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Influence of Ca Content on the Structure and Properties of (Co, Ca)O Thin Films Deposited by PLD Technique

L. CIENIEK* AND S. KAC

Faculty of Metals Engineering and Industrial Computer Science, AGH University of Science and Technology
30 Mickiewicza Ave., 30-059 Cracow, Poland

In this paper the results of investigations of pure and Ca-doped CoO thin films deposited by PLD technique are presented. The studies carried out for variable Ca content allowed to establish optimal conditions for good quality oxide films preparation. The microstructure, chemical/phase composition and morphology of obtained thin films were examined by means of diverse techniques (SEM, EDS, XPS and XRD). For estimation of deposited Ca-doped CoO films quality the nanohardness and scratch tests (adhesion) were performed. Obtained results confirm that using PLD technique it is possible to carry stoichiometric composition of (Co, Ca)O from target to single crystal substrate and allow to conclude that the calcium dopant concentration (chemical composition) influence on the morphology and measured properties of deposited (Co, Ca)O films.

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1. Introduction

In recent years analysis of pure CoO and (Co, Ca)O single crystals, have been made to indicate the influence of Ca content on the structure and properties of ionic oxides [1]. Results of this research allow to conclude that Ca-doped CoO crystals reveal reversible abrupt decrease of electrical conductivity at high temperature (1000–1400 °C) and low oxygen partial pressure (below 10^{-3} atm). The reason for this phenomenon is the presence of more complex defect structure at high temperatures (4:1 clusters apart from simple cation vacancies). Co^+ cations are responsible for the conductivity decrease. Their presence decreases the concentration of electron holes that reduce carrier's amount. The very fine spherical phase, observed by transmission electron microscopy only for specified range of oxygen activity, is responsible for abrupt decrease of the conductivity for (Co, Ca)O oxides. TEM, coupled to EDS analyses, revealed the presence of Co_3O_4 precipitates, whose density, shape and size change with the amount of Ca. The electrical properties change is also the consequence of Co_3O_4 spinel phase concentration decrease (presence of phase boundaries), as well as the dislocations density [2]. Since reversible transport properties changes are observed for very specified range of oxygen partial pressure and high temperature there is much to be said for (Co, Ca)O to be the functional material used for gas sensors. Cobalt oxides (CoO and Co_3O_4) exhibit many interesting electronic and magnetic properties and are widely used as catalysts [3], pigments for glasses and ceramics, electrochromic materials [4], electrochemical anodes [5], electrochemical capac-

itors for high power devices [6]. Contemporary tendency for miniaturization in materials science [7] extort adaptation of the most recent production techniques, like Pulsed Laser Deposition (PLD), to obtain oxides thin films with particular properties. Our goal was to verify the quality of pure and Ca-doped CoO thin films in order to find optimal conditions for their preparation using PLD technique.

2. Experimental procedure

Pulsed Laser Deposition (PLD) process was performed using LOTIS Tii Nd:YAG; Model LS-2147 pulsed laser (wavelength of 266 nm, pump energy 40 J and laser fluency in the range 3.89–5.48 J/cm²). During ablation process a frequency of 10 Hz and a dwell time of the laser pulse of 18 ns were applied. The laser deposition was performed in a vacuum chamber equipped with a rotating target support and a substrate holder, with no heating applied. At first the chamber was kept under dynamic vacuum 5×10^{-6} mbar and next the oxygen atmosphere was used for deposition process ($p_{\text{O}_2} = 5 \times 10^{-2}$ mbar). For all deposition experiments Si single crystals (room temperature) were used as substrates. Time of each film deposition was set to 1 h.

The ablation targets were pure CoO or CoO and CaO oxides mixtures with specific composition ratio: CoO + 1 wt.% of Ca, CoO + 3.5 wt.% of Ca, and CoO + 6 wt.% of Ca. Samples were cold pressed under the pressure of 400 MPa with a little addition of polyvinyl alcohol (6% water solution) and annealed in Ar at the temperature from the range of 100–1100 °C. The quality and chemical composition of obtained targets (Fig. 1) was precisely checked.

* corresponding author; e-mail: cieniek@agh.edu.pl

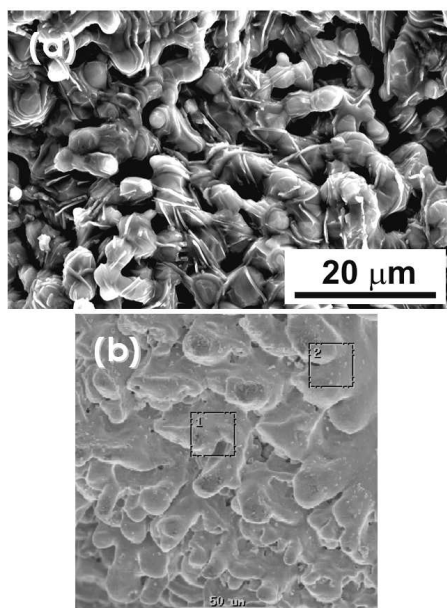


Fig. 1. SEM microstructure of (Co,Ca)O target (a) before and (b) after laser ablation process, with EDS analysis areas.

For characterisation of obtained surface thin films the Scanning Electron Microscopy (HITACHI S-3500N Scanning Electron Microscope), Atomic Force Microscopy (Atomic Force Microscope v 5.01 — built in Institute of Nuclear Physics Polish Academy of Science, Krakow–Muenster), X-ray Diffraction (XRD apparatus model HZG-4) and X-ray Photoelectron Spectroscopy (XPS apparatus Vacuum Scientific Workshop Ltd. England with Galileo electron analyser) investigations have been used to reveal the microstructural details. In addition, Energy-Dispersive X-ray Spectroscopy (EDS) has been applied for chemical microanalysis of the deposited films. Nanohardness measurements and scratch-test have been performed to define the quality and adhesion of oxide films.

3. Results and discussion

Using described deposition conditions all of produced thin films (pure CoO and (Co,Ca)O oxides) were thin, about 50 nm, with no cracks and porosity observed on their surface (Fig. 2). Some droplets are present on the surface of thin films but their amount is limited. The Ca concentration increases their number.

Energy-dispersive X-ray spectroscopy (EDS) studies show, that the surface films deposited on the Si substrate at room temperature are composed generally of CoO and CaO (Fig. 3). Droplets observed on the deposited surfaces are generally calcium rich. The dopant concentration is a little higher than for surface film that can be compared in the Table I. For the highest Ca concentration the amount of dopant is over 50% higher in droplets than in the deposited film.

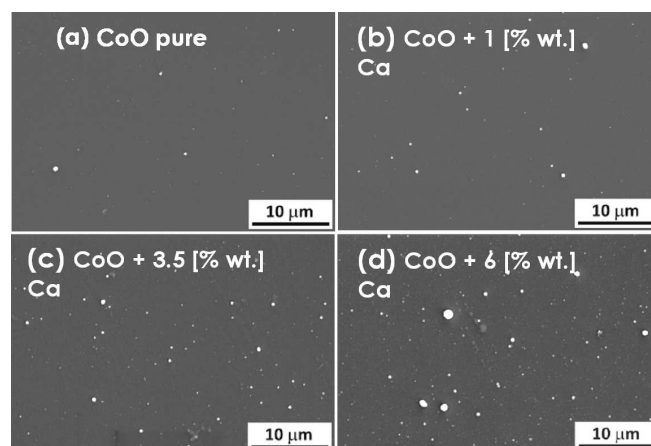


Fig. 2. SEM image of (a) CoO and (b–d) (Co,Ca)O thin layers surface with different Ca concentration: (b) 1 wt.% of Ca, (c) 3.5 wt.% of Ca and (d) 6 wt.% of Ca.

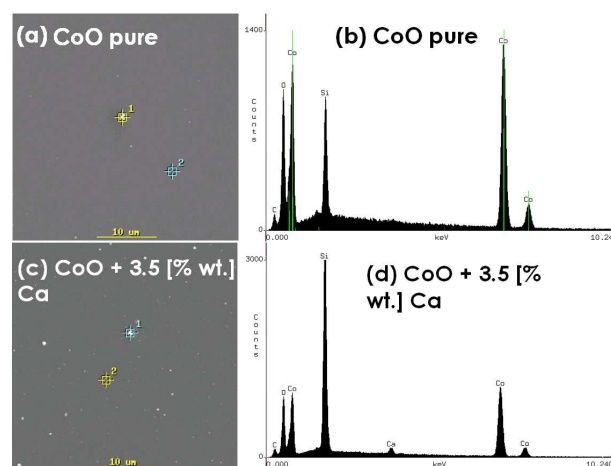


Fig. 3. CoO (a) and (Co,Ca)O (c) thin layers with EDS analysis points and analysis results (b) for CoO pure and (d) CoO + 1 wt.% of Ca respectively.

The results of Atomic Force Microscopy (AFM) investigation indicate that the surface thin films of CoO deposited on silicon substrate at room temperature are quite smooth (Fig. 4a). The separate trapezium in cross-section columns (about 130 nm in height) were observed. However the surface layers of Ca-doped CoO deposited on silicon substrate reveal the topography built from set of columns with the same shape, smooth on the top (Fig. 4b,c). This allows to conclude that during deposition process the column crystal growth takes place on the Si substrate.

In order to study the phase composition of obtained thin films the X-ray Diffraction (XRD) analysis has been made. Figure 5 shows X-ray diffraction diagrams of pure and Ca-doped CoO surface thin films deposited at room temperature. The diagram confirms the presence of CoO and Co₃O₄ in all of samples, however it can be noticed

that with the Ca concentration increase CaO phase appears (for 3.5 wt.% of Ca). For highest Ca concentration (6 wt.% Ca), CaO phase disappears and strong peak from complex calcium cobaltite $\text{Ca}_3\text{Co}_4\text{O}_9$ is revealed. Pres-

ence of SiO_2 phase (between the substrate and the deposited thin film) can be explained as a result of very fast Si oxidation during deposition process.

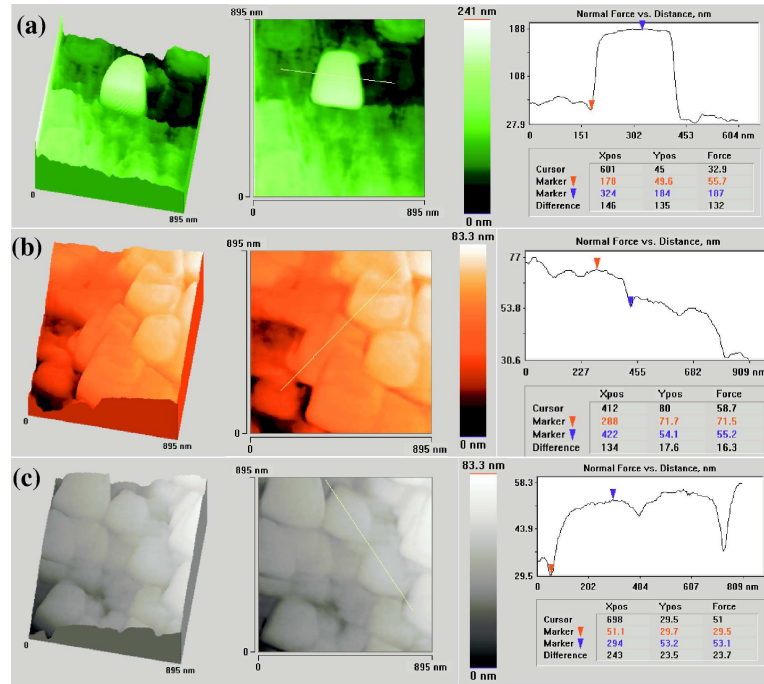


Fig. 4. Image of surface layer topography and vertical section profile with measurements (a) CoO pure, (b) CoO + 1 wt.% of Ca and (c) CoO + 6 wt.% of Ca.

The surface composition was studied using an XPS method instrument equipped with a concentric hemispherical of diameter of 150 mm electron analyser and a two-plate 18-channel detector. The electron analyser was operated in fixed-analyse transmission (FAT) with a constant pass energy of 22.5 eV. As an X-ray source the Mg anode with the $\text{K}\alpha$ (1253.6 eV) radiation of 208 W was applied. The background pressure during the experiments was better than 1×10^{-8} mbar. Calibration of the binding energy scale was done by assuming the position of the C 1s line of C–C and C–H bonding at 284.6 eV. Quantitative analysis has been made for Co and Ca (Table II). The increased Ca concentration observed for all samples may be related to the surface segregation of dopant during epitaxial column growth of deposited films. Figure 6 shows results of XPS analysis made for sample of CoO + 1 wt.% Ca. For all of analysed samples the Co 2p and Ca 2p peaks positions are characteristic for the oxidation state +2, however for cobalt analysis Co_3O_4 phase presence is highly possible (peaks locations are very similar).

In order to verify the quality of obtained thin films nanohardness (Vickers technique nanohardness and nano-scratch tester, CSM Instruments SA) measurements has been performed. The load force 7 mN has been applied during 10 s. It can be seen in Fig. 7 that the hard-

TABLE I
The average concentrations of elements in selected few EDS analysis points for deposited film and droplets.

Sample	Element	Deposited film		Droplets	
		Element [wt.%]	Err. [wt.%]	Element [wt.%]	Err. [wt.%]
CoO pure	Co–K	100.00	± 7.4	99.83	± 2.3
	Ca–K	0.00	± 0.0	0.17	± 0.1
CoO + 1 wt.% of Ca	Co–K	98.85	± 3.2	98.05	± 2.7
	Ca–K	1.15	± 0.2	1.95	± 0.4
CoO + 3.5 wt.% of Ca	Co–K	96.43	± 2.5	93.17	± 3.6
	Ca–K	3.57	± 0.3	6.83	± 0.4
CoO + 6 wt.% of Ca	Co–K	93.92	± 2.9	89.17	± 2.9
	Ca–K	6.08	± 0.2	10.83	± 0.6

ness of pure CoO is lower than for Si substrate (7.94 GPa and 9.87 GPa respectively) but with Ca content it increase to the value of 11.27 GPa. For highest Ca concentration one can notice the decrease of nanohardness value (6.44 GPa) which is the result of calcium cobaltite phase presence ($\text{Ca}_3\text{Co}_4\text{O}_9$).

Measurements of surface films adhesion have been made during scratch-tests. For these experiments of linear scratch the following conditions were applied: ini-

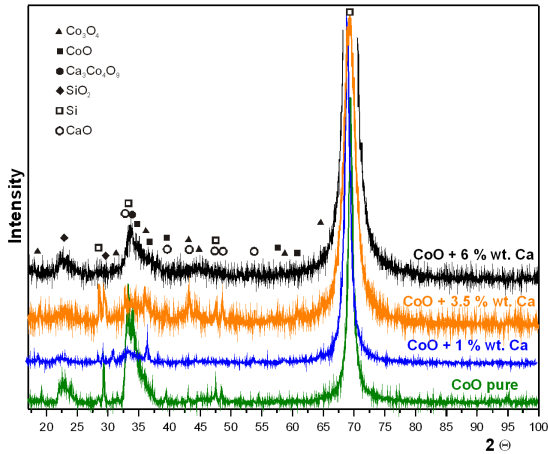


Fig. 5. Diffraction patterns from pure and Ca-doped CoO thin films deposited on Si surface at room temperature.

TABLE II
Results of Ca quantitative analysis in (Co,Ca)O surface layers using XPS technique.

Sample	Ca [wt.%]
CoO + 1 wt.% of Ca	4.1
CoO + 3.5 wt.% of Ca	11.7
CoO + 6 wt.% of Ca	10.7

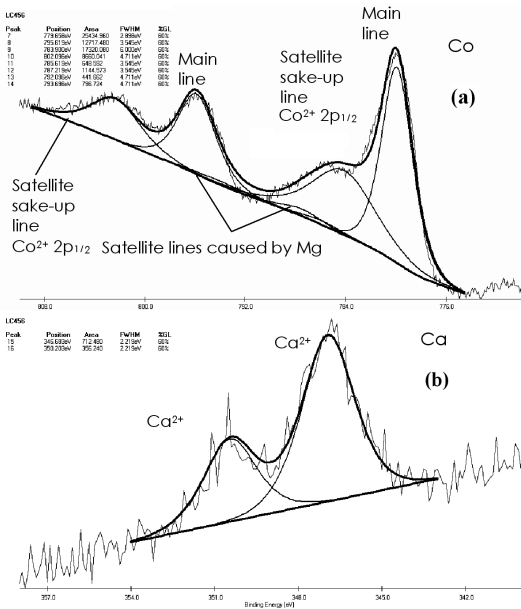


Fig. 6. XPS peaks positions characteristic for oxide state +2, (a) for Co 2p, and (b) for Ca 2p, obtained for CoO + 1 wt.% of Ca sample.



Fig. 7. Results of nanohardness measurements for pure and Ca-doped CoO, as well as for Si substrate.

TABLE III
Results of regular force measurements during pure and Ca-doped CoO thin films scratch tests.

Sample	Critical load [mN]	
	Initial fracture	Delamination
CoO pure	9.60	10.49
CoO + 1 wt.% of Ca	7.82	8.78
CoO + 3.5 wt.% of Ca	8.41	9.15
CoO + 6 wt.% of Ca	11.96	13.32

tial load — 4 mN, final load — 20 mN, loading/unloading rate — 100 mN/min, scratch length — 1 mm and scratch speed — 6.25 mm/min. The values of specific critical loads were estimated for appearance of initial fractures and for complete delamination of deposited films (Table III). In this case the presence of Ca content has the positive influence on the thin films adhesion, with the increase of calcium concentration the greater force is needed to destroy the deposited film.

4. Conclusions

According to results of structure and properties investigations made for pure and Ca-doped thin films (deposited by PLD technique) the following conclusions can be proposed:

- 1. It is possible to carry the chemical composition of pure and Ca-doped CoO from targets to Si substrate at room temperature by Pulsed Laser Deposition technique.
- 2. Obtained thin films are good quality with no visible defects on the surface (cracks or porosity) and little number of Ca rich droplets. For the higher calcium concentration the Ca₃Co₄O₉ phase appears (apart from CoO and Co₃O₄ observed for all samples).

3. The results of Atomic Force Microscopy (AFM) investigation indicate that during deposition process the trapezium in cross-section column crystal growth takes place on the Si substrate.
4. The XPS analysis results show that the concentration of Ca is higher at the surface of deposited films which is a result of Ca surface segregation during epitaxial column growth.
5. The hardness of obtained films depends on the Ca concentration which corresponds to phase formation during deposition. For 6 wt.% of Ca the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase appears and the value of nanohardness decrease.
6. Adhesion of deposited (Co, Ca)O films increases with the Ca concentration.

Acknowledgments

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