SURFACE OF BiSrCaCuO SINGLE CRYSTAL OBSERVED BY MEANS OF SCANNING TUNNELING MICROSCOPE

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The topographic images of a $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ single crystal were studied by means of the scanning tunneling microscope. The structure of terraces and steps seen on the surface reflects the crystallographic structure of bulk.

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1. Introduction

Direct imaging of topographic and electronic surface structures with atomic resolution has been a dream of solid state physicists. This dream was realized after the invention of scanning tunneling microscopy (STM) by Binnig, Rohrer and co-workers in 1981 [1]. After the observation of the real-space image of Si(111)–(7 × 7) [2], which had been an unresolved problem for more than 20 years, scanning tunneling microscopy has been accepted as a powerful tool in the physics of surface science. A huge amount of papers has been published and many specialized conferences have been organized [3].

The STM is one of very few instruments in surface physics giving extremely high atomic resolution and not being confined to the high vacuum environment. Of course, the best results of the STM surface imaging are obtained in vacuum on the specially prepared surfaces, but some chemically inert surfaces like gold or graphite can be successfully observed in the air. Because almost all surfaces interact with atoms of their surroundings, the clean surfaces exposed to the air are covered by foreign atoms. Thus the STM tip sees only these covering layers and not the proper surface.

The discovery of high-T_c superconductivity in the copper perovskites has stimulated the competition in exploring their physical properties and potential applications. The Bi–Sr–Ca–Cu–O, one of the highest T_c superconductor, has been sintered and investigated in many laboratories [4, 5]. The surface properties of high-T_c superconductors are important not only from the physical phenomena's point of view, but also from the point of view of their possible applications. The superconducting shielding currents are generated on the surface of material within a penetration depth, thus the distribution and intensities of these currents can be influenced by the electronic and crystallographic structures in the surface regions. The studies of high-T_c superconductors by means of a STM may give some information concerning the atomic arrangement on the surface and eventually the electronic density of states at grain or twin boundaries.

It is now clear that the conducting and superconducting properties of perovskite superconductors are dramatically sensitive to the presence of oxygen in the lattice. Their surface, where the content of oxide can be different from that in the bulk, can thus have different properties. In general, due to high mobility of oxygen, the surfaces of high-T_c superconductors are covered by non-conducting or semiconducting layers. Removing this layer does not help in the surface analysis. Most of the surface sensitive techniques work only in ultra-high vacuum environment, then the high mobility of the oxygen in a high-T_c superconductor may cause a varying degree of oxygen depletion at the surface. The use of STM working at ambient pressure is thus of great advantage, because the oxygen in the sample is in equilibrium with the oxygen in air.

In the paper, we report on the surface imaging of the $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ single crystals in order to investigate the nature of surface layer. We have obtained well reproducible topographic data resolving the growth steps, grain boundaries and the structure elements in the dimension range of crystallographic unit cell.

2. Experiment

The STM used in these experiments was a modified version of that used by Smith [6] and is described in [7]. Observations of surfaces were performed in the normal air at room temperature. The scans were taken at voltages ranging from 1 V to 1.5 V with tunneling currents in the range of 3 nA to 10 nA. Scanning speeds along the x-axis were in the range of hundreds Å/s. Each surface image was registered in about two minutes.

The observations of $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ surfaces were performed on small single crystals grown from a solution by the flux method [9]. The critical temperature as determined from magnetic susceptibility was 110 K. The small pieces of single crystals of dimensions in the range of millimeters were glued by the conducting silver paste to a sample holder in STM. A cleavage plane of crystal of the best flatness and shine was chosen in an optical microscope as the surface for STM imaging. No special cleaning procedures of investigated surfaces were applied before measurements.

3. Results and discussion

Figures 1 and 2 are the examples of surface images of $Bi_{0.87}Pb_{0.3}SrCaCu_{1.8}O_x$ single crystals. Figure 1 presents the image area 1000 × 1000 Å. The x- and the

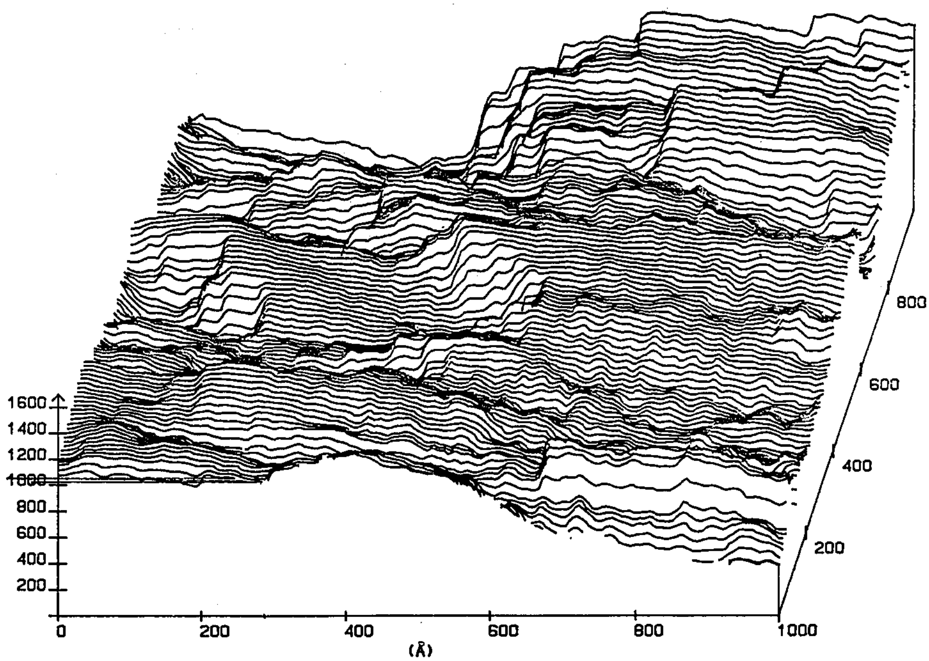

Fig. 1. STM image of a BiSrCaCuO surface. Image area 1000 × 1000 Å.

y-scales are given in the figure, the z-scale corresponds to corrugations in the z direction and should be read for estimation of corrugations registered on particular scans. All scales are given in Å. In Fig. 2 a similar image is presented, but the magnification is doubled compared with that of Fig. 1 and the surface area is now 500 × 500 Å.

It is seen on both images that the surface, which seemed to be ideally flat and regular in optical microscope, after magnification given by STM seems to be markedly corrugated and many terraces and steps can be recognized. The detailed structure of steps cannot be registered precisely because the resolution of the STM image is limited by the size of the tunneling tip, whose curvature was not known in our experiment. The rounding of steps on individual scans are due to the size of the tunneling tip and to the characteristics of electronic circuit. It can be seen, however, in above presented pictures that although the heights of steps are different, they are the multiples of about 30 Å and no steps smaller than 30 Å are visible. Thus we can suggest that 30 Å corresponds to the dimension of a symmetry unit in BiSrCaCuO crystallographic structure which is reflected in the surface structure of the crystal. The dimensions of the orthorhombic unit

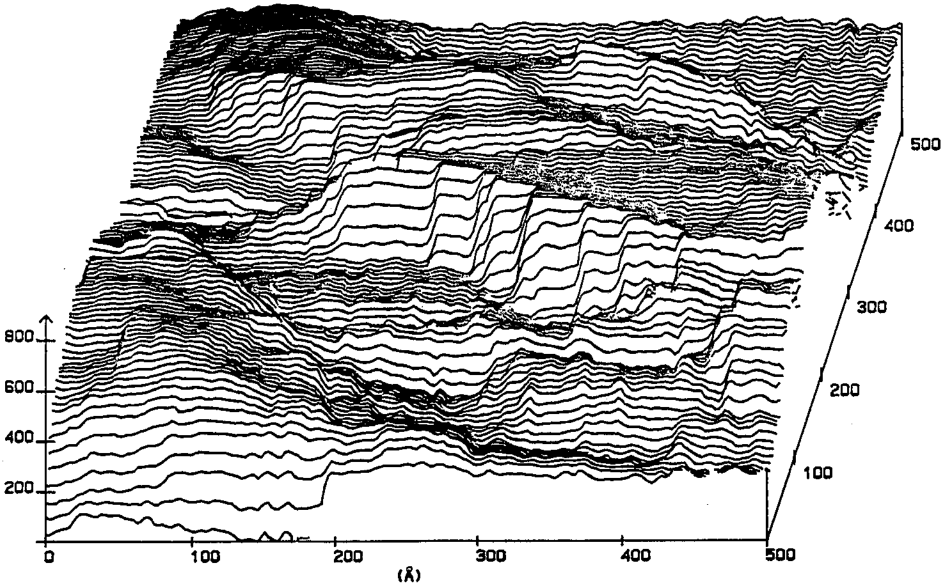

Fig. 2. STM image of the same surface as in Fig. 1, but with magnification 2 times higher. Image area 500 × 500 Å.

cell of the BiSrCaCuO crystal are a = 5.396 Å, b = 5.447 Å and c = 30.673 Å [10]. Therefore, we suggest that the observed steps are connected with the natural cleavage plane of the orthorhombic crystal perpendicular to the c-axis, along the $(Bi_2O_2)^{2+}$ layers, as it was claimed by Kugimiya et al. [11] on the basis of the scanning electron microscope (SEM) pictures.

The correspondence between step heights and the dimension of the unit cell along the c-axis can suggest that the surface of our crystal, observed in several places on the sample, is rather clean and uniform in its electrical properties. Even if there are some contamination layers on the surface, they do not mask or deform substantially the crystal structure of the bulk, which seems to extend to the surface. Unfortunately, we are not able to confirm the assumption of Kugimiya et al. that the cleavage planes responsible for regular, flat SEM and STM images are exactly the $(Bi_2O_2)^{2+}$ layers.

Many other STM images of the BiSrCaCuO surfaces have been observed. Most of them were similar to those presented in Figs. 1 and 2, but there were also images not so regular with visible terraces and steps. These irregular parts of the surface reflect probably the fractures of crystallites in the planes not perpendicular to the c-axis or the parts of the surface covered by some contaminations.

Figure 3 presents the STM image of the same crystal but taken in other place on the surface. Instead of terraces and steps a smooth and clear hill can be recognized. This hill can be connected either with some contamination of the surface or with the presence of a grain of non-crystallized material.

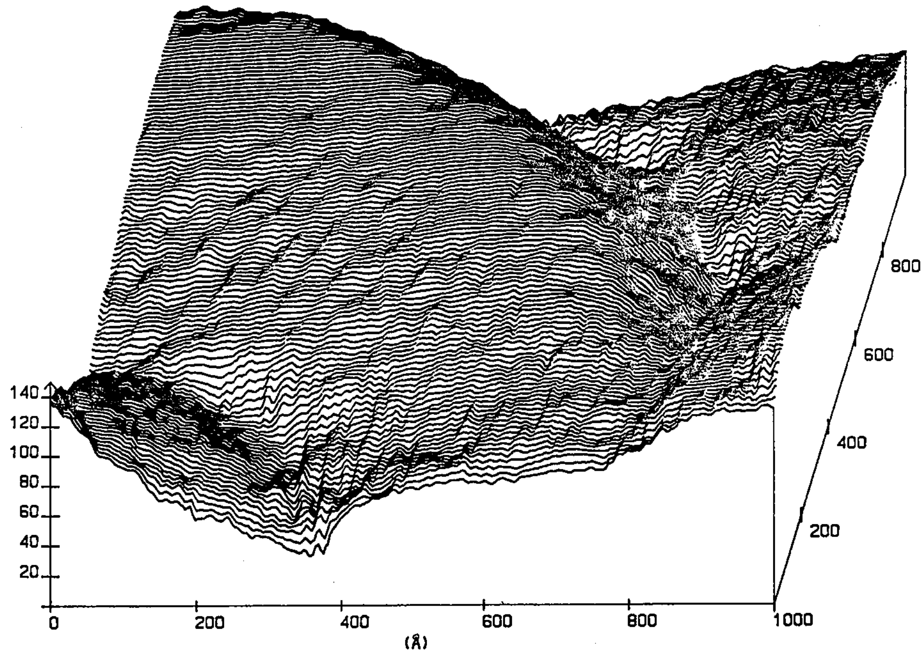

Fig. 3. STM image of the same crystal as in Figs. 1 and 2, but taken in other place on the sample. Image area 1000 × 1000 Å.

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