Growth by MOCVD of (00l) Bi-2223 superconducting thin films on (001) and (110) MgO substrates

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Abstract. Superconducting c-axis thin films of Bi2Sr2Ca2Cu3O10 (Bi-2223) were grown by MOCVD on (001) and (110) MgO substrates. Films on both substrates show, as revealed by AFM investigations, similar morphology composed of regular rectangular grains and relatively low roughness of about two or three half c-axis unit cell order. AFM images also suggest that films might have in-plane epitaxy. The films have zero resistance critical temperatures of 95.1K for the (001) MgO substrate and 75K for the (110) MgO substrate, respectively. Considering very large films-substrate lattice mismatch between (110) MgO and (ab)-plane of the superconducting phase the growth of indicated films is a surprise.

1. Introduction

High Tc superconducting c-axis Bi2Sr2Ca2Cu3O10 (Bi-2223) thin films prepared by metalorganic chemical vapor deposition (MOCVD) have been shown to have high critical current density values Jc at 77K up to high magnetic fields [1]. Considering this result it is expected that this material would have low surface resistance. Especially interesting would be thin films of Bi2Sr2Ca2Cu3O10 phase with the highest critical temperature among the superconducting phases from the Bi-Sr-Ca-Cu-O system. However, it is considered that preparation of this phase is difficult and therefore less attention has been paid to fabrication and investigation of Bi2Sr2Ca2Cu3O10 thin films as a potential candidate for the microwave applications, such as band-pass filters, resonators, etc.

Second important aspect in the microwave applications is the substrate. It should have a low dielectric constant and low tan δ at operating frequencies (>10GHz). Substrate should also have close lattice matching and thermal expansion coefficient with the superconductor. It should be free of twins, chemically stable, available at large areas and low cost. A suitable material that fulfills most of the indicated criteria is MgO, but lattice mismatch between MgO and high temperature superconductor (HTS) is generally considered to be a problem towards growth of high quality HTS thin films, and buffer layers are recommended. However, considering specific features of MOCVD technique that is closer to the equilibrium conditions than others, we have attempted growth of c-axis Bi2Sr2Ca2Cu3O10 superconducting thin films on (001) and (110) MgO substrates without buffer layers. Our results on

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growth and films characterization from the structural, microstructural and electrical resistance vs. temperature viewpoints are presented in this article, leaving the detailed investigation of the films by surface resistance measurements to the future work.

2. Experimental
Films have been grown in a specially designed cold-wall type MOCVD apparatus presented elsewhere [2] using as source materials Bi(C₆H₅), and M(DPM)₂ with M=Sr, Ca and Cu and DPM=di-pivaloyl-methanate. Argon flow was used to transport vapors to the reaction tube and oxygen was introduced directly into reactor. Substrates of (001) and (110) MgO were placed on an Inconel susceptor and inductively heated to 800°C. The relationship between substrate and films is schematically presented in the Fig. 1. Lattice mismatching is also indicated for both substrates.

![Figure 1. Lattice mismatch relationship between (001) film Bi₂Sr₂Ca₂Cu₃O₁₀ and a) – (001)MgO and b) – (110)MgO. Mismatch coefficients along different directions of the substrate are for case a)- [001]=−9.38% and [010]=−9.38%; b)- [001]=−28.6% and [110]=8.47%.](image)

Composition of the as-grown thin films was determined by inductively-coupled-plasma spectroscopy (ICP, SPS 7700, Seiko Instruments Inc.). Film thickness was around 500Å. X-ray diffraction patterns were taken with a D500, Siemens diffractometer. Microstructure was investigated by Atomic force Microscopy (AFM, SPA 300, Seiko Instruments Inc.). Electrical resistance curves vs. temperature R(T) were measured by the standard four-probe method.

3. Results and Discussion
X-ray diffraction patterns of the films are presented in the Fig. 2. The profile of the XRD pattern is approximately the same for the films grown on (001) and (110) MgO substrates. Peaks can be indexed as (00l) of Bi₂Sr₂Ca₂Cu₃O₁₀ phase. This result clearly shows the c-axis epitaxial growth of the Bi₂Sr₂Ca₂Cu₃O₁₀ films. The level of the impurity phases/orientations is relatively low, but considering that the intensity of the (0012) peak in the film grown on (110)MgO is increased relative to the intensity of the other peaks, one can speculate that in the films on (110)MgO intergrowth (probably Bi₂Sr₁Ca₁Cu₂O₈) is present and/or some regions with defect/distorted structure occurs.
AFM images of the films are also similar for both types of substrates (Fig. 3). These images strongly suggest occurrence of the in-plane alignment; rectangular grains of large-area (up to \(0.5\mu m \times 2\mu m\)), sometimes having round edges, are running parallel each other without evidence for twinning or the presence of the grains with different in-plane orientation. Nevertheless, we have not performed yet in-plane detailed structural measurements to confirm in-plane alignment and the quality of the films from this point of view. AFM images also indicate on the two-dimensional nucleation growth mechanism of the films. Roughness of the presented microstructure of the films on (001) and (110) substrate is approximately two and three times the half \(c\)-axis unit cell of the Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) superconductor, respectively.

Electrical resistance curves \(R(T)\) are presented in the Fig. 4. Zero-resistance critical temperature of the films is 95.1K and 75K for the films grown on (001) and (110) MgO substrates, respectively. The difference in the values of \(T_c\) can be explained considering the lower quality as revealed from XRD for the films on (110) MgO that is probably a consequence of the large film-substrate lattice mismatch for these films. The presence of the (Bi\(_2\)Sr\(_2\)Ca\(_1\)Cu\(_2\)O\(_8\)) intergrowth explains also the existence of the shoulder in the \(R(T)\) curve for the films grown on (110) MgO (Fig. 4b). The films on both substrates have a metallic behaviour in the normal state. Normal state values of resistance are higher for the film on (110) MgO (\(R_{300K}=15\times10^{-6}\ \Omega m\)) than for the film on (001) MgO (\(R_{300K}=4\times10^{-6}\ \Omega m\)) and this might
indicate the lower quality of the films grown on (110) MgO. Nevertheless, the ratio \( R_{300K}/R_{Tc(onset)} \) is almost the same for both situations \((001)MgO/R_{300K}/R_{Tc(onset=135K)} = (110)MgO/R_{300K}/R_{Tc(onset=123K)} = 1.42\).

**Figure 4.** Electrical resistance curves vs. temperature for films grown on a) (001)MgO and on b) (110) MgO.

Growth of c-axis and possibly in-plane oriented thin films on (110) MgO of relatively high quality and of apparent single phase Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) is surprising considering the unusually large lattice mismatch between the substrate and superconductor. It is reported for the 3C-SiC MOCVD film on Si substrate [3] and for the GaN MOCVD film on GaAs substrate [4] that a strain resulting from such a large mismatch is relaxed by the formation of stacking faults and/or misfit-dislocation. Currently, an explanation for the mechanism of the strain accommodation or relaxation induced by the mismatch in this system is missing and further investigations are of interest in this regard. Two factors might influence the present behaviour: 1. the layered nature of the Bi-based superconducting phases in which the bonding between layers and especially between the two-neighbouring Bi ones is weak of Van der Waals type so that layers can easily slide and, hence, can release strain (somehow similar to the formation of stacking faults and/or misfit-dislocation) and 2. specific features of the MOCVD process that are closer to the equilibrium processes than in the case of the other deposition techniques. Another important parameter to control growth orientation is probably temperature. Our observation is based on the analogy with our previous results [5] for the growth of Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) superconducting thin films on (110) SrTiO\(_3\) substrates, i.e. when the growth temperature is low films will have (119) orientation due to the small lattice mismatch between (119) Bi\(_2\)Sr\(_2\)Ca\(_2\)Cu\(_3\)O\(_{10}\) and the (110) substrate, while at high growth temperatures (00l) orientation will be obtained. We shall also note that for the superconducting phases from the Bi-Sr-Ca-Cu-O system in-plane orientation relationships observed experimentally are not explained by the classic near coincidence site lattice model between superconducting phase and the substrate [6, 7].

4. Conclusion

We have successfully grown by MOCVD (001) superconducting Bi-2223 thin films on (001) and (110) MgO. Higher critical temperatures are obtained for the thin films grown on (001) MgO \((T_c=95.1K)\) than on (110) MgO \((T_c=75K)\). On the other hand good structural and morphology characteristics of both films, i.e. occurrence of (almost) single phase, c-axis orientation, and relatively low roughness, are similar and make them promising for the future microwave studies. Interestingly, AFM images may suggest that there is also in-plane alignment, but further detailed measurements are required to clarify this aspect. Growth of c-axis BSCCO films on substrates with very large film-
substrate lattice mismatch is puzzling and needs once more further investigations to understand this effect.

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