

Atomic Resolution and Nanostructure of $\text{RE}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (RE = Er, Eu, Ho and Y) Laser-Ablated High T_c Superconductor Films Studied by Scanning Tunneling Microscopy

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We applied scanning tunneling microscopy (STM) to characterize the topography of high quality, epitaxial c-axis-oriented laser-ablated thin film $\text{RE}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, (RE = Eu, Er, Ho and Y) superconductors. We report on atomic resolution in the a-b plane of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ compound indicating an approximately square lattice with a lattice constant of 3.8 Å which will be discussed in relation to the unit cell. The main features of the surface on nanometer scale are steps of one unit-cell height proofing the two-dimensional growth process of the epitaxial film. At larger scale however, island growth is the dominating process. We observed at least two different types of growth hills: circular laminae and screw dislocations. Outgrowths on laser-ablated films are essential features of the topography at micron scale.

The scanning tunneling microscope (STM) developed by Binnig and Rohrer [1] is a very useful tool to study the nanometer topography of clean surfaces in the real space. Impressive results were achieved with layered materials, which can be easily cleaved to give fresh surfaces for STM investigations.

Since the discovery of high T_c superconductors (HTCSC) by Bednorz and Müller [2] in 1986, several other superconducting, layered ceramics were synthesized. The sample quality was improved by choice of different synthesis routes besides powder sintering, e.g. melt-textured growth, growth of single crystals, deposition of thin epitaxial films by magnetron sputtering and laser-ablation [3].

STM was soon applied to high T_c superconductors. Clear atomic resolution by STM of cleaved Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O single crystals was first reported in 1988 [4] and 1989 [5], respectively.

The best investigated high T_c compound as far as its superconducting properties are concerned, is $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with a T_c of 92 K. However, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ is quite reactive which leads to deterioration of the surface, if exposed to humidity.

The atomic arrangement of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ was up to now only studied with well-established methods as high resolution electron microscopy, X-ray, electron, and neutron diffraction experiments. There is only one report on corrugations at the atomic scale on single crystals of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [6] by STM.

Recently, the nano- and microstructure of magnetron-sputtered epitaxial thin films of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ was studied by STM [7, 8]. In this paper, we report on atomic resolution of freshly prepared $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ epitaxial laser-ablated thin films (see also [9, 10]) and their nanometer morphology.

Films investigated in this study were prepared on single crystalline substrates such as $\text{MgO} < 100 >$, $\text{SrTiO}_3 < 100 >$ and $\text{LaAlO}_3 < 100 >$ by laser-ablation. Details of synthesis are described elsewhere [10]. Film thickness is about 200 nm.

The STM used in this study is a standard Nanoscope II with scanners A and D [11] which was operated in air at ambient temperature. $\text{Pt}_{80}\text{Ir}_{20}$ tips were mechanically sharpened. Bias voltage between tip and sample was about 0.8 V and tunneling current was lower than 300 pA. The STM was operated in the constant current mode (Nanoscope Height mode) mapping topography. If not indicated otherwise, the images represent non-filtered data.

Films of $\text{RE}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, RE = Er, Eu, Ho and Y, prepared as described above, have excellent superconducting and structural properties. Inductively measured critical transition temperature T_c above 89 K with a 10 %-90 % transition width of less than 1 K, critical current densities J_c of about $5 \cdot 10^6$ A/cm² at 77 K and up to $3 \cdot 10^7$ A/cm² at 4.2 K [12]. The c-axis orientation of the films is shown by X-ray diffraction.

Scanning electron micrographs of the films show at all attainable magnifications a smooth surface with few crystallites (see figure 1). Simultaneous chemical analysis by energy dispersive scattering of X-rays (EDS) gives the expected 1-2-3 stoichiometry.

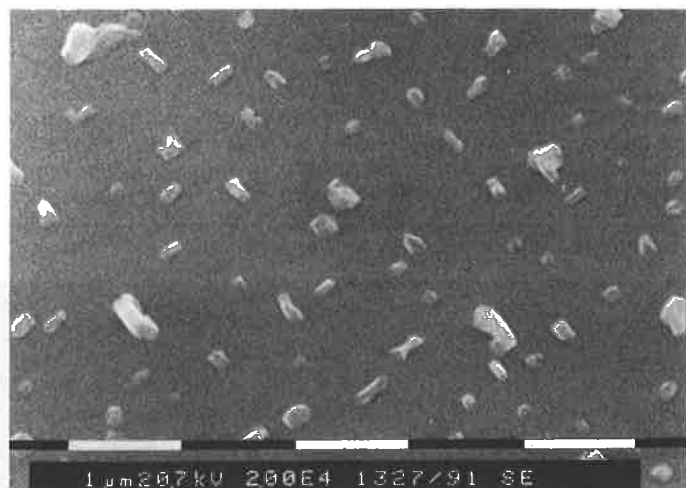


FIGURE 1. - SEM micrograph of an epitaxial $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film. The scale bar is 1 μm .

The STM-topography of the films on a submicron scale is not as smooth as expected from electron micrographs. Apparent features of the surface are steps of unit-cell height (1.18 nm) confirming the X-ray diffraction data. The dominating growth process during laser-ablation is rather island growth than layer by layer growth as found in single crystals. These islands consist of circular

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or rectangular shaped stacked laminae. Frequently, a screw dislocation is found on top of these hills. The occurrence of such lattice defects seems to be related to the temperature on the substrate during deposition. Such phenomena have also been found on magnetron sputtered $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ films by STM [7, 8]. Similarities between laser-ablated and magnetron-sputtered thin films are discussed elsewhere [13].

Figure 2 shows an $400 \text{ nm} \times 400 \text{ nm}$ large area of a $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film and $\text{LaAlO}_3 < 100 >$. The 3D-view shows epitaxial layers with unit cell steps, in the foreground a 6 unit cell deep hole (diameter 80 nm) and near the right border a presumably non c-axis oriented crystallite (see figure 1 for comparison) grown out of the epitaxial layers. Recently, Venkatesan *et al.* [14] have studied the growth of these crystallites by SEM.

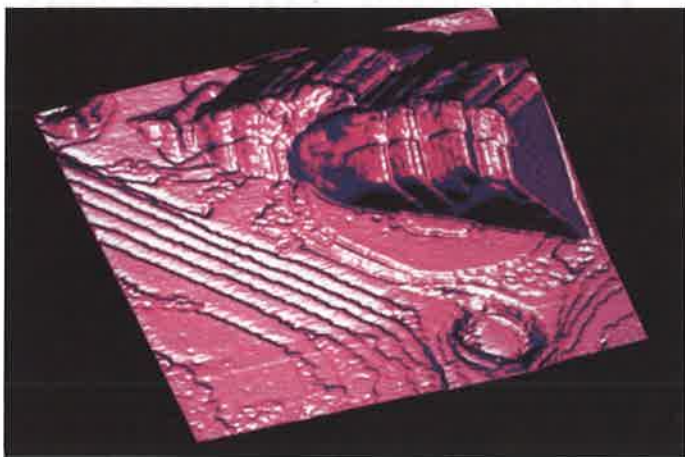


FIGURE 2. - STM illuminated birdview showing epitaxial growth and an emanating crystallite ($400 \text{ nm} \times 400 \text{ nm}$).

The scanning tunneling micrograph shown in figure 3 is a illuminated birdview of a $413 \text{ nm} \times 413 \text{ nm}$ large area of a c-axis oriented laser-ablated $\text{Ho}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film on $\text{SrTiO}_3 < 100 >$ with island-grown stacked layer structures. The steps in the image are of one unit cell height. Figure 4 is a STM topview ($1500 \text{ nm} \times 1500 \text{ nm}$) showing hills with screw dislocations on a $\text{Ho}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film on $\text{MgO} < 100 >$. This screw dislocation mediated growth is another observed basic epitaxial growth mode of laser-ablated thin films besides the above mentioned stacked laminae growth mode. In the middle of the figure 5, a Frank-Read-Source (loop) can be observed on the same film besides unit cell steps. A loop is an introduced extra lattice plane consisting of two screw dislocations of opposite sign.

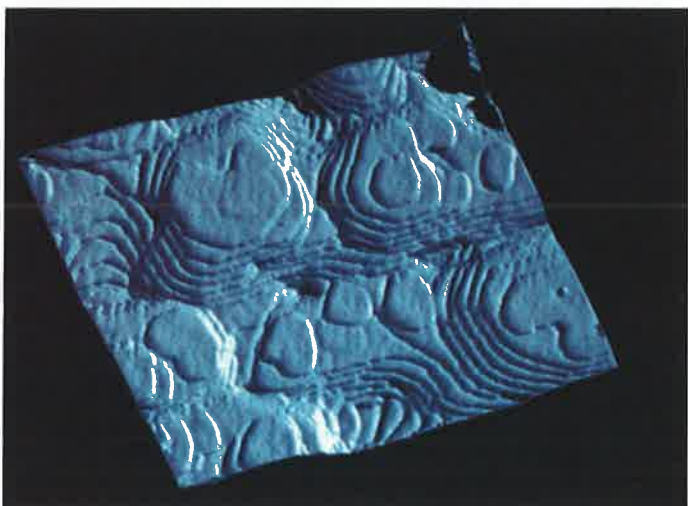


FIGURE 3. - STM topview showing stacked layer laminae structures ($413 \text{ nm} \times 413 \text{ nm}$).

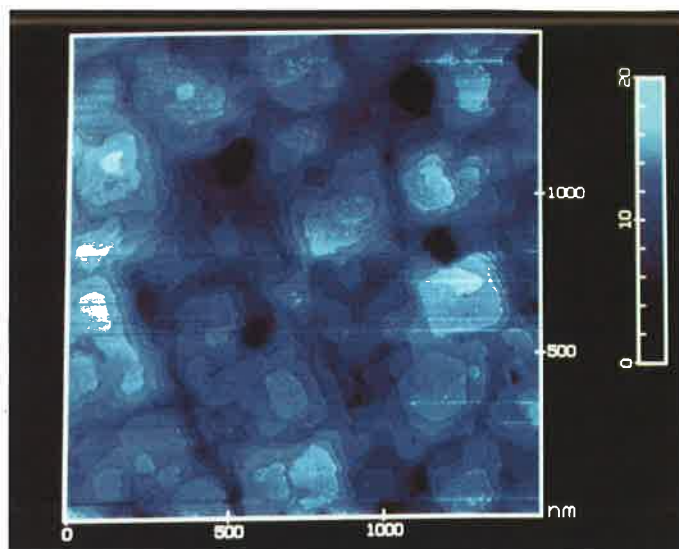


FIGURE 4. - STM topview showing screw dislocation mediated growth ($1500 \text{ nm} \times 1500 \text{ nm}$).

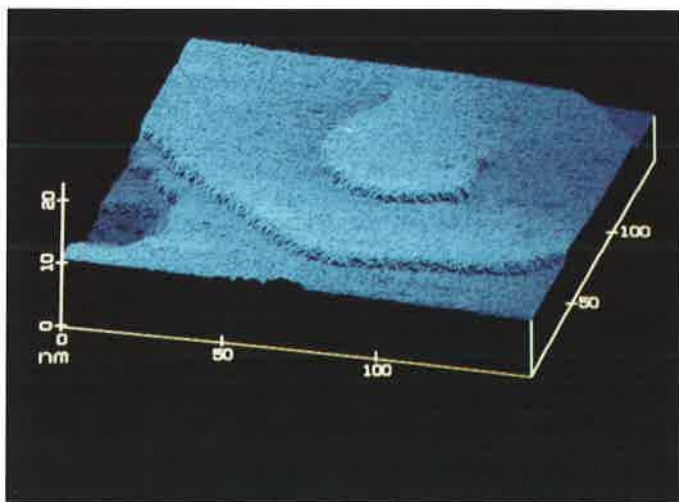


FIGURE 5. - STM illuminated birdview showing a loop ($150 \text{ nm} \times 150 \text{ nm}$).

Figure 6 shows the approximately square atomic arrangement of the (001) face of a $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ film on $\text{SrTiO}_3 < 100 >$. The interatomic distance of about 0.38 nm corresponds to the a- or b-axis length. Possible distances of 0.38 nm in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ crystal structure include Y-Y, Ba-Ba, Cu(1)-Cu(1) respectively O(1)-O(1) in the planes, Cu(2)-Cu(2) and O(4)-O(4) in the chains (see figure 6b). Maybe there exists a so called dead endlayer consisting of parts of the Cu-O chains and the barium layer as was suggested by a group performing angle resolved photoemission experiments on that kind of thin film HTCS samples [15]. We believe that STM cannot solve the problem of what is the toplayer of $\text{RE}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. Suitable experiments might be more accurate angle resolved photoemission or inelastic ion scattering.

Further work on these HTCS laser-ablated films has to be done to understand the growth process in a more detailed way.

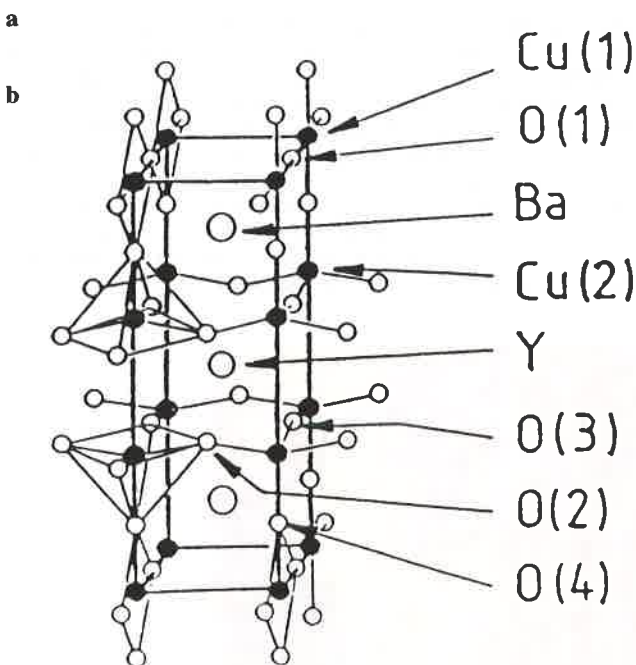
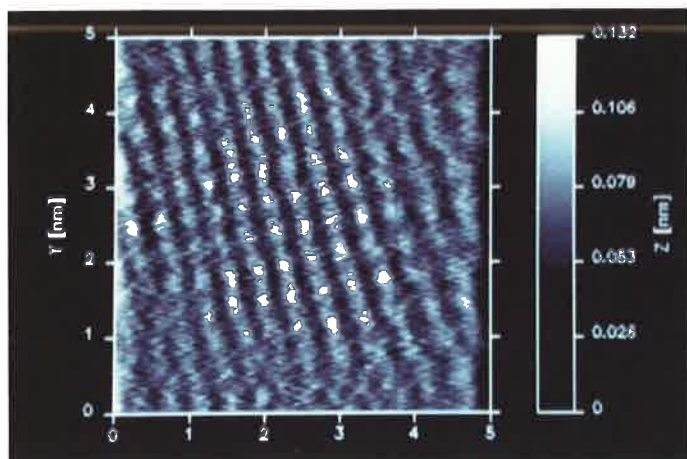


FIGURE 6. - (a) STM topview ($5 \text{ nm} \times 5 \text{ nm}$) showing atomic resolution on $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The image is slightly processed. (b) Crystal structure of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$.

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