

MOCVD of oxides on textured Ni for high temperature superconducting tapes

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High temperature superconducting cables promise several benefits for the performance of magnets, motors, generators, transformers, fault current limiters and transmission cables. MOCVD demonstrated the deposition of YBCO films with high critical current densities on meter long metal tapes. Textured Ni as substrate is a very cost effective approach for the production of Coated Conductors. The buffer layer must be crack-free and must maintain a strong texture. We investigated the deposition of oxides, which are suitable buffers for YBCO, on Ni with metallorganic precursors.

The thermodynamic stability of the phases was calculated by the computer code Chemsage for the deposition conditions. The calculation is important in order to suppress the formation of NiO, La₂O₃, MnO or high oxygen deficient CeO_{2-x}. Therefore the oxygen partial pressure must be adjusted to an intermediate value, controlled by a mixture of ammonia and water or hydrogen and water. The phase diagram was constructed for a mixture of NH₃, N₂, H₂O, La(thd)₃ and Mn(thd)₃, which was used for the further experiments. At high water pressure the LaMnO₃ is thermodynamically stable, while La₂O₃ and MnO is found at low water pressure.

Textured Nickel (Ni 0,1at%W and Ni 5at%W) tapes were produced by the IFW-Dresden. Epitaxial buffer layers were deposited on these substrates in a hot wall reactor of a reel-to-reel MOCVD tape system. Ce-, Y-, Gd-, La- and Mn-(thd) precursors (thd = tetramethyl-heptanedionate) were solved into m-xylene and fed into a Band Evaporator. The Band Evaporator allows to deliver only the precursor vapour without solvent contamination into the reactor. The oxides were deposited at 3-10 mbar total pressure. The temperature in the tape reactor was 800-900°C, while the temperature of the reactor in the microbalance system was 375-725°C. N₂, NH₃ (or H₂), H₂O and precursor mixture flow into the reactors.

The decomposition of different thd-precursors and mixtures of them have been measured by the temperature dependence of the deposition rate on Ni in H₂- and NH₃-H₂O/N₂ atmospheres in a microbalance system. The oxides contained carbon at low temperatures and low H₂O pressures. The calculated activation energies vary in a wide range of 3-70 kJ/mol and strongly depend on the detailed deposition conditions.

Textured CeO₂ films were deposited on Ni and Ni 5%W tapes at temperatures between 800-890°C. Figure 1 shows the XRD measurements of a CeO₂, which was deposited in an NH₃/H₂O/N₂ atmosphere. This film do not contain any CeO₂(111) orientation and no NiO peaks were measured. Additional no cracks and carbon in the films could be detected with REM and WDX.

Only depositions with both water and ammonia flow resulted in formation of the perovskite LaMnO₃ and no oxidation of nickel. LaMnO₃ prepared in the latter case always had a predominant orientation of pseudocubic (001) type (Fig.2). The intensity ratio for (002) and (110) pseudocubic reflections was highly sensitive to the film

stoichiometry, total gas pressure and ammonia/water ratio.

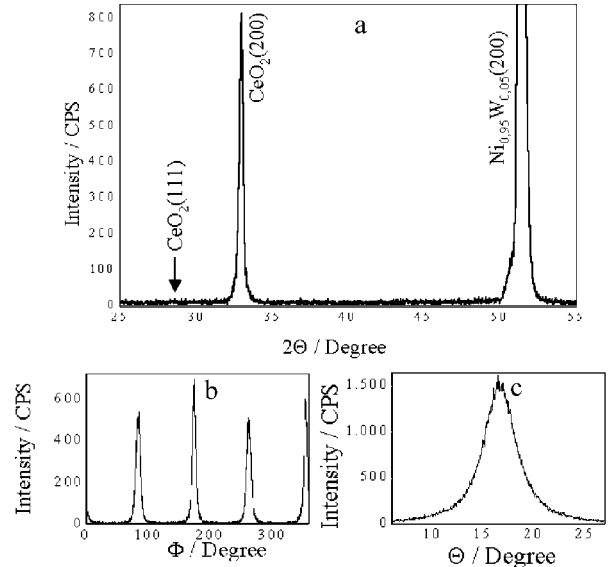


Figure 1. XRD of CeO₂ on a textured Ni 5at%W tape: a) θ -2 θ -scan, b) Φ -scan of CeO₂(111) with FWHM = 5,8°, c) rocking curve of CeO₂(200) with FWHM = 3,5°.

LaMnO₃ film with pure (001) orientation possessed also good in-plane texture of the cube-on-cube type. The best LaMnO₃ films revealed FWHM values of the rocking curves for (001) reflections and ϕ -scans for (110) reflections which are similar to the FWHM values of the corresponding scans for the substrate.

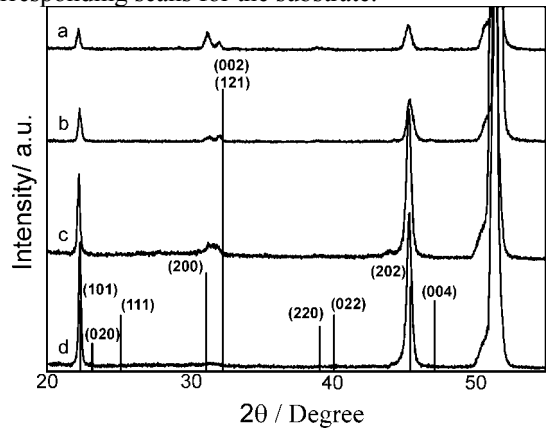


Figure 2. XRD pattern of the LaMnO₃ films prepared under different process conditions with ammonia partial pressure increasing gradually from a) to d). Vertical lines denote the main reflections of the bulk standard of stoichiometric LaMnO₃ (space group *Pnma*).

LaMnO_{3±δ} in the range of $-0.06 \leq \delta \leq 0.09$ is orthorhombic (*Pnma* space group). For P(O₂) – T conditions similar to our deposition experiments the small negative δ can be expected. Only singlet reflections were found in the XRD (Fig.2). The *d*-values of the singlets are close to that of (*h*0*h*) orthorhombic reflections. The orthorhombic unit cell in the pure textured LaMnO₃ films on Ni is oriented in such a way that *b* axis is parallel to the film-substrate interface.

The orientation relations can be refined as follows:

$$(001)[100]_{\text{Ni}} // (101)[010]_{\text{Pnma LaMnO}_3} \text{ and} \\ (001)[010]_{\text{Ni}} // (101)[010]_{\text{Pnma LaMnO}_3}$$

For the future technology it is important that even aqua ammonia can be used for protection of Ni during deposition avoiding application of high pressure tanks with toxic or explosive gases like H₂ or NH₃.

The research was partly supported by VW Foundation (grant I/77821).