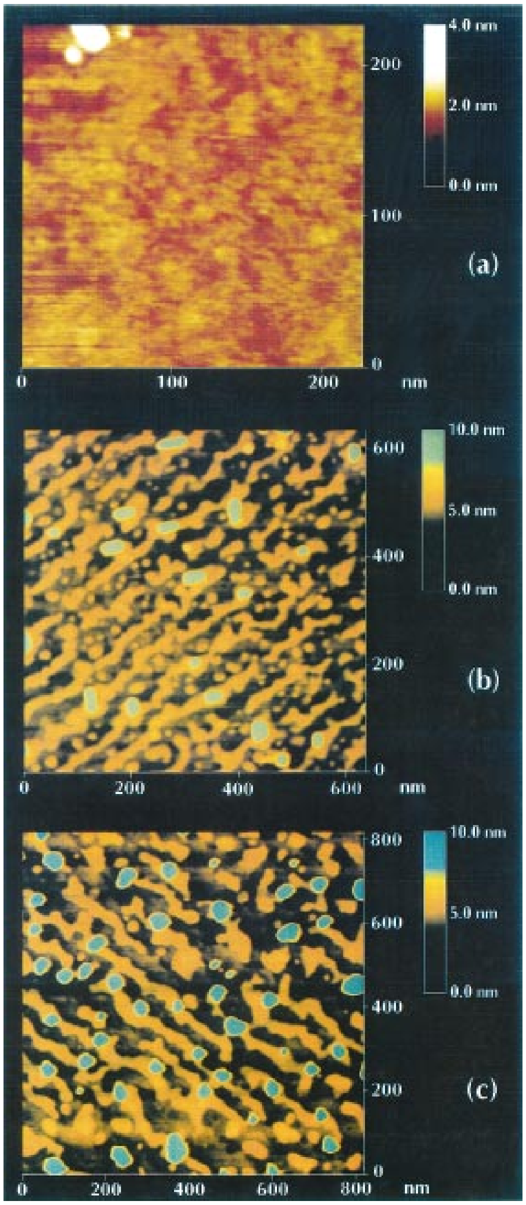

FIG. 2(color). AFM micrographs of $SmBa_2Cu_3O_y$ films after (a) 0.22 uc, (b) 0.75 uc, and (c) 1.0 uc deposition. The film in (b) had an additional 0.5 monolayer of BaO deposited previously.

The width of the terraces for these substrates was previously determined to be 65(5) nm. From the structure of the islands in Fig. 2, it is suggestive to consider that the linearly percolating islands nucleate primarily along the vicinal steps. One can do a more careful height analysis of this picture by doing a plane fit of the height image to the bare areas between the islands. If this is done, we obtain a height difference of 0.40(2) nm between each successive terrace, as can be seen in Fig. 3(a). Therefore, the linear islands have indeed nucleated along the substrate steps. There are also islands in Figs. 2(b) and 2(c) which have roughly the same height, but which have nucleated between the terrace steps.

By comparison with STM of numerous thicker films [6], as well as cross-sectional transmission electron microscopy analysis of such films, we deduce that the orange islands in Figs. 2(b) and 2(c) are the initial stages of growth for the *c*-axis SBCO grains. None of the steps at these islands are observed in excess of 2 nm, consistent with the expectation that no more than a single unit-cell layer has been grown. This is direct evidence that the islands nucleate and then grow as complete molecular units, as opposed to growing in atomic layers. The exact height of these islands can be determined if one does a plane fit of the height image to a bare substrate terrace, and then a line scan across the SBCO grains. The heights of these islands have some variation (0.2 nm), but

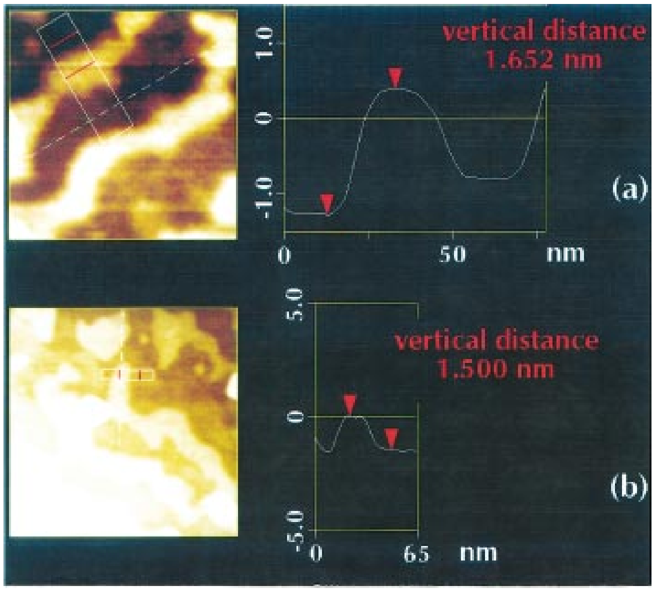

FIG. 3(color). (a) Line scan across an island and a substrate step, as shown in the picture on the left. The line scan is averaged over the width of the rectangle shown on the left. (b) Line scan across an island in the middle of a substrate terrace.

within that variation are the same for the two samples shown in Figs. 2(b) and 2(c). Thus the composition during growth, which is different for the two samples, does not appear to influence the height of the *c*-axis islands. This is a further demonstration that the SBCO grains nucleate in a thermodynamically stable molecular configuration. An example of the results of height analysis is shown in Fig. 3(a). In doing this analysis on many sections of several images, we consistently find a height of 1.7(1) nm for the percolating islands. Since the *c*-axis lattice parameter of SBCO is approximately 1.2 nm, this implies a height of more than one *c*.

The question which then arises is whether the islands are nucleating on top or the bottom of the substrate steps. In order to answer this we can determine the height of the islands which nucleate on or extend into the middle of the substrate terraces. These islands have a height of 1.5(1) nm, slightly less than the islands along the substrate steps, but still in excess of *c*. An example of such a line scan is shown in Fig. 3(b). We conclude that the *c*-axis islands at the $SrTiO_3$ steps nucleate on the bottom of the steps, and we assign an average height to all *c*-axis grains of 1.6(2) nm.

A striking observation from these images is that the coverage area of the *c*-axis islands does not approximate the amount of material which was deposited. Based on thickness measurements of thicker films we know that unity sticking is a good approximation for the thicker films [5]. Nevertheless, it may be that during the nucleation process the effective sticking coefficient is less the unity. Figure 4 shows a plot of the *c*-axis coverage calculated from the AFM images, taking into account tip convolution, versus the deposited material. The dashed line in the figure represents ideal growth without a nucleation threshold and with a unity sticking coefficient. The 0.33 uc sample shows no *c*-axis grains. This, as well as the low *c*-axis coverage in Figs. 2(b) and 2(c), suggests that a certain threshold deposition is needed before nucleation of *c*-axis material begins. We estimate 0.5(1) uc of deposition as the threshold for nucleation in our deposition process [9].

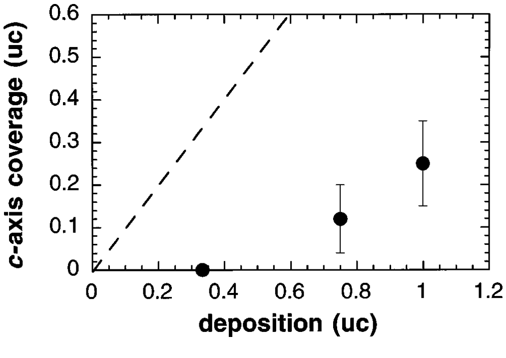

FIG. 4. *c*-axis island coverage as a function of total deposition. Dashed line represents a slope of unity.

From our AFM images of the *c*-axis islands we have concluded that these islands have a height of 1.6(2) nm, somewhat larger than the *c* lattice parameter. Note that at the top of thicker films we observe step heights exactly equal to *c* [6], consistent with unit-cell growth. This result suggests that the initial islands are taller than one unit cell. There is, in fact, no physical reason why these islands have to be exactly one unit cell high. In order to clarify this point we have to understand what is the layer stacking in the initial nucleus [10]. We assume here that the nucleation islands and their surfaces have the same crystal structure as the bulk material. The rules which we believe should be considered in the layer stacking are (i) chemically matched substrate-film interface, (ii) charge neutrality for the complete nucleation island, and (iii) nonpolar (or other) stable surfaces for the nucleation island.

From high-resolution TEM cross-sectional data of *R*BCO films on $SrTiO_3$ [11] we know that the interface layers are the BaO layer in *R*BCO and TiO_2 layer in $SrTiO_3$. The stacking sequence of the layers for our films thus begins as bulk $SrTiO_3$-TiO_2-BaO-CuO_2-Sm-CuO_2-BaO-CuO-bulk RBCO [11]. For a strict crystallographic unit cell, the terminating layer in the nucleation islands would be a CuO chain layer.

X-ray photoemission spectroscopy (XPS) can give additional information on surface layers [12]. Our own angle-resolved XPS measurements, done on samples which were not exposed to air, indicate that BaO is the termination layer of our YBCO and SBCO films [13]. This is consistent with the fact that BaO is the only nonpolar, and therefore lowest-energy surface layer in the stacking sequence. Thermodynamic conditions during synthesis of SBCO lead to very little oxygen in the CuO chain layers. This implies that the CuO layer is just a Cu layer during growth, and as such is polar and less stable as a termination layer. Furthermore, from charge considerations a Cu layer is needed within the nucleation island to balance the negatively charged CuO_2 plane layers; see charges in Fig. 5.

Based on the discussion above, the complete layering sequence of the nucleation island during growth, as shown in Fig. 5, is proposed to be BaO-CuO_2-Sm-CuO_2-BaO-Cu-BaO. The nucleation islands are charge neutral units whose structure depends on the substrate-film interface. Note that compared to one unit cell there is an extra BaO layer in this structure. This extra BaO layer we believe is the origin of the extra height, compared to *c*, observed in the nucleation islands. The expected height from this model is 1.4 nm, but we observe 1.6(2) nm. An explanation for this slight discrepancy is that the surface BaO layer has reacted with CO_2 upon exposure to air and formed a $BaCO_3$ layer, as is commonly observed for *ex situ* samples [12]. This layer gives an additional 0.2 nm, consistent with our data.

We expect this layering sequence in the nucleating island to be applicable to most physical vapor deposition

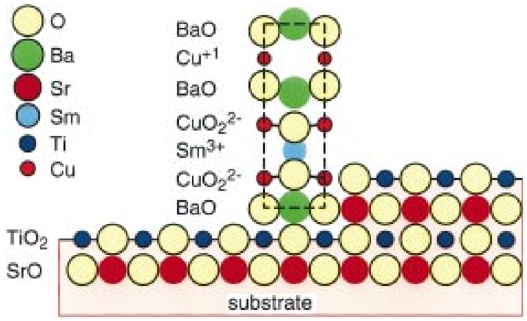

FIG. 5(color). Proposed model for the stacking sequence in the nucleation islands during growth at a step on the (100) $SrTiO_3$ surface. A unit cell of $SmBa_2Cu_3O_6$ is outlined. Ba, Sm, and Sr atoms (circles without outlines) lie out of the plane of the other atoms. The layer charges are based on formal ionic charge.

techniques, since it should be a consequence of the thermodynamically stable structure. However, this applies only for growth on a $SrTiO_3$(100) surface terminated by TiO_2. Other substrates have different terminating layers and the layering sequence can be different due to interface matching. Note that after the nucleation unit each additional molecular unit can be exactly one unit cell.

The proposed model implies that the nucleating islands on $SrTiO_3$ have a cation stoichiometry of 1:3:3, i.e., posses an excess of Ba compared to 1:2:3. Most growth methods, however, utilize a 1:2:3 cation stoichiometry throughout the film deposition process. The extra cations (Cu and Sm, or Y) which are left over after one nucleates 1:3:3 islands during a 1:2:3 cation deposition, can provide nuclei for second phases. R_2O_3 (R = Y or rare earth) and CuO phases are often observed by cross-sectional TEM [14]. We suggest that the nucleation of such second phases may be related to the structure of the nucleating *R*BCO islands. This also appears to be confirmed by our images. Taller grains are seen in Figs. 2(b) and 2(c). The elongated islands in Fig. 2(b), which are at 90° to each other, we assign to *a,b*-axis SBCO. The rounded islands which do not have any particular structure are second phases. The larger ones, at least, are probably CuO, commonly seen on top of our thicker films. The film deposited closer to the 1:3:3 stoichiometry, Fig. 2(b), has fewer second phase islands compared to the one with 1:2:3. This indicates that by tuning the composition during the *initial* stages of film growth, one would be able to eliminate second phases. In a similar, but slightly different approach, Kawasaki has shown that a deposition of a monolayer of SrO prior to 1:2:3 YBCO deposition can help eliminate second phases [15].

In conclusion, we have shown atomic force microscopy images of initial stages of film growth of $SmBa_2Cu_3O_7$ by reactive MBE. These images demonstrate that the nucleation occurs preferentially at the substrate steps and that whole molecular units nucleate at once and irrespective of the exact growth composition. Based on height analysis of the SBCO nucleation islands, as well as other data, we infer a 1:3:3 cation stoichiometry for SBCO nucleation on (100) $SrTiO_3$.

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*Present address: Conductus, Inc., 969 West Maude Ave., Sunnvale, CA 94086 (vlad@conductus.com).

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