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GROWTH MECHANISMS OF $YBa_2Cu_3O_{7-x}$ PLATELET CRYSTALS FROM STM/SEM INVESTIGATIONS

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A scanning tunneling microscope combined with SEM was used to study the growth mechanisms of natural {100} and {001} faces, especially near edges and corners. These two faces of the tetragonal percursor phase of the high-temperature superconductor $YBa_2Cu_3O_7$ (YBCO) have different growth mechanisms. The leading-edge growth mechanism in combination with destabilizing growth conditions explain the platelet growth of YBCO and possibly of other compounds.

In the field of crystal growth, the study of crystal surfaces is of interest to understand growth mechanisms and to relate them to theory. Crystal growth surfaces also indicate the structural perfection and the homogeneity of crystals which are important to numerous electronic and optoelectronic applications. Besides optical and electron microscopes, the scanning tunneling microscope (STM) has found its place in highly resolved analyses of surface topography. Whereas the first STM investigation of an as-grown crystal surface [1] was limited by a maximum scan width of 0.2 to 1 μm, modern instruments allow scans of 70 μm and more. A significant extension of scan width is achieved by a combination of STM with a scanning electron microscope (SEM) and its scan width of several mm [2,3]. This allows additive scans from well-defined regions, for instance near crystal edges and crystal corners. Also, the high-resolution investigation of narrow and small surfaces of crystals with extreme aspect ratios, like thin platelets and whiskers, becomes possible and thus may lead to the understanding of their growth mechanism.

In this study, thin platelets of the tetragonal precursor phase of the high-temperature superconductor $YBa_2Cu_3O_7$ (YBCO) have been studied. The knowledge of growth kinetics and the rate-limiting step may be utilized for reproducible control of the habit, i.e. for growth of bulk crystals and of very thin plates of YBCO, which are needed for critical experiments to understand the new phenomenon of high-temperature superconductivity.

The STM consists of a single-tube scanner mounted vertically on three piezoelectric tubes standing on a translatable and tiltable platform [4]. The scan ranges are 70 μm for the x- and y-directions and 5 μm for the z-direction; the resolution is about 3 Å. A description of the STM system [2] and its limitations and sources of errors [3] is given elsewhere. In particular, while local changes in slope of a surface can be determined with good precision, absolute values of angles measured have to be interpreted with caution.

The YBCO crystals were grown from slowly cooled high-temperature solutions with solvent 28 mol% BaO and 72 mol% CuO [5,6]. Crystal growth details are given elsewhere [3,6]. Two YBCO plates, S46 of 3 mm size and 76 μm thickness and S61 of 4.5×2.5 mm^2 size and 53 μm thickness, were used in this study. They were fixed on a sample holder by means of silver paste with the face of interest (100) or (001) looking upwards and aligned verti-

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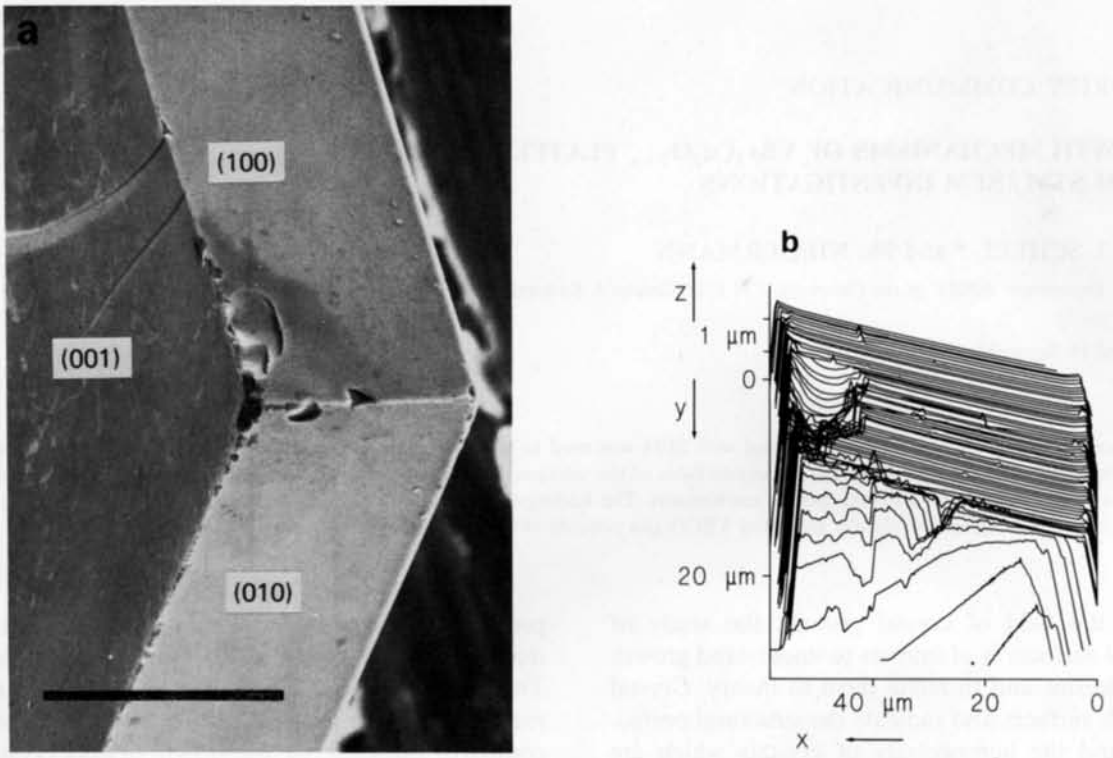

Fig. 1. Two views of the (100)/(010)/(001) corner region of the YBCO crystal S61: a SEM photograph (a) and a STM image (b). Note the different scales and projection angles. Marker in (a) represents 50 μm.

cally to the single-tube scanner with the tip. The SEM and an optical telescope were used to adjust the STM tip slightly above the surface region of interest, then the tip was smoothly moved towards the surface until tunneling occurred.

Fig. 1 presents two images of the corner region of the S61 plate, one taken with a CI Stereoscan 360 (fig. 1a) and the other presenting the STM view (fig. 1b). The latter is somewhat distorted due to differences in scales. Especially the angles of the top (100) face are exaggerated due to the enlarged z scale. The upper (100) face is confined on its sides by the vertical (001) and (001) faces, and in front it forms an edge of 53 μm length with the vertical (010) face. The mechanical damages on the left top edge and on the left side of the horizontal front edge help with finding the orientation and the correlation of figs. 1a and 1b. The interesting features are firstly the slope of the (100) face relative to the crystallographic (100) plane, and secondly the raised side edges of the top (100) face. The real slope of the (100) face is, taking into account the projection angle and the differences in scales, about 1.5°. There is an indication of a raised edge on the left upper edge which may be slightly overemphasized due to piezoelectric drift since the scanning direction is from left to right on the figure. On the other side the edge is clearly elevated above the region of the (100) face near the edge. The upwards trend of the (100) face starts about 4 μm from the edge. A high-resolution STM scan of the front edge between (100) and (010) indicates that this relatively short edge is not raised [3]. Steps of 50 to 60 Å height parallel to the edge are faintly seen, although it was not easy to find these steps because all edges are rough on an atomic scale.

The features of sloped (100) faces and of raised edges have been observed repeatedly. One example of an edge-to-edge STM scan of the (100)

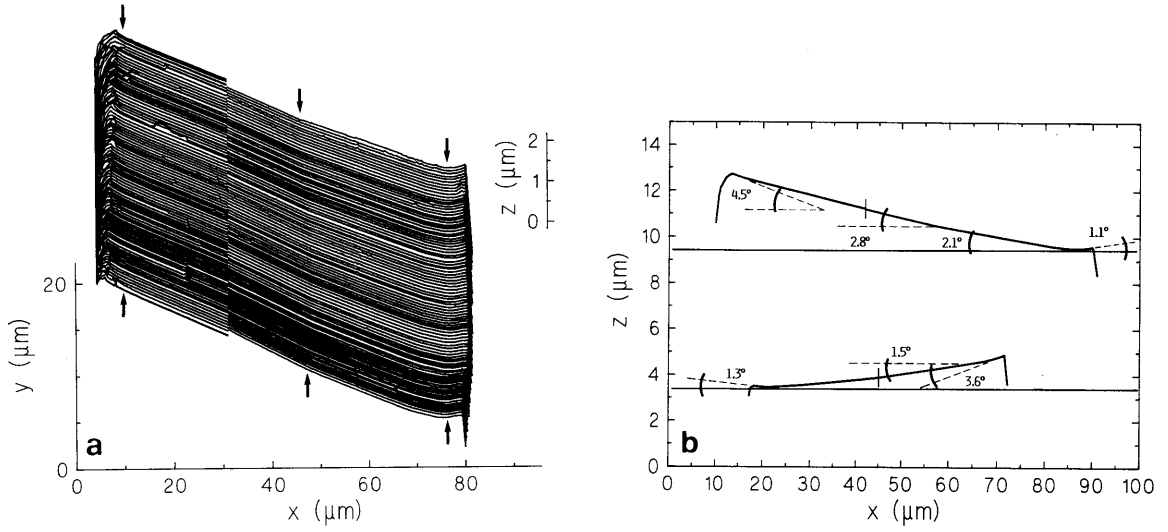

Fig. 2. (a) An edge-to-edge STM plot of the (100) face of the YBCO crystal S46. The changes of slope are indicated by arrows. (b) Profiles of the (100) faces of the crystals S46 (top) and S61 indicating the different slopes with respect to the horizontal lines representing the crystallographic (100) planes. The angles are exaggerated due to the different scales in x and z.

ple of an edge-to-edge STM scan of the (100) surface of crystal S46 is shown in fig. 2a. The slope of the major fraction on the right side of the surface is $2.1° \pm 0.5°$ relative to the (horizontal) crystallographic (100) plane. In the central region this slope changes along a line (indicated by arrows) by $0.7° \pm 0.1°$ to 2.8° from (100). The raised edges are clearly seen: the right-side edge is significantly lower, by about 3 μm, than the left-side edge. The more elevated edge we call the *leading edge*. The average slope of the (100) crystal face is 2.3°.

It is suggested that steps initiate from the (rough) crystal edges and propagate towards the center of the crystal (100) plane. Steps from opposite directions meet in the lowest region of the surface and are "neutralized" here. On this specific crystal this lowest region is near (about 4 μm) to the lower edge. In crystal S46 the leading edge has first a slope of $4.5° \pm 0.5°$, which is reduced at a distance of 4 μm to the slope of 2.8°. Also the lower edge has a width of about 4 μm and an initial slope of 1.1°. Thus the edges can be regarded as two-dimensionally elongated growth hillocks (on solution-grown crystals) which may also abruptly change the slope.

The detailed situation with the various slopes of the (100) crystal faces is shown in fig. 2b which consists of exaggerated height presentations of (100) profiles of crystal S46 (corresponding to fig. 2a) and of crystal S61. In both cases two STM scans were mounted; the link is indicated by a short vertical line. All angles are defined with respect to the crystallographic (100) plane. It is interesting to note that the leading edge had the largest deviation from the crystallographic (100) plane, that the lower edge has the lowest angle, and that there is a regular sequence between these two extremes.

Kossel and Stranski [7,8] established crystal growth on facets by two-dimensional nucleation followed by layer spreading. Burton, Cabrera and Frank [9] could explain growth at low and intermediate supersaturations by spiral growth mechanism. The question now is whether the *leading-edge growth mechanism* can explain facetted crystal growth at very high supersaturation, especially growth of plates and whiskers. Further studies on plates and on tips of whiskers are envisaged in order to evaluate the applicability range of the LEG mechanism.

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