Chemical solution deposition (CSD) of CeO$_2$ and La$_2$Zr$_2$O$_7$ buffer layers on cube textured NiW substrates

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Abstract. We present results of crack free layers of CeO$_2$ and La$_2$Zr$_2$O$_7$ deposited by means of CSD on cube textured Ni-4 at.% W substrates. EBSD-data show histograms with very good in-plane- and out-of-plane textures and were used to simulate the critical current density in the YBCO layer. The surface roughness, a sensitive feature for good deposition results, was analyzed with a profilometer. In the CSD process we applied, the 2,4-pentanedionates of the metal cations in glacial acetic acid and methanol served as starting substances.

1. Introduction
In recent years, the chemistry and dip coating deposition of aqueous or organic solutions has emerged as the most promising route for an economical future preparation of YBCO coated conductors on cube textured substrate tapes, the so-called RABiTS approach [1]. Besides the lower preparation costs, the significant higher coating speed and a wide flexibility in the choice of the chemicals and compositions are the advantages of chemical solution deposition (CSD) compared to physical coating methods. The development of an all solution deposition process (buffer + YBCO (F-free)) is the final goal of the reported investigations.

To prevent diffusion of Ni cations into Y-positions of the superconductor buffer layers are necessary. Although CeO$_2$ and La$_2$Zr$_2$O$_7$ (LZO) as suitable buffer have a lattice misfit of about 8 % with respect to Ni, a very good texture transformation has been observed in divers experiments [2, 3, 6]. The mismatch with the YBCO unit cell is very low with values smaller than 1 %. This paper deals with the deposition of well textured crack free and extraordinary smooth CeO$_2$ and La$_2$Zr$_2$O$_7$ buffer layers on cube textured Ni-4 at.% W substrates that are produced in-house [4].

2. Experimental
As educts for preparation of the coating solutions we used the 2,4-pentandionates of Ce (III), La (III) and Zr (IV) as received from Alfa Aesar. As solvents glacial acetic acid (100 %, p.a.) and methanol (p.a) were used as received from Merck. Trichloroethylene, hydrogen peroxide (30 %) and formic acid (98-100 %) for cleaning the substrates were also bought from Merck and acetone from Roth.

2.1 Devices
2.1.1 Properties of the solutions. The determination of the concentration of the metal cations in solution was carried out with an inductively coupled plasma with optical emission spectrometry (ICP OES) (Iris Intrepid XDL Duo, Thermo Electron Corp.). To get high accuracy we used internal standards and the “bracketing procedure”. The viscosities of the precursor solutions were determined
using a cone-plate viscosimeter (Brookfield, DV III+) at 25 °C with a speed range between 0.01 and 250 min⁻¹. The sample volume was 0.5 ml for each measurement.

2.1.2 Properties of the solid layers. The roughness of the surface of the deposited layers was characterized with a profilometer (Nanopics, NP X 200, Seiko Instruments Inc.). The value of the cutoff-wavelength is fixed to 0.3-fold observation length. Microstructural and texture analyses of the thin films were performed with a scanning electron microscope (FESEM, LEO1530) and an electron backscatter diffraction device (HKL Techn. with software “Channel 5”). The thickness of the layers was determined by EPMA (electron probe microanalysis) with an energy dispersive x-ray spectrometer EDX (Vantage, Thermo Noran), described in detail in [5].

2.2 Procedures

2.2.1 Substrate preparation. To get a good wettability of the metal substrates, the Ni-4 at. %-tapes were at first degreased in trichloroethyen, acetone and methanol. After that a chemical cleaning with a hot mixture of hydrogen peroxide and formic acid followed and finally an ultrasonic purification in methanol. This procedure has been investigated by Van Driessche et al. [6].

2.2.2 Precursor solutions

\[ \text{CeO}_2: 1.0936 \text{ g (2.5 mmol) Ce(CH}_3\text{COCHCOCH}_3\text{)}_3 \times \text{H}_2\text{O was dissolved in 7.5 ml glacial acetic acid by heating and stirring. After that methanol was added up to a total volume of 10 ml. 0.2 ml of the solution was analyzed by ICP OES to check the exact Ce}^{3+}\text{-ion concentration.} \]

\[ \text{LZO: 0.87249 g (2 mmol) La(CH}_3\text{COCHCOCH}_3\text{)}_3 \times \text{H}_2\text{O and 0.975325 g (2 mmol) Zr(CH}_3\text{COCHCOCH}_3\text{)}_4 were in each case dissolved in 7.5 ml glacial acetic acid on a hot plate and the solution was stirred. Every liquid was topped up to 10 ml. 0.2 ml was analyzed by ICP OES with internal standard and “bracketing procedure” to get the exact cation concentration. After that the two solutions were joint in the exact stoichiometric ratio of 1:1.} \]

2.2.3 Coating of the layers and furnace reaction. Cube textured Ni-4 at.% W tapes (3 cm×1 cm×0.01 cm) [4] were used as crystallographically oriented templates. The purified metal stripes were either dip or spin coated. Dip coating was performed with a withdrawing velocity up to 13 cm/min and spin coating with a speed of 3000 rpm for 30 s.

The samples were annealed in a pre-heated quartz tube furnace in reducing forming gas atmosphere of Ar-5 % H₂ at temperatures of 900 °C (CeO₂) and 1000 °C (LZO) for one hour. The LZO-sample was first pre-heated at 180 °C for 20 min in air. Finally, the tapes were quenched to ambient temperature. Also multi-dipping was tested for CeO₂ with heating times of 15 min.

3. Results and discussion

3.1 Viscosity of the liquids and concentration of metal cations.

The precursor solutions showed Newtonian behaviour within the torque interval of 10 to 90 % of the cone. At 25 °C the Cerium-precursor had a value of \( \eta = 1.84(2) \text{ mPa s at a Ce}^{3+}\text{-concentration of 0.25(1) mol/l. The LZO-precursor had a viscosity of 1.68(2) mPa s for concentrations of La}^{3+}\text{ of 0.104(2) mol/l and Zr}^{4+}\text{ of 0.106(2) mol/l. Figure 1 gives an overview of the dependence of the viscosities on the metal ion concentration. The final metal content was determined accurately by means of ICP OES.} \]
3.2 Properties of the buffer layers

3.2.1 Profilometrie and SEM-figures

Figure 2. Profilometer images and SEM micrographs of the CeO$_2$ (left hand) and the LZO (right hand) buffer layer with a thickness of 18(4) nm and 19(4) nm, resp.

The SEM images reveal crack free and homogeneous samples with only a few impurities. The roughness of the surface was checked by means of a profilometer. Within an area of 100 $\mu$m$^2$ the $R_a$ values (arithmetical mean roughness) were 4.3 nm (CeO$_2$) and 3.05 nm (LZO). Within 1 $\mu$m$^2$ areas $R_a$ data smaller than 1 nm could be measured. The thickness of the buffer layers shown in figure 2 was determined to be 18(4) nm (CeO$_2$) and 19(4) nm (LZO). A threefold coated cerium dioxide layer with a sharp crack free cube texture had a thickness of about 120 nm.

Figure 3. Histograms of the misorientation of the grain boundaries and the out-of-plane as well as in-plane-texture of the CeO$_2$ and LZO buffer layers.
3.2.2 Texture analysis by EBSD. The texture of the buffer layers was investigated by EBSD (figure 3). The histograms for the CeO$_2$ sample reveal a maximum of misorientation of the grain boundaries at about 3° and for LZO at about 5°. The in-plane-alignment shows a nearly 45° rotation of CeO$_2$ and LZO with respect to the NiW-substrate. The misorientation of the cube out-of-plane texture exhibits maxima at angles of about 3° and 5°, respectively.

3.3 “Limiting path calculation”
An attribute of the achieved texture quality of the buffer layer may be deduced from “limiting path calculations”. In this model, the experimentally obtained EBSD maps of the CeO$_2$ and the LZO buffer layer are transposed to a virtual YBCO-grain boundary network to find the limiting path of the current and to calculate the $J_c$ in comparison to the maximum value. The exact procedure is described in detail in [7]. The simulations gave $J_c$-values of ca 34 % (LZO) and 52 % (CeO$_2$) of the maximum current density.

4. Conclusion
High quality CeO$_2$ and La$_2$Zr$_2$O$_7$ buffer layers were chemically deposited on cube textured Ni-4 at.-% W substrates with very good c-axis alignment of the unit cells and a smooth and crack free surface. Simulation of the critical current densities resulted in values that show the high potential of these CSD-layers for use in YBCO coated conductor fabrication. The all solution CSD process is actually in work and will be published elsewhere.

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