Quality of YBCO thin films grown on LAO substrates exposed to the film deposition – film removal processes

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Abstract. The characteristics are investigated of high temperature superconducting YBa2Cu3O7 (YBCO) films grown on LaAlO3 (LAO) substrates being exposed a different number of times to YBCO film deposition and acid-solution-based cleaning procedures. Possible mechanisms of degradation of the substrate surface quality reflecting on the growing YBCO film parameters are discussed and analyzed.

1. Introduction

Thin films and layered structures of high temperature superconducting (HTS) YBa2Cu3O7 (YBCO) materials are attractive objects for investigating the problems of superconductivity and for device applications [1]. The characteristics of HTS thin films depend on the deposition conditions and the substrate quality. Defects and roughness of the substrate surface lead to worsening of the HTS film growing conditions and affect the physical and electromagnetic characteristics of the films obtained [2-4]. In experiments, the substrates are exposed to different processes which may result in a gradual degradation of the substrate surface. Different complex procedures are necessary, for example, for developing HTS devices based on multilayer structures. These procedures include nano-lithography, heat treatments, chemical or ion etchings which harm the substrate surface [5]. Frequently HTS films are deposited on such treated substrates or on the treated areas of the substrate. For this reason it is important to investigate the influence of such kind of treatments on the quality of the substrates and the HTS films growing on such substrates.

In this paper we present results of characterization of HTS YBCO films deposited on LAO substrates being exposed different number of times to treatment (i.e. YBCO film deposition and acid-solution-based cleaning) procedures.

2. Experimental

The HTS Y1Ba2Cu3O7 films with thickness ~ 60 nm were grown by DC facing-target off-axis magnetron sputtering on commercial LaAlO3 (LAO) substrates (5mm x 10mm x 0.5mm) produced by CrysTec-GmbH. The average roughness of the substrate was ~ 0.08 nm according to the certificate of

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the producer. The deposition conditions were the same for all the films. The substrate was heated to 780°C during the DC magnetron sputtering (3 h) process. The sputtering gas mixture was Ar:O\textsubscript{2} = 3:1 with total pressure 0.3 mbar. After the film sputtering process, a 30 minutes annealing of the film in oxygen at 800 mbar pressure was performed. Some substrates were exposed several times to YBCO film deposition and film removal (in diluted 5% HCl acid) procedures.

X-Ray Diffraction (XRD) analysis of the YBCO films and substrates were carried out using Phillips “Xpert” XRD equipment with Cu radiation 1.5418 Å. We used a standard Omega-scan (Rocking curves) geometry in which the X-Ray penetration depth is few microns. The surface of the samples was investigated using a scanning electron microscope (SEM). The critical parameters and the microwave surface resistance of the YBCO films were evaluated using AC-contactless methods and the parallel-plate resonator technique, respectively [4].

3. Results

Typical SEM surface images of the YBCO films obtained in the 1st and 5th deposition procedures (samples 1 and 2, respectively) are shown in figure 1. One can see a presence of some “boulders” on the surface of both films. “Boulders” are frequently observed on the surface of HTS YBCO films and consist as a rule of the oxides of copper Cu and yttrium Y [6,7]. The quality of the YBCO films (critical temperature \(T_c\), critical current density \(J_c\), microwave surface resistance \(R_s\)) is believed not to be significantly affected [6] by the presence of such “boulders” if their surface density is not very high.

![Figure 1](image1.png)

**Figure 1.** SEM image of the surface of YBCO films 1, 2 grown on new (a) and on treated (b) LAO substrates.

![Figure 2](image2.png)

**Figure 2.** Rocking curves obtained around YBCO(005) peak for films 1 (curve 1) and 2 (curve 2) and around LAO(002) peak for new (curve 3) and the 4 - times treated (curve 4) substrates.

A few needle-like defects placed perpendicularly to each other was observed on the surface of YBCO film 1 (figure 1a). Such defects are supposed to be grains consisting of a- or b- oriented phases of the YBCO material. Sample 2 does not contain strictly oriented defects and includes chaotically distributed hill-like defects with different diameters (figure 1b).

Results of \(\omega\)-scan (or rocking curves) of the two YBCO films cited above and obtained around the YBCO(005) peak are shown in figure 2. Rocking curve of sample 2 (with the full width at half maximum FWHM = 0.45 deg) prepared on the treated LAO substrate is about twice as broad as that (FWHM = 0.27 deg) of sample 1 prepared on a new substrate. This means poorer quality of YBCO film 2. It can also be noticed that the diffraction peak of sample 2 is slightly shifted to higher values of angle \(\omega\).

Rocking curves of LAO substrates obtained before and after treatment procedures around LAO(002) peak are presented in the same figure 2. One can see a dramatic difference in the substrate quality: while the new substrate demonstrates a narrow rocking curve peak (0.18 deg), the rocking
curve peak of the treated substrate (exposed 4 times to film deposition and film removal procedures) is much broader and shows a presence of domains distributed over ~ 1.5 deg.

Data on the critical temperature $T_C$, the critical current density $J_C$, the microwave surface resistance $R_S$ and the width of the superconducting transition $\Delta T_C$ of YBCO films grown on LAO substrates exposed different number of times to treatment (film deposition - film removal) procedures are summarized in table 1. It can be seen that the YBCO films parameters worsen as the number of treatment procedures is increased.

| Substrate, deposition number, number of films | The film thickness, nm | $T_C$, K | $\Delta T_C$, K | $J_C$ (77 K), MA/cm² | $R_S$ (77 K, 4 GHz), mΩ |
|---------------------------------------------|------------------------|----------|-----------------|----------------------|------------------------|
| New, 1st, 2 films                           | ~60                    | 89.2; 88.3 | 1.5; 2          | 2.1; 1.5             | 4; 8                   |
| Treated, 2nd, 2 films                       | ~60                    | 88.5; 87.9 | 1.5; 2.5        | 1; 0.7               | 10; 16                 |
| Treated, 3rd, 2 films                       | ~60                    | 87.2; 88  | 3.2; 2.3        | 0.4; 0.6             | 36; 24                 |
| Treated, 5th, 1 film                        | ~60                    | ~85       | ~5              | ~0.1                 | ~60                    |

4. Discussion

The worse quality of YBCO films (table 1) grown on the treated LAO (i.e., exposed to YBCO film deposition – film removal procedures) substrates is due to the worse surface of these substrates. Low quality of the surface of the treated substrates can be due to not perfect cleaning procedures when the metal oxides of YBaCuO system remain on the substrate. On the other hand, HCl acid used for cleaning of our LAO substrates is nearly an ideal solvent for these oxides, and, in our opinion, could not produce surface contaminations on the substrate.

Another possible mechanism of substrate degradation is related to the formation of surface defects during the treatment process. Defects like micro-cracks on the substrate surface may arise due to the tensile stress affecting the substrate (tending to “elongate” the substrate in its surface plane) from the side of the growing YBCO film. Such a stress arises because of the lattice mismatch of the LAO substrate and YBCO film (as it is known, $a=0.3788$ nm for pseudocubic LAO and $a=0.3827$ nm, $b=0.3889$ nm for YBCO) along the interface. The heating and cooling processes lead to additional stresses in the substrate because of the difference of the thermal expansion coefficients of the substrate and the film. During the film deposition procedure, some atoms of the growing film can diffuse into the substrate and modify its crystalline structure near the surface, thus creating new defects.

The chemical treating of the structure (by HCl acid in our experiments) removes not only YBCO film from the substrate, but leads to intensive etching of the substrate microareas with defects, as the etching rate of such areas may be significantly higher than that for the smooth surface areas of the substrate. This stimulates an enlargement of the surface defects such as micro-cracks, micro-cavities, micro-pits and the formation of vacancies. The sequence of YBCO film deposition – film removal processes lead to an increase of the defects’ surface density and of the “depth” of these defects causing a gradual isolation of the surface microareas separated from one another by such kind of defects. During the next YBCO film deposition process, the crystal lattice of some isolated and strained microareas of the substrate can relax or re-crystallise into a structure consisting of misoriented grains.

For this reason, the rocking curve of the substrate treated several times is significantly broader than that of a new substrate (see curves 3 and 4 in figure 2) and includes some additional peaks. One can also estimate (from the X-ray penetration depth of the configuration considered) that the thickness of the modified top layer of this treated substrate may reach at least several microns. The low surface quality of the treated substrates hinders the epitaxial growth of YBCO films. The increased surface roughness and the presence of misoriented microareas on the surface limit the planar dimensions of the YBCO film grains and stimulate a 3D growth of YBCO material and, possibly, the formation of the hill-like structure observed in figure 2a.

There are different reasons for growth of $a$- or $b$- oriented grains in the epitaxial YBCO films 1 (figure 1a, needle-like defects). One of them is the stresses arising between the substrate and the film.
described above. The planar dimensions of the grains are small in sample 2 because of the low quality of the substrate, and for this reason the strains in these grains are small as well. For this reason the structures formed by $a$- or $b$- oriented grains are not clearly observed in sample 2 (figure 2a).

The diffraction peak of sample 2 is slightly shifted to the higher values of angle $\omega$ (figure 2, curves 1, 2), which means that the lattice parameter $c$ of this sample is smaller than that of sample 1. Film 2 is characterized by a rougher surface and by a higher number of intergranular boundaries, which provide for better oxidation conditions. It is known that an increase of the oxygen concentration in YBCO film leads to a decrease in its $c$-axis parameter. The more perfect YBCO film 1 is exposed to a stronger compressive stress (in comparison with sample 2) in its $ab$- plane from the LAO substrate. This contributes to an elongation of the $c$– axis of film 1. These two factors explain the difference observed in the positions of the diffraction peaks (figure 2, curves 1 and 2) of samples 1 and 2.

The data given in table 1 demonstrate that the electrical parameters of the YBCO film worsen even after the first treatment procedure, but remain satisfactory for most applications. The difference is more pronounced for the surface resistance $R_S$, which, as it is known, is very sensitive to the roughness and to the presence of the low-quality weak links [8] in the sample. As the number of treatment procedures is increased, the surface roughness of the substrate caused by defects of different kinds increases gradually. The YBCO films grown on such a substrate are characterized by a better developed granular nature and by broader spread orientation angles of the grains (figure 2, curves 1 and 2). This causes the presence of a set of low-quality weak links between the grains and low electrical characteristics (especially, $\Delta T_C$, $J_C$, $R_S$, see table 1) of the samples.

5. Conclusion
High temperature superconducting YBCO thin films with thickness of ~60 nm were grown on LAO substrates being exposed a different number of times to treatment (i.e. YBCO film deposition and acid-solution-based cleaning) procedures. Rocking curves of YBCO film obtained around the YBCO(005) peak and of LAO substrates obtained around the LAO(002) peak were broader in the case of a substrate treated several times in comparison with the case of a new substrate. The electrical parameters of the YBCO films worsened as the number of treatments of the substrate was increased. The stresses arising in the substrate–film structure (due to the lattice mismatch of the LAO and YBCO materials) were assumed to be responsible for the worsening of the surface quality of the substrates in the treatment processes and the experimental results can be interpreted on the basis of this assumption.

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