



## Defect Engineering of SrTiO<sub>3</sub> thin films for resistive switching applications

Sebastian Wicklein

Forschungszentrum Jülich GmbH  
Peter Grünberg Institute (PGI)  
Elektronische Materialien (PGI-7)

# Defect Engineering of SrTiO<sub>3</sub> thin films for resistive switching applications

Sebastian Wicklein

Schriften des Forschungszentrums Jülich  
Reihe Information

Band / Volume 35

---

ISSN 1866-1777

ISBN 978-3-89336-963-8

# Contents

1	Introduction.....	1
2	Background.....	5
2.1	SrTiO <sub>3</sub> .....	5
2.2	Defect chemistry of SrTiO <sub>3</sub> .....	5
2.2.1	Defect chemical equilibrium & reactions for SrTiO <sub>3</sub> .....	6
2.2.2	Conductivity of SrTiO <sub>3</sub> .....	8
2.2.3	Electronic structure of SrTiO <sub>3</sub> .....	10
2.2.4	Electrical doping of SrTiO <sub>3</sub> by B-site cations.....	11
2.3	Space charge considerations.....	11
2.4	Non-stoichiometry, Lattice distortions and 2 <sup>nd</sup> phase formation in SrTiO <sub>3</sub> .....	12
2.5	Resistive switching oxides for future memory devices.....	14
3	Setup of a UHV-oxide Cluster-Tool.....	17
3.1	Deposition-Tools.....	19
3.1.1	PLD (Laser-MBE) with RHEED and OIRD.....	19
3.1.2	Sputtering tool.....	21
3.1.3	E-beam PVD.....	21
3.2	Characterization-Tools.....	22
3.2.1	SPM-Tool with LC-AFM, NC-AFM, STM & Q-plus.....	22
3.2.2	X-ray photoemission spectroscopy (XPS).....	22
3.2.3	Nano-ESCA / PEEM.....	23
3.2.4	LEED.....	23
3.3	Engineering of a high-temperature (HT) holder.....	24
3.3.1	Engineering.....	24
3.3.2	Performance.....	25
4	Experimental.....	27
4.1	PLD process and in-situ analysis methods for thin film defect engineering.....	27
4.1.1	Ablation characteristics.....	27
4.1.2	In-situ film growth analysis by RHEED.....	28

4.1.3	Plume analysis .....	30
4.2	X-ray diffraction analysis.....	33
4.3	Positron annihilation analysis.....	35
4.4	Photo (electron) Emission Spectroscopy.....	37
4.5	SPM Analysis .....	38
5	Defect formation & accommodation in homoepitaxial SrTiO <sub>3</sub> thin films .....	41
5.1	Influence of PLD growth parameters on the defect formation.....	41
5.1.1	Laser fluence variations .....	41
5.1.2	Variation of the Target – Substrate distance.....	49
5.1.3	O <sub>2</sub> background pressure variations.....	50
5.1.4	Influence of substrate temperature on the defect accommodation in STO .....	54
5.2	Origin of non-stoichiometry in homoepitaxial SrTiO <sub>3</sub> thin films.....	56
5.2.1	Non-stoichiometry induced by laser fluence variations.....	56
5.2.2	O <sub>2</sub> background pressure variations.....	64
5.2.3	Effect of substrate temperature on the stoichiometry of STO thin films .....	69
5.3	Discussion and Conclusions .....	72
6	Defect formation & accommodation in Fe doped SrTiO <sub>3</sub> thin films.....	75
6.1	XRD and PLD process analysis .....	75
6.1.1	XPS analysis of the films and the ablation spots on the target.....	77
6.1.2	Positron Analysis .....	78
6.2	PLD Plume Analysis for Fe doped STO.....	83
6.2.1	Plume kinetics.....	83
6.2.2	Plume spectroscopy.....	84
6.2.3	TEM investigations of Fe:STO films .....	84
6.3	Discussion and Conclusions .....	85
7	Influence of defects on the growth mode of SrTiO <sub>3</sub> thin films.....	87
7.1	Laser fluence variations .....	87
7.2	Background pressure variations .....	93
7.3	Effect of substrate temperature.....	95
7.4	Influence of Fe doping on the STO film growth .....	96
7.5	Discussion and Conclusions .....	97

8	Investigations of the resistive switching properties of STO thin films.....	99
8.1	LC-AFM investigations of the RS properties of STO thin films .....	99
8.1.1	Pristine I(V) characteristics of STO thin films .....	101
8.1.2	1D resistive switching characteristics of STO films .....	102
8.1.3	LC-AFM characteristics of SrTiO <sub>3-x</sub> .....	105
8.1.4	Resistive switching mapping (2D) of STO thin films .....	107
8.1.5	I(V) characteristics of the pristine, LRS and HRS area .....	110
8.1.6	Thickness dependence on the RS effect for STO films on Nb:STO .....	114
8.1.7	Discussion .....	117
8.2	STS analysis of resistive states in STO films and Nb:STO .....	120
8.2.1	STS on STO thin films .....	121
8.2.2	STS on Nb:STO single crystal (0.5wt%) .....	122
8.2.3	Discussion .....	123
8.3	In-situ chemical analysis of inscribed areas by PEEM (proof of concept) .....	124
8.3.1	PEEM of inscribed areas.....	124
8.3.2	Discussion.....	124
8.4	Resistive switching dynamics.....	125
8.5	Resistive Switching of MIM structures.....	126
8.5.1	I(V) characteristics of SrTiO <sub>3</sub> thin films .....	126
8.5.2	I(V) characteristics of Fe:STO thin films.....	128
8.5.3	Discussion.....	130
8.6	Discussion.....	131
9	Conclusions.....	133
9.1	Defect engineering.....	133
9.2	Resistive switching properties.....	134



**Information / Information**  
**Band / Volume 35**  
**ISBN 978-3-89336-963-8**

