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Chemical Solution Deposition of LaMnO$_3$ Buffer Layers for Coated Conductors

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Abstract—Chemical solution deposition (CSD) is used to prepare LaMnO$_3$ (LMO) buffer layers on different substrates. The results show that biaxially oriented LMO films can be successfully prepared on single-crystal SrTiO$_3$ (STO) and STO buffered single-crystal LaAlO$_3$ substrates when humid 4%H$_2$–N$_2$ annealing atmosphere is used. The orientation of LMO–Ni is (110)-oriented even when the annealing atmosphere is humid 4%H$_2$–N$_2$. When CSD-derived STO–Ni is used as a template, biaxially oriented LMO buffer layers with c-axis orientation can be successfully prepared. The results provide an effective route to prepare LMO-based buffer layers using CSD.

Index Terms—Buffer layers, chemical solution deposition (CSD), coated conductors.

I. INTRODUCTION

T
HE rolling-assisted biaxially textured substrates (RABiTS) and ion-beam assisted deposition approaches have been identified recently as the leading techniques to fabricate long lengths of high-performance YBCO coated conductors [1]. For the RABiTS approach, if the buffer layer(s) and the superconducting film are both fabricated through chemical solution deposition (CSD), the route is called an all-chemical approach for coated conductors, which is considered as a very promising method for large-scale preparation of coated conductors with low cost since the route is a nonvacuum method [2], [3].

In order to prepare coated conductors using an all-chemical approach, one of the key problems is to fabricate suitable buffer layers. The buffer layers play twofold functions: one is to transmit the biaxial texture of the metallic substrate to the superconducting film; another is to block the interdiffusion between the metallic substrate and the superconducting film [4]. In order to satisfy the above two functions, the buffer layer should have a similar lattice constant and thermal expansion coefficient to both the metallic substrate and the superconducting film. Moreover, the oxygen from the superconducting film should have a low diffusion constant in the buffer layer, and the metallic ions from the metallic substrate also should have a low diffusion constant in the buffer layer.

Many potential buffer layer materials have been identified for coated conductors on cube-textured Ni-based substrates using CSD, including CeO$_2$ [5]–[7], Y-stabilized ZrO$_2$ [7], Y$_2$O$_3$ [8], La$_2$Zr$_2$O$_7$ [9]–[15], Gd$_2$Zr$_2$O$_7$ [16], LaMnO$_3$ (LMO) [17], SrTiO$_3$ (STO) [18]–[21], and so on. For LMO–Ni buffer layers, it is observed that RF-magnetron sputtered buffer layers are highly c-axis oriented, the interdiffusion between the metallic substrate and the superconducting films can be nearly completely blocked when the thickness of LMO is higher than 60 nm, and the critical current density of the YBCO film on the LMO–Ni can be higher than 1 MA/cm$^2$, which indicates that the LMO is a very promising buffer layer for coated conductors [22], [23]. However, in the CSD process, it is reported that the LMO–Ni buffer layers are difficult to crystallization under dry reducing atmosphere, and when annealed in a wet reducing atmosphere the LMO–Ni is highly (110)-oriented [17]. Moreover, there are no relevant reports about CSD for highly c-axis oriented LMO–Ni buffer layers, and the CSD growth mechanism of LMO–Ni is not yet very clear. Additionally, the divalent alkali-earth element Sr-doped LMO, La$_{0.7}$Sr$_{0.3}$MnO$_3$ can be used as conductive buffer layers, which has been prepared by CSD method recently [24].

Currently, highly c-axis oriented STO–Ni buffer layers have been successfully prepared by several groups using the CSD method [18]–[21]. However, it is unfortunate to find that the blooming properties of the pure STO buffer layer are not very good. It is always observed that the NiO phase always appears during the chemical processing of superconducting films even if the STO thickness is about 400 nm, and the critical temperature $T_c$ is much lower than 90 K, which suggests that pure STO is not an ideal buffer layer for coated conductors.

In this paper, LMO films on different substrates have been prepared using CSD under reducing atmosphere, and the growth mechanism is also discussed. The results show that the LMO–STO–Ni is a very promising buffer layer sequence for coated conductors using an all-chemical approach.

II. EXPERIMENTAL PROCEDURE

Commercial LaAlO$_3$ (LAO) and STO single-crystal substrates were cleaned in an ultrasonic cleaner using acetone, methanol, and deionized water before annealing at 1000 °C to obtain a well-defined surface. The purchased Ni substrates were prepared using CSD under reducing atmosphere, and the growth mechanism is also discussed. The results show that the LMO–STO–Ni is a very promising buffer layer sequence for coated conductors using an all-chemical approach.
also cleaned in an ultrasonic cleaner using acetone, methanol, and deionized water, and then the Ni substrates were annealed at 1000 °C under 4%H2–N2 atmosphere in order to eliminate the oxygen atoms at the surface.

The preparation of the STO buffer layers, including the solution preparation, the deposition, and the heat treatment, has been described in detail previously [25]. In this paper, the STO solution concentration is 0.25M, and the thickness of STO–Ni is about 300 nm.

The synthesis of the precursor solution for obtaining LMO films is as follows: La-acetate (Alfa Aesar, 99.9% in purity) was dissolved in propionic acid at 70 °C, and then Mn-acetate (Alfa Aesar, 99% in purity) was added to the solution and stirred at room temperature for more than 20 h to obtain a well-mixed precursor solution. To obtain the desired solution concentration, the LMO solution was diluted by n-butanol to 0.2M. The deposition of LMO films was conducted using a spin coater with a rotation speed of 4000 r/min and a time of 60 s. The deposited films were then dried at 300 °C for 30 min under flowing H2–N2 atmosphere using a flow of 18 sccm for H2 and 450 sccm for N2. The dried LMO films were then annealed at 900 °C for 120 min with the same flux of H2 and N2 as in the drying process. To introduce suitable humidity into the annealing atmosphere, the H2–N2 gas was passed through several bottles filled with deionized water at 30 °C corresponding to a humidity of 2.4%. In order to obtain thicker buffer layers, the depositing, drying, and annealing processes were repeated several times. The thicknesses were checked by ellipsometer (Jobin Yvon-designed Uvisel type), and the results showed that each layer of LMO was about 80 nm in thickness.

To evaluate the crystallization quality as well as the out-of-plane and in-plane orientation, X-ray diffraction (XRD) was carried out using CuKα diffraction (Philips X’pert Pro). Field-emission scanning electronic microscopy [(FE-SEM) FEI-designed, Sirion 200 type] was carried out to investigate the microstructure of the derived samples.

III. RESULTS AND DISCUSSION

Fig. 1 shows the XRD θ–2θ results of the LMO–STO films annealed under dry and humid H2–N2 atmosphere. It can be seen that there are no diffraction peaks corresponding to the LMO phase when the annealing atmosphere is dry 4%H2–N2, which is the same result as previous reports and can be attributed to the very low oxygen partial pressure in the annealing atmosphere. However, when the LMO–STO is annealed under humid 4%H2–N2 atmosphere, the XRD result gives clear evidence that the LMO film is highly (h00)-oriented with pseudocubic structure; moreover, the lattice constant calculated from the LMO (200) diffraction peak using the Scherrer formula is about 3.97 Å, which is larger than that of the stoichiometric LMO (3.88 Å) \(^1\) and can be attributed to the oxygen vacancies in the derived LMO film [28]. The above results suggest that the introduction of humidity into the 4%H2–N2 is beneficial to prepare LMO films using the CSD method.

Based on the above results, we carried out the CSD of LMO on STO–LAO templates, and the XRD θ–2θ result of the LMO–STO–LAO is shown in Fig. 2. In order to show the result more clearly, the XRD θ–2θ result of the STO–LAO is also shown in Fig. 2. From Fig. 2, it is seen that the STO–LAO film is highly (h00)-oriented, and the LMO film is also (h00)-oriented. Moreover, the lattice constant calculated from the LMO (200) diffraction peak using the Scherrer formula is about 3.97 Å, which can be also attributed to the oxygen vacancies in the derived LMO film. Fig. 3 shows the FE-SEM results of the CSD derived STO–LAO and LMO–STO–LAO films. It can be seen that the STO and LMO films are very dense and flat except for some undesired holes shown as black area in the LMO–STO–LAO film, and the root-mean-square roughness is below 8 nm, which is suitable for deposition of superconducting films, such as YBCO [3], [29], [30].

In order to fabricate LMO-based buffer layers suitable for coated conductors using an all-chemical approach, the LMO films are also deposited directly on the Ni substrates under dry and humid 4%H2–N2 annealing atmosphere, and the XRD θ–2θ results are shown in Fig. 4. It can be seen that the LMO–Ni buffer layer annealed under dry atmosphere is not crystallized and without any relevant diffraction peaks;

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Fig. 3. (a) FE-SEM results of CSD-derived STO–LAO and (b) of all CSD-derived LMO–STO–LAO (b).

Fig. 4. XRD $\theta$–2$\theta$ results of LMO–Ni annealed under (a) dry 4%H$_2$–N$_2$ reducing atmosphere and (b) humid 4%H$_2$–N$_2$ reducing atmosphere.

However, the LMO–Ni annealed in a humid atmosphere is highly (110)-oriented, which is different with the results of LMO–LAO or LMO–STO–LAO and is the same as in previous reports [17].

As for the orientation difference between the LMO–Ni and LMO–STO–LAO or LMO–STO, the reasons are not very clear yet. However, this may be explained as follows.

In LMO, the oxygen ratio is different in different planes [31]. As shown in Fig. 5, it is seen that the lowest oxygen ratio is attributed to the (110) plane, that is to say, in a single plane the ratio between the cation and the anion is lowest for the (110) plane. Usually, the orientation of the film is determined by the competition between the interface energy of the film/substrate and the surface energy of the film [32]. As for the orientation of LMO films on STO and STO–LAO, although annealed under humid reducing atmosphere, since of the LMO and STO have the same perovskite structure, the interface energy of LMO–STO is suggested to be the primary factor in determination of the LMO orientation resulting in LMO (h00)//STO (h00)//STO–LAO. However, for the LMO on Ni substrate, since the structure difference between the LMO and Ni, the interface energy factor should be compromised with the surface energy of the LMO. That is to say, the interface energy as well as the surface energy will both play important roles in determination of the LMO orientation. Since the annealing atmosphere is humid reducing, the LMO film will have many oxygen vacancies, which suggests the LMO (110) is the most stable surface with the lowest surface energy; this will be further studied in the next steps.

From the above experimental results, it is obviously seen that although the LMO film is highly (h00)-oriented when STO or STO–LAO templates are used, the LMO–Ni is (110) oriented, which is not suitable for coated conductors. In order to fabricate highly (h00)-oriented LMO-based buffer layers, some effective methods should be applied. From the enlightenments of the above analysis [33], it is suggested that the architecture of LMO–STO–Ni may be a suitable buffer layer structure for an all-chemical approach for coated conductors.

Fig. 6 is the XRD $\theta$–2$\theta$ results of LMO–STO–Ni with different layers of LMO from one to three layers prepared using CSD for both STO and LMO. It should be noted that if the annealing atmosphere is dry 4%H$_2$–N$_2$, the LMO cannot be well crystallized. From Fig. 6, it can be seen that all three samples are highly (h00)-oriented both for the STO and the LMO films. Additionally, the lattice constant of the LMO is also larger than that of the STO, which is similar to the above results about LMO on STO and STO–LAO templates and can also be attributed to the oxygen vacancies in the derived LMO films.

To check the in-plane orientation of the derived LMO–STO–Ni buffer layers, a phi-scan of the (110) plane of LMO (three layers)/STO–Ni was carried out, and the result is shown in Fig. 7. To give a clear relationship between the STO and LMO, a phi-scan of the (110) plane of STO–Ni was also measured and is shown in Fig. 7. It can be seen that the LMO layer grows on the STO–Ni in cube-on-cube mode except for some undesired misoriented LMO domains in the derived buffer layers, which are harmful for the YBCO films. Further experiments are being carried out to eliminate the misoriented LMO domains using several routes, such as higher annealing temperatures, longer annealing times, and a seed layer technique. Moreover, the phi-scan full-width at half-maximum of the LMO layer ($\sim 12^\circ$) is larger than that of the STO layer ($\sim 9^\circ$), which may be attributed to the nucleation within the LMO layers [34].

Fig. 8 shows the FE-SEM result of the LMO (three layers)/STO–Ni and of the STO–Ni. It can be seen that the STO film
Fig. 6. XRD $\theta - 2\theta$ results of LMO–STO–Ni with the different LMO layers. (a) One layer LMO; (b) two layers LMO; and (c) three layers LMO.

is granular with clear grain boundaries; the LMO film shows denser microstructure and a relatively smooth surface. The results indicate that the LMO–STO–Ni buffer layers can be used for the deposition of superconducting films.

IV. CONCLUSION

CSD as a very promising method for coated conductors is used to fabricate LMO films on different substrates. It is found that when single-crystal STO and STO–LAO substrates are used as templates, highly biaxially and c-axis oriented LMO films can be successfully obtained under a humid 4%H$_2$–N$_2$ annealing atmosphere. However, under the same annealing atmosphere, when LaMnO$_3$ is deposited directly on textured Ni substrates, the orientation of LMO buffer layers is (110). When CSD-derived STO–Ni is used as a template, the orientation of LMO can be tuned to highly c-axis oriented. The results provide an effective route to prepare LMO-based buffer layers using CSD.

Fig. 8. (a) FE-SEM results of STO–Ni and (b) LMO (three layers)/STO–Ni.

REFERENCES


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