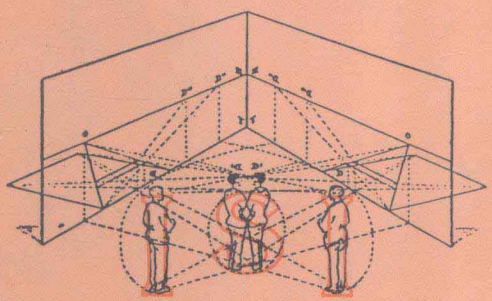
First International Symposium on

PHYSICS AND APPLICATIONS OF AMORPHOUS SEMICONDUCTOR

14-18 September, 1987

Editor

F. DEMICHELIS



INSTITUTE
FOR SCIENTIFIC INTERCHANGE

World Scientific

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PHYSICS AND APPLICATIONS OF AMORPHOUS SEMICONDUCTORS

14-18 September, 1987
Villa Gualino, Torino

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World Scientific
Singapore • New Jersey • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.
P.O. Box 128, Farrer Road, Singapore 9128

U.S.A. office: World Scientific Publishing Co., Inc.
687 Hartwell Street, Teaneck NJ 07666, USA

PHYSICS AND APPLICATIONS OF AMORPHOUS SEMICONDUCTORS

ISBN 9971-50-550-9

Printed in Singapore by Utopia Press.

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on

PHYSICS AND APPLICATIONS OF AMORPHOUS SEMICONDUCTORS

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PREFACE

Since its inception the Institute for Scientific Interchange (I.S.I.) has promoted a well defined programme for the development of Science via Workshops in many branches of Physics. The lectures contained in this volume were delivered by invited and contributed speakers during the Workshop on "Physics and Applications of amorphous semiconductors".

This was the first Workshop organized by the ISI on the subject. It was a truly international event and the level of participation was an indication of the interest in amorphous semiconductors and their applications.

The subject is of great interest in the field of applied physics, in that it offers technological solutions that can be adopted in many applications. Knowledge of the physical properties of these new materials allows to forward their use as optoelectronic devices, solar cells and so on.

The topics have been arranged in logical order. First, the Basic Concepts underlying the physics of amorphous semiconductors have been treated. Some time was spent on Preparation Methods of amorphous semiconductor and devices as well as on the Staebler-Wronski effect influence on the behaviour of amorphous solar cells. Finally, some new materials and their characteristics were examined.

I should like to express my sincere thanks to the sponsors of the Workshop.

First of all to the I.S.I. and, as in duty bound to the President Prof.

T. Regge and to the Director Prof. M. Rasetti, to the Politecnico di Torino, to the Banca Popolare di Milano, to the Cassa di Risparmio di Torino and finally the ENEA represented by Prof. C. Boffa as a member of the Administration Council.

(Prof.sa F. Demichelis)

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1
BASIC CONCEPTS

TOWARDS A SIMPLE DESCRIPTION OF THE ELECTRONIC STRUCTURE OF α-SEMICONDUCTORS

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ABSTRACT

Assuming that an α-semiconductor can be thought of as resulting from an ideal lattice (IL) by a disordering procedure we demonstrate that many important electronic features associated with the band edges (such as the Urbach tails, dc conductivity, etc.) can be obtained in terms of a few gross features of the IL and the variance of the disorder.

I. INTRODUCTION

Amorphous materials in general, and tetrahedral thin films in particular, present great difficulties for their understanding due to the simultaneous influence of several complicating factors. Such factors are : (a) the effects of disorder on the motion of independent electrons; (b) the effects of metastability and partial equilibration, which open up the possibility of new modes involving ionic motion other than phononic; examples of such modes are the so called traveling defects (td); (c) many body effects such as electron-electron interactions (an example of which is the D^- state) electron-phonon interactions (e.g. polaron formation) and electron traveling defect interaction responsible for the so-called S-W mode; and (d) effects due to the synergy of the above.

In this paper we concentrate on one aspect only of the previously mentioned complications, i.e. on the effects of disorder on independent electrons. After two decades of intensive research on this subject a picture has emerged the basic characteristic of which are rather simple and possess a certain degree of universality. The situation is somehow similar to the effective mass approximation in the theory of crystalline materials, where a single parameter, the effective mass (or more precisely the effective mass tensor), determines

the main characteristics near the band edge. In the present case of disordered systems again a few parameters (describing the reference ideal lattice system from which the real system is thought to develop through a disordering procedure and the degree and type of disorder) determine the main characteristics near a pseudoband edge and its tails.

It is also remarkable that, with a little sacrifice in accuracy, one can obtain reasonable quantitative results by using quite elementary theoretical techniques (essentialy the basic quantum mechanics of motion in a constant (or periodic) potential and in the presence of a single local potential well).

II. INPUTS

The motion of an independent electron in a random potential is assumed to be described by a Hamiltonian of the form :

$$H = H_0 + H_1 \; ; \quad \langle H_1 \rangle = 0, \tag{2.1}$$

where H_0 is the Hamiltonian for a reference "unperturbed" system and H_1 incorporates the randomness. Although H_0 may actually be very complicated some features of the disordered system may depend on only two parameters of H_0 : the effective mass m* (which determines the coefficient of the square roof singularity in the DOS, $\varrho_0(E)$, near the band edge) and the real part of the Green's function, G_0, at the band edge E_b^0

$$G_0 = G_0(E_b^0) = \int \frac{\varrho_0(E')dE'}{E_b^0 - E'} \tag{2.2}$$

Of course other aspects of the "unperturbed" part, such as van Hove singularities in the DOS, $\varrho_0(E)$, may influence the behavior of physical quantities.

The most important parameter of the disordered part H_1 is the standard deviation w^2, which as far as certain quantities are concerned, could fully characterize the disorder. Some other important quantities depend not only on w^2 but on the form of the tails of the probability distribution(s) in H_1. Finally there may be quantities which require for their determination the full knowledge of the probability distribution(s) which characterize H_1.

III. MAIN FEATURES OF THE DENSITY OF STATES AND THE EIGENFUNCTIONS

Here we describe briefly how the DOS ϱ of the disordered system results[1-3] from the "unperturbed" DOS, $\varrho_o(E)$. As the disorder sets in, there is first an almost rigid displacement of $\varrho_o(E)$ (near the band edge), widening the band, and moving the unperturbed band edge E_b^o to a new position E_b, by an amount equal to

$$|E_b - E_b^o| = w^2 G_o \qquad (3.1)$$

The approximate result (3.1) is simply the second order perturbation result for the energy levels, as one can easily convince himself by combining (3.1) with (2.2).

The second effect of disorder on the DOS, besides the rigid displacement, is the development of tails extending beyond E_b. One can distinguish three regions in the tail[1-3] : the near tail (NT) or Halperin-Lax[4] region, which lies around E_b; the deep tail (DT) or Urbach[5] region; and the very deep tail (VDT) or deep defect region. The VDT and DT regions correspond to eigenstates bound around a single local potential well (or potential bump for the top of the valence band).

Let us remind the reader the main results concerning the elementary problem of the bound ground state in a three dimensional local (i.e. short range) potential well. We denote by ε the depth of the potential well and by a its linear extent; E is the ground bound state energy and λ is its decay length.

For very deep potential wells ($|\varepsilon| >> \varepsilon_o = \hbar^2/2ma^2$), the bound ground state is essentially inside the well ($\lambda \lesssim 0.1$ a) and $|E|$ is proportional to $|\varepsilon|$, i.e.

$$|E| = |\varepsilon| - \varepsilon_o \qquad (3.2)$$

There is an intermediate regime, where the wavefunction is, roughly speaking, half in half out of the potential well ($0.4 \lesssim \lambda/a \lesssim 1.4$); in this regime the ground bound state energy is approximately proportional to the square of the potential well depth

$$|E| = A\varepsilon^2 - B \quad ; \quad E_1 \lesssim |E| \lesssim E_2 \qquad (3.3)$$

In Table 1 we give the values of A, E_1 and E_2 for various cases[1,2].

TABLE 1 : Values of the constant A and range of validity of Eq.(2.3) for various cases. TB denotes tight binding model with 12 V being the bandwidth.

Case	m^* Description	A	E_1	E_2	Energy
Step Potential Well of 3-d Volume a^3	Yes	0.023	0.5	6	$\hbar^2/2m^*a^2$
Gausssian Potential Well of 3-d Volume a^3	Yes	0.010	0.3	6	$\hbar^2/2m^*a^2$
TB, Semicircular DOS	No	0.064	0.2	3	V
TB, Simple Cubic	No	0.065	0.2	3	V
α-Si:H, Valence Band	No	0.007	0.1	0.3	eV
α-Si:H, Conduction Band	No	0.003	0.1	0.3	eV

Finally, let us mention that there is a critical value of ε, ε_c, such that for $|\varepsilon| < |\varepsilon_c|$ there is no bound state in a 3-d potential well. For $|\varepsilon|$ just above the critical value ε_c, λ tends to blow up ($\lambda \sim |\varepsilon - \varepsilon_c|^{-1/2}$, which means that the bound eigenfunction is essentially outside the potential well) and

$$E \sim |\varepsilon - \varepsilon_c|^2 \; ; \; \varepsilon \to \varepsilon_c \qquad (3.4)$$

Let us now return to the three regions of the tail in the DOS.

The VDT region corresponds to states bounds inside deep fluctuations, where Eq.(3.2) is approximately valid. Due to its linearity (between $|E|$ and $|\varepsilon|$) the distribution of $|E|$ follows the distribution of $|\varepsilon|$, which means that the DOS in the VDT region is the same as the probability distribution of ε, $p(\varepsilon)$

$$\varrho(E) = p(|E| + \varepsilon_o) \; ; \quad \text{VDT or defect region} \qquad (3.2')$$

The DT or Urbach region corresponds to the intermediate regime of bound states in isolated local potential wells for which Eq.(3.3) is valid. Hence the DOS in the Urbach regime is given by

$$\rho(E) \simeq \frac{1}{2} \frac{1}{\sqrt{A(|E| + B)}} \; p\left(\sqrt{\frac{|E| + B}{A}}\right) \; ; \text{ DT or Urbach region} \qquad (3.3')$$

Note that a Gaussian distribution of ε (which is expected to be very common in this intermediate regime), $p(\varepsilon) \sim \exp(-\varepsilon^2/2w^2)$, will give for the DOS

$$\rho(E) \sim \exp(-|E|/2w^2A) \; ; \text{ DT or Urbach region} \qquad (3.3'')$$

Eq.(3.3'') provides a simple explanation for many features observed in the optical absorption of ionic crystals (where the disorder is of thermal nature) and amorphous semiconductors.

One may be tempted to say that the NT or Halperin-Lax region corresponds to loosely band states for which Eq.(3.4) holds. Indeed, Eq.(3.4) combined with a Gaussian probability distribution $p(\varepsilon)$ would give a DOS $\rho(E) \sim \exp(-\sqrt{|E|/C})$ in qualitative agreement with more sophisticated treatments[2,4,6]. In spite of this positive result, the actual situation is considerably more complicated, because the localization length in this regime is larger than the average distance between potential wells. As a result the eigenstates in the Halperin-Lax regime are not localized around a single potential well but around an appropriate cluster of potential wells. One can show[2,6] that this cluster can be replaced approximately by an effective potential well, whose depth has always a Gaussian distribution. It is for this reason that the DOS in this regime is always of the form $\exp(-\sqrt{|E|/C})$.

It is worthwhile to note that the NT or Halperin-Lax region is usually very narrow, and as we approach E_b, the localization (or decay) length becomes very large and finally blows up at the mobility edge E_c[+], which is just inside E_b (the difference $|E_b - E_c|$ is usually less than 10 meV). On the other side of E_c we have extended eigenstates with strongly fluctuating amplitude; however, the linear extent of these fluctuations does not exceed a characteristic length ξ. The length ξ blows up at E_c, but, as we move inside

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[+]The mobility edge is determined by the equation $k(E_c)\, l(E_c) = 0.84$, where k is the wavenumber corresponding to H_0 and l is the mean free path.

the band, rapidly diminishes and, within a region of width comparable to the Halperin-Lax one, drops to interatomic scale. Beyond this we have regular extended states having an essentially uniform amplitude and characterized by l, the phase coherence length (or mean free path).

It is worthwhile to note that the results described above have been obtained by several theoretical techniques ranging from the most elementary (that presented here) to quite sophisticated ones[2,4,6] and including the powerful Coherent Potential Approximation (CPA). Recently, they have been verified by detailed numerical calculations[7].

Before we conclude this section let us make two remarks :

The first concerns the width of the Urbach regime or in other words the range of validity of the exponential behavior in the DOS. Our analysis shows that the narrower the gap, and/or the more disorder, and/or the larger the range of the potential fluctuations, the more limited the range of the exponential behavior is. Thus, in α-Si we expect the exponential behavior to extend over about two orders of magnitude in the DOS and deviations even in this regime to be observable. In α-Ge we expect an even narrower range and more visible deviations. On the contrary for glasses such as As_2Se_3, where the effective[2,3] gap is about 5 eV, the range, according to Table 1, is expected to be a little less than 1 eV for the case of As_2Se_3, in excellent agreement with the experimental results[8].

The second and last remark is referred to the relation of the present approach with the method of equilibrated ensemble. Both start with the general expression for the DOS $\rho(E) = \int \rho'(E; [H])\, p([H])\, d[H]$, where ρ' is the DOS for a particular configuration described by [H] and p([H]) is the probability distribution for the various configurations. Of course p([H]) can always be written as exp(-f([H])), where f is the free energy divided by kT. For a bound state there is a functional relation between the eigenergy E′ and the particular configuration [H] which in principle can be inverted to give a relation of the form [H] = g(E′). Combining the above we obtain

$$\rho(E) = \int \rho'(E;E')\, \exp(-f(g(E')))\, dE' = \exp(-f(g(E))), \qquad (3.5)$$

since $\rho'(E,E')$ is equal to $\delta(E-E')$.

The equilibrated ensemble method assumes that it is usually possible to expand