Series on Directions in Condensed Matter Physics – Vol. 17

INSULATING AND SEMICONDUCTING GLASSES

SERIES ON DIRECTIONS IN CONDENSED MATTER PHYSICS

Published

- Vol. 1: Directions in Condensed Matter Physics — Memorial Volume in Honor of Shang-keng Ma
ed. G. Grinstein and G. Mazenko
- Vol. 2: Ionic Solids at High Temperatures
ed. A. Stoneham
- Vol. 3: Directions in Chaos (Vol. 1)
ed. Hao Bailin
- Vol. 4: Directions in Chaos (Vol. 2)
ed. Hao Bailin
- Vol. 5: Defect Processes Induced by Electronic Excitation in Insulators
ed. N. Itoh
- Vol. 6: Spin Glasses and Biology
ed. D. Stein
- Vol. 7: Interaction of Electromagnetic Field with Condensed Matter
ed. N. N. Bogolubov, Jr., A. S. Shumovsky and V. I. Yukalov
- Vol. 8: Scattering and Localization of Classical Waves in Random Media
ed. Ping Sheng
- Vol. 9: Geometry in Condensed Matter Physics
ed. J. F. Sadoc
- Vol. 10: Fractional Statistics & Anyon Superconductivity
(also published as a special issue of IJMPB)
ed. F. Wilczek
- Vol. 11: Quasicrystals — The State of the Art
ed. D. DiVincenzo and P. Steinhardt
- Vol. 12: Spin Glasses and Random Fields
ed. A. P. Young
- Vol. 13: The Superconducting State in Magnetic Fields
ed. C Sa de Melo
- Vol. 14: Morphological Organization in Epitaxial Growth & Removal
ed. Z.-Y. Zhang and Max G. Lagally
- Vol. 15: Thin Films: Heteroepitaxial Systems
ed. Amy W. K. Liu and Michael B. Santos
- Vol. 16: Quasicrystals — The State of the Art (2nd Edn)
ed. D. DiVincenzo and P. Steinhardt

Series on Directions in Condensed Matter Physics – Vol. 17

INSULATING AND SEMICONDUCTING GLASSES

Editor

P Boolchand

University of Cincinnati

World Scientific

Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.

P O Box 128, Farrer Road, Singapore 912805

USA office: Suite 1B, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Cover Design:

The picture shows a model of an amorphous-Si film grown on a crystalline-Si substrate. It was published in *Journal of Non-Crystalline Solids* **114**, 681 (1989) by Dr. F. Wooten and is reproduced by permission of the author.

INSULATING AND SEMICONDUCTING GLASSES

Series on Directions in Condensed Matter Physics — Volume 17

Copyright © 2000 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 981-02-3673-5

This book is printed on acid and chlorine free paper.

Printed in Singapore by World Scientific Printers

Preface

Most inorganic materials can be rendered noncrystalline by vapor condensation onto cooled substrates, but only a select few can be cooled from the molten state to yield a bulk glass that displays a softening at the glass transition temperature (T_g). A glass is formed by cooling (or supercooling) a melt and is widely regarded as a frozen solution.

The origin of the glass forming tendency has been the subject of discussions and debate in the scientific community for over 60 years. In recent years, the development and maturing of new ideas based on interatomic forces acting as mechanical constraints, the advent of new experimental probes of glass structure and dynamics, and large scale molecular dynamic simulations of covalently bonded networks, is providing, new insights into the morphological structure of network glasses. In Condensed Matter Science, we are used to the notion that atomic scale structure forms the starting point to determine the physical behavior of crystalline solids. One expects that in glassy solids as well, the atomic scale structure will be intimately tied to the physical behavior of glasses, including the glass forming tendency. And while there are important kinetic effects that control the glass formation process, these effects are not decoupled from the structural organization of matter as atomic motion is arrested at T_g . The nature of the glass transition continues to be a subject of profound discussions in basis science.

The scope of this volume is on insulating and semiconducting glasses focussing on inorganic materials that encompass a variety of optical and electronic materials. Glasses based on metallic systems and organic polymers are not covered in this volume, although several reviews on these materials have appeared in the literature.

The book is fortunate to have *Austen Angell* (Chapter 1) and *James Phillips* (Chapter 2) introducing ideas on the nature of the glass transition with the former providing an overview, and the latter commenting specifically on molecular glasses. A more traditional view of glass phenomenology is provided by *Ivan Gutzow* in Chapter 3. Interatomic forces serve as mechanical constraints and play a central role in determining the mechanical and chemical

behavior of glassy networks. When a network structure becomes barely rigid, the glass forming tendency is apparently also optimized. In Chapter 4, *Michael Thorpe* reviews ideas on the onset of rigidity in atypical and generic networks. In the real world, structure of glasses are probed by elastic scattering methods [Chapter 5(A)] as reviewed by *Adrian Wright* and by an array of chemically specific nuclear resonance methods that have proved to be rather powerful in decoding local structures. These include the Mössbauer effect reviewed by *Punit Boolchand* [Chapter 5(B)], Nuclear Quadrupole resonance reviewed by *Phillip Bray* [Chapter 5(C)], and Solid State Nuclear Magnetic resonance reviewed by *Hellmut Eckert* [Chapter 5(D)]. New insights into atomic and molecular dynamics in glasses have emerged from an impressive array of vibrational spectroscopies; including inelastic neutron scattering as reviewed by *Ron Cappelletti* [Chapter 6(A)], Lamb-Mössbauer factors as a probe of low frequency vibrational excitations as reviewed by *Punit Boolchand* [Chapter 6(B)], Raman scattering as reviewed by *Kazuo Murase* [Chapter 6(C)] and very low frequency acoustic excitations probed by Brillouin scattering as reviewed by *Claire Levelut* [Chapter 6(D)].

In the early sixties, one discovered that an excess of very low frequency vibrational excitations over Debye-like ones represents a generic feature of the glassy state of matter. Thirty years later these excitations continue to be identified with tunneling states although their microscopic origin continues to pose a challenge. Model systems for such tunneling states are identified in crystalline solids as well. The subject is reviewed by *Siegfried Hunklinger* and *Christian Enss* in Chapter 7. The physics of electrical transport in disordered semiconductors is reviewed by *Harold Overhof* and *Peter Thomas* in Chapter 8.

Since the early 1990's, the rapid growth of computing power accessible even on small machines, and the development of efficient computing algorithms has made feasible molecular dynamic simulations of covalently bonded random networks, as elegantly illustrated by *David Drabold* in Chapter 9. He develops the interaction from first principles and is able to handle ensembles of typically hundreds of atoms.

Hellmut Fritzsche reviews light induced effects in chalcogenide glasses (Chapter 10), addressing both the scalar and vector effects, an area in which our understanding of the mechanistic details is currently evolving. Chalcogenide glasses, based on alloys of the chalcogens (S, Se and Te) and halogens (Cl, Br and I) with the tathogens (C, Si, Ge, Sn) and the pnictides (P, As, Sb), have gained popularity as low loss infrared optical fiber materials. *Jacques Lucas* has reviewed the subject in Chapter 11.

The economic well-being of a field of scientific endeavor is ultimately tied to the evolution of commercial products. Glass science has been particularly fertile in this regard as illustrated in the last chapter of the book. Apart from xerography and silica fibers, one of the other large applications of glasses resides in rewritable optical memory discs, now in use in several large sized personal computers, as discussed by *Stan Ovshinsky* in Chapter 12(A). Amorphous semiconductors have also found applications in X-ray imaging with important medical benefits as illustrated by *Safa Kasap* and *John Rowland* in Chapter 12(B). Light induced effects in glasses have also served as the base for digital and holographic storage of information, and its reading in real time as reviewed by *Maria Mitkova* in Chapter 12(C). The antiquated cathode ray tube as a display device may be replaced by several new emerging technologies. One such, based on diamond-like carbon films, utilizes their negative electron affinity, and are finding use as active elements in flat-panel displays as reviewed by *James Jaskie* in the final Chapter 12(D) of the book.

I hope the book will be useful to entry level graduate students, and also to established researchers, interested in glass science and applications of these fascinating materials, in a variety of disciplines in the physical sciences (physics, chemistry and geology) and engineering (materials science and engineering, electrical engineering).

Punit Boolchand
Editor
Cincinnati, Ohio

Editorial Consultants

1. Marty Abkowitz	13. Darl McDaniel
2. Austen Angell	14. John Mackenzie
3. Tom Beck	15. Maria Mitkova
4. Wayne Bresser	16. Kazuo Murase
5. Marc Cahay	17. Amar Nath
6. Ronald Cappelletti	18. Robert Pohl
7. John deNeufville	19. James Phillips
8. Hellmut Eckert	20. Kurt Schwartz
9. Hellmut Fritzsche	21. Craig Taylor
10. Bernard Goodman	22. Michael Thorpe
11. Phillip Gradinetti	23. Adrian Wright
12. Prabhat Gupta	24. Richard Zallen

Contents

Preface	v
Editorial Consultants	viii
Chapter 1. Glass Formation and the Nature of the Glass Transitions <i>C.A. Angell</i>	1
Chapter 2. Dual Nature of Molecular Glass Transitions <i>J.C. Phillips</i>	53
Chapter 3. The Generic Phenomenology of Glass Formation <i>I. Gutzow</i>	65
Chapter 4. The Structure and Rigidity of Network Glasses <i>M.F. Thorpe, D.J. Jacobs and B.R. Djordjević</i>	95
Chapter 5. Glass Structure by Scattering Methods and Spectroscopy	
A. X-Ray and Neutron Diffraction <i>A.C. Wright</i>	147
B. Mössbauer Spectroscopy <i>P. Boolchand</i>	191
C. Nuclear Quadrupole Resonance (NQR) Studies of Glass Structure <i>P.J. Bray</i>	249
D. Solid State NMR as a Structural Tool in Glass Science <i>H. Eckert</i>	283
Chapter 6. Vibrational Excitations in Glasses	
A. Inelastic Neutron Scattering <i>R.L. Cappelletti</i>	329

	B. Vibrational Excitations in Glasses: Rigidity Transition and Lamb-Mössbauer Factors <i>P. Boolchand</i>	369
	C. Raman Scattering <i>K. Murase</i>	415
	D. Low Frequency Vibrational Excitations in Glasses by Brillouin and Raman Scattering <i>C. Levelut</i>	465
Chapter 7.	Tunneling Systems in Crystalline and Amorphous Solids <i>S. Hunklinger and C. Enss</i>	499
Chapter 8.	Electronic Transport in Disordered Semiconductors <i>H. Overhof and P. Thomas</i>	553
Chapter 9.	Molecular Dynamics Simulations of Network Glasses <i>D.A. Drabold</i>	607
Chapter 10.	Light-Induced Structural Changes in Glasses <i>H. Fritzsche</i>	653
Chapter 11.	Chalcohalide Glasses <i>J. Lucas</i>	691
Chapter 12.	Applications of Non-Crystalline Materials	
	A. Applications of Glasses, Amorphous and Disordered Materials <i>S.R. Ovshinsky</i>	729
	B. Amorphous Chalcogenide Photoconductors in Imaging Technologies <i>S.O. Kasap and J.A. Rowlands</i>	781

C. Real Time Optical Recording on Thin Films of Amorphous Semiconductors <i>M. Mitkova</i>	813
D. Diamond Based Field Emission Displays <i>J.E. Jaskie</i>	845
Subject Index	869
Materials Index	879