Introduction to Surface and Thin Film Processes

This book covers the experimental and theoretical understanding of surface and thin film processes. It presents a unique description of surface processes in adsorption and crystal growth, including bonding in metals and semiconductors. Emphasis is placed on the strong link between science and technology in the description of, and research for, new devices based on thin film and surface science. Practical experimental design, sample preparation and analytical techniques are covered, including detailed discussions of Auger electron spectroscopy and microscopy. Thermodynamic and kinetic models of electronic, atomic and vibrational structure are emphasized throughout. The book provides extensive leads into practical and research literature, as well as to resources on the World Wide Web. Each chapter contains problems which aim to develop awareness of the subject and the methods used.

Aimed as a graduate textbook, this book will also be useful as a sourcebook for graduate students, researchers and practioners in physics, chemistry, materials science and engineering.

JOHN A. VENABLES obtained his undergraduate and graduate degrees in Physics from Cambridge. He spent much of his professional life at the University of Sussex, where he is currently an Honorary Professor, specialising in electron microscopy and the topics discussed in this book. He has taught and researched in laboratories around the world, and has been Professor of Physics at Arizona State University since 1986. He is currently involved in web-based (and web-assisted) graduate teaching, in Arizona, Sussex and elsewhere. He has served on several advisory and editorial boards, and has done his fair share of reviewing. He has published numerous journal articles and edited three books, contributing chapters to these and others; this is his first book as sole author.

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Preface

This book is about processes that occur at surfaces and in thin films; it is based on teaching and research over a number of years. Many of the experimental techniques used to produce clean surfaces, and to study the structure and composition of solid surfaces, have been around for about a generation. Over the same period, we have also seen unprecedented advances in our ability to study materials in general, and on a microscopic scale in particular, largely due to the development and availability of many new types of powerful microscope.

The combination of these two fields, studying and manipulating clean surfaces on a microscopic scale, has become important more recently. This combination allows us to study what happens in the production and operation of an increasing number of technologically important devices and processes, at all length scales down to the atomic level. Device structures used in computers are now so small that they can be seen only with high resolution scanning and transmission electron microscopes. Device preparation techniques must be performed reproducibly, on clean surfaces under clean room conditions. Ever more elegant schemes are proposed for using catalytic chemical reactions at surfaces, to refine our raw products, for chemical sensors, to protect surfaces against the weather and to dispose of environmental waste. Spectacular advances in experimental technique now allow us to observe atoms, and the motion of individual atoms on surfaces, with amazing clarity. Under special circumstances, we can move them around to create artificial atomic-level assemblies, and study their properties. At the same time, enormous advances in computer power and in our understanding of materials have enabled theorists and computer specialists to model the behavior of these small structures and processes down to the level of individual atoms and (collections of) electrons.

The major industries which relate to surface and thin film science are the micro-electronics, opto-electronics and magnetics industries, and the chemistry-based industries, especially those involving catalysis and the emerging field of sensors. These industries form society's immediate need for investment and progress in this area, but longer term goals include basic understanding, and new techniques based on this understanding: there are few areas in which the interaction of science and technology is more clearly expressed.

Surfaces and thin films are two, interdependent, and now fairly mature disciplines. In his influential book, *Physics at Surfaces*, Zangwill (1988) referred to his subject as an interesting adolescent; so as the twenty-first century gets underway it is thirty-something. I make no judgment as to whether growing up is really a maturing process, or whether the most productive scientists remain adolescent all their lives. But the various stages of a subject's evolution have different character. Initially, a few academics and industrial researchers are in the field, and each new investigation or experiment opens many new possibilities. These people take on students, who find employment in closely related areas. Surface and thin film science can trace its history back to Davisson and Germer, who in effect invented low energy electron diffraction (LEED) in 1927, setting the scene for the study of surface structure. Much of the science of electron emission dates from Irving Langmuir's pioneering work in the 1920s and 1930s, aimed largely at improving the performance of vacuum tubes; these scientists won the Nobel prize in 1937 and 1932 respectively.

The examination of surface chemistry by Auger and photoelectron spectroscopy can trace its roots back to cloud chambers in the 1920s and even to Einstein's 1905 paper on the photo-electric effect. But the real credit arguably belongs to the many scientists in the 1950s and 1960s who harnessed the new ultra-high vacuum (UHV) technologies for the study of clean surfaces and surface reactions with adsorbates, and the production of thin films under well-controlled conditions. In the past 30 years, the field has expanded, and the 'scientific generation' has been quite short; different sub-fields have developed, often based on the expertise of groups who started literally a generation ago. As an example, the compilation by Duke (1994) was entitled *'Surface Science: the First Thirty Years'*. The Surface Science in question is the journal, not the field itself, but the two are almost the same. That one can mount a retrospective exhibition indicates that the field has achieved a certain age.

Over the past ten years there has been a period of consolidation, where the main growth has been in employment in industry. Scientists in industry have pressing needs to solve surface and thin film processing problems as they arise, on a relatively short timescale. It must be difficult to keep abreast of new science and technology, and the tendency to react short term is very great. Despite all the progress in recent years, I feel it is important not to accept the latest technical development at the gee-whizz level, but to have a framework for understanding developments in terms of well-founded science. In this situation, we should not reinvent the wheel, and should maintain a reasonably reflective approach. There are so many forces in society encouraging us to communicate orally and visually, to have our industrial and international collaborations in place, to do our research primarily on contract, that it is tempting to conclude that science and frenetic activity are practically synonymous. Yet lifelong learning is also increasingly recognized as a necessity; for academics, this is itself a growth industry in which I am pleased to play my part.

This book is my attempt to distill, from the burgeoning field of *Surface and Thin Film Processes*, those elements which are scientifically interesting, which will stand the test of time, and which can be used by the reader to relate the latest advances back to his or her underlying knowledge. It builds on previous books and articles that perhaps emphasize the description of surfaces and thin films in a more static, less process-oriented sense. This previous material has not been duplicated more than is necessary; indeed, one of the aims is to provide a route into the literature of the past 30 years, and to relate current interests back to the underlying science. Problems and further textbook reading are given at the end of each chapter. These influential textbooks and monographs are collected in Appendix A, with a complete reference list at the end of the book, indicating in which section they are cited. The reader does not, of course, have to rush to do these problems or to read the references; but they can be used for further study and detailed information. A list of acronyms used is given in Appendix B.

The book can be used as the primary book for a graduate course, but this is not an exclusive use. Many books have already been produced in this general area, and on specialized parts of it: on vacuum techniques, on surface science, and on various aspects of microscopy. This material is not all repeated here, but extensive leads are given into the existing literature, highlighting areas of strength in work stretching back over the last generation. The present book links all these fields and applies the results selectively to a range of materials. It also discusses science and technology and their inter-relationship, in a way that makes sense to those working in inter-disciplinary environments. It will be useful to graduate students, researchers and practitioners educated in physical, chemical, materials or engineering science.

The early chapters 1–3 underline the importance of thermodynamic and kinetic reasoning, provide an introduction to the terms used, and describe the use of ultra-high vacuum, surface science and microscopy techniques in studying surface processes. These chapters are supplemented with extensive references and problems, aimed at furthering the students' practical and analytical abilities across these fields. If used for a course, these problems can be employed to test students' analytical competence, and familiarity with practical aspects of laboratory designs and procedures. I have never required that students do problems unaided, but encouraged them to ask questions which help towards a solution, that they then write up when understanding has been achieved. This allows more time in class for discussion, and for everyone to explore the material at their own pace. A key point is that each student has a different background, and therefore finds different aspects unfamiliar or difficult.

The following chapters 4–8 are each self-contained, and can be read or worked through in any order, though the order presented has a certain logic. Chapter 4 treats adsorption on surfaces, and the role of adsorption in testing interatomic potentials and lattice dynamical models, and in following chemical reactions. Chapter 5 describes the modeling of epitaxial crystal growth, and the experiments performed to test these ideas; this chapter contains original material that has been featured in recent multi-author compilations. Further progress in understanding cannot be made without some understanding of bonding, and how it applies to specific materials systems. Chapter 6 treats bonding in metals and at metallic surfaces, electron emission and the operation of electron sources, and electrical and magnetic properties at surfaces and in thin films. Chapter 7 takes a similar approach to semiconductor surfaces, describing their reconstructions and the importance of growth processes in producing semiconductor-based thin film device structures. Chapter 8 concentrates on the science needed to understand electronic, magnetic and optical effects in devices. The short final chapter 9 describes briefly what has been left out of the book, and discusses the roles played by scientists and technologists from different educational backgrounds, and gives some pointers to further sources of information. Chapters 4–7 give suggestions for projects based on the material presented and cited. Appendices C–K give data and further explanations that have been found useful in practice.

In graduate courses, I have typically not given all this material each time, and certainly not in this 4–8 order, but have tailored the choice of topics to the interests of the students who attended in a given term or semester. Recently, I have taught the material of chapters 1 and 2 first, and then interleaved chapter 3 with the most pressing topics in chapters 4–8, filling in to round out topics later. Towards the end of the course, several students have given talks about other surface and/or microscopic techniques to the class, and yet others did a 'mini-project' of 2000 words or so, based on references supplied and suggested leads into the literature.

With this case-study approach, one can take students to the forefront of current research, while also relating the underlying science back to the early chapters. I am personally very interested in models of electronic, atomic and vibrational structure, though I am not expert in all these areas. As a physicist by training, heavily influenced by materials science, and with some feeling for engineering and for physical/analytical chemistry, I am drawn towards nominally simple (elemental) systems, and I do not go far in the direction of complex chemistry, which is usually implicated in real-life processes such as chemical vapor deposition or catalytic schemes. With so much literature available one can easily be overwhelmed; yet if conflicts and discrepancies in the original literature are never mentioned, it is too easy for students, and indeed the general public, to believe that science is cut and dried, a scarcely human endeavor. In the workplace, employees with graduate degrees in physics, chemistry, materials science or engineering are treated as more or less interchangeable. Understanding obtained via the book is a contribution to this interdisciplinary background that we all need to function effectively in teams.

Having extolled the virtues of a scholarly approach to graduate education in book form, I also think that graduate courses should embrace the relevant possibilities opened up by recent technology. I have been using the World Wide Web to publish course notes, and to teach students off-campus, using e-mail primarily for interactions, in addition to taking other opportunities, such as meeting at conferences, to interact more personally. Writing notes for the web and interacting via e-mail is enjoyable and informal. Qualitative judgments trip off the fingers, which one would be hard put to justify in a book; if they are shown to be wrong or inappropriate they can easily be changed. Perhaps more importantly, one can access other sites for information which one lacks, or which colleagues elsewhere have put in a great deal of time perfecting; my web-based resources page can be accessed via Appendix D. One can be interested in a topic, and refer students to it, without having to reinvent the wheel in a futile attempt to become the world's expert overnight. And, as I hope to show over the next few years, one may be able to reach students who do not have the advantages of working in large groups, and largely at times of their choosing.

It seems too early to say whether course notes on the web, or a book such as this will have the longer shelf life. In writing the book, after composing most but not all of the notes, I am to some extent hedging my bets. I have discovered that the work needed to produce them is rather different in kind, and I suspect that they will be used for rather different purposes. Most of the notes are on my home page http://venables.asu.edu/ in the /grad directory, but I am also building up some related material for graduate

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courses at Sussex. Let me know what you think of this material: an e-mail is just a few clicks away.

I would like to thank students who have attended courses and worked on problems, given talks and worked on projects, and co-workers who have undertaken research projects with me over the last several years. I owe an especial debt to several friends and close colleagues who have contributed to and discussed courses with me: Paul Calvert (now at University of Arizona), Roger Doherty (now at Drexel) and Michael Hardiman at Sussex; Ernst Bauer, Peter Bennett, Andrew Chizmeshya, David Ferry, Bill Glaunsinger, Gary Hembree, John Kouvetakis, Stuart Lindsay, Michael Scheinfein, David Smith, John Spence and others at ASU; Harald Brune, Robert Johnson and Per Stoltze in and around Europe. They and others have read through individual chapters and sections and made encouraging noises alongside practical suggestions for improvement. Any remaining mistakes are mine.

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Arizona/Sussex, November/December 1999

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