Advances in Disordered Semiconductors — Vol. 1

**AMORPHOUS SILICON
AND
RELATED MATERIALS**

ADVANCES IN DISORDERED SEMICONDUCTORS

Editor-in-charge: Hellmut Fritzsche

Volume 1 Amorphous Silicon and Related Materials
edited by Hellmut Fritzsche

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AMORPHOUS SILICON AND RELATED MATERIALS

Volume A

Editor

Hellmut Fritzsche

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PREFACE

The problem of keeping abreast with the important advances in exciting and active fields of physics is still with us. Even experts find it increasingly difficult to keep informed as the familiar channels of communication become overloaded. Monographs and review articles are unable to keep pace with new developments as nearly two years pass between writing a review and seeing it published. Conference proceedings usually manage to shorten this delay time to four months, their page limitation, however, does not permit a clear in-depth exposition of current new ideas and unsolved problems. There is of course a wealth of information in journal articles, but access to these outside one's own specialization requires detailed library search and prior knowledge of what one is looking for. Some of us are fortunate enough to receive such information many months prior to publication in the form of preprints but most researchers remain outside this lucky group.

Advances in Disordered Semiconductors attempts to improve this situation in several ways. The people most actively engaged in a particular subject present here their new results and ideas. The fast publication schedule provides a nearly current overview of the field. The same topics are addressed by different authors, this illuminates problems from different angles and highlights unresolved questions. The purpose of this series is to offer a rapid and more effective way for physicists to teach one another.

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INTRODUCTION

This book presents in a series of articles the rapid advances in our understanding of hydrogenated amorphous silicon (α -Si:H). This material has spawned a rapidly developing amorphous semiconductor industry as it is unmatched as a photoreceptor for electrophotographic and laser printing, as the switching material in large area liquid crystal displays, for large photovoltaic panels and any other application that needs a high quality semiconductor that can be processed on large, curved, or flexible substrates.

During the past year or years new ideas and results have given us a much deeper understanding and with it an appreciation of how fascinating this material is and how we might be able to control and improve its properties. This introduction will outline these novel features by pointing to fundamental differences between α -Si:H and crystalline Si.

In contrast to crystalline Si, whose donor and acceptor concentrations are given and fixed once the crystal is prepared, in α -Si:H these concentrations change with temperature and Fermi level position or carrier concentration in one and the same sample. The dopant atoms can exist in 3-fold or 4-fold coordination and they change their coordination in order to lower the free energy of the material. The same holds for silicon atoms. Hence, even though the number of dopant atoms is fixed once the α -Si:H sample is prepared, the number of donors or acceptors (4-fold coordinated dopant atoms) or of defects (3-fold coordinated silicon atoms) can change with temperature and light- and field-induced carrier density. The time scale of equilibration depends on diffusion of bonded hydrogen and can become much longer than experimental times below a certain temperature, giving rise to glass-like metastabilities that depend on the thermal history, prior light exposure, or carrier injection. The hydrogen diffusion in turn depends on the structure, on the electrochemical potential and on the hydrogen concentration. These factors, as well as the dispersive nature of hydrogen diffusion, led to the understanding of the kinetics of these local bonding changes. Since the properties of semiconductors are intimately linked to the concentrations of donors, acceptors, and defects, one appreciates the variety of new phenomena that arise when these quantities are no longer fixed.

There are other interesting differences. In crystalline semiconductors specific defects have definite energies in the gap and this information is an important design parameter. In α -Si:H in contrast, it appears that from all possible defect configurations those are created which yield a lower total energy. Hence the gap states of the silicon dangling bond defects appearing in n-type α -Si:H are likely to have different energies than those appearing in p-type α -Si:H, or in general, the energy of defects may depend on the electrochemical potential at the temperature

when equilibrium can be established. This novel feature complicates the task of specifying a vital semiconductor parameter, the density of gap states as a function of energy, for a given α -Si:H sample.

Moreover, in contrast to crystalline semiconductors, the length scale characteristic of some electronic processes in α -Si:H and its alloys is less than or equal to the size of heterogeneities and microvoids structures that evolve during the preparation of the material to relieve internal strain. As a consequence, a number of transport properties cannot be described in the same fashion as in crystals and new ways still need be formulated. Remarkable results have been obtained regarding the distribution and clustering of bonded hydrogen as well as structural topologies on the 20–100Å scale. It is a challenging task to explore the effect of these heterogeneities on the properties of amorphous Si and its alloys. Partly because of the relatively high internal strain in α -Si:H and partly because of the low deposition rates, only thin films of α -Si:H are available for investigation. This means that surface states, and native oxide layers as well as adsorbates, affect the measured properties. Moreover, presumably on account of the high diffusivity and the active role of hydrogen, the material properties appear to change along the growth direction and possess anisotropy. Important new results on these phenomena are being reported.

The lack of long range order permits an amorphous structure to accommodate atoms of greatly different sizes. This opens the possibility of achieving desired optical and electrical properties by alloying α -Si:H with various elements such as nitrogen, carbon or germanium. This of course enhances the material's complexity and with it the necessity of determining compositional and structural heterogeneities and their effects on the electronic properties.

The structural adaptability permits, moreover, relatively simple and inexpensive deposition of multilayers, the amorphous analogues of crystalline superlattices. Surprisingly sharp and flat interfaces can be achieved that contain relatively few defects between amorphous materials whose covalent bond lengths mismatch by as much as 25 percent. We now have information about the structure and bonding at surfaces and interfaces at a depth resolution of a few Angstroms. The quality of the interfaces allows clear observations of phonon folding and quantum confinement effects. The latter indicate that the coherence length of the electron and hole extended state wavefunctions is at least 50Å, which is larger than anticipated.

New information about the thermodynamic and growth parameters of amorphous silicon and the conditions at the growth surface that either yield crystalline or amorphous material as well as about the diffusion and solubility of impurities in amorphous silicon forms the basis for future calculations of the energies of the defect and dopant reaction and of the processes that yield the compositional and structural heterogeneities.

For the first time one begins to understand that many strange phenomena in α -Si:H originate from the freedom, probably with the help of hydrogen, to change the bonding coordination and to relax the local structure. Most glasses do that. Different and fascinating in α -Si:H is that these changes are influenced by the electron occupation. This leads to the variety of metastable configuration states which can be induced optically or electronically. The fact that the Fermi level can be shifted by doping and other means in α -Si:H but not so easily in other non-crystalline systems may be the reason why these phenomena were first discovered in α -Si:H.

August 1988

Hellmut Fritzsche
Chicago, Illinois

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