XPS – as a versatile tool in the research of the Department of Inorganic and Physical chemistry, UGent

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Content

- Thin film superconducting materials by sol gel chemistry
- Fibrous transistors, in cooperation with dep. of Textiles, Ugent
- Biogenic nanoparticles, in cooperation with labMET
- Supported metal oxide catalyst for liquid oxidation reactions
**Principle**

**Sol**

- Deposition on substrates by dipcoating, printing
- Gelation, $T \leq 60^\circ$C

**Gel**

**Oxide thin film (5-100 nm)**

- Heat treatment under controlled atmosphere

M$_{n+}$M$_{n+}$M$_{n+}$H$_2$O

M$_{n+}$M$_{n+}$M$_{n+}$
Deposition

- dip-/spin-coating from aqueous solutions
- ink-jet printing from water-based inks
Analysis of solutions, gels and thin films:

- optical analysis: UV/Vis/IR/Raman spectroscopy
- rheology: viscosity, surface tension, contact angle, particle size, ...
- thermal analysis: TGA/DTA/DSC/TMA
- microscopy: AFM, optical, SEM/EDX, (HR)TEM with EELS, STEM, EDX
- structural analysis: XRD, pole figures, BET
- electromagnetic: resistivity measurements
- complexometry: potentiometric titrations
- XPS

Materials

- ceramic high $T_c$ superconductor architectures on NiW tapes: YBCO, CeO$_2$, La$_2$Zr$_2$O$_7$
- TiO$_2$ for self-cleaning surfaces: on ceramic tiles and steel
- YSZ for thermal barrier coatings and solid oxide fuel cells
- mesoporous organosilica layers for low-k dielectrics (through ...)
- Diesel soot catalyst
**High $T_c$ superconductor architecture:**

- Textured, flexible NiW tape
- YBCO by dipcoating or printing from aqueous solutions
- CeO$_2$ (50-100 nm) by dipcoating from aqueous solutions
- LZO (250 nm) by dipcoating from aqueous solutions
- Buffer layers prevent O from diffusing to Ni substrate and Ni-diffusion into YBCO layer

**Applications:**
- Resistance $\sim 0$ at $-180$ °C
- Second generation HTS wires
- Fault current limiter
- Magnets
- Coils for renewable energy
- Induction heaters ...
High $T_c$ superconductor HTS architecture: XPS, TEM, FIB

(HR)-TEM analysis of interface, surface, crystalinity/texture

Ni/W

LZO

Cs-corrected TEM equipped with EELS, STEM, EDX ...

Sputter XPS analysis depth profiling

- Ni - diffusion through buffer layers for $\neq$ processing
- determination of layer thickness
- compositional analysis
- degree of oxidation

Ce⁴⁺ ion : (Xe) = 5p⁶ 4f⁰

Ce⁻⁻⁻ ion: (Xe) 4f¹⁻ = 5p⁶ 4f¹

Ce–O  is not 100 % ionic

ionic:       Ce: 5p⁶ 4f⁰           O: 1s² 2s² 2p⁶
less ionic:  Ce: 5p⁶ 4f¹

Burrough’s notation:

<table>
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<tr>
<th></th>
<th>v₀</th>
<th>v</th>
<th>v’</th>
<th>v”</th>
<th>v””</th>
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<td>Origin</td>
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<td>Ce⁴⁺</td>
<td>Ce³⁺</td>
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<td>Origin</td>
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<td>Ce⁴⁺</td>
<td>Ce³⁺</td>
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<td>FWHM</td>
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<td>5.86</td>
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Study of oxidation state of Cerium and Ni–diffusion, a single layer

XPS narrow scan of the Ce 3d region showing the typical spectrum for Ce$^{4+}$.

Fitting: constraints: doublet separation, peak position, FWHM, peak shape

Top: Ce (IV)
Core: Ce (III)
Due to sputtering?
The objective is to study the role of buffer layers in transferring the texture of Ni-W substrate to YBCO (XRD) and its effective role in prevention of penetration of Ni into YBCO.
Biogenic metals: XPS analysis of cerium from organic origin
B. De Gusseme, Prof. Verstraete (LabMET)

Goal:
In a biological process cerium–ions are removed from a solution into a solid state. The question was to identify the oxidation number of the cerium in the solid state. The paste like substance was spread onto a Sn–substrate. It is shown that the presence of cerium in the sample could be confirmed. The oxidation state of the cerium is Ce(III).

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>BE (eV)</th>
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| Ce(IV)          | 898.4   3d⁵/²  
                 | 916.9   3d⁷/²  
| Ce(IV)          | 888.9   3d⁵/²  
                 | 907.5   3d⁷/²  
| Ce(IV)          | 882.3   3d⁵/²  
                 | 901.0   3d⁷/²  
| Ce(III)         | 880     3d⁵/²   
                 | 899     3d⁷/²   
| Ce(III)         | 886     3d⁵/²   
                 | 904     3d⁷/²   |

Illustration: TEM of zerovalent paladium particles precipitated at the cell surface of Shewanella oneidesis

Goal:
To identify the oxidation number of the cerium in the solid state.

<table>
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<tr>
<th>Oxidation state</th>
<th>Binding Energy (eV)</th>
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<tbody>
<tr>
<td>Ce(III)</td>
<td>880, 899, 904</td>
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</table>

Table 1: Overview literature Ce3d³/² and 3d⁵/²
Determining the thickness of the Cu-layer. Based on differences in etch-rate between Ta$_2$O$_5$ and Cu.
Ultra-stable and zero leaching supported metal oxide catalyst for liquid oxidation reactions

Study of Vanadium oxide on mesoporous fenol resins
Ilke Muylaert, prof. Van Der Voort

Vanadium grafting

Characterization – XPS
Determination oxidation state of Vanadium

(a) $V_2O_5$ Crystalline
(b) $NH_4VO_3$ +5
(c) $VO(acac)_2$ +4
(d) P/F Resin +5 (+4)
Structural information:
C– peak at low energy 281.5 eV: C–OV
Due to low electronegativity and soft center of vanadium atom

XPS and DRIFT spectra before and after grafting with Vanadium
Thanks