Electronic Supplementary Information

for:

Strongly oriented Co_3O_4 thin films on MgO(100) and $MgAl_2O_4$(100) substrates by PE-CVD

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S1. Synthesis

Co_3O_4 depositions were performed on as-received MgO(100) and $MgAl_2O_4$(100) single crystals (Crystal GmbH®, Berlin, Germany) using a two-electrode PE-CVD apparatus powered by a Radio Frequency (RF) generator.[S1] After preliminary experiments aimed at the process optimization, the input power was fixed at 20 W, this value being the optimal one for the obtainment of strongly oriented films characterized by an appreciable growth rate. Electronic grade argon and oxygen were used as plasma sources. The $[Co(dpm)_2]$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) precursor, synthesized according to the literature,[S2] was placed in an external vessel heated at 90°C and transported into the deposition zone by a 60 sccm Ar flow. Two further auxiliary gas-lines were used to introduce Ar (15 sccm) and O_2 (20 sccm) directly into the reactor. To avoid undesired condensation phenomena, the gas lines connecting the precursor reservoir and reaction chamber were heated at 120°C. For all experiments the deposition time, total pressure and inter-electrode distance were 1 h, 1 mbar and 6 cm, respectively. Specimens were grown at temperatures between 100 and 400°C, as summarized in Table 1.

S2. Characterization

XPS measurements were run on a Perkin Elmer Φ 5600ci spectrometer at a working pressure lower than 10^{-8} mbar., using a non-monochromatized AlKα excitation source (1486.6 eV), and performing binding energy (BE) correction by assigning to the C1s signal of adventitious carbon a value of 284.8 eV. Ar^+ sputtering was accomplished at 4.5 kV, with an argon partial pressure of 4×10^{-8} mbar. Peak fitting was carried out by a least-squares procedure, adopting Gaussian-Lorentzian peak shapes. The cobalt Auger parameter was calculated as: $\alpha = BE(Co2p_{3/2}) + KE(CoLMM)$, with KE = kinetic energy.[S2-S4]

SIMS measurements were carried out by means of a IMS 4f mass spectrometer (Cameca, Padova, Italy) using a Cs^+ primary beam (14.5 kV, 10 nA) and by negative secondary ion detection. The profiles were recorded rastering over a 150×150 μm^2 area and detecting secondary ions from a sub-region close to 8×8 μm^2 to avoid crater effects. The signals were collected in beam blanking mode and operating in high mass resolution configuration.[S1] Charge compensation was achieved by means of an electron gun. The dependence of the erosion rate on the matrix composition was also taken into account by evaluating the former at various depths for each sample. The erosion rate was then computed by measuring the crater depth at the end of each analysis by a Tencor Alpha Step profiler (maximum uncertainty = ± 2 nm). Film thicknesses were determined by analysing the dynamics of Mg signal for MgO, and of both Mg and Al for $MgAl_2O_4$-supported samples.

FE-SEM measurements were performed at a primary beam acceleration voltage of 5.0 kV by a Zeiss SUPRA 40VP instrument.

XRD^2 spectra were collected by a D/max-RAPID Rigaku microdiffractometer using a $CuK\alpha$ radiation.[S5] The instrument was equipped with a cylindrical image plate (IP) detector and a collimator having a diameter of 300 μm. Due to the strong orientation of substrates and thin films, making the sample alignment a difficult task, patterns were collected for 1 h by continuously rotating the samples in two directions: a) from 5° to 15° in ω (corresponding to incidence angle); b) from -5° to 5° in ϕ (corresponding to β angle).[S6]

Notes and references

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