Observation of surface superstructure on $Bi_2Sr_2CaCu_2O_x$ single crystal

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The surfaces of $Bi_2Sr_2CaCu_2O_x$ high-T_c superconducting single crystals have been studied by means of low-temperature scanning tunneling microscopy and low-energy electron diffraction. The crystals were synthesized by directed crystallization. A superstructure has been observed along the *a* direction in the *ab* plane with a period of 2.8–3 nm and with relief variations of 0.1–2 nm.

One of the most obvious structural features of the crystalline bismuth-based superconducting oxide materials is a modulated superstructure. Modulations of the positions of atoms have been observed in experiments by electron diffraction and high-resolution electron microscopy.[1] It was clearly of interest to make use of the powerful new tool of high-resolution microscopy—the scanning tunneling microscope[2]—to study both the structure of this material and its superconducting state. In the present letter we are reporting the results of structural studies of $Bi_2Sr_2CaCu_2O_x$ single-crystal samples carried out by low-temperature scanning tunneling microscopy (STM; the

same abbreviation will be used for the microscope) and by low-energy electron diffraction (LEED).

The samples were single-crystal wafers of the compound $Bi_2Sr_2CaCu_2O_x$ with typical dimensions of $2\times2\times0.02$ mm. They were cleaved from bars grown by float zoning in air.[3] According to micro-x-ray diffraction analysis, the concentration ratios of the Bi, Sr, Ca, and Cu atoms in the samples corresponded to 2:2:1:2. The developed surfaces of the samples had the (001) crystallographic orientation. The crystal lattice was a pseudotetragonal lattice with unit-cell parameters $a = b = 0.542$ nm and $c = 3.075$ nm. The superconducting transition temperature of the samples was measured by an rf inductive method and found to be $T_c = 86$ K ($\pm$ 3K). The critical temperature of the surface regions of the samples was 70 K, determined from the disappearance of the gap features on the tunneling current-voltage characteristics recorded by STM at various temperatures. The samples could easily be divided along *ab* planes. It was thus a rather simple matter to obtain a clean surface, accessible to study by STM, before an experiment.

The STM operated in the "fast mode" of an alternating tunneling current.[4] The tip of the microscope was moved along the surface of the sample at line and frame sweep frequencies of 500 and 5 Hz, respectively, in synchronization with the trace of an oscilloscope which displayed an STM image of the surface. After amplification in a frequency band above the scanning frequencies, the tunneling current from the tungsten tip was fed to the oscilloscope brightness modulator. The measurement cell of the STM was immersed in liquid helium ($T = 4.2$ K) during the experiment.

Figure 1 shows a photograph of the oscilloscope screen. The dimensions of the region shown here are 15×15 nm. (The STM was calibrated on the basis of the image

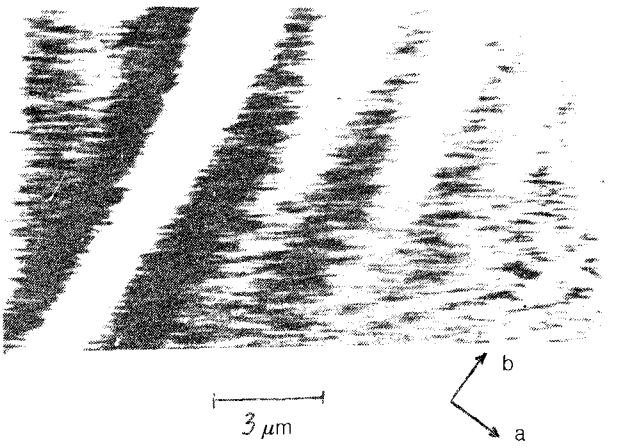

FIG. 1. Scanning-tunneling-microscope image of the surface of a $Bi_2Sr_2CaCu_2O_x$ single crystal cleaved along the *ab* plane (this is a photograph of an oscilloscope screen). The change in brightness from black to white corresponds to 0.2 nm in the vertical direction. The voltage on the STM tip was $V = 200$ mV; the temperature was $T = 4.2$ K.

of the crystal lattice of pyrographite at $T = 4.2$ K.) In Fig. 1 we see bands alternating at a period of 2.8–3.0 nm which correspond to the spatial distribution of the electron state density. The voltage on the microscope tip, $V = 200$ mV, was substantially higher than the voltage corresponding to the energy of the superconducting gap, < 20 mV. (Under the condition $V < 200$ mV, we were not able to obtain a stable STM image.) It can thus be asserted that the bands observed here are a consequence of structural features of the crystal lattice of the sample, rather than of its superconducting properties. A similar superstructure was observed by Kirk *et al.*[5] at room temperature on STM images of BiO planes of ultrahigh-vacuum cleaved faces of $Bi_2Sr_2CaCu_2O_x$ samples grown from the melt.

The samples on which we observed superstructure by means of STM were studied by LEED on an Éskalab-5 electron spectrometer in the temperature range 20–30 K. The surfaces of the $Bi_2Sr_2CaCu_2O_x$ samples were prepared for this study in two ways: 1) cleavage in air followed by annealing at $T = 450$–600 C in the analysis chamber of the spectrometer in a vacuum of 10 Torr; 2) *in situ* cleavage in the analysis chamber of the spectrometer. The chemical compositions of the surfaces prepared by these two methods were analyzed by Auger spectroscopy and were found to be approximately the same. In the LEED study of the surfaces we found clearly defined diffraction patterns (Fig. 2), which corresponded to a modulated superstructure of the $Bi_2Sr_2CaCu_2O_x$ (001) (5×1) type; similar modulated structures were observed in Ref. 6 in a study of $Bi_2Sr_2CaCu_2O_x$ by high-resolution electron microscopy. When we varied the cleavage temperature, and also when we scanned the temperature of the $Bi_2Sr_2CaCu_2O_x$ samples over the range 20–300 K, we found no changes in the diffraction patterns. Repeated heating of the samples to $T \sim 1000$ K again caused no changes in the diffraction patterns and thus no changes in the superstructure on the $Bi_2Sr_2CaCu_2O_x$ (001) surface.

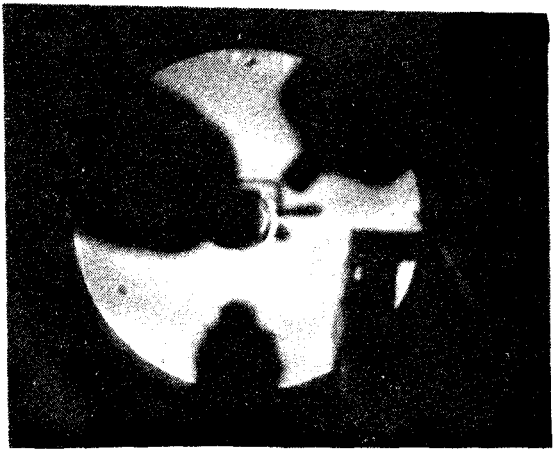

FIG. 2. Electron diffraction pattern from a cleaved surface of a $Bi_2Sr_2CaCu_2O_x$ single crystal (this photograph was taken through a window in the spectrometer chamber). The rows of bright spots on the phosphor were formed by reflections with satellites which arose because of the modulated superstructure.

In summary, the STM studies and also the LEED studies demonstrated that there is a superstructure with a period of 2.8–3 nm on the developed surfaces of $Bi_2Sr_2CaCu_2O_x$ single crystals synthesized by float zoning. The STM measurements demonstrate periodic protuberances of BiO planes, 0.1 nm high. (The samples were divided along specifically these planes.[5]) The appearance of a superstructure of this sort can be linked with a slight excess of Bi atoms over their stoichiometric concentration.[5] The "extra" Bi atoms can occupy Sr or Ca positions; their ordering leads to the formation of a superstructure.

In principle, low-temperature STM is a unique tool for studying the three-dimensional microstructure of the superconducting state.[7] For such studies, the tunneling should be carried out under the condition $eV < \Delta$, where Δ is the energy gap of the superconductor. In the present experiments, unfortunately, we were not able to obtain a stable, reproducible STM image under this conditon, i.e., at $V < 20$ mV. The reason may have been noise which arose upon switching of the tunneling current paths. Switching noise could apparently be eliminated by carefully choosing the working point of the STM on the current-voltage characteristic of the tunneling gap, which has several structural features at $V < 20$ mV.

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