

# Contents

<b>List of Tables . . . . .</b>	<b>XI</b>
<b>List of Figures . . . . .</b>	<b>XIII</b>
<b>1 Introduction . . . . .</b>	<b>3</b>
<b>2 Experimental . . . . .</b>	<b>9</b>
2.1 Electrochemical Experiments (Sample Preparation) . . . . .	9
2.1.1 Theory . . . . .	9
2.1.1.1 The Nernst Equation . . . . .	9
2.1.1.2 Reference Electrodes . . . . .	10
2.1.1.3 Description of the Electric Double Layer .	11
2.1.1.4 Cyclic Voltammetry . . . . .	13
2.2 X-ray Absorption Spectroscopy (XAS) . . . . .	17
2.2.1 Detection Modes in XAS . . . . .	18
2.2.2 Theory of EXAFS Signal Formation . . . . .	21
2.2.2.1 Background Subtraction . . . . .	22
2.2.2.2 Data Analysis . . . . .	23
2.2.2.3 Statistical Considerations . . . . .	26
2.2.3 Setup . . . . .	27
2.2.3.1 Experiments in Total Electron Yield (TEY) Mode . . . . .	27
2.2.3.2 Experiments in Transmission Mode . . . . .	29
2.3 UHV Setup . . . . .	29
2.3.1 Transfer Rod and Sample Mounting . . . . .	29
2.3.2 The UHV Recipient . . . . .	30
2.3.3 The Electrochemical Cell . . . . .	32
2.3.4 The Transfer Process . . . . .	33
2.4 Thermal Desorption Spectroscopy (TDS) . . . . .	34
2.4.1 Theory . . . . .	34

2.4.2	Heating Rate Variation . . . . .	36
2.4.3	<i>Redhead</i> Analysis . . . . .	37
2.4.4	Leading Edge Analysis . . . . .	37
2.5	Photoelectron Spectroscopy (PES) . . . . .	37
2.5.1	The Photoelectric Effect . . . . .	37
2.5.2	X-ray Photoelectron Spectroscopy (XPS) . . . . .	39
<b>3</b>	<b>Results . . . . .</b>	<b>45</b>
3.1	Sample Preparation . . . . .	45
3.1.1	Cleaning . . . . .	45
3.1.2	Preparation of the Au/O Phases . . . . .	46
3.2	XAS Experiments . . . . .	51
3.2.1	$S_0^2$ Determination for Different Gold Oxides . . . . .	51
3.2.2	Experiments with Crystalline $Au_2O_3$ - a Reference Compound . . . . .	53
3.2.3	EXAFS Analysis of Crystalline $Au_2O_3$ . . . . .	55
3.2.4	EXAFS Analysis of Electrochemically Grown $Au_2O_3$ . . . . .	60
3.2.5	XAS Analysis of the Growth Process . . . . .	64
3.2.6	Experiments with an <i>in situ</i> Fluorescence Cell . . . . .	68
3.2.7	Analysis of the Decomposition Process . . . . .	70
3.2.7.1	Crystalline $Au_2O_3$ . . . . .	70
3.2.7.2	Commercial $Au_2O_3$ . . . . .	70
3.2.7.3	Electrochemically Prepared $Au_2O_3$ . . . . .	71
3.3	TPD Experiments . . . . .	74
3.3.1	TPD Experiments with O/Au Phases obtained by Exposure of Au to Oxygen Plasma Discharges . . . . .	74
3.3.2	Experiments with Electrochemically Prepared O/Au Phases . . . . .	78
3.4	XPS Experiments . . . . .	79
3.4.1	Experimental . . . . .	79
3.4.2	XPS Studies of Au/O-Phases Obtained with a Plasma Discharge . . . . .	82
3.4.3	XPS Studies of Au/O-Phases Obtained by electrochemical Oxidation . . . . .	84
3.4.4	Evaluation of the Film Thickness <i>via</i> ARXPS . . . . .	89

<b>4 Discussion</b> . . . . .	<b>93</b>
4.1 EXAFS Results . . . . .	93
4.2 Comparison between EXAFS and XPS Experiments . . . . .	95
4.3 Growth and Decomposition Process . . . . .	95
4.4 TPD Results . . . . .	97
4.5 XPS Results . . . . .	100
<b>5 Summary</b> . . . . .	<b>105</b>
<b>Bibliography</b> . . . . .	<b>109</b>
<b>A Publications and Presentations</b> . . . . .	<b>115</b>
<b>B Curriculum Vitae</b> . . . . .	<b>117</b>