Growth Control of High-Tc Superconducting Thin Films for Future Electronics

Kazuhiro Endo1), Petre Badica2), Hidehito Nanto1),3), Hiroshi Kezuka4), Shunichi Arisawa5) and Tamio Endo6)

1) Research Laboratory for Integrated Technological Systems, Kanazawa Institute of Technology, Hakusan, Ishikawa 924-0838, Japan
Fax: +81-76-274-8273, e-mail: kendo@neptune.kanazawa-it.ac.jp
2) National Institute of Materials Physics, Bucharest-Magurele, POB MG-7, 077125, Romania
3) Advanced Materials Science R&D Center, Kanazawa Institute of Technology, Hakusan, Ishikawa 924-0838, Japan
4) School of Computer Science, Tokyo University of Technology, Hachioji, Tokyo 192-0982, Japan
5) National Institute for Materials Science, 1-2-1, Tsukuba, Ibaraki 305-0047, Japan
6) Graduate School of Engineering, Mie University, Tsu, Mie 514-8507, Japan

Top quality thin films for different applications are always of interest. However, it is not easy to grow such films and many criteria have to be fulfilled. The degree of complexity enhances significantly for multicomponent materials such as high-Tc superconductors, giant magnetoresistive materials, heterostructures, others. This translates into a lower growth control level. Solution resides in identification of the specific details as well as of the general principles of growth and their personalized application towards preparation of optimized thin films of top quality. This is our approach and goal. Examples in this regard will be introduced with a strong emphasis on HTS cuprates for sensor applications such as those working in the terahertz domain and currently considered for construction of future “safe and secure society”.

Key words: MOCVD, Thin Films, Bi-2223, HTS, Lattice Engineering, Artificial-Step Substrate, Periodically Interrupted Growth, Intrinsic Josephson Junction

1. INTRODUCTION

Oxide electronics emerges as one interesting alternative to the current conventional one based on silicon. Many oxides have been already recognized to be superior to conventional silicon when used in fabrication of different electronic devices. Some of them possess unique features, e.g. high temperature superconductors (HTS) allowing exploration of new fields of device physics. Among them, HTS-based “terahertz” device is strongly expected to provide future sensors to realize “safe and secure” society [1-3]. It will be available for a new detector of drugs, chemicals and weapons. However, oxides often impose not only advantages, but also new technical and scientific challenges.

A major role in the development of this field is played by thin films. Growth of high quality oxide thin film is not easy and our efforts are oriented in this direction. Our presentation will discuss growth of oxide thin films such as high-Tc superconductors, insulating infinite-layer-like structures, ferroelectric and their stacked heterostructures, paying attention to surface morphology formation and control since this is one of the limitative factors in device fabrication and integration. We shall present our data in order to observe some general dependencies and extract the necessary information for future developments.

2. EXPERIMENTAL AND DISCUSSION

Thin films were grown by metalorganic chemical vapor deposition (MOCVD). Details and apparatus are presented in our articles [4-6]. Films were with different orientations: (001) Y-123, (103) Y-123, (119) Bi-2223, (001) Bi-2223, (111) SrCaCuO2, (001) SrCaCuO2, (117) Bi4Ti3O12 and (001) Bi4Ti3O12. Heterostructures build as sandwiches of these films were also grown. Use of non c-axis thin films for heterostructures is of high interest considering anisotropic properties of some of the indicated oxides. For example, to use c-axis films for fabrication of structures showing Josephson effect is not a trivial task. Explanation is that due to the small coherence length along c-axis in HTS, to form the Josephson effect, insulating layer should be very thin. An alternative idea would be non c-axis oriented films.

Control of growth, orientation and, hence, of surface morphology can be realized through different methods. One should also keep in mind that these materials are multicomponent and complex processes are likely to occur. In these circumstances we have experimented application of combined methods of control as follows:

1. Film-substrate relationship (lattice matching) can allow growth of c-axis and non c-axis thin films. By selecting the right crystalline plane of the single crystal substrate, a certain plane of the film will match the substrate resulting in a favorable situation for a certain oriented growth (film-substrate lattice engineering) [7].
Figures 1(a) and (b) show the film-substrate lattice relationship for different $c$-axis and non-$c$-axis thin films, respectively. Some examples for $c$-axis and non-$c$-axis thin films growth by MOCVD are presented in Figs 2, 3(a) and 5(a).

AFM images (Figures 2(a) and 5(a)) taken on $c$-axis thin films reveal a 2D layer-by-layer growth mechanism. There are also some deviations as for (001) Y-123 and (001) Bi$_2$Ti$_3$O$_{12}$ (BTO) film showing sometimes some tendency for spiral growth mode (significantly lower for BTO). For $c$-axis thin films terraces may occur and also dot-like precipitates-segregates. The growth direction for the (001) films is $c$-axis that is perpendicular to the surface of the substrate.

Morphology of the non-$c$-axis thin films (Figures. 2(b) and 3(a)) are very similar to each other and consist of roof-range-like-shaped grains, in-plane aligned. This morphology is very different from that of the $c$-axis thin films. However, the growth mechanism in the case of non-$c$-axis thin films is also a 2D layer-by-layer growth along $c$-axis. The difference is that the growth direction, that is parallel to $c$-axis, is inclined and is making a certain angle with the surface of the substrate. The value of this angle is around 45° for our thin films. When two growing symmetrical neighboring fronts merge, they form the specific roof-like-shape grains.

AFM also suggests that films are in-plane aligned. As already introduced in the previous paragraphs, this is obtained for different film materials on (100) and (110) SrTiO$_3$ (STO) substrate for $c$-axis and non-$c$-axis thin films respectively. Furthermore, for $c$-axis as well as non-$c$-axis thin films grown on substrates other than STO, when applying the same principles of the lattice relationship, similar results were obtained. We conclude that the principles of films-substrate relationship play a major role in controlling film orientation. These principles are rather general and do not depend significantly on the material of the substrate or of the film. This provides a powerful tool for thin films orientation and anisotropy engineering.

2. **Template growth**, i.e. subsequent growth at two different temperatures was used in combination with above described method. This approach was necessary to eliminate impurity orientations and secondary nucleation and/or to control uniformity, size and roughness of the grains (Fig. 3(b)), and to improve superconducting characteristics.

3. **Vicinal substrates with controlled miscut angles** can be employed for the growth of $c$-axis and non-$c$-axis films when combined with film-substrate relationship. Step-terraces from the vicinal substrate are useful to control nucleation and growth direction, to avoid island growth, secondary nucleation and formation of precipitates (Fig. 3(c), there are no roof-range-like grains). All of them are leading to a better superconducting characteristics. For some cases growth mechanism of 2D layer-by-layer type shifts to a step-flow-one.

Fig. 1. Film-substrate lattice relationship (a) for different $c$-axis thin films, and (b) for different non-$c$-axis thin films.

Fig. 2. Atomic Force Microscopy (AFM) images of different films (a) on (001) SrTiO$_3$ and (b) on (110) SrTiO$_3$ (2µm x 2µm). Substrates were flat substrates with low miscut angles (typically less than 1°).
The use of substrates with artificial steps of predefined width (equal to double of the migration length of the atomic species arriving on the substrate during growth) and height is effective for the preparation of precipitate-free film of multicomponent materials (Fig. 4(a)) [8]. This allows to gather impurity-precipitates at the step edge where the free energy is minimized. The height of the step is not a critical parameter in this method of growth control and it is rather a limitative one: our experiments have shown that the best results are obtained when the height of the step is about 2-4 times the film thickness.

We have succeeded in fabrication of intrinsic Josephson junction devices on the top quality thin film located on the artificial step (Fig. 4(b)). Intrinsic Josephson junction is a good candidate for future compact solid-state sources of terahertz emission, which are being sought for sensing, imaging, and spectroscopy applications [1-3] including for safety and security equipment.

Interrupted growth consists of cycles of alternative on-off-on deposition when during the ‘off’ state growth atmosphere and temperature of the substrate are the same as for the ‘on’ state. The ‘off’ condition gives time for the atomic species to complete surface migration and through this approach to eliminate island growth and to improve uniformity and to decrease roughness (Fig. 5). Remarkably is that this method was initially thought to be specific for pulse laser deposition (PLD) or molecular beam epitaxy (MBE) layer-by-layer growth methods [9, 10]. Our results demonstrate that it can be successfully applied in the case of conventional MOCVD growth [11].

Bi-2223 thin films were grown on different substrates with lower ferroelectric constant towards terahertz and microwave applications. Substrates of (001) and (110) MgO and NdGaO$_3$ were selected so that there is a certain film-substrate relationship reflected by different degree of lattice mismatch as well as by different lattice mismatch anisotropy. The results are presented in Table 1 (Lattice mismatch anisotropy is given by mismatch ratio, $r$). It was found that the magnitude of the lattice film-substrate mismatch has low influence on the quality of the film, and the strongest influence is given by the mismatch anisotropy (value and sign) [12]. High quality of the films on both substrates and especially on (001) MgO makes them promising for different applications particularly for terahertz and microwave ones.
3. CONCLUSION

Combined 1-6 methods are more powerful than the individual ones. When combined, some of the negative effects of the individual method can be minimized or removed. For example in Fig. 3(b) grains are large for a template approach comparative to one temperature growth of the film for which poorer properties were obtained. Properties are improved and/or roughness is decreased if vicinal substrates are used for one temperature (Fig. 3(c)) or for template growth. Independent control can be realized in some cases and this generates important advantages.

Presented methods were applied for the growth of heterostructures with different orientation, but more research is necessary in this direction. They also point on other less explored directions such as growth of $a$-axis films or heterostructures and thin films on selected substrates with controlled film-substrate mismatch anisotropy. It is expected that these ideas will also produce a significant impact on terahertz device fabrication leading to the realization of safe and secure society.

REFERENCES


(Rceived November 25, 2010; Accepted December 9, 2010)