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Growth and characterization of ternary Ni, Mg–Al and Ni–Al layered double hydroxides thin films deposited by pulsed laser deposition

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ABSTRACT

Layered double hydroxides (LDHs) are a class of layered materials consisting of positively charged brucite-like layers and exchangeable interlayer anions. Layered double hydroxides containing a transition metal which undergoes a reversible redox reaction in the useful potential range have been proposed as electrode coating materials due to their properties of charge transport and redox catalysts in basic solutions.
Ni–Al,(Ni,Mg)–Al and, as reference, non-electronically conductive Mg–Al double hydroxides thin films were obtained via pulsed laser deposition technique. The thin films were deposited on different substrates (Si, glass) by using a Nd:YAG laser (1064 nm) working at a repetition rate of 10 Hz. X-ray diffraction, Atomic Force Microscopy, Energy Dispersive X-ray spectroscopy, Fourier Transform Infra-Red Spectroscopy, Secondary Ions Mass Spectrometry, Impedance Analyzer and ellipsometry were the techniques used for the as deposited thin films investigation. The optical properties of Ni based LDH thin films and the effect of the Ni amount on the structural, morphological and optical response are evidenced.
The optical band gap values, covering a domain between 3.84 eV and 4.38 eV, respond to the Ni overall concentration: the higher Ni amount the lower the band gap value.

1. Introduction

Layered materials, such as anionic and cationic clays are a class of synthetic nano-structured materials who received attention in recent years due to their high ionic exchange capacity and good thermal stability. They are promising candidates for applications in catalysis, optics, chemical sensors and bio-sensors, electronics, medicine and as bioactive materials [1–7].

Also known as hydrotalcites, layered double hydroxides (LDHs) materials consist of divalent and trivalent metals (M), with the general chemical representation: $[Ma_{1-x}Mb_x(OH)_2]^{x+}(A^{n-}{}_{x/n}) \cdot mH_2O$, where Ma represents divalent cations (Mg^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}), Mb represents trivalent cations (Al^{3+}, Cr^{3+}, Fe^{3+}, Mn^{3+}), A^{n-} represents an exchangeable anion (CO_3^{2-}, NO_3^-, Cl^-), x ($=M^b/(Ma+Mb)$) is the layer charge density of LDH with values varying between 0.2 and 0.4 [8] and m is the number of interlayer water molecules.

From this class of materials, the nickel or cobalt/aluminum-layered double hydroxides present a series of advantages, such as low cost and eco-friendliness, while also having good conductivity and the possibility to produce various structure types containing host structure with high proton mobility [9]. Transition metals incorporated in layered double hydroxides are redox-active and a number of papers discussed their potential application as electrode modifier [10–13], amperometric sensor [14], pseudocapacitor [15] or as electrochemical biosensors [16,17]. In order to use LDHs for sensing applications, the fabrication of highly adherent, crystalline and oriented nano-structured films is necessary.

Different methods are proposed to produce LDHs films: electrodeposition [16,18], ion-exchange [19], adsorption and coprecipitation [20], sol–gel [21], hydrothermal synthesis [22], layer-by-layer assembly [23], spin-coating [24], hot-water treatment of sol–gel derived precursor gel films [25], in situ crystallization technique [26]. There are however drawbacks of these methods: a relatively poor adherence to the substrate, a poor crystallinity, the requirement for an appropriate substrate [18–26].

Therefore, it is of great importance to find an alternative deposition technique which allows the obtaining of thin films with good adherence, controlled thickness and structural and morphological properties, with the preservation of the target stoichiometry and purity.

The issue can be solved by using laser methods, such as pulsed laser deposition technique (PLD), which enables to grow thin films of different types of materials with good adherence, controlled thickness and structural and morphological properties, and to preserve the stoichiometry of materials during the deposition process [27]. Very few investigations have been focused on the deposition of LDH films by laser techniques. T.B Hur et al. [28] reported the use of a laser technique to prepare Mg–Al LDH and Zn–Al LDH films using laser ablation in water.

Our group reported on the deposition of LDHs thin films by pulsed laser deposition (PLD) and matrix assisted pulsed laser evaporation

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(MAPLE) [29,30]. We concluded that the formation of Ni–Al and Co–Al based LDH thin films is favored by the 1064 nm wavelength due to its penetration depth [30]. However, small amounts of mixed oxides, Ni(Al)O and Co(Al)O, respectively, could be detected [30]. The advantages of nickel-layered double hydroxides are the low production cost and environmental friendliness.

This work is an extension of the abovementioned studies towards the production of oriented Ni bases LDH with no byproducts starting form ternary Ni_2Mg–Al and $NiMg_2$–Al targets and provides a step forward towards applications of LDH films as sensors.

2. Experimental

In the present work, Ni–Al, (Ni,Mg)–Al and Mg–Al layered double hydroxide powders were synthesized by coprecipitation method at pH = 10, using aqueous solutions of nickel nitrate, magnesium nitrate, aluminum nitrate, sodium hydroxide and carbonate. The obtained gel was dried at 85 °C for 24 h under controlled nitrogen flow. The powders were then pressed as round pellets and used as targets for the pulsed laser deposition experiments. The structural and the chemical compositions of the targets were examined via X-ray diffraction (XRD) using Panalytical X'Pert MPD system (λCuKα = 1.5418 Å) and energy dispersive X-ray spectroscopy (EDX) on scanning microscope (FEI, model Inspect S50). The targets and their corresponding thin films were denoted Ni_3Al, Ni_2MgAl, $NiMg_2Al$ and Mg_3Al, respectively, in accordance with the atomic ratio used in the precipitation step.

The corresponding Ni–Al, (Ni,Mg)–Al and Mg–Al LDH thin films were deposited by pulsed laser deposition technique (PLD) using a Nd:YAG laser (λ = 1064 nm, pulse length of ~5 ns) working at a repetition rate of 10 Hz. The LDHs thin films are deposited in a deposition chamber evacuated down to 2×10^{-2} Pa at ambient temperature. The laser fluence was set at 2 J/cm^2. The number of pulses was set to 12,000, resulting in films with thicknesses of around 100 nm. The target to substrate distance is 4 cm. Samples were grown on double-side polished silicon for infrared detection, Si(001) and glass substrates (1 cm × 1 cm) washed in acetone and ethanol before deposition. The characterization of Ni containing layered double hydroxide (LDH) thin films on glass and silicon substrates was carried out through optical, structural and morphological analysis. Crystalline structure and lattice spacing were determined using X-ray diffraction at grazing incidence (GI-XRD, ω = 0.25°) on Panalytical X'Pert MRD system (λCuKα = 1.5418 Å). A Secondary Ions Mass Spectrometry (SIMS) workstation from Hiden Analytical device with a current of 400 nA rastering in area of about 1 mm^2 and using an Ar ion source was used to check the in-depth uniformity of samples. Fourier transform infra-red spectroscopy (FTIR) measurements, using a JASCO 6300A Spectrometer working in transmission mode and resolution set to 4 cm^{-1}. The chemical composition was evaluated by energy dispersive X-ray spectroscopy (EDX) using a Scanning Electron Microscope (SEM), FEI Co., model Quanta Inspect S, 0–30 kV accelerating voltage, with an EDAX Co. SiLi detector. Optical properties of samples were measured using a spectroscopic ellipsometer (Woolan V-Vase). The double polished Si(001) substrates are appropriate for FTIR measurements while the glass substrates for optical measurements. There are number of pertinent studies on the possibility of developing conductive LDHs in particular Ni-based LDH as sensors or catalysts based on Ni^{2+}/Ni^{3+} redox couple [18,31–36]. The Ni ion environment could be change by Ni ion exchange procedures. In order to get more inside on the structural and optical response of the Ni based LDHs to the modification of Ni ions environment through isomorphous substitution in the "brucite"-type layer or/and intercalation in the interlayer space or/and deposition on the external surface of crystals, the films were immersed for 3 days in a $Ni(NO_3)_2$ aqueous solutions with Ni concentration of 10^{-3}% (w/w) (1 g/L). The immersed films were characterized via XRD, EDX and spectroscopic ellipsometry. Surface morphologies of the obtained thin films were investigated by atomic force microscopy (AFM) using a Park XE 100 system with silicon nitrides cantilevers in non-contact mode.

3. Results and discussion

The XRD patterns of the targets presented in Fig. 1 display the typical structure of layered double hydroxides, with sharp and symmetric reflections for (0 0 3), (0 0 6), (1 1 0) and (1 1 3) planes and broad asymmetric peaks for (0 1 2), (0 1 5) and (0 1 8) planes (JCPDS 70-2151). The reflections were indexed in a hexagonal lattice with a R3m rhombohedral symmetry and the Miller indexation is labeled in Fig. 1. No byproducts were detected.

Table 1 summarizes the crystallographic parameters *a* and *c*, along with the EDX data analysis for targets and thin films and average surface roughness of the films (expressed as RMS) measured by AFM on an area of 20 × 20 μm. The mean crystallite sizes extracted via the Debye–Scherrer formula from the (003) reflection are also shown. The (003) peak is a basal peak related to the *c*-axis along which the layers are stacked and its broadness ascertains for the degree of the organization of the layered structures. It is observed that the Ni_3Al target exhibits the highest degree of organization/crystallinity. It is also to be observed that the values of the lattice constant *a*, related exclusively to the brucite-like sheets, decrease with increasing Ni content in the target following the Vegard's law, in agreement with the difference in the Schannon radii of Ni^{2+}, Mg^{2+} and Al^{3+} in octahedral coordination ($Ni^{2+}/Mg^{2+}/Al^{3+}$ = 0.69/0.72/0.535) (inset in Fig. 1).

The surface morphology (Fig. 2) of deposited samples on Si substrates measured by AFM and SEM reveals a rough surface with big grains randomly oriented with respect to each other distributed onto the surface. The observed grains are due to two reasons: (i) the targets are not sintered just pressed, and (ii) the used laser wavelength for depositions. The penetration depth is greater at higher ablation wavelengths, so that roughness values are expected to increase when working at 1064 nm.

Apparently, the presence of Ni in the films makes the films smoother, barring a few spherical particles on the film surface, than the films deposited from the Ni free target. The result could be related with the highest degree of the layered stacking arrangement/crystallinity of the Ni_3Al target.

Fig. 3 shows X-ray diffraction (XRD) patterns of the films deposited onto Si(001) substrates prepared by PLD. There are no differences in the XRD patterns between the films deposited on Si(001) in comparison with films deposited on glass substrates. The XRD patterns exhibit the formation of oriented LDH phases from all the types of targets, either from the binary systems, as we had already reported [29,30] or in the case of the ternary systems Ni_2MgAl and $NiMg_2Al$. The presence of the basal reflections only accounts for the formation of *c*-axis oriented films. The *c* parameters presented in Table 1 are slightly higher than those in the corresponding targets, probably due to an increase or rearrangement of interlayer carbonates. A broad peak assigned to the cubic

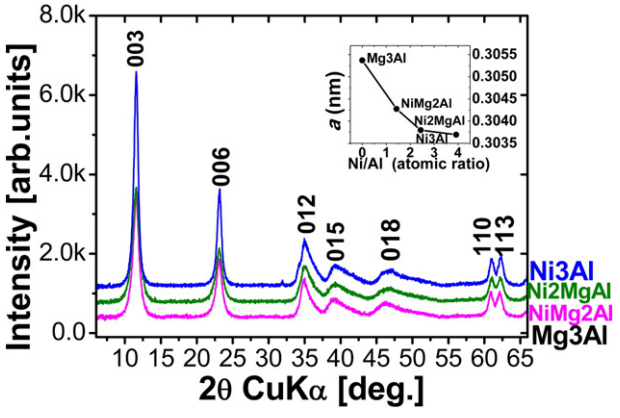

Fig. 1. The XRD patterns of the targets. The values of the lattice constant *a* decrease with increasing Ni content in the target (inset).