ENCYCLOPEDIA OF MATERIALS SCIENCE AND ENGINEERING

Supplementary Volume 1

Editor
ROBERT W CAHN

Senior Advisory Editor
MICHAEL B BEVER

ENCYCLOPEDIA OF MATERIALS SCIENCE AND ENGINEERING

Supplementary
Volume 1

Editor
ROBERT W CAHN
University of Cambridge, UK

Senior Advisory Editor
MICHAEL B BEVER
Massachusetts Institute of Technology
Cambridge, MA, USA

PERGAMON PRESS
OXFORD · BEIJING · FRANKFURT
SYDNEY · TOKYO

THE MIT PRESS
CAMBRIDGE
MASSACHUSETTS

Distributed exclusively in North and South America by The MIT Press, Cambridge, Massachusetts.

Published and distributed exclusively throughout the rest of the world by Pergamon Press:

U.K.	Pergamon Press plc, Headington Hill Hall, Oxford, OX3 0BW, England
PEOPLE'S REPUBLIC OF CHINA	Pergamon Press, Room 4037, Qianmen Hotel, Beijing, People's Republic of China
FEDERAL REPUBLIC OF GERMANY	Pergamon Press GmbH, Hammerweg 6, D-6242 Kronberg, Federal Republic of Germany
AUSTRALIA	Pergamon Press Australia Pty Ltd, P.O. Box 544, Potts Point, N.S.W. 2011, Australia
JAPAN	Pergamon Press, 5th Floor, Matsuoka Central Building, 1-7-1 Nishishinjuku, Shinjuku-ku, Tokyo 160, Japan

First edition 1988

Library of Congress Cataloging in Publication Data
Main entry under title:
Encyclopedia of materials science and engineering supplementary vol. 1.

Includes indexes.

1. Materials—Dictionaries. 1. Cahn, R. W. (Robert W.), 1924. II. Bever, Michael B. (Michael Berliner) III. Encyclopedia of materials science and engineering. TA402.E53 1986 Suppl. 620.1'1'0321.88-12518

ISBN 0–262–03142–6 (v. 1) (MIT Press)

British Library Cataloguing in Publication Data
Encyclopedia of materials science and engineering.—Supplementary vol. 1

1. Materials science—Encyclopaedias

I. Cahn, Robert W. II. Bever, Michael B.
620.1'1'0321

ISBN 0–08–032521–1 (Pergamon Press)

Computer typeset by Page Bros. (Norwich) Ltd.
Printed in Great Britain by A. Wheaton & Co. Ltd., Exeter

ENCYCLOPEDIA OF MATERIALS SCIENCE AND ENGINEERING

SUPPLEMENTARY VOLUME 1

Advances in Materials Science and Engineering

Executive Editor: Robert W Cahn

Forthcoming volumes in this series:

Concise Encyclopedia of Advanced Ceramic Materials
Concise Encyclopedia of Building Materials
Concise Encyclopedia of Composite Materials
Concise Encyclopedia of Electronic & Optoelectronic Materials
Concise Encyclopedia of Magnetic & Superconducting Materials
Concise Encyclopedia of Medical & Dental Materials
Concise Encyclopedia of Metals Processing & Manufacturing
Concise Encyclopedia of Mineral Resources
Concise Encyclopedia of Wood & Wood-Based Materials

HONORARY EDITORIAL ADVISORY BOARD

FOREWORD

In the short time since its publication, the *Encyclopedia of Materials Science and Engineering* has been accepted throughout the world as the standard reference about all aspects of materials. This is a well-deserved tribute to the scholarship and dedication of the Editor-in-Chief, Professor Michael Bever, the Subject Editors and the numerous contributors.

During its preparation, it soon became clear that change in some areas is so rapid that publication would have to be a continuing activity if the Encyclopedia were to retain its position as an authoritative and up-to-date systematic compilation of our knowledge and understanding of materials in all their diversity and complexity. Thus, the need for some form of supplementary publication was recognized at the outset. The Publisher has met this challenge most handsomely: both a continuing series of Supplementary Volumes to the main work and a number of smaller encyclopedias, each covering a selected area of materials science and engineering, will be published in the next few years.

Professor Robert Cahn, the Executive Editor, was previously the editor of an important subject area of the main work and many other people associated with the Encyclopedia will contribute to its Supplementary Volumes and derived Concise Encyclopedias. Thus, continuity of style and respect for the high standards set by the *Encyclopedia of Materials Science and Engineering* are assured. They have been joined by some new editors and contributors with knowledge and experience of important subject areas of particular interest at the present time. Thus, the Advisory Board is confident that the new publications will significantly add to the understanding of emerging topics wherever they may appear in the vast tapestry of knowledge about materials.

The appearance of Supplementary Volumes and the new series *Advances in Materials Science and Engineering* is an event which will be welcomed by scientists and engineers throughout the world. We are sure that it will add still more luster to a most important enterprise.

Walter S Owen
Chairman
Honorary Editorial Advisory Board

SUBJECT EDITORS OF THE MAIN ENCYCLOPEDIA

Willard D. B. Bascom
Hercules Incorporated, USA
[Joining by Adhesives]

Harold Berger
Industrial Quality Incorporated, USA
[Nondestructive Evaluation]

Michael B. Bever
Massachusetts Institute of Technology, USA
[Miscellaneous Materials; Materials Engineering; Materials Economics, Policy and Management]

Jack M. Blakely
Cornell University, USA
[Surfaces and Interfaces]

Richard J. Brook
University of Leeds, UK
[Advanced Ceramics]

Robert W. Cahn
Clare Hall, UK
[Fundamental Physical Metallurgy]

Donald D. Carr
Indiana Geological Survey, USA
[Industrial Minerals]

Gilbert Y. Chin
AT&T Bell Laboratories, USA
[Magnetic Materials]

Philip C. Clapp
University of Connecticut, USA
[Materials Science]

Theodore F. Cooke
Textile Research Institute, USA
[Fibers and Textiles]

Stephen M. Copley
University of Southern California, USA
[Applied Nonferrous Physical Metallurgy]

William D. Davenport
University of Arizona, USA
[Metals Production]

Larry G. DeShazer
Spectra Technology, USA
[Optical Materials]

George E. Dieter
University of Maryland, USA
[Metals Processing and Fabrication]

Robert H. Doremus
Rensselaer Polytechnic Institute, USA
[Glasses]

Thomas S. Ellis
General Motors Research Laboratories, USA
[Polymers: Structure & Properties]

Anthony G. Evans
University of California at Santa Barbara, USA
[Mechanics of Materials]

Brian R. T. Frost
Argonne National Laboratory, USA
[Nuclear Materials]

John W. Glomb
Westvaco Corporation, USA
[Paper and Paperboard]

Evan H. Greener
Northwestern University Dental School, USA
[Dental Materials]

W. Lincoln Hawkins
Plastics Institute of America, USA
[Polymers: Engineering Properties]

Norman Herz
University of Georgia, USA
[Mineral Resources]

Walter R. Hibbard, Jr.
Virginia Polytechnic Institute and State University, USA
[Non-Nuclear Energy Materials]

Frank E. Karasz
University of Massachusetts, USA
[Polymers: Structure & Properties]

Anthony Kelly
University of Surrey, UK
[Composite Materials]

Thomas B. King†
Massachusetts Institute of Technology, USA
[Metals Production]

Jerome Kruger
Johns Hopkins University, USA
[Degradation]

Robert A. Laudise
AT&T Bell Laboratories, USA
[Electronic Materials]

Henry Leidheiser, Jr.
Lehigh University, USA
[Protective Coatings]

Eric Lifshin
General Electric Corporate Research and Development, USA
[Materials Investigation & Characterization]

Margaret L. A. MacVicar
Massachusetts Institute of Technology, USA
[Superconducting Materials]

James E. Mark
University of Cincinnati, USA
[Elastomers]

Koichi Masubuchi
Massachusetts Institute of Technology, USA
[Welding]

Malcolm G. McLaren
Rutgers University, USA
[Traditional Ceramics]

Fred Moavenzadeh
Massachusetts Institute of Technology, USA
[Building Materials]

David D. Mulligan
Westvaco Corporation, USA
[Paper and Paperboard]

J. Merle Nielsen
General Electric Company, USA
[Safety, Health & Environment]

Eli M. Pearce
Polytechnic University, USA
[Polymer Chemistry]

David J. Perduijn
Nederlandse Philips Bedrijven BV, The Netherlands
[Ceramics Process Engineering]

Solomon R. Pollack
University of Pennsylvania, USA
[Biomedical Materials]

Benjamin W. Roberts†
General Electric Corporate Research and Development, USA
[Superconducting Materials]

Philip Ross
National Academy of Sciences, USA
[Biological Materials]

Arno P. Schniewind
University of California at Berkeley, USA
[Wood]

Gilbert R. Speich
Illinois Institute of Technology, USA
[Applied Ferrous Physical Metallurgy]

Leo A. Stuijts†
Philips Research Laboratories, The Netherlands
[Ceramics Process Engineering]

Jack H. Wernick
Bell Communications Research, USA
[Electronic Materials]

Jack H. Westbrook
General Electric Materials Information Services, USA
[Electrical Materials]

James L. White
University of Akron, USA
[Polymers: Processing]

PREFACE

1. Advances in Materials Science and Engineering

As the publication of the *Encyclopedia of Materials Science and Engineering* approached, Robert Maxwell resolved to build upon the immense volume of work which had gone into its creation by embarking on a follow-up project. This project had two components. The first was the creation of a series of Supplementary Volumes to the Encyclopedia itself, with the following objectives.

(a) To cover new materials, techniques and interpretations which had been discovered or developed after mid-1985, when the text of the Encyclopedia was "frozen" in readiness for printing.

(b) To fill the gaps in coverage which are inevitable in any work of such vast scope, as they are gradually revealed.

(c) To bring up to date existing articles in the Encyclopedia, taking into account recent developments.

The first of these Supplementary Volumes is herewith presented to the Encyclopedia's readership.

The second component of the new project was the creation of a series of Concise Encyclopedias on individual subject areas included in the Main Encyclopedia to be called *Advances in Materials Science and Engineering*. These Concise Encyclopedias are intended, as their name implies, to be compact and relatively inexpensive volumes (typically 300–600 pages in length) based on the relevant articles in the Encyclopedia (revised where need be) together with some newly commissioned articles, including appropriate ones from the Supplementary Volumes. Some Concise Encyclopedias will offer combined treatments of two subject fields which were the responsibility of separate Subject Editors during the preparation of the parent Encyclopedia (e.g., dental and medical materials). At the time of writing, nine Concise Encyclopedias have been contracted and others are being planned. These and their editors are listed below.

Concise Encyclopedia of Advanced Ceramic Materials	Prof. Richard J Brook
Concise Encyclopedia of Building Materials	Prof. Fred Moavenzadeh
Concise Encyclopedia of Composite Materials	Dr Anthony Kelly FRS
Concise Encyclopedia of Electronic & Optoelectronic Materials	Dr Lionel C Kimerling
Concise Encyclopedia of Magnetic & Superconducting Materials	Dr Jan E Evetts
Concise Encyclopedia of Medical & Dental Materials	Prof. David F Williams
Concise Encyclopedia of Metals Processing & Manufacturing	Prof. George E Dieter
Concise Encyclopedia of Mineral Resources	Dr Donald D Carr & Prof. Norman Herz
Concise Encyclopedia of Wood & Wood-Based Materials	Prof. Arno P Schniewind

All new or substantially revised articles in the Concise Encyclopedias will be published in one or other of the Supplementary Volumes, which are designed to be used in conjunction with the Main Encyclopedia. The Concise Encyclopedias, however, are "free-standing" and are designed to be used without necessary reference to the parent Encyclopedia.

The Executive Editor is personally responsible for the selection of topics and authors of articles for the Supplementary Volumes. In this task, he has the benefit of the advice of the Senior Advisory Editor and of other members of the Honorary Editorial Advisory Board, who also exercise general supervision of the entire project. The Executive Editor is responsible for appointing the Editors of the various Concise Encyclopedias and for supervising the progress of these volumes.

2. Encyclopedia of Materials Science and Engineering, Supplementary Volume 1

The *Encyclopedia of Materials Science and Engineering*, published in the spring of 1986, is a comprehensive reference work and source of information for a wide readership, including but not restricted to practitioners in the broad domain of materials. It consists of eight volumes containing 1580 articles, the production of which involved almost 1500 experts all over the world. The Encyclopedia has been well received by reviewers and has been acquired by institutions worldwide.

It is the fate of all reference works to be overtaken by new discoveries and developments from the day of their publication—indeed, from a day some months earlier than the publication date, because of the time required for book production.

To maximize the continuing usefulness of a reference work it is necessary to provide its readers with a periodic overview of the new subject matter. This is the prime objective of the Supplementary Volumes of the *Encyclopedia of Materials Science and Engineering*, of which this is the first. The Supplementary Volumes are designed to be used in conjunction with the Main Encyclopedia.

Supplementary Volume 1 contains 113 articles, which fall into three categories: articles covering new materials, processing and characterization techniques, models and interpretations, discovered or developed after the spring of 1985 when the Main Encyclopedia went to press; articles covering mature topics which for a variety of reasons were not treated in the Main Encyclopedia; and articles designed to bring up to date the treatment of topics already covered in the Main Encyclopedia.

In editing the Supplementary Volumes, the Executive Editor has to take decisions of a kind which, when the Main Encyclopedia was being prepared, were distributed among numerous Subject Editors. For the exercise of this responsibility, advice is indispensable. Such advice has come from the following sources.

(a) The Senior Advisory Editor, Professor Michael B Bever, with his unparallelled experience and range of contacts.

(b) Some of the Subject Editors who were responsible for subject areas in the Main Encyclopedia.

(c) Three Special Advisers who undertook critical reviews of specific subject areas in the Main Encyclopedia, recommended topics which in their view needed to be treated in the Supplementary Volumes and also advised on possible authors. These Advisers were Dr A L Challis (former President of the Rubber and Plastics Institute, London, UK), on polymer processing; Professor D F Williams (Director of the Institute of Medical and Dental Bioengineering, University of Liverpool, UK), who has since been appointed the editor of a Concise Encyclopedia; and Professor J Zarzycki (Professor of Materials Science, University of Montpellier, France) on glass.

(d) Numerous individuals in many parts of the world who were consulted by the Executive Editor in connection with particular topics.

(e) Authors of reviews of the Main Encyclopedia in various periodicals; several of these pointed out omissions which needed rectification.

The Executive Editor is greatly indebted to all these people, without whom the task of editing this Supplementary Volume would have been impracticable.

Special care was taken to maintain a proper balance between basic and applied aspects of materials. Authors were evenly spread among universities, industrial firms and government laboratories. Attention was also paid to geographical balance: authors from nine countries are represented in this volume.

In general, the delimitation of the field of materials science and engineering as defined by Professor Bever in the introduction to the Main Encyclopedia was adopted during the editing of this Supplementary Volume. One borderline field is that of liquids: Professor Bever indicated that liquids are usually excluded from the purview of materials science and engineering, but that "some liquids, especially those used because of their physical properties, are considered to be materials and are covered in the Encyclopedia." The decision was taken to commission a series of articles for this Supplementary Volume on various aspects of water and ice, on account of the importance of H_2O in its chemical and mechanical as well as its physical contexts. Two articles on inks (*Inks for Printing* and *Inks for Writing*) are also included, again on the grounds of practical importance.

A number of articles in *Supplementary Volume 1* are aimed at bringing up to date the treatment of topics which were included in the Main Encyclopedia. These are divided into two subsidiary categories.

(a) Supplementary articles which are intended to be read in conjunction with the original article of the same, or similar, title in the Main Encyclopedia; generally a subsidiary phrase such as "recent developments" has been added to the title.

(b) Replacement articles which are intended to substitute entirely for the original article and therefore have the title of that article. These articles generally refer to topics in which there have been rapid recent developments: their inclusion does not imply a critical judgement on the original articles.

These, as indeed all articles in *Supplementary Volume 1*, are furnished with cross-references to relevant articles in the Main Encyclopedia as well as to other articles in this Supplementary Volume itself, where appropriate.

Section 1 above explains the nature and role of the Concise Encyclopedias. During the early stages of the editing of *Supplementary Volume 1*, seven Concise Encyclopedias had already been commissioned: a list of their titles and editors,

together with those of other Concise Encyclopedias commissioned a little later, also appears above.

In the fields of the various Concise Encyclopedias, the editors of those volumes are responsible for selecting novel topics, older topics for updating and mature topics which were not dealt with in the Main Encyclopedia. With a few minor exceptions, the Executive Editor does not make such selections (although he does discuss those proposed with the Editors of the Concise Encyclopedias). This is why *Supplementary Volume 1* contains very few articles on topics such as superconducting materials, advanced ceramics, wood, etc. (Some articles on medical and dental materials are included here because this Concise Encyclopedia was commissioned late in the editing of *Supplementary Volume 1*.)

All new or substantially updated articles in the Concise Encyclopedias, whether by the original authors who treated them in the Main Encyclopedia, or by new authors, will automatically be included in future Supplementary Volumes. The contribution by the editors of Concise Encyclopedias will thus progressively grow in successive Supplementary Volumes.

Supplementary Volume 1 contains subject and name indexes (to both article authors and authors of bibliographic citations) prepared according to the same scheme as in the Main Encyclopedia, and articles are also classified according to the Systematic Outline of the Encyclopedia, as set out by Professor Bever in Volume 8 of the Main Encyclopedia. The present intention is to treat all these listings on a cumulative basis in future Supplementary Volumes so that readers in search of an elusive entry will need to refer to only two listings: those in Volume 8 of the Main Encyclopedia and those at the back of the latest Supplementary Volume.

As Executive Editor, I wish to express my gratitude to all those numerous individuals who have helped me in preparing *Supplementary Volume 1*. First of all are the authors of the articles. Among these, I would particularly like to thank those who have valiantly struggled with a language not their own.

Next, I would like to thank Professor Michael B Bever, the Senior Advisory Editor, for his ready counsel and practical help in various ways; his monumental achievement in bringing the Main Encyclopedia to fruition has been a model for my own endeavors, hard though it has been to emulate.

My thanks also go to the three Special Advisers for their crucial help and also to numerous other people who gave me ad hoc advice as needed, and to members of the Honorary Editorial Advisory Board—particularly its Chairman, Professor Walter S Owen—for helpful comments.

I am grateful to Mr A B Britton for his assiduity in checking every one of the approximately one thousand bibliographic citations in this volume.

Finally, I am deeply indebted to Dr Colin Drayton and Mr Michael Mabe of the editorial staff of Pergamon Press, and to the copy-editors working with them, for their prompt, cheerful and efficient cooperation in the creation of this volume.

Robert W Cahn
Executive Editor
February 1988

An invitation to readers. The Executive Editor cordially invites readers of this Supplementary Volume to advise him of topics which in their view deserve coverage or updating, or to offer criticism of their treatment here. This can only be of benefit to him and to readers of future volumes. He undertakes to acknowledge all such communications. Letters should be sent to Professor R W Cahn, Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK. Telephone: (44) ((0)223) 334381.

GUIDE TO USE OF THE ENCYCLOPEDIA

Readers of this Supplementary Volume are referred to the "Guide to Use of the Encyclopedia" printed on p. xxv of Volume 1 of the *Encyclopedia of Materials Science and Engineering*. Guidance given here is in addition to that already given in the Main Encyclopedia.

A virtually identical titling policy has been adopted with minor adjustments to take into account the updating nature of this publication. Completely new articles have been given titles which accord with the policy of the Main Encyclopedia. Some articles have inevitably become out of date since the publication of the Main Encyclopedia and two classes of article were commissioned to update them: those intended to be read in conjunction with the original article and those intended to completely replace it. In the case of the former, the title of the original article has been used with some qualifying phrase indicating that it is updated or expands the scope of the original. In the case of the latter, the title of the original article has been used unchanged. For both these categories of article a statement appears in the first paragraph indicating whether the article supplements or replaces an existing article in the Main Encyclopedia.

The existing system of cross-referencing has been adopted and expanded. As this Supplementary Volume is intended to sit alongside the Main Encyclopedia as an extra volume, cross-references to articles within the Main Encyclopedia are given as before and without qualification. Cross-references to articles within this Supplementary Volume are qualified by the addition of "Suppl. 1" to the title. The following forms thus appear:

> The effect of this phenomenon on the creep curve is to initiate a new primary regime at a dramatically higher creep rate (see *Dynamic Recovery and Recrystallization of Metals*).

> The unusual mechanical strength of the intermetallic compound Ni_3Al ($L1_2$ structure) is caused by the atomic long-range order (see *Aluminides for Structural Use*, Suppl. 1).

As before, a high degree of uniformity in terminology and notation has been imposed upon the text. In general, the International System of Units and the recommendations on *Quantities, Symbols and Units* of the Royal Society of London have been used. Where this has not been possible, notation has been standardized throughout a particular field. In all cases, symbols are defined at their first appearance in the text of an article.

Following the Main Encyclopedia, the name/date system of bibliographic citation has been used. All the authors cited in this Supplementary Volume are listed in the Author Citation Index. The contributor's name appears at the end of an article. All contributors are listed along with their affiliations and the titles of the articles which they submitted in the alphabetical List of Contributors. The Subject Index follows the same principles as the Main Encyclopedia.

For the convenience of the reader all the above indexes will be cumulated in future Supplementary Volumes. A supplement to the Systematic Outline of the Encyclopedia, which appears in Volume 8, is contained in this Supplementary Volume and, like the indexes, will be cumulative in later Supplementary Volumes. By these means the reader has only to look in two places, namely the Main Encyclopedia indexes or Systematic Outline, and the indexes or Systematic Outline in the latest Supplementary Volume, to find the information required.

An alphabetical list of all the articles contained in this Supplementary Volume is also provided.

ALPHABETICAL LIST OF ARTICLES

CONTENTS

A

Adhesion: Enhancement by Ionizing Radiation

An important application of surface modification techniques has been in the area of thin-film coatings on various substrate materials. Such coatings are intended for a number of purposes, for instance, improved wear or corrosion resistance, the minimizing of the use of precious or strategic materials, the establishment of contacts and conducting paths on electronic devices, and the modification of reflectance properties. Often, the best choices for film and substrate are not consistent with their natural proclivity for adhesion; in this event there are a few general rules by which a technique can be devised to improve adhesion.

1. Adhesion Enhancement Technique

Recently, what appears to be a universal adhesion enhancement technique was found. The work of Griffith et al. (1982) shows that the passage of MeV ions through the film–substrate interface can greatly increase the adhesion. Since in this energy range the deposition of energy is through electronic excitation processes rather than through atomic recoil, one infers that the mechanism involves ion-induced interface chemistry rather than collisional processes. This was subsequently confirmed by the observations that the film–substrate interface remained very thin (see Tombrello 1984) and that the process could be induced by keV electrons (Mitchell et al. 1984); both of these results show that atomic displacements that mix the film and substrate atoms cannot be important in achieving the adhesion improvement.

The overall systematic trend of the data obtained shows that the dose at which a certain fixed threshold of adhesion could be achieved varies as $(dE/dx)^{-n}$ with $1.5 \leq n \leq 4$, where dE/dx is the energy lost per unit length of the ion's path to electronic excitation degrees of freedom in the target material (Tombrello 1984, Stokstad et al. 1986). However, when the data are viewed in finer detail the variation is somewhat more complicated; careful studies with a single ion type show distinct departures from this overall trend (Tombrello 1984, Wie et al. 1985).

2. Adhesion Tests

One of the difficulties in assessing the influence of various variables on adhesion is the primitive nature of most adhesion tests. Although there are a number of methods for measuring adhesion, none is thought to be either universally applicable or reliable. The use of the Scotch tape test is ubiquitous because of its simplicity and reproducibility (this test consists in firmly attaching Scotch tape to the film and pulling the tape away quickly). This test is useful but it establishes only a threshold for adhesion and that threshold is not a particularly high level of adhesion. Of course, an object of known area can be cemented to the film and the force required to pull the film away can be measured. Such tests are common but do not have a high degree of reproducibility, probably because of stresses introduced in the film by the cementing agent. If the film is relatively thick or can be made thick enough (greater than several micrometers) without introducing new stresses, peel testing is perhaps the easiest to interpret in terms of film–substrate forces (Baglin et al. 1984).

A routine, but nonquantitative, test is provided by scrubbing or abrasion of the film. For example, the "cotton-bud" test is easy to perform and quickly shows whether any enhancement has been achieved (Mitchell et al. 1984). A variant of this method that is both quantitative and reproducible is the scratch test. In this test a smooth hard tip is loaded with a known mass and pulled across the film. The measurement of the load threshold for film removal and/or the width of the strip removed provide a measure of adhesion (Chopra 1969). There is no direct connection, however, between the observations and force of adhesion, but there are models for making such a connection (Benjamin and Weaver 1960).

3. Mechanisms Affecting Adhesion Enhancement

The effect of film–substrate chemistry on the ion bombardment parameters is not well established. There are small differences, for example, in the threshold doses required for different metallic films on the same substrate; however, these effects are not large and even in cases where no compounds exist (e.g., silver on silicon), a high degree of adhesion can be attained. The chemical–physical nature of the bond between the film and substrate is unknown. This is a consequence of the thinness of the bonded layer. Mendenhall (1983) has shown, for example, that for silver on silicon this layer is less than 20 Å thick. Headrick and Seiberling (1984) have shown that the bonded region is no more than two to four atomic layers in thickness.

A number of investigations have considered the role played by adsorbed contaminants or the presence of oxide layers at the film–substrate interface.

In cases where the adhesion is excellent for atomically clean substrates, the presence of such interface contaminants usually drastically reduces the adhesion. However, even in that case, the ion/electron-beam irradiation can produce adhesion comparable to that for a clean surface (Jacobson et al. 1983, Dallaporta and Cros 1986, Carbucicchio et al. 1986). It has been shown (Dallaporta and Cros 1986, Carbucicchio et al. 1986) that the irradiation tends to break up oxide and carbide bonds, respectively, thus allowing film–substrate bonds to form. The data of Headrick and Seiberling (1986) also indicate that the breaking of C–H bonds in the contaminant layers induces the formation of C–Si bonds that distort the surface layer of the Si crystal.

Several other effects that arise in the bombardment also contribute to the adhesion enhancement. For example, Wie et al. (1985) have shown that irradiation-induced surface cracking in SiO_2 produces an adhesion improvement at low fluence levels. The relaxation of surface strain under bombardment also plays an important role (Carbucicchio et al. 1986, Livi et al. 1985, Wie et al. 1986). Wie et al. (1986) show that collisional energy loss effects are important in the strain relaxation, whereas the new bond formation arises from electronic excitation processes.

The data of Wie et al. (1985) provide an example of the occurrence of the adhesion enhancement effect. In this experiment, thin Au films on fused silica (SiO_2) were bombarded with high-energy Cl ions. The data shown in Fig. 1 are the dose thresholds to pass the Scotch tape test versus the ion energy. The columns of connected full circles for doses less than 5×10^{13} $^{35}Cl^{4+}$ ions cm^{-2} represent the low-dose adhesion range where beam spots pass the Scotch tape test. In this dose range the opening and subsequent closing of surface cracks coincide with the adhesion enhancement and thus may be related to it. The unconnected full circles represent the threshold dose for the high-dose adhesion using the same test. The adhesion fails the Scotch tape test at doses between the high dose threshold and the largest dose (about 5×10^{13} $^{35}Cl^{4+}$ ions cm^{-2} of low-dose adhesion). As this figure indicates, there was enhanced adhesion at low doses, followed by worsened adhesion at higher doses, which in turn became enhanced adhesion at still higher doses. A closer examination of the substrate behavior versus ion dose showed that the low-dose enhanced adhesion was connected with the formation of surface cracks in the substrate under bombardment; when these cracks closed at higher doses, the adhesion became worse again. At still higher doses another enhancement mechanism seems to come into play. These effects can be seen in a more continuous fashion in Fig. 2, where the scratch width from a scratch test of the Au films versus dose at a fixed ion energy was performed. (The scratch width is a function of the adhesion, with large width associated with low adhesion and vice versa.) For the dose range from 5×10^{12} to 5×10^{13} $^{35}Cl^{4+}$ ions cm^{-2}, where the width shows a minimum, the beam spots pass the Scotch tape test. The beam spots also pass the tape test for doses higher than about 2×10^{14} $^{35}Cl^{4+}$ ions cm^{-2}. The two dose ranges that produce the adhesion improvement now stand out more clearly, and one may even use the Scotch tape test results to "calibrate" the adhesion measured by the scratch test.

One thus sees that a definite assignment of a mechanism is complicated by the probable presence of a number of coincident effects that cannot easily be resolved owing to the lack of adequate precision in

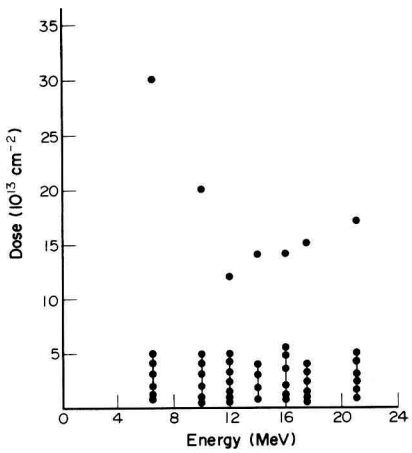

Figure 1
Threshold dose against $^{35}Cl^{4+}$ ion bombarding energy for gold films on SiO_2 (after Wie et al. 1985)

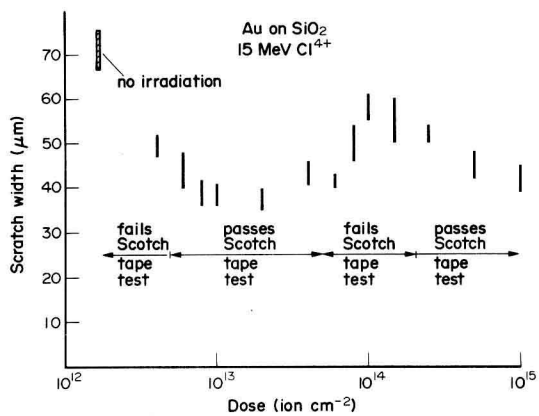

Figure 2
Scratch width as a function of beam dose for gold films on SiO_2 for 15 MeV $^{35}Cl^{4+}$ ion bombardment (after Wie et al. 1985)