HTS thin films: a convenient method for removal of precipitates-segregates

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Abstract. High quality superconducting thin films of HTS have been grown by MOCVD on substrates with artificial steps of predefined height and width. The surface of the films grown on the steps having width equal to the ‘double of the migration length’ of the atomic species depositing on the substrate is totally free of precipitates: precipitates are gathered at the step edges where the free energy is lowest. The method has several advantages: it is simple, universal (it is independent of the materials, substrates, deposition technique or application) and allows control of precipitates segregates so that the quality and growth conditions of the films are the same as for the films grown on conventional substrates. The method is expected to result in new opportunities for the device fabrication, design and performance.

1. Introduction

For devices or integration purposes, component thin films should fulfill several requirements:
   a) Certain relationship between substrate-film or film-film is necessary (e.g. lattice matching, wetting and chemical stability and compatibility).
   b) A certain morphology/roughness is necessary (optimum growth conditions should be found and knowledge of the growth mechanism are useful in this respect).
   c) Controlled properties, usually uniform and reproducible have to be obtained
   d) Relatively large clean surfaces are desired; no precipitates-segregates.
   e) Fabrication cost should be low.

Sometimes this is not a trivial problem especially for the multicomponent materials such as high-Tc superconductors (HTS), manganites or other electronic materials.
For example, in-situ, as-prepared BSCCO thin films have shown excellent quality (high $T_c$ and $J_c$ and low and uniform morphology [1]), but on the surface of the film Cu-rich precipitates-segregates are usually found. This is a serious problem toward (layered) device fabrication and/or integration! Currently, to avoid precipitates-segregates several methods are available:

a) introduction of buffer layers
b) changes in the chemical composition of the films
c) complex heat treatments/ post-annealings.
d) use of vicinal substrates combined with layer-by-layer deposition techniques such as molecular beam epitaxy [2, 3] and by applying interrupted growth [4].

However, these methods are not always convenient since they might influence the quality of the films and usually they are not generally applicable.

We propose a new approach and method using artificial substrates with steps.

2. Experimental

In order to generate steps with controlled width and height, commercial (001) SrTiO$_3$ single-crystal substrates (Crystec GmbH, 15mm x 15mm x 0.5mm) have been processed in a dry etching apparatus [5] by Ar-plasma generated through electron cyclotron resonance. Pressure of Ar-gas in the chamber is 0.1Pa, microwave power is 350W, and ion extraction voltage and current density are $-240$V and 0.15mA/cm$^2$, respectively. Dry etching rate for SrTiO$_3$ is 3nm/min.

On the substrates with and without steps, thin films of Bi-Sr-Ca-Cu-O superconductor were grown by MOCVD [1]. Source materials were Bi$(C_6H_5)_3$ and M(DPM)$_2$ with M=Sr, Ca and Cu and DPM is the abbreviation for dipivaloylmethanate ligand. Source materials are heated between 60 and 200° C. Pressure in the source vessels is between 80 and 196hPa. Carrier gas is Ar with the flow rate of 70-300 sccm in individual source vessel. The pipes connecting to the reactor are heated above 200° C in order to avoid condensation of the vapours. Oxygen is supplied to the reactor at 36hPa and total pressure in the reactor is 65hPa. Deposition temperature is 800° C. Composition and thickness of the thin films were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPS 7700, Seiko Instruments Inc.). X-ray diffraction (D500, Siemens) have shown that films are epitaxial, c-axis aligned and composed of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ (Bi-2223) phase, or of Bi-2212/Bi-2223 (Bi-2212 is abbreviation for Bi$_2$Sr$_2$CaCu$_2$O$_8$) superlattice with apparent c-axis equal to 3.4nm. Morphology of the thin films was inspected on large areas by optical microscopy and locally by atomic-force-microscopy (AFM) by using a commercial microscope SPA 300, Seiko Instruments Inc. Superconductivity of the thin films was checked by standard four-probe method.

3. Result and Discussion

Our method consist in generation of artificial steps on the surface of the substrate with a predefined width and height, so that occurring precipitates-segregates will migrate and gather at the edge of the step where the free energy is lowest. Superconducting thin films are deposited on such substrates in the same conditions as for step-free substrates and have similar properties. Schematically, process is shown in figure 1. All precipitates will gather at the step edge if the width of the step is equal to the ‘double of the migration length’ of the atomic species depositing on the substrate (figure 2a). For our growth conditions, migration length is about 10μm and hence the surface of the film on a step with the width of 20μm is free of precipitate-segregates.
Figure 1 Schematic image showing formation of the precipitates at the step edge during growth of thin films.

Figure 2 Microscope image of Bi-2223 thin films grown on (100)SrTiO$_3$ substrate with artificial steps: (a)- step width $w=20\mu m$, step height $h=2000A$, film thickness $t=490A$, ratio $n=h/t=4.08$; (b)- step width $w=60\mu m$, step height $h=2000A$, film thickness $t=490A$, ratio $n=h/t=4.08$.

For a step width of 60\(\mu m\) (figure 2b), precipitates within 10\(\mu m\) from the step edge (marked with dashed line) will migrate to the edge, while the for the other precipitates the distance is above the migration length so that they will be formed randomly on the surface of the film, on the step and within 40\(\mu m\) delimited by the two arbitrary dashed lines. We conclude that steps of 20\(\mu m\) width are suitable for the growth of clean high quality BSCCO thin films to be used in electronics (figure 3). Height of the step is not a crucial parameter, but it introduces some limitations to the thickness of the film: if the height of the precipitate is large relative to the height of the step (and this occurs usually for thicker films), situation is close to that of having no steps. Best results are obtained when the step height is 2-4 times the value of the film thickness ($n=2-4$).
Advantages of the method are:

1. Simplicity.
2. Universality: it is independent of the materials, substrates, deposition methods, applications.
3. It allows independent control of precipitate-segregation without changes in the growth conditions and quality of the films.
4. Steps can have any shape as long as “double migration rule” is applied. Term ‘steps’ does not necessarily conform to the classic definition. Domains delimited by scratches could also work.
5. It allows to determine migration parameters that might be useful in the optimization process of the films: by producing steps with different width, for certain growth conditions and materials migration length can be experimentally determined, and by changing growth temperature the migration energy can be extracted.
6. All above advantages are working against the necessity of complex, sophisticated, expensive growth technologies and is removing some of the limitations in the design and fabrication of thin films growth for various applications.
7. Optimum growth conditions determined for the conventional substrate are same for the substrates with steps: this is advantageous in terms of time- and energy/materials-saving comparative to other methods requiring extra optimization experiments.

Figure 3. AFM image (10μm ×10μm) of a Bi-2223 thin film on a substrate with artificial step (B is on the step). Inset shows the morphology (AFM image, 2μm × 2μm ) of the precipitate-free thin film with roughness about half c-axis unit cell of Bi-2223. Note large precipitates-segregates gathered at the step edge.
Films presented in this article are showing zero-resistance critical temperature of 91 and 89K for Bi-2223 and Bi2223/Bi2212 films, respectively (figure 4).

![Resistance vs. temperature for Bi-2223 (left) and Bi-2223/Bi2212 (right) thin films as-grown by MOCVD on (001)SrTiO3 substrates with steps.](image)

**Figure 4.** Resistance vs. temperature for Bi-2223 (left) and Bi-2223/Bi2212 (right) thin films as-grown by MOCVD on (001)SrTiO3 substrates with steps.

4. Conclusions
A new concept and method for the growth of high quality precipitate-free multicomponent thin films suitable for applications is proposed. Our approach has several important advantages that open new opportunities for films growth and their application in electronics.

5. References
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