Disorder and Order in the Solid State

Concepts and Devices

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To
Professor Heinz K. Henisch
with great respect and affection
on the sixty-fifth anniversary of his birth

PREFACE

This Festschrift is an outgrowth of a collection of papers presented as a conference in honor of Professor Heinz K. Henisch on his sixty-fifth birthday held at the Institute for Amorphous Studies, Bloomfield Hills, Michigan. It is our great pleasure to be editors of the Festschrift volume to honor Heinz and his work.

Professor Henisch has a long and distinguished career and has many accomplishments in semiconductor materials and devices. He has made seminal contributions to the understanding of semiconductor switching devices and contact properties. He has an outstanding reputation as an expositor of science. His seminars and lectures are always deep, lucid and witty. He received his doctorate in Physics from the University of Reading and then joined the faculty. In 1963, he accepted a position in the Department of Physics at Pennsylvania State University. While at Penn State, Dr. Henisch broadened his research interest to include the History of Photography. At the present time, Dr. Henisch holds parallel appointments as a Professor of Physics and a Professor of the History of Photography at Pennsylvania State University. He is a Fellow of the American Physical Society, the Institute of Physics, London, the Royal Photographic Society and is a Corresponding Member of the Deutsche Gesellschaft fur Photographie. In addition to his considerable publication in the fields of physics and the history of photography, Dr. Henisch is the founder and editor of the Journal of the History of Photography published quarterly by Taylor and Francis, Ltd., London.

The papers in this Festschrift reflect only a small portion of the breadth of the total scientific contribution of Professor Henisch, his students and his associates. The papers are a selection of "snapshots" of the activities and influences of Heinz Henisch. This volume contains 17 papers by 30 authors from 6 countries around the world. We are grateful to the many friends and associates of Dr. Henisch for their contributions to this volume.*

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* A number of excellent papers related to the history of photography were also presented at the Henisch Festschrift conference at the Institute for Amorphous Studies. Those papers are published as a separate volume and edited by Dr. Kathleen Collins.

The topics discussed in this volume range from superconductivity theory to experimental measurements of piezoresistivity, and from the long-range disorder of the amorphous state to various types of short-range order and disorder. The largest number of papers, 11, address the measurement and the modeling of different aspects of the electronic properties of solid-state devices and thin solid films, both single and multilayer. Other papers consider the various effects of order/disorder on the properties of solids and the fabrication of amorphous films and fibers.

The editors wish to express their gratitude to Ghazaleh Koefod for her many contributions, without which this volume would not have been completed.

Roger W. Pryor

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Stanford R. Ovshinsky

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INTRODUCTION

The HENISCH FESTSCHRIFT is a collection of papers presented in honor of the sixty-fifth birthday of Professor Heinz K. Henisch. His contributions to the understanding of semiconductors, their contacts and to the science of electronic materials has been extensive. His book on "Rectifying Semiconductor Contacts" has long been considered the definitive document in that field. The papers in this collection only partially reflect the extent of the total scientific contribution that he, his students and his associates have made. These papers are presented as a brief summary of the current activities of a great scientist and his associates.

This volume is international in scope and contains 17 papers by 30 authors from 6 different countries around the world. The topics covered in this volume range from superconductivity to piezoresistivity and include many different kinds of states of disorder such as the amorphous states and the state with long-range order but with no short-range order. The largest number of papers, 11, on amorphous thin film concepts and devices, address the measurement and modeling of different aspects of the electronic properties of solid state devices and thin solid films, both single and multilayer. The second largest number of papers, 4, consider the various effects of order/disorder on the properties of solids. The topics discussed include superconductivity, piezoresistivity, magnetism, and the various types of short-range order and disorder. The last category, on films and fibers, contains 2 papers that treat the fabrication of amorphous films and fibers.

The initial section in this volume is titled "AMORPHOUS THIN-FILM CONCEPTS & DEVICES." The first two papers in this section concern the conductivity of thin amorphous films. The first paper is by Sir Nevill Mott of the University of Cambridge on the "Mobility of Electrons in Non-crystalline Materials." Sir Nevill discusses the validity of the polaron hypothesis as it relates to the question of the fundamental conduction mechanism in amorphous semiconductors. He calculates an expression for the mobility based on the inelastic diffusion length and the time between inelastic collisions with phonons. He obtains a value of the mobility for amorphous silicon that agrees well with current experimentally derived values. Sir Nevill concludes by suggesting areas of research that are in need of further experimental exploration. The next paper is by H. Fritzsche, H. Ugur, J. Takada, and S. H. Yang of the University of Chicago on "Metastable Nonlinear Conductance Phenomena in Amorphous Semiconductor Multilayers". In this paper, Fritzsche et. al. present a series of experimental observations on amorphous semiconductor multilayer films and the conclusions that can be made from their measurements. The films used were of two types: compositionally modulated multilayers (a-Si:H-a-SiN:H) and doping-modulated multilayers (a-Si npnp). The compositionally modulated multilayer films exhibit no unusual behavior at low applied biases (<1 volt). At high applied bias (300 volts), excess dark conductance was observed after brief photoillumination. The excess dark conductance can be removed by photoillumination of the sample at no bias or by heating. The doping-modulated multilayer films also show field related conductance anomalies. This paper shows that the persistent photoconductivity (PPC) effect is reduced by applied bias during light exposure. It is concluded that there may be a link between these effects and the glass-like behavior of the bonded hydrogen network in a-Si:H films that mediates the equilibration of defects and dopants.

The next seven papers in the "AMORPHOUS THIN FILM CONCEPTS & DEVICES" section are on device technology, device behavior and device theory. The first paper is by Roger W. Pryor of Energy Conversion Devices entitled "Recent Developments in Ovonic Threshold Switching Device Technology." This paper discusses the development of two new device designs and processing techniques for the fabrication of thin film, high current, DC stable, chalcogenide glass threshold switches and presents the first results showing hydrogen as an electronically active material modifying the behavior of the chalcogenide switching glasses. It is shown that hydrogen significantly improves the threshold voltage stability and reproducibility. Experimental data are presented on the current density during the ON-State, which confirms the principle of the expanding filament.

The next device paper is by D. N. Bose of the Indian Institute of Technology. His paper discusses the use of chalcogenide glasses in "Amorphous Chalcogenide Microwave Switches." He shows that thin chalcogenide films can act as microwave switches in the X-band. Measurements were made on both threshold and memory glass compositions using the switches to modulate an applied X-band signal. A mechanism for the change in conductance is presented.

Melvin P. Shaw of Wayne State University presents a paper on "Switching and Memory Effects in Thin Amorphous Chalcogenide Films - Thermophonic Studies." In this paper, the author briefly reviews the experimentally observed characteristics of threshold switching devices before presenting his additional observations by electroacoustic spectroscopy (thermophonics). Data taken simultaneously on the voltage, current and acoustic signals demonstrate that electronic switching occurs well before the thermally generated acoustic signals under normal conditions. Data and analysis are also presented on devices operated under other than normal conditions.

The role of relaxation semiconductors is considered in next two papers. "Interpretation of Recent ON-State and Previous Negative Capacitance Data in Threshold Chalcogenide Amorphous Switch" is the title of the first such paper by G. C. Vezzoli of U. S. Army Materials Technology Laboratory and M. A. Shoga of Hughes. These authors show that the blocked on-state requires approximately 65 ns to form in thin chalcogenide threshold switching devices. For times less than the critical time of formation, the I/V curve of the switch appears to be metallic in nature. It is argued that these results support a recombination single injection model for the mechanism of threshold switching. In the paper "Carrier Injection into Low Lifetime (Relaxation) Semi-Conductors" by J. C. Manifacier, Y. Moreau, and R. Ardebili, the mechanism of conduction in relaxation semiconductors is the main theme. The authors review the equations governing the behavior of electrons and holes in the general case for semiconducting materials. They proceed to do a comparison between an analytical and a numerical solution to these equations for both the lifetime and relaxation cases for two types of junctions. The calculations presented agree well with previously published experimental data.

Peter T. Landsberg of the University of Florida and the University of Southampton, U.K. contributed a paper on "A Semiconductor Model for Electronic Threshold Switching." The author presents a model for a method of electronic switching based on electron and hole concentration using the stability criterion of the recombination, generation parameters in impact ionization space to explain the occurrence of switching. In this model, a switching transition occurs as a result of a field-driven boundary crossing from one region of stability to a region in which different stability criteria apply.

In the next paper, "Proper Capacitance Modeling for Devices with Distributed Space Charge" by Roberto C. Callarotti of INTEVEP S. A., a detailed method of modeling device capacitance is presented. The primary feature of this model is that the bulk of the device is divided into slices and each slice is electrically modeled as a parallel resistor and capacitor. All the electrical analogs are then connected in series for calculation. An example is given using a Metal-Insulator-Metal device.

P. E. Schmidt of IVIC and R. C. Callarotti contributed a paper on "On the Impedance Calculation of Thick MIM Barriers". This paper demonstrates methods for the calculation of the incremental AC characteristics of thick metal-insulator-metal barriers. A generalized approach results in the formulation of coupled ordinary differential equations in terms of a complex AC carrier density. This simplified approach utilizes an incremental circuit representation as a reasonable approximation. A low frequency model is presented and discussed in detail.

K. B. R. Varma, K. J. Rao and C. N. R. Rao present the final paper in the "AMORPHOUS THIN FILM CONCEPTS & DEVICES" section entitled "Dielectric Behavior of Amorphous Thin Films." They present an analysis of the dielectric behavior and the ultramicrostructures of RF sputtered amorphous and recrystallized high dielectric constant films. The behavior of these films are analyzed using a cluster model. It is concluded that amorphous films of ionic dielectrics exhibit large dielectric constants and ferroelectric-like dielectric anomalies in the region of crystallization. It is also concluded that the dielectric anomalies in the crystallized state and in the amorphous films are not directly related.

"ORDER & DISORDER" is the next section of this volume and includes those papers that analyze the influence of the relative degree of order or disorder on some of the observable properties of solids. The topics that are included within this section are superconductivity, various kinds of short- and long-range order and disorder, piezoresistivity and magnetic domain patterns.

The first paper in this section is by S. R. Ovshinsky (inventor of the threshold switch) of Energy Conversion Devices entitled "A Personal Adventure in Stereochemistry, Local Order, and Defects: Models for Room Temperature Superconductivity." The author presents a new and unique approach to the theory of superconductivity. In his discussion, he covers primarily two topics. The possibility of room temperature superconductivity being the mechanism of conduction in the Ovonic Threshold Switch (OTS) during the ON-State and the establishment of high-temperature superconductivity by a simultaneous, two-atom valence transformation process. In the case of the OTS, the formation of the superconductive filament occurs in the solid state plasma. Bose particles are formed when the carriers can pair as a result of the negative correlation energy in the lone pair configurations. It is proposed that "such pairs should exhibit a Bose condensation well above room temperature." In the new ceramic oxide high-temperature superconductors, a different mechanism is proposed. The basis of that mechanism is the establishment of a simultaneous, two-atom valence transformation. This is accomplished by the interaction of copper "sheets" and the copper "chains" through the oxygen "pump." This results in "superexchange coupled spin pairs on the chains and sheets" that "are mobile, strongly bound, spinless composite particles which obey Bose statistics."

A. H. Majid, W. F. Anderson and R. L. Osgood of the Pennsylvania State University and T. Madjid of the Department of the Air Force present the next paper entitled "Phenomenology of Antiamorphous Order." This paper treats the phenomenology of metal/insulator/metal superlattice structures, where the layers are sufficiently thin to be aggregates. Such aggregates are an experimental approach to the formation of a state in which the material has long-range order without having short-range order. These multilayer aggregate structures exhibit a broad range of interesting phenomena, including switching. The methods of fabrication and the observed results are discussed.

The "Piezoresistivity in Semiconducting Ferroelectrics" paper by Ahmed Amin of Texas Instruments reviews the piezoresistive effect in semiconducting polycrystalline barium titanate and its solid solutions with lead and strontium titanate under different elastic and thermal boundary conditions. An analysis of this phenomenology is presented in terms of current ferroelectric and grain boundary potential models. The results are compared to that for silicon and germanium.

The final paper in the section is by Walter M. Fairbairn of the University of Lancaster, U. K. on "Domain Patterns in Helical Magnets". The author presents an analysis of helical domains in rare earth materials. He discusses the effects of static, time-varying, and non-uniform applied fields in addition to temperature related effects and concludes that helically-ordered domain structures are very stable and not easily altered.

The last section in this volume is on "FILMS & FIBERS" and contains two papers. The first paper is on "Silicon Nitride Films Formed with DC-Magnetron Reactive Sputtering" by Napo Formigoni of Energy Conversion Devices. The author discusses the development of both the hardware and the process to make silicon nitride films using a DC-magnetron sputtering system with a silicon target in a reactive nitrogen/argon gas environment. Detailed information is presented on the design of the equipment and the quality and uniformity of the deposited films. These films are used as the passivation layer on the new thin film Ovonic Threshold Switching devices.

The final paper is "Optical Fibers for Infrared from Vitreous Ge-Sn-Se" by L. Haruvi, J. Dror, D. Mendleovic and N. Croitoru of Tel-Aviv University. The authors discuss the experimental methods and data obtained during the fabrication of chalcogenide fibers for use at a wavelength of 10.6 microns. Several compositions were formed into glass. The glass drawn into fibers showed an attenuation of 6 db/cm, as compared to 10 db/cm for GeSe(4).

The three sections of this volume represent an important collection of new results and analyses in a broad cross-section of solid state science and technology. These papers honor Professor Henisch for his many contributions to science and technology. It is hoped that this Festschrift will contribute to the stimulation of further work toward the understanding of the phenomenology of solids, devices and contacts.

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HEINZ HENISCH FESTSCHRIFT

MOBILITY OF ELECTRONS IN NON-CRYSTALLINE MATERIALS

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INTRODUCTION

On the occasion of Heinz Henisch's retirement I remember him for many things. His early book, published by the Oxford University Press, on rectifying semiconductor contacts, written I think when Heinz was still at Reading University in the U.K.; his creation and editorship of the hugely enjoyable journal, "The History of Photography"; but above all for his experimental work on the Ovonic threshold switch, which I followed with close interest while trying to make a theory of what was happening in this device (Mott 1969, 1971, 1975).

Finally we brought together the work of Heinz and of Dave Adler (of whose sad death I learned recently) and my theoretical speculations in a review article (Adler, Henisch & Mott 1978). We were far from getting a complete answer, particularly about the switching process itself. But we did obtain a consistent, if speculative, model of the on-state of the switch. In the last ten years I have not seen further work on the basic mechanism; I would like, then, to look back on this paper and to see how it stands up to more recent work on the conduction process in non-crystalline materials.

THEORY

In the conducting channel in the layer of chalcogenide glass electrons and holes are injected from the electrodes, forming a plasma. Both the density of electrons and the current density are independent of the total current; it is the cross-sectional area that varies. The thickness of the channel is normally greater than the thickness of the film. Some dynamical process is responsible for the voltage across the contacts which allows injection. The channel is not hot, and its conductivity is not due to temperature. It is also suggested that the density of carriers, in the range 10^{18}-10^{19} cm^{-3}, might be that at which the density of the electron-hole gas is a minimum, though this is perhaps doubtful; the existence of a minimum depends on the electron and hole gases being degenerate, and this is unlikely at the temperature slightly above room temperature in the conducting channel, unless the density of states is rather low; however as we shall see below, this is possible.

I want particularly to discuss the high mobility of the carriers, shown by the experiments described to be about 10 cm^2/V sec. This has always seemed to me the strongest evidence that the carriers are not polarons. Emin, Seeger and Quinn (1972) give evidence for an activated mobility and seek to explain it by postulating the existence of polarons; Mott and Davis (1979) give arguments to show that it can be explained, as is usual in hydrogenated amorphous silicon (a-Si-H), through the presence of a mobility edge. These high mobilities seem hardly consistent with polaron formation. On the other hand the high density of electrons in the channel could ensure that the Fermi energy lies above the mobility edge E_c. In a-Si-H extensive recent research shows that the density of states at the mobility edge is given by

$$N(E_c) \sim 2 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$$

and that N(E) drops linearly towards zero over a range of E of perhaps 0.05 eV, below which the small values characteristic of the exponential tail begin. There are thus $\sim 10^{20}$ cm^{-3} states in the conduction band below the mobility edge. This differs by 10 from the highest estimate of electrons and holes in the switch, but we do not know the density of states near E_c in the chalcogenide glasses; it could well be lower than in a-Si-H.

We do - as we did not in 1978 - know how to calculate the mobility just above E_c. This follows from the scaling theory of Abrahams et al. (1979). If we write the conductivity

$$\sigma = \sigma_o \exp\{-(E_c-E_F)/kT\} ,$$

where E_F is the Fermi energy, then we believe (Mott 1987) that

$$\sigma_o \simeq 0.03 \ e^2/\hbar L_i ,$$

where L_i is the <u>inelastic</u> diffusion length for an electron with energy just above E_c. L_i is given by

$$L_i = (D\tau_i)^{1/2}$$

where τ_i is the time between (inelastic) collisions with phonons and D the diffusion coefficient resulting from elastic scattering by disorder. We find D from the equation

$$\sigma_o = e^2 N(E) \ D ,$$

giving

$$\sigma_o = (0.03)^{2/3} e^2 (N/\hbar^2\tau_i)^{1/3}.$$

The value of μ at the mobility edge is given by

$$\sigma_o = eN(E_c)kT\mu ,$$

so

$$\mu = \{e(0.03)^{2/3}/kT\} \ (1/\hbar\tau_i N(E_c)^2)^{1/3} .$$

In a-Si-H reasonable values of these quantities lead to $\mu \sim 10$ cm^2/V sec, in agreement with experiment; a smaller value of $N(E_c)$ which we have suggested might be the case for a chalcogenide glass would increase τ_i, so the dependence on the density of states will not be great. We have no experimental value of τ_i, but since it appears only to the power $^1/_3$ we should not expect any large difference from the value of μ for a-Si-H, which is what Adler et al. deduce from the experimental work of both Henisch and Adler.

Experimental values of the quantities concerned would, we believe, be of considerable interest in elucidating the conduction process in those materials, particularly in the switch.

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