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Bulk and surface structure of epitaxial $YBa_2Cu_3O_{7-\delta}$ thin films grown on Mg_2TiO_4 (001) substrate layers

Part II. Orientation and surface structure

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Abstract

Thin films of $YBa_2Cu_3O_{7-\delta}$ (YBCO) have been grown on Mg_2TiO_4 substrate layers by pulsed laser deposition. The substrate temperature T_s has been varied between 600 and 800°C in order to optimize the YBCO film growth. All samples were characterized by means of X-ray diffraction, scanning electron microscopy (SEM) and scanning tunneling microscopy (STM). We have found an optimum T_s in the range of 675-700°C where the YBCO thin films show perfect (001) orientation. SEM and STM reveal that the (001) oriented YBCO films have very flat surfaces. STM shows a large number of spiral growth hills and steps of unit cell height. These films exhibit a superconducting transition temperature T_c(onset) at 88.5 K and a zero resistance at 86.5 K. Films grown at lower substrate temperatures show no (001) orientation, but (100) and (110)/(103) orientations. At higher T_s additional (100) oriented grains occur.

1. Introduction

Since the discovery of high-temperature superconductors (HTSC) [1] many efforts have been made to optimize thin film growth of these materials. Namely $YBa_2Cu_3O_{7-\delta}$ (YBCO) – being the most investigated HTSC compound – has been grown as high quality thin films on various substrate materials.

In the last years not only the deposition processes but also the substrate materials have been optimized. However, single-crystal substrates having a small lattice mismatch to YBCO are rather expensive.

For industrial applications it is important to find a compromise between cost and perfection of the substrate materials used. Therefore it is very interesting to study low-cost substrates such as MgO. Unfortunately MgO reacts with the ambient forming hydroxide and carbonate. In order to preserve the advantages of MgO it is necessary to cover the MgO surface with a protection or buffer layer, such as Mg_2TiO_4 [2]. Therefore, studying buffer layers is an important task with respect to future HTSC device fabrication.

We have used Mg_2TiO_4 buffer layers as substrates for thin film growth of YBCO by pulsed laser deposition. The effect of the substrate temperature on the orientation and surface morphology of YBCO thin films has been studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM) and scanning tunneling microscopy (STM), respectively. A series of YBCO films has been prepared at substrate temperatures of 600 up to 800°C.

2. Experimental

Mg_2TiO_4 substrate layers were grown on cleaved as well as on polished MgO single crystals by a topotaxial solid-state reaction [3]. Using transmission electron microscopy and selected area electron diffraction it was shown that the Mg_2TiO_4 substrate layers were grown in perfect epitaxy.

2.1. Thin-film growth

YBCO thin films were prepared by pulsed laser deposition [4] using a KrF excimer laser (λ=248nm, 1.2 J/shot) running at a repetition rate of 8 Hz. The laser beam was focused to an energy density of 2.5 J/cm^2 onto a stoichiometric high density YBCO pellet which was rotated to ensure continuous ablation. Mg_2TiO_4/MgO substrates were mounted onto a heater block at a distance of 7.5 cm to the YBCO target. With this experimental setup growth rates of about 0.4 nm/s were realized.

The substrate temperature was measured using a pyrometer (λ=960nm) aligned at an angle of 45° to the substrate surface. A chromel-alumel thermocou-

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ple embedded into the heater block was used as a sensor for the computer controlled feedback loop of the heating system. All temperatures above 600°C were determined by pyrometer.

Prior to YBCO evaporation the substrates were preheated in vacuum (10^{-4} Pa) at 800°C for 10 min and then equilibrated to the substrate temperature T_s. After introducing 27 Pa oxygen into the preparation chamber, YBCO was deposited to a film thickness of about 150 nm. Following the deposition the sample was cooled in 10^5 Pa oxygen to 600°C at a cooling rate of 4 K/min, then annealed at 500°C for 30 min and finally cooled down to room temperature.

2.2. Film orientation

The orientation of the YBCO thin films was determined by means of XRD using Cu K_α radiation. Conventional Bragg-Brentano (Θ-2Θ) XRD was performed on each sample in order to determine the crystallographic orientation. The distribution of grain rock (mosaic spread) was determined by Θ-scans of the YBCO(006) reflection.

2.3. Surface morphology

The surface morphology was investigated by STM. It has been shown that STM is an appropriate method to image the surface structure from the microscopic to the atomic scale [5-7]. The YBCO films were examined in ambient air at room temperature. STM images were taken in constant current mode applying a tip bias voltage of +800 mV and a tunneling current of 300 pA. Using several different mechanically prepared $Pt_{90}Ir_{10}$ tips for every sample tip-geometry induced artifacts could be widely excluded. Roughness was given by the maximum height differences (peak-to-valley value) determined by STM line sections.

For comparison with STM the YBCO film surfaces were also imaged by means of SEM.

3. Results and discussion

3.1. Film orientation in dependence on T_s

Figure 1(a) shows the XRD data for the YBCO(006) and (200) reflections. The YBCO film deposited at T_s=675°C (denoted as Y-675 in fig. 1(a)) exhibits (001) orientation (demonstrated by the YBCO(006) reflection). YBCO films deposited at T_s=600°C show no (001) orientation, but (100) and (110)/(103) orientations. At T_s above 700°C, e.g. at T_s=725°C (see curve labeled Y-725 in fig. 1(a)) additionally the (100) orientation appears demonstrated by the YBCO(200) reflection.

Mosaic spread (YBCO(006) reflection) of the YBCO film deposited onto Mg_2TiO_4/MgO(cleaved) at T_s=675°C (dashed curve in fig. 1(b)) exhibits a full width at half maximum (FWHM) of about 2° whereas the YBCO film grown on Mg_2TiO_4/MgO(polished) under the same conditions shows a lower FWHM of about 1° (solid curve in fig. 1(b)).

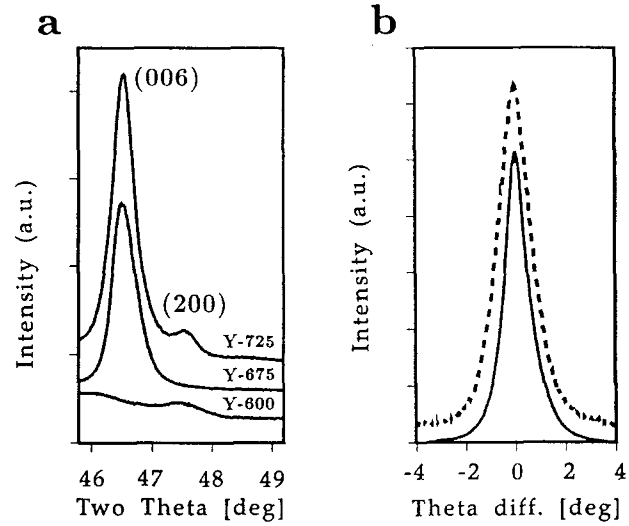

Figure 1. (a) Θ-2Θ X-ray scans showing the YBCO(006) peak for laser deposited films as a function of substrate temperature. (b) Mosaic spread for YBCO(006) reflection indicating a FWHM of about 2° for YBCO grown on Mg_2TiO_4/MgO(cleaved) (dashed curve) and about 1° for YBCO grown on Mg_2TiO_4/MgO(polished) (solid curve).

3.2. Surface structure in dependence on T_s

Figure 2 shows STM images of YBCO thin films grown at different substrate temperatures, *viz.* 600, 625, 650, 675, 700 and 725°C, respectively.

Figure 2(a) shows the surface of a YBCO film grown at 600°C indicating typical growth structures for (100) and (110)/(103) orientations. The slab-like grains are attributed to (100) growth, whereas the platelet structures are assigned to (110)/(103) growth. The SEM image (fig. 3(a)) of the same YBCO film shows similar surface features but with inferior vertical resolution.

When T_s is increased to T_s=625°C the YBCO films are grown in (001) orientation. Figure 2(b) shows numerous (001) oriented spiral growth hills (about $10^{10}/cm^2$) originating from screw dislocations. The step heights were determined to be one unit cell spacing in crystallographic [001] direction, i.e. 1.17 nm. Due to the large number of screw dislocations some grains are tilted (marked by arrows in fig. 2(b)).

YBCO thin films deposited at T_s=650°C show less spiral growth hills (about $6\times10^9/cm^2$) having diameters of about 100 nm (fig. 2(c)).

The morphology of films grown at T_s=675°C is

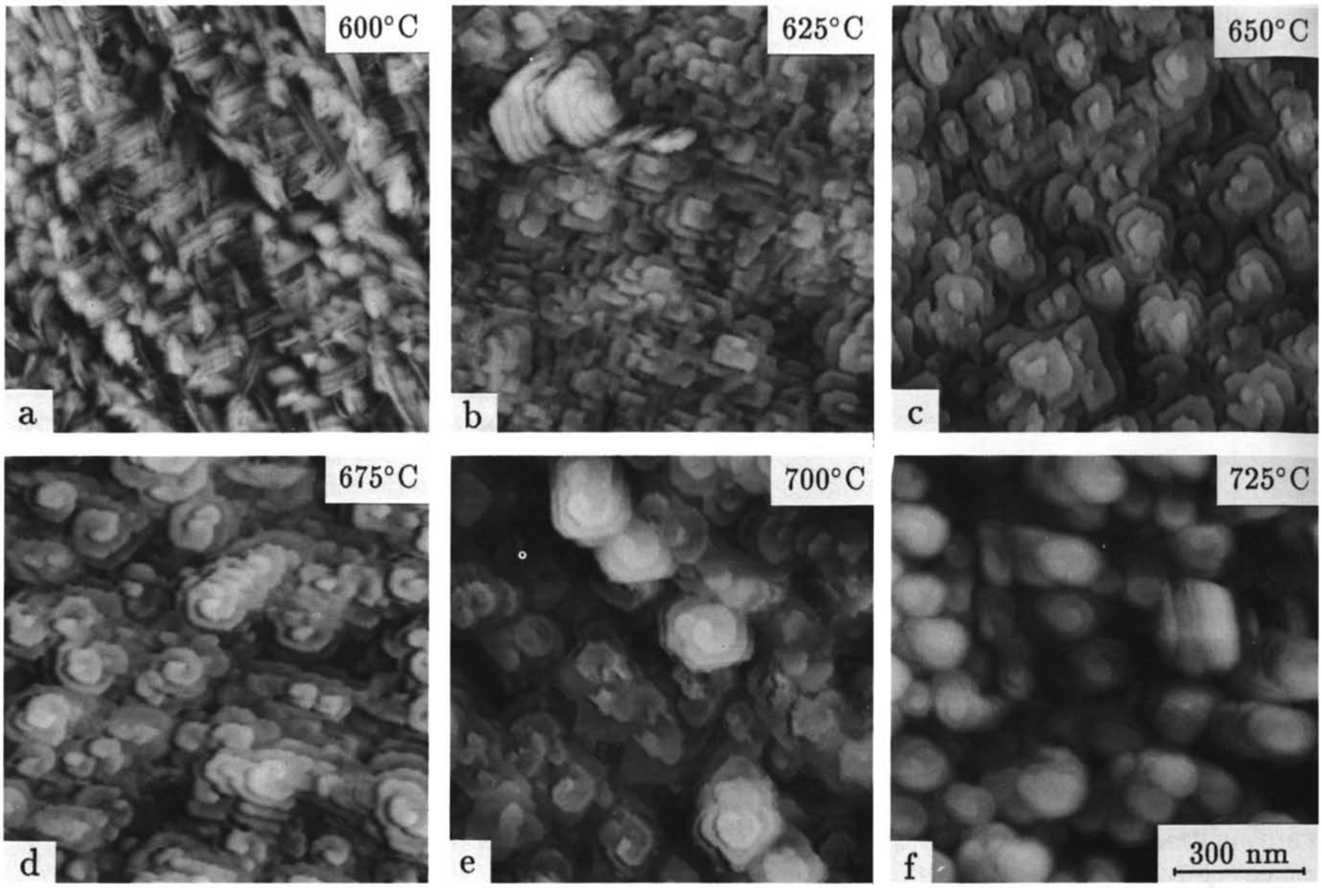

Figure 2. STM images of YBCO thin films laser deposited at different substrate temperatures: (a) 600°C, (b) 625°C, (c) 650°C, (d) 675°C, (e) 700°C and (f) 725°C. The z-scale is for (a) 50 nm, (b)–(e) 15 nm, (f) 50 nm respectively.

dominated by spiral growth hills with larger diameter. The roughness of the samples grown between 625 and 675°C is less than 15 nm.

SEM images (fig. 3(b)) show a smooth film surface. At higher substrate temperatures, i.e. at 700°C, the average terrace width as well as the roughness increases (see fig. 2(e)).

The YBCO film shown in fig. 2(f) was prepared at 725°C. It shows a higher roughness, typically 30 nm, and additionally (100) oriented grains (marked by an

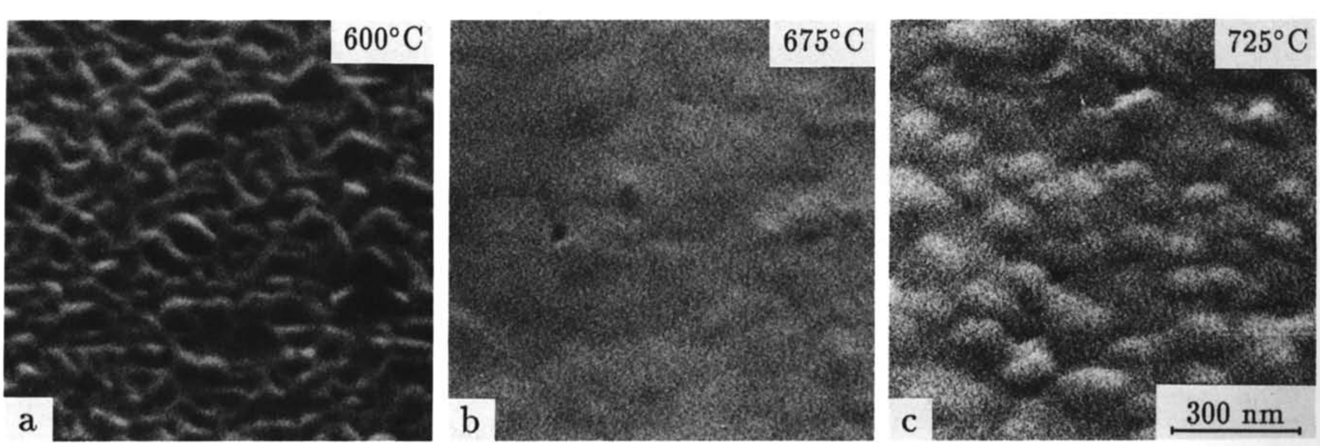

Figure 3. SEM images of YBCO thin films deposited at substrate temperatures of: (a) 600°C, (b) 675°C and (c) 725°C.

arrow in fig. 2(f)) are observed. The higher roughness can also be seen in the SEM image in fig. 3(c) revealing a grainy surface structure.

3.3. Electrical properties

Transition temperatures of the YBCO thin films have been measured resistively using a standard DC four probe method. Films grown at 675 °C have transition temperatures T_c (onset) up to 88.5 K and T_c (R=0) of 86.5 K.

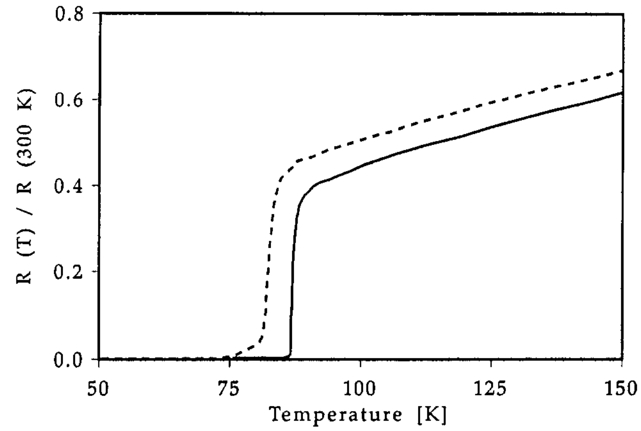

Figure 4. Temperature dependence of resistivity for YBCO thin films on Mg_2TiO_4/MgO(polished) (solid line) and on Mg_2TiO_4/MgO(cleaved) (dashed line).

YBCO films grown on Mg_2TiO_4/MgO(cleaved) have lower T_c(onset) (about 85 K) than films grown on Mg_2TiO_4/MgO(polished). In fig. 4 resistivity vs. temperature of these samples was plotted.

The rather low value of YBCO films on Mg_2TiO_4/MgO(cleaved) may be caused by high cleavage steps on the MgO(001) faces as shown by a SEM image in fig. 5.

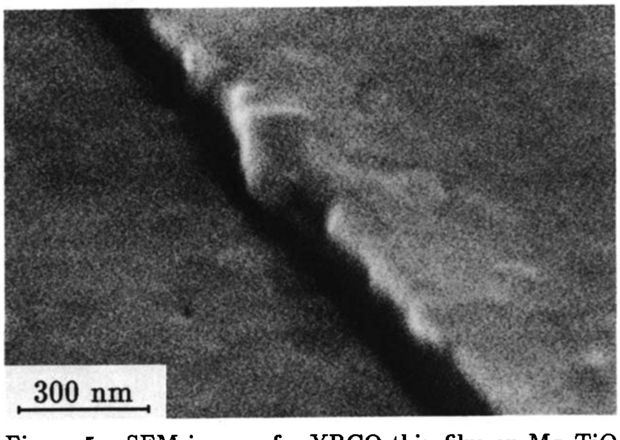

Figure 5. SEM image of a YBCO thin film on Mg_2TiO_4 which was grown on a cleaved MgO (001) face.

Maximum step heights determined by STM were found to be 200 nm which is comparable to the YBCO film thickness of about 150 nm. Therefore it will be necessary to examine the film growth of YBCO close to the edges of the cleavage steps.

4. Conclusion

In summary, we have studied the growth of YBCO films on novel Mg_2TiO_4 spinel layers topotaxially grown on MgO cleavage faces and on polished MgO (001) faces. XRD, SEM and STM have been applied to YBCO samples prepared at different substrate temperatures between 600 and 800°C in order to investigate orientation and surface morphology. At T_s=675°C YBCO films have been grown in perfect (001) orientation. Below 675°C both (100) and (103) orientations appear whereas YBCO films grown above 675°C are (001) oriented and exhibit additionally (100) orientation.

(001) oriented YBCO films on Mg_2TiO_4/MgO (polished) show T_c (onset) up to 88.5 K and T_c (R=0) at 86 K. Films deposited on Mg_2TiO_4/MgO(cleaved) exhibit lower T_c values due to high cleavage steps on the MgO(001) surfaces.

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