Comparisons of the growth properties of CeO_2 and Y_2O_3 buffer layers on Ni tapes

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Abstract – The growth properties of Y_2O_3 and CeO_2 films for the buffer layers on Ni tapes were studied comparatively. The water vapor larger than $2x10^{-5}$ Torr and the substrate temperature higher than 700°C were required for the proper growth of Y_2O_3 films, while the upper limits of the water vapor and the lower limit of the substrate temperatures for the proper growth of CeO_2 were $1x10^{-5}$ Torr and 500°C, respectively. These imply that the windows of the growth conditions of CeO_2 are wider than those of Y_2O_3. However the formation of cracks in CeO_2 films were its disadvantage, while Y_2O_3 showed no cracks.
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1. Introduction

The recent progresses in the fabrication technologies of coated conductors using biaxially textured metallic substrates such as Ni alloy tapes indicate that their practical applications are very promising [1]. Since the superconducting $Re_1Ba_2Cu_3O_7$ (ReBCO) films can be grown at the temperature as high as 700°C, appropriate buffer films are necessary between the ReBCO film and the substrate surface in order to prevent them from chemical reaction at the interface [2]. Various appropriate materials for those buffer layers were reported. Among them, the best-known buffer layer is the triple structured oxide film, $CeO_2/YSZ/CeO_2$ [2]. Since the bottom oxide layer, CeO_2, should be grown epitaxially on the metallic substrate, it is important to prevent the substrate surface from oxidation during depositions. This can be easily done for CeO_2 depositions on Ni tapes. One of the serious disadvantages of this film is the formation of cracks when its thickness is larger than a certain value [3]. It was reported that the bottom layer can be replaced by Gd_2O_3, Y_2O_3, Yb_2O_3, etc [4]. It is known that the Y_2O_3 films show no cracking [5], but the detailed growth features of this film have not been reported. It is interesting to compare the properties of Y_2O_3 and CeO_2. For instance, due to the chemical differences between CeO_2 and Y_2O_3, the growth conditions of them might be also different. Since their advantages and disadvantages are different from each other, it is not clear which is the better buffer layer. In this paper we report the results of the comparative studies on the relation between the growth conditions and the textures/morphologies for these two types of films.

2. Experiment

A 3mm thick Ni plate were rolled to 80μm tape and annealed in vacuum with 10mTorr H_2 at 850°C for 1hour for each part of tape. The texture quality of this RABiTS Ni tapes were measured by XRD pole figures, which indicated that the in-plane alignment was 8-9°. Y_2O_3 films and CeO_2 films were deposited on the Ni tapes using thermal evaporation method. We used W boat and Ta boat for the evaporations of the metallic lumps of Y and Ce, respectively. The base pressure of the chamber $1x10^{-7}$Torr and the partial pressure of oxygen was less than $1x10^{-9}$ Torr. To oxidize the films, water vapor was supplied into the chamber, where the partial pressure of water vapor was varied from $1x10^{-4}$ to $1x10^{-7}$ Torr. The oxygen solved in the water was removed by heating, freezing, and pumping many times. Since we could see the H_2 partial pressure was increased during depositions of film in the water vapor, Ce or Y must react with water and produced H_2 gas in the chamber. Hence the oxidation rates were controlled by the partial pressure of the water vapor. This method of oxidation using water vapor has an important advantage that we could oxidized the films with keeping the Ni surfaces from oxidation. This was possible because the electron negativity of Ni substrate is smaller than H, while Y and Ce are much more reactive with oxygen than H. The substrate temperature (Ts) was varied from 400°C to 730°C. The thickness of the Y_2O_3 films and

CeO2 were varied from 20nm to 150nm. We measured XRD θ-2θscans and pole figures to find the textures, and we measured SEM to check the surface morphologi

3.Results and discussions

Fig.1 shows the partial pressures of water $P(H_2O)$ vs XRD θ-2θscans of Y_2O_3 films, which were deposited at the substrate temperature (Ts), 730°C, and the deposition rate, 0.2nm/sec. When $P(H_2O)$ was larger than $2x10^{-5}$ Torr, the [100] axes were normal to the surfaces. The deficiency of the water vapor resulted in [111] axis normal growth for $P(H_2O)$ less than $7.5x10^{-6}$ Torr. We also observed that too much water vapor resulted in [111] axis normal growth for $P(H_2O)$ larger than $4x10^{-5}$Torr. In order to increase the deposition rate, the more water vapor might be necessary and we opened the gas value more for the more introduction of the water vapor. However we observed that $P(H_2O)$ was kept as the same value, which was due to the fact that the observed $P(H_2O)$ was for the remnant water vapor after it reacted with the depositions of Y on the substrate and on the wall of the chamber. Hence the fast deposition rate required a large supply of water vapor with the same partial pressure read by the gauge. Hence the best $P(H_2O)$was independent of the deposition rate.
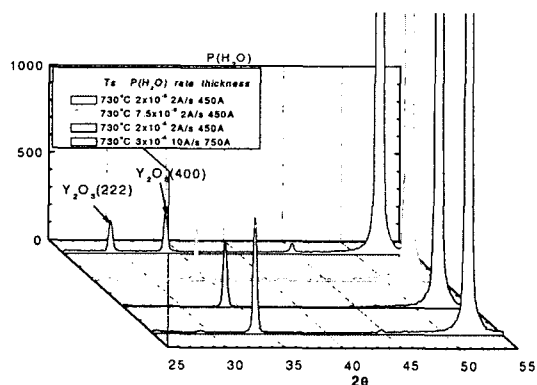

Fig. 1. $P(H_2O)$ vs XRD θ-2θ scans of Y_2O_3 films, which were deposited at 730°C and with the deposition rate, 0.2nm/sec

Fig.2 shows Ts vs XRD θ-2θscans of Y_2O_3 films, which were deposited in $P(H_2O)=2x10^{-5}$Torr and the deposition rate, 0.2nm/sec. These data indicate that Ts should be higher than 700°C for the high quality of textures.
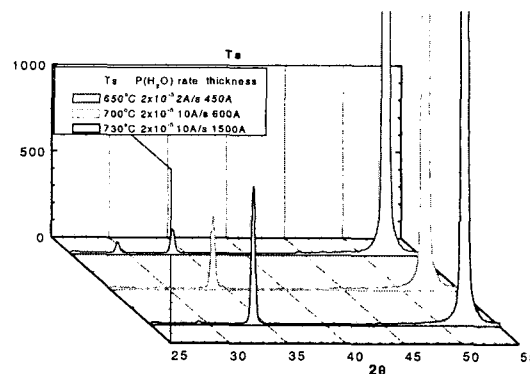

Fig. 2. Ts vs XRD θ-2θscans of Y_2O_3 films which were deposited in $P(H_2O)=2x10^{-5}$ Torr and the deposition rate, 0.2nm/sec

Fig.3 shows a pole figure of a typical Y_2O_3 film, which was grown in the water vapor of $P(H_2O)=2x10^{-5}$Torr and at Ts=730°C. This pole figure shows that 10% line was indistinguishable from the background noise.

Fig.4 shows the absence of cracks, where this is the SEM micrograph of the surface of a 35nm thick Y_2O_3 film grown at 700°C and $2x10^{-5}$ Torr. We checked SEM micrographs of several samples whose thickness were varied from 20nm to 150nm. All of them showed no cracks. This micrograph shows many small grains whose sizes are less than 100nm. We don't know exactly what they are. EDS measurement indicate no chemical difference. We think that they might be the domains of (111) growths. Those (111) growths seemed to be due to the native oxide surface of Ni. The rolled Ni tapes underwent heat treatments in the hydrogen gas so that their surfaces were deoxidized. However when they were exposed to air during we brought them to the chamber, the slight oxidations of their surfaces were inevitable. From our experience, we found that it is desirable to deoxidize the Ni surface again in-situ in the chamber just before Y_2O_3 deposition. If the water vapor was not too sufficient during the deposition of the first atomic layer on Ni, they might react with the oxygen atoms, which were in the NiO surface layer, and resulted in deoxidizing the native oxide surface. The evidence of this is our empirical observations that the best texture were obtained in the water vapor pressure less than a certain value, $3x10^{-5}$Torr. This upper limit of $P(H_2O)$ depends on the chemical reactivity's, i.e. the upper limit of $Y_2O_3$was different from those of CeO_2 because their reactivity with oxygen are different to each other.
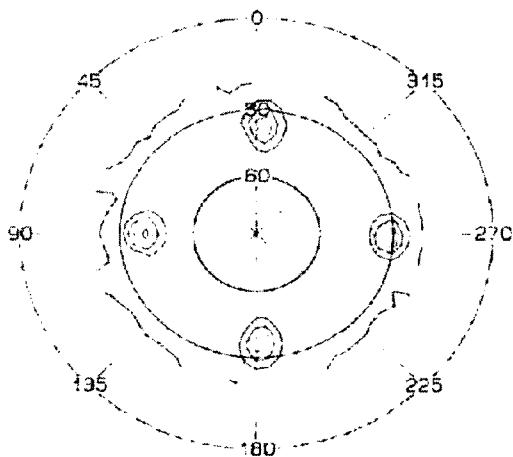
Fig. 3. Pole figure of the typical Y2O3 film, which indicate a good quality of (100) growth. The 10% line is the background noise.

Fig. 4. SEM micrograph of the surface of 35nm thickness Y_2O_3film, which were grown at $700°C$ and $2x10^{-5}$ Torr. This figure showed no cracks.

In order to compare the various properties of Y_2O_3 films with those of CeO_2 films, we carried out similar measurements on the several CeO_2 films. Fig.5a shows $P(H_2O)$ vs XRD θ-2θscans of CeO_2 films, which were grown at $3x10^{-6}$- $2x10^{-5}$Torr of $P(H_2O)$ with Ts fixed as $650°C$. $P(H_2O)$'s less than $1x10^{-5}$Torr were required for (100) growth of CeO_2. We tested the growth of CeO_2 films on a long Ni tape at very low $P(H_2O)$, which was $1x10^{-6}$Torr. For the initial few tens of cm, the film growths were good, but then the film quality got worse gradually. This indicates that $P(H_2O)$ should be kept at few times 10^{-6}Torr, which is lower than that of CeO_2. This might be due to the higher reactivity of Ce than that of Y. It'll be interesting research to find out the effects of these differences on the de-oxidation of the native oxide surfaces of Ni by the deposition of those metallic films.
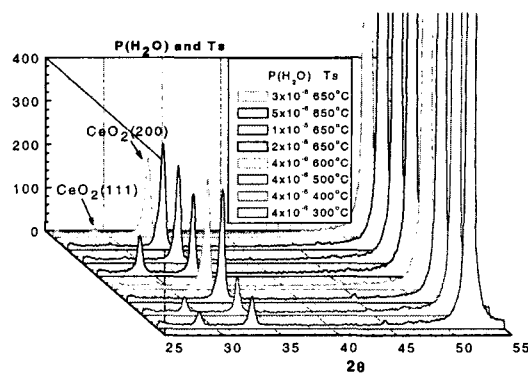

Fig. 5. (a) $P(H_2O)$ vs XRD θ-2θ scans of CeO_2 films grown at a Ts fixed as $650°C$. The films grown below $1x10^{-5}$ Torr show good (100) grown. (b) Ts vs XRD θ-2θ scans of CeO_2 films grown in $P(H_2O)$ fixed as $4x10^{-6}$ Torr. The films grown below $4x10^{-6}$ Torr show good (100) growths.
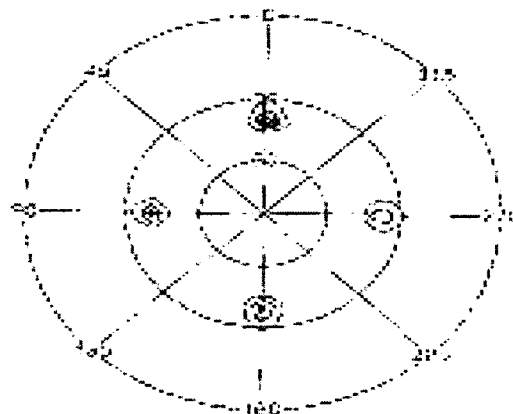

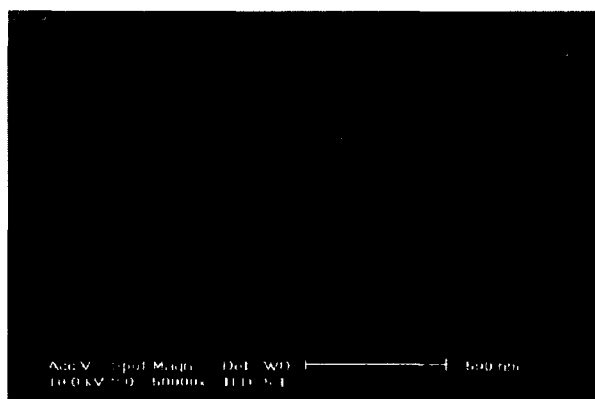Fig. 6. Pole figures of the typical CeO_2 film

Fig. 7. SEM micrographs of the surfaces of thick CeO_2 film grown at $650°C$ and $4x10^{-6}$ Tc $P(H_2O)$. One can see a crack is the centr figure.

Fig.5b shows Ts vs XRD θ-2θscans of CeO_2 films, which were grown at $300°C$ $600°C$ with

P(H_2O) fixed as 4×10^{-6}Torr. The lower limit of Ts for the (100) growths of CeO_2 films is 400°C-500°C, which is smaller than that of Y_2O_3. This means the window Ts is much wider than that of Y_2O_3. This seems to be due to the lower melting temperature of Ce, which results in the lower temperature of crystal growth.

Fig.6 shows the pole figures of the typical CeO_2 film. It showed good textures of the films. The phi-scan indicated that FWHM of in-plane alignment was 8-9. Fig.7 shows SEM micrographs of the surfaces of the 30nm thick CeO_2 film. When the thickness was as thin as 10nm, it was hard to see the crack formations. When the thickness was larger than 20nm, we could see the cracks clearly.

In order to find out the origins of cracks, we check the changes of texture and morphology as functions of time in air. Fig.8 shows the changes of XRD θ-2θscans of a CeO_2/YSZ film as a function of time in the range of 1hour to 14 hour, which was measured just after taking out the sample from the chamber to air.
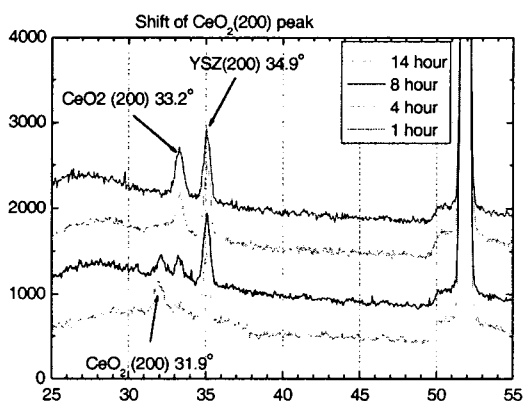

Fig. 8. Changes of XRD θ-2θscans of a CeO_2 film as a function of time. As time was going by after the sample was taken out of the chamber, the 2θ of the peak move from 31.9 to 34.9.

Initially the peak at 2θ=31.9° indicated the film was the (100) growth of Ce_2O_3, which has +3 for the valence of Ce ion. As time was going by, the 2 of the peak move from 31.9 to 33.2, which indicated that the chemical composition of the film changed from Ce_2O_3 to CeO_2. Without YSZ overlayer, this conversion in air was so fast that we could only barely observed the shift of XRD peak. Hence this was due to the additional reaction with the oxygen absorbed from air, which cause that

the valence of Ce increased from +3 to +4. Both of them are cubic crystals and the lattice parameter of Ce_2O_3, 5.93, is smaller than that of CeO_2, 5.41. Hence during the chemical and structural changes in air, they underwent the volume reduction. This seems to cause the cracks. This phenomenon was more salient for thick CeO_2 films. When the thickness was smaller than 10nm, it was hard to see those cracks. However for the proper growths of YSZ overlayers, the thickness of CeO_2 film was at least 20nm according to our experience. For the triple layer of CeO_2/YSZ/CeO_2, usually 200nm thick YSZ films are deposited on CeO_2. For this thickness of CeO_2, it show small crack. Since the thickness of YSZ is as large as 200nm, those small cracks might give negligible effects on the surface of YSZ. Actually we couldn't see any cracks or grooves on the surface of YSZ. This implies that the small cracks in CeO_2 of the triple layer may not cause troubles.

4.Conclusions

The windows of the growth conditions for Y_2O_3 films were narrower than CeO_2. Furthermore it was more difficult to grow Y_2O_3 films with perfect textures than CeO_2. The advantages of Y_2O_3 are the absence of cracks. Meanwhile the small cracks of the bottom CeO_2 layer in CeO_2/YSZ/CeO_2 gives negligible effects on the surface if YSZ is thick enough. Hence if the YSZ overlayer on Y_2O_3 is necessary, their merits and demerits might be comparable.

Acknowledgement

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