

First-principles Statistical Mechanics Approach to Step Decoration at Solid Surfaces

von
M. Sc.
Yongsheng Zhang

im Fachbereich Physik der Freien Universität Berlin eingereichte
Dissertation zur Erlangung des akademischen Grades

DOCTOR RERUM NATURALIUM

Berlin 2008

Erstgutachter: PD Dr. Karsten Reuter

Zweitgutachter: Prof. Eberhard K. U. Gross

Disputationstermin: 14. May 2008

Abstract

As prominent defects at solid surfaces atomic steps are commonly perceived as playing some kind of special, if not decisive role for the surface properties or functions in materials science applications. When aiming to qualify this role at the atomic scale an important first task is to identify the structure and composition at the step edge under realistic gas-phase conditions that are representative for the targeted application. From the modeling side, this requires two ingredients: A reliable description of the energetics at the surface, in other words of the chemical bonds that are formed there. And on the other side a proper treatment of the manifold of processes that can occur, in particular also due to the contact with the gaseous environment at finite temperatures.

In this thesis this problem is addressed with a first-principles statistical mechanics approach, *i.e.* with an approach that is based entirely on a reliable first-principles energetics. Since the evaluations of the partition functions required to at least thermodynamically account for the statistical interplay at finite temperatures would necessitate on unfeasible amount of first-principles total energy calculations, the approach relies on parameterizing as intermediate between the electronic and mesoscopic regime a coarse-grained lattice model, which is then employed in the statistical simulations. The approach is illustrated using the interaction of an oxygen atmosphere with a close-packed (111) step at Pd(100) as example. Apart from the methodological advances that are achieved the major result for this application is then that the specific way how oxygen atoms decorate the step even in environments with pressures of the order atmospheres and elevated temperatures around 1000 K is obtained. Since such gas phase conditions are representative for an important catalytic application like the high-temperatures combustion of methane, this work thus provides first first-principles insight into the structure and composition at a prominent defect at the surface of a working model catalyst.

*For Yuanyuan
and my parents*



Contents

1	Introduction	1
I	Theoretical Background	5
2	Density-functional Theory	7
2.1	The Many-electron Problem	7
2.2	Density-functional Theory	9
2.2.1	Original Idea: Thomas-Fermi Model	9
2.2.2	Hohenberg-Kohn Theorems	10
2.2.3	Kohn-Sham Equation	12
2.2.4	Present-day Exchange-correlation Functionals	13
3	(L)APW+lo	15
3.1	Bloch's Theorem	15
3.2	Augmented Plane Wave (APW)	16
3.3	LAPW	17
3.4	LAPW with Local Orbital (LAPW+LO)	18
3.5	APW+lo	18
3.6	Full Potential (L)APW+lo Method	19
3.7	Two Important Basis Set Parameters: Energy Cutoff and K-mesh	19
3.8	WIEN2k Code	20
4	DFT Calculations for Solid Surfaces	23
4.1	Vicinal Surfaces	23
4.2	Surface Models	25
4.3	Surface Minimization	27
4.4	Two Key Surface Energetic Properties: γ and E_b	29
4.5	Step Formation Energy	30
4.6	Local Density of States (LDOS)	31
4.7	Surface Core-level Shifts	31

5	First-principles Statistical Mechanics	37
5.1	Ab-initio Atomistic Thermodynamics	38
5.2	Ab-initio Statistical Mechanics	39
5.2.1	Canonical Monte Carlo (CMC) [61, 62]	39
5.2.2	Grand-Canonical Monte Carlo (GCMC)	41
5.2.3	First-principles Lattice-gas Hamiltonian (FP-LGH)	43
5.2.4	Leave-one-out Cross-validation: Identify Optimum Lateral Fig- ures	44
5.2.5	Direct Enumeration: Validate the Set of DFT Input Structures .	45
5.2.6	Two Properties to Monitor Phase Transitions: Ψ and C_V	47
 II Ordering Behavior of Oxygen Atoms at the Pd(100) Surface		53
6	On the Accuracy of First-Principles Lateral Interactions: Oxygen at Pd(100)	55
6.1	Computational Details	56
6.1.1	Lattice-Gas Hamiltonian for O-Pd(100)	56
6.1.2	Static and Vibrational Average Binding Energy	57
6.1.3	Total Energy Calculations	58
6.1.4	Monte Carlo Simulations	59
6.2	First-Principles Lattice-gas Hamiltonian for O at Pd(100)	60
6.2.1	Energetics of On-Surface Adsorption	60
6.2.2	Lateral Interactions	62
6.2.3	Order-disorder Transition	67
6.2.4	Population of Bridge Sites	68
6.3	Accuracy of First-principles Lateral Interactions	70
6.3.1	Uncertainties in the LGH Expansion Procedure	71
6.3.2	Uncertainties in the First-principles Energetics	72
6.4	Comparison to Empirical Parameters	76
6.5	Conclusions	79
 III Ordering Behavior of Oxygen Atoms under the Influ- ence of a Step		81
7	Oxygen Adsorption at Pd(11<i>N</i>)(<i>N</i>=3,5,7) Vicinal Surfaces	83
7.1	Computational Details	85
7.2	Clean Vicinal Surfaces	86
7.2.1	Geometric Structure	86
7.2.2	Energetics and Electronic Structure	87

7.3	Oxygen Adsorption at Vicinal Surfaces	92
7.3.1	Binding Energy	92
7.3.2	Geometric and Electronic Structure	94
7.4	Conclusions	99
8	Decoration of a (111) Step at Pd(100) by Oxygen Atoms	101
8.1	Computational Details	102
8.1.1	Total Energy Calculations	102
8.1.2	Lattice-gas Hamiltonian for O-Pd(117)	103
8.2	First-principles Lattice-gas Hamiltonian for O at Pd(117)	105
8.2.1	Energetics for O–Pd(117)	105
8.2.2	Lateral Interactions for O–Pd(117)	106
8.2.3	Vibrational Contribution to the Lateral Interactions	108
8.2.4	Validation by Direct Enumeration	108
8.2.5	Treating the Boundary for Surfaces with Wider Terrace Width	109
8.3	Ordering Behavior of Oxygen Near a (111) Step at Pd(100)	111
8.3.1	Simulated Annealing Simulation: Identify Low-energy Step structures	111
8.3.2	Stability of Zigzag Decorated Step	112
8.4	Conclusion	115
9	Summary and Outlook	119
IV	Appendix	121
A	Bulk Pd	123
B	Low-index Pd Surfaces	127
B.1	Clean Surfaces	127
B.2	Oxygen at Pd(100)	131
C	Pd(11<i>N</i>) Vicinal Surfaces	135
C.1	Clean Pd(11 <i>N</i>) Vicinal Surfaces	135
C.2	Oxygen at Pd(11 <i>N</i>) Vicinal Surfaces	139
D	Monte Carlo Simulations	145
D.1	Equilibration	145
D.2	Simulation Cell for O-Pd(100)	145
D.3	Identical T_c from Ψ and C_V	146
D.4	Simulation Cell for Stepped Pd(100)	149
E	Computed Ordered Configurations for O-Pd(100)	151

CONTENTS

F Computed Ordered Configurations for O-Pd(117)	167
Bibliography	195
Acknowledgments	203
Curriculum Vitae	205
Publications	207

List of Figures

3.1	Schematic division of space into atomic sphere and interstitial	16
3.2	Flow chart of the WIEN2k code.	21
4.1	Top view of a fcc (100) surface, and a real surface	24
4.2	Cartoon scheme to create a (113) vicinal surface in a fcc bulk.	24
4.3	Top view of the family of Pd(11 <i>N</i>) vicinal surfaces,	25
4.5	Striped and two types of triangular islands on a fcc(111) surface.	26
4.4	Supercell model, including slabs and vacuum.	26
4.6	Model explaining the geometrical view behind Eq. 4.13.	31
4.7	Local density of states of bulk fcc Pd	32
4.8	Cartoon to illustrate the <i>d</i> -band surface shift in late TM	34
4.9	Local density of states of different layers for Pd(111) and Pd(100)	35
5.1	Schematic view of three regimes in the (length,time) space	37
5.2	Phase diagram of on-surface oxygen atom adsorption at the Pd(100)	40
5.3	θ vs. $\Delta\mu$ from the Langmuir adsorption isotherm	42
5.4	Schematic view of lateral interaction figures for adatoms at a fcc (100)	43
5.5	Schematic illustration of periodic image lateral interactions	44
5.6	Schematic illustration of the idea behind a of convex hull	46
5.7	Schematic top view illustrating the division into sub-lattices	50
5.8	Illustration of how Ψ and C_V identify the order-disorder transition	50
6.1	Illustrating the considered pool of 17 lateral interactions between O	57
6.2	Top view of 5 ordered adlayers with O in on-surface hollow sites.	60
6.3	Coverage (θ) dependence of the calculated DFT binding energies	62
6.4	Formation energies ΔE_f as computed with DFT	66
6.5	$\theta - T$ diagram using different functionals	68
6.6	Considered lateral interaction figures for bridge-bridge sites	69
6.7	Critical temperatures for 0.25, 0.35 and 0.45 ML coverages	70
6.8	$\theta - T$ diagram using different lateral interaction groups	72
6.9	$\theta - T$ diagram comparing to the empirical approach	78
7.1	Top and side views of the atomic geometry of the family of Pd(11 <i>N</i>)	84
7.2	Smoluchowski smoothing picture	88

LIST OF FIGURES

7.3	Local density of states in the different layers in Pd(11N)	89
7.4	Geometry side views for adsorption in the Sh2 and Thu	96
7.5	Oxygen-induced changes in the LDOS and initial-state SCLSs	97
8.1	70 step-influenced lateral interaction figures	104
8.2	Phase diagrams of DFT calculations and of corresponding DE data . . .	109
8.3	Schematic top view of the site types at wider terrace width	110
8.4	Schematic top views showing the results of simulated annealing	111
8.5	Computed Gibbs free energy ΔG^{ad} for O at a (111) step at Pd(100) . .	112
8.6	Schematic view of a Pd(100) surface with (111) steps.	113
8.7	Average coverage and order parameter for the terrace and step	114
8.8	Two Pd vicinal structures used to calculate the O 1s SCLS	116
8.9	Schematic perspective view of the surface under gas-phase conditions . .	116
A.1	Determination of the equilibrium lattice constant for the fcc Pd	124
A.2	Determination of the equilibrium lattice constant for the fcc Pd	124
B.1	Schematic figures of the Pd(111) and Pd(100)	127
B.2	Convergence test for the optimal energy cutoff and \mathbf{k} -points	128
B.3	Convergence test for the optimal energy cutoff and \mathbf{k} -points	128
B.4	Convergence test for the optimal energy cutoff and \mathbf{k} -points	129
B.5	Convergence test for the optimal layer number for Pd(111) and Pd(100)	130
B.6	Cutoff convergence test and k-mesh test for the O at Pd(100)	133
C.1	$E_{\text{max}}^{\text{wf}}$ and irreducible k-point convergence tests for Pd(113)	136
C.2	$E_{\text{max}}^{\text{wf}}$ and irreducible k-point convergence tests for Pd(115).	136
C.3	$E_{\text{max}}^{\text{wf}}$ and irreducible k-point tests for Pd(117)	136
C.4	Surface energy convergence with number of slab layers for the Pd(113)	138
C.6	Absolute binding energies of oxygen adsorbed at the Sh2 and Thu . . .	141
C.7	Binding energy vs. energy cutoff for oxygen adsorbed at Pd(11N) . . .	141
C.8	E_{b} vs. number of slab layers for O-Pd(113)	143
C.9	E_{b} vs. number of slab layers for O-Pd(115) and O-Pd(117)	143
D.1	Illustration of the evaluation of the total energy with MC steps	146
D.2	E vs. MC step and $\langle E \rangle$ vs. MC step	147
D.4	Critical temperatures determined by Ψ and C_V	148
D.5	Cell size tests for two coverages, $\theta=0.1$ ML and $\theta=0.15$ ML	150

List of Tables

5.1	$\Delta\mu_{\text{O}}(T, p^0)$ in the temperature range of interest to our study.	39
6.1	Calculated E_{b} for O adsorption in on-surface hollow or bridge sites . . .	59
6.2	$E_{\text{b}}^{\text{DFT}}$ for ordered O-Pd(100) with O in the hollow sites	61
6.3	List of the sets containing m lateral interactions	64
6.4	Lateral interactions obtained using the LDA and the GGA-PBE	75
7.1	Comparison of the multilayer relaxation sequence of the Pd(11 N)	87
7.2	Computed surface energies of the low-index surfaces and Pd(11 N)	87
7.3	Step formation energies at the different vicinal surfaces	91
7.4	Initial-state $\Delta_{\text{initial}}^{\text{SCLS}}$ for the topmost layers	92
7.5	E_{b} of O at the different highly-coordinated terrace and step	92
7.6	E_{b} of oxygen adsorption at different sites on Pd(113)(1 \times 1)	93
7.7	O-Pd bond lengths at the different sites in (1 \times 1) overlayers	95
7.8	Surface relaxation pattern of the Pd(11 N) ($N = 3, 5, 7$)	97
8.1	Total binding energies of one O at different sites in Pd(117)	105
8.2	Extracted on-site energies and lateral interactions of O-Pd(117)	107
8.3	Comparison of equivalent lateral interaction figures of O-Pd(117)	107
A.1	Comparison of calculated lattice constant and bulk modulus	125
B.1	Optimized basis set parameters for the clean Pd(111) and Pd(100)	130
B.2	Surface energies for various vacuum thicknesses	131
C.1	Surface energies of the Pd(11 N) ($N=3, 5, 7$) vicinal surfaces	139
C.2	Computed surface energies of different low-index and vicinal surfaces	139
C.3	E_{b} for various vacuum thicknesses in supercells for O at the Sh2 site.	142
C.4	Optimal basis set parameters of oxygen adsorption on Pd(11 N)	142

