

# Contents

|                                         |           |
|-----------------------------------------|-----------|
| <b>Preface</b>                          | <b>9</b>  |
| <b>1. A Brief History</b>               | <b>13</b> |
| <b>2. The Nature of Plasma</b>          | <b>16</b> |
| 1. General                              | 16        |
| 2. Types of Known Plasmas               | 18        |
| 3. Types of Discharges                  | 19        |
| A. General Description                  | 19        |
| B. Ionization                           | 20        |
| C. The Glow Discharge                   | 23        |
| 1. General Description                  | 23        |
| 2. Effect of Pressure                   | 25        |
| 3. Effect of Electrode Distance         | 26        |
| 4. Effect of Voltage                    | 26        |
| 5. Effect of the Nature of Gas          | 26        |
| 6. The Cathode Zone                     | 27        |
| 7. Negative Glow and Faraday Dark Space | 28        |
| 8. The Positive Column                  | 28        |
| 9. The Anode Region                     | 29        |
| 10. Effect of Electromagnetic Radiation | 29        |
| 11. Other Phenomena                     | 31        |
| D. The Corona Discharge                 | 31        |
| E. Arc Discharge                        | 31        |
| 4. Plasma Temperature                   | 32        |
| <b>3. Glow-Discharge Chemistry</b>      | <b>36</b> |
| 1. Techniques                           | 36        |
| 2. Plasma Components                    | 37        |
| 3. Physical Processes                   | 38        |
| 4. Bimolecular Discharges               | 45        |
| A. General                              | 45        |
| B. Free Radicals                        | 45        |

| 6         | Contents                                                 | Contents | 7          |
|-----------|----------------------------------------------------------|----------|------------|
|           | C. Hydrogen                                              |          | 47         |
|           | D. Oxygen                                                |          | 49         |
|           | E. Nitrogen                                              |          | 51         |
|           | F. Summary                                               |          | 52         |
| 5.        | Reactions of Diatomic Gases                              |          | 53         |
|           | A. General                                               |          | 53         |
|           | B. Reactions of Hydrogen                                 |          | 54         |
|           | C. Reactions of Oxygen                                   |          | 57         |
|           | D. Reactions of Nitrogen                                 |          | 59         |
|           | E. Reactions of Halogens                                 |          | 62         |
|           | F. Reactions of Free Radicals                            |          | 63         |
| 6.        | Synthesis of Organic Compounds in Plasma                 |          | 66         |
|           | A. General                                               |          | 66         |
|           | B. Isomerizations                                        |          | 66         |
|           | C. Eliminations                                          |          | 67         |
|           | D. Bimolecular Reactions                                 |          | 68         |
|           | E. Reaction Mechanisms                                   |          | 70         |
| 7.        | Synthesis of Inorganic Compounds                         |          | 71         |
| <b>4.</b> | <b>Plasma Polymerization</b>                             |          | <b>75</b>  |
|           | 1. Coupling of Electrical Energy into Plasma             |          | 75         |
|           | 2. Mechanistic Aspects                                   |          | 77         |
|           | A. Nature                                                |          | 77         |
|           | B. Kinetics                                              |          | 90         |
|           | C. Energy Transfer                                       |          | 93         |
|           | D. Diffusion of Charged Species                          |          | 93         |
|           | E. Wattage and Mass Flow Rate                            |          | 94         |
|           | F. Inductive versus Resistive Plasma                     |          | 97         |
|           | 3. Plasma Polymerization of Hydrocarbons                 |          | 98         |
|           | A. Saturated Aliphatic Hydrocarbons                      |          | 98         |
|           | B. Aromatic Hydrocarbons                                 |          | 102        |
|           | C. Unsaturated Hydrocarbons                              |          | 105        |
|           | D. Vinyl Monomers                                        |          | 109        |
| <b>5.</b> | <b>Plasma Deposition of Films</b>                        |          | <b>122</b> |
|           | 1. Introduction                                          |          | 122        |
|           | 2. Plasma Parameters in Film Deposition                  |          | 122        |
|           | A. Electric Field and Gas Density                        |          | 122        |
|           | B. Effective Electric Field Strength                     |          | 123        |
|           | C. Breakdown Parameters                                  |          | 124        |
|           | D. Parameters for Discharge Maintenance                  |          | 124        |
|           | E. Constriction of the Discharge                         |          | 125        |
|           | F. Excited-State Concentrations                          |          | 126        |
|           | 3. Effect of Pressure on Deposition Rate                 |          | 126        |
|           | A. Introduction                                          |          | 126        |
|           | B. Experimental Data                                     |          | 129        |
|           | 4. Effect of Flow Rate                                   |          | 136        |
|           | 5. Effect of Carrier Gases on Deposition                 |          | 148        |
|           | 6. Effect of Discharge Power $W$ , $W/F$ , and $W/FM$    |          | 153        |
|           | 7. Effect of Electrode Temperature on Deposition         |          | 158        |
|           | 8. Effect of Frequency on Deposition                     |          | 160        |
|           | 9. Effect of Reactor Design                              |          | 162        |
|           | 10. Effect of a Magnetic Field                           |          | 166        |
|           | 11. Effect of Pulsed Discharge                           |          | 168        |
| <b>6.</b> | <b>Structure of Plasma Polymers</b>                      |          | <b>173</b> |
|           | 1. Introduction                                          |          | 173        |
|           | 2. Plasma Oils                                           |          | 173        |
|           | 3. Plasma Films                                          |          | 179        |
|           | A. Microstructure                                        |          | 179        |
|           | B. Morphology of Plasma-Deposited Films                  |          | 188        |
|           | 4. Plasma Powder                                         |          | 190        |
| <b>7.</b> | <b>Properties of Plasma Polymers</b>                     |          | <b>199</b> |
|           | 1. Wettability                                           |          | 199        |
|           | 2. Adhesion                                              |          | 204        |
|           | A. Introduction                                          |          | 204        |
|           | B. CASING                                                |          | 205        |
|           | C. Composition of the Surface                            |          | 209        |
|           | D. Zeta Potential and Adhesion                           |          | 218        |
|           | E. Effect of Corona Treatment on Adhesion                |          | 219        |
|           | F. Contaminant Removal by Plasma                         |          | 222        |
|           | G. Adhesion to Metals                                    |          | 225        |
|           | 1. Adhesion of Plasma-Deposited Films to Metals          | 225      |            |
|           | 2. Adhesion of Plasma-Treated Polymer Surfaces to Metals | 226      |            |
|           | H. Adhesion of Plasma-Treated Polymer to Polymer         |          | 233        |
|           | 3. Abrasion Resistance and Wear                          |          | 238        |
|           | 4. Hardness                                              |          | 240        |
|           | 5. Friction Characteristics                              |          | 241        |
|           | 6. Diffusion Characteristics                             |          | 242        |
|           | 7. Permselectivity and Reverse Osmosis                   |          | 244        |
|           | A. Introduction                                          |          | 244        |
|           | B. Permselectivity for Gases                             |          | 244        |
|           | C. Reverse Osmosis                                       |          | 245        |
|           | 8. Ion-Exchange Properties of Plasma Membranes           |          | 249        |

|           |                                                     |            |
|-----------|-----------------------------------------------------|------------|
| <b>8</b>  | <b>Contents</b>                                     |            |
| 9.        | Electrical Properties                               | 251        |
|           | A. Introduction                                     | 251        |
|           | B. Dielectric Constant                              | 251        |
|           | C. Capacitance                                      | 253        |
|           | D. Conductivity                                     | 255        |
| <b>8.</b> | <b>Additional Applications of Plasma Technology</b> | <b>260</b> |
| 1.        | Ion Implantation                                    | 260        |
|           | A. Introduction                                     | 260        |
|           | B. Properties                                       | 263        |
|           | 1. Hardness and Wear                                | 263        |
|           | 2. Fatigue                                          | 264        |
|           | 3. Corrosion and Oxidation Resistance               | 264        |
|           | 4. Optical Properties                               | 264        |
|           | C. Ion Nitriding                                    | 265        |
| 2.        | Effects of Carbon on Ion Nitriding                  | 271        |
|           | A. Ion Carbonitriding                               | 274        |
|           | B. Ion Carburizing                                  | 274        |
|           | C. Ion Borizing                                     | 276        |
| 3.        | Microcircuit Fabrication                            | 277        |
|           | A. Description                                      | 277        |
|           | B. Plasma Photoresist Stripping                     | 278        |
|           | C. Silicon Nitride Deposition                       | 281        |
| 4.        | Membranes                                           | 282        |
| 5.        | Biomedical Applications                             | 283        |
| 6.        | Optical Applications                                | 283        |
| 7.        | Review of Surface Treatments                        | 284        |
| 8.        | Plasma Cleaning of Metal Surfaces                   | 284        |
| 9.        | Plasma Etching                                      | 285        |
|           | A. Etching of Polymer Surfaces                      | 285        |
|           | B. Etching of Inorganic Surfaces                    | 287        |
|           | 1. Introduction                                     | 287        |
|           | 2. Aluminum                                         | 288        |
|           | 3. Silicon Dioxide                                  | 288        |
|           | 4. Silicon Nitride                                  | 289        |
|           | 5. $\text{LiNbO}_3$                                 | 289        |
| 10.       | Low-Temperature Ashing                              | 289        |
| 11.       | Textile Treatment                                   | 291        |
| 12.       | Plasma Detoxification and Air Purification          | 292        |
|           | <b>Index</b>                                        | <b>297</b> |