IN-SITU MICROSCOPY IN MATERIALS RESEARCH

**Leading International Research in
Electron and Scanning Probe
Microscopies**

IN-SITU MICROSCOPY IN MATERIALS RESEARCH

Leading International Research in Electron and Scanning Probe Microscopies

edited by

PRATIBHA L. GAI

Central Research and Development
DuPont Wilmington, Delaware, USA

Springer Science+Business Media, LLC

Library of Congress Cataloging-in-Publication Data

In-situ microscopy in materials research : leading international research in electron and scanning probe microscopies / edited by Pratibha L. Gai.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-7923-9989-6 ISBN 978-1-4615-6215-3 (eBook)

DOI 10.1007/978-1-4615-6215-3

1. Materials--Microscopy. 2. Electron microscopy. 3. Scanning probe microscopy. I. Gai, Pratibha L., 1948-

TA417.23.I524 1997

620.1'127--dc21

97-26282

CIP

Copyright © 1997 by Springer Science+Business Media New York

Originally published by Kluwer Academic Publishers in 1997

Softcover reprint of the hardcover 1st edition 1997

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, mechanical, photo-copying, recording, or otherwise, without the prior written permission of the publisher, Springer Science+Business Media, LLC.

Printed on acid-free paper.

Cover Illustration: Direct high resolution electron microscopy image of a gold on carbon test sample, showing a gold particle with twin defects and $\sim 2.3 \text{ \AA}$ (111) gold lattice plane spacings, recorded in EHREM. (By: P.L. Gai, Central Research & Development, Dupont).

CONTENTS

List of Contributors		xi
Foreword	David B. Williams	xv
Preface	Pratibha L. Gai	xvii
1. IN-SITU APPLICATIONS OF LOW ENERGY ELECTRON MICROSCOPY (LEEM) :		1
by E. Bauer		
1. Introduction		1
2. Phase Transitions on Clean Surfaces		1
3. Segregation		3
4. Gas-Surface Interactions		4
5. Epitaxy		6
6. Summary		10
Acknowledgements and References		11
2. ENVIRONMENTAL SCANNING ELECTRON MICROSCOPY		13
by Gerasimos Daniel Danilatos		
1. Introduction		14
2. Gas Dynamics		15
3. Electron Beam Transfer		19
4. Contrast and Resolution		23
5. Detection		25
6. Cathodoluminescence		29
7. X-rays		29
8. Beam Irradiation Effects		31
9. Operation and Applications		33
10. Conclusions		41
Acknowledgements and References		42

3. ESEM DEVELOPMENT AND APPLICATION IN CULTURAL HERITAGE CONSERVATION 45

by Eric Doehne

1.	Introduction	45
2.	Applications	47
	2.1 Sodium Sulfate Dynamics	47
	2.2 Formaldehyde Corrosion	49
	2.3 Cleaning the Sistine Chapel	53
	2.4 Dead Sea Scrolls	53
3.	ESEM and SEM: Operational Differences	55
4.	ESEM/EDS Development (1990-1997)	57
	4.1 Dynamic Imaging System	57
	4.2 Still Image System	58
	4.3 EDS Analysis	59
5.	Future Work	60
	Acknowledgements and References	61

4. INTRINSIC POINT DEFECT CLUSTERING IN Si: A STUDY BY HVEM AND HREM IN-SITU ELECTRON IRRADIATION 63

**by Ludmila Fedina, Anton Gutakovskii
Alexander Aseev, Joseph Van Landuyt
and Jan Vanhellemont**

1.	Introduction	63
2.	Experimental Details	65
3.	Results and Discussion	66
	3.1 Point Defect Clustering	66
	3.2 Point Defect Clustering (500°C - 700°C) by HVEM	81
4.	Conclusion	90
	Acknowledgements and References	91

5. IN-SITU OBSERVATION AND QUANTITATIVE ANALYSIS OF ELECTROMIGRATION VOID DYNAMICS 93

by Richard Frankovic and Gary H. Bernstein

1.	Introduction	94
2.	Sample Fabrication and In-Situ Test Technique	96
3.	Single Void Behavior	99
	3.1 Direct Void Shape Changes	99
	3.2 Secondary, Induced Voids and Hillocks	103

4.	Void-Void Interactions	108
4.1	Qualitative Results	110
4.2	Quantitative Results	110
5.	Void-Hillock Interactions	117
5.1	Qualitative Results	119
5.2	Quantitative Results	120
6.	Summary and Conclusions	120
	Acknowledgements and References	122

6. ENVIRONMENTAL HIGH RESOLUTION ELECTRON MICROSCOPY (EHREM) IN MATERIALS SCIENCE 123

by Pratibha L. Gai and Edward D. Boyes

1.	Introduction	124
2.	Experimental: In-Situ Controlled Environmental High Resolution Transmission EM (EHREM) Development for Gas-Solid Reactions on the Atomic Scale	126
3.	Applications	128
3.1	Gas Molecule - Solid Surface Interactions	128
3.2	Silica based Ceramics	131
	Chemically Stabilized Cristobalite Ceramics	131
3.3	EHREM of Complex Catalysts:	141
4.	Conclusions	146
	Acknowledgements and References	146

7. IN-SITU TRANSMISSION ELECTRON MICROSCOPY OF THIN FILM GROWTH 149

by J. Murray Gibson

1.	Introduction	149
2.	Role of TEM in Studies of Thin Film Growth	150
3.	Instrumental Approaches	159
4.	Some Results	165
5.	Conclusions	169
	Acknowledgements and References	169

8. HREM IN-SITU EXPERIMENT AT VERY HIGH TEMPERATURES 173

by Takeo Kamino and Hiroyasu Saka

1.	Introduction	173
2.	Specimen-Heating Holders	174

3.	Electron Microscope	177
4.	HREM Observation of Si Particle just below the Melting Point	179
5.	Formation of SiC through Solid State Chemical Reactions between Si and Graphite	181
	5.1 Specimens	181
	5.2 Results and Discussion	181
6.	Sintering of SiC Crystals	186
7.	Surface Reconstruction of Au-deposited Si	191
	7.1 Specimens	191
	7.2 Results and Discussion	191
	Acknowledgements and References	199

9. **IN-SITU REM AND TEM STUDIES OF HOMO AND HETERO-EPITAXY ON Si SURFACES** **201**

by **Hiroki Minoda and Katsumichi Yagi**

1.	Introduction	201
2.	Experimental	204
	2.1 General Remarks on REM and TEM	204
	2.2 Sample Preparation	204
3.	Results and Discussion	206
	3.1 Growths of Si on Si (111) Surfaces	206
	3.2 Growths of Ge on Si (111) Surfaces	208
	3.3 Growths of Ge on Si (001) Surfaces	215
4.	Conclusions	223
	References	223

10. **ATOMIC-SCALE FABRICATION OF METAL SURFACES BY ADSORPTION AND CHEMICAL REACTION** **225**

by **Ken-ichi Tanaka, Yuji Matsumoto,
Takaya Fujita and Yuji Okawa**

1.	Introduction	226
2.	Fabrication of Metal Surfaces by Physical Processes	228
3.	Fabrication of Metal Surfaces by Chemical Reaction	240
4.	Nano-meter Scale Patterning by Chemical Reactions	251
	References	259

11. **HIGH TEMPERATURE DYNAMIC BEHAVIOR OF SILICON SURFACES STUDIED BY SCANNING TUNNELING MICROSCOPY (STM)** **263**

by **Hiroshi Tokumoto**

1.	Introduction	263
2.	High Temperature UHV-STM System	264
3.	Hydrogen Desorption Process on Si (111) Surface	264
4.	(7x7) - (1x1) Phase Transition on Si (111) Surface	271
5.	Step Shifting under dc Electric Fields	275
6.	Conclusions	280
	Acknowledgements and References	281

12. DYNAMIC OBSERVATION OF VORTICES IN SUPERCONDUCTORS USING ELECTRON WAVES 283

by Akira Tonomura

1.	Introduction	283
2.	Experimental Method	284
	2.1 Interference Microscopy	284
	2.2 Lorentz Microscopy	287
3.	Observation of Superconducting Vortices	288
	3.1 Superconducting Vortices Observed by Interference Microscopy	288
	3.1.1 Profile Mode	288
	3.1.2 Transmission Mode	291
	3.2 Superconducting Vortices Observed by Lorentz Microscopy	293
	3.3 Observation of Vortex Interaction with Pinning Centers	294
	3.3.1 Surface Steps	295
	3.3.2 Irradiated Point Defects	296
4.	Conclusion	298
	References	299

13. TEM STUDIES OF SOME STRUCTURALLY FLEXIBLE SOLIDS AND THEIR ASSOCIATED PHASE TRANSFORMATIONS 301

by Ray L. Withers and John G. Thompson

1.	Introduction	301
2.	Tetrahedrally Corner-Connected Framework Structures	302
3.	Tetragonal α -PbO	311
4.	Compositionally Flexible Anion-Deficient Fluorites and the "Defect Fluorite" to C-type Sesquioxide Transition	320
5.	Summary and Conclusions	327
	Acknowledgements and References	327

Author Index 331

Subject Index 333

List of Contributors

A. ASEEV

Institute of Semiconductor Physics, Russian Academy of Sciences
Novosibirsk, 630090, pr.ac., Lavrentjeva 13, RUSSIA

E. BAUER

Department of Physics and Astronomy, Arizona State University
Tempe, AZ 85287-1504, U.S.A.

G. H. BERNSTEIN

University of Notre Dame, Department of Electrical Engineering
275, Fitzpatrick Hall, Notre Dame, Indiana, IN 46556, U.S.A.

E. D. BOYES

Central Research & Development, DuPont Experimental Station
Wilmington, Delaware DE 19880-0356, U.S.A.

G. D. DANILATOS

ESEM Research Laboratory,
Sydney, N.S.W 2026, AUSTRALIA

E. DOEHNE

The Getty Conservation Intitute, Los Angeles
California 90049-1684, U.S.A.

L. FEDINA (a,b)

(a) Institute of Semiconductor Physics, Russian Academy of Sciences
Novosibirsk, 630090, pr.ac., Lavrentjeva 13, RUSSIA

(b)University of Antwerpen, RUCA EMAT, Groenenborgerlaan 171,
B-2020, Antwerp, BELGIUM

R. FRANKOVIC

University of Notre Dame, Department of Electrical Engineering,
275, Fitzpatrick Hall, Notre Dame, Indiana, IN 46556, U.S.A.

T. FUJITA

Institute of Solid State Physics, University of Tokyo
7-22-1, Roppongi, Minato-ku, Tokyo 106, JAPAN

P. L. GAI

Central Research and Development, Science and Engineering Laboratories
DuPont, Experimental Station, Wilmington, DE 19880-0356, U.S.A.

J. M. GIBSON

University of Illinois, Materials Research Laboratory
104, S. Goodwin Avenue, Urbana, IL 61801, U.S.A.

A. GUTAKOVSKII

Institute of Semiconductor Physics, Russian Academy of Sciences
Novosibirsk, 630090, pr.ac., Lavrentjeva 13, RUSSIA

T. KAMINO

Techno-Research Laboratory, Hitachi Instruments Engineering Co. Ltd.,
882, Ichige, Hitachinaka, Ibaraki, 312, JAPAN

M. MATSUMOTO

Institute of Solid State Physics, University of Tokyo
7-22-1, Roppongi, Minato-ku, Tokyo 106, JAPAN

H. MINODA

Department of Physics, Tokyo Institute of Technology
Oh-Okayama, 2-12-1, Meguro-ku, Tokyo 152, JAPAN

Y. OKAWA

Institute of Solid State Physics, University of Tokyo
7-22-1, Roppongi, Minato-ku, Tokyo 106, JAPAN

H. SAKA

Department of Quantum Engineering, Nagoya University
Furo-Cho, Chikusa-ku, Nagoya, 464-01, JAPAN

K. TANAKA

Institute of Solid State Physics, University of Tokyo
7-22-1, Roppongi, Minato-ku, Tokyo 106, JAPAN

J. G. THOMPSON

Research School of Chemistry, Australian National University
Canberra, A.C.T. 0200, AUSTRALIA

H. TOKUMOTO

Joint Research Center for Atom Technology, (JRCAT), National Institute for
Advanced Interdisciplinary, Research (NAIR),
Higashi 1-1-4, Tsukuba, Ibaraki-305, JAPAN

A. TONOMURA

Advanced Research Laboratory, Hitachi Ltd.
Hatoyama, Saitama, 350-03, JAPAN

J. VAN LANDUYT

University of Antwerpen, , RUCA EMAT, Groenenborgerlaan 171,
B-2020, Antwerp, BELGIUM

J. VANHELLEMONT ^(c,d)

(c) IMEC, Kapeldreef 75, B3001, Leuven, BELGIUM

(d) Present address: Wacker Siltronic, A.G., P.O. Box 1140, D-84479,
Burghausen, GERMANY

R. L. WITHERS

Research School of Chemistry, Australian National University
Canberra, A.C.T. 0200, AUSTRALIA

K. YAGI

Department of Physics, Tokyo Institute of Technology
Oh-Okayama, 2-12-1, Meguro-ku, Tokyo 152, JAPAN

FOREWORD

A fundamental limitation of almost all microscopy investigations of materials is that the images are static and taken when the specimen is at room temperature. More particularly, in electron microscopy (EM), the technique which constitutes most of this text, the specimen is also in a high or ultra-high vacuum and under intense radiation. Unfortunately, all these conditions rarely represent the treatment that the material has received during its processing to final form, or the conditions it will suffer during its service life. Consequently, we microscopists often make assumptions about a material's ability to retain its high-temperature structure and chemistry during rapid cooling to room temperature; also we generally ignore surface effects in thin specimens and assume that no changes take place during bombardment with intense radiation. Obviously all these assumptions can be seriously wrong in many practical studies and this text presents a broad overview of methods by which some or all of these limitations can be overcome.

Specifically in the case of EM, in-situ microscopy is a mature field that blossomed in the 1960s and 70s with the development of the first megavolt TEMs. These instruments had sufficient space in their specimen stages to accommodate heating, tensile and gas-reaction stages, and also were powerful enough to permit observation of specimens that were thick enough to mimic bulk behavior. However, no comprehensive review has been written in the last couple of decades, even though some of the old MeV microscopes continue to perform and dozens of 300-400 keV ones, well capable of in-situ studies, have been delivered in recent years. So this book represents an essential addition to the microscopists' library, because of the extraordinary instrument developments that have taken place. New microscopes and microscopies have appeared, but of equal importance are the improvements in our ability to record dynamic images with modern video/CCD cameras as well as store the images and process them digitally. Unique instruments have also been created in a few microscopy laboratories around the world, and results from several of these are described here in detail. In many cases, such instruments have been designed with very specific materials problems in mind, such as the need for extremely high temperatures to study ceramics and the combination of gas reactions with atomic resolution to understand catalysis.

Another remarkable development, that of environmental SEMs is properly emphasized. The ESEM has generated a wide array of related low-vacuum or variable-pressure SEMs. Now we have a whole new field of materials characterization, combining our long-standing abilities to heat, cool and deform bulk specimens in the SEM with the ability to image their surfaces under significant pressure of a gas, that may also react chemically with the specimen. More recent tools such as scanning probe microscopes have been able to build on the many hardware developments in the

EM field.

In a truly diverse field that represents one of the last technical frontiers in microscopy, this text both educates and informs the materials scientist and the microscopist with a well-chosen spectrum of chapters from internationally renowned scientists.

David B. Williams
Lehigh University
Bethlehem PA

PREFACE

The ability to study dynamic materials directly, in-situ, close to their natural state as they undergo reactions is a very important goal in materials research and technology. In-situ microscopy under dynamic conditions with real-time monitoring of events provides information on material processes that can not be obtained directly by other methods. Material scientists who include physicists, chemists, ceramicists, biologists and conservation scientists associated with the preservation of cultural heritage, often want to know how materials behave in their true state under reacting conditions, what structural changes there are and how they affect their properties. This is because post-reaction examination of static sample (cooled to room temperature from a higher reaction temperature, or taken out of its natural reaction environment) is not often representative of the dynamic system. Striking breakthrough developments in in-situ microscopy instrumentation and applications are making the dream of observing materials directly and dynamically, a reality. The purpose of this book is to provide an authoritative and informative account of the interdisciplinary developments and applications of in-situ microscopy in materials and surface science research. The chapters are written by renowned international scientists who have pioneered many of these outstanding fields of research at leading laboratories in the world. They address fundamental materials and process issues in semiconductor technology, ceramics, superconductors, integrated circuits, heterogeneous catalysis, polymeric materials, biological research and conservation science. Major and novel opportunities in materials research have continued to evolve directly as a consequence of in-situ microscopy studies.

In this regard, we have attempted to incorporate several fields of in-situ microscopy, namely, environmental scanning electron microscopy (ESEM) and field emission-SEM, low energy EM (LEEM), scanning tunneling microscopy (STM), reflection EM (REM), in-situ high voltage EM (HVEM), ultra high vacuum (UHV)-TEM, environmental-high resolution transmission EM (EHREM) to study gas molecule-solid surface interactions on the atomic scale, atomic level-HREM with very high temperature holders, electron holography and Lorentz microscopy. LEEM is an important surface science technique used to image bulk surfaces with low energy electron diffraction (LEED) to study phase transitions on clean surfaces of semiconductors, segregation of impurities, gas chemisorption and molecular beam epitaxy (MBE). Striking ESEM developments highlight expanding uses of the technology in diverse fields such physical sciences, biological sciences, fibers, wet samples and describe conditions for optimum electron beam transfer from high vacuum to high pressure environments whilst preserving secondary imaging, X-ray detection and cathodoluminescence. Practical development and applications of ESEM in the important fields of Museum and Conservation Science describe conservation studies of cultural heritage and property including the Sistine Chapel in Rome and Dead Sea Scrolls. Electromigration void nucleation and growth is a failure mechanism of integrated circuits (IC) metallization. Using in-situ SEM, void growth and interaction dynamics have been explored to study electromigration performance of IC interconnects. A

significant approach is the in-situ studies of point defect reactions and point defect clustering during intense electron irradiation in an HVEM which are relevant to the fundamental understanding of intrinsic point defect behavior in technologically important silicon semiconductors, ion implantation and thermal oxidation. Notable EHREM development enables key studies of live gas molecule - solid surface interactions at elevated temperatures on the atomic scale. It allows access to metastable intermediate phases and local chemistry, to both surface and bulk (subsurface) microstructural changes which are often interrelated and to novel reaction mechanisms crucial to chemical processes. Diverse applications of EHREM include studies of samples in reducing / oxidizing gases or in moist environments, technologically important complex catalysts, defect structures and new ceramics. The important role of in-situ and UHV TEM in thin film semiconductor growth is elucidated allowing visualization both of the surface structure and internal film microstructure. Impressive sample holders have been developed which allow observations at near atomic resolution of reactions taking place at very high temperatures ($\sim 1500^\circ\text{C}$). Using powerful in-situ REM and TEM methods, surface structure (atomic height steps) and dramatic surface reconstruction during semiconductor thin film growth in very wide areas, as well as interface dynamics between substrates and overgrowth films have been elucidated. Elegant developments in scanning tunneling microscopy (STM) studies describe a high temperature-UHV-STM, and atomic scale fabrication of metal surfaces by adsorption and chemical reaction. The high temperature UHV-STM is used to study dynamic behavior of Si (111) surfaces upto 950°C . The utility of STM for exploration of surface restructuring describes reactions between the STM tip and the sample surface where selective atom-transportation via chemical reaction to a desired area on the surface known as "atom-painting" is viable, leading to important new concepts and possibilities of designing fundamental new surfaces and atomic-scale patterning. The development of "coherent" field emission electron beam has been utilized to directly and dynamically observe superconducting vortices, including magnetic lines of force by in-situ holography and dynamics of vortices by Lorentz microscopy. The unique role of electron diffraction is elucidated in studies of phase transformations in structurally flexible silica based ceramic solids including in revealing the existence of highly structured diffuse intensities in reciprocal space. The chapters are arranged in an alphabetical order.

It is hoped that the book will be a rich source of information to both the newcomers and practising scientists in this rapidly expanding field of in-situ microscopy of dynamic processes and their relationship to material properties.

I am most grateful to all the contributors of this book for their excellent and elegant chapters. As editor, it has been my great privilege and pleasure to work with the internationally eminent researchers. I would like to express my thanks to John Bodt who has been responsible for the successful realization of this project and to Kluwer Academic Publishers for the opportunity. I am deeply indebted to Urmila Chandr and Laxman for the encouragement.

Pratibha L. Gai

Wilmington, Delaware
U.S.A.