Applied Surface Science 255 (2009) 6656–6660

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Sn–CeO_2 thin films prepared by rf magnetron sputtering: XPS and SIMS study

Karel Mašek [a,*], Michal Václavů [a], Petr Bábor [b], Vladimír Matolín [a]

[a] Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, 18000 Prague 8, Czech Republic
[b] Brno University of Technology, Faculty of Mechanical Engineering, Institute of Physical Engineering, Technická 2896/2, 616 69 Brno, Czech Republic

ARTICLE INFO

Article history:
Received 17 April 2008
Received in revised form 5 January 2009
Accepted 23 February 2009
Available online 6 March 2009

PACS:
68.47.Gh
82.80.Pv
68.49.Sf
81.15.Cd

Keywords:
Cerium oxide
Tin–cerium mixed oxide
SIMS
XPS
Magnetron sputtering

ABSTRACT

Sn addition in the CeO_2 thin film by simultaneous Sn metal and cerium oxide magnetron sputtering causes growth of Ce^{3+} rich films whilst pure cerium oxide sputtering provides stoichiometric CeO_2 layers. $Ce^{4+} \rightarrow Ce^{3+}$ conversion is explained by a charge transfer from Sn atoms to unoccupied orbital Ce $4f^0$ of cerium oxide by forming Ce $4f^1$ state. XPS and SIMS revealed a formation of a new chemical $Ce(Sn)^+$ state, which belongs to $SnCeO_2$ species.

1. Introduction

The electronic structure of the CeO_2 oxide is characterized by unoccupied 4f states of Ce^{4+} ($4f^0$) whilst the Ce_2O_3 oxide has a Ce^{3+} ($4f^1$) configuration. Different 4f configurations for Ce^{4+} and Ce^{3+} result in different core level and valence band structures. One of the important properties of ceria is its oxygen storage capacity, which can provide oxygen to the gas mixture in catalytic contexts. The key factor for this property is the reversible transformation from Ce^{4+} to Ce^{3+}.

The cerium chemical state may be determined by a photoelectron spectroscopy. Using a conventional laboratory X-ray source, Ce 3d levels can be analysed [1–3]. The Ce 3d spectrum of partially reduced ceria consists of three $3d_{3/2}$–$3d_{5/2}$ spin–orbit–split doublets representing different $4f^0$ (Ce^{4+}) configurations in the photoemission final state. Two other doublets represent $4f^1$ (Ce^{3+}) states.

The previous X-ray photoelectron spectroscopy (XPS) and resonance photoelectron spectroscopy (RPES) studies on epitaxial CeO_2 thin films grown on Cu(1 1 1) showed that the Sn deposition on cerium oxide causes Ce^{3+} intensity to appear in the Ce 3d spectra [4,5]. The mixed oxide Sn–Ce–O has been found to be efficient CO oxidation catalyst which was more active than the individual oxides.

The purpose of this study was to contribute to the elucidation of the Sn–Ce interaction mechanism in mixed oxides prepared by simultaneous magnetron sputtering of ceria and tin.

There are several reports concerning the deposition of CeO_2 films using sputtering, mainly for superconducting and microwave applications, e.g., [6–9].

Secondary ion mass spectroscopy (SIMS) study of the chemical nature of ceria thin films showed the possibility to determine depth profiles by analysing different positive ion clusters [10].

We report that the Sn introduction in the CeO_2 thin film causes Ce^{3+} concentration enhancement and complete $Ce^{4+} \rightarrow Ce^{3+}$ conversion could be caused by a charge transfer from Sn atoms to unoccupied orbital Ce $4f^0$ of cerium oxide by forming Ce $4f^1$ state.

2. Experimental

Non-reactive rf magnetron sputtering was used to deposit CeO_2 and Sn–CeO_2 thin films on Si(1 0 0) wafer substrates. CeO_2 sputtering was performed using a pure CeO_2 target (Kurt J. Lesker Company, 99.99% purity) at a distance of 90 mm from the Si substrate (Si wafer covered by natural oxide layer) with rf power of

* Corresponding author. Tel.: +420 22191 2753.
E-mail address: karel.masek@mff.cuni.cz (K. Mašek).

0169-4332/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2009.02.080

20 W. Sn–CeO_2 thin films sputtering was performed from the composite target prepared by partial covering of the ceria target with a Sn foil (Goodfellow Cambridge Limited, 99.99+% purity). Deposition was carried out at room temperature of the substrate in Ar atmosphere keeping the total pressure in the deposition chamber constant at 6×10^{-1} Pa.

XPS and SIMS study were performed ex-situ in two analysis chambers. All photoemission data acquisition was done with the sample at 300 K using K_α photons from the Al anode of the X-ray source (1486.6 eV). The spectra were acquired under the emission angle perpendicular to the sample surface. SIMS analysis was performed in PHI 600 series instrument by using a scanned Ar^+ ion beam with following parameters: ion current: 60 nA, spot size 200 μm, crater raster area 1.5×1.5 mm^2. As the source of the primary beam the Specs IQE 12/38 ion gun was used and quadrupole mass analyser was used for detection of secondary ion signal. In order to obtain well resolved depth profiles and minimize crater effects, the technique of gating of the secondary ion beam was used together with secondary ion optics focused to area of 0.5×0.5 mm^2 [11].

3. Results

3.1. Pure cerium oxide

The 3d core level spectrum of continuous CeO_2 film deposited without adding Sn is presented in Fig. 1(a) (upper spectrum). It consists of three $3d_{3/2}$–$3d_{5/2}$ spin–orbit–split doublets (u‴-v‴, u″-v″ and asymmetric u-v). The appearance of a high u‴-v‴ signal, together with u-v peaks which are less intense than the u″-v″ peaks, is evidence of the formation of CeO_2 oxide.

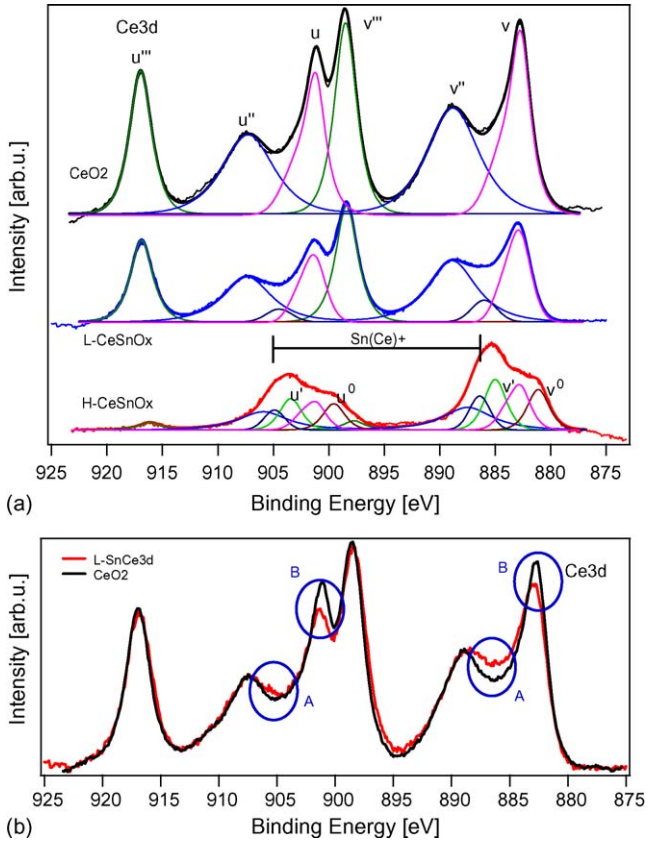

Fig. 1. (a) XPS Ce 3d core level spectra of continuous pure cerium oxide (CeO_2), low Sn content (L-$SnCeO_x$) and high Sn content (H-$SnCeO_x$) cerium oxide films including their deconvolution. (b) Comparison of XPS Ce 3d spectra of pure (CeO_2) and low Sn content (L-$SnCeO_x$) cerium oxide.

The thickness of this layer was estimated to be 2.3 nm taking to the account a very low intensity of Si 2p XPS signal and a value of inelastic mean free path of signal electrons in ceria (2.4 nm for Si 2p electrons and Al K_α X-ray source [12]. The Ce 3d emission peaks were fitted by pseudo-Voigt functions (combination Gaussian and lorentzian functions). The asymmetry of u-v doublet was modelled using two components with energy shift 1.6 eV. Further details and resulting fitting parameters are introduced in Table 1.

3.2. Sn–cerium oxide – XPS

Similarly to the Sn deposition on CeO_2(1 1 1) [4,5], the interaction of the added metal resulting in a partial reduction of CeO_2 to Ce_2O_3 was observed. Examples of the Ce 3d spectra for two Sn contents are plotted in Fig. 1(a) (L stands for a low Sn content, H for higher Sn content). The spectra were fitted by using the same

Table 1
List of resulting fitting parameters of Ce 3d core level spectrum for all samples.

	H-CeO_x	L-CeO_x	CeO_2
u‴-v‴ Ce 3d doublet			
Position	897.74	898.40	898.50
Amplitude	375.80	4738.85	7797.00
Width	2.30	2.41	2.42
Shape	1.00	0.80	0.76
Split	18.43	18.49	18.48
Ratio	1.24	1.42	1.34
u″-v″ Ce 3d doublet			
Position	887.49	888.89	888.82
Amplitude	919.99	2497.86	4315.57
Width	5.30	5.23	5.66
Shape	0.90	0.82	0.69
Split	18.43	18.49	18.48
Ratio	1.24	1.36	1.34
u-v Ce 3d asymmetrical doublet			
1st component			
Position	882.92	882.80	882.69
Amplitude	1455.64	3513.60	6803.41
Width	2.26	2.48	2.17
Shape	0.60	0.44	0.85
Split	18.43	18.49	18.48
Ratio	1.46	1.36	1.30
2nd component			
Position	884.32	884.40	884.49
Amplitude	393.02	948.67	1836.92
Width	2.00	2.26	3.11
Shape	0.60	0.60	0.60
Split	18.43	18.49	18.48
Ratio	1.21	1.35	1.21
u′-v′ Ce 3d doublet			
Position	885.00	xxxx	xxxx
Amplitude	2061.17	xxxx	xxxx
Width	2.40	xxxx	xxxx
Shape	0.60	xxxx	xxxx
Split	18.43	xxxx	xxxx
Ratio	1.61	xxxx	xxxx
u^0-v^0 Ce 3d doublet			
Position	881.12	xxxx	xxxx
Amplitude	1648.94	xxxx	xxxx
Width	2.38	xxxx	xxxx
Shape	0.60	xxxx	xxxx
Split	18.43	xxxx	xxxx
Ratio	1.54	xxxx	xxxx
Ce–Sn + Ce 3d doublet			
Position	886.40	885.99	xxxx
Amplitude	1386.36	883.98	xxxx
Width	2.26	2.70	xxxx
Shape	0.26	0.00	xxxx
Split	18.51	18.49	xxxx
Ratio	1.70	1.70	xxxx