



PROCEEDINGS OF THE INTERNATIONAL WORKSHOP ON
**AMORPHOUS
SEMICONDUCTORS**

held in Beijing, China from 13 — 18 October, 1986

Editors

Hellmut Fritzsche

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PREFACE

This International Workshop on Amorphous Semiconductors was the first meeting held at the newly built International Training Center in Beijing, China, between the 13th and the 18th of October, 1986. The workshop was a satellite conference of the International Conference on Semiconductor and Integrated Circuit Technology that took place in Beijing a week later.

150 scientists from five countries attended the workshop. With 26 invited lectures and 25 contributed papers the workshop covered the current areas of research on amorphous semiconductors with a special emphasis on hydrogenated amorphous silicon and on multilayers made with amorphous silicon. These Proceedings have been organized into the following chapters:

Theory and General Aspects

Preparation and Structure

Electron Spin Resonance

Density of States and Electronic Transport

Photoluminescence and Photoconductivity

Metastable Defects

Multilayers and Interfaces

Device Physics

D. X. Han served as the Secretary of the workshop. The Organizing Committee consisted of: G. H. Chen (Lanzhou, China), R. G. Cheng (Shanghai, China), R. C. Fang (Hefei, China), H. Fritzsche (Chicago, USA), D. X. Han (Beijing, China), G. L. Kong (Beijing, China), L. Y. Lin (Beijing, China), K. Y. Liu (Xian, China), S. Q. Peng (Guangzhou, China), C. C. Tsai (Palo Alto, USA), and W. Y. Xu (Tianjin, China).

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Lanzhou University
Institute of Semiconductors (Beijing)
Shandong University (Jinan)
Northwestern University (Xian)
Hunan University (Changsha)
Xian College of Telegraphic Dispatch and Engineering (Xian)

This workshop was made successful by the lively discussions and the valuable contributions of the participants.

Daxing Han
Chuang Chuang Tsai
Hellmut Fritzsche
Chicago, Illinois
December 1986

The Chinese contributors would like to take this opportunity to extend their warmest congratulations to Hellmut Fritzsche on his 60th birthday as well as to thank him for his help in Amorphous Semiconductor research in China.

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Chapter 1

THEORY AND GENERAL ASPECTS

THEORY OF AMORPHOUS SEMICONDUCTORS

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ABSTRACT

A thermodynamic view of the structure of covalent amorphous semiconductors is presented, in which local configurations of higher free energy that are accessible at high temperatures are frozen in below the glass transition temperature. It is shown how this leads to exponential band tails, defect states, and the possibility of doping. Given the resulting density of states, the possible mechanisms of electronic transport are analyzed.

1. INTRODUCTION

It has long been known that there are often two paths from the liquid to the solid state, depending on the rate of cooling. At temperatures above the melting point, T_m , a sufficient concentration of higher energy local configurations are accessible that the structure cannot withstand shear stresses and behaves like a fluid. If the temperature is reduced slowly, a first-order transition occurs at T_m to a state with lower energy and entropy that resists finite shear stresses and thus retains its shape. The structure then ordinarily exhibits a long-range periodicity which reflects the chemical nature of the constituent atoms, and the material is called a crystal. For simple materials, the crystal represents the absolute minimum energy arrangement, and thus is the stable phase at very low temperatures. However, for complex alloys, it often represents a

compromise between the optimal chemical bonding and the strain energy. When such an alloy is cooled rapidly, a different series of processes can then take place. Since first-order phase transitions entail finite entropy changes, they require a finite time to occur. If kT is decreased sufficiently rapidly that the time required for nucleation and growth of the crystal is longer than that to freeze out the array of states necessary to sustain fluid flow, then a disordered phase with the large viscosities characteristic of a solid results. Depending somewhat on the thermal history, a small range of temperatures exist over which the viscosity increases by many orders of magnitude; the point at which it exceeds about 10^{14} poise (corresponding to a structural relaxation time of about a day), is called the glass transition temperature, T_g . Below T_g , the material retains its shape and thus must be characterized as a solid, despite its long-range structural disorder. This phase is called a glass. Glasses are not ordinarily the state of lowest free energy at any temperature and pressure. They form only when the cooling rate is so rapid that the time required to overcome the potential barrier to crystallization is not available while the temperature is between T_m and T_g . Thus, it can be said that although glasses lose thermodynamically, they win kinetically.

2. STRUCTURE OF GLASSES

In the absence of long-range order, determination of the local structure of glasses is difficult and often ambiguous. In general, however, glasses try to optimize the chemical bonding around as many of their constituent atoms as possible. Thus, the vast majority of atoms in a glass have their optimal values. Most of the remaining strains are taken up by bond-angle distortions, often as much as $\pm 10\%$, reflecting the much smaller energy increase resulting from such distortions relative to those from similar bond-length variations. It is the spread in bond angles that directly leads to the lack of long-range periodicity of glasses.

3. THERMODYNAMIC VIEW OF AMORPHOUS SOLIDS

Thermodynamics requires that for any system at a given temperature and pressure, the Gibbs free energy, $G = E - TS + PV$, must be a minimum at equilibrium. At atmospheric pressure, the PV term does not contribute significantly if we restrict ourselves to condensed phases, so it is sufficient to minimize the Helmholtz free energy, $F = E - TS$. Clearly, the lowest-energy state is favored at low temperatures, while the state of highest entropy eventually prevails at sufficiently high temperatures. As a system is cooled, from the high-entropy gas phase, several first-order phase transitions ordinarily occur, at which points both the energy and entropy discontinuously decrease. However, if the cooling rate is sufficiently rapid and the activation barrier between the two phases is sufficiently high, the transition can be kinetically retarded, a phenomenon known as supercooling. Glasses represent a liquid phase cooled sufficiently rapidly that the crystallization kinetics are retarded indefinitely.

Above the glass transition temperature, we anticipate that thermal equilibrium prevails within the supercooled liquid phase. Thus, the concentration of atoms of type X in a particular local configuration i with Helmholtz free energy above that of the optimal configuration for X , $F_0 = E_0 - TS_0$, is given by:

$$N_i = N_X \exp(-\Delta F_i/kT_g) \quad (1)$$

where N_X is the concentration of X and $\Delta F_i = F_i - F_0$. Since structural relaxations are frozen out below T_g , we expect that Eq. (1) remains applicable for all temperatures below T_g .

4. IDEAL COVALENT NETWORKS

In order to apply Eq. (1), it is necessary to define a reference phase, one which all the atoms have their optimal local configurations. This phase is called the ideal covalent network. In order to analyze the structure of such a network, first consider a

single-component covalent material, such as Se, As, or Si. Its column in the Periodic Table immediately suggests an optimal coordination number, Z , while the details of its electronic structure determines the optimal values of the bond length, a , and the bond angle, θ . A subclass of ideal networks, which possess the optimal values of Z , a , and θ for each atom, exhibits long-range periodicity and represents the structure of crystalline solids. When the ideal network exhibits no long-range order, it forms the basis for the structure of amorphous solids.

Phillips¹ called attention to the fact that the actual value of Z has major practical significance. Since each bond connects two atoms, fixing all the bond lengths introduces $Z/2$ constraints per atom. In addition, setting the bond angles adds another $Z(Z-1)/2$ constraints per atom, resulting in a total of $Z^2/2$ such constraints. Since each atom in ordinary three-dimensional space has three degrees of freedom, then only if $Z \leq \sqrt{6} \approx 2.4$ can all the required constraints be fulfilled in a random network. When $Z > 2.4$, the ideal networks are possible, in general, only in curved spaces that represent projections from spaces with higher dimensionality. For amorphous Se ($Z = 2$), there is no problem in forming flat ideal networks, and, in fact, the material often exhibits intermediate-range order. In contrast, for amorphous Si ($Z = 4$), an eight-dimensional space may be necessary to avoid strains. In any event, the local configuration around each atom in the ideal network determines the value of F_0 needed to apply Eq. (1).

For multicomponent alloys, the chemical nature of the different types of atom requires the introduction of a much wider array of parameters, Z_i , a_{ij} , and θ_{ijk} . Nevertheless, for any particular alloy, there are optimal average values for all these parameters, and we can evaluate F_0 , even if the ideal network is inaccessible in flat three-dimensional space.

5. EXCITED STATES

In general, several types of local structural deviations away from the ideal covalent network are possible. These include

continuous variations in bond lengths or bond angles (distorted bonds), and discrete deviations in either coordination number or the nature of the nearest neighbors (defects). In each case, we can, in principle, determine the creation energy, ΔE_i , and free energy, ΔF_i , for the deviant structure, relative to those of the ideal configuration. At any given temperature, T , if thermal equilibrium prevails, the probability of any such structure is proportional to $\exp(-\Delta F_i/kT)$. As recently pointed out by Bar-Yam et al.,² some networks that incorporate these excited states lie flat in three-dimensional space, and these represent the accessible states of the system. Thus, the actual structure above T_g reflects both the ideal configurations and those excited states with relatively low excess free energy compared to kT_g . Below T_g , we expect a freezing in of the structure, the excited configurations being given by Eq. (1).

6. ELECTRONIC STRUCTURE

Derivation of the electronic structure for the case of disordered systems follows the same logic as for periodic crystals.³ First, the many-body Hamiltonian is used to write down the Schrodinger Equation for the ion cores and the outer electrons. As a first approximation, only the electrostatic interactions among these charged particles need be considered. Below T_g , the high viscosity enable us to postulate that the ion cores possess an equilibrium structure, which is frozen in at T_g . If we now adopt the adiabatic approximation, a first-order expansion in the small parameter $(m/M_a)^{1/4}$, where m is the electronic mass and M_a the masses of the constituent ion cores, we can separate the problem into three parts: (1) structure, or the equilibrium positions of the ion cores; (2) phonons, or the normal modes of vibrations of the ion cores around their equilibrium positions; (3) electronic structure, or the states available to the outer electrons as they move in the field of the ion cores at equilibrium. The adiabatic approximation neglects electron-phonon interactions, which allow for specific shifts of the equilibrium structure in response to