Physical Properties of Amorphous Materials

Institute for Amorphous Studies Series

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PREFACE

The Institute for Amorphous Studies was founded in 1982 as the international center for the investigation of amorphous materials. It has since played an important role in promoting the understanding of disordered matter in general. An Institute lecture series on "Fundamentals of Amorphous Materials and Devices" was held during 1982-83 with distinguished speakers from universities and industry. These events were free and open to the public, and were attended by many representatives of the scientific community. The lectures themselves were highly successful inasmuch as they provided not only formal instruction but also an opportunity for vigorous and stimulating debate. That last element could not be captured within the pages of a book, but the lectures concentrated on the latest advances in the field, which is why their essential contents are here reproduced in collective form. Together they constitute an interdisciplinary status report of the field. The speakers brought many different viewpoints and a variety of background experiences to bear on the problems involved, but though language and conventions vary, the essential unity of the concerns is very clear, as indeed are the ultimate benefits of the many-sided approach.

The impact of amorphous materials on the worlds of science and technology has been enormous, covering such diverse applications as solar energy, image processing, energy storage, computer and telecommunication technology, thermoelectric energy conversion, and new materials synthesis. If the subject is to reach its full fruition, its role in educational programs will have to be commensurate. To an astonishing extent, the teaching of solid state physics is still restrictively tied to crystalline concepts, and the time has come for a change and a balance. Both will undoubtedly come but reform and reorientation take time. It is one of the Institute's purposes to accelerate the process.

We reconfirm our belief and confidence that amorphous materials will serve humankind in a variety of important ways, and we recognize that the scientists who are now in the forefront of this field are in effect social as well as technological pioneers. My special thanks are due to the contributors to this volume, to whom I wish continued success in the realms of new scientific ideas and technological achievement.

S.R. Ovshinsky
Troy, Michigan

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INTRODUCTION

It is no surprise to note that the technological importance of amorphous solids has mushroomed over the past few years. Of course, this is not to say that they have been insignificant in the past. In fact, the use of glass in decorative and packaging applications has a history of more than 10,000 years. However, it was not until the advent of electrophotographic copying only about 25 years ago that the electronic properties of amorphous materials began to be exploited. In the very brief time since this breakthrough, we have seen the development of commercial computer memories, television pick-up tubes, solar cells, x-ray mirrors, thermoelectric devices, and imaging films based on amorphous materials, and we are on the verge of adding batteries, catalysts, video disks, displays, transient suppressors, and an array of other applications to this list. Yet most solid-state scientists appear to be unaware of even the existence of these materials, much less of their importance. Few textbooks deal with anything but crystalline solids and there is little evidence that even graduate-level courses at all but a handful of universities devote much time to their properties.

There has never been a dearth of technical review papers dealing with specialized properties of amorphous solids, but the same cannot be said of coherent books suitable for student texts. It is true that Mott and Davis's work, Electronic Properties of Non-Crystalline Materials, has gone through two editions and Zallen's recent The Physics of Amorphous Solids has just appeared, but neither of these is exhaustive in scope.

With the creation of the Institute for Amorphous Studies, devoted to both the training of scientists and the dissemination of information relating to amorphous materials and devices, we now have the opportunity to fill all of the gaps in the written as well as

oral avenues of pedagogic instruction. This volume represents the first step in the direction of making the state of the art accessible to those who were not able to attend either the lecture series or the various mini-courses held at the Institute. This book can serve either as an initial introduction to the field or as the basis of a comprehensive in-depth course. Much of the cited literature is quite recent, reaching to the late 1984 publication of the Proceedings of the International Conference on Transport and Defects in Amorphous Semiconductors (J. Noncryst. Solids, Vol. 66) held at the Institute.

The 14 papers in this volume are arranged in five parts. Part One, dealing with all aspects of the materials, can serve as a general introduction to the whole field. The Adler paper is an attempt at outlining a new approach to the study of solid-state physics, in which periodicity is not considered to be fundamental. Both the conventional and alternative viewpoints are discussed, and the effects of disorder are analyzed in detail. Brief reviews of the properties of amorphous silicon-based and chalcogenide alloys are included. This paper is followed by one by Ovshinsky, primarily dealing with his broad view of the chemical basis for controlling the properties of amorphous materials and the tailoring of these materials to optimize their use in specific applications. This paper provides the rare opportunity to understand some aspects of the original thinking which revolutionized the field.

Any problem in solid-state physics can be broken down into three sub-problems. The first is that of the equilibrium positions of the atoms constituting the solid, i.e., its structure. The structure not only determines the mechanical properties of the material but also controls the other two sub-problems. One of these is the nature of the vibrations of the atoms around their equilibrium positions, i.e., the phonon modes of the solid. These determine the thermal properties of the material. The other problem is that of the states available to the electrons as they propagate through the solid, i.e., the electronic structure. This controls the electrical and optical properties of the material. Part Two of this volume is concerned with the structure of amorphous solids. Weaire's paper discusses the conceptual basis of disordered structures in general, while those of Bienenstock, Stern, and Boolchand deal with detailed experimental results on real systems. Bienenstock provides a general introduction to studies of both simple and complex systems, pointing out the contrasts between the analyses of crystalline and amorphous materials. Stern concentrates on the use of extended x-ray absorption fine structure (EXAFS)

to determine the structure of disordered solids, while Boolchand discusses the results of Mössbauer experiments in detail. Finally, Chakraverty presents a novel approach to the structure of silicon-metal interfaces, an important subject in many device applications of silicon-based materials.

Part Three, dealing with the analysis of phonon modes in amorphous materials, consists of the comprehensive paper by Lucovsky. This paper analyzes the vibrational properties of both network glasses and amorphous silicon-based alloys in detail.

The important problem of electronic structure is the basis of both Parts Four and Five. Part Four is primarily concerned with the density of states available to electrons as they move through the disordered system, g(E), as a function of their energy, E. Once g(E) is known, the near-equilibrium electrical and optical properties of the material as functions of the temperature can be derived from the known probability of occupation of these states, the Fermi-Dirac distribution function, f(E). Fritzsche's paper presents an elementary introduction to the various experimental methods that have been developed for the determination of g(E). In contrast, the paper of Cohen is primarily concerned with the theoretical basis for understanding the behavior of g(E) and how the observed transport and optical properties can be explained.

One of the major advances of the past decade has been a detailed understanding of the approach to re-equilibration after the perturbation of a semiconductor away from its equilibrium distribution function, f(E). This perturbation can be accomplished, e.g., by the application of an intense light pulse that creates excess free electrons and holes or an applied electric field that injects free carriers from one or both contacts. The resulting time dependence of the response, e.g., i(t), can be quite complex, but recent theoretical models have been developed which can sort it out and, in fact, use this response as a sensitive probe of the density of localized electronic states, g(E), in the material under investigation. Part Five is devoted to several aspects of these nonequilibrium phenomena. Henisch discusses the processes in general, paying particular attention to the complex issue of carrier injection and extraction via the contacts. Kastner's paper provides an elementary introduction to the subject of excess-carrier trapping and recombination, and shows how a simple model can explain the complex transient photoconductivity data. Silver is primarily concerned with the additional information that can be

learned from sorting out the primary excess-carrier recombination mechanisms and the effects of high-level injection, in particular the use of such experiments to obtain a handle on the mobility of carriers in extended states. Finally, Guha discusses the important problem of light-induced variations in properties of amorphous semiconductors, paying special attention to hydrogenated amorphous silicon.

All of the lectures reproduced here stimulated a great deal of lively discussion, both during and after their presentation. We hope this volume does the same.

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CHEMISTRY AND PHYSICS OF COVALENT AMORPHOUS SEMICONDUCTORS

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I. INTRODUCTION

Although, as Ovshinsky [1] has often noted, the history of civilization is intimately connected with advances in materials research (e.g., the Stone, Bronze, Iron, and Steel Ages), a quantitative theory of materials did not evolve until after the development of quantum mechanics in 1925. When Bloch [2] developed the quantum theory of solids in 1930, physicists were unduly influenced by the discovery less than 20 years previous that many solids were periodic arrays of atoms. By making use of the mathematical simplifications resulting from periodicity, Bloch was able to derive some general properties of the electronic states in crystals, from which Wilson [3] developed the band theory of electronic transport. There is no question that this theory has been very successful in providing a detailed understanding of the properties of crystalline solids, including the electrical and optical properties of a wide array of commercially important semiconductors and metals. However, it has long been known that many solids are not crystalline but are amorphous, and do not exhibit any long-range periodicity. Furthermore, these amorphous solids have been shown to exhibit the same range of electrical and optical properties as do crystalline materials, strongly suggesting that the band theory of solids is much more general than its original derivation indicates. Nevertheless, even now, over 15 years after the publication of Ovshinsky's landmark paper [4],