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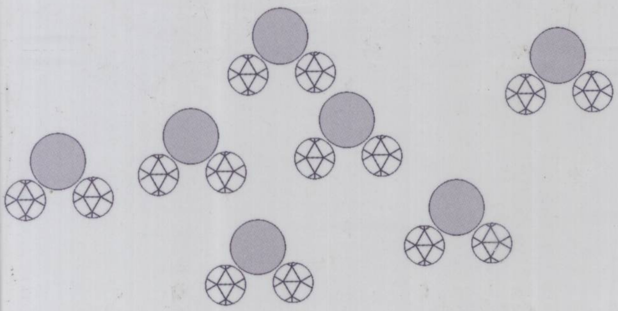
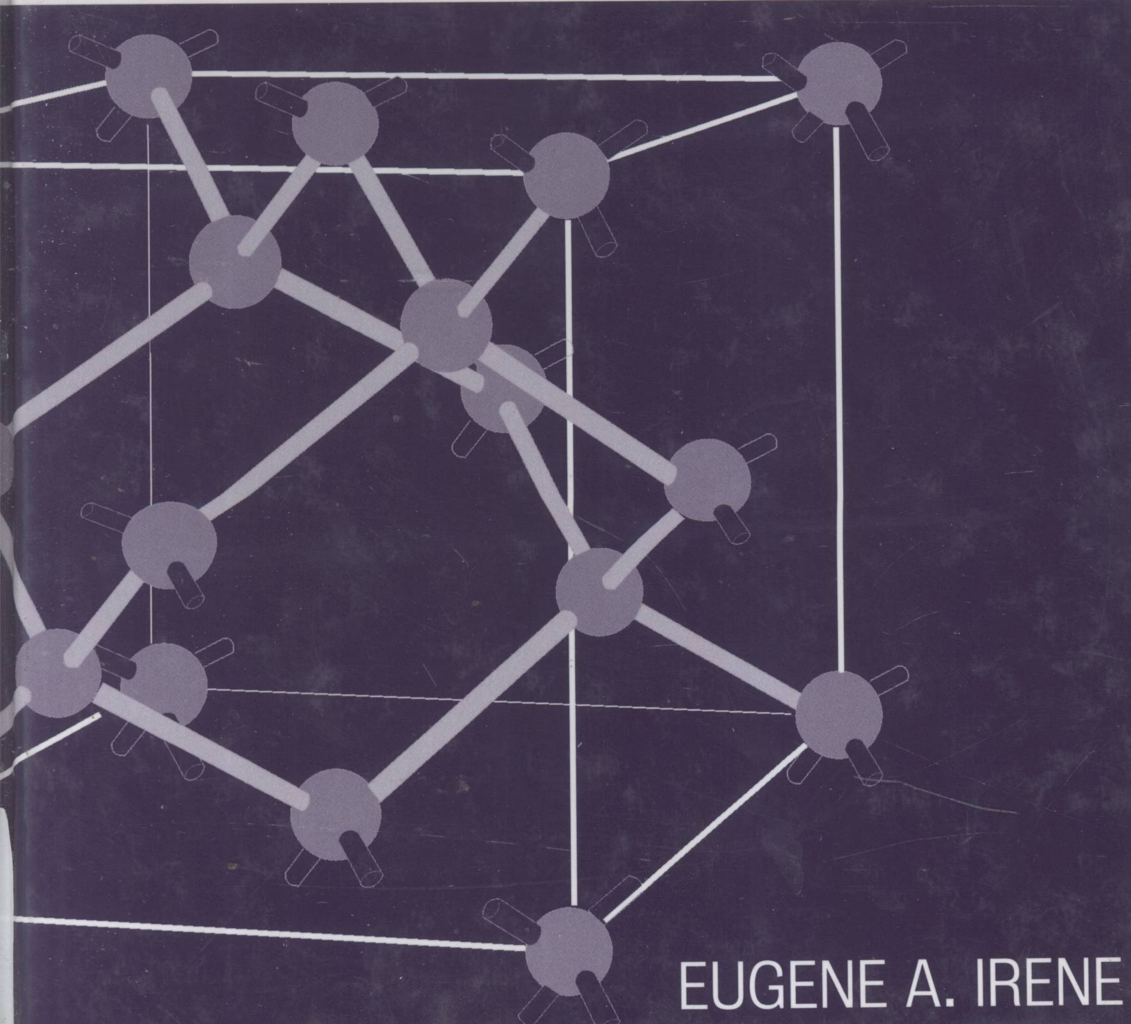


SURFACES, INTERFACES, AND THIN FILMS FOR MICROELECTRONICS



EUGENE A. IRENE

SURFACES, INTERFACES, AND THIN FILMS FOR MICROELECTRONICS

EUGENE A. IRENE

WILEY-INTERSCIENCE
A JOHN WILEY & SONS, INC., PUBLICATION

Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

Library of Congress Cataloging-in-publication Data:

Irene, Eugene A.
Surfaces, interfaces, and thin films for microelectronics / Eugene A. Irene.
p. cm.
Includes index.
ISBN 978-0-470-17447-0 (cloth)
1. Surface chemistry. 2. Interfaces (Physical sciences) 3. Thin films.
4. Microelectronics—Materials. I. Title.
QD506.I74 2008
621.381—dc22 2007024692

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

SURFACES, INTERFACES, AND THIN FILMS FOR MICROELECTRONICS

PREFACE

This book is first and foremost a text for classroom use or self-study aimed at providing an understanding of surfaces and interfaces that are important in the broad area of microelectronic materials. The subject matter selected for inclusion derives from a series of three courses offered at UNC that I have taught over 25 years on the materials science aspects of microelectronics. The first course in the series deals with the fundamentals of electronic materials. The content of that course is embodied in my previous text, *Electronic Materials Science*, published by Wiley, and this text is covered in its entirety in the first course. This first course and text introduces structure, diffraction, reciprocal and **k** spaces, defects, diffusion, phase equilibria, mechanical properties of materials, electronic structure, electronic properties, and some devices. This introduction to these subjects comprises the prerequisites to the two following courses and this text, which contains about two thirds of the material covered in the two following courses. These two courses include the fundamental aspects of surfaces and interfaces in one course and the physics and chemistry of microelectronics processing in the other.

The second course is a surface science course where surface structure, both geometric and electronic structure, surface thermodynamics, morphology, and a sampling of surface science techniques provide the main topics. These subject areas are covered in Part I of the present text in Chapters 1 through 9. With the exception of vacuum technology, which is also covered in our UNC course, Chapters 1 to 9 are the main subject matter in the fundamentals of surface and interface science course at UNC. Vacuum technology is a crucial aspect of modern surface science and is discussed in the course but not included in this text. The reason is that there are several excellent texts available written by experts whose knowledge is extensive and current and that provide both the science and technology of vacuum science that cannot be presented in a chapter or part of a chapter. In fact, surface and interface science covers such a vast area of science and technology that I found it difficult to find a single book or even two that together contained all the aspects of electronic materials and microelectronics that I wanted to present. Hence, course notes were developed that were supplemented with parts of available textbooks. Finally, the course notes evolved into the present text. At the end of each chapter (except for Chapter 4) is a short list of my favorite texts in the areas covered in the chapter, and many of these texts were used in the courses over the years. The selection of the material for Part I of this book presented a challenge because of my attempt to present a reasonably complete picture of the field. Since I found this objective impossible to attain, the material selected is that which is covered in the courses with some omissions that particular instructors include as their areas of particular interest. For example, I also include ellipsometry as a sensitive surface, interface and thin-film technique, and include a full chapter on ellipsometry and optical properties while other instructors barely mention the topic.

The final course that is addressed by this text is the course dealing with microelectronics processes. At UNC this course has been co-taught by at least three instructors who lectured on various important topics such as crystal growth and silicon wafer fabrication and testing, thin-film growth and deposition, film measurements, substrate measurements, defects, ion beam analysis, electronic measurements, doping, and mechanical properties of films, and the topics sometimes varied year to year and instructor to instructor. Therefore, rather than trying to capture that elusive course, I have chosen to liberally add microelectronics applications (e.g., electronic measurement applications in Chapter 7, thin-film processing in Chapter 10, modern techniques in Chapters 6 and 12, and the like) and separate the text into Parts I and II. Part I captures the surface and interface course, and Part II has more applications on microelectronics materials studies that further illustrate the fundamentals presented in Part I.

A few words about applications are warranted. The UNC courses were originally aimed at microelectronics graduate students. Consequently, the applications used are predominantly from the field. I have found that I can use one device to discuss and illustrate almost all the surface and interface science that I present, and this device is the metal–oxide–semiconductor field–effect transistor, the MOSFET. In almost every chapter some aspect of the MOSFET is mentioned and applications discussed, and thus the entire book hinges on the MOSFET. I begrudgingly admit that there are other microelectronic devices, but none is so pervasive and none can be used better as a focus point for this book.

For this course material there are an enormous number of original studies to choose from that deal directly with various aspects of the fundamental issues addressed in this text. Obviously, I have included only a small subset of the available original research studies and reviews that I have used in the courses, but I have included the ones I used most often. I had passed out the articles for classroom discussion during lectures, excerpted problems and text for use in class notes, and/or assigned studies to be read and then discussed in class. Many of the articles that I have used repeatedly in the courses are listed in the References at the end of each chapter, and used figures and the authors units from the original studies (consequently, several different units are used for the same variables and constants throughout the book and especially in Part II). I have tried to include some experimental techniques and experimental details to give students a better feel for experiments and the experimental results. With the use of Internet search capability at universities, I am hopeful that students will be encouraged to access the original studies and examine the original research and results while they read the text. Many of the included studies are from my own research over the years since in using these I was able to include insights often missed in the details when reading articles, and I was able to extract the important points for this book without insulting or misrepresenting the authors. For these research studies I owe a great debt of gratitude to all my graduate students and postdoctorals that have been in my research group since 1982 when I came to UNC and before that to my colleagues at the IBM Research Center at Yorktown Heights where I learned about microelectronics. Most of these people are included in the citations to specific studies and figures. Many of the drawings and figures were developed in my research group for various talks, papers, and theses and usually referenced, but some origins are unknown.

The courses and this text are aimed at first- and second-year graduate students, and it is assumed that the students have had introductory courses in thermodynamics and quantum mechanics that are typical of chemistry and physics undergraduate curricula as well as the material in my introductory text mentioned above.

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PART 1

FUNDAMENTALS OF SURFACES AND INTERFACES

1

INTRODUCTION TO SURFACES

1.1 INTRODUCTION

A surface is intuitively defined as the boundary of a condensed phase, liquid, or solid. In this text the main concern is with solid surfaces. Typically, a solid surface displays many properties that are different from the bulk material. Surface structure is often different, and compared to the bulk material usually leads to a density and stoichiometry difference at the surface. With both structural and chemical differences, it is straightforward to conclude that the potential at the surface that binds the constituent atoms is different from that in the bulk, that is, the bonding at the surface is different from the bulk. The direct consequence is a different electronic structure and the subsequent altered properties derived therefrom. Among the most important surface properties that are different from the bulk material properties are chemical reactivity resulting from different thermodynamic and kinetic properties and different electronic properties resulting from different electronic energy band structure. Therefore, in the study of surfaces it is important to first understand the structure of surfaces. Structure can be understood from different perspectives. First is the geometric structure that is essentially the arrangement of atoms or molecules. Many properties are dependent upon the specifics of this arrangement since different surface sites result from different arrangements. The arrangement of atoms and/or molecules and the nature of the atoms and molecules at a surface yield a potential specific to the surface. This potential leads to different surface electronic structure and different electronic states than those that exist in the bulk. Both perspectives, sites and states, yield a measure of

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understanding about surface chemical and physical properties. In this text different perspectives will be considered as well as techniques that yield information about surface sites and states. In addition, relevant examples mostly from the arena of microelectronics and the author's research experiences are included mainly in Part II to illustrate various surface and interface principles. Chapter 1 will present several of the overarching ideas that will be covered in more depth throughout the text with the intent in Chapter 1 being the introduction of ideas that help to define surfaces and interfaces and some tools for evaluating those differences and examples from the research literature.

With different geometrical and electronic structure at surfaces and the resulting alteration of thermodynamic and kinetic properties, it is useful to question why one often encounters the chemical reactivity of solids being described using only bulk thermodynamic properties. It is clear that a reaction among solids first involves the contact of the solids, which is via their respective surfaces. Furthermore, it is obvious that the contact of surfaces and the prediction of surface reactivity will involve the use of surface properties rather than bulk properties. One explanation for the use of bulk properties rather than surface properties is that often the relevant surface properties are unknown. Thus, one uses bulk properties to achieve a first approximation. Surface properties usually require special techniques, and many of the most powerful techniques have been developed in the past 30 years. Therefore, much of the older literature on surface science and interfaces does not benefit from the modern advanced techniques, and with a relatively short history of measurement many surface properties are unknown. Often these surface-sensitive techniques involve the use of high (below about 10^{-4} atm) or ultra-high (below about 10^{-8} atm) vacuum, so as to preserve a pristine surface for examination. Thus, knowledge of vacuum techniques is a part of the study of surfaces. For the most part this text will introduce surface characterization techniques that are useful for various surface measurements, along with the major surface topic with which the technique(s) is associated. For example, surface structure techniques will be introduced in Chapter 2 that deals with geometrical surface structure and electronic structural techniques are introduced in Chapter 5 that deals with electronic structure. Chapter 6 discusses several techniques that are also useful for surface analysis. Chapter 9 discusses ellipsometry, which is useful for films and interfaces. There is no attempt to be exhaustive relative to surface and interfaces science techniques but rather to introduce techniques that are both popular and that are used to obtain results used in this book. It should be understood that there are many surface, interface, and film techniques that are not covered in this book.

Surfaces are typically more reactive than the same bulk material. For example, it is difficult to maintain a pristine metal surface for study in air, and as was mentioned above ultra-high vacuum is necessary to prevent or retard surface oxidation or nitridation and enable surface properties to be assessed. For this reason it is rare to actually deal with pristine surfaces in applications. Usually, there is at least a thin oxide on metals, a reaction layer on nonmetals, and almost always a film of contamination on all surfaces exposed to laboratory ambient. Thus, real solid materials comprise a surface covered with some kind of a film. Underneath the surface film there is an