





# **Influence of Conduction Mechanism Changes and Related Effects on the Sensing Performance of Metal Oxide Based Gas Sensors**

## **Dissertation**

der Mathematisch-Naturwissenschaftlichen Fakultät

der Eberhard Karls Universität Tübingen

zur Erlangung des Grades eines

Doktors der Naturwissenschaften

(Dr. rer. nat.)

vorgelegt von

Diplom Chemikerin Julia Margarete Rebholz

aus Horb am Neckar

Tübingen

2016

Gedruckt mit Genehmigung der Mathematisch-Naturwissenschaftlichen Fakultät der  
Eberhard Karls Universität Tübingen.

Tag der mündlichen Qualifikation:

01.08.2016

Dekan:

Prof. Dr. Wolfgang Rosenstiel

1. Berichterstatter:

Prof. Dr. Udo Weimar

2. Berichterstatter:

Prof. Dr. Günter Gauglitz

Berichte aus der Chemie

**Julia Margarete Rebholz**

**Influence of Conduction Mechanism Changes and  
Related Effects on the Sensing Performance of  
Metal Oxide Based Gas Sensors**

D 21 (Diss. Universität Tübingen)

Shaker Verlag  
Aachen 2016

**Bibliographic information published by the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Zugl.: Tübingen, Univ., Diss., 2016

Copyright Shaker Verlag 2016

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

ISBN 978-3-8440-4832-2

ISSN 0945-070X

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen

Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9

Internet: [www.shaker.de](http://www.shaker.de) • e-mail: [info@shaker.de](mailto:info@shaker.de)

## Table of Content

<b>1</b>	<b>Introduction</b>	1
1.1	Development of SMOX gas sensors	3
1.2	Motivation and preliminary work	5
<b>2</b>	<b>Theoretical background</b>	11
2.1	Important definitions	11
2.2	SnO <sub>2</sub> – a wide band gap n-type semiconductor	12
2.3	Reception	13
2.3.1	General aspects	13
2.3.2	Adsorption of oxygen	14
2.3.3	Carbon monoxide reactions	15
2.3.4	Humidity	16
2.4	Transduction in n-type semiconductors	19
2.4.1	Space charge effects	19
2.4.2	Layer morphologies	23
2.4.3	Conduction mechanism	24
<b>3</b>	<b>Experimental</b>	30
3.1	Sensor fabrication and material characterization	30
3.1.1	Material synthesis and sensor fabrication	30
3.1.2	Doping	31
3.1.3	Sol gel produced sensing materials (IPC1000 and IPC450)	32
3.1.4	Sensors produced from commercial nanopowders (SA)	33
3.2	Operando investigation techniques	34
3.2.1	DC electrical resistance measurements	34
3.2.2	Simultaneous DCR/WF measurements	36
<b>4</b>	<b>Conduction mechanism switch in application relevant conditions – implications for modeling and sensing</b>	45
4.1	Motivation	45
4.2	Operando investigations using DCR and DCR/WF measurements	47
4.3	Implications for modeling of sensing	49
<b>5</b>	<b>Modeling of sensing</b>	52
5.1	Motivation	52
5.2	Influence of the electrical semiconducting properties	54
5.3	Reaction of CO with pre-adsorbed oxygen ions	58
5.3.1	Modeling the calibration curve of IPC1000	58
5.3.2	Experimental validation	64
5.4	The influence of humidity	66
5.4.1	Modeling the calibration curve in the presence of humidity	66
5.4.2	Experimental validation	68

5.5	Impact of changing the conduction mechanism for the reaction of CO with lattice oxygen .....	70
<b>6</b>	<b>Impact assessment of reception and transduction in the sensing performance of SMOX based gas sensors .....</b>	<b>74</b>
6.1	Influence of an intrinsic surface band bending .....	75
6.1.1	The effect of an intrinsic surface band bending on the transduction function ...	76
6.1.2	The effect of Ni loading.....	77
6.1.3	A self-doping surface effect and its influence on the sensor performance of undoped SnO <sub>2</sub> based gas sensors .....	83
6.2	Impact of conduction mechanism changes on the sensing performance .....	89
6.3	Influence of gold doping .....	91
6.3.1	General knowledge about noble metal doping .....	91
6.3.2	Results and discussion.....	92
<b>7</b>	<b>Summary .....</b>	<b>97</b>
7.1	Understanding the relationship between conduction mechanism and sensor signal ...	99
7.2	Understanding the relationship between surface chemistry and sensor signal .....	103
7.3	Comparison of the investigated materials in normal application conditions .....	105
<b>8</b>	<b>Outlook .....</b>	<b>107</b>
<b>9</b>	<b>References .....</b>	<b>108</b>
<b>10</b>	<b>Annex.....</b>	<b>112</b>
10.1	Fitting curves DCR/WF measurements.....	112
10.1.1	IPC1000 .....	112
10.1.2	SA dry .....	114
10.1.3	Ni SA dry .....	116
10.1.4	IPC450 .....	117
10.1.5	0.2wt.% Au doped IPC1000.....	118
10.2	List of Abbreviations .....	119
10.3	List of Variables .....	120
10.4	List of Constants .....	122