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## A MICROSCOPIC AND SPECTROSCOPIC INVESTIGATIONS IN $\text{CuO}_x\text{-CeO}_{2-\delta}$ /Si THIN FILMS

### MIKROSKOPOWE I SPEKTROSKOPOWE BADANIA CIENKICH WARSTW $\text{CuO}_x\text{-CeO}_{2-\delta}$ /Si

$\text{CuO}_x\text{-CeO}_2$  thin films for gas sensor application were elaborated by pulsed laser deposition technique. Targets were prepared from compacted Cu and  $\text{CeO}_2$  powder. The films were deposited on oriented Si (100) substrates with variable deposition times ( $t = 90, 240, 360$  s) and atomic fractions of Cu ( $\Phi = 0, 15, 21.5, 27\%$  at.), using excimer laser system (Compex 301 L = 248 mm from Lambda Physics Germany). The  $\text{CuO}_x\text{-CeO}_2$  thin films were characterized by means of the X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS) and High Resolution Transmission Electron Microscopy (HREM). The XPS analysis has shown that  $\text{Ce}^{4+}$  and  $\text{Cu}^{+1}$  ions were present at the surface of all samples. The argon ion sputtering has indicated that the surface of samples was enriched in copper. The high concentration of copper on the surface has been confirmed by SIMS.

*Keywords:* XPS, SIMS, thin films, gas sensors,  $\text{CuO}_x\text{-CeO}_2$

Warstwy  $\text{CuO}_x\text{-CeO}_2$  do zastosowań jako czujniki gazów, wytworzono techniką ablacji laserowej. Tarcze przygotowano z proszków Cu i  $\text{CeO}_2$ . Warstwy osadzano na podkładkach Si (001) przy różnych czasach ekspozycji  $t = 90, 240, 360$  s i różnej zawartości Cu (0, 15, 21.5, 27% at.), z zastosowaniem lasera excimerowego Compex 301 o długości fali  $\lambda = 248$  nm, firmy Lambda Physics Germany. Warstwy poddano badaniom struktury za pomocą Spektroskopii Elektronów Wzbudzonych Promieniowaniem Rentgenowskim (XPS), Spektroskopii Elektronów Wtórnych (SIMS) oraz Wysokorozdzielczej Mikroskopii Elektronowej (HREM). Analiza XPS wykazała obecność ceru na +4 stopniu utlenienia i miedzi na +1 stopniu utlenienia. Rozpylanie warstw jonami argonu wykazało iż miedź znajduje się na powierzchni warstwy. Potwierdziły to badania za pomocą SIMS. Analiza HREM wykazała iż miedź występuje w warstwach w postaci dwóch związków  $\text{CuO}$  i  $\text{Cu}_2\text{O}$ .

## 1. Introduction

In order to detect toxic gas traces in air, industrial devices making use of non-stoichiometric cerium dioxide  $\text{CeO}_2$  were previously developed. In fact, this dioxide has also been involved in a lot of diversified applications. Over the last 20 years, intensive researches on oxygen conduction in non-stoichiometric ceria led to development of new fuel cells. Doped ceria films were used in the manufacture of electrochemical cells (SOFC) operating at low temperatures ( $500^\circ\text{C}$ ) and in the oxygen storage or transport [1-2]. Ceria has also been currently used as an active component in the so-called three-way catalyst (oxidation of CO, oxidation of  $\text{C}_n\text{H}_m$ , reduction of  $\text{NO}_x$ ), for automotive exhaust [3]. In addition, ceria based catalysts were investigated for catalytic redox reactions, such as catalytic oxidation of CO and methane or

catalytic reduction of sulfur dioxide by carbon monoxide [4].

In previous works [5] we have reported the evolution of texture in  $\text{Cu-CeO}_2$  thin films obtained by pulsed laser deposition technique, with increasing copper content and with increasing deposition time. A change from (111) to (200) in the preferred orientation of the  $\text{CeO}_2$  grains have been observed with increasing copper amount. The catalytic properties strongly depended on the Cu atomic fraction. Full oxidation of methane has been observed only for thin films with 27%at. Cu [6].

In order to understand the role of copper in these sensors regarding the catalytic properties, we have studied localization of copper by coupling XPS and SIMS measurements and chemical composition of copper by electron microscopy observations.

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## 2. Experimental details

Thin films were elaborated by pulsed-laser deposition technique, the details of which have been described previously [5]. The targets were initially prepared by compacting powders of  $\text{CeO}_2$  and Cu under a pressure of 140 MPa during 5 min. Then the pellets were sintered at  $T = 1200^\circ\text{C}$  for 2 hours. The nominal composition of the pellets varied with copper fraction  $\phi = 0, 15, 21.5, 27\%$  at. The thin films were deposited on [100] oriented Si substrates using an excimer laser system (Compex 301,  $\lambda = 248$  nm from Lambda Physics, Germany) with different deposition time  $t = 90, 240, 360$  s. To define each sample, the simplified following specific notations were chosen: at.% Cu-t.

The oxidation state of Cu and Ce ion of the films and distribution of copper at different depth have been studied by X-ray Photoelectron Spectroscopy (XPS). The mean concentration depth profile and the lateral distribution maps of cerium and copper were determined by the SIMS method. The chemical composition of the copper in the thin films was determined by HREM.

## 3. Results and discussion

### 3.1. Chemical composition of the films

The XPS spectrum for the sample 27Cu-240 is presented in Fig. 1a. Generally, the shape of Ce 3d spectral line in cerium oxides is rather complex due to the overlapping of several component doublet lines (3d5/2 and 3d3/2) resulting from different final states of cerium ion after the emission of photoelectron [7]. The  $\text{Ce}^{4+}$  ions are represented by  $3d^9 4f^2 L^{-2}$ ,  $3d^9 4f^1 L^{-1}$  and  $3d^9 4f^0 L$  while  $\text{Ce}^{3+}$  ion are represented by  $3d^9 4f^2 L^{-1}$  and  $3d^9 4f^1 L$  configurations, where L denotes a ligand. Thus, the presence of  $\text{Ce}^{4+}$  ions lead to the appearance of three doublets in the XPS spectrum and the  $\text{Ce}^{3+}$  ions produce two doublet lines. These ten single lines (five doublets) are necessary to fit the Ce 3d region when these two types of ions are present. Only one line situated at 916.7 eV is well separated from others and correspond to Ce 3d3/2 ( $3d^9 4f^0 L$ ) [7, 8]. The relative intensity of this separated line is 14% of the total Ce 3d line intensity [9] for the pure  $\text{CeO}_2$  compound. As this line is absent in the pure  $\text{Ce}_2\text{O}_3$  compound, it can be used to determine the oxidation state of cerium in oxides. Our results, for all samples doped and undoped with copper, indicated that the relative intensity of this peak was 14% within the experimental error. More than the Ce 3d region was very well fitted with only by three 3d doublet lines characteristic for  $\text{Ce}^{4+}$  ion (Fig. 1b).

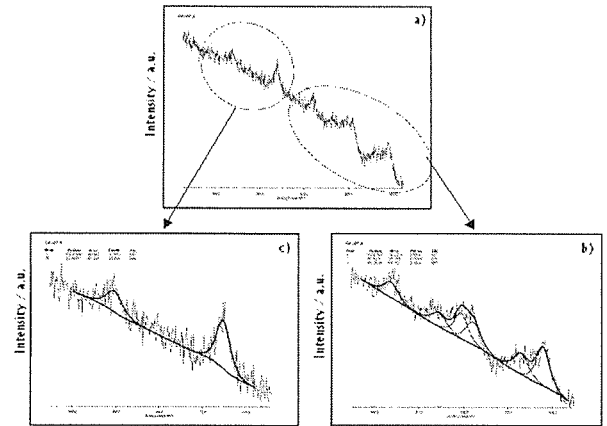


Fig. 1. XPS spectrum for sample 27%Cu-240 a) 3dCe and 2p Cu binding energies region b) three 3d doublet lines for  $\text{Ce}^{4+}$  ion and c) one 2p doublet line for  $\text{Cu}^{+1}$

Analyses of the Cu 2p binding energy region have shown only one 2p doublet line (Fig. 1c) of the binding energy for 2p3/2 at about 932.5 eV and for 2p1/2 at about 952.7 eV. The oxidation state of copper has been identified as  $\text{Cu}^{1+}$ . No shake-up satellites have been detected in any Cu 2p spectrum, which should appear if only the  $\text{Cu}^{2+}$  ions were present [9]. These results clearly indicated that copper formed  $\text{Cu}_2\text{O}$  grain.

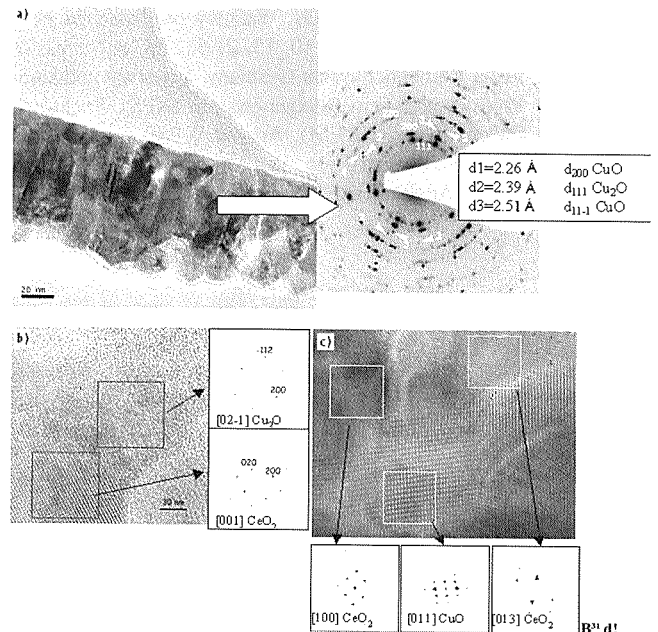


Fig. 2. Transmission microstructure of a cross-section and accompanying diffraction pattern (a), high resolution plan-view and Fourier Transforms from areas marked with squares (b, c) for sample 27Cu-90

The microstructure of the cross-section and electron diffraction of the sample 27Cu-90 are presented on Fig. 2a. We can observe a few extra spots, marked by arrows.

The corresponding distances were precisely determined, using the (220) ring from  $\text{CeO}_2$  for the calibration of the diffraction pattern. Thus, extra spots could be indexed as  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ . Individual grains of copper oxides were identified by HREM (fig. 2b, c) in plane view samples. By means electron diffraction and HREM imaging we have identified two type of copper oxides, namely  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ .

### 3.2. Distribution of the copper

Each Cu-doped sample was argon sputtered and subsequent XPS analyses were done at two different depth distances from the surface. The argon ion etching caused strong reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ , what is a well known effect [8]. We have noticed that after several minutes of sputtering the relative intensity of the Ce 3d3/2 separated peak at about 916.7 eV dropped up to 7% for undoped sample and up to 5-6% for copper-doped samples. For these cases five 3d doublet lines were necessary to well fit the Ce 3d region (Fig. 3). The Cu 2p spectra after sputtering has shown also only one 2p doublet line without any traces of the shake-up satellites as for non-sputtered samples. The ratios of the Cu 2p doublet intensity to the total intensity of Ce 3d line for all samples after each argon etching were recalculated using atomic sensitive factors (ASF). This factors have been determined by the photoionization process and condition of experiment [10, 11]. In this study the ASF was equal to 27.1 for Cu 2p and 51.1 for Ce 3d. In Table the atomic ratios of [Cu]:[Ce] are presented. The results clearly indicated that the surface of samples is enriched in copper. Unfortunately, the quantitative conclusions were not possible, because of lack of data concerning the sputtering rates of copper and cerium in oxides. The copper-enriched near-surface layer was roughly estimated to be about 30-50 nm.

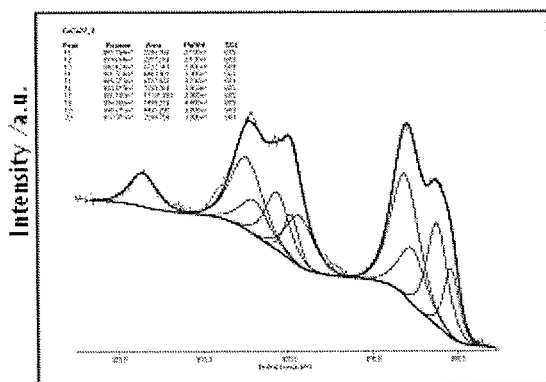


Fig. 3. XPS spectra of five 3d doublet lines for  $\text{Ce}^{+4}$  ion after sputtering for sample 27%Cu-240

TABLE  
Atomic ratio of Cu:Ce after subsequent argon ion etchings (2 keV  $\text{Ar}^+$  energy) determined by XPS

15% Cu-240		27% Cu-240	
$\text{Ar}^+$ sputtering conditions	Cu:Ce	$\text{Ar}^+$ sputtering conditions	Cu:Ce
before sputtering	0.41	before sputtering	0.46
20 min, 2.0 $\mu\text{A}/\text{cm}^2$	0.10	20 min, 2.1 $\mu\text{A}/\text{cm}^2$	0.12
45 min, 2.3 $\mu\text{A}/\text{cm}^2$	0.08	45 min, 2.3 $\mu\text{A}/\text{cm}^2$	0.09
45 min, 2.5 $\mu\text{A}/\text{cm}^2$	0.08	45 min, 2.5 $\mu\text{A}/\text{cm}^2$	0.08

The SIMS lateral distribution maps and depth profile of cerium and copper are present on Figure 4. The analyses have shown the uniform distribution of these elements on the surface. The depth profile is presented in the form of the secondary ion intensity ratio of  $^{140}\text{Ce}$  and  $^{63}\text{Cu}$  isotopes. The analysis confirmed the higher concentration of copper at the surface. The copper enriched layers are about 40 nm.

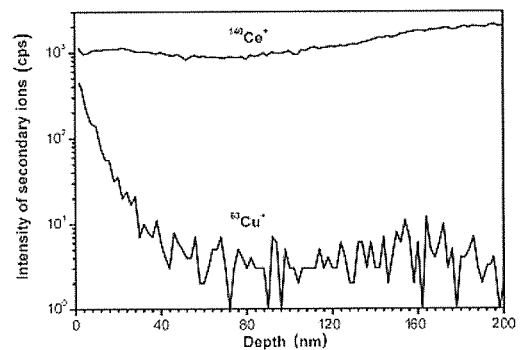
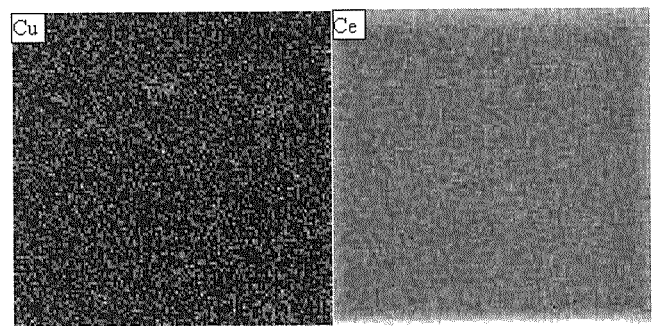


Fig. 4. The SIMS lateral distribution maps and depth profile of Ce and Cu for sample 15%Cu-360s

## 4. Conclusion

In this study two types of copper oxides have been identified in the various  $\text{CuO}_x\text{-CeO}_{2-\delta}/\text{Si}$  films. The  $\text{Cu}_2\text{O}$  was observed by XPS analysis. Using electron

diffraction and HREM imaging we have identified two type of copper oxides, CuO and Cu<sub>2</sub>O. Both XPS and SIMS study have shown the presence of copper-enriched near-surface layer of 30 to 40 nm. Enrichment of the surface of thin films in copper explained the oxidizing methane by system CuO<sub>x</sub>-CeO<sub>2-δ</sub>/Si [6]. These results correspond with the literature data. The better catalytic properties in oxidizing carbon monoxide have been observed in the system CuO<sub>x</sub>/CeO<sub>2</sub> with different atomic fraction of copper 5-25% at. by Skarman [12]. In this research the copper concentrated on the surface of CeO<sub>2</sub> crystalline in the form CuO and Cu<sub>2</sub>O. They have suggested that the superior catalytic activity of the CuO<sub>x</sub>/CeO<sub>2</sub> catalyst system in oxidizing carbon monoxide at low temperatures can be explained by a quick reversible redox process of surface Cu(I)/(II) couples in strong synergistic interaction with the nanocrystalline ceria support.

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