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# An improvement of surface smoothness and lattice match of CeO<sub>2</sub> buffer layers on R-sapphire processed by MOCVD

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#### Abstract

Epitaxial thin films of CeO<sub>2</sub> and Ce<sub>1-x</sub>R<sub>x</sub>O<sub>2-v</sub> (R=Y, Nd; x=0-0.32) on R-sapphire were prepared by band flash evaporation MOCVD. It was demonstrated that the smoothness of the films can be improved by a decrease of deposition rate and by post deposition annealing at 1000 °C. The lattice match of buffer layers with R-Al<sub>2</sub>O<sub>3</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.6</sub> was improved by doping of ceria with yttrium and neodymium correspondingly. A bilayer structure Ce<sub>0.7</sub>Nd<sub>0.3</sub>O<sub>2-y</sub>/Ce<sub>0.68</sub>Y<sub>0.32</sub>O<sub>2-v</sub>/R-Al<sub>2</sub>O<sub>3</sub> is proposed as potential substrate material for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.6</sub> deposition.

Keywords: MOCVD; Post deposition annealing; Deposition rate decrease

#### 1. Introduction

Chemical reactivity of high temperature superconductor (HTSC) materials to single crystalline sapphire, which is a most promising substrate material for microwave applications, can be avoided by the deposition of buffer layers.  $CeO_2$  has a low reactivity with YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.8</sub> and has the ability to epitaxial growth with  $R-Al_2O_3$  (1102) and  $YBa_2Cu_3O_{7:\delta}$  phase making it a very effective buffer layer material [1]. However, the critical properties of superconducting layer are strongly dependent on the single crystalline quality and the smoothness of buffer layer: smooth surface and low density of mismatch dislocations of the buffer layer facilitate the epitaxy of HTSC layer with high crystallinity and consequently high  $T_c$  and  $j_c$  characteristics [2]. The aim of this work was to find the conditions of MOCVD preparation of very smooth CeO<sub>2</sub> buffer layers and to improve its match with both sapphire and  $YBa_2Cu_3O_{7,\delta}$  layers by doping with rare earth oxides.

## 2. Experimental

Buffer layers  $Ce_{1-x}R_xO_{2-x}$  (R=Y, Nd; x=0-0.32)

were prepared by MOCVD technique using single source flash evaporation of the precursors from the inert carrier band [3]. The advantages of this technique to the conventional MOCVD with continuous evaporation from separate sources are: (1) the ability to produce in one deposition run the thin multilayers consisting of any number of sublayers with varied composition, (2) easy regulation of the deposition rate and (3) lower requirements to the thermal stability of the precursors. The later advantage is especially important for CeO<sub>2</sub> deposition because according to our experience Ce(thd), [tetrakis(2,2,6,6-tetramethy]-3,5-heptane-dionato) Ce(IV)] used as precursor, remarkably decomposes during continuous evaporation from a boat. The resulting CeO<sub>2</sub> covers the particles of Ce(thd)<sub>4</sub> and the evaporation rate decreases very drastically. The flash evaporation of Ce(thd)<sub>4</sub> in micro portions helps to avoid this obstacle.

The solution of  $Me(thd)_4$  (Me=Ce, Y, Nd) in tetrahydrofuran was dripped in separate small droplets (1 µl) on the glass fibre carrier band heated to 140 °C, the solvent being instantaneously evaporated; dry small specs of precursors were thus formed. One by one evaporation of the precursors specks by the hot carrier gas flow (argon) was performed in the specially designed vacuum chamber. One speck is evaporated during 2 s, the pulses of the precursors vapors are evolved by carrier gas to the hot wall horizontal reactor where the deposition takes place. The

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Fig. 1. X-ray diffraction pattern of CeO<sub>2</sub> film on R-Al<sub>2</sub>O<sub>3</sub>.

deposition rate in pulse process is easily regulated by the amount of the precursor in one speck. The deposition temperature was 850 °C, oxygen partial pressure -4 mbar, total pressure -13 mbar. The films were characterized by X-ray diffraction ( $\theta$ -2 $\theta$ ,  $\phi$ -scanning, and rocking curves), secondary neutral mass-spectrometry (SNMS), Rutherford backscattering (RBS), atomic force microscopy (AFM) and high resolution electron microscopy (HREM).

#### 3. Results and discussion

CeO<sub>2</sub> buffer layers of a thickness 30 nm were deposited using deposition rates: 3 nm/pulse and 0.15 nm/pulse, corresponding quantities of Ce(thd)<sub>4</sub> evaporated per pulse were 0.08 and 0.004 mmol.  $\theta$ -2 $\theta$  diffraction patterns of these films show only the peaks of (002) and (004) reflections of CeO<sub>2</sub> which indicate that only a CeO<sub>2</sub>(001)||Al<sub>2</sub>O<sub>3</sub>(1102) orientation of the films is present (Fig. 1). In-plane orientation was analyzed by  $\phi$ -scanning of asymmetric reflections (113) of CeO<sub>2</sub> and (3030) of Al<sub>2</sub>O<sub>3</sub>. For both types of the films it was found that the reflection peaks were separated exactly 90° of rotation angle (Fig. 2). Hence, the films have only one type of



Fig. 2.  $\phi$ -Scanning for (113) plane of CeO<sub>2</sub> film on R-Al<sub>2</sub>O<sub>3</sub>.

in-plane orientation corresponding to the epitaxial relation  $CeO_2[010]$   $AI_2O_3[1210]$ . It should be stressed that the orientation of the films is not sensitive to the deposition rate in the interval studied. In contrast, the full widths at the half maximum (FWHM) of (004) reflections are strongly dependent on the deposition rate changing from 0.85° to 0.45° for the films deposited with the rates 3 nm/pulse and 0.15 nm/pulse correspondingly. Moreover, the deposition rate drastically effects the buffer layers surface morphology. As it was calculated from AFM data (Fig. 3) the  $R_1$  factor which is the vertical distance between the deepest and the highest points of the surface profile decreases from 26.9 nm to 3.4 nm together with the decrease of CeO<sub>2</sub> deposition rate (the measurements were done at the length 1500 nm). We assume that this effect is caused by slow diffusion of Ce atoms along the growing  $CeO_2$  surface at the deposition temperature. Indeed, postdeposition annealing of these films at higher temperature (1000 °C, 1 h, O<sub>2</sub>) activates the surface diffusion and leads to substantial smoothing of the surface: R,-factor decreases from 26.9 nm to 4.1 nm and from 3.4 nm to 2.2 nm for films deposited at high and low deposition rate correspondingly. The density of the hills on the surface also decreases. A similar annealing effect was observed in [1]. It should be noted that the films deposited at low deposition rate are smoother even after the annealing. The smoothness of the slow deposited and annealed buffer layer is considerably better than that of initial substrate surface ( $R_1 = 2.2$  nm and 4.2 nm correspondingly). RBS data also show that high temperature annealing results in considerable improvement of the films crystallinity: the channelling minimum yields are 16% and 8.5% for asreceived and the annealed buffer layer correspondingly (deposition rate of 3 nm/pulse).

HREM on the CeO<sub>3</sub>/R-Al<sub>3</sub>O<sub>3</sub> interface (films were deposited with the rate 3 nm/pulse and annealed at 1000 °C) show three different arrangements: (1) an almost atomically flat interface which is present at more than 95% of the areas investigated, (2) a straight interface but with some differently oriented small (about 5 nm into the substrate) sapphire particles adjacent to the interface, and (3) a very rough interface occurring at areas with a contrast which suggests the presence of a rather deep hole in the substrate, which is filled with sapphire grains of random orientations. At the first two types of interfaces the CeO<sub>2</sub>, surface layer is smooth (not more than a single unit cell roughness) and the layer is single crystalline. Thus also at a rather rough sapphire surface a smooth CeO<sub>2</sub> surface is formed. At the last type of interface the  $CeO_2$ buffer layer is irregular in thickness and often also thicker. and the CeO<sub>2</sub> consists of grains with orientations which differ from that of the single crystalline part of the buffer layer.

The lattice deviations due to the misfit between the  $CeO_2$  and sapphire lattices are situated within 0.5 nm from the  $CeO_2/R-Al_2O_3$  interface as can be seen in Fig. 4. No indication of a strain field could be observed again



Fig. 3. AFM pictures of CeO<sub>2</sub> films on R-Al<sub>2</sub>O<sub>3</sub>: (A) and (B) films prepared at 850 °C and deposition rates 3 nm/pulse and 0.15 nm/pulse correspondingly; (C) and (D) the same films annealed at 1000 °C. Picture size  $1000 \times 1000$  nm<sup>2</sup>. The inserts show the surface profile across the picture diagonal.

indicating that the accommodation to the misfit is very local.

In order to decrease the mismatch between the lattice



Fig. 4. A HREM image of the main type of  $CeO_2/R-Al_2O_3$  interface, showing a clean interface.

parameters of buffer layer and the substrate, films of solid solutions  $Ce_{1=x}Y_{x}O_{2=x}$  (x = 0.16, 0.20, 0.32 according SNMS) were deposited on R-Al<sub>2</sub>O<sub>3</sub> at deposition rate 0.15 nm/pulse. The observed decrease of the lattice parameter from 0.5411 nm for x=0 to 0.5375 nm for x=0.32 was the natural result of the Y substitution by Ce. The epitaxy of the films was proved using  $\theta$ -2 $\theta$  and  $\phi$ -scans. Nevertheless, the reflection peak (004) for the film with x = 0.32was abnormally broad (FWHM≈0.8°) and splitted (Fig. 5). This feature is attributed to the fact that the compositions  $Ce_{1-x}Y_xO_{2-x}$  with x > 0.3 at the films deposition conditions are inside the immiscibility region of the phase diagram. According to the data [4] the  $CeO_2$ -based solid solutions of fluorite structure co-exist in this region with solid solutions on the base of C-type Y<sub>2</sub>O<sub>3</sub>. Single phase solid solution was obtained after the film was annealed at 1000 °C (1 h,  $O_3$ ), as it can be seen from disappearance of the splitting and the decrease of FWHM to  $0.5^{\circ}$  (Fig 5). The effect of annealing is also correlating with phase diagram CeO,-Y,O, [4]. In order to obtain single phase  $Ce_{1,2}, Y, O_{2,2}$ , fluorite solid solutions with higher yttria concentration (x > 0.32) the annealing at much higher temperatures is needed. The buffer layers thus obtained



Fig. 5. The reflection peak (004) of  $Ce_{0.68}Y_{0.32}O_{2-3}$  film before (solid line) and after (dashed line) the annealing at 1000 °C.

should be strained and unstable with respect to the phase decay. Thus, the limited solubility of  $Y_2O_3$  in CeO<sub>2</sub> matrix allowed us to decrease the lattice parameter of buffer layer only up to 0.5375 nm and to decrease the mismatch at the interface with R-sapphire from 5.4% and 12.0% (for pure CeO<sub>2</sub>) to 4.7% and 11.4% for the composition Ce<sub>0.68</sub>Y<sub>0.32</sub>O<sub>2-v</sub>.

An attempt to improve the lattice mismatch at the interface  $CeO_2/YBa_2Cu_3O_{7-\delta}$  by doping  $CeO_2$  with Nd<sub>2</sub>O<sub>3</sub> was undertaken. Single phase  $Ce_{1-x}Nd_xO_{2-x}$  fluorite solid solutions can be obtained for the values of x up to 0.5 [4]. These solutions demonstrate the monotonous growth of lattice parameter with the concentration of Nd. mismatch with tetragonal minimal lattice The composition corresponding 10 the YBa<sub>2</sub>Cu<sub>1</sub>O<sub>2.8</sub>  $Ce_{0,7}Nd_{0,3}O_{2-\gamma}$  is 0.15% while in case of pure CeO<sub>2</sub> it is 0,89%. The improvement of the match with tetragonal phase is important since the crystallization of this particular phase takes place at high temperature on the substrate surface. At room temperature fully oxidized  $YBa_2Cu_3O_{7.\delta}$  is orthorombic and its mismatch parameters with  $Ce_{0.7}Nd_{0.3}O_{2-v}$  are +0.9% and -0.8% (corresponding values for pure CeO<sub>2</sub> are +1.6% and -0.1%). The film of the composition Ce<sub>0.7</sub>Nd<sub>0.3</sub>O<sub>2-y</sub> was deposited on Ce<sub>0.68</sub>Y<sub>0.32</sub>O<sub>2-y</sub>/R-Al<sub>2</sub>O<sub>3</sub>, both layers of doped CeO<sub>2</sub> being 30 nm thick. SNMS measurements showed that this film has the intended Y and Nd concentration profile. AFM data give evidence that R<sub>t</sub> of these bilayer structures does not differ from that of pure CeO<sub>2</sub> layers deposited at the same conditions. The study of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7.8</sub> deposition on Ce<sub>0.7</sub>Nd<sub>0.3</sub>O<sub>2-y</sub>/Ce<sub>0.68</sub>Y<sub>0.32</sub>O<sub>2-y</sub>/R-Al<sub>2</sub>O<sub>3</sub> is in progress.

## 4. Conclusion

The smoothness of CeO<sub>2</sub>-based buffer layers prepared by MOCVD was improved by the decrease of deposition rate and the post deposition annealing at 1000 °C. The lattice match of buffer layers with R-Al<sub>2</sub>O<sub>3</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7. $\delta$ </sub> was improved by doping of ceria with yttrium and neodymium correspondingly. The bilayer structure Ce<sub>0.7</sub>Nd<sub>0.3</sub>O<sub>2-y</sub>/Ce<sub>0.68</sub>Y<sub>0.32</sub>O<sub>2-y</sub>/R-Al<sub>2</sub>O<sub>3</sub> is proposed as potential substrate material for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7. $\delta$ </sub> deposition.

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