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Towards functional advanced materials based using filling of ordered anodic oxides supports and templates

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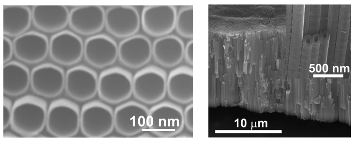
1. Motivation

- Highly-ordered nanostructures of valve metal oxides have recently attracted huge scientific and technological interest motivated by their possible use in many applications.
- The nanoporous Al_2O_3 membranes have been prepared by anodic oxidation of Al under suitable electrochemical conditions into perfectly ordered, honeycomb-like porous structures [1].
- Owing to the flexibility of the pore diameter/length and easy Al_2O_3 dissolution, its porous membranes have been since than widely used as templating material for a range of materials [2,3].
- It is the TiO_2 that has received the highest attention after Al_2O_3 motivated by its range of applications, including photocatalysis, water splitting, solar cells and biomedical uses.
- Self-organized TiO_2 nanotube layers have been prepared by anodization in suitable electrolytes, during which the Ti substrate is converted into highly-ordered nanotubular layer [4-6].
- Although many applications of ordered oxides have been presented [2,3,7,8] their potential for the synthesis of advanced functional nanomaterials has not at all been exploited.
- This in particular applies for exploration of all possible shapes and geometries due to a variety of anodization conditions.
- Our work aims to exploit these structures for various functional devices.

2. Preparation of ordered anodic oxides

TiO_2 NANOTUBES



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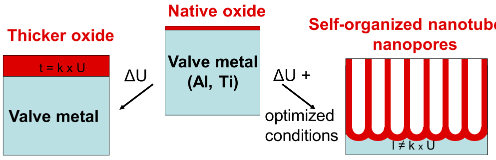
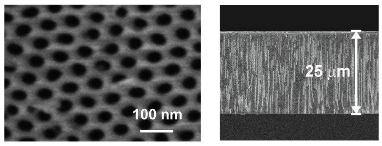
J.M. Macak et al., *Curr. Opin. Solid State Mater. Sci.* 1-2 (2007) 3.



- High-field anodization
- Electrochemical anodization / dissolution
- Chemical dissolution

Al_2O_3 NANOPORES



More in
W. Lee, R. Ji, U. Gösele, K. Nielsch, Nat. Mater. 5 (2006) 741

3. Controlled filling of ordered anodic oxides

These approaches have been used:

- selective electrochemical reduction of the tubes, pulse deposition of metals
- pulse deposition of polymer monomers and subsequent polymerization.
- chemical bath deposition of nanoparticles

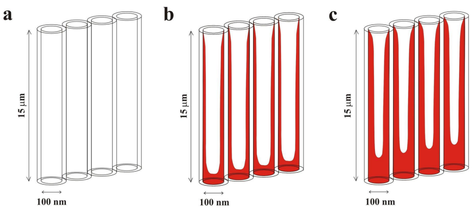
- selective electrochemical filling of pores using suitable electrode (metal)
- physico-chemical techniques (ALD, CVD, …)
- chemical bath deposition of nanoparticles

These approaches are very limited in terms of choice of materials, and were only successful for certain types of layers with specific dimensions

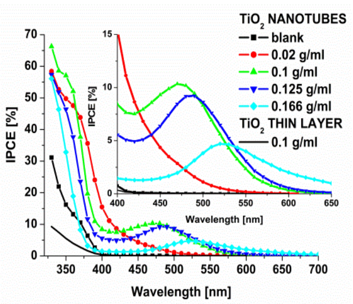
4. Applications of filled anodic oxides

Enhancing visible light response of TiO_2 nanotubes using new chalcogenide sensitizers

- Thin chalcogenide layers (Se, As, S, Te…) have been used in many applications (memories, optics, etc) - typically **spin-coated** from solution, or sputtered
- Chalcogenide glasses could have VIS-sensitizing effect as known from DSSC.



The infiltration concept of the titania nanotubes achieved by tailored spin-coating procedure. (a) plane tubes, (b) tubes with low material content, (c) tube with high material content.



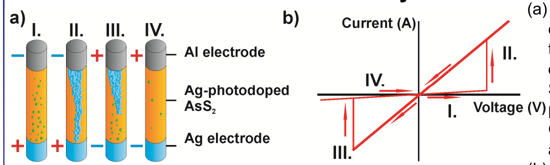
After coupling As_3S_7 to TiO_2 by infiltrating the titania nanotubes:

1) Photocurrent response in the UV light is enhanced by the factor of two(for all As_3S_7 concentrations) as compared to pristine TiO_2 nanotubes

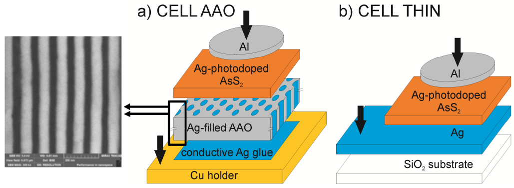
2) Significant photocurrent response can be observed in the visible light range, in particular for medium sensitizer concentrations (0.1 and 0.125 g/ml),

J.M. Macak, T. Kohoutek, L. Wang, R. Beranek, Nanoscale, 5 (2013) 9541

Exploring Ag-filled Al_2O_3 membranes for the resistive switching memory cells



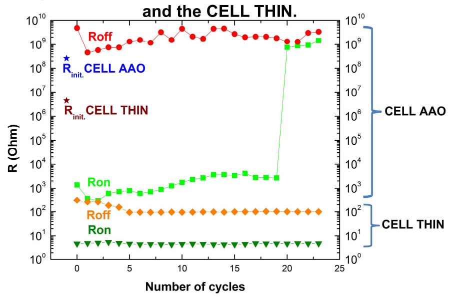
(a) the scheme of operation of memory cell based on ionic resistive switching, thicknesses of all layers are on the order of hundreds of nanometers. Symbols + and – represent applied polarities during each particular stage. Green and blue points represent Ag+ and Ag^0 species, respectively;
(b) 4 stages through which the cell passes within each cycle of operation.

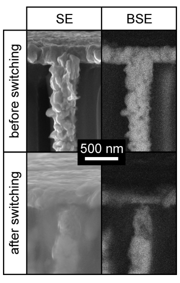


a) scheme of CELL AAO
b) scheme of CELL THIN

Arrows indicate contacting points.

Comparison of resistance data between the CELL AAO and the CELL THIN.





SEM images of CELL AAO sample showing the interface of the ionic conductor and Ag nanowires embedded in the AAO matrix.

The sample "after switching" was observed after recording 21 cycles and stopping the experiment afterwards.

J. Kolar, J.M. Macak, K. Terabe, T. Wagner, J. Mater. Chem. C, 2 (2014) 349

5. Summary

- Highly ordered valve metal oxide nanostructures can be prepared by anodization under optimized conditions.
- Owing to their ordering and defined structure, they can be used for a range of functional applications.
- They may be used directly (part of the final product) or as a templating material for various devices.

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