

# Contents

Preface	ix
<i>Chapter 1 (J.A. Venables)</i>	
<b>Surface processes in epitaxial growth</b>	
1. Introduction	1
1.1 Growth modes and surface energies	2
1.2 Surface processes in crystal growth	3
1.3 Thermodynamics and kinetic arguments	5
2. Microscopy and surface physics techniques	7
2.1 Transmission and scanning electron microscopy	7
2.2 Surface-sensitive electron microscopy and analysis	8
2.3 Field ion microscopy	9
2.4 Tunnelling and force microscopies	10
3. Nucleation and growth theory	11
3.1 Rate equations for cluster densities	11
3.2 Adatom capture and regimes of condensation	13
3.3 Competing sinks: step capture and nucleation	15
3.4 Pattern formation: ripening and other effects	17
4. Island growth: metals on insulators	19
4.1 Ag, Au and Pd on alkali halides	19
4.2 Metals on oxide surfaces	21
4.3 Defect-induced nucleation on insulator surfaces	22
4.4 Comparison with theory	24
5. Layer growth: metal and semiconductor homoepitaxy	24
5.1 Metal-metal systems	24
5.2 Semiconductor homoepitaxy	27
5.3 Compound semiconductors and other compounds	29
6. Layer plus island growth examples	31
6.1 Metal heteroepitaxy: Ag/W, Ag/Fe(110) and Ag/Pt(111)	31
6.2 metal/semiconductor systems: Ag/Si and Ge(111)	33
6.3 Semiconductor heteroepitaxy: Ge/Si(100)	36
6.4 Metallic systems involving interdiffusion	39
7. Discussion and conclusions	41
Acknowledgements	42
References	42

*Chapter 2 (E. Bauer)***The many facets of metal epitaxy**

1. Introduction	46
2. Metals on metals	48
2.1 General considerations	48
2.2 The submonolayer range	48
2.2.1 The bcc(110) surface	48
2.2.2 The bcc(100) surface	52
2.3 Coverages above one monolayer	53
2.3.1 The bcc(110) surface	53
2.3.2 The bcc(100) surface	56
3. Metals on semiconductors	59
3.1 Some results from microscopic studies	59
4. Concluding remarks and acknowledgements	62
References	63

*Chapter 3 (G. Rosenfeld, B. Poelsema and G. Comsa)***Epitaxial growth modes far from equilibrium**

1. Introduction	66
2. A kinetic model for homoepitaxial growth	68
2.1 Ideal growth modes in homoepitaxy: intralayer versus interlayer mass transport	68
2.2 Atomistics of intra- and interlayer mass transport	70
2.3 Growth modes in real systems	72
2.4 Dependence of growth modes on deposition parameters	75
3. Experimental studies of metal homoepitaxy	79
3.1 Homoepitaxy on fcc(100) metal surfaces	81
3.2 Homoepitaxy on fcc(111) metal surfaces	84
3.3 A special system: the growth of Pt/Pt(111)	88
3.4 Discussion: why are fcc(100) and fcc(111) metal surfaces so different?	92
4. Kinetic concepts for growth manipulation	94
4.1 Controlled reduction of the step-edge barrier	95
4.2 The concept of two mobilities	95
5. Conclusions	97
Acknowledgements	97
References	98

*Chapter 4 (T.T. Tsong and C. Chen)***Dynamics and diffusion of atoms at stepped surfaces**

1. Introduction	102
2. Field ion microscopy	104
3. Random walk of single atoms and atom-clusters	106
3.1 Random walk of single atoms on a terrace	109
3.2 Mechanisms of atomic jumps: hopping vs. exchange-displacement	111
3.3 Field induced surface diffusion	114
3.4 Diffusion of clusters	117
4. Effects of lattice steps and defects	118
4.1 Step structures and ledge atom diffusion	119
4.2 Equilibrium island shape	123
4.3 Relative binding energy of ledge atoms at different steps	127
4.4 Descending steps	131
4.5 Ascending motion of step-edge atoms and in-layer atoms	133
4.6 Dissociation of step edge atoms to remain on the lower terrace	138
4.7 Impurity traps	143
5. Summary	143
References	145

*Chapter 5 (H. Brune, and K. Kern)***Heteroepitaxial metal growth: the effects of strain**

1. Introduction: heteroepitaxial metal growth	149
2. Thermodynamic growth mode and structural mismatch	150
3. Strain relief and strain induced structures	153
3.1 Dislocations and strain relief at hexagonal close-packed interfaces	155
3.2 Strain relief mechanisms at interfaces with square symmetry	162
3.3 Anisotropic strain relief	169
4. Effects of strain on nucleation kinetics in metal epitaxy	171
4.1 Nucleation and surface diffusion	175
4.2 Effect of isotropic strain on surface diffusion and nucleation	184
4.3 Nucleation on anisotropically strained substrates	188
4.4 Strain and interlayer diffusion	194
Acknowledgement	201
References	201

*Chapter 6* (F. Besenbacher, L.P. Nielsen and P.T. Sprunger)**Surface alloying in heteroepitaxial metal-on-metal growth**

1. Introduction	207
2. Thermodynamic considerations	210
3. Growth of bulk miscible systems	213
3.1 Surface alloying of Pd on Cu(100)	213
3.2 Surface alloying of Pd on Cu(110)	214
4. growth of bulk immiscible systems	215
4.1 Surface alloying of Au on Ni(110)	216
4.2 Theoretical predictions for the Au-Ni system	217
4.3 Surface dealloying of Au on Ni(110)	221
4.4 Surface alloying of Au on Ni(111)	222
4.5 Strain relief at the buried Au-Ni(111) interface	224
4.6 Surface alloying of Au on Ni(111) at high Au coverages: Vegards law in 2-D	226
4.7 Surface alloying of Ag on Cu surfaces	229
4.7.1 Surface alloying of Ag on Cu(110)	230
4.7.2 Surface alloying of Ag on Cu(100)	231
4.7.3 Surface structure and alloying of Ag on Cu(111)	233
4.7.4 Surface alloying of Ag-Cu on Ru(0001)	234
4.8 Surface alloying of Ag on Ni surfaces	236
4.8.1 Surface alloying of Ag on Ni(110)	236
4.8.2 Surface structure of Ag on Ni(111)	237
4.9 Surface alloying of Pb on Cu surfaces	238
4.9.1 Pb on Cu(110)	238
4.9.2 Pb on Cu(100)	240
4.9.3 Pb on Cu(111)	240
4.10 Surface alloying of alkali metals on Al(111)	242
5. Surface alloying: general trends	243
6. Implications for surface reactivity	248
7. Concluding remarks	251
Acknowledgements	252
References	252

*Chapter 7 (F. Liu and M.G. Lagally)*

**Epitaxial growth of Si on Si(001)**

1. Introduction	258
2. Background	259
2.1 The silicon (001) surface	259
2.2 Kinetic processes during vapor deposition	261
3. Adatom adsorption: theoretical predictions	262
4. Direct measurement of Si self-diffusion with STM	264
4.1 Dependence of island number density and denuded-zone width on the diffusion coefficient	265
4.2 Diffusional anisotropy	269
4.3 Diffusion coefficient and activation energy	271
5. Nucleation: energetics and dynamics of Si ad-dimers	274
6. Growth: adatom-step interaction	277
7. Coarsening	280
8. Real-time measurements of kinetics of surface defects	283
8.1 Activation energy for step fluctuation and step motion	284
8.2 Dimer-vacancy migration	286
9. Thermodynamic properties and equilibrium surface morphology	288
9.1 Equilibrium shape of Si islands and energetics of steps	288
9.2 Equilibrium step configurations	289
9.2.1 Nominal surface	289
9.2.2 Vicinal surface	290
10. Conclusion	292
References	293

*Chapter 8 (G. Le Lay)*

**Monolayer films of unreactive metals on semiconductors**

1. Introduction	297
2. Ultra low metal coverage regime	300
2.1 Cs/InAs(110)	300
2.2 Pb/Si(111)7x7 at RT	302
3. Submonolayer regime	304
3.1 Pb, Sn/Si, Ge(111) mosaic phases	305
3.2 The R3 alpha phase	305
4. The dense 2D phases	311
4.1 RT structures	312
4.2 The R3β <sub>z</sub> 1x1 phase transition	319

4.3 Equilibrium formation of 2D-adlayers	320
5. Thin metal films	322
5.1 Quantum size effects in thin Ag and Pb films	322
5.2 Hydrogen-termination effects	323
5.3 Influence of buried interface structures on Schottky-barrier heights	326
6. Unreactive metals on Si(001)	328
6.1 Bismuth adsorption	329
6.2 Lead adsorption	330
6.3 Thin silver (111) films on Si(100)	334
7. Future prospects	335
References	336

*Chapter 9 (H. Kuhlenbeck and H.-J. Freund)*

**Structure and electronic properties of ultrathin oxide films on metallic substrates**

1. Introduction	340
2. Preparation of thin oxide films	342
3. Experimental results for different oxide-metal systems	344
3.1 NiO(100)/Ni(100), NiO(111)/Ni(111) and NiO(111)/Au(111)	344
3.1.1 Geometric structure	344
3.1.1.1 NiO(100)/Ni(100)	344
3.1.1.2 NiO(111)/Ni(111)	347
3.1.2 Electronic structure	352
3.1.2.1 Band structure of NiO(100)/Ni(100)	352
3.1.2.2 Electronic excitations	355
3.2 Cr <sub>2</sub> O <sub>3</sub> (0001)/Cr(110)	357
3.3 Al <sub>2</sub> O <sub>3</sub> (111)/NiAl(110)	364
4. Summary	370
Acknowledgements	371
References	371

*Chapter 10* (S.C. Street and D.W. Goodman)

**Chemical and spectroscopic studies of ultrathin oxide films**

1. Introduction	375
2. Magnesium oxide	376
2.1 Synthesis and characterisation of MgO(100) ultrathin films	376
2.1.1 Adsorption of CO on MgO(100) ultrathin films	378
2.1.2 Acid/base and Li-doped properties of MgO(100) ultrathin films	378
2.2 Synthesis and characterisation of MgO(111) ultrathin films	381
2.2.1 Adsorption on MgO(111) ultrathin films	382
3. Nickel Oxide	384
3.1 Synthesis and characterisation of NiO(100) ultrathin films	384
3.1.1 Adsorption of CO on NiO(100) ultrathin films	384
3.1.2 Acid/base properties of NiO(100) ultrathin films	385
3.2 Synthesis and characterisation of NiO(111) ultrathin films	387
3.2.1 Adsorption on NiO(111) ultrathin films	388
4. Alumina	389
4.1 Synthesis and characterisation of Al <sub>2</sub> O <sub>3</sub> ultrathin films	389
4.2 Interaction of benzene with Al <sub>2</sub> O <sub>3</sub> and MgO ultrathin films	390
5. Layered and mixed oxide ultrathin films	392
5.1 The MgO/NiO mixed oxide system	392
5.2 The CaO/NiO mixed oxide system and comparison to the NiO/MgO system	394
5.3 NiO ultrathin film supported on Al <sub>2</sub> O <sub>3</sub>	395
5.4 Mixed Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> ultrathin films	397
6. STM imaging of oxide surfaces	398
7. Oxide supported metal particles	401
9. Conclusion	402
References	404

*Chapter 11* (R. Persaud and T.E. Madey)

**Growth, structure and reactivity of ultrathin metal films on TiO<sub>2</sub> surfaces**

1. Introduction	407
2. Overview of metals on TiO <sub>2</sub> (110)	408
2.1 Stoichiometric TiO <sub>2</sub> (110)	408
2.2 Thermodynamics of metal/TiO <sub>2</sub> interactions	411
2.3 Experimental procedures	414
2.4 Growth modes for metals/TiO <sub>2</sub>	414
2.5 Interfacial reactivity for metals/TiO <sub>2</sub>	417
2.6 Structure	419

2.7 Thermal stability of overlayer films: encapsulation	420
3. Element-by-element survey of metals on TiO <sub>2</sub>	421
3.1 Non-transition metals on TiO <sub>2</sub> (110)	421
3.1.1 Alkali metals on TiO <sub>2</sub> (110)	421
3.1.1.1 Na/TiO <sub>2</sub> (110)	422
3.1.1.2 K/TiO <sub>2</sub>	423
3.1.1.3 Cs/TiO <sub>2</sub> (110)	424
3.1.2 Al/TiO <sub>2</sub>	425
3.2 Transition metals on TiO <sub>2</sub> (110)	425
3.2.1 Ti/TiO <sub>2</sub> (110)	425
3.2.2 Hf/TiO <sub>2</sub> (110)	426
3.2.3 V/TiO <sub>2</sub> (110)	426
3.2.4 Cr/TiO <sub>2</sub> (110)	428
3.2.5 Mn/TiO <sub>2</sub> (110)	429
3.2.6 Fe/TiO <sub>2</sub> (110)	430
3.2.7 Rh/TiO <sub>2</sub> (110)	432
3.2.8 Ni/TiO <sub>2</sub> (110)	432
3.2.9 Pd/TiO <sub>2</sub> (110)	433
3.2.10 Pt/TiO <sub>2</sub> (110)	434
3.2.11 Cu/TiO <sub>2</sub> (110)	436
3.2.12 Ag/TiO <sub>2</sub> (110)	437
3.2.13 Au/TiO <sub>2</sub> (110)	437
4. Summary and outlook	442
Acknowledgements	443
References	443

## *Chapter 12 (R. Koch)*

### **Intrinsic stress of epitaxial thin films and surface layers**

1. Introduction	448
2. Nomenclature, definitions of stress	449
2.1 Intrinsic stress of thin films in one dimension	449
2.2 Intrinsic stress of thin films in three dimensions	450
2.3 Surface tension and surface stress	455
3. Measurement of misfit strain and stress	457
3.1 Techniques to determine misfit strain	457
3.2 Techniques to determine misfit stress	458
4. Intrinsic stress upon equilibrium epitaxy	461
4.1 Film growth in thermodynamic equilibrium	461
4.2 Volmer-Weber epitaxy	464



4.3 Stranski-Krastanov epitaxy	471
4.4 Frank-Van der Merwe epitaxy	475
5. Intrinsic stress upon pyramidal growth	477
5.1 Film growth at presence of Ehrlich-Schwoebel barriers	477
6. Intrinsic stress of surface layers	482
6.1 Stress of clean surfaces	482
6.2 Changes of surface stress induced by adsorbates	483
7. Summarising discussion	484
Acknowledgements	486
References	486

*Chapter 13 (P. Ruggerone, C. Ratsch and M. Scheffler)*

**Density-functional theory of epitaxial growth of metals**

1. Introduction	490
2. Atomistic processes and rate equations	494
2.1 Atomistic processes	494
2.2 Rate equations	502
2.3 Critical island area and the action of surfactants	504
3. Total energy and the description of growth	507
3.1 Bond-cutting methods	508
3.2 Density-functional theory	509
3.3 Implementation of DFT into state-of-the-art computations	514
3.4 Kinetic Monte Carlo approach	518
4. Results for fcc(111) and fcc(100) surfaces	520
4.1 Growth at Al(111)	521
4.1.1 Microscopic processes	521
4.1.2 Ab initio KMC study of growth	524
4.2 Ag(111)	530
4.2.1 The influence of strain on surface diffusion	530
4.2.2 The role of antimony as a surfactant	533
4.3 Microscopic processes at Al(100)	536
4.4 Ag(100)	537
4.4.1 Microscopic processes	537
4.4.2 The influence of strain on surface diffusion	539
References	540

*Chapter 14 (P.D. Johnson)***Electronic structure of ultrathin magnetic films**

1. Introduction	545
2. Itinerant magnetism and the Stoner model	546
3. Transition metal films	548
3.1 Theoretical studies	538
3.2 Experimental studies	551
3.3 Other ultrathin ferromagnetic systems	562
4. Noble metal films on ferromagnetic substrates	563
4.1 The Ag/Fe(001) interface	564
4.2 The Cu/Co(001) interface	570
5. Summary	577
Acknowledgements	578
References	578

*Chapter 15 (J.A.C.Bland)***Ultrathin magnetic structures - magnetism and electronic properties**

1. Introduction	583
2. Ultrathin magnetic film magnetometry	585
2.1 The magneto-optic Kerr effect: an introduction	586
2.2 The magneto-optic Kerr effect	587
2.3 A macroscopic description of the Kerr effect	588
2.4 Vector MOKE	590
2.5 Polarised neutron reflection: an introduction	590
2.6 Polarised neutron reflection	591
3 Absolute magnetic moments	594
3.1 3-d metal magnetic moments - an overview	594
3.2 Volume dependence of the magnetic moment	600
3.3 Magnetic moments and surface stability	601
3.4 Measurements of absolute magnetic moments in ultrathin transition metal films	602
3.5 X/Fe(001) films on Ag(001) substrates	603
3.6 Fe(110) films on W(110) substrates	607
4 The two dimensional magnetic phase transition	607
4.1 Critical behaviour of Co/Cu(001)	608
4.2 Effect of Cu overlayers on the magnetism of Co/Cu(001)	609
5 Thickness dependence of magnetic anisotropies and vector spin reversal processes	612

5.1 bcc Fe/GaAs	613
5.2 Vector switching processes in Fe/GaAs(001)	617
5.3 Vector spin reversal of coupled Fe/Cr/Fe trilayers	620
5.4 Anisotropy and reversal behaviour of Fe/Ag(001)	622
6 Conclusions	627
Acknowledgements	628
References	628
Index	635