HREM Surface Profile Images of Bi$_2$Sr$_2$CaCu$_2$O$_8$

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Surface profile images of Bi$_2$Sr$_2$CaCu$_2$O$_8$ have been obtained using high-resolution electron microscopy. The cleaved (001) surface of the crystals terminates with a single Bi-O atomic layer. The modulated structure developed in this surface atomic layer was observed directly. The (hk0) surfaces were found to decompose in air into an amorphous coating layer. This coating layer was unlikely recrystallized into the original structure under electron beam irradiation. The amorphous layer on the (hk0) surface formed in pure Ar atmosphere was relatively thin and could be recrystallized into some secondary phases in which a Bi loss was observed. The original (001) surface might also be covered by an amorphous-like layer. This disordered layer could be recrystallized under electron beam irradiation into BiSr$_2$Ca$_2$Cu$_3$O$_{y}$, BiSr$_2$CuO$_3$, etc. which intergrow with the parent crystal perfectly on the (001) planes.

KEY WORDS: Superconductor; Bi$_2$Sr$_2$CaCu$_2$O$_8$; surface structure; electron microscopy.

1. INTRODUCTION

In comparison with other high-$T_c$ superconducting oxides, surface investigation of Bi$_{2}$Sr$_{2}$Ca$_{n-1}$Cu$_n$O$_{2n+6}$ by scanning tunnelling microscopy (STM) is relatively easier, since the crystals of these materials are usually cleaved in between two Bi-O layers and a large flat (001) surface terminating on the single Bi-O atomic plane can be obtained. In addition, cleaning such surface is not too difficult due to the chemical stability of the single Bi-O atomic plane. Consequently, high-quality STM images showing Bi atomic arrangement on the (001) surface have been reported previously [1–4]. Nevertheless, STM studies on other surfaces of these materials are still difficult.

STM gives us a direct image of the topmost surface atomic layer of a solid-state compound. However, information of the underlying structure cannot be revealed by this technique. On the other hand, high-resolution electron microscopy (HREM) has been developed in the last 15 years to enable us to obtain surface profile images of metal oxide crystals at atomic resolution and the near surface structures of the crystals can be studied simultaneously. Using this technique, the surface chemistry of many high-$T_c$ superconducting oxides have been investigated [5–9]. Amorphous coating, reconstruction, recrystallization, formation of secondary phase etc. on the surfaces of the crystals were often observed.

The (001) surface of the Bi$_2$Sr$_2$CaCu$_2$O$_8$ crystals with the single Bi-O atomic layer as the terminal plane was also observed previously by HREM [10]. The results were in agreement with the STM observations. No surface reconstruction nor secondary phases was detected. This is not surprising because, to prepare the specimen for the HREM studies, the specimen is usually crushed into wedge-shaped small crystals, or ion thinning technique is applied to pare the crystals to create thin edges. Therefore, almost of all the surfaces observed were not original but created during the specimen pretreatment.

With respect to the relationship between the surface structures and the superconducting properties, information on the surface structures of superconducting oxides is essential. In this report, the surface chemistry of Bi$_2$Sr$_2$CaCu$_2$O$_8$ is discussed based on the examination of HREM profile images of the original surfaces as well as the cleaved surfaces formed in air and in Ar.
2. EXPERIMENTAL

Sample preparation conditions for Bi$_2$Sr$_2$Ca$_x$Cu$_2$O$_y$ were similar to those described in a previous report [11]. The polycrystalline specimen was prepared by solid-state reaction of Bi$_2$O$_3$, CaCO$_3$, SrO$_2$/Sr(NO$_3$)$_2$, and CuO in appropriate proportions at 800°C in air for 20 h followed by quenching to room temperature. Initial characterization of the specimen was by X-ray powder diffraction and the structure was determined to be pseudotetragonal with the unit cell parameters $a = 5.4$ and $c = 30.7$ Å. The produced specimen was also tested for superconductivity and a $T_c$ value of 83 K was detected.

For the HREM studies, the first specimen (sample A) was prepared by grinding the synthesized powder in an agate mortar and pestle in air. The dry powder was spread on a copper grid coated with a holey carbon film before being transferred into a Jeol JEM-200CX electron microscope. Instead of grinding in air for sample A, the second specimen (sample B) was prepared by carefully pressing the synthesized powder in Ar atmosphere in a glove box. The dry powder was spread on a grid also coated with a holey carbon film. The grid was then transferred into the microscopic vacuum system by means of an specially designed air-lock specimen holder.

HREM images were obtained from the electron microscope operating at 200 kV with a modified specimen stage [12] with objective lens parameters $C_1 = 0.41$ mm and $C_2 = 0.95$ mm, giving an interpretable point resolution of about 1.85 Å. The vacuum in the microscope was maintained at around $2 \times 10^{-7}$ Torr. Beam current was set at 10–20 μA and screen brightness was in the range 10–50 Pa cm$^{-2}$. Computer image simulation was according to the multislice method [13,14] using the CERIUS HRTEM program developed by Cambridge Molecular Design Ltd.

3. RESULTS AND DISCUSSION

The crystals of sample A were crushed into very small fragments, which were well spread on the specimen grid. Therefore, most surfaces observed were freshly created just before the HREM examination. In sample B, however, most crystals were expected to be still stuck together, a large amount of the original surfaces of the as-prepared crystals being therefore maintained. Although the area where many crystals overlapped each other along the electron beam direction was not suitable for the HREM studies, high-resolution images could be obtained from single crystals with various orientations on the edge of a cluster of the crystals.

Like all other two-dimensional superconducting oxides, the most interesting profile images of Bi$_2$Sr$_2$CaCu$_2$O$_y$ are those projected along the [001] and (hk0) zone axes, from which different atomic layers can be observed clearly along the $c$ direction. Figure 1 shows HREM images from sample A viewed down the [110] and [100] directions respectively. The crystal shown in Fig. 1a is only a single $c$ lattice vector thick and that in Fig. 1b 1.5$c$ lattice vector thick. Computer image simulations were then performed, and it was confirmed that both the top and bottom (001) surfaces of the crystals terminated with a single Bi-O atomic layer without further coating of a secondary phase. The (001) surface was relatively clean and stable under the electron beam irradiation.

In comparison with other high-$T_c$ superconductors, a very distinctive characteristic of the Bi-containing materials is the existence of incommensurate superstructures, often called modulated structures, along the [010] directions. This type of superstructure appears to be developed in the Bi–O layer as detected by low-energy electron diffraction (LEED) [15] and STM [1–4] from Bi$_2$Sr$_2$CaCu$_2$O$_y$. Two models have been proposed previously to describe the origin of the incommensurate superstructure. The first model contains some missing Bi–O rows parallel to the $a$ axis in the double Bi–O layers, the remaining atoms in these layers displacing in both the $a$ and $c$ directions [1,2]. The second model contains wavy Bi–O layers without any missing atomic rows, and some Bi atoms are depressed along the $c$ axis. According to Ting et al.’s STM observations [3], the average depression of the atoms was 0.015 nm with the largest value of 0.034 nm. The mechanism of formation of this depressed Bi–O layers is still not well established. Zandbergen et al. [16] believed that there were extra oxygen atoms in the double Bi–O layers, which resulted in the displacement of the Bi atoms.

In the HREM images, the superstructure cannot be observed when viewed down the [110] direction (Fig. 1a), since the modulated structure is only developed along the [010] direction. Although the displacement of the Bi atoms along the $c$ axis must result in some degree of enlargement of the dark spots corresponding to the Bi columns in the structural image, this effect seems to be not significant. However, when viewed down the [100] zone axis (Fig. 1b), a wavy pattern of the image contrast can be observed at the positions of the Bi–O atomic planes both inside the