MOCVD deposition of CoAlO$_2$ thin films

N. El Habra$^1$, G. Carta$^1$, M. Natali$^1$, L. Crociani$^1$, G. Rossetto$^1$, P. Zanella$^1$, C. Sada$^2$, S. Restello$^3$, V. Rigato$^3$, M. Casarin$^4$

1 ICIS-CNR Padova, 2 Dipartimento di Fisica INFM, Università Padova, 3 INFN, Laboratori Nazionali di Legnaro, 4 Dipartimento di Scienze Chimiche, Università Padova

I. INTRODUCTION

Transition metal spinels are of great importance in different fields ranging from semiconductor and sensor technology to heterogeneous catalysis. In this class of materials, an important role is played by cobalt aluminate (CoAlO$_2$, the well known Thernard’s Blue) which, as a consequence of its thermal, chemical, and photochemical stability as well as of its optical properties, is widely used as pigment coating, catalyst and, in optical devices, as color filter and pigment layer on luminescent materials [1-5]. CoAlO$_2$ is usually produced in powder form through methods based on dry or wet routes generally requiring high temperatures and accurate control of starting reagents. In the present work, we report the MOCVD growth of CoAlO$_2$ using cobalt and aluminium precursors. The films were characterized by XRD, RBS and UV–Vis spectroscopy in order to evaluate the influence of deposition parameters and post-deposition treatments on the compositional, morphological, structural and optical properties.

II. EXPERIMENTAL SET-UP

CoAlO$_2$ depositions were performed in a horizontal hot wall LP-MOCVD reactor at a total pressure of 2 Torr and different growth temperatures (500 °C and 900 °C), using bis-(η$^5$-cyclopentadienyl) Co(II) [Co(η$^5$-C$_5$H$_5$)$_2$] and aluminium dimethylisopropoxide [AlMe$_2$(OPr)$_3$], OPr = –OCH(CH$_3$)$_2$, and Me = –CH$_3$ as Co and Al sources, respectively. The synthesis and the characterization of cobalt and aluminium precursors were carried out as described in the literature [6-8]. The carrier gas was nitrogen, flowing through two distinct bubblers containing Co and Al precursors. The co-reactant gas was an oxygen/water vapour mixture, incorporated into the main flow after the precursors evaporation zone, in close proximity to the entry of the reaction zone, to avoid the undesired decomposition of the precursors. Substrates used for film depositions were small rectangular pieces of polished Si (1 0 0) and fused quartz, previously washed with hot trichloethylene and then rinsed with acetone. After film depositions, the samples were exposed to a thermal annealing in air in a 800–1200 °C temperature range. The annealing treatment was performed in a muffle furnace. The structure of the deposited films was determined by X-ray diffraction with a Philips PW1830 powder diffractometer using Ni filtered Cu Kα radiation. Rutherford backscattering spectroscopy measurements were performed at the CN accelerator at LNL-Legnaro using a 2MeV He$^{3+}$ beam. Fixed random spectra were recorded and the film stoichiometry and composition profile were evaluated by simulating the spectra using the RUMP software. UV–Vis spectra were recorded on a UV500-spectrometer (Spectronic Unicam) based on a Vision 32 software and operating in transmission mode.

III. RESULTS

Fig.1 reports X-ray diffraction patterns of as grown samples and of samples annealed at different temperatures. The evolution of the spectra can be interpreted as follows: at 500 °C polycrystalline Co$_3$O$_4$ and amorphous Al$_2$O$_3$ are deposited. Annealing in air at 800 °C causes the progressive reduction to CoO, which reacts with Al$_2$O$_3$ to form CoAlO$_2$ phase. Indeed at this temperature a new small peak at 2θ=49° corresponding to the (3 3 1) Bragg reflection appears which is considered diagnostic of the CoAlO$_2$ phase [9]. After the annealing at 1200 °C, in addition to a series of small peaks which are unidentified till now, a new peak is observed at 2θ=22.0°, which corresponds to the (1 0 1) Bragg reflection of cristobalite phase. The CoAlO$_2$, crystallite sizes, calculated for the (3 1 1) Bragg reflection from the XRD patterns using the Scherrer’s equation, increased with the annealing temperatures from 33 nm for the sample annealed at 800 °C to 45 nm for that annealed at 1000 °C and finally to 66 nm after the annealing at 1200 °C. In Fig. 2, the UV–vis spectra of the as-grown and annealed samples are reported. The as-grown film, of dark brown colour, showed a continuum of absorbance in the whole UV–vis range, while after annealing at 800°C two weak absorption bands appeared in the 500–650 and 650–800 nm ranges. Moreover, increasing the annealing temperatures to 1000 and 1200 °C, the spectrum clearly showed a three band absorption pattern in the 540–630 nm range and correspondingly, the colour changed from green-blue at 1000 °C to bright blue at 1200 °C. Such a behaviour could be interpreted as a d-d electronic transition of Co(III) ions in octahedral coordination [1T1g– 1A1g transition] [10] for the absorption in the 650–800 nm range, whereas for
the 500 – 640 nm range, it could be assigned to
\( ^1T_1(P) \leftrightarrow ^4A_2(F) \) transition [11], which is characteristic for
tetrahedral Co(II) transitions allowed by the spin and it is
to be considered as the origin of the deep blue colour. The
visual observation and spectrum evolution after the
annealing treatments could be interpreted as a progressive
transformation of Co(III) ions into Co(II) ions in
tetrahedral coordination.

![XRD patterns of sample as-grown (T=500°C) and
annealed at different temperatures in air for 12 h.](image1)

**FIG. 1**: XRD patterns of sample as-grown (T=500°C) and
annealed at different temperatures in air for 12 h.

![UV–Vis absorbance spectra of sample grown on quartz
at 500°C and annealed in the 800–1200°C temperature range.](image2)

**FIG. 2**: UV–Vis absorbance spectra of sample grown on quartz
at 500°C and annealed in the 800–1200°C temperature range.

To verify the correct stoichiometric Co/Al/O ratio, RBS
measurements were performed on samples deposited on Si.
In Fig.3a is shown the RBS spectrum of a sample annealed
at 1200°C together with the RUMP simulation. The
simulation gave the composition profile reported in Fig.
3b. The Al:Co:O ratio on surface was 1:2:4, but cobalt
content decreases going from the surface to the substrate,
probably due to a diffusion of the cobalt, in the deep
layers, towards the silicon substrate forming cobalt silicates.

![RBS spectrum of sample (2) CoAl2O4 deposited on Si
(1 0 0) after annealing at 1200°C with corresponding simulation
(dashed line) and (b) composition profile deriving from the
simulation of the RBS spectrum.](image3)

**FIG. 3**: (a) RBS spectrum of sample (2) CoAl2O4 deposited on Si
(1 0 0) after annealing at 1200°C with corresponding simulation
(dashed line) and (b) composition profile deriving from the
simulation of the RBS spectrum.