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While the state-of-the-art has advanced dramatically in the ten years since publication of our first edition, the fundamentals still abide. The first, nine chapters on fundamentals of low pressure partially ionized plasmas (Chapters 2–6) and gas-phase and surface physics and chemistry (Chapters 7–9) have been revised mainly to clarify the presentation of the material, based on the authors’ continuing teaching experience and increased understanding. For plasmas, this includes significant changes and additions to Sections 5.2 and 5.3 on diffusion and diffusion solutions, 6.2 on the Bohm criterion, 6.4 on sheaths with multiple positive ions, and 6.6 on Langmuir probes in time-varying fields. For gas phase and surface physics and chemistry it includes revised presentations in Sections 9.2 and 9.3 of sputtering physics, loss rates for neutral diffusion, and loss probabilities. The argon and oxygen rate coefficient data sets in Chapters 3 and 8 have been brought up to date.

Chapters 10–14 on discharges have been both revised and expanded. During the last decade, the processing community has achieved a more thorough understanding of electronegative discharge equilibrium, which lies at the core of the fluorine-, chlorine-, and oxygen-containing plasmas used for processing. Electronegative discharges are described in the new or revised Sections 10.3–10.5. An important new processing opportunity is the use of pulsed power discharges, which are described in a new Section 10.6. Chapter 11 on capacitive discharges has been expanded to incorporate new material on collisionless sheaths, dual-frequency, high-frequency, and electronegative discharges. New Sections 11.5 and 11.6 have been added on high-density rf sheaths and ion energy distributions, which are important for rf-biased, high-density processing discharges. Chapter 12 on inductive discharges now incorporates the electron inertia inductance in the discharge model and includes a new subsection on hysteresis and instabilities, whose effects can limit the performance
of these discharges for processing. Section 13.2 on helicon discharges has been expanded to incorporate new understanding of helicon mode absorption and neutral gas depletion, both important for helicon discharge modeling. Two Sections 14.4 and 14.6 have been added on hollow cathode discharges and on ionized physical vapor deposition. Hollow cathode discharges have important applications in both processing and for gas lasers, and serve as an example of low pressure dc discharge analysis. Ionized physical vapor deposition has some important applications for thin film deposition and illustrates the combined use of dc and rf discharges for processing.

Chapters 15 and 16 on etching, deposition, and implantation have been brought up to date. In Section 15.4, a brief subsection on copper etching has been included. A new Section 15.5 on charging effects has been added, since differential substrate charging is now fairly well understood and is known to damage thin film oxides.

During the last decade, particulates in discharges have been studied both with a view to controlling their formation, to avoid generating defects during processing, and for producing powders and nanocrystalline materials. In a new Chapter 17 on dusty plasmas, the physics and technology of this important area is described, including particulate charging and discharge equilibrium, particulate equilibrium, particulate formation and growth, diagnostics, and removal and production techniques.

Also during the last decade, discharge analysis based on kinetic theory has advanced considerably, and kinetic techniques have found increasing use. In a new Chapter 18, we give an introduction to the kinetic theory of discharges, including the basic concepts, local and nonlocal kinetics, quasi-linear diffusion and stochastic heating, and examples of discharge kinetic modeling.

Errors in the first and second printings of the first edition have been corrected. All topics treated have been brought up to date and incorporate the latest references to the literature. The list of references has been expanded from about 6 to 14 pages.

Because we emphasize the development of a strong foundation in the fundamental physical and chemical principles, our one-semester course teaching this material to a mixed group of mainly graduate students in electrical, chemical, and nuclear engineering, materials science, and physics has not changed much over the years. The outline in the first preface for a 30, 1.5 hour lecture course is still relevant, with, perhaps, some additional emphasis on electronegative plasma equilibria and on pulsed plasmas. (Some sections have been renumbered.)

Our colleagues C.K. Birdsall and J.P. Verboncoeur and the plasma theory and simulation group (PTSG) at Berkeley continue to maintain a set of user-friendly programs for PCs and workstations for computer-aided instruction and demonstrations. The software and manuals can be downloaded from their web site http://ptsg.eecs.berkeley.edu.

In preparing this revision, we have received encouragement and benefited from discussions with many friends and colleagues. We thank I.D. Kaganovich for carefully reviewing Chapter 18 on kinetic theory. We are indebted to J.T. Gudmundsson for assistance in updating the argon and oxygen rate coefficient data sets (for more complete data, see his web site http://www.raunvis.hi.is/tumi/), and to Z. Petrović
and D. Marić, who provided assistance in updating the field-intensified ionization coefficient and the breakdown voltages given in Chapter 14. We thank B. Cluggish, R.N. Franklin, V.A. Godyak, and M. Kilgore for their comments clarifying various calculations. We have benefited greatly from the insight and suggestions of our colleagues C.K. Birdsall, J.P. Booth, R.W. Boswell, P. Chabert, C. Charles, S. Cho, T.H. Chung, J.W. Coburn, R.H. Cohen, D.J. Economou, D. Fraser, D.A. Graves, D.A. Hammer, Y.T. Lee, L.D. Tsendin, M. Tuszewski, J.P. Verboncoeur, A.E. Wendt, and H.F. Winters. Our recent postdoctoral scholars S. Ashida, J. Kim, T. Kimura, K. Takechi, and H.B. Smith, and recent graduate students J.T. Gudmundsson, E. Kawamura, S.J. Kim, I.G. Kouznetsov, A.M. Marakhtanov, K. Patel, Z. Wang, A. Wu, and Y. Wu, have taught us much, and some of their work has been incorporated into our revised text. The authors gratefully acknowledge the hospitality of R.W. Boswell at the Australian National University, Canberra, and M.G. Haines at Imperial College, London, where considerable portions of the revision were written.

MICHAEL A. LIEBERMAN
ALLAN J. LICHTENBERG

September, 2004
This book discusses the fundamental principles of partially ionized, chemically reactive plasma discharges and their use in thin-film processing. Plasma processing is a high-technology discipline born out of the need to access a parameter space in materials processing unattainable by strictly chemical methods. The field is interdisciplinary, combining the areas of plasma physics, surface science, gas-phase chemistry, and atomic and molecular physics. The common theme is the creation and use of plasmas to activate a chain of chemical reactions at a substrate surface. Our treatment is mainly restricted to discharges at low pressures, <1 Torr, which deliver activation energy, but not heat, to the surface. Plasma-based surface processes are indispensable for manufacturing the integrated circuits used by the electronics industry, and we use thin-film processes drawn from this field as examples. Plasma processing is also an important technology in the aerospace, automotive, steel, biomedical, and toxic waste management industries.

In our treatment of the material, we emphasize the development of a strong foundation in the fundamental physical and chemical principles that govern both discharges and gas- and surface-phase processes. We place little emphasis on describing state-of-the-art discharges and thin-film processes; while these change with time, the fundamentals abide. Our treatment is quantitative and emphasizes the physical insight and skills needed both to do back-of-the-envelope calculations and to do first-cut analyses or designs of discharges and thin-film processes. Practical graphs and tables are included to assist in the analysis. We give many examples throughout the book.

The book is both a graduate text, including exercises for the student, and a research monograph for practicing engineers and scientists. We assume that the reader has the usual undergraduate background in mathematics (2 years), physics (1 1/2 years), and, chemistry (1/2 or 1 year). Some familiarity with partial differential equations as
commonly taught in courses on electromagnetics or fluid dynamics at the junior or senior undergraduate level is also assumed.

After an introductory chapter, the book is divided into four parts: low-pressure partially ionized plasmas (Chapters 2–6); gas and surface physics and chemical dynamics (Chapters 7–9); plasma discharges (Chapters 10–14); and plasma processing (Chapters 15 and 16). Atomic and molecular collision processes have been divided into two relatively self-contained chapters (Chapters 3 and 8, respectively) inserted before the corresponding chapters on kinetics in each case. This material may be read lightly or thoroughly as desired. Plasma diagnostics appear in concluding sections (Sections 4.6, 6.6, 8.6, and 11.6) of various chapters and often also serve as applications of the ideas developed in the chapters.

For the last five years, the authors have taught a one-semester course based on this material to a mixed group of mainly graduate students in electrical, chemical, and nuclear engineering, materials science, and physics. A typical syllabus follows for 30 lectures, each $1\frac{1}{2}$ hours in length:

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The core ideas of the book are developed in the sections of Chapters 2, 4–7, 9, and 10 listed in the syllabus. Atomic and molecular collisions (Chapters 3 and 8) can be emphasized more or less, but some coverage is desirable. The remaining chapters (Chapters 11–16), as well as some sections within each chapter, are relatively self-contained and topics can be chosen according to the interests of the instructor. More specialized material on guiding center motion (Section 4.3), dynamics (Section 4.4), waves (Section 4.5) and diffusion in magnetized plasmas (Sections 5.4 and 5.5) can generally be deferred until familiarity with the core material has been developed.
Our colleagues C.K. Birdsall and V. Vahedi and the plasma simulation group at Berkeley have developed user-friendly programs for PCs and workstations for computer-aided instruction and demonstrations. A number of concepts in discharge dynamics have been illustrated using various output results from these programs (see Figures 1.11, 2.2, and 6.3). We typically do four or five 20-minute simulation demonstrations in the course during the semester using this software. The software and manuals can be obtained by contacting the Software Distribution Office, Industrial Liaison Program, Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, CA 94720; the electronic mail address, telephone, and fax numbers are software@eecs.berkeley.edu, (510) 643-6687, and (510) 643-6694, respectively.

This book has been three years in writing. We have received encouragement and benefited from discussions with many friends and colleagues. We acknowledge here those who contributed significantly to our enterprise. We are indebted to D.L. Flamm who was a MacKay Visiting Lecturer at Berkeley in 1988–89 and co-taught (with A.J.L.) an offering of our course in which he emphasized the chemical principles of plasma processing. One of the authors (M.A.L.) has taught abbreviated versions of the material in this book to process engineers in various short courses, along with his colleagues C.K. Birdsall, D.B. Graves, and V. Vahedi. We have benefited greatly from their insight and suggestions. Our colleagues N. Cheung, D. Graves, D. Hess, and S. Savas, our postdoctoral scholars C. Pico and R. Stewart, and our graduate students D. Carl, K. Kalpakjian, C. Lee, R. Lynch, G. Misium, R. Moroney, K. Niazi, A. Sato, P. Wainman, A. Wendt, M. Williamson, and B. Wood have taught us much, and some of their work has been incorporated into our text. Some of the material in Chapters 10, 12, and 13 is based on a review article by R.A. Gottscho and one of the authors (M.A.L.) in Physics of Thin Films, Vol. 18, edited by M. Francombe and J.L. Vossen, Academic Press, New York, 1994. We thank V.A. Godyak, M.B. Lieberman, and S. Brown for reviewing several chapters and suggesting clarifications of the text. W.D. Getty has used a preprint of our manuscript to teach a course similar to ours, and the final text has benefited from his comments and suggestions. Many of the ideas expressed in the book were developed by the authors while working on grants and contracts supported by the National Science Foundation, the Department of Energy, the Lawrence Livermore National Laboratory, the State of California MICRO Program, the California Competitive Technology Program, SEMATECH and the Semiconductor Research Corporation, IBM, Applied Materials, and Motorola. The authors gratefully acknowledge the hospitality of M.G. Haines at Imperial College, London (M.A.L.), and of R. Boswell at the Australian National University, Canberra (A.J.L.), where much of the manuscript was developed. We gratefully thank E. Lichtenberg and P. Park for typing portions of the manuscript.
SYMBOLS AND ABBREVIATIONS

SYMBOLS

a  radius (m); atomic radius; \( a_0 \), Bohr radius; \( a_j \), chemical activity of species \( j \); \( a_v \), etching anisotropy

a  acceleration (m/s^2)

A  area (m^2); a constant; \( A_R \), reduced mass (amu)

b  impact parameter (m); radius (m)

B  magnetic induction (T); a constant; \( B_{\text{rot}} \), rotational constant of molecule

c  velocity of light in vacuum

C  a constant; capacitance (F/m); \( C_V \), specific heat at constant volume (J/mol K); \( C_p \), specific heat at constant pressure

C  a contour or closed loop

d  denotes an exact differential

delta  denotes a nonexact differential (Chapter 7)

d  distance (m); plasma size (m)

D  diffusion coefficient (m^2/s); displacement vector (C/m^2); \( D_a \), ambipolar diffusion coefficient; \( D_{a+} \), ambipolar diffusion coefficient in the presence of negative ions; \( D_v \), velocity space diffusion coefficient (m^3/s^3); \( D_E \), energy diffusion coefficient (V^2/s); \( D_{\text{SiO}_2} \), deposition rate of silicon dioxide (m/s)

e  unsigned charge on an electron (1.602 \times 10^{-19} \text{ C})

e  the natural base (2.718)

E  electric field (V/m); etch (or deposition) rate (Å/min)

E  the voltage equivalent of the energy (V); i.e., energy(J) = eE (V)

f  frequency (Hz); distribution function (m^{-6} s^{-3}); \( f_m \), Maxwellian distribution; \( f_{\text{pe}} \), electron plasma frequency; \( f_{\text{pi}} \), ion plasma frequency
Symbols and Abbreviations

f_c  collisional force per unit volume (N/m^3)
F  force (N)
g  degeneracy; \bar{g}, statistical weight; energy distribution function; gravitational constant
g  denotes a gas
G  Gibbs free energy (J); volume ionization rate (m^{-3} s^{-1}); G_f, Gibbs free energy of formation; G_r, Gibbs free energy of reaction; conductance (\Omega^{-1}); particle density source (m^{-3} s^{-1})
h  center-to-edge density ratio; h_y, axial ratio; h_R, radial ratio
H  enthalpy (J); magnetic field (A/m); height (m); H_f, enthalpy of formation; H_r, enthalpy of reaction
H  Boltzmann H function
i  integer
I  electrical current (A); differential scattering cross section (m^2/sr); I_{AB}, I_{mol}, moment of inertia of molecule (kg m^2)
I  modified Bessel function of the first kind
j  \sqrt{-1}; integer
J  electrical current density (A/m^2); rotational quantum number
J  Bessel function of the first kind
\mathcal{J}  \mathcal{J}_j denotes chemical species j
k  Boltzmann’s constant (1.381 \times 10^{-23} J/K); wave number or wave vector (m^{-1})
K  first-order (s^{-1}), second-order (m^3/s), or third-order (m^6/s) rate constant
K  modified Bessel function of the second kind
K  equilibrium constant
l  discharge length (m); antenna length (m); quantum number; integer
l  denotes a liquid
\ell  denotes length for a line integral
L  length (m); volume loss rate (m^{-3} s^{-1}); inductance (H); particle density sink (m^{-3} s^{-1})
m  electron mass (9.11 \times 10^{-31} kg); mass (kg); azimuthal mode number; m_l, m_s, and m_J, quantum numbers for axial component of orbital, spin, and total angular momentum
M  ion mass (kg)
\mathcal{M}  number of chemical species
n  particle density (m^{-3}); principal quantum number (an integer); n_i, ion density; n_e, electron density; n_g, neutral gas density
n'  area density (m^{-2}); n'_0, area density of surface sites
N  quantity of a substance (mol); index of refraction of a wave
N  number of turns
p  pressure (N/m^2); particle momentum (kg m/s); p', standard pressure (1 bar or 1 atm); p_d, electric dipole moment (C m); p_{ohm}, ohmic power density (W/m^3)
P  power (W); probability
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q )</td>
<td>electric charge (C)</td>
</tr>
<tr>
<td>( \mathbf{q} )</td>
<td>heat flow vector (W/m²)</td>
</tr>
<tr>
<td>( Q )</td>
<td>heat (J); electric charge (C)</td>
</tr>
<tr>
<td>( \dot{Q} )</td>
<td>resonant circuit or cavity quality factor</td>
</tr>
<tr>
<td>( r )</td>
<td>radial position (m); ( r_c ), gyroradius; ( r_{ce} ), electron gyroradius</td>
</tr>
<tr>
<td>( R )</td>
<td>gas constant (8.314 J/(K mol)); cylinder radius (m); center-of-mass coordinate (m); nuclear separation (m); reaction rate (m⁻³ s⁻¹); resistance (Ω)</td>
</tr>
<tr>
<td>( s )</td>
<td>sheath thickness (m); sticking coefficient; ( \tilde{s} ), thermal sticking coefficient; ( s_v ) or ( s_h ), etching selectivity</td>
</tr>
<tr>
<td>( S )</td>
<td>denotes a solid</td>
</tr>
<tr>
<td>( S )</td>
<td>energy flux (W/(m² s)); entropy (J/K); closed surface area (m²); ( S_p ), pumping speed (m³/s)</td>
</tr>
<tr>
<td>( S )</td>
<td>denotes a closed surface</td>
</tr>
<tr>
<td>( t )</td>
<td>time (s)</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature (K); ( T_0 ), standard temperature (298 K)</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature in units of volts (V)</td>
</tr>
<tr>
<td>( u )</td>
<td>average velocity (m/s); ( u_B ), Bohm velocity; ( u_E ), ( \mathbf{E} \times \mathbf{B} ) velocity; ( u_D ), diamagnetic drift velocity</td>
</tr>
<tr>
<td>( U )</td>
<td>energy (J); internal energy (J); potential energy (J)</td>
</tr>
<tr>
<td>( v )</td>
<td>velocity (m/s); vibrational quantum number; ( \tilde{v} ), average speed; ( v_{th} ), thermal velocity; ( v_R ), relative velocity; ( v_{ph} ), phase velocity</td>
</tr>
<tr>
<td>( V )</td>
<td>voltage or electric potential (V); ( \tilde{V} ), rf voltage; ( \overline{V} ), dc or time-average voltage</td>
</tr>
<tr>
<td>( Y )</td>
<td>volume (m³)</td>
</tr>
<tr>
<td>( W )</td>
<td>energy per unit volume (J/m³); width (m)</td>
</tr>
<tr>
<td>( W )</td>
<td>kinetic energy (J); work (J)</td>
</tr>
<tr>
<td>( x )</td>
<td>rectangular coordinate (m); ( x_j ), mole fraction of species ( j ); ( x_{iz} ), fractional ionization</td>
</tr>
<tr>
<td>( X )</td>
<td>reactance (Ω)</td>
</tr>
<tr>
<td>( y )</td>
<td>rectangular coordinate (m)</td>
</tr>
<tr>
<td>( Y )</td>
<td>admittance (Ω⁻¹)</td>
</tr>
<tr>
<td>( z )</td>
<td>rectangular or axial cylindrical coordinate (m)</td>
</tr>
<tr>
<td>( Z )</td>
<td>relative charge on an ion, in units of e; impedance (Ω)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>spatial rate of variation (m⁻¹); spatial attenuation or decay constant (m⁻¹); first Townsend coefficient (m⁻¹); ratio of negative ion to electron density; ( \alpha_j ), stochiometric coefficient of species ( j ); ( \alpha_p ), atomic or molecular polarizability (m³)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>spatial rate of variation (m⁻¹); a constant</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>secondary electron emission coefficient; wall loss probability; ratio of electron-to-ion temperature; ratio of specific heats; complex propagation constant; ( \gamma_{se} ), secondary electron emission coefficient; ( \gamma_{sput} ), sputtering coefficient</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>particle flux (m⁻² s⁻¹)</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>the Gamma function</td>
</tr>
</tbody>
</table>
δ  Dirac delta function; layer thickness (m); δ_p, collisionless skin depth (m); δ_c, collisional skin depth (m); δ_e, anomalous skin depth (m)
Δ  denotes the change of a quantity
ε  dielectric constant (F/m); ε_0, vacuum permittivity (8.854 × 10^{-12} F/m);
    ε_p, plasma dielectric constant
ξ  a small displacement (m); ξ_L, fractional energy loss for elastic collision
θ  angle (rad); spherical polar angle; scattering angle in laboratory system;
    fractional surface coverage
Θ  scattering angle in center of mass system (rad)
η  efficiency factor
κ  relative dielectric constant; κ_p, relative plasma dielectric constant; κ_T,
    thermal conductivity
λ  mean free path (m); λ_c, collisional mean free path; λ_e, electron mean free path;
    λ_i, ion mean free path; λ_{De}, electron Debye length (m)
Λ  diffusion length (m); ratio of Debye length to minimum impact parameter
μ  mobility (m^2/V s); chemical potential (J/mol); μ_0, vacuum permeability
    (4π × 10^{-7} H/m); μ_{mag}, magnetic moment
ν  collision or interaction frequency (s^{-1} or Hz); ν_c, collision frequency
ζ  a constant
τ  3.1416
Π  stress tensor (N/m^2)
ρ  volume charge density (C/m^3); ρ_s, surface charge density (C/m^2)
σ  cross section (m^2); σ_{dc}, dc electrical conductivity (Ω^{-1} m^{-1}); σ_{rf}, rf
electrical conductivity
τ  mean free time (s); time constant (s); τ_c, collision time
φ  angle (rad); spherical azimuthal angle
ψ  magnetic flux (T m^2)
Φ  electric potential (V); Φ_p, plasma potential; Φ_w, wall potential
χ  angle (rad); χ_{01}, first zero of zero order Bessel function
ψ  spherical polar angle in velocity space
Ψ  helix pitch (rad)
ω  radian frequency (rad/s); ω_{pe}, electron plasma frequency; ω_c, gyration
    frequency; ω_{ce}, electron gyration frequency
Ω  solid angle (sr)
∇, ∇_r  vector spatial derivative; ∇_v, vector velocity derivative; ∇_T, vector
derivative in total energy coordinates
A  scalar
A  vector
A  unit vector (has unit magnitude)
A  oscillating or rf part
A  average or dc part; equilibrium value
A  dA/dt
A  d^2A/dt^2
⟨A⟩  average