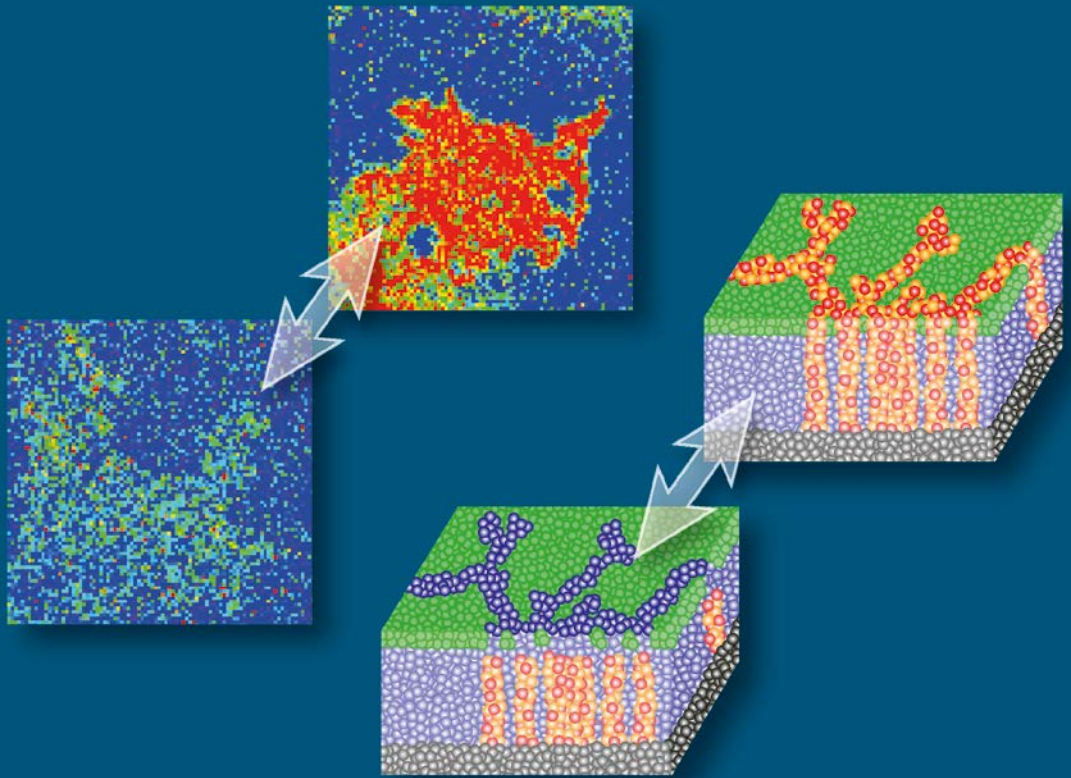


# Redox processes and ionic transport in resistive switching binary metal oxides

Katharina Skaja



Information  
Band/ Volume 49  
ISBN 978-3-95806-236-8

Forschungszentrum Jülich GmbH  
Peter Grünberg Institute (PGI)  
Electronic Materials (PGI-7)

# **Redox processes and ionic transport in resistive switching binary metal oxides**

Katharina Skaja

Schriften des Forschungszentrums Jülich  
Reihe Information / Information

Band / Volume 49

---

ISSN 1866-1777

ISBN 978-3-95806-236-8

# Contents

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Fundamentals</b>	<b>5</b>
2.1	Resistive switching . . . . .	5
2.2	Structure of $Ta_2O_{5-x}$ and $TiO_{2-x}$ . . . . .	7
2.2.1	$TiO_{2-x}$ . . . . .	7
2.2.2	$Ta_2O_{5-x}$ . . . . .	8
2.3	Defect Chemistry . . . . .	9
2.3.1	$TiO_{2-x}$ . . . . .	10
2.3.2	$Ta_2O_{5-x}$ . . . . .	16
2.4	Diffusion in solids . . . . .	20
2.4.1	Ideal step response . . . . .	20
2.4.2	Non ideal step response . . . . .	24
2.4.3	Chemical diffusion in $TiO_{2-x}$ . . . . .	26
<b>3</b>	<b>Experimental methods</b>	<b>31</b>
3.1	DC magnetron sputter deposition . . . . .	31
3.2	Atomic force microscopy (AFM) . . . . .	32
3.3	X-ray photoelectron spectroscopy (XPS) . . . . .	33
3.4	Photoemission electron microscopy (PEEM) . . . . .	35
3.5	High temperature equilibrium conductance (HTEC) measurements .	37
3.6	Electronic conductivity relaxation (ECR) measurements . . . . .	39
<b>4</b>	<b>Growth and characterization of thin oxide films</b>	<b>45</b>
4.1	Surface morphology and structure of sputtered thin films . . . . .	45
4.2	Spectroscopic characterization of thin films . . . . .	48
4.2.1	Engineering the oxygen content in $Ta_2O_{5-x}$ . . . . .	48
4.2.2	Engineering the oxygen content in $TiO_{2-x}$ . . . . .	54
4.2.3	Spectroscopic characterization of $Nb_2O_{5-x}/Ta_2O_{5-x}$ heterosys- tems . . . . .	57
4.3	Resistive switching in tantalum oxide based MIM structures . . . . .	59
4.3.1	Sample preparation . . . . .	59
4.3.2	Sample preparation for spectromicroscopy . . . . .	59

4.3.3	Stoichiometry dependent switching characteristic in Pt/Ta <sub>2</sub> O <sub>5-x</sub> /Ta layer structures . . . . .	60
4.3.4	Influence of different top electrodes on the resistive switching properties . . . . .	63
4.3.5	Electrical characterization of Nb <sub>2</sub> O <sub>5-x</sub> /Ta <sub>2</sub> O <sub>5-x</sub> heterosystems	66
4.3.6	Comparison of resistive switching behavior . . . . .	68
4.4	Summary . . . . .	69
<b>5</b>	<b>Surface sensitive investigation of the active interface in MIM structures</b>	<b>73</b>
5.1	Morphological changes of the bottom electrode . . . . .	74
5.1.1	Ta <sub>2</sub> O <sub>5-x</sub> MIM structures . . . . .	74
5.1.2	Nb <sub>2</sub> O <sub>5-x</sub> /Ta <sub>2</sub> O <sub>5-x</sub> heterosystem . . . . .	81
5.2	Studying the active MIM interface of Ta <sub>2</sub> O <sub>5-x</sub> based devices by spectromicroscopy . . . . .	83
5.2.1	Dendrite-like structures investigated with a laboratory source	83
5.2.2	Electroforming process in Ta <sub>2</sub> O <sub>5-x</sub> . . . . .	88
5.2.3	Dendrite-like structures investigated by synchrotron radiation	95
5.3	Investigation of the active interface of Nb <sub>2</sub> O <sub>5-x</sub> /Ta <sub>2</sub> O <sub>5-x</sub> heterosystems	98
5.3.1	Pt/5 nm Nb <sub>2</sub> O <sub>5-x</sub> /10 nm Ta <sub>2</sub> O <sub>5-x</sub> /Ta . . . . .	99
5.3.2	Pt/10 nm Nb <sub>2</sub> O <sub>5-x</sub> /5 nm Ta <sub>2</sub> O <sub>5-x</sub> /Ta . . . . .	108
5.3.3	Discussion . . . . .	111
5.4	Summary . . . . .	112
<b>6</b>	<b>Point defects and ionic transport in TiO<sub>2-x</sub></b>	<b>115</b>
6.1	High temperature conductivity in TiO <sub>2-x</sub> . . . . .	116
6.1.1	TiO <sub>2-x</sub> single crystals . . . . .	116
6.1.2	High temperature conductivity in TiO <sub>2-x</sub> thin films . . . . .	120
6.2	Chemical diffusion in TiO <sub>2-x</sub> . . . . .	128
6.2.1	TiO <sub>2-x</sub> single crystals . . . . .	128
6.2.2	Orientation dependent relaxation in TiO <sub>2-x</sub> single crystals . .	136
6.2.3	TiO <sub>2-x</sub> thin films . . . . .	138
6.3	Summary . . . . .	151
<b>7</b>	<b>High temperature conductivity of Ta<sub>2</sub>O<sub>5-x</sub></b>	<b>153</b>
7.1	Sample preparation of polycrystalline Ta <sub>2</sub> O <sub>5-x</sub> . . . . .	153
7.2	High temperature conductivity measurements of polycrystalline Ta <sub>2</sub> O <sub>5-x</sub> . . . . .	155
7.3	High temperature conductivity of polycrystalline Ta <sub>2</sub> O <sub>5-x</sub> thin films	158
7.3.1	Sample preparation of Ta <sub>2</sub> O <sub>5-x</sub> thin films . . . . .	159
7.3.2	High temperature conductivity measurements of Ta <sub>2</sub> O <sub>5-x</sub> thin films . . . . .	161
7.4	Summary . . . . .	164

<b>8 Summary and Conclusion</b>	<b>167</b>
<b>A Appendix</b>	<b>171</b>
A.1 Sputterdeposition parameters . . . . .	171
<b>List of abbreviations</b>	<b>173</b>
<b>Bibliography</b>	<b>175</b>
<b>Acknowledgement</b>	<b>201</b>

**Information**  
**Band / Volume 49**  
**ISBN 978-3-95806-236-8**

