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A TEM Study of Microstructures of Ultrathin $YBa_2Cu_3O_7$ Films on $SrTiO_3$ (100) and MgO (100)

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We have examined microstructures of the growth interface in ultrathin $YBa_2Cu_3O_7$ (YBCO) (001) films on $SrTiO_3$ (100) and MgO (100) substrates. On both substrates, YBCO films are completely *c*-axis oriented, and surface is flat within ± one unit cell thickness. On $SrTiO_3$ the atomic stacking sequence is usually SrO-TiO_2-BaO-CuO_2-Y-CuO_2-BaO-CuO. In contrast, on the MgO substrate various sequences appear, because there are many narrow steps on the substrate. On both substrates the influence of steps tends to disappear even in the first unit cell layer. The surface structure of YBCO is same on both substrates: the film is always terminated by the BaO-CuO_2-Y-CuO_2-BaO-CuO sequence.

KEY WORDS: Transmission electron microscopy (TEM)/ $YBa_2Cu_3O_7$/ Ultrathin film/ Interface/ Terminating layer

INTRODUCTION

Recently, ultrathin films[1] and superlattices[2-4] of high-T_c oxides, especially $YBa_2Cu_3O_7$ based systems have attracted much attentions. When we discuss the superconductivity in the ultrathin layers, it is of essential importance to understand the microstructures of the films on atomic scales. From the observation of reflection high-energy electron diffraction (RHEED) intensity oscillations, we have found that YBCO is grown by two-dimensional (2D) unit cell-by-unit cell growth mode.[5] The 2D growth mode implies that the growth unit should have the same stacking sequence of atomic layers, and therefore the terminating layer in the growth unit should always be the same.

Figure 1 shows a schematic diagram of the unit cell of YBCO. YBCO consists of six atomic layers. Initial stage of the epitaxial growth and interface atomic layer would be affected by the surface state of the substrate, especially, atomic species of the terminating layer of the substrate. We have used two kinds of substrates; one is $SrTiO_3$ (100) which has a perovskite structure with a lattice misfit of ~2%, and the other is MgO (100) which has a NaCl structure with a lattice misfit of ~9%.

In this paper we report the results of the transmission electron microscope (TEM) observation for the ultrathin YBCO films. We will, especially, focus on the stacking sequence of atomic layers at the interface and surface regions.

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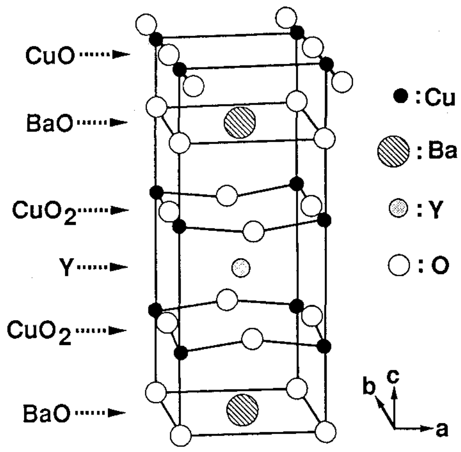


Fig. 1. Schematic diagram of the crystal structure of $YBa_2Cu_3O_7$.

EXPERIMENTAL

c-axis oriented ultrathin YBCO films were grown by reactive evaporation.[6] The typical deposition conditions were the following: The substrate were $SrTiO_3$ (100) and MgO (100). MgO was etched by HNO_3/ethanol. The substrate temperature was 680°C and the deposition rate was 0.5Å/s. The thickness of YBCO films were 120 – 140Å (10 – 12 unit cells). The ultrathin YBCO films were covered with Y_2O_3 or La_2CuO_4 for protecting the surface.

The cross-sectional TEM specimens were produced by gluing two films face to face, followed by slicing, polishing, dimpling and argon ion-milling in liquid nitrogen cooled stage. We have made a special care to avoid irradiation damage during ion-milling by milling at low angles and low voltage for last several hours. The TEM experiments were carried out using JEOL 2000EX electron microscope operated at 200 kV.

RESULTS AND DISCUSSION

$SrTiO_3$ (100) substrate

Figure 2 (a) shows a high-resolution TEM image of La_2CuO_4/YBCO (120Å) film on the $SrTiO_3$ (100) substrate. The image reveals that YBCO film is completely *c*-axis oriented and the surface is flat within ± one unit cell thickness. A step can be seen at the marked position. Figure 2 (b) is an enlargement of the marked area in Fig. 2 (a). Height of surface steps on the $SrTiO_3$ (100) substrate is found to be one unit cell (3.9Å). The one-unit-cell high steps have been also found by the recent scanning tunneling microscope (STM) observation.[7]

Ramesh *et al.*[8] have reported the formation of *c*/3 (two atomic layer) translational boundary due to the presence of unit-cell high steps on the substrate surface. In this case, interface atomic layer of YBCO is the same everywhere. Figure 2 (b), however, shows that each atomic layer of YBCO is continuous in *a*-*b* plane even in the first unit-cell layer.

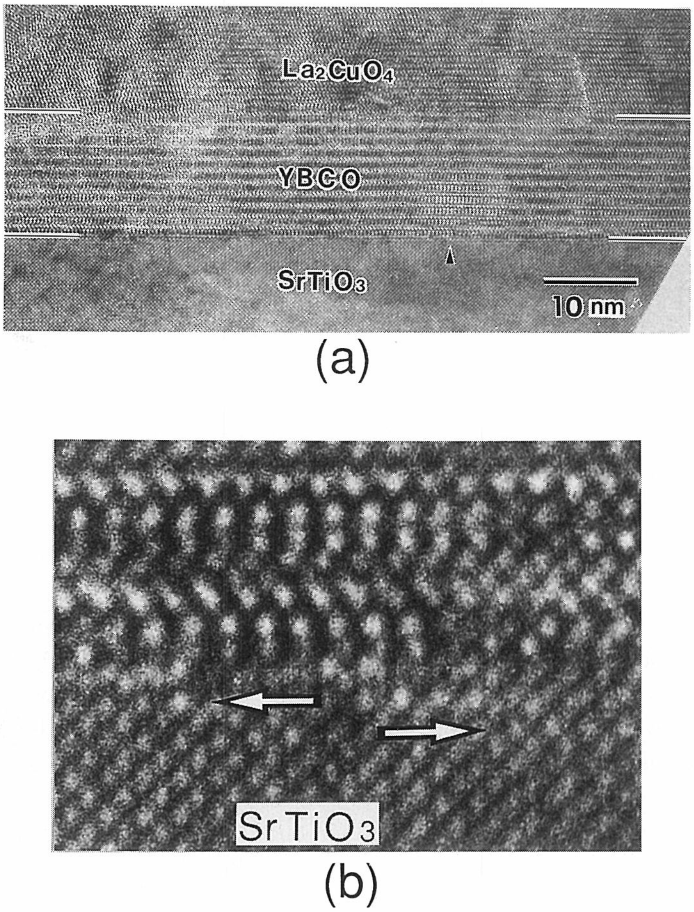
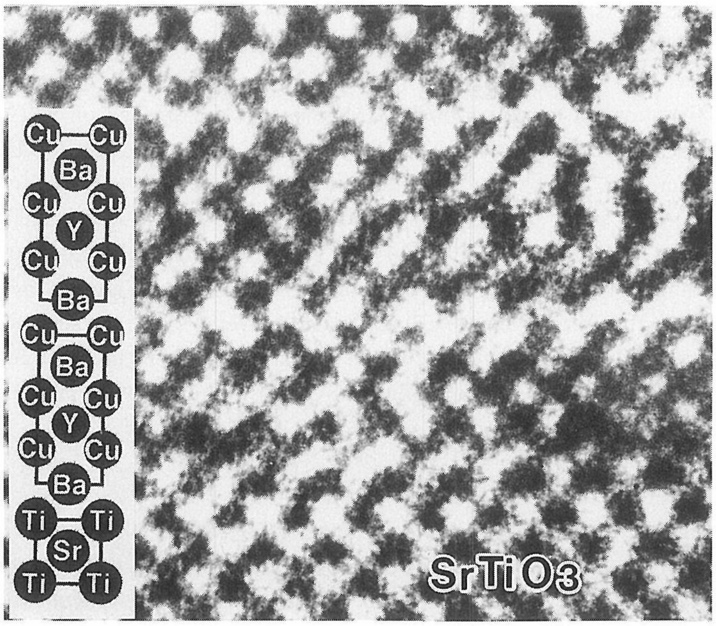


Fig. 2. (a) High-resolution TEM image of a YBCO (120Å) film on the $SrTiO_3$ (100) substrate. One-unit-cell high step is shown by a marker. (b) Enlargement of the marked area shown in (a). The arrows indicate the $SrTiO_3$ surface.

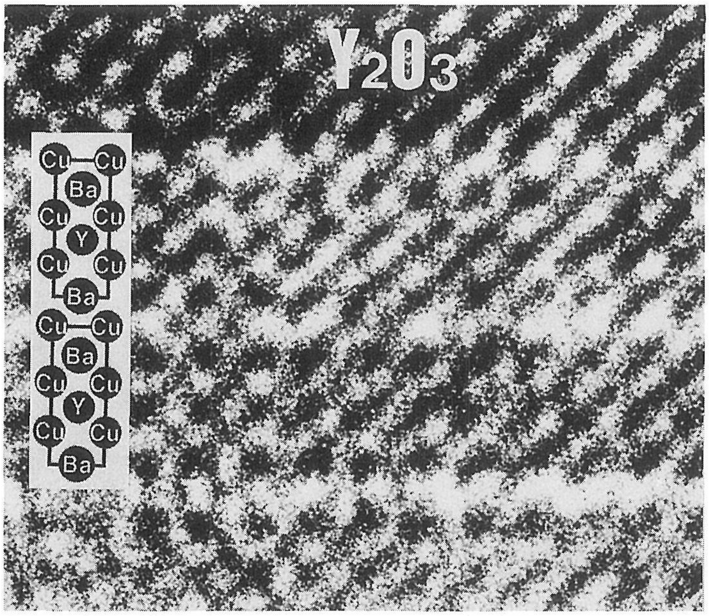
This result means that interface atomic layers of YBCO on $SrTiO_3$ substrate are different on both sides around the step. The growth with the translational boundary has never been observed in our observation. The difference in the growth manner may be caused by the difference of the deposition conditions.

As YBCO has a pseudo-perovskite structure and the lattice mismatch between YBCO and $SrTiO_3$ is rather small (2.1% and 0.5% for *a* and *b* directions, respectively), interface layer of YBCO would be determined by atomic species of the substrate surface. Terminating atomic layer of $SrTiO_3$ substrate is revealed to be dominantly TiO_2 layer by angular dependence of the intensity ratio of Sr 3p and Ti 2p in the X-ray photoelectron spectroscopy.[9)]

Figure 3 (a) shows a cross-sectional high-resolution TEM image at the YBCO/$SrTiO_3$ interface where the first unit cell layer has a complete 1:2:3 structure. The stacking se-



(a)



(b)

Fig. 3. (a) Atomic-resolution TEM image of the YBCO/$SrTiO_3$ interface. (b) Atomic-resolution image of the Y_2O_3/YBCO interface.

quence of atomic layers can be determined to be SrO-TiO_2-BaO-CuO_2-Y-CuO_2-BaO-CuO. This stacking sequence implies that the terminating layer of YBCO grown on $SrTiO_3$ is CuO chain layer.

Figure 3 (b) shows a cross-sectional TEM image at the surface of YBCO film. The surface of YBCO was covered with Y_2O_3 in order to protect the surface layer from the damage by ion-milling. Since Y_2O_3 protection layer was deposited on YBCO at a substrate temperature of about 600°C, YBCO and Y_2O_3 have following epitaxial relationship: YBCO [001] // Y_2O_3 [001] and YBCO [100] or [010] // Y_2O_3 [110]. Distinct contrast between YBCO and Y_2O_3 enables us to determine the terminating atomic layer of YBCO. The image reveals that the terminating layer is CuO layer. The results in Figs. 3 (a) and (b) clearly show that the stacking sequence of the growth unit in the unit cell-by-unit cell growth of YBCO is BaO-CuO_2-Y-CuO_2-BaO-CuO and the terminating layer of YBCO film is CuO layer.

MgO (100) substrate

Figure 4 shows a low-magnification image of YBCO (140Å) film grown on MgO (100) substrate. Since the lattice misfit between YBCO and MgO in the *a-b* plane is ~9%, YBCO is grown by island mechanism in the initial stage of the growth and the islands coalesce after the growth of 4 unit cells.[10] The image in Fig. 4 shows that the YBCO film with 140Å on MgO (100) has a continuous structure and good smoothness.

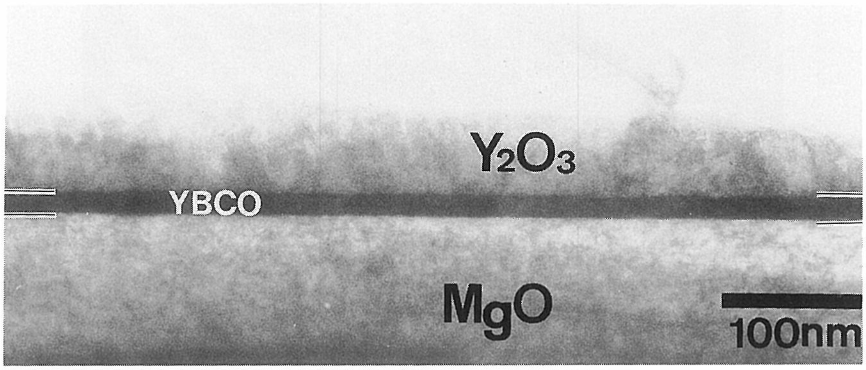
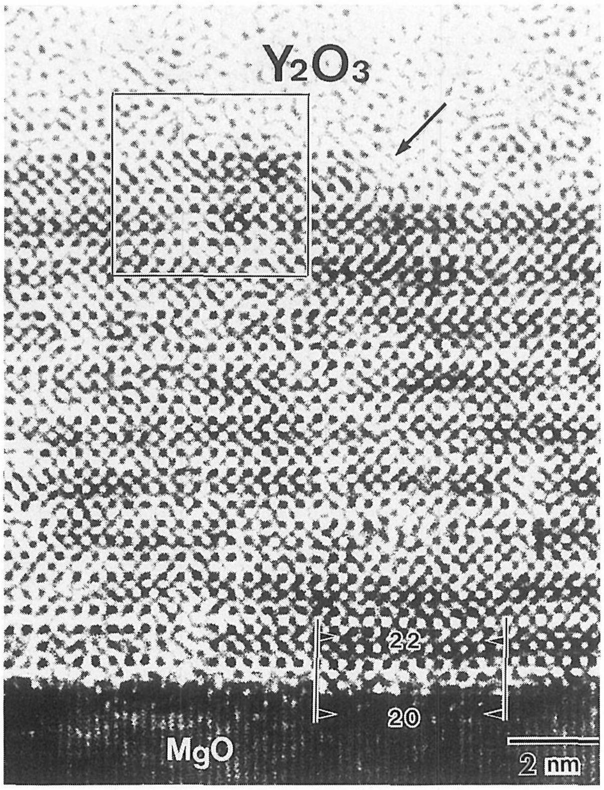


Fig. 4. Low-magnification TEM image of a YBCO (140Å) film on the MgO (100) substrate.

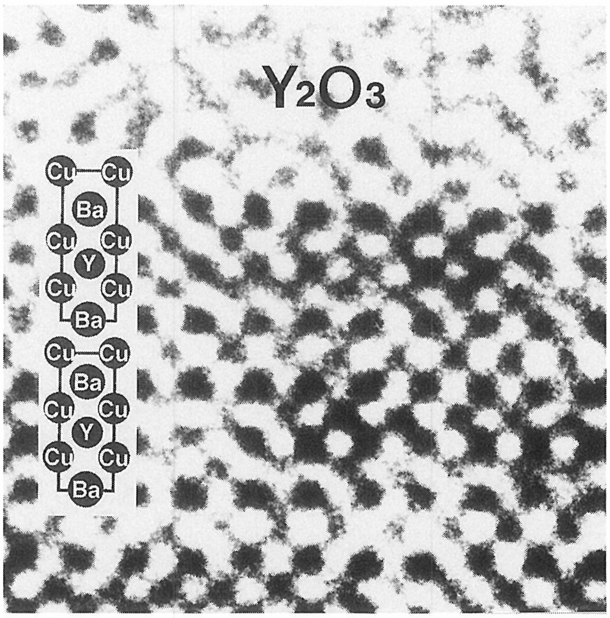
Figure 5 (a) is a high-resolution TEM image of the YBCO (120Å) film on MgO substrate. As Y_2O_3 protection layer was deposited on the YBCO at room temperature, Y_2O_3 layer consists of amorphous and polycrystals. Many narrow steps are seen on MgO substrate. In contrast to the result on the $SrTiO_3$, there is not a definite interface layer due to the various height of the steps. The influence of steps, however, tends to disappear and each atomic layer of YBCO is continuous even in the first unit cell layer.

The misfit between the YBCO and MgO in the *a-b* plane would be accommodated by the introduction of the interfacial dislocation. The lattice misfit of ~9% corresponds to an



(a)

interfacial dislocation spacing of about 10 atomic layers. Counting the number of atomic layers in the film and substrate within the marked region in Fig. 5 (a) shows that the spacing of 20 layers in the MgO substrate is in agreement with that of 22 layers in the YBCO film. Since this dislocation occurs between the first atomic layer of YBCO and MgO surface, YBCO with 10-unit-cells thick has original lattice constants of *a,b*-axis from the first unit cell layer. There is a step on YBCO surface corresponding to one unit cell height of YBCO (marked by arrow in the figure). This result also provides an evidence for the unit cell-by-unit cell growth. Figure 5 (b) shows an enlargement of YBCO surface area in Fig. 5 (a). It is also confirmed that the terminating layer of YBCO on MgO (100) substrate is CuO layer.



(b)

Fig. 5. (a) High-resolution TEM image of a YBCO (120Å) film on the MgO (100) substrate. The arrow shows a unit-cell-high step (12Å) on the YBCO surface. (b) Enlargement of the YBCO surface area. Inset: Stacking sequence of the atomic layers in YBCO.

CONCLUSION

The microstructures of the growth interface in ultrathin YBCO films deposited on $SrTiO_3$ (100) and MgO (100) substrate have been studied by TEM. There are one-unit-cell high steps on $SrTiO_3$ substrate surface. It has been found that only one-unit-cell layer of YBCO is enough to accommodate for the steps by introducing additional atomic layers. On the $SrTiO_3$ substrate the atomic stacking sequence is usually SrO-TiO_2-BaO-CuO_2-Y-CuO_2-BaO-CuO.

In contrast, on the MgO substrate, various sequences appear because there are many narrow steps on the substrate. The influence of steps, however, tends to disappear even in the first unit cell layer. The terminating atomic layers of YBCO films are found to be CuO layer for both substrates.

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