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Defects in Glasses

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Defects in Glasses

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Preface

In the last few years, several advances have been made in our conceptual and quantitative understanding of imperfections in amorphous solids. This has been particularly true of *glasses,* which are amorphous materials that can be formed by quenching from the melt, but are often fabricated in other ways, including methods of thin film deposition, gel dehydration and by geophysical processes.

To review the current state of the field, a symposium entitled Defects in Glasses was held at the Materials Research Society meeting in Boston, Massachusetts, December 2-4, 1985. The original program of 11 invited and 31 contributed talks is reproduced in the Appendix. The resultant manuscripts appear in rearranged order in the present record. Since this is the first book length compendium of information on the subject area, the authors have been encouraged to provide tutorial presentations, containing extensive lists of references. Many have succeeded. To make their subjects and references more accessible, we have created a relatively complete Subject Index with over 700 entries.

For this symposium, a defect was any significant departure from the *idealized* continuous random network (CRN) model appropriate for the nominal chemical composition. This was done *not* because we believe the CRN is the best model for all glasses, but to provide a crisp definition of the meaning of "defect" in a glass. Thus, a central theme was the nature of deviations or extensions from the (Zachariasen) CRN model *in real glasses*. This emphasis will help to delineate the limits of applicability of the ZCRN, which presently plays the same role for glass science as does the (unrealized) perfect crystal in crystallography. In a limited way, these proceedings are about the *defects* in the ZCRN model.

The papers reflect well the areas in which contributions were solicited. They cover intrinsic or deliberately induced defects in the form of impurities and dopants (atomic, ionic, molecular . . .), short range order (point defects, wrong bonds, wrong coordination . . .), intermediate range order (rings, rafts, cages . . .) and extended defects (voids, internal and external surfaces . . .). Many of the defects are induced by radiations, ranging in energy from meV to MeV and including infrared, visible, U.V., X-ray, γ-ray, electrons, protons and neutrons.

Although defects in other *inorganic* amorphous materials such as amorphous Si and Ge and amorphous metals are very important, these materials were explicitly excluded -- largely because they have been the subjects of recent conferences. The materials covered therefore include oxide, halide and chalcogenide bulk glasses, xero gels, fibres and amorphous thin films. The full extent of materials covered can be judged from entries in the Subject Index.

As usual in materials research, the papers reflect a lively interest in structure, bonding, kinetics, mechanisms of formation, modeling, computer simulation, relation to device performance and methods of characterization. The latter include electron microscopy, liquid chromatography, transport properties, and the following spectroscopies: nuclear magnetic resonance, electron spin resonance, optical absorption, luminescence, infrared, Raman, X-ray absorption and Mössbauer. There is also an extensive discussion of the causes of color in glasses, many of which are related to the kinds of defects considered in this symposium.

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Frank Galeener
David Griscom
Marvin Weber

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PART I

Theory and Modeling

THEORY OF INTRINSIC DEFECTS IN a-SiO_2

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ABSTRACT

In this paper we discuss recent advances in the theory of intrinsic defects in amorphous SiO_2. We pay particular attention to the E′ centers, and to the oxygen-related hole traps.

I. INTRODUCTION

Silicon dioxide is a remarkably versatile material. In its crystalline form it is used in precision oscillators, it is drawn into fibers for use in optical communications and it is the principal dielectric in silicon electronic technology. From a fundamental point of view, silicon dioxide is equally useful as a model amorphous material because of its chemical simplicity. It is not surprising, then, that much research effort has been expended to understand the properties of this material.

In this paper we focus on point defects in a-SiO_2. We will pay particular attention to those that occur naturally, and to those that are generated by irradiation. The defects we consider here involve only silicon, oxygen and hydrogen (As was discussed elsewhere [1], we consider hydrogen to be an intrinsic component of all forms of SiO_2). Furthermore, as the title indicates, we are interested in theoretical contributions to this field, so that, while we will discuss some experimental results at length, our primary goal is to demonstrate the increasingly important role of theory. At this point, we will digress and explain our picture of the role of theory in defect studies.

The goal of any study of defects is to elucidate the microscopic structure and chemical constituents, as well as the electronic structure, that is to say, the defect wave function and energy levels. Once these features are determined, formation and annihilation mechanisms can be addressed. In Table I, we outline the various experimental and theoretical approaches available for obtaining this information.

TABLE I. Important Experimental Techniques and the Associated Theoretical Results for the Study of Point Defects.

Experiments	Relevant Observables	Calculated Parameters
ESR	Defect Geometry	Defect Geometry
Isotope Enrichment	Principle Chemical species Orbital composition of defect wave function	Spin Densities
Optical Spectroscopy	Energy Levels Transition Strengths	Excited States Optical Matrix Elements
Thermal Annealing	Defect formation, annihilation and transformation (growth or decay of signal intensity)	Heats of Formation Reaction paths
IR and Raman Spectroscopy	Vibrational Frequencies Defect Symmetry	Vibrational Frequency Selection Rules

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We place a box around Electron Spin Resonance and the associated isotope enrichment experiments because these are the most revealing techniques. In fact, they have historically been the only techniques that led to unambiguous defect identification. All of the calculations listed in Table I obviously assume a microscopic model which is usually derived from ESR. While one of the primary roles of theory is to verify microscopic models derived from experiment, only recently have theoretical techniques and computational resources been developed that make quantitative verification possible. Furthermore, these techniques are powerful enough to allow theorists to develop their own models through computer experiments that in turn will be tested experimentally. Our central goal is to demonstrate that this iterative give-and-take between experiment and theory has led to a solid understanding of several of the important intrinsic defects in a-SiO_2.

The balance of this paper is organized in six sections. In section II, we briefly outline our model of a-SiO_2. In Section III, we review the theoretical techniques used in calculating the electronic structure and geometry of defects. Sections IV through VI are the core of the paper, where we discuss the principal theoretical achievements in interpreting experimental results, as well as in predicting the correct defect models. We conclude in section VII.

II. THEORETICAL PICTURE OF SiO_2

Our understanding of amorphous silicon dioxide begins with an appreciation of its similarity to crystalline SiO_2. Most common spectroscopies (XPS, UPS, X-ray absorption and emission) performed on both crystalline and amorphous SiO_2, yield results that are virtually indistinguishable (See reference [2]). Theoretical calculations confirm this similarity. The band structures of the various crystalline polymorphs of SiO_2 [3-8] are different in detail, but give rise to almost identical predicted optical properties. This is so because, while the long range order varies, the fundamental bonding unit, shown in Fig. 1, changes only through the variation of the Si-O-Si bond angle, theta. Several theoretical studies [9-11] demonstrate that this angle is extremely flexible, i. e., the entire experimental range for theta (180° - 120°) can be accessed by expending a maximum of 0.3 kcals/mole. In fact, the remarkable flexibility of this bonding unit is consistent with the distribution of bond angles found in a mechanical model for a continuous random network of silicon dioxide[12]. In this model, the Si-O bond length and the O-Si-O and Si-O-Si bond angles were initially held fixed. The model was constructed appealing only to intuitive ideas of randomness. However, upon completion, it was discovered that distortions had taken place. These were strikingly reflected in the above mentioned bond angle distribution. We should point out that the experimental radial distribution functions for both X-ray diffraction and neutron diffraction were reproduced quite faithfully by this mechanical model[12].

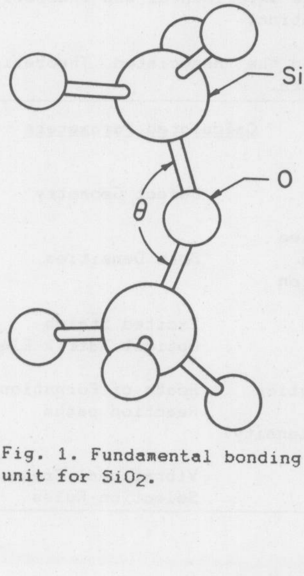

Fig. 1. Fundamental bonding unit for SiO_2.

There is a competing microcrystallite model, wherein the glass is composed of crystallites of diameter 100 angstroms surrounded by a monolayer of nonbridging-oxygen atoms that are double-bonded to silicon atoms [13]. This model was proposed to account for two very narrow peaks in the Raman and IR spectra for a-SiO_2.

These two models are the subject of