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Scanning tunneling microscopy of pulsed-laser-deposited $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films: Surface microstructure and growth mechanism

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Scanning tunneling microscopy suggests that epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films grow unit cell by unit cell, by a terraced-island-growth mode. Although films grown at low temperatures exhibit a spiral-growth surface microstructure, films with high critical current densities (grown at high temperatures on nearly-lattice-matched substrates) do not. The terraced microstructure explains the steps found in ultrathin $YBa_2Cu_3O_{7-\delta}$ layers in $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$ superlattices. These steps may act as superconducting weak links, providing support for Josephson-coupled-array models of superconducting superlattices.

High-quality epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films have been obtained on single-crystal substrates using several deposition techniques, including coevaporation, off-axis magnetron sputtering, and pulsed-laser deposition.[1-4] Such films exhibit outstanding superconducting properties including superconducting transition temperatures T_c, greater than 90 K and critical current densities J_c, in excess of 10^6 A/cm^2 at 77 K in zero magnetic field and greater than 10^5 A/cm^2 in $H=8$ T.[3,4] Nevertheless, many fundamental questions remain unresolved, including an understanding of the nucleation and epitaxial growth mechanism. In addition, the vortex pinning centers, responsible for the much higher J_c for epitaxial thin films than for bulk $YBa_2Cu_3O_{7-\delta}$ single crystals in high magnetic fields, have not yet been identified. An understanding of these fundamental issues is critical for device applications, with the growth mechanism of particular importance for multilayered film structures.

Studies of the nucleation and growth mechanism of $YBa_2Cu_3O_{7-\delta}$ using microscopy have produced some understanding of how epitaxial growth is initiated and proceeds. Norton *et al.* have used transmission electron microscopy (TEM) to study the initial phase of epitaxy for $YBa_2Cu_3O_{7-\delta}$ on (100) MgO.[5] Their results suggest that c-axis oriented $YBa_2Cu_3O_{7-\delta}$ growth on MgO proceeds by the Volmer-Weber island-growth mechanism with substrate surface steps important as nucleation sites. Two other groups recently used scanning tunneling microscopy (STM) to study the surface microstructure of sputter-deposited $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films, in which a high density of growth spirals was observed.[6,7] Each growth spiral produced a well-defined grain, presumably with a screw dislocation at the center, suggesting an island-growth mode. However, in a recent reflection high-energy electron-diffraction (RHEED) study, Terashima *et al.* observed RHEED oscillations during the growth of $YBa_2Cu_3O_{7-\delta}$ on (100) $SrTiO_3$ by means of reactive evaporation.[8] They interpreted the RHEED oscillations as being due to the nucleation of two-dimensional (2D) islands and their growth into flat terraces in a cyclic fashion. Terashima *et al.* also found that each RHEED oscillation, when compared to the resulting film thickness (determined by precision x-ray analysis), corresponded to a layer thickness increment of one c-axis unit cell ($\sim$1.17 nm). This implies that the minimum structural unit satisfying stoichiometry and electrical neutrality is the full unit cell, and that epitaxial c-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films grow unit cell by unit cell.

In this paper, we report the surface microstructures, determined by STM, in epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films grown by pulsed-laser deposition (PLD). The STM images suggest that c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ films grow by a terraced-island-growth mechanism, in which the islands consist of flat terraces with step heights that are multiples of the c-axis lattice parameter, in agreement with the RHEED studies of Terashima *et al.* For some of the films, we also observe spiraling growth patterns, similar to those reported for sputter-deposited epitaxial $YBa_2Cu_3O_{7-\delta}$ films. However, we have not been able to unambiguously identify these spiral structures in $YBa_2Cu_3O_{7-\delta}$ films that were grown at high temperatures on nearly-lattice-matched substrates [i.e., (100) $SrTiO_3$ and (100) $LaAlO_3$], where the superconducting properties and c-axis growth are optimized. The fact that our smoothest c-axis $YBa_2Cu_3O_{7-\delta}$ films exhibit a surface roughness on the order of 10 nm implies that undulations and/or step discontinuities should exist in the connectivity of ultrathin $YBa_2Cu_3O_{7-\delta}$ layers within $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$ superlattice structures. This has important implications for the interpretation of superlattice electrical transport properties, and may be direct evidence of the structural defects needed to justify a weak-link model, whereby the ultrathin $YBa_2Cu_3O_{7-\delta}$ layers in these structures act as an array of Josephson-coupled-superconducting grains.[9–12]

The PLD method used to grow our epitaxial thin films and superlattices has been described elsewhere.[4,13] Films were grown on (100) $SrTiO_3$, (100) $LaAlO_3$, and (100) MgO at substrate (heater) temperatures T_{sub} of ~640 °C–730 °C (690 °C–780 °C) in 200 mTorr of oxygen. The laser repetition rate was 1.1 Hz with each laser pulse depositing ~0.1 nm. Total thickness of the films was 200–300 nm. Film growth on (100) $SrTiO_3$ at the optimum substrate temperature (~730 °C) results in $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films with $T_c(R=0)$ ~90–92 K, transition widths of 1 K or less, and J_c(77 K) ~1–4 MA/cm^2.

STM images were obtained using a Nanoscope I STM with typical scanning parameters of 0.3-nA tunneling current and −1.0 V bias. No special treatment of the film surface was required, and all of the images were obtained in air at room temperature. The samples were stored in a dessicator prior to being scanned. Figure 1 shows a STM image of a c-axis oriented epitaxial $YBa_2Cu_3O_{7-\delta}$ thin film grown at T_{sub}~730 °C on (100) $SrTiO_3$. Well-defined islands are clearly evident, with each island composed of stacks of terraces. The terrace step heights are multiples of the c-axis unit-cell height (1.17 nm). The islandlike appearance seen in Fig. 1 was common to c-axis-oriented films, with the most symmetric, well-defined, and largest grains obtained at higher growth temperatures. The terrace width, defined as the distance between terrace steps, is ~10 nm, which is the same order of magnitude as the distance between "kinks" in the $YBa_2Cu_3O_{7-\delta}$ layers of $YBa_2Cu_3O_{7-\delta}/PrBa_2Cu_3O_{7-\delta}$ superlattices, as observed by cross section Z-contrast TEM.[11,14]

The STM images demonstrate the effect of substrate temperature on surface microstructure. Figure 2 shows a STM image of a $YBa_2Cu_3O_{7-\delta}$ thin film grown at T_{sub}~680 °C on (100) $SrTiO_3$. c-axis-oriented epitaxial growth is achieved at this temperature, although the superconducting transport properties, such as T_c and J_c, are not as good as for films grown at T_{sub}=730 °C. Nevertheless, the STM image indicates a smoother film, with a maximum feature height of ~10 nm, although granularity is still present. All of the ~200–300-nm-thick films we have investigated exhibit a granular morphology, suggesting that these $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films grow by an island growth (Volmer-Weber or Stranski-Krastanov) mechanism. The islands consist of stacks of atomically flat terraces, constructed unit cell by unit cell, with the island-height variation being a function of the substrate temperature. Pure layer-by-layer growth is difficult to achieve when any lattice mismatch of the substrate and film exists, and will be the dominant growth mode only for very thin films.[15] Thus, island growth for $YBa_2Cu_3O_{7-\delta}$ on $SrTiO_3$ is not unexpected since lattice mismatch is present. The multiple-unit-cell terrace steps observed here are in agreement with the principal conclusion of the RHEED studies by Terashima *et al.*, although the layer-by-layer growth mode they propose is not completely consistent with the granular surface microstructure observed by STM for relatively thick films. Note that Terashima *et al.* report RHEED oscillations only during the initial stages of epitaxy using reactive evaporation at a relatively

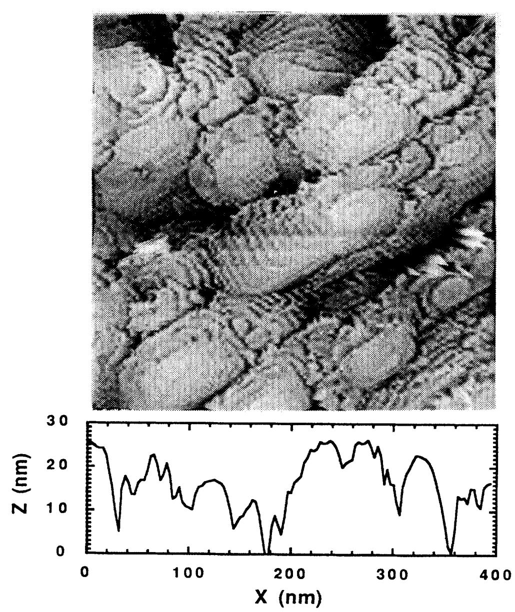

FIG. 1. STM image (upper) and line-scan profile (lower) of a c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $SrTiO_3$ at T_{sub}~730 °C. The dimensions of the STM image are 400×400 nm^2.

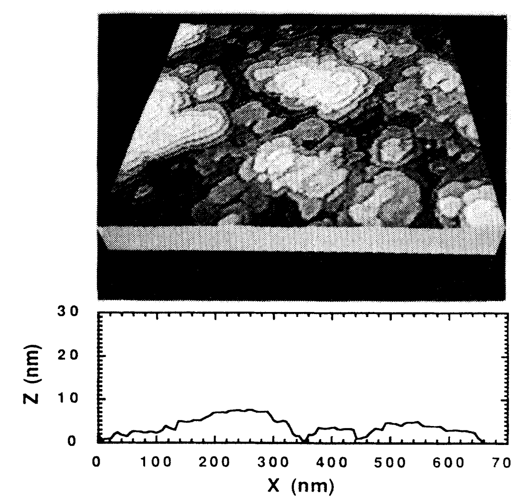

FIG. 2. STM image (upper) and line-scan profile (lower) of a c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $SrTiO_3$ at T_{sub}~680 °C. The dimensions of the STM image are 670×670 nm^2.

low substrate temperature (680 °C). This is consistent with a Stranski-Krastanov growth mode, in which film growth is initially layer by layer, but changes to an island-growth mechanism at some finite film thickness due to strain. This may explain the existence of RHEED oscillations during the initial states of lower-temperature growth, with the 3D island morphology dominating for greater film thickness, as shown here.

It is useful to compare the STM images obtained for $YBa_2Cu_3O_{7-\delta}$ films grown by PLD with those recently reported for sputter-deposited films.[6,7] In both cases, the $YBa_2Cu_3O_{7-\delta}$ films appear to be quite granular, with atomically flat terraces that are multiples of the c-axis unit cell in height. For the films grown by pulsed-laser deposition at ~0.1 nm/sec, the average $YBa_2Cu_3O_{7-\delta}$ grain diameter on (100) $SrTiO_3$ is 100–300 nm. This is smaller than the grain size reported for films sputter-deposited at lower deposition rates (1.5 nm/min),[4] but comparable to the grain diameter in films sputtered at comparable deposition rates (0.13 nm/sec).[5] We also have observed the spiral grain microstructure that was reported for sputter-deposited $YBa_2Cu_3O_{7-\delta}$ thin films.[6,7] However, for films grown on (100) $SrTiO_3$ and (100) $LaAlO_3$, we have been able to identify these spiral structures unambiguously only in films that were grown at substrate temperatures that were less than optimal for superconducting properties ($T_{sub} \leq 680$ °C). At least three spiral structures can be identified in the STM image shown in Fig. 2. Figure 3 shows spiral microstructures in a $YBa_2Cu_3O_{7-\delta}$ film grown on (100) MgO at T_{sub} =640 °C. The spiral structures' areal density for this film is ~10^9/cm^2. As with the film grown at 680 °C on (100) $SrTiO_3$, this film is significantly smoother than the film grown at 730 °C, although the transport properties are measurably worse with T_{c0}~85 K. For most c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ films with superior transport properties [grown on (100) $SrTiO_3$ and (100) $LaAlO_3$ at T_{sub}~730 °C], the grains resemble those shown in Fig. 1, being composed of very flat terraces with no growth spirals.

It has been suggested that screw dislocations associated with these spiral structures could be responsible for the strong flux pinning observed in epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films at low magnetic fields, although the density of screw dislocations is insufficient to account for the pinning observed at high vortex densities and high magnetic fields (~8 T).[6,7] Although it may be possible to obtain $YBa_2Cu_3O_{7-\delta}$ films with both outstanding superconducting properties and growth spirals, the apparent lack of spiral structures in $YBa_2Cu_3O_{7-\delta}$ films grown by PLD at the optimal deposition temperature would seem to exclude their importance in flux pinning, since these films have very high critical current densities. Thus, it may prove more relevant for identification of flux-pinning sites to understand the defect structures that are produced at the intersection of adjacent $YBa_2Cu_3O_{7-\delta}$ grains.

We also investigated the surface microstructure of a-axis-oriented thin films. Figure 4 shows a STM image of an a-axis-oriented $Pr_{0.6}Ca_{0.4}Ba_2Cu_3O_{7-\delta}$ thin film grown at T_{sub}=640 °C on (100) $LaAlO_3$. $Pr_{0.6}Ca_{0.4}Ba_2Cu_3O_{7-\delta}$ has the same "1:2:3" crystal structure as $YBa_2Cu_3O_{7-\delta}$, with the Y site occupied by Pr and Ca. However, Pr containing 1:2:3 thin films tend to grow in the a-axis-perpendicular orientation more easily than do those of $YBa_2Cu_3O_{7-\delta}$, and thus was chosen for this STM image. The surface morphology of the a-axis film differs strikingly from that observed for c-axis-oriented films, with no indication of the terrace or spiral structures that are so prominent in the c-axis films. As is true for the c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ film grown at 640 °C, this a-axis-oriented film is smoother than c-axis-oriented films grown

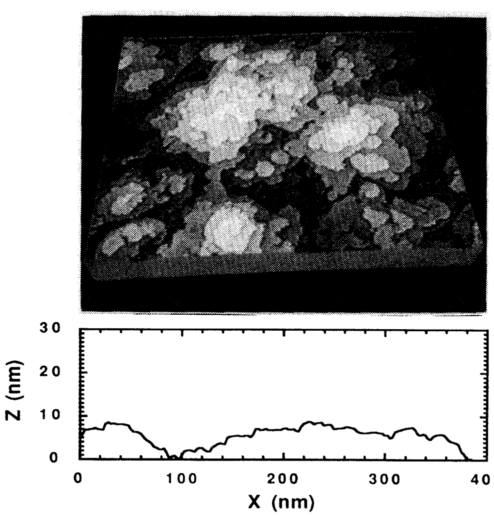

FIG. 3. STM image (upper) and surface profile (lower) of a c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) MgO at T_{sub}~640 °C. The dimensions of the STM image are 440×440 nm^2.

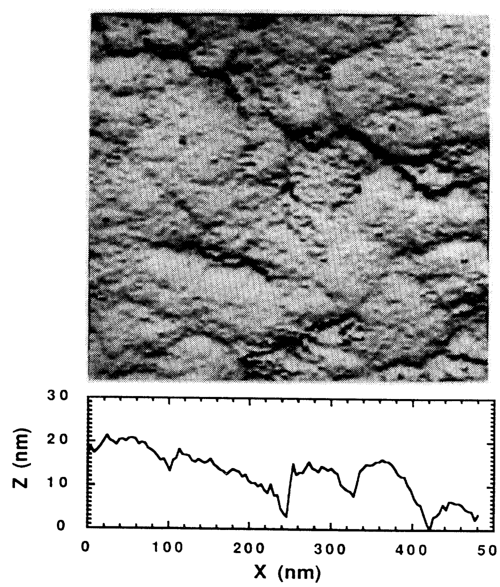

FIG. 4. STM image (upper) and surface profile (lower) of an a-axis-oriented $Pr_{0.6}Ca_{0.4}Ba_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $LaAlO_3$ at T_{sub}~640 °C. The dimensions of the STM image are 500×500 nm^2.

at 730 °C.

The surface microstructure observed in the *c*-axis-oriented thin films may have important implications concerning the transport properties of $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ superlattice structures. For *c*-axis-oriented $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ superlattices, the superconducting properties are a function of both the superconducting ($YBa_2Cu_3O_{7-\delta}$) and the barrier ($PrBa_2Cu_3O_{7-\delta}$) layer thicknesses.[13,16,17] T_c decreases as the $YBa_2Cu_3O_{7-\delta}$ layer thickness is decreased or as the $PrBa_2Cu_3O_{7-\delta}$ layer thickness is increased, and is accompanied by a significant broadening of the superconducting transition for the thinnest $YBa_2Cu_3O_{7-\delta}$ layers. Several models have been suggested to explain the transport properties of these superlattice structures.[10,12,18,19] However, the terraced "roughness" that is present on the growing surface (Figs. 1–3) will be translated into the individual layers in a multilayered structure. The individual $YBa_2Cu_3O_{7-\delta}$ layers in the structures will not be flat, but will contain significant undulations relative to the crystal axes as well as steps or kinks occurring when the $YBa_2Cu_3O_{7-\delta}$ layers are viewed in cross section. For $YBa_2Cu_3O_{7-\delta}$, the *c*-axis superconducting coherence length ($\xi_c \sim 3$–6 Å) is much shorter than the *c*-axis lattice parameter. Consequently, at the kinks, where *c*-axis conduction is necessary, perturbation of at least the phase of the superconducting wave function should occur, and may dominate the transport properties of these structures (especially so for the $1\times N$ structures with single-cell-thick $YBa_2Cu_3O_{7-\delta}$ layers). Based on the observed surface microstructure, together with *Z*-contrast TEM images of the superlattice structures,[11,14] it appears that a complete theory of the transport properties of $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ superlattice structures must include the effects of these kinks, and that perhaps one should regard the $YBa_2Cu_3O_{7-\delta}$ layers as an array of superconducting terraces connected by weak links. Such a model predicts a significant broadening of the superconducting transition,[9] similar to that observed.[13,16,17] Ariosa and Beck recently proposed a model to explain the variation of T_c in $YBa_2Cu_3O_{7-\delta}$/$PrBa_2Cu_3O_{7-\delta}$ superlattices, in which the $YBa_2Cu_3O_{7-\delta}$ layers were treated as an array of Josephson-coupled grains with additional electrostatic coupling between conducting layers along the *c* direction.[10]

In conclusion, a STM study of the surface microstructure of $YBa_2Cu_3O_{7-\delta}$ epitaxial thin films grown by PLD reveals a terraced-island morphology. The grains consist of stacks of terraces that are multiples of the *c*-axis unit cell in height. The surface roughness of these films is a function of substrate temperature, although the smoothest films (grown at lower temperatures) do not give the best superconducting properties. Spiral growth structures[6,7] were observed on the surface of several *c*-axis-oriented $YBa_2Cu_3O_{7-\delta}$ thin films. However, no spiral microstructures were observed for the films with the best superconducting transport properties, suggesting that screw dislocations associated with these spirals play a little role in flux pinning. Although an islandlike morphology was observed for these films, the possibility of achieving layer-by-layer $YBa_2Cu_3O_{7-\delta}$ growth cannot be ruled out. In addition, the terraced-island morphology implies that ultrathin $YBa_2Cu_3O_{7-\delta}$ layers in superlattice structures should contain a high density of steps or kinks. These may play a significant role as superconducting weak links in broadening the resistive transition in such multilayered structures.[11,12]

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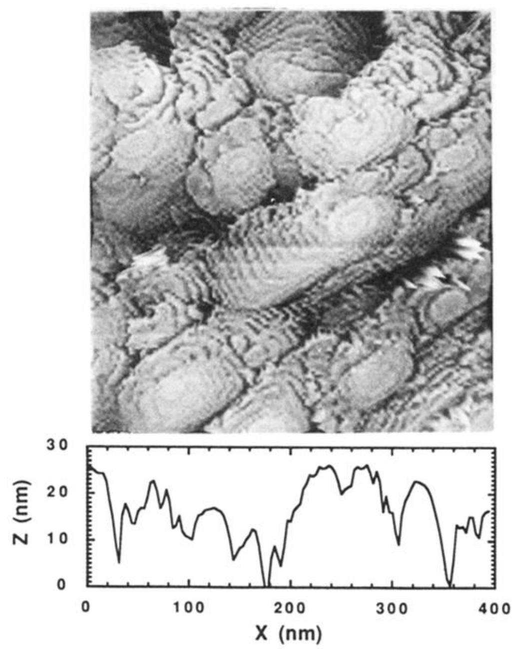

FIG. 1. STM image (upper) and line-scan profile (lower) of a c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $SrTiO_3$ at $T_{sub} \sim 730\,°C$. The dimensions of the STM image are $400 \times 400\ nm^2$.

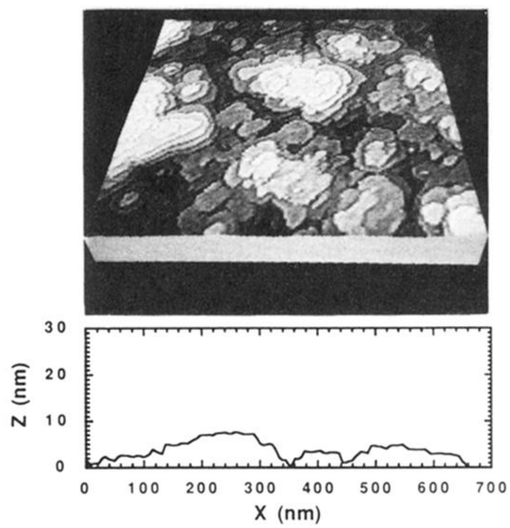

FIG. 2. STM image (upper) and line-scan profile (lower) of a c-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $SrTiO_3$ at $T_{sub} \sim 680\,°C$. The dimensions of the STM image are $670 \times 670\ nm^2$.

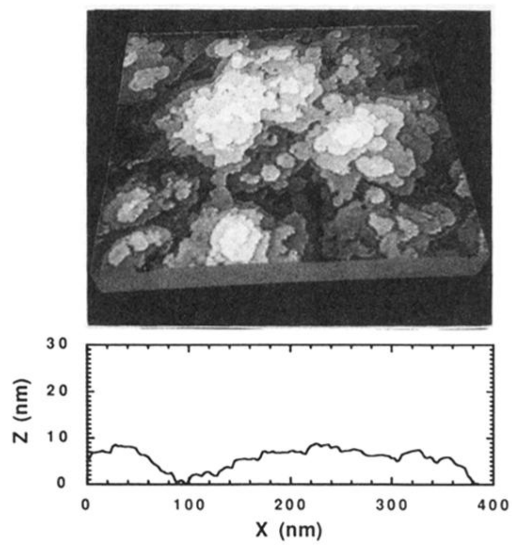

FIG. 3. STM image (upper) and surface profile (lower) of a *c*-axis-oriented $YBa_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) MgO at $T_{sub} \sim 640\,°C$. The dimensions of the STM image are $440 \times 440\ nm^2$.

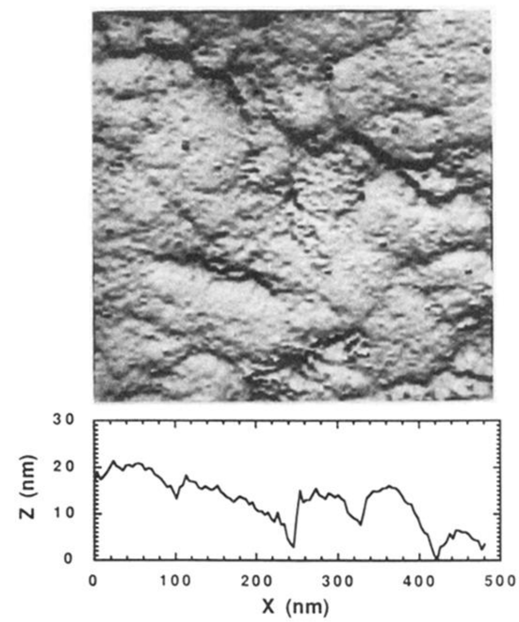

FIG. 4. STM image (upper) and surface profile (lower) of an *a*-axis-oriented $Pr_{0.6}Ca_{0.4}Ba_2Cu_3O_{7-\delta}$ epitaxial thin film grown on (100) $LaAlO_3$ at $T_{sub} \sim 640\,°C$. The dimensions of the STM image are $500 \times 500\ nm^2$.