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Preface

Our motivation for writing this book was to provide materials scientists with a guide to the power and utility of atom probe microscopy, particularly, to atom probe tomography. We have sought to provide the beginner with a rigorous background, together with the practical information necessary to initiate successful experiments. Well-experienced practitioners should see this book as an up-to-date source containing complementary knowledge that supports and enables their research. A balance has been sought between providing a fundamental organisation of the main theories, a practical experimental guide and a source of valuable references.

For the past 20 years, atom probe techniques have been at the forefront of atomic-scale microscopy, producing unique atomically resolved tomographic maps of the distribution of the elements within small, but consistently increasing, volumes of material, and their use has markedly and steadily been expanding. We have, when possible or appropriate, discussed the complementarity of other atomic-resolution microscopy techniques. We have highlighted that atom probe microscopy provides unique insights into the structure and chemistry of a vast range of technological and scientific materials, ranging from steels for power plant applications to semiconducting nanoelectronics devices and, progressively, to organic and biological materials.

In several places in this book, we have directed the reader to various excellent textbooks that provide details of particular theories or practice that we have not treated. Over the last decade, the implementation of micro-electrode systems and wide-field-of-view detectors, along with the renaissance of pulsed-laser atom probe approaches, has transformed the capability of atom probe microscopy. This has brought the technique into the microscopy mainstream, and it is now widely recognised as a key enabler of materials science. We feel that this has generated the need for an up-to-date textbook that offers a framework for the many recent developments and focuses on instrumentation, experimental methods, tomographic reconstruction, data analysis and simulation.

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We would like, first, to acknowledge and pay respect to the Gadigal people of the Eora Nation, the traditional owners of the land on which most of this book has been written. It is upon their ancestral lands that the University of Sydney is built.

We acknowledge the support of the Australian Centre for Microscopy and Microanalysis (ACMM) at the University of Sydney for providing a stimulating and supportive environment to write this book. The ACMM is a node of a much larger network linking microscopy laboratories around Australia, the Australian Microscopy and Microanalysis Research (AMMRF). Indeed, the atom probes are flagship instruments within AMMRF, and this network brings an array of exciting research ideas and challenges to our doorstep that have, in part, inspired the writing of this text.

We are enormously grateful and indebted to Dr Kyle Ratinac for his invaluable help and advice on writing, as well as his bravery for reviewing and help us with editing the manuscript.

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List of Acronyms and Abbreviations

(GM-)SRO	(Generalised multi-component-) short-range order
3DMF	3D Markov field
3DAP	3D Atom probe
APM	Atom probe microscopy
APT	Atom probe tomography
BIF	Best image field
BIV	Best image voltage
COM	Centre-of-mass
CW	Continuous wave
DBSCAN	Density-based scanning
DC	Direct current
EDS	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectrometry
eFIM	Digital-FIM
FDM	Field desorption microscopy
FEEM	Field electron emission microscopy
FEM	Finite-element method
FFT	Fast Fourier transform
FIB	Focused ion-beam
FIM	Field ion microscopy
FW1%M	Full-width at 1%-maximum
FW9/10M	Full-width at nine tenths maximum
FWHM	Full-width at half-maximum
FWTM	Full-width at tenth-maximum
hcp, bcc, fcc, dc	Hexagonal close-packed, body-centred cubic, face-centred cubic, diamond cubic
HV	High voltage

IAP	Imaging atom probe
ICF	Image compression factor
ICME	Integrated computational materials engineering
LE	Local-electrode
LEAP	Local-electrode atom probe
MCP	Microchannel plate
MSDS	Material safety data sheets
NN, 1NN, kNN	Nearest neighbour, first NN, *k*th NN
NSOM or SNOM	Near-field scanning optical microscopy or scanning near-field optical microscopy
PoSAP	Position sensitive atom probe
ppb	Part per billion
ppm	Part per million
PSF	Point-spread function
RDF	Radial distribution function
ROI	Region-of-interest
SDM	Spatial distribution map
SEM	Scanning electron microscope
SEM-FIB	Scanning electron microscope–focused ion-beam
SIMS	Secondary-ion mass spectrometry
SNIP	Sensitive nonlinear iterative peak
SPM	Scanning probe microscopy
SRIM	Stopping range of ions in matter
STEM	Scanning transmission electron microscope
TAP	Tomographic atom probe
TEM	Transmission electron microscope
tof-SIMS	Time-of-flight SIMS

List of Terms

$<\rho^2>$	Mean square surface displacement
α	Specimen shank angle
α_{P}	Surface atom polarisability
α_{T}	Thermal diffusivity
c	Light celerity
χ_{e}^2	Experimental value of χ^2 for significance testing
c_p	Specific heat
D	Distance between features on the screen/detector
δ	Depth resolution
$d(\mathrm{p}, \mathrm{p}^{\mathrm{kNN}})$	Distance between two solute atoms p and their kNN
$d(\mathrm{p,q})$	Distance between two solute atoms p and q
$\delta(r-r_{\mathrm{i}})$	Dirac delta function
$d(\zeta, \psi)$	Histograms of atomic positions in the computation of the Hough transformation
δ_0	Size of the ionisation zone
D_0	Surface diffusivity
D_{a}	Analysed depth
d_{diff}	Distance of heat diffusion
d_{erode}	Distance over which the clusters are eroded
$\mathrm{d}_{\mathrm{kNN}}$	Distance between an atom and its *k*th NN
d_{link}	Distance between core and linked atoms of a cluster and in the core-linkage algorithm
d_{max}	Maximal distance separating two solutes belonging to a cluster
d_{p}	Distance of penetration of the static field
δ_{s}	Skin depth
ΔT_{rise}	Maximum increase of temperature-induced laser illumination
$\mathrm{d}z$	Depth increment
e	Elementary charge

$e(n)$	Experimental measured number of voxels
ε_0	Dielectric permittivity of the vacuum
E_C	Kinetic energy
ε_D	Detection efficiency
E_F	Fermi energy
ε_N	Absorption coefficient in the direction normal to the specimen axis
E_P	Potential energy
ε_P	Absorption coefficient in the direction parallel to the specimen axis
F	Electric field
$f(M)$, $g(M)$, $h(M)$	Respectively object, point-spread function and imaged function
$f(r)$, $F(R)$, $I(R)$	Structure function, Fourier transform and intensity respectively
$f_b(n)$	Expected number of blocks each containing n atoms of a given element
$f_{CT}(n_{ij})$	Expected contingency table
Φ_e	Work function
F_{evap}	evaporation field of a species
Φ_{evap}	Field evaporation rate
F_i	Intrinsic electric field of the electromagnetic wave
$f_{LBM}(n)$	Frequency distribution from LBM model
$f_{Pa}(n)$	Frequency distribution from a sinusoidal model
$f_{Sq}(n)$	frequency distribution from a square-wave model
$g_{AB}(r)$	Value of the A–B pair-correlation function at a distance r from the A atom
η	Detection efficiency
$\hbar$	Planck constant
I	Light intensity
I_0	Energy of first ionisation
I_n	nth ionisation energy
κ	Thermal conductivity
k_B	Boltzmann constant
k_f	Field factor
L	Flight path
λ	Lateral resolution
Λ	Sublimation energy
L_1, L_2, L_3	Characteristic length of the best-fit ellipsoid of a cluster with $L_1>L_2>L_3$
λ_e	Electron mean free path
L_{erode}	Radius of a sphere used to include matrix atoms within a cluster prior to performing erosion
L_{flight}	Flight distance

l_g	Radius of gyration of a cluster
$L_x/L_y/L_w$	Physical length of the delay-line
l_x, l_y, l_z	Length of the block along the x, y and z directions, respectively
m	Atomic mass
M	Mass-to-charge ratio
μ	Pearson-coefficient
μ_e	Magnetic permeability
M_{proj}	Magnification
n	Number of atoms in a given block of a given species
N	Number of blocks
n_{Ai}	Number of A atoms in the ith block
N_{at}	Number of imaged atoms over the specimen surface
n_b	Population of atoms occupying a block
n_d	Number of atoms detected
N_{diff}	Number of surface diffusion related hops
N_{double}	Number of atoms evaporated from the specimen that have induced a double event
n_e	Electron density
n_{evap}	Number of field evaporated atoms
N_I	Number of isotopes
n_i	Number of atoms in the ith block
N_{min}	Minimum number of atoms in a cluster
N_R	Number of ranges
$n_{RDF}(r)$	Average number of atoms in the shell at a distance of r around each atom
N_{spec}, N_C	Number of atoms in the cluster in the specimen and that detected by the atom probe
P_a	Peak–peak amplitude of the compositional fluctuations
$P_b(n)$	Probability from a binomial distribution of having n atoms of a given element in a block
P_{evap}	Field evaporation probability
$P_k(r,\rho)$	probability distribution of finding the kth NN at r for an atomic density ρ
$P_k(r, \rho, \alpha)$	Probability distribution of finding the kth NN at r for an atomic density ρ and a relative weight α
$Q(F)$	Energy barrier for field evaporation under electric field
Q_0	Energy barrier for field evaporation without electric field
θ_{crys}	Crystallographic angle between two sets of atomic planes
Q_{diff}	Energy barrier for surface diffusion
θ_{obs}	Observed angle between two sets of atomic planes
R	Radius of curvature
ρ	Material atomic density
$\rho_{average}$	Average atomic density

$RDF(r)$	Value of the RDF at a distance r from the central atom
ρ_{filter}	Threshold value of ρ_{kNN} for density-filtering
r_{filter}	Threshold value of d_{kNN} for density-filtering
ρ_i	Atomic density in the ith block
ρ_{kNN}	Atomic density derived from the kth NN distribution
r_{sphere}	Radius of a spherical cluster derived from its radius of gyration
σ	Standard deviation of a Gaussian function
S_{a}	Analysed area
σ_{e}	Electrical conductivity
σ_{heat}	Size of the Gaussian-shaped heated zone
σ_{v}	Surface normal stress resulting from the electric field
σ_{q}	Surface charge density
σ_{spot}	Laser spot diameter
T	Absolute temperature
t_0	Time shift for time-of-flight measurement
τ_0	Time of observation in surface diffusion experiments
T_{apex}	Temperature of the specimen apex
t_{d}	Instant of departure of the ion from the surface
t_{flight}	Time-of-flight
τ_{P}	Laser pulse duration
$\text{Tp}_x/\text{Tp}_y/\text{Tp}_w$	Total propagation time along a delay-line
Tx_{1-2} / Ty_{1-2}/Tz_{1-2}	Propagation time at the end of a delay-line
V	High voltage
v	Ion velocity
V_{evap}	Field evaporated volume
V_i	Volume of the ith block
$v_{\text{p}}(i)$	Mass spectrum histogram for the SNIP method
Ω	Atomic volume
ω	Wave pulsation
$w_{\text{R}}(z)$	Function describing the change in the specimen's radius during the analysis
$w_{\text{V}}(z)$	Function describing the increase in the analysed volume during the analysis
ξ	Image compression factor
x, y, z	Coordinates of an atom in the tomographic reconstruction
$X_{\text{A/B}i}$	Concentration of A atoms relative to B atoms in the ith block
$X_{\text{A}i}$	Concentration of A atoms in the ith block
x_{c}	Critical distance of ionisation
$x_{\text{COM}}, y_{\text{COM}}, z_{\text{COM}}$	Coordinates of the centre-of-mass of a cluster in the tomographic reconstruction
$X_{\text{D}}/Y_{\text{D}}$	Detector coordinates

x_i, x_{max}, Δx	Respectively position of the *i*th bin along the composition profile, total length of the profile and width of sampling bins
ζ, ψ	Rotation angle around the *z*- and *y*-axes respectively to compute Hough transformation
z_{tip}	Depth of the virtual surface
Δr	Thickness of the shell for RDF calculation
Δz	*z*-Offset between atoms used to compute SDM
$\Delta z'(\phi, \theta)$	*z*-Offset after rotation around the *x*- and *y*-axis between atoms used to compute SDM
v_0	Surface atom vibration frequency
ϕ, θ	Angles by which a dataset is rotated around the *x* and *y* axes, respectively

List of Non-SI Units and Constant Values

Description	Symbol	Value
Angstroms	Å	10^{-10} m
Atomic mass unit	amu	1.660×10^{-27} kg
Boltzmann constant	k_B	1.380×10^{-23} m^{2}kg s^{-2} K^{-1}
Dalton	Da	1 atomic mass unit per coulomb
Dielectric permittivity of the vacuum	ε_0	8.854×10^{-12} F m^{-1}
Elementary charge	e	1.602×10^{-19} C
Planck constant	$\hbar$	6.626×10^{-34} m^{2}kg s^{-1}
Torr	Torr	1 torr=133.322 Pa

Contents

Part I Fundamentals