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A new growth method of high-quality precipitate-free HTS thin films applied for electronics

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Abstract We report successful growth of high-quality thin films with clean and completely precipitate-free surface, suitable for device applications, by applying a new concept and method to the substrates. The concept consists in generation of artificial steps of controlled height and width, and desired shape on the surface of the substrate. The width of the step is chosen so that it is equal to the double of the migration (surface diffusion) length of the atomic species in the growth process of the film. If precipitates occur, they will be selectively gathered to the step edge where the free energy is lowest. Using this new method, we have successfully obtained by MOCVD high-quality precipitate-free Bi-2223 and Bi-2223/Bi-2212-superlattice thin films on (100) $SrTiO_3$ substrates with artificial steps of controlled width and height. These as-grown films have been further used to fabricate patterned intrinsic Josephson junctions. Completely precipitate-free films offer a strong advantage for integration, and generate new possibilities for the device fabrication.

Keywords Precipitate-free · Thin films · Oxides · Multicomponent materials · Superconductor

Introduction

For oxide electronics applications such as MRAM, non-volatile FeRAM, HTS micro-wave filter and Josephson computer, etc. using perovskite-related layered oxide films, impurity-phase precipitates are a fatal problem working against high-performance of devices. In particular, this precipitate-problem is very important for ultra-thin films, sandwich-type structures and superlattices exhibiting through the stacked layers certain effects, (e.g. Josephson or magnetoresistance tunneling) and/or for integrated devices.

For devices or integration purposes, component thin films should fulfill several requirements:

(a) 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 is useful in this respect);
(c) Controlled properties, usually uniform and reproducible have to be obtained;
(d) Relatively large clean surfaces are desired, e.g. no precipitates-segregates should occur;
(e) Fabrication cost should be low.

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Sometimes this is not a trivial problem especially for the multicomponent materials such as high-T_c 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, low roughness 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) Layer-by-layer growth by *Molecular-Beam-Epitaxy* combined with the use of vicinal substrates and/or interrupted growth [2–4].

However, these methods are not always convenient since they might influence the quality of the films. Some of them are also local, e.g. suitable just for a certain technique or conditions. To solve this problem we propose a new approach and method using artificial substrates with steps. To test the viability of our method we have fabricated intrinsic Josephson Junctions using films grown on artificial substrates.

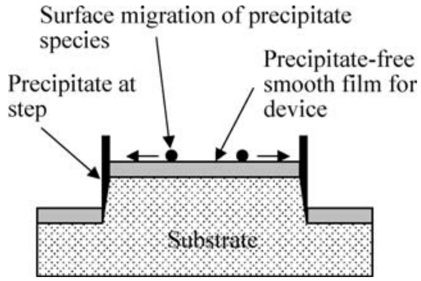


Fig. 1 Schematic image showing formation of the precipitates at the step edge during growth of thin films

Experimental

In order to generate steps with controlled width and height, commercial (100) $SrTiO_3$ single-crystal substrates (Crystec GmbH, 15 mm × 15 mm × 0.5 mm) have been processed in a liquid-nitrogen cooled dry etching apparatus [5] by Ar-plasma generated through electron cyclotron resonance. Pressure of Ar-gas in the chamber is 0.1 Pa, microwave power is 350 W, and ion extraction voltage and current density are –240 V and 0.15 mA/cm^2, respectively. Dry etching rate for $SrTiO_3$ is 3 nm/min.

On the substrates with and without steps, thin films of Bi-Sr-C-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 8000 and 19600 Pa. 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 vapors. Oxygen is supplied to the reactor at 3600 Pa and total pressure in the reactor is 6500 Pa. 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 oriented and composed of $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) phase, or of Bi-2212/Bi-2223 (Bi-2212 is abbreviation for $Bi_2Sr_2CaCu_2O_8$) superlattice with apparent c-axis equal to 3.4 nm. 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.

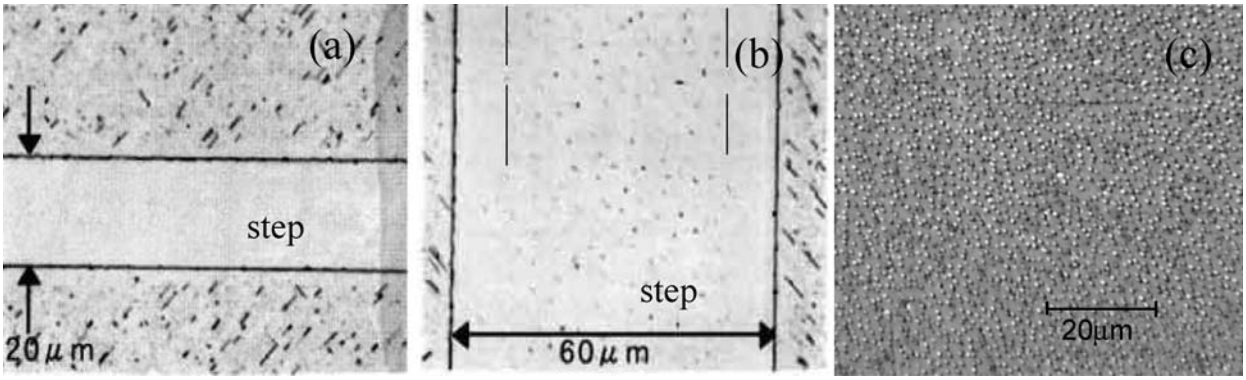


Fig. 2 Optical microscopy of the Bi-2223 thin films grown on (100)$SrTiO_3$ substrate with artificial steps: (a) step width $w = 20\,\mu$m, step height $h = 2000$ A, film thickness $t = 490$ A, ratio $n = h/t = 4.08$; (b) step width $w = 60\,\mu$m, step height $h = 2000$ A, film thickness $t = 490$ A, ratio $n = h/t = 4.08$; (c) surface of a Bi-2223 film grown on conventional substrate (without steps)

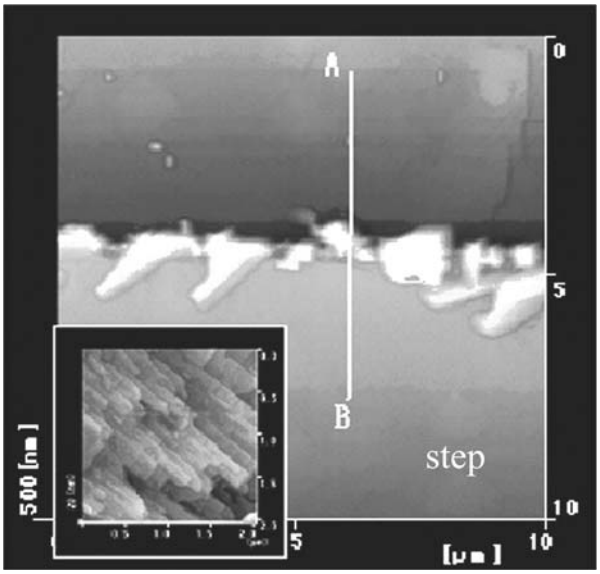


Fig. 3 AFM image (10 μm × 10 μm) of a Bi-2223 thin film on a substrate with artificial step (B is on the step). Inset shows the morphology (AFM image, 2 μm × 2 μm) of the precipitate-free thin film with roughness less than half *c*-axis unit cell of Bi-2223. Note large precipitates-segregates gathered at the step edge

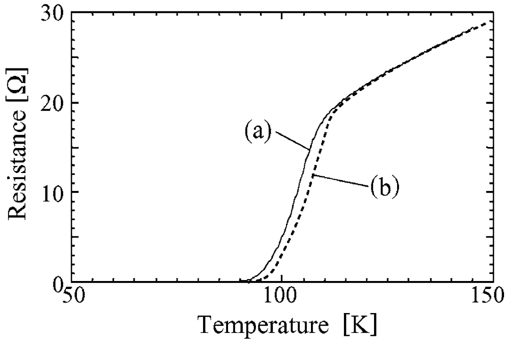


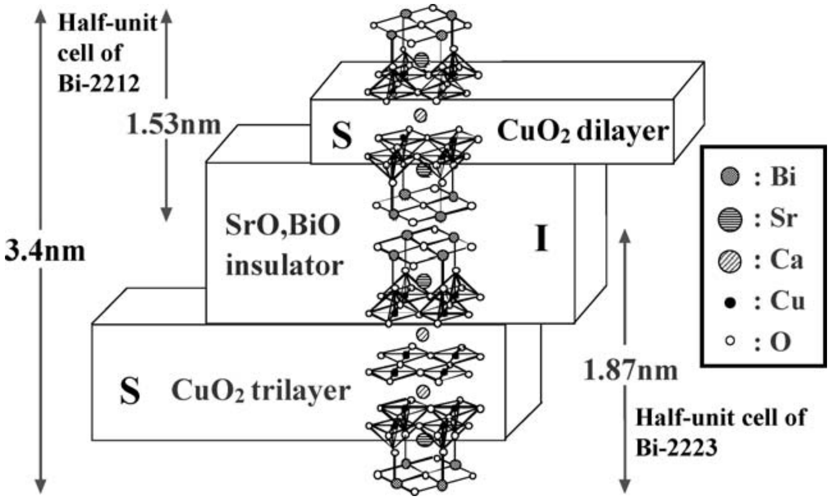
Fig. 4 Resistance vs. temperature for Bi-2223 thin films grown on (a) - artificial substrate and (b) conventional substrate

Results and discussion

Our method consists 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 Fig. 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 (Fig. 2(a)). For our growth conditions, migration length is about 10 μm and hence the surface of the film on a step with the width of 20 μm is free of precipitate-segregates. For a step width of 60 μm (Fig. 2(b)), precipitates within 10 μm from the step edge (i.e. between the step-edge and arbitrary dashed lines) will migrate to the edge. For the other precipitates located within the 40 μm central region (between dashed lines) on the step, the distance is beyond the migration length, so these precipitates will form randomly, and the case is similar to that of the growth on conventional substrate without steps (Fig. 2(c)). We conclude that steps of 20 μm width are suitable for the growth of clean high quality BSCCO thin films to be used in electronics (Fig. 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;

Fig. 5 Schematic figure of Intrinsic Josephson junction (Superconductor-Insulator-Superconductor) on as-grown film of Bi2212/Bi2223 superlattice with apparent *c*-axis lattice parameter of 3.4 nm



3. It allows *independent control* of precipitate-segregation without changes in the growth conditions and quality of the films. For example, in Fig. 4 are presented resistance curves (R-T) for two films grown on different substrates (films from Fig. 2(a) and (c)). Zero resistance critical temperature, $T_{c(R=0)}$, is 92 K and 94 K for the film on artificial and conventional $SrTiO_3$ substrate, respectively. The difference is within the reproducibility of our MOCVD growth. From one run to another and depending on the location of the substrate films on both substrates are showing $T_{c(R=0)}$ between 90 and 97 K;
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 estimation of the *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 the same as for the substrates with steps: this is advantageous in terms of time- and energy/materials- saving comparative to other methods requiring extra optimization experiments;

Using a Bi-2212/Bi-2223 superlattice thin film (50 nm thickness and with $T_{c(R=0)} = 89$ K) grown on (100) $SrTiO_3$ substrate with steps of 20 μm, a Superconducting-Insulating-Superconducting (SIS) (Fig. 5) stacked Josephson junction (JJ) was successfully made. Mesa was fabricated using liquid-nitrogen cooled dry etching method [5] described in section Experimental. Schematic image of the mesa is presented in Fig. 6. Current-Voltage characteristics are shown in Fig. 7, while current -magnetic field dependence is given in Fig. 8. Multiple branches and hysteresis were observed. The number of branches coincides with the number of stacked SIS junctions within the mesa height. Maximum voltage jump was 2 mV, critical current was 5 μA and critical current density was 5 A/cm^2. Critical current dependence with reduced temperature ($1-T/T_c$) is linear (not shown). Critical current is also showing oscillations with magnetic field (Fig. 8). All presented features confirm that

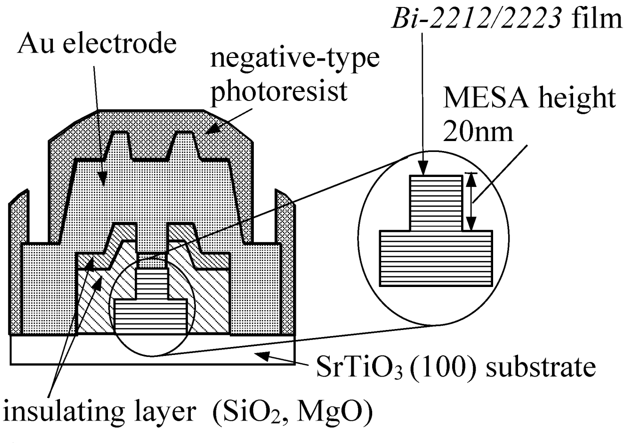


Fig. 6 Schematic figure of mesa structure

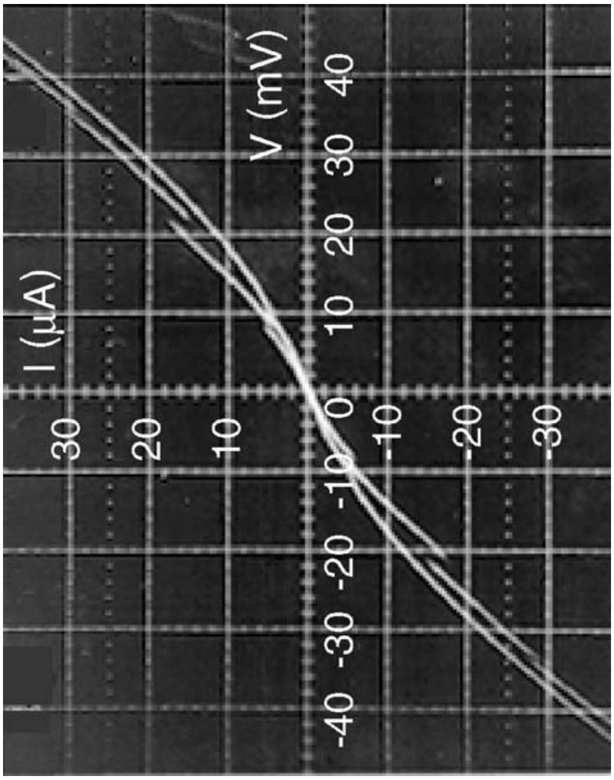


Fig. 7 Current-Voltage characteristics at 4.2 K of the intrinsic JJ on Bi-2212/Bi2223 thin films grown on (100) $SrTiO_3$ substrate with 20 μm width step (junction size 10×10 μm^2, mesa height = 20 nm)

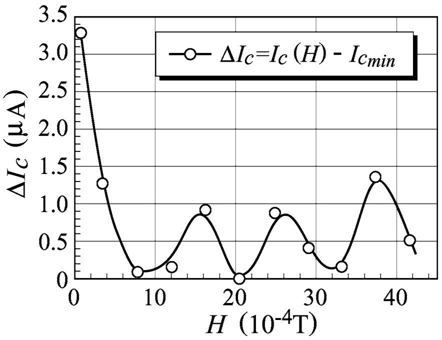


Fig. 8 Current-magnetic field dependence of the intrinsic JJ on Bi-2212/Bi-2223 thin films (same JJ from Fig. 7)

we have successfully fabricated a SIS intrinsic Josephson junction.

Conclusion

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.

Using this new approach we have successfully fabricated intrinsic Josephson junctions based on a Bi-2212/Bi-2223 superlattice thin film.

Method can be easily applied for fabrication of devices based on other materials than superconductors.

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