Silicon Processing

for the VLSI Era Volume 1 – Process Technology

S. Wolf and R.N. Tauber

Micron Ex. 1042, p. 1 Micron v. YMTC IPR2025-00119



WEIL, GOTSHAIL & MANGES, LLP LIBRARY

JUL 0 1 1999

NENLU PARK

Micron Ex. 1042, p. 2 Micron v. YMTC IPR2025-00119

SILICON PROCESSING FOR THE VLSI ERA VOLUME 1: PROCESS TECHNOLOGY

.

.

Micron Ex. 1042, p. 3 Micron v. YMTC IPR2025-00119

SILICON PROCESSING FOR THE VLSI ERA

VOLUME 1:

PROCESS TECHNOLOGY

STANLEY WOLF Ph.D.

Professor, Department of Electrical Engineering California State University, Long Beach Long Beach, California and Instructor, Engineering Extension, University of California, Irvine

RICHARD N. TAUBER Ph.D.

Manager of VLSI Fabrication TRW - Microelectronics Center Redondo Beach, California and Instructor, Engineering Extension, University of California, Irvine

LATTICE PRESS

Sunset Beach, California

Micron Ex. 1042, p. 4 Micron v. YMTC IPR2025-00119

DISCLAIMER

This publication is based on sources and information believed to be reliable, but the authors and Lattice Press disclaim any warranty or liability based on or relating to the contents of this publication.

Published by:

Lattice Press Post Office Box 340 Sunset Beach, California 90742, U.S.A.

Cover design by Roy Montibon and Donald Strout, Visionary Art Resources, Inc., Santa Ana, CA.

Copyright © 1986 by Lattice Press

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system without written permission from the publisher, except for the inclusion of brief quotations in a review.

Library of Congress Cataloging in Publication Data Wolf, Stanley and Tauber, Richard N.

Silicon Processing for the VLSI Era Volume 1 : Process Technology

Includes Index 1. Integrated circuits-Very large scale integration. 2. Silicon. I. Title

86-081923

ISBN 0-961672-3-7

11 12 13 14 15

PRINTED IN THE UNITED STATES OF AMERICA

Micron Ex. 1042, p. 5 Micron v. YMTC IPR2025-00119 To my wife, Carrol Ann, and my children, Jennifer Laura and Stanley Charles Ross

Stanley Wolf

To my wife, Barbara

Richard N. Tauber

•

.

_

Micron Ex. 1042, p. 6 Micron v. YMTC IPR2025-00119

PREFACE

SILICON PROCESSING FOR THE VLSI ERA is a text designed to provide a comprehensive and up-to-date treatment of this important and rapidly changing field. The text will consist of two volumes of which this book is the first, subtitled, *Process Technology*. Volume 2, subtitled, *Manufacturing Technology* is scheduled for publication in 1988. In this first volume, the individual processes utilized in the fabrication of silicon VLSI circuits are covered in depth (e.g. epitaxial growth, chemical vapor and physical vapor deposition of amorphous and polycrystalline films, thermal oxidation of silicon, diffusion, ion implantation, microlithography, and etching processes). In addition, chapters are also provided on technical subjects that are common to many of the individual processes, such as vacuum technology, properties of thin films, material characterization for VLSI, and the structured design of experiments for process optimization. The topics covered in the book are listed in more detail in the Table of Contents. In Volume 2, *Manufacturing Technology*, other issues related to VLSI fabrication such as process integration, process simulation, manufacturing yield, VLSI manufacturing facilities, assembly, packaging, and testing will be covered.

The purpose of writing this text was to provide professionals involved in the microelectronics industry with a single source that offers a complete overview of the technology associated with the manufacture of silicon integrated circuits. Other texts on the subject are available only in the form of specialized books (i.e. that treat just a small subset of all of the processes), or in the form of edited volumes (i.e. books in which a group of authors each contributes a small portion of the contents). Such edited volumes typically suffer from a lack of unity in the presented material from chapter-to-chapter, as well as an unevenness in writing style and level of presentation. In addition, in multi-disciplinary fields, such as microelectronic fabrication, it is difficult for most readers to follow technical arguments in such books, especially if the information is presented without defining each technical "buzzword" as it is first introduced. In our book we hope to overcome such drawbacks by treating the subject of VLSI fabrication from a unified and more pedagogical viewpoint, and by being careful to define technical terms when they are first used. The result is intended to be a *user friendly* book for workers who have come to the semiconductor industry after having been trained in but one of the many traditional technical disciplines.

An important technical breakthrough has occurred in publishing, that the authors also felt could be exploited in creating a unique book on silicon processing. That is, revolutionary electronic publishing techniques have recently become available, which can cut the time required to produce a published book from a finished manuscript. This task traditionally took 15-18 months, but can be now reduced to less than 4 months. If *traditional* techniques are used to produce books in such fast-breaking fields as VLSI fabrication, these books automatically possess a built-in obsolescence, even upon being first published. The authors took advantage of the *rapid production techniques*, and were able to successfully meet the reduced production-time schedule. As a result, they were able to include information contained in technical journals

Micron Ex. 1042, p. 7 Micron v. YMTC IPR2025-00119

PREFACE

and conferences which was available within four months of the book's publication date. Earlier books written on silicon processing, unfortunately, suffer from having had to undergo an 15-18 month production cycle. This is the first book on the subject in which such time-delay effects have been eliminated from the production process!

Written for the professional, the book belongs on the bookshelf of workers in several microelectronic disciplines. *Microelectronic fabrication engineers* who seek to develop a more complete perspective of the subject, or who are new to the field, will find it invaluable. *Integrated circuit designers, test engineers*, and *integrated circuit equipment designers*, who must understand VLSI processing issues to effectively interface with the fabrication environment, will also find it a uniquely useful reference. The book should also be very suitable as a text for graduate-level courses on silicon processing techniques, offered to students of electrical engineering, applied physics, and materials science. It is assumed that such students already possess a basic familiarity with semiconductor device physics. Problems are included at the end of each chapter to assist readers in gauging how well they have assimilated the material in the text.

The book is an outgrowth of an intensive seminar conducted by the authors through the Engineering Extension of the University of California, Irvine. In the first three years that it was offered, over three hundred engineers and managers from more than 75 companies and government agencies, enrolled in the course. Its fine reputation is attested to by the fact that many firms have sent participants each time the course has been offered, presumably based on the recommendations of earlier enrollees.

In setting out to create a comprehensive text on VLSI fabrication, the authors each contributed a set of unique and complementary skills to the project. Professor Wolf's proficiency as a teacher and writer were utilized to produce a clearly written and logically organized book. Some of this expertise was gained in authoring an earlier best-selling text *Electronic Measurements and Laboratory Practice*, Prentice-Hall, 1983. Dr. Tauber brought a technical expertise acquired from his long involvement in the semiconductor industry. He used this background to insure that the most important topics of VLSI fabrication were addressed, and that the information was up-to-date and presented in a technically correct fashion. Note that for over twenty years, Dr. Tauber has held positions at Bell Telephone Laboratories, Xerox, And Hughes Aircraft Company. Currently he directs advanced VLSI Fabrication efforts at the Microelectronics Center of TRW. The labor of the writing effort was divided between the authors in the following manner: Professor Wolf was responsible for writing Chapters 1, 2, 3, 9, 10, 12, 13, 15, 16, 17, and 18, and Dr. Tauber undertook the writing of Chapters 4, 5, 7, 8, 11, and 14. Material for Chap. 6 was jointly contributed by Andrew R. Coulson and Dr. Tauber.

A book of this length and diversity would not have been possible without the indirect and direct assistance of many other workers. To begin with, virtually all of the information presented in this text is based on the research efforts of a countless number of scientists and engineers. Their contributions are recognized to a small degree by citing some of their articles in the references given at the end of each chapter. The direct help came in a variety of forms, and was generously provided by many people. The text is a much better work as a result of this aid, and the authors express heartfelt thanks to those who gave of their time, energy, and intellect.

Each of the chapters was reviewed after the writing was completed. The engineers and scientists who participated in this review were numerous. Special thanks are given to Leonard Braun and Ethelyn Motley, who provided extensive and incisive editing services. We also thank Warren Flack, Stephen Franz, Kenneth Tokunaga, Dean Denison, Simon Prussin, and Vitus Matare for their critical reviews. Simon Prussin also provided clarification of many concepts during the course of numerous technical discussions with the authors, and can be rightly considered as being the technical underpining of Chapters 1, 2, 8, and 9. Extra thanks are also

extended to Mark Miscione for bringing valuable technical input on the subject of the physics of microlithography, to Susan Curry for donating SEM photographs, and to Andrew Coulson for creating some of the drawings. Ada Mae Hardeman, of the Engineering Extension of the University of California, Irvine is owed special thanks for helping to make a success of the seminar from which this book grew. Otto Gruneberg, of QBI, Inc. was also a benefactor of the project. He graciously agreed to share his exhibition space with Lattice Press at Semicon-West, 1986, where the book made its debut.

Superlative computer support and access to computer resources was generously made available by Donald E. Carlile, Harry T. Hayes, and Dale Lambertson of the Personal Computer Support Section of the Electronic Systems Group of TRW. Henry Nicholas was a computer expert and friend who lit the fire of inspiration that led to the undertaking of the project. The management of the Electronics Systems Group and the Microelectronics Center of TRW, including most notably Dr. Barry Dunbridge and Phillip Reid, are warmly thanked for providing a supportive environment, conducive to producing such an intensive technical project. They made available technical literature and other resources to the authors, especially S. Wolf, who was able to avail himself of this generosity while writing during a Sabbatical leave from his teaching duties at California State University, Long Beach. Roy Montibon and Donald Strout of Visionary Art Resources, Inc., Santa Ana, CA designed the cover. Finally, we wish to thank Shirley Rome, Carrol Ann Wolf, and Barbara Tauber for typing the manuscript.

Stanley Wolf and Richard N. Tauber

P.S. Additional copies of the book can be obtained from:

Lattice Press, P.O. Box 340-V Sunset Beach, CA, 90742

An order form, for your convenience, is provided on the final leaf of the book.

PREFACE	v ii
PROLOGUE	xxi
1. SILICON: SINGLE-CRYSTAL GROWTH AND WAFERING	ř 1
 TERMINOLOGY OF CRYSTAL STRUCTURE, 1 MANUFACTURE OF SINGLE-CRYSTAL SILICON, 5 From Raw Material to Electronic Grade Polysilicon CZOCHRALSKI (CZ) CRYSTAL GROWTH, 8 Czochralski Crystal Growth Sequence Incorporation of Impurities into the Crystal (Normal Freezing) Modifications Encountered to Normal Freezing in CZ Growth Czochralski Silicon Growing Equipment Analysis of Czochralski Silicon in Ingot Form Measuring Oxygen and Carbon in Silicon Using Infrared Absorbance Spectroscopy FLOAT-ZONE SINGLE-CRYSTAL SILICON, 21 FROM INGOT TO FINISHED WAFER: SLICING; ETCHING; POLISHING, 2: SPECIFICATIONS OF SILICON WAFERS FOR VLSI, 26 TRENDS IN SILICON CRYSTAL GROWTH AND VLSI WAFERS, 30 	3
 2. CRYSTALLINE DEFECTS, THERMAL PROCESSING, AND GETTERING CRYSTALLINE DEFECTS IN SILICON, 37 Point Defects One-Dimensional Defects (Dislocations) Area Defects (Stacking Faults) Bulk Defects and Precipitation INFLUENCE OF DEFECTS ON DEVICE PROPERTIES, 51 Leakage Currents in pn Junctions Collector-Emitter Leakage in Bipolar Transistors Minority Carrier Lifetimes Gate Oxide Quality Threshold Voltage Control Wafer Resistance to Warpage 	36

xi

- CHARACTERIZATION OF CRYSTAL DEFECTS, 55

- THERMAL PROCESSING, 56 Rapid Thermal Processing (RTP)
- OXYGEN IN SILICON, 59
- GETTERING, 61 Basic Gettering Pinciples Extrinsic Gettering Intrinsic Gettering

3. VACUUM TECHNOLOGY FOR VLSI APPLICATIONS

- FUNDAMENTAL CONCEPTS OF GASES AND VACUUMS, 73 Pressure Units
 - Pressure Comms Pressure Ranges Mean Free Path and Gas Flow Regimes
- LANGUAGE OF GAS /SOLID INTERACTIONS, 77
- TERMINOLOGY OF VACUUM PRODUCTION AND PUMPS, 78
- ROUGHING PUMPS, 85
 - Oil-Sealed Rotary Mechanical Pumps Pump Oils

Roots Pumps

- HIGH VACUUM PUMPS I: DIFFUSION PUMPS, 89
- HIGH VACUUM PUMPS II: CRYOGENIC PUMPS, 92
- HIGH VACUUM PUMPS III: TURBOMOLECULAR PUMPS, 95
- SPECIFICATION OF VACUUM PUMPS FOR VLSI, 97
- TOTAL PRESSURE MEASUREMENT, 97
- MEASUREMENTS OF PARTIAL PRESSURE: Residual Gas Analyzers, 101 Operation of Residual Gas Analyzers (RGA) RGAs and Non-High Vacuum Applications: Differential Pumping Interpretation of RGA Spectra RGA Specification List

 HIGH GAS FLOW VACUUM ENVIRONMENTS IN VLSI PROCESSING, 104 Medium and Low-Vacuum Systems Throttled High-Vacuum Systems

4. BASICS OF THIN FILMS

109

73

- THIN FILM GROWTH, 110
- STRUCTURE OF THIN FILMS, 111
- MECHANICAL PROPERTIES OF THIN FILMS, 113 Adhesion Stress in Thin Films

Other Mechanical Properties

- ELECTRICAL PROPERTIES OF METALLIC THIN FILMS, 118 Electrical Transport in Thin Films

5. SILICON EPITAXIAL FILM GROWTH	124
 SILICON EPITAXIAL FILM GROWTH FUNDAMENTALS OF EPITAXIAL DEPOSITION, 125 The Grove Epitaxial Model Gas Phase Mass Transfer Atomistic Model Of Epitaxial Growth CHEMICAL REACTIONS USED IN SILICON EPITAXY, 133 DOPING OF EPITAXIAL FILMS, 136 Intentional Doping Autodoping and Solid-State Diffusion DEFECTS IN EPITAXIAL FILMS, 139 Defects Induced During Epitaxial Deposition and their Nucleation Mechanisms Techniques for Reducing Defects in Epitaxial Films PROCESS CONSIDERATIONS FOR EPITAXIAL DEPOSITION, 142 Pattern Shift, Distortion, and Washout EPITAXIAL DEPOSITION EQUIPMENT, 145 CHARACTERIZATION OF EPITAXIAL FILMS, 147 Optical Inspection of Epitaxial Films Electrical Characterization Epitaxial Film Thickness Measurements Infrared Reflectance Measurement Techniques 	124
- SILICON ON INSULATORS, 151 Silicon on Sapphire Silicon on Other Insulators MOLECIII AR BEAM EPITAXY OF SILICON 156	
6. CHEMICAL VAPOR DEPOSITION OF AMORPHOUS AND POLYCRYSTALLINE FILMS	161
 BASIC ASPECTS OF CHEMICAL VAPOR DEPOSITION, 162 CHEMICAL VAPOR DEPOSITION SYSTEMS, 164 Components of Generic CVD Systems Terminology of CVD Reactor Design Atmospheric Pressure CVD Reactors Low-Pressure CVD Reactors 	
 Plasma-Enhanced CVD: Physics; Chemistry; and Reactor Configurations Photon-Induced CVD Reactors POLYCRYSTALLINE SILICON: PROPERTIES AND CVD DEPOSITION, 175 Properties of Polysilicon Films CVD of Polysilicon Dening Tachniques for Polysilicon 	
Oxidation of Polysilicon - PROPERTIES AND DEPOSITION OF CVD SiO ₂ FILMS, 182 Chemical Reactions for CVD Formation Step Coverage of CVD SiO ₂ Undoped CVD SiO ₂	

Micron Ex. 1042, p. 12 Micron v. YMTC IPR2025-00119 Phosphosilicate Glass

Borophosphosilicate Glass

- PROPERTIES AND CVD OF SILICON NITRIDE FILMS, 191
- OTHER FILMS DEPOSITED BY CVD (OXYNITRIDES and SIPOS), 195

7. THERMAL OXIDATION OF SINGLE-CRYSTAL SILICON 198

- PROPERTIES OF SILICA GLASS, 199
- OXIDATION KINETICS, 200
- The Linear-Parabolic Model - THE INITIAL OXIDATION STAGE, 207
 - Growth of Thin Oxides
- THERMAL NITRIDATION OF SILICON AND SiO₂, 210
- FACTORS WHICH AFFECT THE OXIDATION RATE, 211
 Oxidation Growth Rates: Crystal Orientation Dependence
 Oxidation Growth Rates: Dopant Effects
 Oxidation Growth Rates: Water (H₂O) Dependence
 Oxidation Growth Rates: Chlorine Dependence
 Oxidation growth Rates: Pressure Effects
 Oxidation Growth Rates: Plasma and Photon Effects
- MASKING PROPERTIES OF THERMALLY GROWN SiO₂, 219
- PROPERTIES OF THE Si /SiO₂ INTERFACE AND OXIDE TRAPS, 220 Interface Trap Charge Fixed Oxide Charge Mobile Ionic Charge Oxide Trapped Charge
 - Nature of the Si /SiO₂ Interface
- STRESS IN SiO₂, $2\overline{2}8$
- DOPANT IMPURITY REDISTRIBUTION DURING OXIDATION, 228
- OXIDATION SYSTEMS, 230
 - Horizontal Furnaces Suspended Loading Systems Vertical Furnaces
- MEASUREMENT OF OXIDE THICKNESS, 234

8. DIFFUSION IN SILICON

242

MATHEMATICS OF DIFFUSION, 242
 Ficks First Law
 Ficks Second Law
 Solutions to Ficks Second Law
 Concentration Dependence of the Diffusion Coefficient

 TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT, 250
 DIFFUSION CONSTANTS OF THE SUBSTITUTIONAL
 IMPURITIES: B; As; and P, 251
 Arsenic Diffusion

Boron Diffusion Phosphorus Diffusion **ATOMISTIC MODELS OF DIFFUSION IN SILICON, 256** The Vacancy Model The Vacancy-Interstitial Model - DIFFUSION IN POLYCRYSTALLINE SILICON, 261 - DIFFUSION IN SiO₂, 262 - ANOMALOUS DIFFUSION EFFECTS IN SILICON, 262 Emitter Push Effect Lateral Diffusion Under Oxide Windows Diffusion in an Oxidizing Ambient DIFFUSION SYSTEMS AND DIFFUSION SOURCES, 264 Gaseous Sources Liquid Sources Solid Sources - MEASUREMENT TECHNIQUES FOR DIFFUSED LAYERS, 267 Sheet Resistivity Measurements Junction Depth Measurements Doping Profile Measurements

9. ION IMPLANTATION FOR VLSI

- ADVANTAGES (AND PROBLEMS) OF ION-IMPLANTATION, 282

IMPURITY PROFILES OF IMPLANTED IONS, 283
 Definitions Associated with Ion Implantation Profiles
 Theory of Ion Stopping
 Models for Predicting Implantation Profiles in Amorphous Solids
 Implanting into Single-Crystal Materials: Channeling
 Boltzmann Transport Equation and Monte-Carlo Approaches to Calculating Profiles

 ION IMPLANTATION DAMAGE AND DAMAGE ANNEALING IN SILICON, 295
 Implantation Damage in Silicon
 Electrical Activation and Implantation Damage Annealing

- ION IMPLANTATION EQUIPMENT, 309

Components of an Ion Implantation System Ion Implanter Types Ion Implantation Equipment Limitations Ion Implantation Safety Considerations

- CHARACTERIZATION OF ION IMPLANTATIONS, 318 Measurement of Implantation Dose and Dose Uniformity Measurement of Implantation Depth Profiles

Measurement of Implantation Depin Projects Measurement of Implantation Damage and Damage Annealing Efficacy - ION IMPLAN TATION PROCESS CONSIDERATIONS, 321

Selecting Masking Layer Material and Thickness Implanting Through Surface Layers Shallow Junction Formation by Ion-Implantation Multiple Implantations 280

Micron Ex. 1042, p. 14 Micron v. YMTC IPR2025-00119

10. ALUMINUM THIN FILMS AND PHYSICAL VAPOR DEPOSITION IN VLSI

- ALUMINUM THIN FILMS IN VLSI, 332

- SPUTTER DEPOSITION OF THIN FILMS FOR VLSI, 335

Properties of Glow-Discharges
Physics of Sputtering
Sputter Deposited Film Growth
Radio-frequency (RF) Sputtering
Magnetron Sputtering
Bias Sputtering
Sputter Deposition Equipment
Commercial Sputtering System Configurations
Process Considerations in Sputter Deposition
Reactive Sputtering
Future Trends in Sputter Deposition
PHYSICAL VAPOR DEPOSITION BY EVAPORATION, 374
Evaporation Basics
Evaporation Methods

Evaporation Methods Evaporation Process Considerations - METAL FILM THICKNESS MEASUREMENT, 380

11. REFRACTORY METALS and THEIR SILICIDES in VLSI 384

- CANDIDATE SILICIDES FOR VLSI APPLICATIONS, 386 Silicide Resistivities
- SILICIDE FORMATION, 388

Direct Metallurgical Reaction Co-Evaporation Sputter Deposition: Co-Sputtering and Sputtering from Composite Targets Chemical Vapor Deposition

- STRESS IN SILICIDES, 394
- OXIDATION OF SILICIDES, 395
- PROCESS INTERACTION, 397
- SELF-ALIGNED SILICIDE (SALICIDE) TECHNOLOGY, 397
- REFRACTORY METAL INTERCONNECTIONS FOR VLSI, 399

Deposition of CVD Tungsten Selective Deposition of Tungsten Properties of CVD Tungsten for VLSI Contacts Future Trends

12. LITHOGRAPHY I: OPTICAL PHOTORESISTS -MATERIAL PROPERTIES AND PROCESS TECHNOLOGY 407

- BASIC PHOTORESIST TERMINOLOGY, 407

Micron Ex. 1042, p. 15 Micron v. YMTC IPR2025-00119

331

xvi

- PHOTORESIST MATERIAL PARAMETERS, 409

Resolution Sensitivity Etch Resistance and Thermal Stability Adhesion Solids Content and Viscosity Particulates and Metals Content Flash Point and TLV Rating Process Latitude, Consistency, and Shelf-Life

- OPTICAL PHOTORESIST MATERIAL TYPES, 418

Postive Optical Photoresists Negative Optical Photoresists Image Reversal of Positive Resist Multilayer Resist Processes Contrast Enhancement Layers Inorganic Resists Dry-Developable Resists Mid-UV and Deep-UV Resists Photosensitive Polyimides

PHOTORESIST PROCESSING, 429
 Resist Processing: Dehydration Baking and Priming
 Resist Processing: Coating
 Resist Processing: Soft-Bake
 Resist Processing: Exposure
 Resist Processing: Development
 Resist Processing: After Develop Inspection and Linewidth Measurement
 Resist Processing: Post Bake and Deep UV Hardening
 PHOTORESIST SELECTION, 454

13. LITHOGRAPHY II: OPTICAL ALIGNERS AND PHOTOMASKS

 OPTICS OF MICROLITHOGRAPHY, 460 Diffraction, Coherence, Numerical Aperture, and Resolution Modulation Transfer Function
 OPTICAL METHODS OF TRANSFERRING PATTERNS TO A WAFER: OPTICAL ALIGNERS, 468 Light Sources and Light Meters for Optical Aligners Contact Printing Proximity Printing Projection Printing: Scanning Aligners and Steppers
 PATTERN REGISTRATION, 473 Automatic Alignment
 MASK AND RETICLE FABRICATION, 476 Glass Quality and Preparation Glass Coating (Chrome) 459

Micron Ex. 1042, p. 16 Micron v. YMTC IPR2025-00119 Mask Imaging (Resist Application and Processing) Pattern Generation (Optical and Electron-Beam) Mask and Reticle Defects and their Repair Pellicles Critical Dimension and Registration Inspection of Masks and Reticles

14. ADVANCED LITHOGRAPHY

 ELECTRON BEAM LITHOGRAPHY, 493 Electron Beam Systems Writing Strategies Electron Scattering in Resists Resist Development Proximity Effects
 X-RAY LITHOGRAPHY, 504 X-Ray Sources X-Ray Masks X-Ray Masks
 ION BEAM LITHOGRAPHY, 510

15. WET PROCESSING: CLEANING; ETCHING; LIFT-OFF 514

- WAFER CLEANING, 516 Sources of Contamination

Wafer Cleaning Procedures

- TERMINOLOGY OF ETCHING, 520

Bias, Tolerance, Etch Rate, and Anisotropy Selectivity, Overetch, and Feature-size Control Determining Required Selectivity with Respect to Substrate, S_{fs} Determining Required Selectivity with Respect to Mask, S_{fm} Loading Effects

- WET ETCHING TECHNOLOGY, 529 Wet Etching Silicon Wet Etching Silicon Dioxide Wet Etching Silicon Nitride Wet Etching Aluminum

- LIFT-OFF TECHNOLOGY FOR PATTERNING, 535

16. DRY ETCHING FOR VLSI

- BASIC PHYSICS AND CHEMISTRY OF PLASMA ETCHING, 542 The Reactive Gas Glow Discharge Electrical Aspects of Glow Discharges

xviii

Micron Ex. 1042, p. 17 Micron v. YMTC IPR2025-00119

539

Heterogeneous (Surface) Reaction Considerations Parameter Control in Plasma Processes - ETCHING SILICON AND SiO₂ in CF₄ /O₂ /H₂, 547 Fluorine-to-Carbon Ratio Model ANISOTROPIC ETCHING AND CONTROL OF EDGE PROFILE, 552 - DRY ETCHING VARIOUS TYPES OF THIN FILMS, 555 Silicon Dioxide (SiO_2) Silicon Nitride Polysilicon Refractory Metal Silicides and Polycides Aluminum and Aluminum Alloys Organic Films PROCESS MONITORING AND END POINT DETECTION, 565 Laser Reflectometry and Laser Reflectance **Optical Emission Spectroscopy** Mass Spectroscopy - DRY ETCHING EQUIPMENT CONFIGURATIONS, 568 Commercial Dry Etch System Configurations Comparison of Single Wafer and Batch Dry Etchers PROCESSING ISSUES RELATED TO DRY ETCHING, 574 Plasma Etching Safety Considerations Uniformity and Reproducibility Considerations Contamination and Damage of Etched Surfaces Process Gases for Dry Etching

17. MATERIAL CHARACTERIZATION TECHNIQUES FOR VLSI FABRICATION

 WHAT ARE WE TRYING TO DETECT, AND HOW IS IT DONE?, 586 Energy Regimes and Energy Levels in Material Characterization Definitions of Material Characterization Terminology Vacuum Requirements of Compositional Analysis
 MICROSCOPY FOR VLSI MORPHOLOGY, 589 Optical Microscopes Scanning Electron Microscopes (SEM) Transmission Electron Microscopy
 ELECTRON /X-RAY COMPOSITIONAL ANALYSIS TECHNIQUES, 599 Auger Emission Spectroscopy X-Ray Emission Spectrocopy X-Ray Photoelectron Spectroscopy (XPS, ESCA) X-Ray Fluorescence

- ION BEAM EXCITED COMPOSITIONAL ANALYSIS, 606 Secondary-Ion Mass Spectroscopy (SIMS) Laser Ion Mass Spectroscopy (LIMS) Rutherford Backscattering Spectroscopy (RBS) 586

- CRYSTALLOGRAPHIC STRUCTURE ANALYSIS, 610 X-Ray Diffraction X-Ray Lang Topography Neutron Activation Analysis (NAA)
- SUMMARY OF CHARACTERIZATION TECHNIQUE CAPABILITIES, 612
- SUGGESTIONS FOR HOW TO ACCOMPLISH AN EFFECTIVE ANALYSIS, 614

18. STRUCTURED APPROACH to DESIGN of EXPERIMENTS FOR PROCESS OPTIMIZATION 618

- FUNDAMENTALS OF STATISTICS, 619

Samples, Populations, Means, Variance, and Standard Deviation Pooled Variance and Degrees of Freedom Normal Distributions Distributions of Averages, t-Distributions, and Confidence Levels

- DESIGN OF EXPERIMENTS: BASIC DEFINITIONS, 625
- CHARACTERISTICS OF FACTORIAL EXPERIMENTS, 627
- STRATEGY OF DESIGNING EXPERIMENTS, 632
- DESIGNING and ANALYZING 2-LEVEL FULL-FACTORIAL EXPERIMENTS, 634 Method for Designing 2-Level Full-Factorial Experiments Analysis of the Measured Data
- SCREENING EXPERIMENTS, 641
- RESPONSE SURFACES, 643

APPENDICES

1. MATERIAL PROPERTIES OF SILICON at 300°K	647
2. PHYSICAL CONSTANTS	648
3. ARRHENIUS RELATIONSHIP	649
DEX	651

INDEX

XX

DRY ETCHING for VLSI FABRICATION

In Chapter 15 the procedure of transferring patterns onto regions of silicon wafers by wet etching was described. Wet etching was the standard pattern transfer technique in the process sequences used to fabricate early generations of integrated circuits. Its widespread use stemmed from the facts that the technology of wet etching was well established, and that liquid etchant systems are available with very high *selectivity* to both substrate and the masking layer (defined in Chap. 15). As noted in Chap. 15, however, wet etching processes are typically isotropic. Therefore, if the thickness of the film being etched is comparable to the minimum pattern dimension, undercutting due to isotropic etching, becomes intolerable (Fig. 1a & b). Since many films used in VLSI fabrication are 0.5-1.0 μ m thick, reproducible and controllable transfer of patterns in the 1-2 μ m range becomes difficult if not impossible with wet etching. Alternative pattern transfer processes must therefore be employed to fabricate devices with such dimensions.

One alternative pattern transfer method that offers the capability of non-isotropic (or *anisotropic*) etching is "dry" etching. As a result, considerable effort has been expended to develop dry etch processes as replacements for wet etch processes. Dry etching also offers the important manufacturing advantage of eliminating the handling, consumption, and disposal of the relatively large quantities of dangerous acids and solvents used in wet etching and resist stripping processes. Dry etching and resist stripping operations utilize comparatively small amounts of chemicals (although, as will be discussed later, some of these may still be quite toxic or corrosive). This chapter deals with the technology of dry etch processes for VLSI fabrication, although many of the terms generic to both wet and dry etching are defined in Chap. 15.

Before launching into a description of the details of dry etching, it is worthwhile to identify the characteristics that a useful etching process should exhibit. This approach helps to define the problems that must be overcome when developing adequate dry etch processes, and shows why some types of dry etch processes may not be suitable for all VLSI applications.

The overall goal of an etch process for VLSI fabrication is to be able to reproduce the features on the mask with fidelity. This should be achievable together with control of the following aspects of etched features: a) the slope of the feature sidewalls (e.g. the slope of the sidewalls of the etched feature should have the desired specific angle, in some cases vertical, Fig. 1c - f); and b) the degree of undercutting (i.e. usually the less undercutting the better). In addition to this capability, a useful etch process should have the following characteristics:

- 1) It should be highly selective against etching the mask layer material;
- 2) It should be highly selective against etching the material under the film being etched;
- The etch rate should be rapid, or the throughput of a machine performing the etch should be suitably high;
 5.39

Micron Ex. 1042, p. 20 Micron v. YMTC IPR2025-00119 540 SILICON PROCESSING FOR THE VLSI ERA



Fig. 1 (a) and (b) Isotropic etching of narrow and deep grooves. (a) shows the desired pattern and (b) shows how the mask must be dimensioned in order to obtain a pattern which resembles the desired pattern. (c) - (f) SEM micrographs show the results of highly anisotropic etching for several materials. (c) Anisotropically etched contact hole in an SiO₂ layer over Si. (d) Anisotropically etched poly-Si film over SiO₂. (e) 1 μ m-wide features in single-crystal Si. (f) Anisotropically etched 1.5 μ m thick Al-0.7% Cu film, with an SiO₂ substrate³³. Copyright 1983, Bell Telephone Laboratories, reprinted with permission.

- 4) The etching should be uniform across the entire wafer, from wafer-to-wafer, and from run-to-run;
- 5) The process should be safe;
- 6) The etch process should cause minimal damage to substrates;
- 7) The etch mask material should be easily removable after the etching is completed;
- 8) The process should be clean (i.e. low incidence of particulate and film contamination);
- 9) The process should be conducive to full automation.

As shown in Fig. 2 there is a variety of dry etch process types. This figure also indicates that the mechanism of etching in each type of process can have a physical basis (e.g.

Micron Ex. 1042, p. 21 Micron v. YMTC IPR2025-00119 glow-discharge sputtering [Chap. 10], or ion milling), a chemical basis (e.g. plasma etching), or a combination of the two (e.g. reactive ion etching, RIE, and reactive ion beam etching, RIBE).

In processes that rely predominantly on the physical mechanism of sputtering (including RIBE), the strongly directional nature of the incident energetic ions allows substrate material to be removed in a highly anisotropic manner (i.e. essentially vertical etch profiles are produced). Unfortunately, such material removal mechanisms are also quite non-selective against both masking material and materials underlying the layers being etched. That is, the selectivity depends largely on sputter yield differences between materials. Since the sputter yields for most materials are within a factor of three of each other, selectivities are typically not adequate. Furthermore, since the ejected species are not inherently volatile, redeposition and trenching (see Chap. 10) can occur. Another major problem of pattern transfer by physical sputtering involves the redeposition of nonvolatile species on the sidewalls of the etched feature⁷. As a result of these drawbacks, dry etch processes for pattern transfer based on physical removal mechanisms have not found wide use in VLSI fabrication applications.

On the other hand, dry processes relying strictly on chemical mechanisms for etching can exhibit very high selectivities against both mask and underlying substrate layers. Such purely chemical etching mechanisms, however, typically etch in an isotropic fashion. Although some applications in VLSI fabrication (e.g. photoresist stripping in oxygen plasmas) utilize such processes, the problem of undercutting associated with isotropic etching is not solved by them.

By adding a physical component to a purely chemical etching mechanism, however, the shortcomings of both sputter-based and purely-chemical dry etching processes can be surmounted. Dry etch processes based on a combination of physical and chemical mechanisms offer the



Fig. 2 The dry-etching spectrum.



Fig. 3 Primary processes occurring in a plasma etch process. Reprinted with permission of Ref. 1, Copyright, 1983, the American Chemical Society.

potential of controlled anisotropic etching, together with adequate selectivity.

In this chapter we primarily focus on *plasma etching processes* (i.e. purely chemical) and *reactive ion etching (RIE) processes* (i.e. physical /chemical processes, which are more aptly described as *ion-assisted etching processes*). Even though purely chemical processes find less application than RIE for VLSI pattern transfer, an understanding of RIE processes is facilitated if the mechanisms which underlie plasma etching processes are understood first. Sputter-based etching processes receive little attention here, as their use for pattern transfer in VLSI production is limited, and substantial information on sputtering processes is presented in Chap. 10.

BASIC PHYSICS and CHEMISTRY of PLASMA ETCHING

The basic concept of plasma etching is rather direct. A glow discharge is utilized to produce chemically reactive species (atoms, radicals, and ions) from a relatively inert molecular gas. The etching gas is selected so as to generate species which react chemically with the material to be etched, and whose reaction product with the etched material is volatile. An ideal dry etch process based solely on chemical mechanisms for material removal, can thus be broken down into six steps, as shown in Fig. 3. These steps are listed as: 1) reactive species are generated in a plasma; 2) these species diffuse to the surface of the material being etched; 3) the species are adsorbed on the surface; 4) a chemical reaction occurs, with the formation of a volatile by-product; 5) the by-product is desorbed from the surface; and 6) the desorbed species diffuse into the bulk of the gas¹. If any of these steps fails to occur, the overall etch cycle ceases. Product desorption is the most important step. Many reactive species can react rapidly with a solid surface, but unless the product has a reasonable vapor pressure so that desorption occurs, no etching takes place. Steps 1, 2, and 6 involve events occurring in the gas phase and plasma, while steps 3, 4, and 5 are steps that take place at the surface of the solid layer being etched.

Micron Ex. 1042, p. 23 Micron v. YMTC IPR2025-00119 Hence, it is useful to briefly consider the physics and chemistry of events that involve the etching process that occur in a) the plasma, and b) the etched surface.

The Reactive Gas Glow Discharge

In Chap. 10, the methods for producing a glow-discharge using a dc diode and an rf diode configuration are described. In plasma-etching processes an rf diode configuration is normally used to establish the glow discharge, for the reasons listed in Chap. 10. The glow discharge in Chap. 10 was treated primarily as a source of energetic ions which are used to bombard target surfaces and cause sputtering. In plasma etching applications the glow discharge can be used to produce energetic ionic bombardment of the etched surface, but it also has another even more important role, that of producing reactive species for chemically etching the surfaces of interest. Thus, it is necessary to examine the properties of glow discharges related to this function.

Since plasmas consisting of fluorine-containing gases are extensively used for etching Si, SiO₂, and other materials used in VLSI fabrication, it is appropriate to study the glow discharge of CF₄ gas as an example. Before a glow discharge is established, the only species present are CF₄ molecules. Over the pressure range at which an rf glow discharge can be maintained, 1 Pa (7.5 mtorr) - 750 Pa (5.6 torr), the gas density ranges from 2.7×10^{14} - 2×10^{17} molecules /cm³. When a glow-discharge exists, some fraction of the CF₄ molecules are dissociated into other species. As will be described in a later section dealing with the *utilization factor*, it is better to have a CF₄ flow rate that is much larger than the dissociation rate. For moderately sized etching systems this represents a flow rate of $\geq 10 \text{ sccm}^2$.

A plasma is defined to be a partially ionized gas composed of ions, electrons, and a variety of neutral species. A glow discharge is a plasma that exists in the pressure range given above, containing approximately equal concentrations of positive particles (positive ions) and negative particles (electrons and negative ions). The density of these charged particles in glow discharges ranges from 10^9 - 10^{11} /cm³, and the fraction of ions-to-neutral species is thus ~ 10^{-4} - 10^{-6} . The average energies of electrons in glow discharges is between 1-10 eV. The reactions that occur in the gas phase (plasma) are called *homogeneous* reactions, while those that occur at the surface are termed *heterogeneous* reactions. Table 1 lists the general types of homogeneous electron-impact

Table 1. HOMOGENEOUS REACTIONS (ELECTRON-IMPACT) and HETEROGENEOUS REACTIONS THAT OCCUR IN PLASMAS

<u>Homogeneous Reactions -</u> Electron Impact Reactions	•	<u>Heterogeneous Reactions</u>
Excitation (rotational, vibrational) $e + A_2 \Rightarrow A_2 + e$ (e (1) Dissociation: $e + A_2 \Rightarrow A + A + e$ (e Ionization: $e + A_2 \Rightarrow A_2^+ + 2e$ (e Dissociative Ionization: $e + A_2 \Rightarrow A^+ + A + 2e$ (e Dissociative Attachment: $e + A_2 \Rightarrow A^+ + A^- + e$	al, electronic): + F \Rightarrow F* + e) F* \Rightarrow F + hv _F) + O ₂ \Rightarrow O + O + e) O ₂ \Rightarrow O ₂ ⁺ + 2e) + O ₂ \Rightarrow O ⁺ + O + 2e)	Atom Recombination: $S - A + A \Rightarrow S + A_2$ Metastable deexcitation: $S + M^* \Rightarrow S + M$ Atom abstraction (etching): $S - B + A \Rightarrow S^+ + AB$ Sputtering (etching): $S - B + M^+ \Rightarrow S^+ + B + M$

Micron Ex. 1042, p. 24 Micron v. YMTC IPR2025-00119 reactions and heterogeneous surface-plasma reactions that can take place.

The properties listed above, impart glow discharges with unique and useful capabilities. The first ionization potential of most gas atoms and molecules is $\geq 8 \text{ eV}$. Since the energies of the plasma electrons have a distribution whose *average* is between 1-10 eV, some of these electrons will be energetic enough to cause such ionization. Collisions of these energetic electrons with neutral etch gas molecules (Table 1), in fact, are primarily responsible for the production of the reactive species in a plasma (*electron-impact reactions*). These reactive species, however, can also react with themselves in the plasma (*inelastic collisions among heavy particles*, Table 1), and alter the overall plasma chemistry.

The most abundant *ionic specie* found in CF_4 plasmas is CF_3^+ , and such ions are formed by the electron-impact reaction³: $e + CF_4 \Rightarrow CF_3^+ + F + 2e$. Other ionization reactions also occur, but the products of these reactions are found in less abundance than CF_3^+ ions, because the probability that such reactions occur is smaller, and their products also react with CF_4 , while CF_3^+ ions do not. In addition to CF_4 molecules, ionic species, and electrons, there are a large number of radicals that are formed. A radical is an atom, or collection of atoms, which is electrically neutral, but which also exists in a state of incomplete chemical bonding, making it very reactive. Some examples of radicals include F, Cl, O, H, and CF_y , where x = 1, 2, or 3. In CF_4 plasmas, the most abundant radicals are CF_3 and F, formed by the reaction: $e + CF_4 \Rightarrow CF_3 + F + e$. In general, radicals are thought to exist in plasmas in much higher concentrations than ions, because they are generated at a faster rate, and they survive longer than ions in the plasma. This view is substantiated by measurements of radical concentrations in plasmas, but in fact, only a few such measurements have been reported. One measurement determined that the F atom pressure was 20 percent of the total gas pressure in the system⁴. To summarize, the gas in an etch chamber when plasma etching is underway, generally consists of the following species⁵ (in order of decreasing concentration, and estimated concentration ranges): a) etch gas molecules (70-98% of the total species in the chamber); b) etch-product molecules (2-20%); c) radicals 0.1-20%); charged species, including positive ions, electrons, and negative ions (0.001-0.01%).

The radicals, in fact, are responsible for most of the actual chemical etching phenomena that occur at the surface of the material being etched (except for the etching of Al, which is apparently etched by molecular Cl_2). As will be described later, the ionic species are believed primarily to enhance the etching that occurs, by causing events that are not in them- selves chemical reactions. Thus, the term *reactive ion etching*, that is commonly used to denote processes in which plasma etching is accompanied by ionic bombardment, is actually somewhat of a misnomer. Since the etching by the reactive radicals is principally *enhanced* by the ionic bombardment, these processes would more aptly be described as *ion-assisted etching processes*.

Electrical Aspects of Glow Discharges

It is important to have some information about the electrical potential distribution in systems containing glow discharges. In Chap. 10, details about this subject were given for both dc and rf diode glow discharges, and the information was used to explain how glow discharge sputtering occurs. In plasma etching systems, high frequency (13.5 MHz) rf diode configurations are primarily used, and readers are directed to Chap. 10 for more general information on rf glow discharges. In plasma etching systems, knowledge about the potential distribution is useful because the energy with which particles impinge on the etched surface depends on the potential distribution. In addition, the plasma potential determines the energy with which ions strike other surfaces in the chamber, and high energy bombardment of these surfaces can cause sputtering and consequent redeposition of the sputtered material (as contamination on the wafers).



Fig. 4 (a) Schematic view of an rf glow discharge. (b) Potential distribution in a parallel plate plasma etcher with a grounded surface area larger than the powered electrode area.

As shown in Fig. 4 the potential of the plasma is positive relative to that of the grounded electrode (which is usually connected electrically to the chamber walls, grounding them as well), and the powered electrode develops a negative dc self-bias voltage relative to ground, as described in Chap. 10^6 . The magnitude of the self-bias voltage depends on the amplitude of the rf signal applied to the electrodes. As also noted in Chap. 10, if the electrodes of the rf plasma system are of comparable area, the potential difference across the dark space of both electrodes will be equal. Since the powered electrode develops a negative dc self-bias voltage, in order for a potential difference of equal magnitude to exist across the dark space of the grounded electrode, the plasma must assume a positive potential of comparable magnitude. Thus, even if wafers are placed on the grounded electrode of such systems, they will be subjected to substantial energetic ion bombardment. In systems in which the area of the powered electrode is much smaller than that of the grounded electrode, smaller potential differences exist between the plasma and the grounded electrode, and thus grounded surfaces are subjected to less energetic bombardment.

If a 13.56 MHz frequency is used for the applied rf power, this frequency is high enough so that the ions require several rf cycles to traverse the dark space between the bulk plasma region and the wafer surface. Some investigation of systems using lower frequency power has also been conducted (100-450 kHz). Under such circumstances, the ions can cross the dark space in a relatively small fraction of an rf cycle. This can enable ions to strike the surface with greater energies than in the high frequency case, a condition that can be useful in some applications.

Heterogeneous (Surface) Reaction Considerations

The reactive etch species that undergo chemical reactions at the surface that result in etching, and the ionic species that bombard the surface to enhance such etching are produced in the plasma. The events that take place at the surface are interactions between the gas phase species and the solid material to produce etching. The issues related to the mechanisms that occur on the surface include³²: a) the sticking probabilities of radicals and ions; b) chemical recombination processes that form films, cause species to be adsorbed, or lead to other gas phase species; c) reaction paths which are followed, from adsorption to the eventual formation of volatile products; d) desorption of species from the surface; e) effect of ion and electron fluxes on the surface; and f) the synergistic effects on the surface of of multiple species bombardment (i.e. by ions, electrons, and photons). As shown in Fig. 5, some of the parameters that impact heterogeneous reactions⁸, include the surface temperature, the surface electrical potential, the nature of the surface, and

SOLID	ETCH GAS	ETCH PRODUCT
Si, SiO ₂ , Si ₃ N ₄	CF ₄ , SF ₆ , NF ₃	SiF ₄
Si	Cl_2, CCl_2F_2	SiCl ₂ , SiCl ₄
Al	BCI_3 , CCI_4 , $SiCI_4$, CI_2	$A1Cl_3, Al_2Cl_6$
Organic Solids	ŏ ₂	CO, CO_2, H_20
	$O_2 + CF_4$	$CO, CO_2, H\overline{F}$
Refractory Metals (W, Ta, Mo)	CF ₄	wf ₆ ,

Table 2 EXAMPLES OF SOLID-GAS SYSTEMS USED IN PLASMA ETCHING

geometrical aspects of the surface (e.g. the angle of incidence of impinging ions depends upon whether they are striking the bottom, or the sidewall of an etched feature).

The gases adopted for plasma etching processes have been selected on the basis of their ability to form reactive species in a plasma, which then react with the surface materials being etched and lead to volatile products. Table 2 lists the gas-solid systems for various solids to be etched in VLSI fabrication, together with their resultant etch products.

Parameter Control in Plasma Processes

One of the more challenging aspects of implementing a useful and reproducible etch process



Fig. 5 Representation of the parameter problem in plasma etching systems (n_e is the electron density, f (E) is the electron energy distribution function, N is the gas density, and τ is the residence time⁸. Reprinted with permission of Springer-Verlag Publishing Company.

Micron Ex. 1042, p. 27 Micron v. YMTC IPR2025-00119 involves the control of the large number of parameters that affect the process. Figure 5 illustrates some of the parameters that impact the gas-phase interactions, as well as the surface-plasma interactions. Although many macroscopic parameters can be controlled, such as the type of feed gas, power, and pressure, the precise effect of making any changes in these parameters is usually not well understood. In fact, a change in a single macroscopic parameter typically alters two or more basic *plasma* parameters, and possibly one or more of the surface parameters, such as temperature or electrical potential. This makes process development in plasma systems a challenge, and the use of factorial experimental design techniques for such tasks very useful⁹ (see Chap. 18). In the introduction to the section on *Dry-Etch System Configurations*, a discussion is presented on how gas flow, pumping speed, and pressure are interrelated, and how this interrelationship is used to control pressure.

ETCHING SILICON and SILICON DIOXIDE in FLUOROCARBON-CONTAINING PLASMAS

The etching of silicon and SiO₂ in fluorocarbon plasmas is described in this section in substantial detail. This is done because these etching processes are very important in silicon VLSI fabrication. In addition, when the mechanisms of plasma etching were being first studied, the etching of silicon and SiO₂ in plasmas containing CF₄, mixtures of CF₄ + O₂, and mixtures of CF₄ + H₂, yielded important data about many of the fundamental mechanisms that are operative in plasma etching, as well as information about the specific materials system under investigation. The conclusions from these studies led to the development of two models for organizing chemical and physical information on plasma etching. These models are the *fluorine-to-carbon ratio model* (or F /C model)¹⁰, and the *etchant-unsaturate model*¹¹. Since the models are conceptually similar, although they emphasize different aspects of plasma etching, we describe only the F /C model. Details of the etchant-unsaturate model are given in Ref. 25.

We begin the discussion by considering several basic phenomena related to plasma etching processes. First, it is known that in the absence of a glow discharge, the gases commonly used in plasma etching do not react with the surfaces to be etched. For example, CF_4 does not etch silicon without a discharge. This is due to the fact that CF_4 does not chemisorb on Si, and thus



Fig. 6 The fluorine pressure dependence of the etch rate of amorphous silicon at room temperature 12 . Reprinted with permission of the publisher, the Electrochemical Society.

Micron Ex. 1042, p. 28 Micron v. YMTC IPR2025-00119



Fig. 7 Proposed mechanism for F-atom reaction with a silicon film leading to the products SiF_2 and SiF_4^{13} . Reprinted with permission of the American Physical Society.

the step 3 of the dry-etching process described earlier does not occur. On the other hand, fluorine has been found to spontaneously etch Si, even without the presence of a discharge (Fig. 6)¹². Thus, when a discharge of CF_4 is created, it is not the CF_4 molecules themselves that participate in the etching reaction. Instead, the etching is accomplished by the radical species which are created by the dissociation of CF_4 molecules; namely fluorine atoms. The products of the Si-etching reaction are SiF₄ and SiF₂. A mechanism for the F-atom reaction with a Si film leading to gasification products has been proposed¹³, and is summarized in Fig. 7. The



Fig. 8 The normalized etch rate for Si and the normalized intensity of the emission from electronically excited F atoms (703.7 nm line) versus the O_2 concentration in the CF_4 - O_2 etch gas⁴. Reprinted with permission of the American Physical Society.

Micron Ex. 1042, p. 29 Micron v. YMTC IPR2025-00119 steady-state surface seems to be a stable "SiF₂-like" that must be penetrated by impinging F atoms in order for the SiF₄ to be formed. The etch rate of silicon (and SiO₂) in pure CF₄, however, is relatively low.

If small concentrations of O_2 are added to the CF₄ feed gas, however, the etch rates of both Si and SiO₂ are observed to dramatically increase (Fig. 8)¹⁴. The addition of the O₂ is also accompanied by an increase in the density of F-atoms in the discharge. Although several reasons have been advanced for this effect, it is certain that reactions between the oxygen atoms (or molecules) and the CF₄ molecules are responsible for the increased F-concentration. One of these reactions might be the gas phase oxidation of CF₃, to first form COF₂ + F, which then dissociates into CO + F₂. Another suggested reaction could involve CF₃ radicals that reach the silicon surface, and upon adsorption, contribute one C atom and 3 F-atoms to the surface. If an oxygen atom reacts with the adsorbed C atom, the 3 remaining F atoms are available to etch the Si. In any case, the etch rate of Si continues to increase until ~12% O₂ (by volume) is added. The etch rate of SiO₂ reaches its maximum value when ~20% O₂ is added. At greater concentrations, the additional O₂ dilutes the F concentration, and causes the etch rate to decrease. Figure 8 also shows that Si is etched much more rapidly than SiO₂ in CF₄-O₂ plasmas, and thus high selectivity of Si over SiO₂ is in such plasmas is easy to obtain.

If H_2 is added to the CF₄ feed gas, the etch rate of silicon decreases monotonically to almost zero for H_2 additions $\ge 40\%$. The etch rate of SiO₂, however, remains nearly constant for H_2 additions of up to 40% (Fig. 9)¹⁵. The silicon etch rate decrease occurs because the molecular hydrogen reacts with fluorine to form HF, and this drastically reduces the F atom concentration in the plasma. (It is said that the hydrogen *scavenges* F atoms). Although the effect of the Si etch rate decrease by itself may not be useful, the fact that the SiO₂ etch rate does not substantially decrease at the same time is valuable, because the SiO_2 -to-Si etch rate ratio increases. As a result, this allows a higher *selectivity* with respect to the substrate to be achieved when etching SiO₂ over Si. This selectivity is necessary when SiO₂ films must be etched down to an underlying Si layer, without significantly etching the Si.

The mechanism responsible for the high SiO₂-to-Si etch rate selectivity involves the



Fig. 9 The etch rate of Si, resist, and SiO₂ (measured in a reactive ion etching configuration) as a function of the concentrations of H₂ in the CF_4 -H₂ etch gas¹⁵. Reprinted with permission of the publisher, the Electrochemical Society.

Micron Ex. 1042, p. 30 Micron v. YMTC IPR2025-00119 combination of two phenomena: 1) the deposition of a nonvolatile residue; and b) the role of oxygen in the etching of SiO₂. If an nonvolatile layer (e.g. carbon residue) deposits on a surface during etching, and it is not removed, etching will cease. While such carbon residues are found to deposit on all surfaces inside an etch chamber containing CF_4 -H₂ plasmas, less accumulation is observed to occur on oxide surfaces than on non-oxide surfaces. There are several ways in which carbon can be deposited on a surface in fluorocarbon discharges. One way involves the dissociation of CF_3 , or other fluorocarbon radicals, upon being chemisorbed on a surface. Less residue accumulates on SiO₂ surfaces because some of the carbon combines with the oxygen in the SiO₂ to form CO and CO₂, which are volatile. This in turn allows the SiO₂ layer to continue to be etched under conditions when etching of the Si has ceased. Nevertheless, if the deposition rate of the carbon residue becomes too great, etching eventually stops on *all* surfaces in the chamber, including SiO₂ surfaces. Other gases which also consume F atoms have been found to produce high SiO₂-to-Si selectivities¹⁶ (even without the use of H₂), including CHF₃, C_3F_8 , and C_2F_6 . The reason for this effect is described as a part of the discussion on the *F* /*C ratio model*.

In practice, the exact process conditions that produce selective etching of SiO₂ over Si are generally empirically derived for each reactor. This is due to the fact that high selectivity requires that the process be operated very close to the demarcation between etching and polymerization (where etching abruptly ceases). Although the adjustment of plasma conditions to achieve high SiO₂ /Si selectivity remains an art, high selectivity is achievable. For example, selectivities of >20:1 at oxide etch rates of 600-1000Å / min have been reported¹⁷.

Fluorine-to-Carbon Ratio Model

The fluorine-to-carbon ratio $(F/C) \mod l^{10}$ is one of the two models which have been evolved to assist in assimilating the large amount of information on chemical and physical mechanisms observed in plasma etching. That is, the model represents an attempt to organize such information into a framework that allows processes to be developed more efficiently, by providing some basis for predicting the effects of various parametric variations. The F/C ratio is the ratio of the fluorine-to-carbon species, which are the two "active species" involved in the etching of Si and SiO₂ (as well as other materials etchable in fluorocarbon plasmas, including Si₃N₄, Ti, and W). The F/C ratio model does not attempt to account for the specific chemistry taking place in the glow discharge, but instead treats the plasma as a ratio of F to C species which can interact with the Si or SiO₂ surface. The generation or elimination of these "active species" by various mechanisms or gas additions then alters the initial F/C ratio lowers them.

For example, a pure CF_4 feed gas has an F /C ratio equal to four. If the plasma environment causes Si etching, however, this phenomenon consumes F atoms without consuming any carbon, and thus the F /C ratio is reduced. If more Si surface is added to the etching environment, the F /C ratio is further decreased, and the etch rate is also reduced. The addition of H₂ to the CF₄ feed gas causes the formation of HF, but does not consume any carbon, thereby the F /C ratio is <4, such as CHF₃ or C₃F₈, also has the effect of producing an F /C ratio smaller than that present in a plasma of pure CF₄. Their use is found to produce very similar effects in the etching chemistry as the other two procedures. Plasmas in which the F /C ratio is decreased to less than 4, are termed *fluorine-deficient plasmas*.

Conversely, the addition of O_2 has the effect of *increasing* the F /C ratio, because the oxygen consumes more carbon (by forming CO or CO_2), than F atoms (by the formation of COF_2). Other feed gases that can be added to increase the F /C ratio include CO_2 , F₂, and NO₂.

The cause of the high selectivity of SiO₂-to-Si in $CF_4 + H_2$ plasmas can be elucidated

Micron Ex. 1042, p. 31 Micron v. YMTC IPR2025-00119



Fig. 10 Illustrative plot of the boundary between polymerizing and etching conditions as influenced by the fluorine-to-carbon ratio of the chemically reactive species and the bias applied to a surface in the discharge 10. Reprinted with permission of the American Physical Society.

with the aid of the F /C ratio model. That is, even though the F /C ratio in such plasmas is less than 4, the SiO₂ contributes oxygen (which consumes carbon), thus locally compensating for the decreased F /C ratio at the SiO₂ surface¹⁹. As long as the F /C ratio at the oxide surface has a value close to that which exists in a pure CF₄ plasma, SiO₂ etching continues to proceed at the same rate. Meanwhile, since the F /C ratio at the Si surface is less than 4, the local etch rate decreases. To summarize, the F /C ratio model is useful for linking together the effects of a diverse set of phenomena, including the effects of many feed gases and SiO₂ /Si selectivity.

The F/C ratio can also be used to qualitatively portray the demarcation between etching and polymerization as it varies according to changes in some process condition (Fig. 10). In this figure the boundary between polymerization (x-axis) is shown to vary as a bias voltage (y-axis) is applied to the substrate. The bias voltage has the effect of causing increased bombardment of the surface by energetic ions, which removes the nonvolatile residue layer by sputtering. This allows etching to occur at lower F/C ratios than if the carbonaceous polymer film were not simultaneously removed by sputtering and etching. This effect, as will be described in the following section, may be utilized as a technique to control sidewall profiles of etched layers.

ANISOTROPIC ETCHING and CONTROL OF EDGE PROFILE

Up to this point in our discussion we have considered the etching of Si and SiO₂ in fluorocarbon plasmas largely as a mechanism that proceeds by chemical action (i.e. the reaction of Si by F-atoms generated by the plasma to form SiF₄). If etching action is purely chemical, however, the removal of material is isotropic, and no advantage in dimensional control is gained over wet etching (Chap. 15). In such processes, the plasma plays no role other than to produce

Micron Ex. 1042, p. 32 Micron v. YMTC IPR2025-00119 the etchant. The attractiveness of dry-etching for VLSI patterning, however, is based on its potential to etch in an anisotropic manner (defined in Chap. 15), and the mechanisms that are believed to produce anisotropic etching need to be considered.

It should be mentioned before discussing details of the directional etching mechanisms, that the desired degree of directionality varies with the specific application in the final device. For example, if the lines etched from a deposited film are designed to carry current, steep-walled profiles are preferred, so that the cross-sectional area of the conductor is maximized. On the other hand, if an etched feature must be subsequently covered by another film, tapered profiles on the walls of the etched feature are more desirable, since highly anisotropic profiles in underlying topography may result in poor step coverage by the overlying film. As also mentioned in Chap. 15, a highly anisotropic etch will cause "stringers" in the overlying film to be left behind at the base of steep underlying steps (Fig. 9, Chap. 15). Since such stringers represent regions of incomplete etching between adjacent lines, the etch process must remove them. This can be done in several ways including: a) overetching the overlying film; b) introducing a finite lateral etching component into the etch process; and c) insuring that the underlying feature steps have tapered wall profiles. Achieving wall profiles with the desired degree of slope may require the use of a multi-step etch process, in which each of the sub-processes would employ of an etch mechanism with its own degree of anisotropy. A multi-step etch process for producing arbitrarily shaped wall profiles by such piece-wise anisotropic etching is described in Ref. 19.

The ability to achieve anisotropic etching is thought to depend in some way or another on the bombardment of the etched surface with energetic ions. Other parameters, such as the chemical nature of the plasma, may influence the degree of anisotropy, but unless energetic particles strike a surface, only isotropic etching can be expected. The directional etching effects in ion-assisted etching processes, however, cannot be due to sputtering alone, as product yields of over several hundred substrate atoms per incident ion have been reported in ion-assisted etch processes. Such product yields are much greater than those of typical sputtering yields (e.g. <2



ION - ASSISTED ETCHING OF SI

Fig. 11 An example of ion-assisted gas-surface chemistry in the etching of silicon with XeF₂. The XeF₂ flow is $2x10^{15}$ molecules /sec and the Ar energy and current are 450 eV and 2.5 μ A, respectively²⁰. Reprinted with permission of the American Physical Society.

Micron Ex. 1042, p. 33 Micron v. YMTC IPR2025-00119



Fig. 12 (a) Surface damage, and (b) surface inhibitor mechanisms, for ion-assisted anisotropic etching¹³. Reprinted with permission of the American Physical Society.

for 400 eV Ar ions, see Chap. 10). This is fortunate, for as was discussed at the outset of the chapter, purely sputter etch mechanisms result in processes with inadequate selectivities.

The fact that sputtering alone is not operative in such processes, was elegantly demonstrated in an experimental manner by Coburn and Winters²⁰. In one experiment, they first exposed a Si surface to a gas of XeF_2 (not a plasma of XeF_2), and observed a low etch rate (Fig. 11). Next, while continuing to expose the surface to XeF_2 , an Ar^+ ion beam with an energy of 450 eV was directed at the Si. The observed etch rate was ~10 times as great as with the XeF_2 alone. Finally, when the Ar^+ beam alone was directed at the surface, the smallest etch rate of the three conditions was produced. The results of this experiment demonstrate that a strong cooperative effect can be result if the etching surface is simultaneously exposed to a reactive gas and bombardment by energetic particles. The microscopic details of exactly how the ion bombardment enhances the reaction between a reactive gas and a surface, is the subject of substantial research efforts. Evidence indicates that different mechanisms exist for specific chemical systems.

Two principal mechanisms by which energetic ions assist in enhancing the etch rate produced by reactive gases, however, have been postulated to be operative in directional etching processes (Fig. 12)²¹. They are: a) Relatively high energy impinging ions (> 50 eV) produce lattice damage at the surface being etched, extending several monolayers beneath the surface. Reaction at these damaged sites is enhanced compared to reaction at surfaces at which no damage has occurred; and b) lower energy ions (\leq 50 eV) provide enough energy to desorb *nonvolatile polymer layers* (also referred to as *surface inhibiting*, or *blocking* layers) that deposit on the surfaces being etched. In processes in which such polymer deposition occurs, surfaces not struck by the ions do not have the blocking layer removed, and hence are protected against etching by the reactive gas. In features being etched on a wafer, the incident energetic particles generally arrive in a direction perpendicular to the wafer surface, and hence they strike the bottom surfaces of the etched features. The sidewalls of the etched features, meanwhile, are subjected to little or no bombardment. As a result, the bottom of the features exhibit enhanced etching. Ion bombardment effects are enhanced by decreasing the pressure in a high frequency (> 5 MHz)

Micron Ex. 1042, p. 34 Micron v. YMTC IPR2025-00119 plasma, or by decreasing the frequency of the discharge.

Examples of specific data that illustrates anisotropic etching are given in the discussions on the etching of the various types films, but two idealized examples will be given here to illustrate the kind of approaches that have been suggested to achieve directional etching.

In the first case, shown in Fig. 13, hypothetical Si and SiO₂ surfaces are subjected to positive ion bombardment as a result of a negative bias voltage of -150 V being applied to the wafers²². Since the etch rate of SiO₂ is zero without ionic bombardment, but finite rate under ion bombardment (Fig. 13), the SiO₂ film etches anisotropically. The silicon etch rate is finite but smaller on surfaces that receive no ionic bombardment, and thus the lateral etch rate is slower than the vertical etch rate. The etched feature ends up having a profile in which the sidewalls are not vertical.

In the second example, the chemistry of the discharge together with ionic bombardment is used to control the directionality of etching²². As was shown in the first hypothetical example, Si is etched more rapidly under energetic ion bombardment (e.g. from 150 eV ions) than when no bombardment occurs. If H_2 is added to the CF₄ feed gas, the Si etch rate decreases (Fig. 14). At some value of H_2 concentration, the non-bombarded surface etch rate decreases to zero, but the bombarded surfaces continue to be etched. Thus, under those conditions, the bottom of the feature is etched, while the non-bombarded sidewalls are not etched, and the resulting etched profile is vertical.

One other technique suggested for introducing a non-vertical shape to a feature being etched by a completely anisotropic process, involves the introduction of some rounding to the sidewall angle of the resist mask^{23,24}. The selectivity of the etch process is then adjusted, so that the resist and the layer to be patterned are both etched anisotropically at the same rate. In this manner the slope of the resist wall is replicated in the walls of the etched layer (Fig. 15). In practice, this technique is difficult to successfully implement, because stringent control of all



Fig. 13 Illustrative figure which shows the relationship between the shape of the etched wall profile and the dependence of the etch rate on the wafer potential¹⁰. Reprinted with permission of the American Physical Society.

Micron Ex. 1042, p. 35 Micron v. YMTC IPR2025-00119



Fig. 14 Illustrative figure which shows the way in which the shape of a wall profile can be influenced by decreasing the fluorine-to-carbon ratio (in this example by H_2 addition)¹⁰. Reprinted with permission of the American Physical Society.

plasma parameters must be maintained (temperature, ion energy distributions, etc.). It is a particularly formidable process to control when wafers are etched in a batch mode.

DRY-ETCHING VARIOUS TYPES of THIN FILMS

Silicon Dioxide (SiO_2)

It was described earlier how fluorocarbon-containing plasma can be used to etch SiO₂, and how selectivity with respect to silicon can be obtained by using fluorine-deficient plasmas. An example approach for producing anisotropic etching of SiO₂ was also illustrated. When etching contact holes in SiO₂, however, it is advantageous to have sloped contact sidewalls for easier filling by the following conductor layer. One method for producing such a slope is by controlled resist erosion, as described earlier²⁴. By adjusting the resist : oxide etch ratio, the slope can be transferred to the oxide. A technique for adjusting the *resist : oxide* etch rate ratio, is to add O₂ or SF₆ to the fluorocarbon feed gas. A second method for achieving sloped walls is the use of a reflow step, but this is not an etching procedure (see Chap. 6). Controllably producing tapered sidewalls on small SiO₂ contacts by an etching process remains a difficult task.

The etch rate of the oxide films depends on several factors including pressure, power, feed gas composition, and film characteristics. For a given set of etching conditions, the film characteristics impact the etch rate. For example, thermal SiO_2 generally etches more slowly than CVD SiO_2 films, and the etch rate may depend on the dopant concentration in the SiO_2 layer.

555



Fig. 15 SEM photograph of a contact hole in a 1 μ m thick phosphorus-doped CVD SiO₂ with tapered profile achieved by controlled resist erosion during etching²³. Reprinted with permission of the Applied Materials.

Silicon Nitride

Fluorine atoms isotropically etch silicon nitride with a selectivity of silicon nitride : Si ~1:8 in the temperature range of 30-100°C²⁵. As described in Chap. 6, two more or less distinct types of silicon nitride are used in VLSI fabrication. The first type is usually deposited by low pressure CVD (LPCVD) at 700-800°C, and results in a stoichiometric compound Si₃N₄ film. The second type is deposited by plasma-enhanced CVD techniques at \leq 350°C, and such plasma deposited nitrides are really polymer-like Si-N-H materials. Although both nitrides are usually etched in CF₄-O₂ plasmas, the plasma nitride films normally etch more rapidly than the LPCVD films^{23,25}.

In most applications, nitride films are patterned with relatively coarse lateral dimensions (e.g. the opening of bonding pads in nitride passivation layers, or the patterning of a thin nitride layer [~1000 Å thick] in the LOCOS process), and thus a high degree of anisotropy is not usually necessary for patterning the nitride. In the LOCOS application, however, sufficient selectivity with respect to SiO₂ must exist so that the thin oxide layer under the nitride (~250 Å thick) is not etched away. This would expose the silicon under the SiO₂ to a fast-etching plasma, which as noted above, would etch the silicon ~8 times as rapidly as the nitride. The selectivity of a CF₄ isotropic Si₃N₄ etching process with respect to SiO₂ is ~2-3, but more favorable selectivity (e.g. 9-10) can be obtained with the use of NF₃ plasmas²⁶.

Polysilicon

In MOS applications, the gate length is a critical, fine line dimension that determines the channel length of the devices. Thus, when polysilicon serves as the gate material, it is paramount that the etched linewidth dimension faithfully reproduces the dimension on the mask (e.g. to within $\pm 5\%$). A polysilicon etch process must therefore exhibit excellent linewidth control, and high uniformity of etching. In addition, a high degree of anisotropy is also generally required, as the doping of the source-drain and the polysilicon itself is typically performed by ion implantation. If the etch process produced sloped sidewalls in the polysilicon, then portions of the gate would not be thick enough to effectively mask the substrate against the

Micron Ex. 1042, p. 37 Micron v. YMTC IPR2025-00119 implanation. This would produce devices whose channel length depended on the degree of sidewall taper, and unless the taper could be accurately controlled, would cause a manufacturing control problem.

The degree of anisotropy, however, is dictated by other considerations as well, including the extent of overetching required to remove stringers at the base of steep steps in the inderlying topography (Fig. 9, Chap. 15), and the coverage of the etched polysilicon features by subsequently deposited layers. In the first of these cases, completely anisotropic etching will require extensive overetching to remove the stringers, while in the second, it will produce features that may be difficult for overlying films to cover. Thus, in general, an important characteristic of a process is its ability to produce a profile with the desired degree of slope.

Finally, the polysilicon layer is usually deposited over thin SiO_2 (e.g. gate oxides, 250-500 Å thick). Thus, the etch process must be selective over SiO_2 etching, since if this oxide layer was removed, the shallow source-drain junction regions in the underlying Si substrate would be rapidly etched by the reactants that cause polysilicon etching. In some cases, where buried contacts between polysilicon and the single crystal substrate are made, high selectivity over single crystal Si must also be exhibited (a subject discussed in Ref. 30).

As described in the earlier section on etching of Si with fluorine-based plasmas, fluorine atoms etch Si isotropically, and hence controlled anisotropic etching of Si with fluorine-based chemistries, such as CF_4 or SF_6 , is difficult. In addition, such processes exhibit a large loading effect, also an undesirable characteristic in etching processes (see later section on *Loading Effects*). As a result, several other methods have been investigated to overcome these limitations. First, chlorine plasmas were found to etch polysilicon very anisotropically and exhibited excellent selectivty over SiO₂, but they etch Si more slowly than fluorine containing gases. Thus, etch gases containing both chlorine and fluorine have come to be preferred for polysilicon etching²⁷. For example, a detailed description of an etching process utilizing SF₆ and Cl₂ is given in Ref. 28. In that study, undercutting was controlled to less than 0.3 μ m, while maintaining high etch rates and good selectivity over SiO₂, by adding small amounts of chlorine to SF₆ plasmas. It was concluded that the chlorine together with the resist mask material reacted, to form a thin polymer that deposits on the sidewalls of the etching polysilicon, to produce less etching at the sidewalls. Other proposed process for etching polysilicon with all of the required etching parameters, involve multi-step etching processes^{27, 29}.

Refractory Metal Silicides and Polycides

Refractory metal silicides are deposited onto polysilicon to form a low resistance polycide



Fig. 16 Polysilicon etching²⁹. Reprinted with permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet.

structure that can serve as both a gate and an interconnect layer (Chap. 11). In many applications, etching is used to pattern such polycide structures, but this is a difficult etching task^{25,33}. As in polysilicon etching, the process must provide a vertical profile on the etched polycide, good selectivity over oxide (i.e. >10), and minimal resist erosion. Etching of refractory metal silicides with both fluorine and chlorine based plasmas has been investigated, as both the fluorides and the chlorides of the refractory metals are relatively volatile (Fig. 17a). Etch gases that result in high concentrations of F atoms, however, are not suitable, as they tend to undercut either the n⁺ polysilicon or the silicide (or both). On the other hand, fluorine-deficient plasmas can produce anisoropic etching of both the polysilicon and the silicides, but the etch ratio with respect to SiO₂ is less than one.

Chlorine plasmas are known to etch SiO_2 quite slowly, and anisotropic etching of n⁺ polysilicon and silicides is easier to obtain. Unfortunately, the vapor pressures of the refractory metal chlorides are much lower than those of the fluorides, and so to assist the etching process, the use of mixtures of gases that consist of both fluorine and chlorine containing gases have been studied (e.g. $SF_6: Cl_2$). Reference 31 describes the results of etching tantalum silicides and polycides with such mixtures (Fig. 17). It is reported that etch profiles vary widely with process parameters, especially the gas composition. As the silicide etch rates also vary with silicide composition, the successful implementation of a polycide etching process requires stringent process that produces an appropriately-shaped polycide profile, together with high selectivity over SiO₂, a multi-step etch process may need to be employed.



Fig. 17 (a) Vapor pressures of transition metal halides. (b) Polycide etching³¹. Reprinted with permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet.

Micron Ex. 1042, p. 39 Micron v. YMTC IPR2025-00119



Fig. 18 Vapor pressure of AlF₃, AlCl₃, and AlBr₃ as a function of temperature³⁴.

Aluminum and Aluminum Alloys

The etching of aluminum and aluminum alloy films is a very important step in the fabrication of integrated circuits. The device density, on many of the most advanced circuits, is limited by the area occupied by the interconnect paths. Anisotropic etching of the metal layers permits the use of smaller minimum metal pitches (i.e. the *pitch* is the sum of the dimensions of a metal line and the space between lines), which increases the interconnect capability. Thus, the isotropic nature of aluminum wet etching processes renders them inadequate for VLSI applications, and there is a need for a directional dry etching process.

The fluorine-containing gases used to etch Si and SiO₂, however, are not suitable for etching aluminum since the etch product, AlF₃, has a very low vapor pressure (Fig. 18)³⁴. On the other hand, other halides of Al (e.g. AlCl₃, Fig. 18) have sufficiently high vapor pressures to allow plasma etching of Al, and thus chlorine-containing gases have been exploited to develop dry-etch processes for aluminum films. The chlorine containing gases used to etch aluminum, BCl₃, CCl₄, SiCl₄, and Cl₂, however, are all either carcinogenic or highly toxic. They also have a propensity to dissolve and become concentrated in pump oils. Consequently, special care must be taken during system servicing to avoid skin contact or inhalation of vapors from cold traps, oil filters, pumps or pump oils of aluminum etching systems. The reactive compounds, AlCl₃ and BCl₃, also degrade silicone and hydrocarbon pump fluids, and to avoid pump fluid decomposition, perfluoropolyethers are often used (see Chap. 3). In addition, oxidation of AlCl₃, BCl₃, or SiCl₄ results in particulate formation (e.g. Al₂O₃, SiO₂). Such particles, together with polymeric residues in the oil, can produce vacuum pump bearing failure by plugging lubrication ducts³⁵. Hence, it is recommended that oil filters be utilized to prolong pump life and allow longer intervals between oil changes.

It has been determined that a freshly exposed aluminum surface, uncovered by aluminum oxide (Al_2O_3) will react spontaneously with Cl or molecular Cl₂ to form AlCl₃, even in the absence of a plasma³⁶. If, however, the surface of the aluminum is covered with a thin layer of

 Al_2O_3 (i.e. a native oxide of ~30 Å), it will not react with Cl or Cl_2 . Thus, etching of Al films is two-step process, involving removal of the native oxide layer, and etching of the Al film.

The successful removal of the native oxide is one of the most important steps in achieving an effective aluminum etching process. This is because removal of Al₂O₃ is far more difficult than the etching of pure aluminum, and the thickness of this oxide can vary from run-to-run, depending on several factors. Thus, an aluminum etch cycle is observed to begin with an *initiation period*, during which the native oxide and the moisture from the chamber is slowly removed. The removal can be accomplished by sputtering with energetic ions, a condition that can be established in reactive ion etching systems, or by chemical reduction. The chemical reduction of the Al_2O_3 requires the availability of oxide reducing species. The dissociation of BCl₃ or CCl₄, for example, produces fragments capable of reducing Al₂O₃. That is, CCl_x (where x <4) can reduce the oxide according to $Al_2O_3 + CCl_x -> AlCl_3 + CO$, but ion bombardment is still apparently necessary to assist these reducing reactions. If there is water vapor present in the etch chamber, however, it will scavenge the oxide-reducing species and react with the exposed aluminum to form new Al₂O₃. This represents one of the factors which contribute to non-reproducible initiation times. \tilde{BCl}_3 has become the preferred source gas for the role of native oxide removal in many processes³⁷. BCl₃ is a much better getter of oxygen or water vapor than is CCl₄, and the etch products of CCl₄ have been identified as carcinogenic (see section on Plasma Etching Safety Considerations). Figure 19a shows the results of one report in which the aluminum initiation period was reduced to a relatively short interval, by increasing the flow rate of BCl₃. It should be noted, however, that BCl₃ is highly reactive and



Fig. 19 a) Time necessary for initiation of Al etching vs. BCl₃ flow. Other parameters include: 20 sccm Cl₂, 200 sccm He, 200 Pa total pressure, 1.75 W /cm². Reprinted with permission of the publisher, the Electrochemical Society³⁸. b) Effect of small concentrations of H₂O on the initiation period (designated as the Al₂O₃ etching rate)³⁹. This figure was originally presented at the Fall, 1981 Meeting of the Electrochemical Society, held in Denver, Colorado.

Micron Ex. 1042, p. 41 Micron v. YMTC IPR2025-00119 forms nonvolatile residues upon contact with oxygen or water, for example in the pump exhaust line.

Water vapor, nevertheless, must be excluded from the etch chamber in order to achieve reproducible Al etch processes. As shown in Fig. 19b, the etch rate of Al₂O₃ decreases rapidly with increasing partial pressure of water vapor³⁹. If an etch chamber is exposed to ambient after an etch run, moisture can be adsorbed on the chamber walls. This condition becomes more severe if the etch product of aluminum, AlCl₃, is allowed to deposit on the chamber walls⁴⁰. Such deposition occurs on surfaces maintained at room temperatures. AlCl₂ is very hygroscopic, and thus absorbs considerable moisture on exposure to atmosphere. This moisture may be desorbed after the plasma is struck. The deposition of AlCl₃ also has other deleterious effects on the etch process, which are described later, and so minimizing its deposition is important. Techniques used to manage AlCl₃ in plasma etching applications include maintaining the temperature in the etch chamber above 35°C (as the AlCl₃ evaporation rate at such temperatures is high enough to assist in removing it from the chamber), and using large gas flow rates to keep its partial pressure low. Water vapor in the etch chamber is most effectively reduced by load lock chamber designs. In non-load locked designs, water vapor is decreased by use of extended pumpdowns, heating the chamber walls when the chamber is open (e.g. to 40°C), surrounding the chamber with a nitrogen purge box, use of BCl_3 , and minimizing AlCl₃ buildup⁴⁰.

It should also be noted at this point that the oxygen content of the aluminum film can also play a significant role in determining the etch rate⁴¹, as shown in Fig. 20. This oxygen can be incorporated during the aluminum sputter deposition step, as a result of the partial pressure of oxygen in the sputter chamber during deposition. Since oxygen concentrations of <5% in



Fig. 20 (a) Effect of oxygen content in Al films on plasma etch rate⁴¹. (b) Vapor pressure of copper chloride as function of temperature⁴⁴. Reprinted by permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet.

Micron Ex. 1042, p. 42 Micron v. YMTC IPR2025-00119



Fig. 21 Etch rate of Al vs. Cl_2 flow for different BCl₃ flows. Other parameters include: 250 sccm He, 9.4 sccm CHCl₃, 160 Pa total pressure⁴². This figure was originally presented at the Fall, 1981 Meeting of the Electrochemical Society, held in Denver, Colorado.

aluminum do not alter the resistivity of the film, this contamination may go unnoticed. In addition, since the oxygen tends to segregate to the grain boundaries, the aluminum in these regions will etch more slowly, leaving a "stencil" of the grains. If a large concentration of oxygen is present, complete etching of grain boundary regions may require undue overetching.

After the native oxide is removed, the aluminum etching proceeds at a rate and with a resultant profile, that is affected by the gases used (e.g. Fig. 21³⁸). In general, the demands of high throughput require the highest etch rate consistent with good results. Processes with high concentrations of Cl_2 in the feed gas exhibit isotropic etching, and the etch rate in such processes is not enhanced by energetic ionic bombardment. Thus, it is postulated that anisotropic etching of aluminum occurs as a result of the formation of an inhibiting layer on the aluminum surface⁴², which is removed on surfaces struck by energetic ions, allowing etching to occur there (Fig. 12b). Such inhibiting layers are believed to arise from the formation of chlorocarbon polymers (e.g. CCl_x), originating from the carbon in CCl_4 or resist etch products. In fact, CCl₄, CHCl₃, and other chlorocarbon gases are added to Cl₂ plasmas to reduce undercutting. It has also been observed that if aluminum is etched with an SiO₂ etch mask, with gases containing large concentrations of Cl_2 and no carbon containing species, isotropic etching occurs⁴³. A partial list of the gases and gas mixtures (neglecting rare gas diluents) which have been reported to successfully etch aluminum include: CCl₄, BCl₃, Cl₂, CCl₄ + BCl_3 , $CCl_4 + Cl_2$, $BCl_3 + Cl_2$, $BCl_3 + Cl_2 + O_2$, $CCl_4 + Cl_2 + O_2$, $SiCl_4$, and BBr_3 .

Selectivity with respect to SiO_2 is sufficient for VLSI applications. Selectivity with respect to silicon (or polysilicon), however, is typically inadequate with chlorine-containing gases (e.g. aluminum /silicon selectivities are typically only 2-5:1). As a result, Al patterns must overlap contact windows, and this serves to restrict the density of Al conductor lines.

Small quantities of other materials are added to aluminum to improve some of its properties. That is, 1-2 at% silicon is often added to prevent the aluminum from spiking through shallow junctions (see Chap. 10), and 2-4 at% copper, or 0.1-0.5 at% Ti (often together with Si), are added to enhance the electromigration resistance. Since SiCl₄ is volatile at room temperature, Al-Si films are readily etchable in chlorine-containing gases. Titanium also forms volatile etch products (TiCl₄, Fig. 17a), and thus also does not pose a problem, provided the titanium is not oxidized. That is, titanium readily oxidizes, and TiO₂ is difficult to etch in chlorine plasmas.

Copper, on the other hand, forms an etch product with chlorine, CuCl, that is relatively non-volatile below temperatures of 175°C (Fig. 20b)⁴⁴. Thus, copper containing residues often remain after these alloy films have been dry-etched. This makes Al-Cu more difficult to etch in chlorine plasmas. The degree of difficulty increases with increasing Cu concentration, and 4% Cu-containing films pose quite a formidable dry etching challenge. Two methods are used to promote CuCl desorption: increasing the substrate temperature, commensurate with the maximum temperature allowed with the resist material being used; and enhancing the ionic bombardment of the surface, so that significant sputtering occurs. In batch etchers, low pressure operation together with a slower etch rate, promotes high energy bombardment while allowing more time for the sputtering to remove CuCl⁴⁵. In single wafer etchers, higher power is needed to produce sufficient ion bombardment under the conditions of greater operating pressure. This causes the unwanted effect of eroding the resist during etch. In addition, the etch product, AlCl₃, is highly reactive, and it can also attack and degrade the resist^{40,46}. Thus, it is necessary to employ special UV-thermal resist stabilization steps to enable the resist to withstand such harsh etching environments. See Chap. 12 for more information on UV-stabilization procedures.

Another problem with etching Al is that of post-etch corrosion. The effect arises from the hydrolysis of the chlorine or chlorine-containing residues (mostly AlCl₃) which remain on the film sidewalls, substrate, or resist after etch. Upon absorbing moisture, these residues form HCl which corrodes the aluminum. The reaction of HCl and Al produces more AlCl₃, and thus as long as moisture is available, corrosion will continue (Fig. 22)⁴⁷. The problem is even more severe in Al-Cu alloys⁴⁸, since Al-Cu compounds formed in the film (primarily CuAl₂) create a galvanic couple with the Al (Fig. 23), and this drives the corrosion even more rapidly than in pure aluminum films. Consequently, the residual chlorine and ambient moisture levels necessary to induce corrosion are much lower when Cu is present in the aluminum films.

Various techniques have been suggested to deal with the post-etch corrosion problem, all involving the removal of the chlorinated species. These include: a) removing the wafers from the chamber and rinsing in cold deionized water. It has been suggested, however, that this method is not likely to be effective for alleviating corrosion in Al-Cu alloy films⁴⁰; b) plasma ashing of the resist in an O₂ plasma before removal from the etch chamber, which removes the chlorine present in the resist, and restores the passivating Al₂O₃ layer; and c) exposing the aluminum to a fluorine-containing plasma before removal from the chamber (e.g. CF₄ or



Fig. 22 Corrosion of etched Al lines⁴⁷. Reprinted by permission of Semiconductor Internat'l.

Micron Ex. 1042, p. 44 Micron v. YMTC IPR2025-00119



Fig. 23 Corrosion of Al-Cu films in Cl-containing plasmas⁴⁸. Reprinted with permission of the American Physical Society.

 CHF_3)⁴⁶. The CF₄ exposure is believed to cause the chemisorbed chlorine to be replaced with fluorine, thereby passivating the Al by the formation of nonhydroscopic AlF₃. The CHF₃ exposure is thought to deposit a polymer film over the aluminum, thus "sealing" the surface and preventing moisture from penetrating to the chlorine residues. Long term reliability studies on the effectiveness of these treatments, especially on circuits in plastic packages, have yet to be reported in detail.

Organic Films

Organic films are exposed to plasma etching environments in many applications during VLSI fabrication. Photoresist is most commonly used as an etch mask, and in such applications it is usually desired that the resist not be etched by the plasma. In some cases, however, the resist is deliberately etched as part of a technique used to produce directional etching effects in underlying films (e.g. sloped contact sidewalls), or as a method for producing planarization of layers under the resist. In some of these instances, the etch rate of the resist must be accurately known and controlled. At the conclusion of the pattern etching step the resist must be removed, and this can be achieved by a plasma etch process as well. Organic film etching is also performed in dry-developable resist and tri-layer resist processes (see Chap. 12), and in etching polyimide films.

Plasmas containing pure oxygen at moderate pressures produce species that attack organic materials to form CO, CO₂, and H₂O as end products^{1,25,49}. Such oxygen plasmas provide a highly selective method for removing organic materials, since the O₂ plasmas do not etch Si, SiO₂, or Al. The addition of fluorine-containing gases to the O₂ causes the etch rate of organic materials to significantly increase. This occurs because the F atoms extract hydrogen from the organic films to form HF, producing sites that react more rapidly with molecular oxygen.

Ion bombardment can also be used to accelerate organic film etching. Under conditions in

Micron Ex. 1042, p. 45 Micron v. YMTC IPR2025-00119

565

which the concentrations of oxygen atoms are small (e.g. low pressure and loading), the etched profiles are completely anisotropic²⁵.

The resistance of organic materials (e.g. resists) to plasma conditions depends on the chemical composition of the organic layer and the type of plasma. There are some plasma conditions, however, in which the durability of commonly used positive resists is quite high, espcially those used for the selective etching of SiO₂ and Si₃N₄.

PROCESS MONITORING and END POINT DETECTION

Dry etch equipment used in a VLSI production environment requires the availability of effective diagnostic and etch end point detection tools. Extremely tight control of all process parameters must be maintained to ensure wafer-to-wafer and run-to-run reproducibility. In typical production facilities, some of these parameters can be controlled, while others cannot. For example, as will be described, reactor wall conditions, which contribute to the heterogeneous destruction of active reactants, become a *bona fide* variable, if the walls are exposed to atmosphere after every run. Similarly outgassing, virtual leaks, and backstreaming from pumps can sufficiently change the chemistry, so that a calibrated etch-time approach to reproducibility generally proves to be inadequate. Thus, techniques for determining the end point of a cycle become highly valuable as procedures for reducing the degree for overetching, and for increasing throughput and run-to-run reproducibility. In this section we describe four common methods for determining the end point of dry etch processes: 1) laser interferometry and reflectivity; 2) optical emission spectroscopy; c) direct observation of the etched surface through a viewing port on the chamber, by a human operator; and d) mass spectroscopy, which of the four, is least widely used^{1,50,51}.

Laser Interferometry and Laser Reflectance

Laser interferometry monitors the thickness of optically transparent films on reflective substrates by making use of interference effects.⁹ The laser reflectance method exploits the difference in the reflectivity between a nontransparent material being etched and an underlying layer.



Fig. 24 (a) Experimental apparatus for using emission spectroscopy as an end point detector; (b) Typical apparatus for the optical reflection method of end point detection⁵⁰. Reprinted by permission of Solid State Technology, published by Technical Publishing, company of Dun & Bradstreet.

Micron Ex. 1042, p. 46 Micron v. YMTC IPR2025-00119 The same apparatus can be utilized to carry-out both techniques, and is shown in Fig. 24b. The system is designed to measure the intensity of light reflected from films being monitored.

In the case where a transparent film is being etched (e.g. SiO_2), the amplitude of the intensity of the reflected light varies, in approximately a sinusoidal manner, as interference conditions change with decreasing film thickness. If the incident light is normal to the surface, the film thickness change, Δd , between any two adjacent maxima or minima is given by $\Delta d = \lambda/2n$, where λ is the wavelength of the incident light, and n is the index of refraction of the etched layer. As a result, if the etch time between two adjacent maxima is known, *in situ* etch rates can be inferred. Laser interferometry can also provide end point detection. That is, the interface between two dielectrics is identifiable as a change in slope caused by the different refractive indices, and by a change in the frequency of the reflectance variations, due to the etch rate variations of the two materials.

Opaque /transparent interfaces (e.g. metal /dielectric) are distinguished by a variation from an approximately constant reflectivity to an oscillating one. In the case when two nontransparent films are etched there is a change in the reflected signal when the end point is reached, if the reflectivity of the underlying layer differs significantly from the film being etched. This change is proportional to the ratio of the reflectivity of the layer being etched to the underlying layer. Of course, the *laser reflectance* method does not provide any information on the *in situ* etch rate, and therefore does not provide as much information as *laser interferometry*.

These techniques, however, do have several limitations. First, the laser must be focused on a flat region of the wafer on which the film being etched is exposed. Thus, in many etching applications, where the area being etched is too small for good reflectivity measurements (e.g. etching of contacts in an SiO_2 film), a larger test site (>0.5 mm) must be added to the wafer patterning to facilitate this measurement. This requirement can be costly, as the open space must be located in a prime area of the wafer. Even when such a test area is present, each wafer must then be accurately aligned, so that the laser is incident on this area during the etch process. Second, this method provides etching information only on that specific area on a single wafer. If a large batch of wafers is being processed, non-uniformities in the batch etching process cannot be compensated for by this technique. Finally, in some cases, enhanced etching occurs at locations upon which the laser is focused, which yields inaccurate etch rate data.

FILM	SPECIES MONITORED	WAVELENGTH (NM)	
Resist	CO	297.7, 483.5, 519.8	
	OH	308.9	
	H	656.3	
Silicon, Polysilicon	F	704	
	SiF	777	
Silicon Nitride	F	704	
	CN	387	
	N	674	
Aluminum	AlCl	261.4	
	A1	396	

 Table 3.
 SPECIES and EMISSION WAVELENGTH

 for OPTICAL EMISSION END POINT DETECTION⁵⁰

Optical Emission Spectroscopy

Optical emission spectrocopy is the most widely used method for end point detection, because it is easy to implement, can offer high sensitivity, and provides useful information about both etching species and etch products. The technique relies on the change in the emission intensity of characteristic optical radiation, from either a reactant or product in a plasma. Light is emitted by excited atoms or molecules in a plasma when electrons relax from one energy state to another. Atoms and molecules emit a series of spectral lines that is unique to each species. The emission intensity is a function of the relative concentration of a species in the plasma, and emitted light is observed through a viewing port on the etch chamber. A typical apparatus utilized for end point detection is shown in Fig. 24a. It operates by recording the emission spectrum during the etch process in the presence and absence of the material that is to be etched. The comparison of these two spectra indicates the emission lines that are sensitive to the etching process. To detect the end point, the emission intensity of the process-sensitive line (or band) is monitored at a fixed wavelength. When the end point is reached, the emission intensity changes. The change in emission intensity at end point depends on the species being monitored; the intensity due to reactive species increases, while the intensity due to etch products decreases. It is useful to monitor emission from both reactive species and product species simultaneously (Table 3), as in some etching applications one or the other of these measurements may yield a stronger signal¹. Optical emission spectroscopy is widely used for determining the end point of SiO₂, polysilicon, and aluminum layers. In batch etch processes, the end point signal is derived from the average of etch conditions in the process. As a result, a degree of overetching is still required to insure that all wafers have been completely etched.

Optical emission spectroscopy also some drawbacks, one of the most important being that its sensitivity is determined by the etch rate and the total area being etched. Thus, for slow etch processes, the end point may be difficult to detect. The fact that the sensitivity is also dependent on the total area being etched, in some instances requires that a special test site be established to provide sufficient exposed area to cause a detectable end point signal (e.g. $\sim 1 \text{ cm}^2$ of exposed Si⁵⁰). Separate test sites are most necessary when small contacts are being etched (i.e. the total area of etched surface is small), or when the etch depths become comparable to the separation between features. In the latter case, the total area (side wall + bottom) of material being etched can remain almost constant, even after the bottom of the film has been reached and only undercutting is occurring.

Mass Spectroscopy

Like emission spectroscopy, mass spectroscopy is a gas phase measurement method that offers the ability to detect and identify individual species in a plasma discharge. It is also able to provide information about the presence of species in the chamber prior to igniting the plasma, or in the effluent extracted from the etching chamber. A diagram of a mass spectrometer apparatus used for monitoring chamber effluents is shown in Fig. 25. Although mass spectroscopy is a useful technique, it is more difficult to implement than emission spectroscopy, and is limited to the sampling of species removed from the plasma, whereas emission spectroscopy obtains its data from the bulk plasma.

As shown in Fig. 25, a small orifice is utilized to sample the process effluent, and electron impact is used to create ions. The species present are analyzed in much the same manner as in a residual gas analyzer (described in Chap. 3), or in a secondary ion mass spectroscopy instrument (described in Chap. 17). Mass spectroscopy is very useful for gaining insights into plasma reactions. For example, the development of the etchant-unsaturate model, that elucidates the mechanism of radical production and quantifies the role of added oxidants in halocarbon plasmas, was evolved with the assistance of experimental data obtained from this method.

Micron Ex. 1042, p. 48 Micron v. YMTC IPR2025-00119



Fig. 25 Diagram for mass spectrometric monitoring of effluents from a plasma etching reactor. Reprinted with permission of Ref. 1, copyright, 1983, the American Chemical Soc.

DRY-ETCH EQUIPMENT CONFIGURATIONS

Plasma etching systems consist of several components: a) an etching chamber, that is evacuated to reduced pressures; b) a pumping system for establishing and maintaining the reduced pressure; c) pressure gauges to monitor pressure in the chamber; d) a variable conductance between the pump and etching chamber so that the pressure and flow rate in the chamber can be controlled independently; e) an rf power supply to create the glow discharge; f) a gas handling capability to meter and control the flow of reactant gases; and g) electrodes. Detailed assembly of such systems from these components has evolved a variety of configurations, depending upon which parameters of a process need to be controlled, as well as the specific applications of the system⁵². In this section we describe several of the most important commercially available plasma etch /RIE etch system configurations, together with some of their applications, advantages, and limitations. They include: 1) barrel etchers; 2) "downstream" etchers 3) parallel-electrode (planar) reactor etchers; 4) stacked parallel-electrode etchers; 5) hexode batch etchers; 6) magnetron ion etchers. After describing each of these configurations, a brief comparison of the characteristics single wafer and batch etchers is given.

Some general comments on two equipment related topic are presented before starting a more detailed look at the various systems. These are: a) the impact of electrode materials on dry etch processes; and b) available procedures for adjusting pressure in the etch chamber.

The type of electrode material can have an impact on the etch process in a number of ways. First, in some systems sputtering of the electrodes can occur, and the sputtered material can redeposit on the wafer surfaces. If these products are nonvolatile, they become a source of contamination. Thus, use of electrodes containing materials that will result in nonvolatile sputter etch products, should be avoided. For example, an aluminum electrode in a system utilized to etch Si and SiO₂ with fluorocarbon gases may be prone to causing such problems. Second, some materials can suppress loading effects (see later section on this topic) which can be advantageous, but may also influence the discharge chemistry. For example, carbon and silicon electrodes may suppress loading effects in fluorine-based plasmas, but they may also decrease the F /C ratio. Third, the etching of some electrode materials may cause etch products that impact

or even obscure end point information. Finally, the electrode material may contribute to etch rate non-uniformity effects across the wafer, as is described in a later section.

The pressure in an etch chamber may be adjusted in two ways². The pressure dependence of the etch rates can depend on which of these pressure variation procedures is followed. To adjust the pressure, either the flow rate can be kept constant and the the pumping speed can be varied, or the pumping speed kept constant and the flow rate adjusted. In the former method, the residence time in the chamber changes, while in the latter it remains constant. Possibly the best method for operating a dry-etch system, from the point of view of controlling the gas variables, is to set a fixed flow rate and then maintain a constant pressure by adjusting the pumping speed with a variable conductance and an automatic pressure controller (see Chap. 3). In this manner an adequately high flow rate can be chosen, thereby avoiding the unwanted situation of operating under conditions of a high *utilization factor* (see subsequent section on this topic).

Commercial Dry-Etch System Configurations

Barrel Etchers

The first, and simplest, plasma etchers to be developed⁵³ were barrel etchers (Fig. 26a). This configuration consists of a cylindrical reaction vessel, usually made of quartz, with rf power supplied by metal electrodes placed above and below the cylinder, as shown in Fig. 26a. A perforated metal cylindrical *etch tunnel* is placed within the etch chamber. This serves to confine the glow discharge to the annulur region between the etch tunnel and the chamber wall. Wafers are placed in a holder or *boat* at the center of the cylinder, and usually no electrical connection is made to them. The reactive species created by the discharge diffuse to the region within the etch tunnel, but the energetic ions and electrons of the plasma do not enter this region. The reactive



Fig. 26 Schematic of: (a) a barrel-type plasma etching system. (b) a downstream plasma etcher.

Micron Ex. 1042, p. 50 Micron v. YMTC IPR2025-00119



Fig. 27 Parallel-electrode (planar) type dry etcher. (a) When wafers are placed on the grounded electrode, the system is configured in the plasma etch mode. (b) When wafers are placed on the powered electrode, the system is operated in the reactive ion etch, or RIE, mode.

species from the plasma diffuse to the surfaces to be etched, and since there is no ionic bombardment, the etching is almost purely chemical. As a result, the etching tends to be isotropic, and it is possible to obtain good selectivity, with little or no radiation damage. Most barrel etchers are operated in the high pressure range of dry etching (0.5-2.0 torr). The isotropic nature of the etch, however, limits barrel etchers to such applications as resist stripping and "non-critical" etch steps. Nevertheless, these applications are well served by such systems. In fact, for processes that do not require ion bombardment for directional etching, barrel etchers should be considered. Some materials, such as Al, however, cannot be successfully etched in barrel etchers.

Downstream Etchers

Downstream etchers⁵⁴ derive their name from the fact that the reactive species are created in a plasma, and are then transported to the etching chamber downstream of the plasma (Fig. 26b). Microwave sources have been used to create the long lived chemical species necessary for this configuration. Since the reactive species are created outside of the etching region, as in barrel reactors, temperature control and radiation damage problems can be minimized or avoided⁵⁵. These systems are mostly operated in the high pressure range (0.5-2.0 torr). In order to obtain directional etching, however, some form of bias must still be applied to wafers in downstream etchers, otherwise etching again proceeds in a purely chemical manner.

Parallel Electrode (Planar) Reactors

As described earlier, wafers exposed to energetic ions of a plasma can be subjected to ion-assisted etching processes. Etcher configurations that utilize parallel electrodes can direct energetic ions at the surfaces being etched, by causing them to be accelerated across the potential difference that exists between the plasma and the electrode surfaces (Fig. 4b). As a result, both a physical and a chemical component can impart directionality to the etch process.

In parallel-electrode systems, the electrodes have a planar, circular shape, and are of

Micron Ex. 1042, p. 51 Micron v. YMTC IPR2025-00119

approximately the same size⁵⁶. One of the two electrodes of the planar reactor configuration is connected to the rf supply, and the other to ground. Wafers can be placed on either of the electrodes (Fig. 27). When wafers are etched in such systems by placing them on the grounded electrode, the system is said to be operated in the *plasma etch mode*. When wafers are placed directly on the rf-powered electrode, these systems are said to configured in an reactive ion etch mode. As discussed in Chap. 10, however, a potential difference between the plasma and the grounded electrode can still exist, since the plasma potential is always above ground potential. Thus, even in the plasma etch mode, wafers are subject to energetic ionic bombardment, although usually to a lesser degree than in the RIE mode. For example, energies of bombarding ions are 1-100 eV in the plasma etch mode, and 100-1000 eV in the RIE mode. Since the chamber walls are also grounded, in the plasma etch mode they may be subject to significant ionic bombardment, causing sputtering and redeposition to occur within the etch chamber (i.e. on wafer surfaces). In the RIE mode, only the powered electrode is subject to energetic positive ion bombardment, and there is less likelihood of sputtering nonvolatile products onto the wafers. Etching in both modes in such systems, nevertheless, is affected by the fact that both physical and chemical mechanisms are operative. Typically operation in the RIE mode is conducted at low pressures (<100 mtorr), while plasma etching is carried out at pressures >100 torr.

Commercial systems built in the parallel-electrode configuration can be batch systems or single wafer systems. Batch systems are typically manually loaded, and usually have the capability of being operated in either the plasma etch or RIE mode. This provides such systems with a useful flexibility. Some such systems, have been offreed with a low frequency (450 kHz) power supply. Single wafer parallel electrode etchers are described later.

Stacked Parallel-Electrode Etchers

The stacked parallel-electrode etcher is a small batch machine capable of handling 6 wafers at a time. Its unique design provides an individual pair of electrodes for each wafer (Fig. 28),



Fig. 28 (a) Stacked electrode etcher²³. Reprinted with permission of Semiconductor International. (b) Magnetron ion etching system⁶⁰. Courtesy of MRC, Inc.

Micron Ex. 1042, p. 52 Micron v. YMTC IPR2025-00119



Fig. 29 (a) Schematic of the electrode configuration of the hexode batch etcher. (b) Photograph of a hexode batch etcher. Courtesy of Applied Materials.

thereby combining some of the advantages of single-wafer and batch etchers⁵⁷. (Although, others may hold that it offers less benefits than larger batch systems, while maintaining the same disadvantage of end point detection from only a single wafer). Operating chamber pressures and rf power densities can be kept in the ranges between those of low-pressure, low- power-density hexode batch etchers, and high pressure, high power-density single wafer RIE machines. The system operates cassette-to-cassette, and does not offer load-locks. The major applications of this machine are for etching SiO₂, Si₃N₄, and polysilicon.

Cylindrical Batch Etch Reactors (Hexode Etchers)

Cylindrical batch etchers are designed with a hexagonal inner electrode 45,58,59 (hexode), and the chamber walls serve as the opposite electrode (Fig. 29). Up to 24-150 mm wafers per run are mounted on the hexode, which is the powered electrode, while the other electrode (chamber walls) is grounded. The result is a system in which the area of the hexode is much smaller than the area of the grounded electrode (typically one-half the area). This is just the kind of *highly asymmetrical electrode configuration* needed to cause ionic bombardment of the powered electrode, while minimizing ion bombardment of the grounded electrode and other chamber surfaces (see Chap. 10, *RF Sputtering*, which explains why). Thus, hexode etchers are well designed to operate in the RIE mode and to provide good directional etching capability, but not for operation in the plasma etch mode. Most hexode models are not load-locked and must be manually loaded. Some of the newer models have been designed with load-locks and robotic autoloading. In those non-loadlocked models, more elaborate pumping systems must be provided to remove water vapor from the chamber after exposure to atmosphere (although the load-locked models are also equipped with comparably elaborate pumping systems). Etching is conducted at low pressures (20-100 mtorr) and low power densities.

Micron Ex. 1042, p. 53 Micron v. YMTC IPR2025-00119

Comparison of Single-Wafer and Batch Dry Etchers

Dry etchers capable of anisotropic etching are available as systems configured for single wafer or batch processing (the latter being primarily hexode-type designs). Each type of system has its advantages and limitations. In this section, we compare their capabilities, which are summarized in Table 4.

Hexode batch etchers can accommodate a group of wafers (batch) in each run. Because they can process multiple wafers in a single run, their operating power and pressure can be kept low, while maintaining high throughput. The low pressure allows more energetic bombardment of the surface at lower powers. Thus, non-volatile species that must be removed by the physical component of the etching, such as CuCl, are effectively etched without having to resort to the higher power density levels that promote resist erosion, reduced selectivity, and radiation damage. In addition, multi-step etch processes can be performed in the reaction chamber, as sufficient time is available to change the gas composition in the chamber.

The disadvantages of hexode batch etchers are the following: a) an entire batch of wafers can be lost if the etch process is somehow incorrectly performed, while in single wafer etchers the loss due to a flaw in any cycle can be limited to one wafer; b) end point detection is determined from the average of the etching conditions over the entire batch (emission spectroscopy), or from a single wafer in the batch, while a single wafer etcher can monitor the end point of each wafer; c) more laboratory space is required for batch etchers; d) automation and load-locking of hexode etchers is more complex and expensive than in single-wafer etchers; e) the etching characteristics of the batch etcher may depend on the load of wafers in the chamber, and thus several process recipes might have to be developed for the machine, depending on batch size; and f) the batch uniformity represents an extra variable.

Single wafer etchers have the advantage that wafer-to-wafer uniformity problems of large batch systems is avoided. In addition, since only one wafer is at risk at any time, if a flaw in the process is detected, theoretically it can be corrected before allowing the next wafer to be etched. Likewise, end point detection, load-locking, and automation are more easily achieved. New etch processes can usually be more more rapidly developed on single wafer etchers, and the establishment of multiple recipes dependent on batch size is unnecessary. Finally, capital equipment costs are lower, and equipment space requirements smaller.

On the other hand, single wafer etchers must perform their etching at high rates in order to achieve adequate throughputs. There may be unwanted side effects of such rapid etching requirements, such as: a) excessive resist erosion (see *Dry Etching of Aluminum Thin Films*); b) reduced selectivity; and c) multi-step etches may require multi-chamber etching systems, as the time to evacuate a chamber after each sub-step may be prohibitively long. It is therefore likely that single wafer etchers will be utilized in processes that can tolerate the harsher etching environ-

	SINGLE	BATCH
Pressure	Low - High (often high)	Low
Throughput	Depends on Pressure	High
Etch Uniformity	Good	Adequate?
End Point Detection	Good Control	Average over
Automation	Relatively Easy	More Difficult
Laboratory Space	Smaller	Larger

Table 4. SINGLE WAFER versus BATCH ETCHING

ments of high-rate etching, but that other, more critical steps, will continue to be performed by the less damaging batch etch processes.

Magnetron Ion Etchers

Magnetron ion etchers (MIE) are single wafer machines in which the magnetron principle from sputter deposition is adapted to make the primary electron excitation process in plasma etchers more efficient at lower gas pressures⁶⁰. As a result, both higher reactant species production and ion bombardment rates of the surfaces being etched can be achieved at lower powers and pressures, than are required in non-MIE single wafer etchers. Thus, some of the drawbacks of single wafer etchers associated with having to operate at high power densities and pressure (such as bulk radiation damage and resist erosion), can be reduced, while still maintaining the high etch rates necessary for adequate throughputs in single wafer etchers.

As shown in Fig. 28b, a band magnetron cathode is utilized to create a uniform magnetic field above the wafer. This causes the electrons emitted by the cathode to be constrained from traversing the discharge region to the collecting surfaces. These electrons are thus more likely to collide with, and ionize, gas particles in a low pressure gas. Etch rates of SiO₂ of 6,000 Å /min have been reported using various fluorocarbon-based gas mixtures, with a 5% uniformity over a 125 mm wafer, and at a low voltage. Polysilicon etch rates of 1 μ m /min have also been reported, using an SF₆/CF₄ gas mixture.

PROCESSING ISSUES RELATED TO DRY-ETCHING

Plasma Etching Safety Considerations

Many dry etching processes require the use of potentially hazardous and /or toxic gases. It is important that these gases be used safely in the course of operating and maintaining dry-etching systems. This section provides a brief, but far from complete introduction to this subject and other dry-etching safety issues. Readers are directed to references 61 and 62, as well as to the Semiconductor Safety Association, and to local safety representatives for further information on these topics. The following safety aspects of dry etching are presented in this section: a) working with compressed gases; b) working with toxic and /or corrosive gases; and c) some safety design considerations in plasma etching equipment.

Gases contained in cylinders at high pressures (>225 psig @ 70° F) should be treated with extreme respect. The total force that could be exerted during the release of the gas in a cylinder 48 inches high with a diameter of 9 inches and a pressure of 2000 psig, is in excess of 24 million pounds. The correct regulator should be used to make connection to the cylinder. Compressed-gas cylinders should be securely fastened in properly designed cabinets. The exhaust capacity of a gas cabinet should be able to rapidly handle the entire contents of the cylinder to limit the exposure area. Cylinders containing flammable materials should be electrically grounded to avoid static charge.

One of the most probable times when a life or health threatening accident can occur is when gas cylinders are being changed, and thus safe procedures must be carefully followed when performing this operation. In some plants, *only* engineers responsible for a particular operation can change cylinders, and the procedure is performed using the "buddy" system.

The constituents of the feed stock gases used in common plasma processes are listed in Refs. 61 and 62. Many of these constituents are toxic. Some of them (e.g. ammonia) cause immediate noticeable symptoms at concentrations below the *immediately dangerous to life and health levels* (IDLH), but many others (e.g. phosgene [COCl₂] an impurity constituent gas found

in BCl_3 supplies) are colorless and odorless at concentrations well above the IDHL level. This demands that suitable gas detectors be used to monitor and warn of gas leaks, as a means of protecting the work environment from hazardous materials. All personnel that work with hazardous gases should attend safety courses dealing with such subjects as respirator use, spill clean-up procedures, and fire procedures.

If a toxic gas is accidentally inhaled, both *emergency* and *extended* action needs to be taken. For example, the inhalation of chlorine produces only slight irritation in the first 6 hours. During the following period of up to 8 days, however, *edema* (a swelling of the mucous membrane) may result and acute reaction set in. Thus, *close observation* during this entire period is mandatory to insure the well-being of anyone who has come into contact with chlorine (or any other toxic substance).

Carbon tetrachloride (CCl_4) is an etch gas used in some aluminum dry-etch processes. This etch products from this gas have been identified as being carcinogenic, and its use in *non-load-locked* systems has been pronounced unacceptable⁶¹. On the other hand, others have suggested that utilization of CCl_4 in *load-locked* systems can be safe⁶², provided that NIOSH (part of OSHA) approved respirators with organic vapor and acid gas cartridge, and gloves (made of nitrile rubber, polyvinyl alcohol, or viton) are worn by personnel whenever performing maintenance or cleaning procedures on such systems.

Plasma systems should also be designed for no-fail operation. For example, the shut off valve of gas cylinders should be normally off, and only driven on by high pressure nitrogen that is interlocked to the gas monitor and electrical alarm systems. Thus, if either N_2 pressure or electrical power fails, these cylinders will be isolated. The gas line between the cylinder valve and the last valve in a line should be purged by cycling between over pressure and under pressure conditions, to rapidly dilute the gas trapped in the line to low values. This procedure is much more effective in reducing the concentration of the gas in the line than merely flowing a purge gas through the line.

Plasma system pumps should be oversized and use N_2 ballast (see Chap. 3) to eject corrosive gases quickly, and to prevent condensation of corrosive vapors. Pumps should be well marked so that maintenance personnel will follow proper protective procedures when performing oil changes or repairs. Use of synthetic pump oils is recommended, because they require much less frequent oil changes. The spent oil and filter cartridges must be treated as hazardous waste.

The rf emissions from plasma etchers are normally below the U.S. recommended limit for rf exposure (4.9 mW /cm² of body area over a 6 min period). However, damage to an etching unit door or housing misalignment can result in excessive rf leakage. Thus, whenever an etcher installed, moved, or modified, its rf emissions should be monitored to ensure the units integrity.

Uniformity and Reproducibility Considerations

It is important that dry etch processes are uniform across a wafer (and from wafer-to-wafer in batch etch systems), and are reproducible from run-to-run. The following factors influence the uniformity and reproducibility of dry etch processes: a) exposure of the etching chamber to room ambient; b) gas distribution within the system; c) gas flow rates; d) end point detection; e) loading effects; and f) electrode-related efffects.

Exposure of Etching Chamber to Room Ambient

If the etching chamber is periodically exposed to room ambient, the reproducibility of the etch conditions from run-to-run may be impacted. The exposed chamber surfaces adsorb moisture which may affect the next etch cycle in a nonreproducible way. This problem is avoided in systems that keep the etch chamber isolated from exposure to the ambient by use of load locks,

576 SILICON PROCESSING FOR THE VLSI ERA



Fig. 30 Etch rate of sputtered quartz, demonstrating the utilization factor $concept^{63}$. Reprinted with permission of the American Physical Society.

but often batch systems, such as some hexode reactor models, are not load-locked, but are opened to atmosphere after every run. Several techniques are employed to reduce the above mentioned problems in such systems⁴⁵, including using a cryopump to more completely remove moisture from the chamber before beginning the etch cycle, employing etch gases that are effective moisture getters (e.g. BCl₃), and surrounding the etch chamber with a nitrogen purged box.

Gas Distribution

A uniform supply of reactive species to the wafer surfaces is necessary to bring about uniform etch rates across a wafer, and from wafer-to-wafer in batch etchers. Thus, reactors must be designed with gas feed systems that produce such uniform reactant distributions. This is a challenging task, as viscous flow prevails over the range of working pressures and reactor dimensions. In viscous flow, the local molecular interactions are strong, and gas mixing is poor. Various gas distributions designs have been evolved, depending on the reactor configuration. Batch-type planar etchers usually use gas rings to distribute the gas uniformly around the perphery of the circular electrodes. Some single wafer etchers, that have smaller chambers utilize a shower head electrode, that emits gas from the top electrode. Hexode etchers employ a gas tree distribution design along the axis of the hexagonal electrode.

Gas Flow Rates (Utilization Factor)

Not only must a *uniform* quantity of reactants be provided to all wafer surfaces in order to achieve uniform and reproducible etch rates, but an *adequate quantity* of reactant must also be supplied. That is, if the etch rate is limited by the supply of reactant, small variations in flow rate or gas distribution uniformity may lead to etch rate nonuniformities. As a result, there is a minimum flow rate of reactant gas that must be supplied to prevent the process from being

Micron Ex. 1042, p. 57 Micron v. YMTC IPR2025-00119 limited by the reactant supply. A concept known as the *utilization factor* has been developed to quantify this situation. For example, in a CF_4 based etching process, the utilization factor is defined to be the ratio of the rate at which fluorine is consumed in the etching process, to the rate at which the fluorine enters the system as CF_4 . If the etch rate is limited by the supply of reactants, then all the fluorine is consumed, and the utilization factor = 1 (Fig. 30)⁶³. It has been determined that etching processes exhibit optimum behavior if the utilization factor is of the order of 0.1 or less. It is therefore recommended that the utilization factor be determined whenever an etching process parameter is changed⁴. Relatively simple techniques for measuring the utilization factor are given in Reference 63.

Loading Effects

In plasma etching systems, etch gas is fed into the reaction chamber. There, a plasma creates reactive species. The etch rate is generally proportional to their concentration, and the concentration in turn is reflected by the partial pressure of the species, P_x . The reactive species are removed from the chamber by one of the following events: a) consumption, by the etching reactions, taking place at a rate S_{etch} ; b) recombination, an event most likely to occur when the reactive species come in contact with the non-etchable surfaces within the chamber, and such recombination removes reactants at a rate, S_{recomb} ; and c) pumping of the species from the chamber before one of the other two events occurs, and this removal rate is given by the pumping speed, S_{pump} .

In the steady-stafe, reactive species are being created and removed at equal rates, and the partial pressure of the reactive species, $P_x = G_x/S$, where G_x is the generation rate of these species, and S is the sum of the three removal rates, $S = S_{etch} + S_{recomb} + S_{pump}$. In processes in which the etch reaction is the dominant removal mechanism, the partial pressure, and hence etch rate, is controlled by S_{etch} . Since S_{etch} is directly proportional to the area of exposed etch surface, the etch rate decreases as more etched surface is added to the chamber. This effect is known as the *loading effect*, and an example of the loading effect is shown in Fig. 31b. In this figure, the etch rate of polysilicon decreases with exposed area when the temperature is increased to 140°C. Note that an increase in the gas flow will not alleviate the loading effect. The concentration of reactive species will be increased by a higher flow rate, and for a constant area of etched surface, the etch rate will be faster. But if S_{etch} remains dominant, when more wafers are added the etch rate will still decrease.

In most etch processes the loading effect is undesirable for the followng reasons: 1) since the etch rate drops, some of the throughput benefits of batch processing are lost; 2) since the etch rate depends upon the amount of etchable area in the chamber, this becomes another parameter that leads to process non-uniformities from run-to-run; and 3) when the end point of an etch step is reached, the etchable area undergoes a precipitous decrease, as the material in the field is removed, and only the sidewalls of the etched features remain exposed. The loading effect at that time causes the etch rate to increase. As a result, during any overetch time, the sidewalls are etched at a higher rate than the nominal process etch rate, and this aggravates the undercutting problem. There are several methods that can be utilized to alleviate loading effects, mostly based on increasing the rate of removal of reactive species by other mechanisms than the etching reactions on wafers.

To quantify the procedures utilized to reduce loading effects, a mathematical model that relates the various parameters involved in with the loading effect has been constructed^{25,65}. The model provides a good description of silicon etching in CF_4/O_2 discharges, and expresses the etch rate of m wafers, R_m , in terms of the etch rate of an empty reactor, R_0 (which represents the etch rate when the etchable area approaches zero), by the following expression:



Fig. 31 (a) Reciprocal of Si etch rate vs. number of 3" wafers, demonstrating the loading effect⁶⁵. Reprinted with permission of the publisher, the Electrochemical Society. (b) The etch rate of Si is increased sufficiently and /or the reactivity is increased sufficiently by increasing temperature⁶⁶. Reprinted with permission of the Japanese Journal of Applied Physics.

$$R_{o}/R_{m} = 1 + m\Phi = 1 + m[A_{w}k_{etch}/(A_{ch}k_{recomb} + Vk_{v})]$$
(1)

where: Φ is the ratio of reactant species consumed by etching a wafer to the rate of removal of reactant species by all other mechanisms; k_{etch} is the reactant species consumption rate per unit area of etched surface; A_w is the area of exposed etched surface per wafer; k_{recomb} is the removal rate per unit area due to recombination at reactor wall surfaces; A_{ch} is the area of the chamber wall surfaces; k_v is the volumetric removal rate per unit volume due to pumping; and V is the volume of the chamber. When Φ is small, the etch rate approaches that of an empty chamber.

In plasma etching processes for which the above model is applicable, the sensitivity of etch rate to loading conditions can be reduced by several procedures, including: a) conducting the etching in a chamber with a large volume and high surface area; b) utilizing large gas flows, (large k_v) which will cause the removal rate due to pumping to dominate; c) using an electrode constructed of the same material as that being etched, thereby maintaining a fully-loaded condition in the chamber, regardless of the number of wafers present (in the latter method, however, end pont detection by optical emission spectroscopy becomes difficult); and d) in processes in which the etch rate is controlled by ionic bombardment, it may be possible to reduce Φ by maintaining a sufficiently slow etch rate.

Not all plasma etching processes are well modeled by Eq. 1, and some of those that are not do not exhibit loading effects. For example, the concentration of chlorine atoms, a reactive species in some chlorine-containing plasmas, is limited by recombination, rather than by the atom-substrate reaction that causes etching. In these plasmas the etching is independent of etchable area²⁵.

Micron Ex. 1042, p. 59 Micron v. YMTC IPR2025-00119

Electrode-Related Effects

Etching rate nonuniformity effects across a wafer, arising from aspects of the electrode material and configuration, can also occur. Two examples of such effects are: 1) the degree to which the electrode material is etched can play a role. That is, if the electrode is inert, no consumption of reactive species occurs above regions where the electrode surfaces are uncovered. These species then represent an additional supply of reactants near the wafer edge that is not available to central wafer regions. Hence, etching occurs more rapidly near the edges, and the wafer clears from the outside to the center (*bullseye pattern*). Conversely, if the electrode material etches more rapidly than the wafer surface, reactant at the wafer edges may become depleted, causing the center of the wafer to etch more rapidly; 2) With the wafer located on the electrode, the electric field lines of the dark space are disturbed at the wafer edge. This leads to an increase in the ion bombardment near the edge. If the etch rate increases with increasing ionic bombardment flux, etching again becomes greater near the edge than at the center. Techniques suggested for reducing this effect include recessing of the wafers into the electrode surface, or surrounding the wafer with conducting or insulating rings.

End Point Detection

After an etch cycle is completed, it is necessary to terminate the etching action. There are usually too many variables in an etch process performed in a production environment to merely use the etch time as a measure of when the cycle is complete. Instead, the process must be monitored with an end point detection technique, as described earlier, and information obtained from such monitoring must be utilized to decide when the etching action should be terminated. (It should be noted, however, that in processes in which end point detection techniques are not effective, timed etches are used.) Effectively determining the end point of an etch cycle prevents insufficient etching as well as overetching, and can also be used to compensate for film thickness and etch rate variability. End point detection techniques are described in an earlier section.

Contamination and Damage of Etched Surfaces

Contamination

Wafers etched by dry processes can be subjected to contamination from a number of sources including: a) polymeric residues from the etch process; b) deposition of nonvolatile contaminants from sputtering events associated with the etch process; and c) particulate contamination.

Polymeric residue contamination is caused by halogen deficiency in halocarbon plasmas, as described earlier in the section dealing with the etching model of Si and SiO₂ in CF₄, O₂, and H₂. Such contamination can produce rough surfaces on the films being etched (or on underlayers), can lead to high contact resistance, and in the case of Al etching, serve as a "reservoir" for corrosion causing halogens. A technique for avoiding such residues is to somehow increase the F/C ratio near the end of a dry-etching cycle, thereby allowing any residue film to be removed, and not reformed.

Surfaces being etched can be contaminated by deposits of nonvolatile solids sputtered from surfaces in the etching chamber. Sputtering events occur in etching chambers as a result of the potential difference that exits between the plasma, and the surfaces being etched and chamber walls. If the chamber surfaces consist of materials containing heavy metals (e.g. Fe, Cr, Ni), they can be sputtered, and then end up being deposited on the surfaces being etched. To reduce this type of contamination: 1) the chamber walls and electrode surfaces should be made of (or coated with) materials compatible with the surfaces being etched (e.g. aluminum, or SiO_2); and 2) the system should be designed so that sputtering events are minimized from surfaces of nonvolatile solids. The latter is accomplished by electrically connecting together the chamber

580 SILICON PROCESSING FOR THE VLSI ERA

walls and non-wafer holding electrode, and making their combined area large relative to that of the wafer-holding electrode.

Four main sources of *particulate contamination* have been identified in dry-etching systems⁶⁷: 1) wafer transport materials and operation; 2) processing by-products; 3) particulates from paper products utilized nearby the etcher (e.g. operations manuals and strip chart recorders); and 4) the environment. *Wafer transport related particulates* are kept to a minimum by effective system design. *Processing by-product particulate* densities depend on the specific process. In those processes that are prone to particulate production from polymer build-up and subsequent separation from the reactor walls, however, more frequent system cleaning to maintain low particulate densities is required. *Paper product related particulates* can be reduced by using low particulate stationary, or by keeping paper products entirely out of the clean room in which the etchers are located. *Clean room environment particulates* are minimized by a host of elaborate procedures, and these are described in detail in Vol. 2 of this text.

Radiation Damage

As described earlier, in reactive ion etching (RIE), surfaces being etched are subject to bombardment by energetic ions, electrons, and photons. These incident species can produce various forms of radiation damage in the materials being etched including: a) electron traps in gate oxides, which if not annealed out, cause shifts in the threshold voltages of MOS devices; b) displaced atoms and implanted atoms in the surface due to ion bombardment; and c) under some etching conditions, destruction of the gate oxide.

The type of *trapping sites generated by RIE* is reported to depend on the specific process⁶⁸. For example, CF_4 plasmas have been shown to induce bulk trapping sites with a centroid of approximately one half the thickness of the oxide, while exposure to O₂ plasmas leads to surface



Fig. 32 Gate oxide breakdown⁷⁰. Reprinted with permission of Solid State Technology, published by Technical Publishing, a company of Dun & Bradstreet.

Micron Ex. 1042, p. 61 Micron v. YMTC IPR2025-00119

MATERIAL	GASES
Silicon (including polysilicon) Si O_2 Si $_3N_4$ Organic Solids Aluminum W, WSi ₂ , Mo TaSi ₂ Au	$\begin{array}{c} \hline & \text{CF}_4, \ \text{CF}_4 \ /\text{O}_2, \ \text{CF}_3\text{Cl}, \ \text{SF}_6 \ /\text{Cl}, \ \text{Cl}_2 + \text{H}_2, \ \text{C}_2\text{ClF}_5 \ /\text{O}_2 \\ & \text{SF}_6 \ /\text{O}_2, \ \text{SiF}_4 \ /\text{O}_2, \ \text{NF}_3, \ \text{ClF}_3, \ \text{Ccl}_3\text{F}_5, \ \text{C}_2\text{ClF}_5 \ /\text{SF}_6 \\ & \text{CF}_4 \ /\text{H}_2, \ \text{C}_2\text{F}_6, \ \text{C}_3\text{F}_8, \ \text{CHF}_3 \\ & \text{CF}_4 \ /\text{O}_2, \ \text{CF}_4 \ /\text{H}_2, \ \text{C}_2\text{F}_6, \ \text{C}_3\text{F}_8 \\ & \text{O}_2, \ \text{O}_2 + \text{CF}_4, \ \text{O}_2 + \text{SF}_6 \\ & \text{BCl}_3, \ \text{Ccl}_4, \ \text{SiCl}_4, \ \text{BCl}_3 \ /\text{Cl}_2, \ \text{Ccl}_4 \ /\text{Cl}_2, \ \text{SiCl}_4 \ /\text{Cl}_2 \\ & \text{CF}_4, \ \text{CF}_4 \ /\text{O}_2, \ \text{C}_2\text{F}_6, \ \text{SF}_6 \\ & \text{SF}_6 \ /\text{Cl}_2, \ \text{CF}_4 \ /\text{Cl}_2 \\ & \text{C}_2\text{Cl}_2\text{F}_4, \ \text{Cl}_2 \end{array}$

IADIC D ETCH GADED COED FOR VARIOUS HVIEVGRAIED CIRCUIT MATERIA	Table 5	ETCH	GASES	USED	FOR	VARIOUS	INTEGRATED	CIRCUIT	MATERIAI
---	---------	------	-------	------	-----	---------	------------	---------	----------

layer trapping sites. The bulk traps are removed by a 600°C anneal, and so are of concern only if an RIE step is performed after an Al thin film is in place. Polysilicon and Al gate materials also effectively shield the oxide from such radiation damage. Such radiation damage is minimized by low power or low dc voltages, or by placing the wafers on the grounded electrodes⁶⁹. Batch etch systems tend to use lower power than conventional single wafer etchers, but magnetron ion etching single wafer systems employ low power as well.

The gate oxide can also be destroyed by dielectric breakdown during RIE of polysilicon gate layers under some conditions. Watanabe and Yoshida⁷⁰ propose that as polysilicon is being etched (Fig. 32), it builds up a positive charge in response to the electrons from the discharge, which accumulates on the wafer and then become stored in the resist and blocking capacitor (see Chap. 10 for an explanation as to how electrons accumulate ion the surfaces in contact with an rf plasma). As long as the poly-Si layer is continuous, it contacts the backside of the wafer, and there is no potential difference across the gate oxide. Once the poly-Si is etched, the gate and the substrate are no longer in contact and a sufficient voltage may develop across the gate oxide to result in dielectric breakdown. In addition, whenever the power is turned off, positive ions in the dark space recombine with the electrons in the resist, and negative charges stored on the blocking capacitor recombine with the darkspace positive ions through the conductive material of the cathode. If, however, the negative charges on the blocking capacitor are attracted by the positive charges on the isolated gate material, before enough recombination takes place, the transient surge current may also produce a sufficiently large potential difference across the SiO₂ gate to cause breakdown. It is noted, that in conventional RIE processes the cause of such breakdown cannot be removed, and that a solution to this problem requires a more complete understanding of the details of this failure mechanism.

Process Gases for Dry Etching

Many different gases are used in dry etching processes for VLSI fabrication, either individually or as the components of mixtures of several gases⁷³. Table 5 lists most of the important gases used in dry etching applications. Chlorine-based gas mixtures (e.g. containing Cl₂, BCl₃, CCl₄, and SiCl₄- usually in some combination of Cl₂ and one of the other species) are primarily used to etch aluminum and aluminum alloys. Earlier we discussed the use of fluorocarbon-based plasmas for etching Si, SiO_2 , and Si_3N_4 , and also described the use of various flourochlorocarbon gas mixtures for etching polysilicon. In dry etching processes for Si and SiO₂ that utilize CF₄, it was found that the active etching species is atomic fluorine. More recently SF₆ and NF₃⁷¹ have been exploited as sources of atomic fluorine for dry

581

etching Si and SiO₂. These gases exhibit the advantages of higher Si and SiO₂ etch rates than CF₄ (up to 5000 Å /min vs. ~1000 Å /min), excellent silicon to silicon dioxide selectivities (e.g. 50:1), and the fact that they exhibit a smaller loading effect than CF₄ etching processes. The NF₃ etching processes reportedly suffer from more pronounced loading effects than SF₆-based etching processes, but the NF₃ etching by-products formed from side reactions consist of only volatile compounds⁷². Therefore, polymer deposition on the silicon surface is minimal when etching with NF₃. Etching polysilicon with either SF₆ or NF₃, alone, is typically isotropic, but anisotropic etching has been successfully performed by: a) adding small amounts of chlorine-containing gases, such as CFCl₃ or CHCl₃, to the SF₆; or b) by decreasing the pressure of the NF₃ plasma to ~100 mtorr, causing higher ion bombardment energies. Furthermore, highly anisotropic etching of MoSi₂ in such low-pressure NF₃ plasmas has been reported⁷².

REFERENCES

- 1. J. A. Mucha and D.W. Hess, "Plasma Etching", in *Introduction to Microlithography*, Advances in Chemistry Series, Vol. 219, American Chemical Society, 1983, p. 215.
- 2. J.W. Coburn, "Plasma Etching and Reactive Ion Etching", American Vacuum Society, New York, 1982, p. 15.
- 3. *ibid.*, Ref. 2, p. 15.
- 4. C.J. Mogab, A.C.Adams, and D.L.Flamm, J. Appl. Phys., 49, 3796 (1978).
- 5. J.W. Coburn, from foils presented in the American Vacuum Society Education Course,"Plasma Etching and Reactive Ion Etching", 1986, foil 3-16, not published.
- 6. J.L. Vossen, J. Electrochem Soc., 126, 319 (1979).
- 7. J.W. Coburn, "Pattern Transfer", Solid State Technol., April, 1986, p. 117.
- 8. E. Kay, J.W. Coburn and A. Dilks, *Topics in Current Chemistry*, Vol. 94, Springer-Verlag Publishing Co., Heidelburg, W. Germany, 1980, p. 1.
- M.W. Jenkins, et al., "The Modelling of Plasma Etching Processes Using Response Surface Methodology", Solid State Technol., April, 1986, p. 175.
- 10. J.W. Coburn and H.F. Winters, J. Vac. Sci. Technol., 16, 391 (1979).
- 11. D.L. Flamm, Plasma Chem., Plasma Process, 1, 37 (1981).
- 12. M. Chen, V.J. Minkiewicz, and K. Lee, J. Electrochem. Soc., 126, 1946, (1979).
- 13. D.L. Flamm and V.M. Donnelly, Plasma Chem. Plasma Process, 1, 317, (1981).
- 14. ibid., Ref. 4.
- 15. L.M. Ephrath and E.J. Petrillo, J. Electrochem. Soc., 129, 2282, (1982).
- 16. R.A. Heineke, Solid State Electronics, 18, 1146, (1975).
- 17. J.S Chang, "Selective Reactive Ion Etching of SiO2", Solid State Technol, April, '84, p. 214.
- 18. G. Francis, Handbuch der Physik, 22, 53 (1956).
- 19. A.S. Bergendahl, D.L. Harmon, and N.T. Pascoe, Solid State Technol., Nov. '84, p. 107.
- 20. J.W. Coburn and H.F. Winters, J. Appl. Phys., 50, 3189 (1979).
- 21. ibid., Ref. 13.
- 22. ibid., Ref. 10.
- 23. A. Weiss, "Plasma Etching of Oxides and Nitrides" Semiconductor Internat'l, Feb., '83, p. 56.
- 24. J. Poisson, et al., "Via Contact Dry Etching Using a Plasma Low Resistance Photoresist", Proc. Third VLSI Multilevel Interconnection Conf., Santa Clara, CA., June, 1986, IEEE.
- 25. D.L. Flamm, V.M. Donnelly, and D.E. Ibbotson, "Basic Principles of Plasma Etching", in VLSI Electronics, Microstructure Science, Vol. 8, Academic Press, Chap. 8, p. 190.
- 26. ibid., Ref. 25, p. 227.
- 27. A. Weiss, "Plasma Etching of Poly-Si: Overview", Semiconductor Internat'l, May, '84, p. 215.
- 28. M. Mieth, et al., "Plasma Etching Using SF₆ and Chlorine Gases", Semiconductor International, May, 1984, p. 222.

- 29. U. Winkler, "VLSI Polysilicon Etching: A Comparison of Different Techniques", Solid State Technol., April, 1983, p. 169.
- 30. P. Chang and S. Hsia, "Selective Plasma Etching of Polysilicon", Solid State Technology, Aug., 1984, p. 225.
- 31. W. Beinvogel and B. Hasler, "Reactive Ion Etching of Polysilicon and Tantalum Silicide", *Solid State Technology*, April, 1983, p. 125.
- 32. H.F. Winters, J.W. Coburn, and J.T. Chang, "Surface Processes in Plasma Assisted Etching Environments", J. Vac. Sci. Technol., B1, (2), 469, 1983.
- C.J. Mogab, "Dry Etching", in VLSI Technology, Ed. S.M. Sze, McGraw-Hill, NewYork, 1983, Chap. 8, p. 303.
- 34. D.R. Stull, Ind. Engr. Chem., 39, 517, (1947).
- 35. J.F. O'Hanlon, Solid State Technol., October, 1981, p. 86.
- 36. D.L. Smith and R.H. Bruce, Ext. Abs. of the Electrochem. Soc., Abs. No. 258, Fall Meeting, 1981, Denver, CO., Electrochem. Soc., Pennington, N.J.
- 37. K. Tokunaga and D.W. Hess, J. Electrochem. Soc., 127, 928 (1980).
- 38. R.H. Bruce and G.P. Malafsky, J. Electrochem. Soc., 130, 1369 (1983).
- 39. T. Tsukuda, et al., in Plasma Processing, Eds. J. Dieleman, R.G. Frieser, and G.S. Mathad, The Electrochemical Society, Inc., Pennington, N.J.
- J.E. Spencer, "The Management of AlCl₃ in Plasma Etching Aluminum and Its Alloys", Solid State Technol., April, 1984, p. 203.
- 41. M. Pender and P.C. Lindsey, 1982, Zylin Corp., unpublished results.
- 42. R.H. Bruce and G. Malafsky, Ext. Abs. of the Electrochem Soc. Meeting, Fall, 1981, Denver, CO., Oct. 1981, Abs. No 288, Electrochemical Society, Pennington, N.J.
- 43. M. Oda and K. Hirata, Jap. Jnl. Appl. Phys., 19, 405 (1980).
- 44. F. Daniels and R. Alberty, Physical Chemistry, John Wiley & Sons, New York, 1981, p. 126.
- 45. S. Broydo, "Important Considerations in Selecting Anisotropic Plasma Etching Equipment", Solid State Technol., April, 1983, p. 159.
- D.W. Hess and R.H. Bruce, "Plasma Assisted Etching of Al and Al Alloys", in Dry Etching for Microelectronics, Ed. R.A. Powell, North Holland Publishing Co., 1984.
- 47. B. Chapman and M. Nowak, "Troublesome Aspects of Aluminum Plasma Etching", Semiconductor International, November, 1980, p. 139.
- 48. W.Y. Lee, et al., J. Appl. Phys., 52, 2994 (1981).
- M. Sternheim, W. van Gelder, and A.W. Hartman, "A Laser Interferometer System to Monitor Dry Etching of Patterned Si", J. Electrochem. Soc., 130, 655, 1983.
- 50. P.J. Marcoux and P.D. Foo, "Methods of End Point Detection for Plasma Etching", Solid State Technol., April, 1981, p. 115.
- 51. A.D. Weiss, "End Point Monitors", Semiconductor International, Sept. 1983, p. 98.
- 52. S.J. Fonash, "Advances in Dry Etching Processes- A Review", Solid State Technol., January, 1985, p. 150.
- 53. D.L. Tolliver, "Plasma Etching in Microelectronics-Past, Present, and Future", Solid State Technol., Nov., 1980, p. 99.
- 54. D.L. Smith, "High Pressure Etching", in VLSI Electronics, Vol. 8, N.G. Einspruch, Ed., Academic Press, Orlando, FL., 1984, Chap. 9, p. 253.
- 55. J. Dieleman and F.H.M. Sanders, "Plasma Efluent Etching: Selective and Non-Damaging", Solid State Technol., April, 1984, p. 191.
- 56. A.R. Reinberg, "Dry Processing for Fabrication of VLSI Devices", in N.G. Einspruch, Ed., VLSI Electronics, Vol. 2, Academic Press, New York, 1981, Chap. 1, p. 1.
- 57. J. Maher, "Selective Etching of SiO₂ Films", Semiconductor Int'l., May, 1983, p. 110.
- 58. A. Weiss, "Plasma Etching of Aluminum: Review of Process Equipment and Technology",

584 SILICON PROCESSING FOR THE VLSI ERA

Semiconductor International, Oct., 1982.

- 59. A. Weiss, "Etching Systems", Semiconductor International, Oct., 1982, p. 69.
- 60. D.C. Hinson, et al., "Magnetron-Enhanced Plasma Etching of Silicon and Silicon Dioxide", Semiconductor International, Oct., 1983.
- 61. G.K. Herb, et al., "Plasma Processing: Some Safety, Health, and Engineering Considerations", Solid State Technology, Aug., 1983, p. 185.
- 62. G. Corn and D.G. Baldwin, "Safety Considerations for Plasma Aluminum Etching", J. Vac. Sci. Technol., 83 (3), 909, (1985).
- 63. B.N. Chapman, T.A. Hansen, and V.J. Minkiewicz, J. Appl. Phys., 51, 3608 (1980).
- 64. ibid., Ref. 2, p. 2.
- 65. C.J. Mogab, "Loading Effect in Plasma Etching", J. Electrochem. Soc., 124, 1262 (1977).
- 66. T. Enomoto, et al., "Loading Effect and Temperature Dependence of Etch Rate in CF₄ Plasma", Jpn. J. Appl. Phys., 18, 155 (1979).
- 67. R. Lachenbruch, T. Wicker, and J. Peavey, "Contamination Study of Plasma Etching", *Semiconductor International*, May, 1985, p. 164.
- 68. L.M. Ephrath and D.J. DiMaria, "Review of RIE Induced Radiation Damage in SiO₂", Solid State Technology, April, 1981,
- 69. S.W. Pang, "Dry Etching Induced Damage in Si and GaAs", Solid State Technology, April, 1984, p. 249.
- 70. T. Watanabe and Y. Yoshida, "Dielectric Breakdown of Gate Insulator Due to RIE", Solid State Technol., April, 1984, p. 213.
- 71. A.J. Woytek, et al., "Nitrogen Trifluoride-A New Dry Etchant Gas", Solid State Technol., March, 1984, p. 172.
- 72. C.S. Korman, et al., "Etching Characteristics of Polysilicon, Silicon Dioxide, and MoSi₂, in NF₃ and SF₆ Plasmas, Solid State Technol., Jan., 1983, p. 115.
- 73. J. Webber, "Choosing Gases for Plasma Dry Etching", Microel. Mfg. & Test., Jan. 85, p.40.
- 74. R.F. Reichelderfer, et al., J. Electrochem. Soc., 124, 1926 (1977).

PROBLEMS

1. Cite five advantages that dry-etching possesses when compared to wet etching. Also list three of the most important disadvantages associated with dry-etching when compared to wet etching.

2. Why have *ion-milling* and *reactive ion beam etching* found little application in the fabrication of silicon VLSI circuits.

3. Explain the difference between the terms glow discharge and plasma.

4. Explain why the term *ion-assisted etching* is a more apt description of dry-etching processes which rely on both chemical and physical etching effects, than is the term *reactive-ion etching*.

5. Explain why the potential of a glow discharge used in dry-etching or sputter deposition, is positive relative to ground.

6. When etching Si over SiO₂ in a CF_4 plasma, the problem of obtaining an adequately high S_{fs} does not usually exist. Explain why this is the case.

7. Explain why a short-lived reactive species, such as atomic chlorine, does not exhibit loading effects when used to perform dry-etching.

8. If the selectivity of SiO₂ over Si can be improved by adding H₂ to the CF₄ feed gas, why have processes that use gases that contain no H₂, but still offer improved selectivity compared to pure CF₄ (e.g. C₂F₆), been investigated as alternatives?

9. The addition of H_2 to a CF_4 plasma is accompanied by the deposition of polymers (*polymerization*) on surfaces within the reaction chamber. Discuss the chemistry of such polymer formation. Note that it may be necessary to consult a chemistry text or the technical literature to

completely answer this problem.

10. Cite an etch process that is apparently controlled by the surface damage mechanism, and another that is apparently controlled by the surface inhibitor mechanism.

11. Explain why the formation of sloped sidewall in etched features by controlled resist erosion is such a difficult process to implement in a batch-etch production manufacturing environment.

12. Discuss some of the reasons why the development of an adequate dry-etch process for polycide layers is such a challenging task.

13. If a dry-etch process for an Al-4at% Cu alloy is conducted at 70°C, use the vapor pressure of CuCl versus temperature curve, given in Fig. 20b, to calculate the maximum etch rate of such a film which would still allow the CuCl etch product to completely evaporate as the film is being etched.

14. In practice, the evaporating CuCl molecules of problem 13 would suffer collisions with the argon sputter gas to a signifiant degree, and therefore be returned to the surface from which they evaporated in relatively large numbers, in effect making the apparent evaporation rate substantially lower. Calculate the mean free path of a CuCl molecule in an Ar plasma at a pressure of 2 torr.

15. In some cases a loading effect is necessary in order to be able to monitor an etch process. Cite at least one important aspect of a dry-etch process that takes advantage of loading effects.

16. Explain the difference between the utilization factor and loading effects.

n/a TK7874/.W831

Silicon processing for the VLSI era / Stanley Wolf, Richard N. Tauber. Process integration. V. 2 1990 bfdn c. 1 SVO

n/a TK7874/.W831 T Silicon processing for the VLSI era / Stanley Wolf, Richard N. Tauber. Process integration. V. 2 1990 bfdn c. 1 SVO

> WEIL, GOTSHAL & MANGES, LLP LIBRARY

> > SEP 1 3 .Joy

WENLU FAHK

Micron Ex. 1042, p. 67 Micron v. YMTC IPR2025-00119

THE COMPANION VOLUMES TO THIS BOOK

Silicon Processing

for the VLSI Era

Volume 2 - Process Integration By STANLEY WOLF

TABLE of CONTENTS - Ch. 1 Process Integration for VLSI and ULSI;
Ch. 2 Isolation Technologies for Integrated Circuits; Ch. 3 Contact Technology and Local Interconnects for VLSI; Ch. 4; Multilevel Interconnect Technology for VLSI and ULSI; Ch. 5 NMOS Devices and Process Integration;
Ch. 6 CMOS Process Integration; Ch. 7 Bipolar and BiCMOS Process Integration; Ch. 8 Semiconductor Memory Process Integration;
Ch. 9 Process Simulation.

1990 LATTICE PRESS 752 pp. ISBN 0-9616721-4-5

Volume 3 - The Submicron MOSFET By STANLEY WOLF

TABLE OF CONTENTS - Ch. 1 Role of Process & Device Models in Microelectronics Technology; **Ch. 2** Numerical Methods for Solving the Partial Differential Equations which Model Submicron Devices and Processes; **Ch. 3** Basic MOS Physics & MOS Capacitors; **Ch. 4** Long-Channel MOSFETs; **Ch. 5** The Submicron MOSFET; **Ch. 6** Isolation Structures in CMOS; **Ch. 7** Thin Gate Oxides: Growth & Reliability; **Ch. 8** Well Formation in CMOS; **Ch. 9** Hot-Carrier Resistant Processing & Device Structures.

1995 LATTICE PRESS 722 pp. ISBN 0-9616721-5-3

Order by using form on last page of book

ISBN 0-9616721-3-7

Micron Ex. 1042, p. 68 Micron v. YMTC IPR2025-00119