The Physics and Technology of Amorphous SiO_2

Edited by
Roderick A. B. Devine

The Physics and Technology of Amorphous SiO_2

Edited by

Roderick A. B. Devine

National Center for Telecommunications Studies
Meyland, France

Plenum Press • New York and London

Library of Congress Cataloging in Publication Data

Symposium on the Physics and Technology of Amorphous SiO_2 (1987: Les Arcs, France)

The physics and technology of amorphous SiO_2 / edited by Roderick A. B. Devine.

p. cm.

"Proceedings of a Symposium on the Physics and Technology of Amorphous SiO_2, held June 29–July 3, 1987, in Les Arcs, France"—T.p. verso.

Includes bibliographical references and indexes.

ISBN 0-306-42929-2

1. Silica—Congresses. 2. Surfaces (Physics)—Congresses. 3. Surface chemistry—Congresses. I. Devine, Roderick A. B. II. Title.

QC585.75.S55S95 1987

620.1'93—dc19 88-17464

CIP

Proceedings of a symposium on the Physics and Technology of Amorphous SiO_2, held June 29–July 3, 1987, in Les Arcs, France

A Division of Plenum Publishing Corporation
233 Spring Street, New York, N.Y. 10013

Printed in the United States of America

The Physics and Technology of Amorphous SiO_2

FOREWORD

The contents of this volume represent most of the papers presented either orally or as posters at the international conference held in Les Arcs, Savoie, from June 29th to July 3rd 1987. The declared objective of the conference was to bring together specialists working in various fields, both academic and applied, to examine the state of our understanding of the physics of amorphous SiO_2 from the point of view of its structure, defects (both intrinsic and extrinsic), its ability to transport current and to trap charges, its sensitivity to irradiation, etc. For this reason, the proceedings is divided, as was the conference schedule, into a number of sections starting from a rather academic viewpoint of the internal structure of idealized SiO_2 and progressing towards subjects of increasing technological importance such as charge transport and trapping and breakdown in thin films. The proceedings terminates with a section on novel applications of amorphous SiO_2 and in particular, buried oxide layers formed by ion implantation. Although every effort was made at the conference to ensure that each presentation occured in its most obvious session, in editing the proceedings we have taken the liberty of changing the order where it seems that a paper was in fact more appropriate to an alternative section. In any event, because of the natural overlap of subjects, many papers could have been suitably placed in several different sections.

The successful operation of any conference is always the result of a group effort and Les Arcs was no exception. The groundwork for the conference resulted from discussions with Jörg Arndt, Akos Revesz, Guy Ghibaudo and Jean-Jacques Niez whilst the on-site smooth running was assured by Julia, Bob and Neil Devine and Bernadette Bonnefond - sincere thanks go to all of these people for their unflagging help. A special word of thanks goes also to the session chairmen who, without recourse to buzzers, bells or flashing lights, steered the sessions to a timely end so that coffee breaks were not delayed and nobody suffered from malnutrition.

Finally, the conference could not have been held were it not for the kind support, both financial and moral, obtained from the following organisations to whom we are sincerely grateful:

Bull S. A.
Centre National d'Etudes des Télécommunications
Department of the Army (European Research Office)
Department of the Navy (European Research Office)
Direction des Recherches, Etudes et Techniques
Heraeus (France)
IBM (France)

Laboratoire d'Electronique et de Physique Appliquée
Laboratoire d'Electronique et de Technologie de l'Informatique
Thomson CSF
Universität Tübingen (Federal Republic of Germany)

R. A. B. Devine
Grenoble, February 1988

CONTENTS

STRUCTURE: THEORY AND EXPERIMENT

INTRINSIC AND EXTRINSIC DEFECTS: THEORY

INTRINSIC AND EXTRINSIC DEFECTS: EXPERIMENT

INTERFACES

OXIDATION, OXYNITRIDES AND DEPOSITED FILMS

TRANSPORT, TRAPPING AND BREAKDOWN

RADIATION EFFECTS

BURIED DIELECTRIC LAYERS AND NOVEL APPLICATIONS

CURRENT MODELS FOR AMORPHOUS SiO_2

Frank L. Galeener

Department of Physics
Colorado State University
Fort Collins, CO 80523, USA

ABSTRACT

I discuss central questions of glass structure and define four ranges of order in an amorphous solid : short, intermediate, long and global. These concepts are used to catalog all of the elements of order in the Zachariasen-Warren model for a-SiO_2, in preparation for a later deduction of the logically possible improvements in that model. Six existing approximate forms of the ZW model are discussed using the language developed in the paper. This provides a fundamental background regarding structure for the rest of the papers in this volume.

INTRODUCTION

The description and determination of the structure of amorphous materials is a ubiquitous and fundamental problem for those who wish to understand and predict their properties. In this paper I will discuss conceptual aspects of the problem, using a-SiO_2 as a vehicle for the presentation. The content will build on ideas recently reported elsewhere[1].

SOME CENTRAL QUESTIONS OF GLASS STRUCTURE

It is clear that glasses contain sufficient disorder that their structure must ultimately be defined statistically. There are too many slightly different structural units for a complete enumeration, so an approximate and statistical description of structure is needed, just as one is needed for treating the properties of gases. How completely can one specify the structure of a real glass ? What is the best "language" for doing this ? How precise must be the description - for adequate understanding of each of various physical properties ? What are useful simplifications of these structural models, for purposes of facilitating calculations or conceptual reasoning ? How does structure vary with the conditions and mode of preparation[2] of the amorphous solid ? Previous reports[3] and several papers at this conference show that numerous properties of a-SiO_2 vary importantly with preparation conditions ; the statistical description of structure must be sensitive enough to account

for these changes. Most of the questions just raised are not yet well-answered.

THREE KINDS OF STRUCTURAL MODELS

Occasionally an author will present evidence against a particular model and then infer erroneously that the parent class of models has been disproven. Thus, a specific inadequacy of the Bell and Dean model[4] for a-SiO_2 does not[5] necessarily invalidate[6] the parent continuous random network hypothesis. To help avoid this logical error, I will classify models as conceptual, specific or approximate.

A conceptual model consists of conceptual statements only, is very general in nature, typically stating the topology, connectivity or order with no quantitative detail. It is insufficiently specified for quantitative comparison with experiment. Examples are models that simply assert that an amorphous solid is "not crystalline", is a "continuous random network" or is an "array of microcrystals".

A specific model is characterized by conceptual statements plus sufficient quantitative specifications to be compared quantitatively with one or more experiments. To the extent that there is disagreement, the model may be wrong only in the quantitative specifications, or it may also be wrong conceptually if the conceptual aspects require quantitative specifications in the range tested[7] : this is, of course, simple logic, but it is all too frequently violated.

An approximate model is a specific model which is simplified from its pristine form in order to enable physical or mathematical construction of the model or to enable or facilitate mathematical calculations of properties that will be compared with experiment. A Bethe lattice[8] may be viewed as an approximate form of some specific continuous random network, and is used to calculate properties like the vibrational spectra of a-SiO_2 [9]; if those predictions cannot be made to agree with experiment the fault may lie in the Bethe lattice approximation, not in the specific structure it is used to model, or in the conceptual model that lies underneath. In more subtle situations this distinction is also too often overlooked. In fact, most structural models used to compare with experiment are approximate in the present sense : the Bell and Dean models are highly approximate because of the small size and large surface area of the clusters actually built and used for calculations.

SOME IMPORTANT FACTS ABOUT STRUCTURAL STUDIES

It is important to note some general facts about experimental studies of the structure of amorphous solids.

While the diffraction of x-rays, neutrons or electrons gives definite information about the structure of crystalline solids, such measurements give much less information about the structure of amorphous solids[10]. The diffraction pattern of an a-solid consists of diffuse rings whose radial variation of intensity provides a merely 1-dimensional representation of the 3-dimensional glass structure. Clearly some information about the structure is "averaged out" in the experiment, and the structure is surely not 1-1 with the diffraction data. In practice, then, one imagines a likely a-structure, predicts experiment and compares with observation. If comparison is poor, the specific model is rejected ; however, good comparison merely qualifies the model as an acceptable candidate and leaves

open the possibility that some other model would do as well, or better.

This illustrates the fact that statistical structural models are almost impossible to prove uniquely. All probes will involve averages over statistical structural models. A poor fit to data with one probe implies rejection of the specific model used for calculation, but the conceptual form of the specific model may still be correct. A good fit is encouraging, but may in principle be had with other models not yet considered.

This discussion illustrates the need for the use of many different experimental probes of structure. Diffraction, NMR, vibrational spectroscopy and other techniques emphasize different aspects of structure, such as interatomic distances, or angles, or local symmetry, or range of order, and the like. Each technique provides an alternate view of the structure and generally averages the structure differently, thus revealing aspects that may be de-emphasized or obscured by another technique. Observation of ordered rings of bonds in a-SiO_2 by Raman spectroscopy is a vivid example[11]. Although each probe gives limited information, the results of several different probes can dramatically reduce the number of possible models, leading to a conviction of truth (if not its proof).

RANGES OF ORDER IN AMORPHOUS SOLIDS

This logical process of elimination of possible models would also be greatly helped by the development of clearer concepts and more certain theoretical principles concerning the structure of a-solids. To this end I have tried to develop a more precise set of terms for categorizing the scales (or ranges) of order in amorphous solids[1]. The resultant four ranges of order are as follows.

Short Range Order

Short range order (SRO) describes the nearest neighbor (nn) bonding environment of each atomic species. It involves bond types, distances, and angles, extends over a volume whose dimension is about twice the typical nn

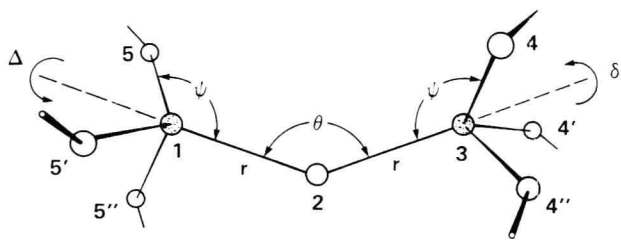

Fig. 1. The relative orientation of two corner-sharing tetrahedra in a-SiO_2, showing the short range order and one aspect of the intermediate range order. Each Si atom (dark) is surrounded tetrahedrally at distance r by four O atoms and each O atom bridges between two Si atoms with an angle θ that varies from site to site ; these two molecule-like arrangements specify the SRO in its usual "simplified" form. The dihedral angles δ and Δ, giving the angular orientation of the tetrahedra about their bridging O-Si bonds (relative to the Si-O-Si plane) are defined in this paper as elements of IRO.

structure of B_2O_3 glass[17]. The model is based on regular planar "boroxol" rings within which the dihedral angles of the BO_3 units on either side of an O atom are equal and thus completely correlated. On the other hand the dihedral angles of BO_3 units on either side of an O atom bridging between two rings are not equal, are much less correlated and are generally assumed to be random and independent in recent studies[18] (which are quantitatively consistent with that assumption).

Similarly, the assumption of random dihedral angles in fig. 1, used in the Zachariasen-Warren model[19-26] for a-SiO_2 is also a specification of an element of IRO.

SRO and IRO will specify the relative atomic positions over a volume whose dimension is several nearest neighbor distances, and is therefore in the range 5-10 Å, or larger.

Long Range Order

At larger distances we must consider the possibility of crystal-like arrangements of atoms which we will call long range order (LRO). We will define two mutually exclusive kinds of order on this next larger scale of distances, namely crystalline LRO and morphological LRO.

Crystalline Long Range Order

Crystalline LRO recognizes the possibility of periodic repetition of an IRO over several repeat lengths, and thus accounts for the possible existence of microcrystals in the structure of amorphous solids. Its existence shows clearly as sharp features in a diffraction pattern at positions related closely to those for more macroscopic crystals.

Roughly speaking, microcrystallinity over dimensions of 10 Å or more will be revealed as diffraction features that are sharper than those seen in glasses which are not microcrystalline. In a-SiO_2 it has been argued that microcrystals larger than about 8 Å would produce diffraction lines narrower than those seen[5]. Clearly, microcrystalline LRO specifies, SRO, IRO and other elements of structure - over the range of the particle size. (Note, as I have shown elsewhere[1], that the surface or interface layers between such particles comprise a very large fraction of the entire sample).

The important idea here is that we operationally define a distance d_{LRO}, which is the dimension of a microcrystal that would give sharp enough diffraction lines to be revealed by the narrowness of those lines. Clearly, d_{LRO} varies from material to material, and for different crystal structures of the same material.

Order on this scale or larger will be called LRO, thus defining a lower limit for the scale of LRO and an upper limit for the scale of IRO. We will use the same d_{LRO} to define a scale for LRO in amorphous materials that are not microcrystalline.

Morphological Long Range Order

This category accounts for order in non-microcrystalline structures on a longer range scale than that of IRO, ie on a scale larger than the minimum dimension d_{LRO} just defined. This is useful in order to catalog structures that are clearly not covered by the previously defined notions of IRO. Morphological LRO includes extended voids, channels, spherulites,

distance, and is therefore in the range 3-5 Å for most materials, 3 Å for a-SiO_2. It is usually well determined from the radial distribution function (rdf) obtained from x-ray or neutron diffraction.

In a-SiO_2, the SRO is commonly specified by stating that each Si atom is surrounded almost tetrahedrally by four oxygen atoms at bonding distance r of 1.61 Å, while each O atom bridges between two Si atoms at the same distance. There is a small spread in the bond distance r, a small spread in the O-Si-O angles Φ, and a much larger spread in the Si-O-Si angles θ. These elements of SRO in a-SiO_2 can be visualized with the help of fig. 1, where one can see schematically the SRO around the Si and that around the O atomic species.

For the present definition of SRO, all neighbors of a species are treated as if they are spherically symmetric. This allows logical separation of SRO from intermediate range order (which recognizes that the neighbors are not spherically symmetric, and have orientations associated with them).

Intermediate Range Order

Intermediate range order (IRO) involves specification of relative atomic positions over several nn distances, given the SRO. Most fundamentally, it recognizes that nearest neighbors are not spherically symmetric. IRO may take the form of specification of the dihedral angles[12] δ, Δ shown in fig. 1 for the two corner sharing tetrahedra, distributions of the sizes of rings of completed bonds, properties of network connectivity[13] or some presently unformulated measure. There can be distributions of dihedral angles[12,14] and correlations [15] among dihedral angles if there are regular structures such as rings [16] embedded in the a-solid.

An example of IRO involving both correlated and uncorrelated dihedral angles is illustrated in fig. 2, which shows elements of the likely

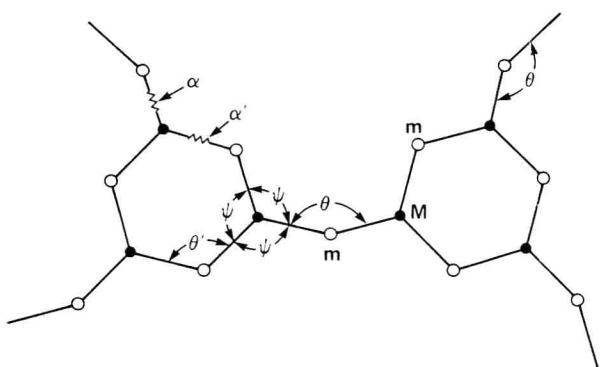

Fig. 2. Schematic (planarized) drawing of some elements of IRO in B_2O_3 glass, where • = boron and ○ = oxygen. The hexagonal B_3O_3 "boroxol" θ varies from site to site. The dihedral angles of the BO_3 units at each end of this bridging O atom are assumed random (the rings are generally not in the plane of the figure), while those within the rings all have the same value (δ = 0), and are thus highly correlated.