

Contents

III/42 Physics of Covered Solid Surfaces

A: Adsorbed Layers on Surfaces

Part 1: Adsorption on Surfaces and Surface Diffusion of Adsorbates

1	Introduction to physical and chemical properties of adlayer/substrate systems (H.P. BONZEL)	1
1.1	General background	1
1.2	Surface thermodynamics	3
1.3	Kinetics of adsorption/desorption and adsorption isotherms	9
1.3.1	Thermal rates of adsorption/desorption	9
1.3.2	Isotherms	15
1.3.3	Non-thermal desorption	16
1.4	Physical and chemical properties of adsorbed species	17
1.4.1	Sticking coefficient	17
1.4.2	Heat of adsorption	18
1.4.3	Orientation of adsorbed molecules	19
1.4.4	Surface diffusion coefficients	22
1.4.5	Long-range order	25
1.4.6	Vibrational frequencies	27
1.4.7	Structure and adsorption site	30
1.4.8	Molecular orbital energies, dispersion and 2d band structure	32
1.4.9	Core level binding energies	34
1.4.10	Two-dimensional phase diagrams and order-disorder transitions	38
1.4.11	Chemical state	39
1.4.12	Influence of surface structural defects	40
1.4.13	Influence of chemical surface additives ("promoters")	42
1.5	Adsorbate-induced changes of substrate properties	44
1.5.1	Changes of structure: surface relaxation and surface reconstruction	44
1.5.2	Changes of electron work function	46
1.5.3	Electron binding energy changes, core and valence levels	48
1.5.4	Changes of surface free energy and surface stress	50
1.5.5	Changes of surface phonon dispersion	53
1.5.6	Changes of surface optical properties	54
	References for 1	59
2	Characterization of adsorbate overlayers: measuring techniques (CH. WÖLL)	see subvolume III/42A2
3	Data: Adsorbate properties	67
3.1	Adsorption of noble gases	67
3.1.1	Noble gases on metals and semiconductors (P. ZEPPENFELD)	67
3.1.1.1	Introduction	67
3.1.1.1.1	General remarks	67
3.1.1.1.2	The interaction of noble gases at surfaces	67
3.1.1.1.3	Sticking and accommodation	68
3.1.1.1.4	Adsorption energies	69
3.1.1.1.5	Desorption energies and desorption kinetics	70
3.1.1.1.6	Structure and phase diagram	70

3.1.1.1.7	Adsorption site	71
3.1.1.1.8	Electronic structure	72
3.1.1.1.9	Diffusion kinetics	73
3.1.1.1.10	Lattice dynamics	73
3.1.1.2	Data	75
3.1.1.2.1	Sticking coefficients of the noble gases	76
3.1.1.2.2	Binding energies, thermodynamic quantities and phase diagrams	77
3.1.1.2.3	Monolayer structures and phase diagrams	82
3.1.1.2.4	Electronic structure	87
3.1.1.2.5	Surface diffusion coefficients	94
3.1.1.2.6	Vibration frequencies and phonon dispersion	95
	Figures for 3.1.1	96
	References for 3.1.1	111
3.1.2	Noble gases on graphite, lamellar halides, MgO and NaCl (M. BIENFAIT)	117
3.1.2.1	Thermodynamics	117
3.1.2.1.1	Rare gases adsorbed on graphite (0001)	117
3.1.2.1.1.1	Xenon on graphite	117
3.1.2.1.1.2	Krypton on graphite	117
3.1.2.1.1.3	Argon on graphite	118
3.1.2.1.1.4	Neon on graphite	118
3.1.2.1.1.5	Rare gas mixtures on graphite	118
3.1.2.1.1.6	Helium on graphite	118
3.1.2.1.2	Rare gases on BN	118
3.1.2.1.3	Rare gases on lamellar halide surfaces	118
3.1.2.1.4	Rare gases on MgO(100) and NaCl(100)	119
3.1.2.2	Structure	119
3.1.2.2.1	Xenon on graphite	119
3.1.2.2.2	Krypton on graphite	119
3.1.2.2.3	Argon on graphite	119
3.1.2.2.4	Neon on graphite	120
3.1.2.2.5	Rare gas mixtures on graphite	120
3.1.2.2.6	Rare gas on lamellar halides	120
3.1.2.2.7	Rare gases on MgO(100) and NaCl(100)	120
3.1.2.3	Influence of structural defects	120
3.1.2.3.1	Thermodynamics and phase transitions	120
3.1.2.3.2	Structure	120
3.1.2.4	Vibrations	121
3.1.2.5	Kinetics of adsorption and desorption	121
	Figures for 3.1.2	122
	References for 3.1.2	128
3.2	Adsorption of alkali metals	131
3.2.1	Alkali metals on metals (R.D. DIEHL, R. McGRATH)	131
3.2.1.1	Introduction	131
3.2.1.2	Adsorbed alkali metals: Data	132
3.2.1.2.1	Adsorption bonds	132
3.2.1.2.2	Work function changes	133
3.2.1.2.3	Electronic structure of adatoms	138
3.2.1.2.4	Heats of adsorption/desorption	140
3.2.1.2.5	Adatom vibrational frequencies	141
3.2.1.2.6	Adsorption sites and bond lengths (commensurate structures)	143
3.2.1.2.7	Incommensurate overlayer rotations	147
3.2.1.2.8	Monolayer saturation lattice parameters	149
3.2.1.2.9	Condensation transition parameters	150

3.2.1.2.10	Two-dimensional phase diagrams	152
3.2.1.2.11	Adsorbate substrate intermixing	154
	Figures for 3.2.1	157
	References for 3.2.1	169
3.2.2	Alkali metals on semiconductors (E.G. MICHEL, R. MIRANDA)	179
3.2.2.1	Introduction	179
3.2.2.1.1	Historical layout and general background	179
3.2.2.1.2	Alkali metal/semiconductor interfaces	180
3.2.2.1.3	Experimental techniques	180
3.2.2.2	Adsorption on covalent semiconductors: physical and chemical properties	180
3.2.2.2.1	Adsorption site, structure and long range order	181
3.2.2.2.2	Adsorption energy and saturation coverage	185
3.2.2.2.3	Metallization and electronic structure	186
3.2.2.2.4	Overlayer plasmons and electron excitations	189
3.2.2.2.5	Core level binding energies and components	189
3.2.2.2.6	Chemical state and nature of the bond	191
3.2.2.3	Adsorption on III-V semiconductors: physical and chemical properties	193
3.2.2.3.1	Long range order, structure and adsorption site	193
3.2.2.3.2	Metallization and electronic structure	193
	Figures for 3.2.2	195
	References for 3.2.2	210
3.3	Adsorption of metals	217
3.3.1	Metals on metals (H. BRUNE)	217
3.3.1.1	Introduction	217
3.3.1.2	Adsorption energies	218
3.3.1.3	Atom condensation	225
3.3.1.3.1	Transient mobility	225
3.3.1.3.2	Neighbor-driven mobility	226
3.3.1.4	Adsorbate – adsorbate interactions	227
3.3.1.4.1	Dimer bond energies	228
3.3.1.4.2	Long range interactions	230
3.3.1.5	Overlayer structure	231
	Acknowledgements	243
	Figures for 3.3.1	244
	References for 3.3.1	251
3.3.2	Metals on semiconductors (V.G. LIFSHITS, K.OURA, A.A. SARANIN, A.V. ZOTOV)	259
	List of Abbreviations	259
3.3.2.1	Introduction	260
3.3.2.1.1	Outline	260
3.3.2.1.2	Metal adsorption and surface phase formation	261
3.3.2.1.3	Notations for surface structures and adsorption sites	263
3.3.2.1.4	Preparation	265
3.3.2.1.5	Techniques of surface characterization	267
3.3.2.2	List of structures	268
3.3.2.3	Metallic adsorbates on silicon	284
3.3.2.3.1	Ag (Silver) on Si	284
3.3.2.3.2	Al (Aluminum) on Si	292
3.3.2.3.3	As (Arsenic) on Si	299
3.3.2.3.4	Au (Gold) on Si	303
3.3.2.3.5	Ba (Barium) on Si	310
3.3.2.3.6	Bi (Bismuth) on Si	311
3.3.2.3.7	Ca (Calcium) on Si	316

3.3.2.3.8	Ce (Cerium) on Si	317
3.3.2.3.9	Co (Cobalt) on Si	317
3.3.2.3.10	Cu (Copper) on Si	320
3.3.2.3.11	Eu (Europium) on Si	324
3.3.2.3.12	Ga (Gallium) on Si	324
3.3.2.3.13	Gd (Gadolinium) on Si	331
3.3.2.3.14	Hg (Mercury) on Si	331
3.3.2.3.15	In (Indium) on Si	332
3.3.2.3.16	Mg (Magnesium) on Si	340
3.3.2.3.17	Ni (Nickel) on Si	342
3.3.2.3.18	Pb (Lead) on Si	347
3.3.2.3.19	Pd (Palladium) on Si	353
3.3.2.3.20	Pt (Platinum) on Si	354
3.3.2.3.21	Sb (Antimony) on Si	355
3.3.2.3.22	Sm (Samarium) on Si	362
3.3.2.3.23	Sn (Tin) on Si	362
3.3.2.3.24	Sr (Strontium) on Si	368
3.3.2.3.25	Te (Tellurium) on Si	369
3.3.2.3.26	Tl (Thallium) on Si	370
3.3.2.3.27	Yb (Ytterbium) on Si	372
3.3.2.4	Metallic adsorbates on germanium	372
3.3.2.4.1	Ag (Silver) on Ge	372
3.3.2.4.2	Al (Aluminum) on Ge	374
3.3.2.4.3	As (Arsenic) on Ge	374
3.3.2.4.4	Au (Gold) on Ge	375
3.3.2.4.5	Bi (Bismuth) on Ge	376
3.3.2.4.6	Cu (Copper) on Ge	377
3.3.2.4.7	Ga (Gallium) on Ge	378
3.3.2.4.8	In (Indium) on Ge	381
3.3.2.4.9	Pb (Lead) on Ge	384
3.3.2.4.10	Sb (Antimony) on Ge	389
3.3.2.4.11	Sn (Tin) on Ge	392
	References for 3.3.2	396
3.4	Non-metallic atomic adsorbates on metals and semiconductors	see subvolume III/42A3
3.4.1	Chemisorbed hydrogen on metals and semiconductors (K. CHRISTMANN)	see subvolume III/42A3
3.4.2	C, N, O on metals and semiconductors (H. OVER)	see subvolume III/42A3
3.4.3	Halogens on metals and semiconductors (E.I. ALTMAN)	421
3.4.3.1	Introduction	421
3.4.3.2	General features of halogen adsorption	422
3.4.3.3	Halogen adsorption on metal surfaces	423
3.4.3.3.1	FCC transition metals	423
3.4.3.3.1.1	FCC (100) surfaces	423
3.4.3.3.1.2	FCC (111) surfaces	426
3.4.3.3.1.3	FCC (110) surfaces	429
3.4.3.4	BCC transition metals	431
3.4.3.4.1	BCC (100) surfaces	432
3.4.3.4.2	BCC (110) surfaces	434
3.4.3.4.3	BCC (111) surfaces	437
3.4.3.5	HCP transition metals	438
3.4.3.6	Semiconductor surfaces	439
3.4.3.6.1	Diamond cubic semiconductors	439

3.4.3.6.1.1	Diamond cubic (100) surfaces	439
3.4.3.6.1.2	Diamond cubic (111) surfaces	440
3.4.3.6.2	Zinc blende III-V semiconductor surfaces	441
3.4.3.6.2.1	Zinc blende (110) surfaces	441
3.4.3.6.2.2	Zinc blende (100) surfaces	441
3.4.3.6.2.3	Zinc blende (111) surfaces	442
	Figures for 3.4.3	443
	References for 3.4.3	450
3.4.4	P, S, As, Sb on metals and semiconductors (M. ENACHESCU, M. SALMERON)	see subvolume III/42A3
3.5	Surface segregation of atomic species (non-metal on metal) (H.-J. GRABKE, CH. UEBING, H. VIEFHAUS)	see subvolume III/42A3
3.6	Molecules on graphite, BN, MgO (except noble gases) (H. WIECHERT, J. SUZANNE)	see subvolume III/42A3
3.7	Molecular diatomic adsorbates on metals and semiconductors	see subvolume III/42A3
3.7.1	CO and N ₂ on metals (A. FÖHLISCH, A. NILSSON, H.P. BONZEL)	see subvolume III/42A3
3.7.2	NO, CN, O ₂ on metals (W.A. BROWN)	see subvolume III/42A3
3.7.3	Diatomic molecules on alloys (B. E. NIEUWENHUYNS)	see subvolume III/42A3
3.7.4	Diatomic molecules on semiconductors (K. HORN)	see subvolume III/42A3
3.8	Molecular polyatomic adsorbates on metals and semiconductors	see subvolume III/42A3
3.8.1	H ₂ O and OH on metals (G. PIRUG)	see subvolume III/42A3
3.8.2	H ₂ O and OH on semiconductors (W. JAEGERMANN, T. MAYER)	see subvolume III/42A3
3.8.3	NH ₃ and PF ₃ on metals and semiconductors (E. HASSELBRINK)	see subvolume III/42A3
3.8.4	CO ₂ , NO ₂ , SO ₂ , OCS, N ₂ O, O ₃ (B.E. KOEL)	see subvolume III/42A3
3.8.5	Substituted hydrocarbons on metals (W.T. TYSOE, D.R. MULLINS)	see subvolume III/42A3
3.8.6	Linear hydrocarbons and CH ₄ on metals and semiconductors (G. SOMORJAI, G. RUPPRECHTER)	see subvolume III/42A3
3.8.7	Cyclic hydrocarbons on metals and semiconductors (G. HELD, H.P. STEINRÜCK)	see subvolume III/42A3
3.8.8	Oxygenated hydrocarbons on metals and semiconductors (J. VOHS)	see subvolume III/42A3
3.8.9	Halogen-substituted hydrocarbons on metals and semiconductors (J. FIEBERG, J.W. WHITE)	see subvolume III/42A3
3.8.10	Polyatomic chain-like hydrocarbons on metals and semiconductors (M. GRUNZE)	see subvolume III/42A3
3.8.11	Large aromatic adsorbates on metals and semiconductors (M. SOKOLOWSKI, E. UMBACH)	see subvolume III/42A3
3.9	Adsorption on oxides (H. KUHLENBECK, H.J. FREUND)	see subvolume III/42A3
3.10	Adsorption on alkali halides (J. HEIDBERG)	see subvolume III/42A3
3.11	Surface diffusion on metals, semiconductors, and insulators (E.G. SEEBAUER, M.Y.L. JUNG)	455
3.11.1	Introduction	455

3.11.1.1	General remarks	455
3.11.1.2	Intrinsic and mass transfer diffusion	456
3.11.2	Methodology	458
3.11.2.1	Experimental techniques	458
3.11.2.1.1	Single-atom imaging	458
3.11.2.1.2	Field emission	459
3.11.2.1.3	Electron diffraction	459
3.11.2.1.4	Chemical state relaxation	460
3.11.2.1.5	Spin axis relaxation	460
3.11.2.1.6	Profile evolution	461
3.11.2.1.7	Capillarity-driven effects	463
3.11.2.1.8	Island growth	463
3.11.2.1.9	Miscellaneous	464
3.11.2.2	Classification of experimental techniques	464
3.11.2.3	Computational techniques	466
3.11.2.3.1	Molecular dynamics	466
3.11.2.3.2	Monte Carlo method	467
3.11.2.3.3	<i>Ab initio</i> methods	467
3.11.2.3.4	Classical interatomic potentials	467
3.11.2.3.5	Semi-empirical potentials	469
3.11.2.3.6	Quantum mechanical potentials	470
3.11.3	Tables of data	470
3.11.3.1	Commentary to tables	470
3.11.3.2	Surface diffusion tables	472
3.11.3.2.1	Thermal diffusion in vacuum	472
3.11.3.2.1.1	Intrinsic diffusion	472
3.11.3.2.1.2	Mass transfer diffusion	486
3.11.3.2.1.3	Impurity-influenced diffusion	489
3.11.3.2.2	Non-thermal diffusion	490
3.11.3.2.3	Diffusion under liquids	491
3.11.3.2.4	Computational data	492
3.11.4	Discussion and correlations	495
3.11.4.1	Thermal diffusion in vacuum	495
3.11.4.1.1	Intrinsic diffusion on metals	495
3.11.4.1.2	Intrinsic diffusion on semiconductors	496
3.11.4.1.3	Intrinsic diffusion on insulators	497
3.11.4.1.4	Mass transfer diffusion on metals	497
3.11.4.1.5	Mass transfer diffusion on semiconductors	498
3.11.4.1.6	Mass transfer diffusion on insulators	498
3.11.4.1.7	Comparison of mass transfer diffusion on various substrates	499
3.11.4.1.8	Adsorbate concentration dependence	499
3.11.4.1.9	Impurity-influenced diffusion	500
3.11.4.2	Non-thermal diffusion	500
3.11.4.2.1	Tunneling diffusion	500
3.11.4.2.2	Ion- and photon-influenced diffusion	500
3.11.4.3	Diffusion under aqueous liquids	501
3.11.4.4	Computational results	501
	Acknowledgements	501
	Figures for 3.11	502
	Special references: review articles for 3.11	517
	References for 3.11	519
3.12	Dynamics of activated adsorption (A.C. LUNTZ)	see subvolume III/42A3

4	Data: adsorbate-induced changes of substrate properties	see subvolume III/42A2
4.1	Surface structure on metals and semiconductors (M.A. VAN HOVE, P.R. WATSON, K. HERMANN)	see subvolume III/42A2
4.2	Electron work function of metals and semiconductors (K. JAKOBI)	see subvolume III/42A2
4.3	Electron binding energy of metals and semiconductors (R. DENECKE, N. MARTENSSON, A. NILSSON)	see subvolume III/42A3
4.4	Surface free energy and surface stress (D. SANDER, H. BACH)	see subvolume III/42A2
4.5	Surface phonon dispersion (M. ROCCA)	see subvolume III/42A2
4.6	Surface optical properties (N. ESSER, W. RICHTER)	see subvolume III/42A3