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Fabrications of Y-ZrO_2 buffer layers of coated conductors using dc-sputtering

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Abstract **-- The detailed conditions of dc-sputtering for depositions of yttria-stabilized ZrO_2 (YSZ) films were investigated, while the films were grown on the CeO_2 template layers on biaxially textured Ni-tapes. The window of oxygen pressures for proper growth of YSZ films, which was dependent on sputtering powers, was determined by sufficient oxidations of the YSZ films and the de-oxidation of the target surface, which was required for rapid sputtering. The window turned out to be fairly wide under certain values of argon pressure. When the sputtering power was raised, the deposition rate increased without narrowing the window. The fabricated YSZ films showed good texture qualities and surface morphologies.**

Keywords : coated conductor, buffer layer, YSZ, sputtering

1. INTRODUCTION

The recent progresses in the fabrication technologies of coated conductors, for which biaxially textured metallic substrates such as Ni alloy tapes are used, indicate that their practical applications are very promising [1]. Since the superconducting $RE_1Ba_2Cu_3O_7$ (REBCO, RE=Rare Earth) films can be grown at the temperatures as high as ~700℃, appropriate buffer films are necessary between the REBCO film and the substrate surface in order to prevent them from chemical reaction [2].

Usually the buffer film is comprised of several layers of different oxide materials. For instance, the best-known one is CeO_2/YSZ/CeO_2 [3]. Each layer of these triple films plays different role for the proper growth of high quality superconductive over-layers. The lowest oxide layer, which is grown epitaxially on the metallic tape, provides the continuation of crystalline textures from the metallic substrate. The best-known materials for this template layer are CeO_2 and Y_2O_3 [4]. The over-layer on the template film provides the role of blocking the atomic diffusion from substrates to superconducting films, while the atoms of the metallic substrate come out easily if there are pinholes in the template buffer layers. Usually this blocking layer should be thick and atomically dense. In many cases, the appropriate material for this is yttria-stabilized zirconia (YSZ). The top layer is for lattice matching with the superconducting film. Without this lattice-matching layer, the REBCO superconducting films might be textured in two different orientations, while one crystalline orientations are rotated by 45° in the plane with respect to the other [5].

To prevent the atoms of the metallic substrate from coming out, it is desirable that the blocking layers are deposited to be atomically dense without pinholes. This requirement becomes more important when it takes long time to deposit thick superconducting films or when the substrate temperature is high for the rapid growth of superconducing film. There are several methods for depositions of YSZ such as e-beam evaporation, sputtering, and MOCVD...etc., but among these, sputtering is the best suited to produce the dense films required for this. This property of sputtering is related to the high energy of impingement during depositions.

Since the deposition rate should be as large as possible, it should be the dc-sputtering with a Y-Zr metallic target rather than the rf-sputtering with a YSZ ceramic target. This is due to the large difference of sputtering yields between a metallic target and an oxide target. Some conditions are required for the fast deposition of YSZ films on the template layer. The important parameters to control are the density of oxygen ion and the partial pressure of oxygen gas, which are correlated to each other. The density of oxygen ion, which is produced by the plasma near the sputtering target, should be as small as possible around the substrates. This is because the oxygen ions, which diffuse easily through the buffer layer and oxidize the metallic substrate excessively, deteriorate the template film as well as the substrate. The partial pressure of oxygen gas should be within a certain window. When it exceeds the upper limit of the window, the surface of the sputtering target is oxidized too much and it results in the slow-down of sputtering rate. When it is smaller than the lower limit, the reaction with oxygen in depositions is not completed and some non-oxidized zirconium can exist in the film.

In this paper, we report the detailed structure of our dc-sputtering system and the conditions of rapid growth of high quality YSZ films on biaxially textured Ni tapes.

2. EXPERIMENTS

A 3mm thick Ni plate was rolled to a ~80μm thick tape and annealed in ~10mTorr hydrogen gas at 850℃ for ~1hour. Then we measured XRD pole figures of Ni (111) peaks. The Ni tape was found to be biaxially textured with

8~9° of in-plane alignments of crystalline orientations. The template layer, which is CeO_2, was reactively deposited by means of thermal evaporation in the chamber, in which the reel-to-reel system was set up. It was evaporated from metallic lumps using a tungsten boat. In most cases, the Ni tapes were heat-treated in H_2 gas again in the chamber just before the depositions of CeO_2 films to ensure the removal of possible NiO layers at the metal surface.

The blocking layers were deposited by dc-sputtering, followed by the depositions of the top CeO_2-layer by rf-sputtering. Fig.1 shows the schematic diagram of the dc-sputtering system for depositions of YSZ films. Two magnetron sputtering guns and reel-to-reel system were installed in the chamber. We used Zr disks of 5cm diameter for the sputtering targets. Two small Y-disks of 1cm diameter were pinned in each Zr-disk. The final top layer, CeO_2 film, was deposited in the same sputtering chamber using CeO_2 disks for sputtering targets and rf-power suppliers. The deposition conditions of rf-sputtering for the top layer are simple [6]. Hence the detailed description of the depositions of the CeO_2 films is not necessary. However the conditions for dc-sputtering of YSZ layers are not simple at all and we'll explain it in detail.

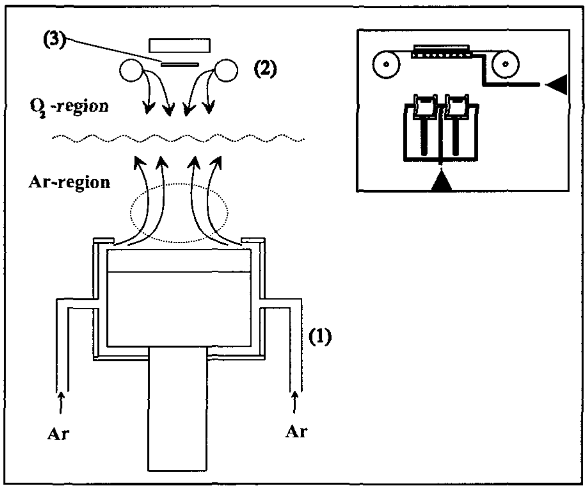

Fig. 1. Schematic diagram of the dc-sputtering system for the depositions of YSZ films. Two magnetron sputtering guns are installed. The Ar gas-tubes (1) are connected to the caps of the sputtering guns. The injection holes (2) of oxygen gas were placed very closed to the tape substrate. Inset; side view of the sputtering system, which shows the structure of reel-to-reel system.

In the schematic diagram of Fig.1, the Ar gas-tubes were connected to the caps of the sputtering guns, which were grounded electrically, so that Ar gas could be supplied into the sputtering gun and flow around the metallic target as shown in the figure. This route of gas flow prevents the oxygen gas from approaching the target surfaces. The injection holes of oxygen gas were placed near the tape substrate as shown in the figure, where many holes were distributed along the heating zone of the tape for the uniform distribution of the oxygen gas pressure on the tape. Since the Ar-gas comes out from the gun, the oxygen gas hardly approaches the plasma area around the targets. Fig.1 shows that the space between the tape substrate and the sputtering gun was roughly divided into two regions. The upper region near the tape is occupied mostly by oxygen gas flow and the lower region near the guns is occupied mostly by argon gas flow. Of course they undergo mixing with each other in the mid-region. Since the vacuum gauge was placed ~30cm away from the substrate region, the measured value of gas pressure was a nominal one rather than the one at the substrate. The tape substrate was heated to a temperature of 700°C using several halogen lamps. We could measure the deposition rate using a microbalance with a quartz crystal oscillator, which was water-cooled and placed near the substrate. The thickness of the YSZ layer was about 300nm. Finally we checked the texture qualities of the film using XRD and SEM measurements.

There were two purposes of this type of structure for the gas supplies. (1) One is to prevent the target surface from oxidation and consequently to increase the sputtering rate. As explained in the introduction, the oxidations of the surface of sputtering targets results in slow-down of sputtering rate. The larger the Ar pressure is, the more effective the protection of the targets against oxidation can be, but it results in the reduction of mean free path and consequently slow-down of deposition rate. Hence an appropriate value of Ar pressure must be chosen. (2) The other is to reduce the ionization rate of oxygen gas near the substrates. The oxygen ions diffuse so easily through the hot buffer layers and heavily oxidize the metallic substrate, which results in the deterioration of the template film. Hence the pressure of oxygen ions (not neutral oxygen molecules) on the tape should be reduced as much as possible.

After deposition of a CeO_2 top-layer, we deposited a ~100nm thick YBCO film on it using the hollow cathode dc-sputtering. We checked the quality of the superconductive film by measuring XRD pole figures, R-T curves, and the critical current densities.

3. RESULTS

Fig.2 shows the minimum partial pressure of oxygen gas (P_m) for proper formations of YSZ film as a function of

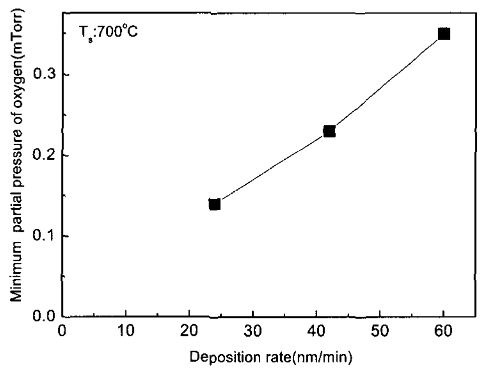

Fig. 2. Minimum partial pressure of oxygen gas (P_m) for proper formations of YSZ film as a function of deposition rate

deposition rate (DR), while T_s is 700°C. When P_{O2} was lower than P_m(DR) for a given DR, the YSZ films were not properly oxidized. We could easily recognize it by the color of films and the height of XRD peaks [7]. The color of the YSZ films oxidized insufficiently was not highly transparent and the height of XRD (200) peak of them was smaller than those of sufficiently oxidized films. When P_{O2} was increased to exceed P_m, the height of the XRD peaks reached the saturated value. From this we could determine the well defined P_m for given DR. P_m was only slightly dependent on the pressure of Ar (P_{Ar}) and the sputtering power, but was strongly dependent on T_s. We measured P_m for the off-axis deposition as well as the on-axis deposition, and found similar P_m for both cases.

Figure 3 shows DR as functions of P_{O2} for various sputtering powers and Ar pressures for on-axis sputtering [8]. In any case, DR's were almost constant until they sharply dropped to very small ones at certain values of P_{O2} (P_d). One can find the similar features of reactive sputtering in Ref.7. In Fig.3, the arrow indicates P_d for each case. Those abrupt drops at P_d imply that the sputtering yields quickly decreased when the surfaces of targets were oxidized by sufficient oxygen gas higher than P_{O2}.

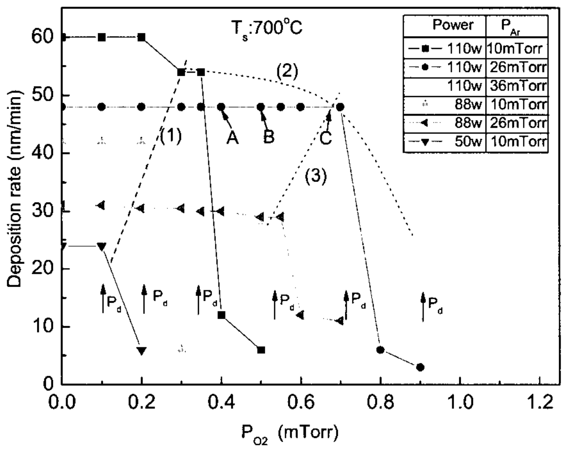

Fig. 3. Deposition rates (DR) as functions of oxygen pressure for various sputtering powers and P_{Ar}. DR's are constant until they sharply dropped to very small values at certain values of P_{O2}, which is defined as Pd for each case. The three dashed lines, (1), (2), and (3) indicate (1) Pm for given DR, the trends of (2) the changes of (P_d, DR) as a function of Argon pressure (P_{Ar}), (3) the changes of (P_d, DR) as functions of power and with P_{Ar} fixed as 26mTorr, respectively.

In Fig.1, one can see that Ar gas came out from the gap between the cap of the gun and the target and prevented the oxygen gas from approaching to the target surface, which kept the target surface to be metallic for the high yield of sputtering. As P_{O2} was increased up to P_d, the oxygen gas finally reached the target surface by making its way through the counter-flow of Ar gas. Then the target surface was oxidized, that resulted in the abrupt drop of sputtering yield. The three cases for 50W, 88W, and 110W of sputtering power with 10mTorr of P_{Ar} indicate that P_d as well as DR increased as the power increased. This is easy to understand because the occasional formations of oxide on the target surface can be removed by sputtering for high sputtering power. When the Ar pressure was increased up to 36mTorr, DR decreased, which must be due to the decrease of mean free path, and P_d increased, which must be better protection against the oxygen gas.

The dashed line (1) in Fig.3 is P_m for the given DR, which is re-plot of the same data of Fig.2. For given deposition rate, the window of P_{O2} is between P_m and P_d. Hence except the case of 26mTorr and 36mTorr, the windows were very narrow or even absent. However the window of P_{O2} for 26mTorr and 36mTorr of P_{Ar} was relatively wide. The window of P_{O2} in this case is from ~0.3 to ~0.7mTorr, which is fairly wide for easy control of film growth. The dashed line (2) indicates the trend of the changes of (P_d, DR) when P_{Ar} is increased and the power was fixed as 110W. This dashed line indicates that the window of P_{O2} can be widened when P_{Ar} is increased, but DR decreased at the same time. The dashed line (3) indicates the trend of the changes of (P_d, DR) as the power is increased and P_{Ar} is fixed as 26mTorr. This line implies that DR can be increased without reduction of the window of P_{O2} if the power is increased. Based on these results, we believe further increases of DR and the window can be achieved by higher power. All the parameters of these results shown in Fig2, and 3 are dependent on the structure in the chamber.

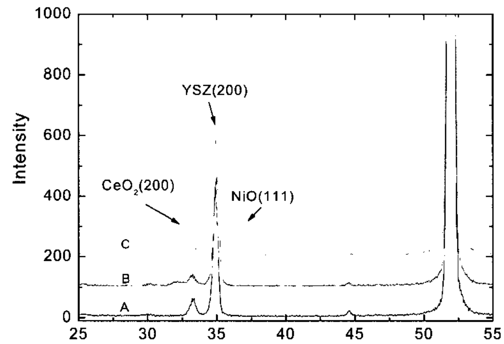

Fig. 4. The XRD 2-θ scans for these three cases, A, B, and C, which are defined in Fig.3..

For the case of 26mTorr of P_{Ar} and 110W, we take the three cases of conditions, which are indicated by A, B, and C in Fig.3. The XRD 2-θ scans in Fig. 4 shows good qualities of growths for these three cases. The peak of NiO(111) for the case C shows that the oversupplied oxygen gas caused the oxidation at the interface of the Ni substrate and the buffer layer. This oxidation of Ni is allowed, because the buffer layer, which was already sufficiently thick, is stable. Fig.5a shows the typical ϕ-scan of YSZ(111) peak for the case of A, where FWHM was 14.6°. Fig.5b shows the ω-scan of YSZ(002) peak for the same sample. FWHM was 9.1°. The out-of-plane alignment was better than that of in-plane.

Fig.6 is the SEM micrograph of the YSZ surface. The surface looked flat and we couldn't see any cracks although there were lots of cracks in the template CeO_2 layer. Those crack formations in CeO_2 template films are well known [9]. Since the width of the opening of the cracks was ~5nm and the thickness of the YSZ film

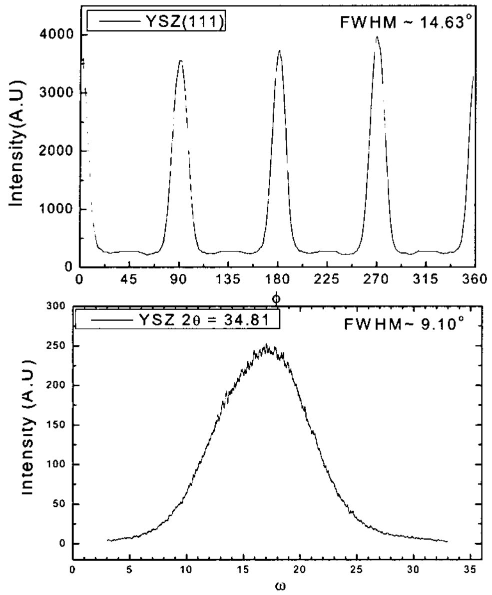

Fig. 5. (a) and (b) (a) XRD ϕ-scan of YSZ(111) peak and (b) ω-scan of YSZ(002) peak for the case A.

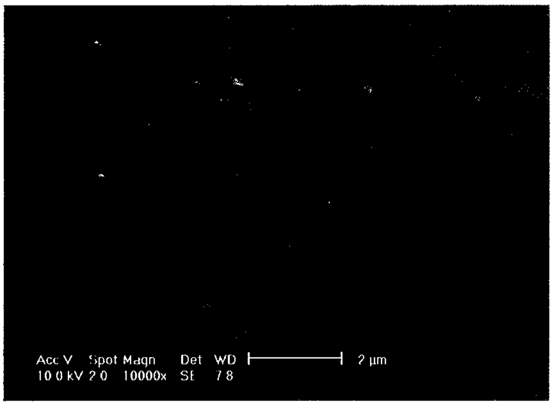

Fig 6. SEM micrograph for a typical YSZ sample

was ~300nm, the cracks seemed to be completely covered with the YSZ films. Similar phenomena have been reported in Ref. [6].

4. CONCLUSION

The detailed conditions of dc-sputtering for the depositions of YSZ films were investigated, while the films were grown on the CeO_2 template layers on biaxially Ni tapes. The window of the oxygen pressure for proper growth of YSZ films, which was dependent on sputtering powers, was determined by the sufficient oxidation of the depositions and the de-oxidation of the target surface. The window turned out to be fairly wide under certain values of argon pressure. When the sputtering power was raised, the deposition rate increased without narrowing the window. The YSZ films fabricated showed good texture and surface morphologies. Even though there were cracks in the CeO_2 films templates, we couldn't see any cracks in the YSZ film surfaces.

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