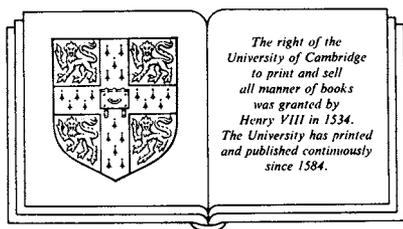


R. A. STREET

*Xerox Corporation, Palo Alto Research Center*

# Hydrogenated amorphous silicon



CAMBRIDGE UNIVERSITY PRESS

*Cambridge*

*New York Port Chester Melbourne Sydney*

Published by the Press Syndicate of the University of Cambridge  
The Pitt Building, Trumpington Street, Cambridge CB2 1RP  
40 West 20th Street, New York, NY 10011, USA  
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1991

First published 1991

*British Library cataloguing in publication data*

Street, Robert A.

Hydrogenated amorphous silicon.

1. Amorphous silicon semiconductors

I. Title

537.6223

*Library of Congress cataloguing in publication data*

Street, R. A.

Hydrogenated amorphous silicon/R. A. Street.

(Cambridge solid state science series)

Includes bibliographical references and index.

ISBN 0 521 37156 2 (hardcover)

1. Silicon. 2. Amorphous semiconductors. 3. Surface chemistry.

I. Title. II. Series.

QC611.8.S5S76 1991

621.381'52 - dc20 90-2387 CIP

ISBN 0 521 37156 2 hardback

Transferred to digital printing 2002

# Contents

	<b>Preface</b>	xiii
<b>1</b>	<b>Introduction</b>	1
1.1	Early research	1
1.2	Basic concepts of amorphous semiconductors	3
	1.2.1 Atomic structure	4
	1.2.2 Chemical bonding, the $8 - N$ rule and defect reactions	7
	1.2.3 Electronic structure	9
	1.2.4 Electronic properties	11
	1.2.5 Localization, the mobility edge and conduction	13
<b>2</b>	<b>Growth and structure of amorphous silicon</b>	18
2.1	Growth of a-Si:H	18
	2.1.1 The morphology of film growth	20
	2.1.2 Growth mechanisms	29
2.2	The silicon bonding structure	34
	2.2.1 Silicon-silicon atomic bonding	35
	2.2.2 Intermediate range order, network voids and stress	36
	2.2.3 Network vibrations	40
2.3	The hydrogen bonding structure	44
	2.3.1 Silicon-hydrogen bonds	44
	2.3.2 The hydrogen local order	48
	2.3.3 Hydrogen diffusion, evolution and rehydrogenation	51
	2.3.4 The role of hydrogen in the growth of a-Si:H	58
	2.3.5 Hydrogen in amorphous and crystalline silicon	60
<b>3</b>	<b>The electronic density of states</b>	62
3.1	The conduction and valence bands	63
	3.1.1 Measurements of the conduction and valence band density of states	66

3.2	The band tails	70
	3.2.1 Dispersive trapping in a band tail	72
	3.2.2 The band tail density of states distribution	81
3.3	Optical band-to-band transitions	83
	3.3.1 The Urbach edge	88
	3.3.2 Thermal and static disorder	91
<b>4</b>	<b>Defects and their electronic states</b>	<b>95</b>
4.1	Defects in amorphous semiconductors	95
	4.1.1 Lattice relaxation at defects	97
	4.1.2 Correlation energies	99
	4.1.3 Valence alternation pairs – the example of selenium	102
4.2	Experimental measurements of defects	104
	4.2.1 Electron spin resonance (ESR)	104
	4.2.2 ESR hyperfine interactions	109
	4.2.3 Defect level spectroscopy – thermal emission energies	114
	4.2.4 Defect level spectroscopy – optical transition energies	123
	4.2.5 Summary	129
4.3	Defect Models	130
<b>5</b>	<b>Substitutional doping</b>	<b>135</b>
5.1	Growth and structure of doped a-Si:H	138
5.2	The electronic effects of doping	142
	5.2.1 Defects induced by doping	145
	5.2.2 Shallow electronic states	147
	5.2.3 The doping efficiency	155
	5.2.4 Compensated a-Si:H	158
5.3	The doping mechanism	160
	5.3.1 Discussion of the doping model	165
<b>6</b>	<b>Defect reactions, thermal equilibrium and metastability</b>	<b>169</b>
6.1	Evidence of structural equilibration	171
6.2	Thermal equilibrium models	179
	6.2.1 Theory of chemical equilibrium	179
	6.2.2 Defect and dopant equilibrium with discrete formation energies	181
	6.2.3 Distributions of formation energies – the weak bond model	185
	6.2.4 The role of the band tails and deposition conditions	190

6.2.5	Doping dependence of gap state energies	194
6.2.6	Compensated a-Si:H	195
6.2.7	Defect and dopant pairing	196
6.2.8	The dopant distribution coefficient and equilibrium growth	199
6.3	Kinetics of structural relaxation and equilibrium	202
6.3.1	Stretched exponential relaxation	203
6.3.2	The hydrogen glass model	209
6.4	Metastability	211
6.4.1	Light-induced defects	213
6.4.2	Other metastable phenomena	220
<b>7</b>	<b>Electronic transport</b>	<b>224</b>
7.1	Measurements of dc conductivity	227
7.1.1	Doped a-Si:H above the equilibration temperature	230
7.1.2	Doped a-Si:H below the equilibration temperature	232
7.1.3	Undoped a-Si:H	234
7.2	Carrier mobility	237
7.3	Thermopower and Hall effect	242
7.3.1	The Hall effect	245
7.4	Theories of electronic conduction	247
7.4.1	Early models of extended state conduction	249
7.4.2	Scaling theory	254
7.4.3	Inelastic scattering and phonon effects	258
7.4.4	Hopping conductivity	262
7.4.5	Potential fluctuations and percolation	266
7.4.6	Conduction mechanisms in a-Si:H	271
<b>8</b>	<b>The recombination of excess carriers</b>	<b>276</b>
8.1	Thermalization and recombination mechanisms	277
8.1.1	Radiative recombination	278
8.1.2	Electron-phonon interactions	279
8.1.3	Thermalization and non-radiative transitions	281
8.1.4	Geminate electron-hole pairs	284
8.2	Carrier thermalization	288
8.2.1	Thermalization in extended states	288
8.2.2	Thermalization in localized states	291
8.3	Band tail recombination	292
8.3.1	Photoluminescence	293
8.3.2	Luminescence spectra	294
8.3.3	Recombination kinetics	297

- 8.3.4 Geminate and non-geminate recombination 300
- 8.3.5 Thermal quenching of luminescence 302
- 8.3.6 Auger and surface recombination 305
- 8.4 Recombination at defects 307
  - 8.4.1 Low temperature non-radiative tunneling 308
  - 8.4.2 High temperature trapping at defects 311
  - 8.4.3 Radiative recombination at defects 314
- 8.5 Photoconductivity 315
  
- 9 Contacts, interfaces and multilayers 321**
- 9.1 Metallic contacts 321
  - 9.1.1 Models of the Schottky barrier 321
  - 9.1.2 Electrical transport across the barrier 325
  - 9.1.3 Measurement of depletion layers 328
  - 9.1.4 Material dependence of the Schottky barrier 330
- 9.2 Surfaces 334
  - 9.2.1 Oxidation and surface states 334
  - 9.2.2 Gases adsorbed on the surface 338
- 9.3 Interfaces with dielectrics and semiconductors 340
  - 9.3.1 Band offsets 342
  - 9.3.2 Electronic properties 344
- 9.4 Multilayers 348
  - 9.4.1 Recombination in compositional multilayers 348
  - 9.4.2 Quantum confinement of electronic states 350
  - 9.4.3 Quantum confinement of phonons 356
  - 9.4.4 Doping multilayers 359
  
- 10 Amorphous silicon device technology 363**
- 10.1 Light sensors 363
  - 10.1.1 p-i-n sensors 364
  - 10.1.2 Response to illumination 366
  - 10.1.3 Electrical characteristics 369
- 10.2 Thin film transistors (TFTs) 372
  - 10.2.1 TFT electrical characteristics 374
  - 10.2.2 Other TFT structures 378
- 10.3 Other devices 378
  - 10.3.1 Light emitting diodes (LEDs) 378
  - 10.3.2 Memory switching devices 380
- 10.4 Applications of amorphous silicon devices 383
  - 10.4.1 Solar cells 383
  - 10.4.2 Active matrix arrays 391
  - 10.4.3 Photoreceptors 396

<i>Contents</i>	xi
10.4.4 Vidicon	399
10.4.5 High energy radiation imaging	399
10.4.6 Position sensors	403
<b>References</b>	404
<b>Index</b>	413

# 1 Introduction

## 1.1 Early research

Hydrogenated amorphous silicon (a-Si:H) was a late arrival to the research on amorphous semiconductors, which began to flourish during the 1950s and 1960s; studies of insulating oxide glasses, of course, go back much further. Interest in the amorphous semiconductors developed around the chalcogenides, which are materials containing the elements sulfur, selenium and tellurium; examples are  $\text{As}_2\text{Se}_3$ ,  $\text{GeS}_2$  etc. The chalcogenides are glasses which may be formed by cooling from the melt, with structure similar to the oxides but with smaller energy band gaps. Research in these amorphous semiconductors addressed the question of how the disorder of the non-crystalline structure influences the electronic properties. The study of chalcogenides was further promoted by the introduction of xerographic copying machines. Xerography was invented in 1938 and the first successful copier was made in 1956, using selenium as the photoconductive material.

A-Si:H was first made in the late 1960s. Before that time there was research on amorphous silicon without hydrogen, which was prepared by sputtering or by thermal evaporation. The unhydrogenated material has a very high defect density which prevents doping, photoconductivity and the other desirable characteristics of a useful semiconductor. Electronic measurements were mostly limited to the investigation of conduction through the defect states.

Chittick and coworkers in the UK were the first to make a-Si:H, using glow discharge as the deposition technique (Chittick, Alexander and Sterling 1969). Silane gas ( $\text{SiH}_4$ ) is excited by an electrical plasma which causes the gas molecules to dissociate and deposit on heated substrates. The technique is essentially the same as is used currently, although the design of the deposition systems has evolved. The first reactor was inductive: the plasma is excited by a coil outside the quartz chamber. Most reactors now are capacitive, consisting of two parallel electrodes within a stainless steel chamber, but the deposition mechanism is not substantially different.

These early experiments demonstrated the deposition of silicon films, the lack of conduction in defect states (implying a low defect density) and increased conduction due to impurities (Chittick *et al.* 1969,

Chittick and Sterling 1985). The infra-red (IR) vibrations of silicon–hydrogen bonds were observed, although they were not recognized as such, and also some metastable phenomena which are now being widely studied. However, the significance of this early work was evidently missed by the sponsors of the research and the project was terminated.

The significance of the results was not lost on Spear at the University of Dundee, who saw the promise of this new method of making amorphous silicon and arranged to take Chittick's reactor to Dundee. In the following years this group documented in considerable detail the superior properties of the amorphous silicon made by this deposition technique (Spear 1974). The research showed that the material had good electrical transport properties with a fairly high carrier mobility (LeComber and Spear 1970) and also strong photoconductivity resulting from a very low defect density (Spear, Loveland and Al-Sharbaty 1974). A major turning point in the development of a-Si:H was the report in 1975 of substitutional n-type or p-type doping by the addition of phosphine or diborane to the deposition gas (Spear and LeComber 1975). The significance of all these observations was widely acknowledged and the subsequent years saw a period of rapidly increasing interest in this form of amorphous silicon.

The essential role of the hydrogen in a-Si:H was first recognized by Paul's group at Harvard, who had studied sputtered amorphous silicon and germanium since the late 1960s (Lewis *et al.* 1974). They understood that the high defect density of amorphous silicon and amorphous germanium prevented these materials from being useful for electronic devices and tried to find ways of eliminating the defects, eventually succeeding by introducing hydrogen into the sputtering system. The hydrogen caused a similar improvement in the material properties as was found for glow discharge a-Si:H, with a high photoconductivity, low defect density and doping. The Harvard group demonstrated that the hydrogen concentration in the films was about 10 atomic %, by observing its characteristic IR vibration, which has a frequency close to  $2000\text{ cm}^{-1}$  for Si–H bonds and  $1800\text{ cm}^{-1}$  for Ge–H bonds. These were actually the same absorption lines seen earlier by Chittick, but not identified as hydrogen vibrations. Shortly after the Harvard experiments, it was confirmed that the glow discharge material also contained hydrogen (Fritzsche 1977). This is now recognized as an essential component of the films which is responsible for suppressing defects. Research on both glow discharge and sputtered a-Si:H continued, but the glow discharge technique has become increasingly dominant because it seems to give slightly better material.

A-Si:H device research was started by Carlson and Wronski (1976)

at RCA Laboratories with the development of photovoltaic devices. They demonstrated the feasibility of a-Si:H solar cells and initially obtained conversion efficiencies of 2–3%. Subsequent research by RCA and by many other groups, increased the cell efficiency by roughly 1 percentage point each year to 12–14% in 1989. Although RCA began the development of solar cells, Sanyo in Japan was the first company to market devices. RCA was primarily interested in large scale electric power production, a topic which was popular in the oil crises of the late 1970s. Economically viable solar cells for power production need to have high conversion efficiency (although the actual value was debated for several years). Sanyo, however, recognized that even quite low efficiency cells could power hand-held calculators. In fact the efficiency of a-Si:H solar cells is larger under fluorescent light compared to sunlight, so that the calculators work well in an office environment. Sanyo began producing cells in 1979, and Japanese companies have dominated this market for a-Si:H ever since. Solar cells for large scale power production are still not in significant use, although the intermediate scale power markets are developing.

Research on large area electronic arrays of a-Si:H devices started a few years later after the first field effect transistors were reported (Snell *et al.* 1981). These devices take advantage of the capability to deposit and process a-Si:H over large areas. Applications include liquid crystal displays, optical scanners and radiation imagers. Present devices contain up to  $10^6$  individual elements and are presently used in hand-held televisions and FAX machines.

## 1.2 **Basic concepts of amorphous semiconductors**

The disorder of the atomic structure is the main feature which distinguishes amorphous from crystalline materials. It is of particular significance in semiconductors, because the periodicity of the atomic structure is central to the theory of crystalline semiconductors. Bloch's theorem is a direct consequence of the periodicity and describes the electrons and holes by wavefunctions which are extended in space with quantum states defined by the momentum. The theory of lattice vibrations has a similar basis in the lattice symmetry. The absence of an ordered atomic structure in amorphous semiconductors necessitates a different theoretical approach. The description of these materials is developed instead from the chemical bonding between the atoms, with emphasis on the short range bonding interactions rather than the long range order.

The structural disorder influences the electronic properties in several different ways which are summarized in Fig. 1.1. The similarity of the

covalent silicon bonds in crystalline and amorphous silicon leads to a similar overall electronic structure – amorphous and crystalline phases of the same material tend to have comparable band gaps. The disorder represented by deviations in the bond lengths and bond angles broadens the electron distribution of states and causes electron and hole localization as well as strong scattering of the carriers. Structural defects such as broken bonds have corresponding electronic states which lie in the band gap. There are also new phenomena which follow from the emphasis on the local chemical bonds rather than the long range translational symmetry. The possibility of alternative bonding configurations of each atom leads to a strong interaction between the electronic and structural states and causes the phenomenon of metastability.

The following brief survey of the properties of amorphous semiconductors is intended to provide an introduction to the subsequent more detailed discussion.

1.2.1 *Atomic structure*

Amorphous semiconductors are not completely disordered. The covalent bonds between the silicon atoms are much the same as in crystalline silicon, with the same number of neighbors and the same average bond lengths and bond angles. The disorder is represented by the atom pair distribution function, which is the probability of finding an atom at distance  $R$  from another atom. Schematic pair distribution functions for crystalline, amorphous (or liquid) and gaseous phases are illustrated in Fig. 1.2. The relative positions of atoms in a dilute gas are random (except at very close spacings), whereas a perfect crystal is completely ordered to large pair distances. The amorphous material has the same short range order as the crystal but lacks the long range order. The first few nearest neighbor distances are separately distinguished, but the correlation between atom pairs loses structure after a few interatomic spacings. The material properties of amorphous semi-

Fig. 1.1. The correspondence between features of the atomic structure and the resulting electronic properties.

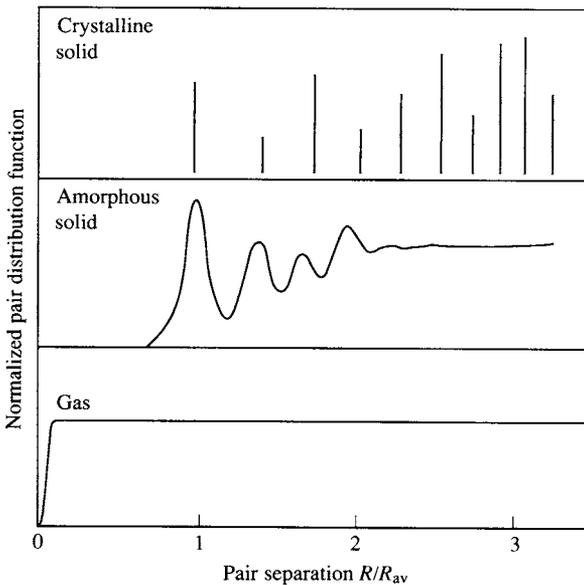
<u>STRUCTURE</u>	→	<u>ELECTRONIC PROPERTIES</u>
Bonding disorder	→	Band tails, localization, scattering
Structural defects	→	Electronic states in the band gap
Alternative bonding configurations	→	Electronically induced metastable states

conductors are similar to their crystalline counterparts because they share the same local order. In contrast, there is often little connection between the properties of gaseous and condensed phases.

The short range order and long range disorder lead to the model of the continuous random network, introduced by Zachariasen (1932) to describe glasses such as silica. The periodic crystalline structure is replaced by a random network in which each atom has a specific number of bonds to its immediate neighbors (the coordination). Fig. 1.3. is a two-dimensional illustration of such a network, containing atoms of different coordination (4, 3 and 1). The random network has the property of easily incorporating atoms of different coordination, even in small concentration. This is in marked contrast to the crystalline lattice in which impurities are generally constrained to have the coordination of the host because of the long range ordering of the lattice. This difference is most distinctly reflected in the doping and defect properties of a-Si:H, discussed in Chapter 4 and 5.

A real crystal contains defects such as vacancies, interstitials and dislocations. The continuous random network may also contain defects, but the definition of a defect has to be modified. Any atom

Fig. 1.2. Schematic diagram of the atom pair distribution functions for a crystalline and amorphous solid and a gas, scaled to the average separation of nearest neighbor atoms,  $R_{av}$ , showing the different degree of structural order.



which is out of place in a crystal is a defect – the simplest such defects are vacancies and interstitials. The only specific structural feature of a random network is the coordination of an atom to its neighbor. Thus the elementary defect of an amorphous semiconductor is the coordination defect, when an atom has too many or too few bonds. The ability of the disordered network to adapt to any atomic coordination

Fig. 1.3. An example of a continuous random network containing atoms of different bonding coordination, as indicated.

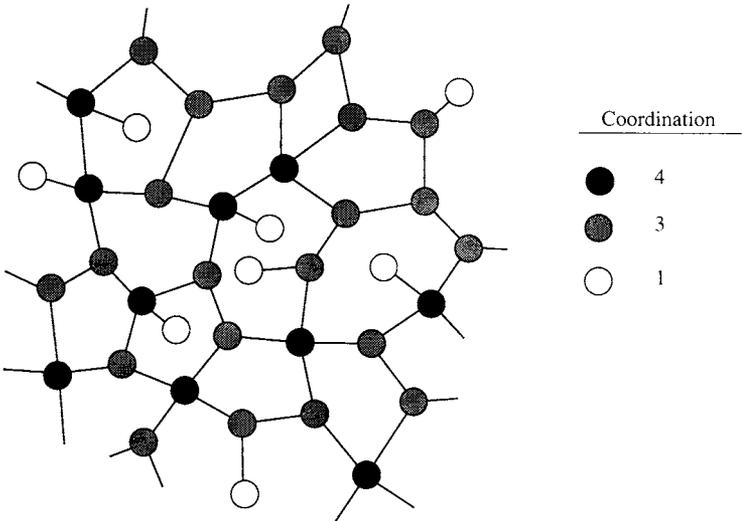
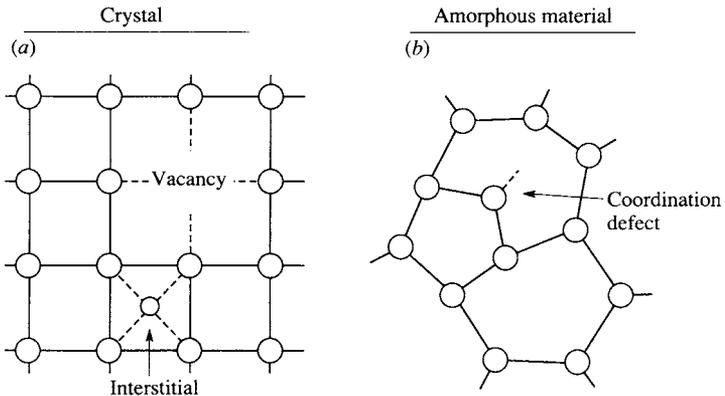


Fig. 1.4. An illustration contrasting the different types of simple defects in (a) crystalline and (b) amorphous networks.



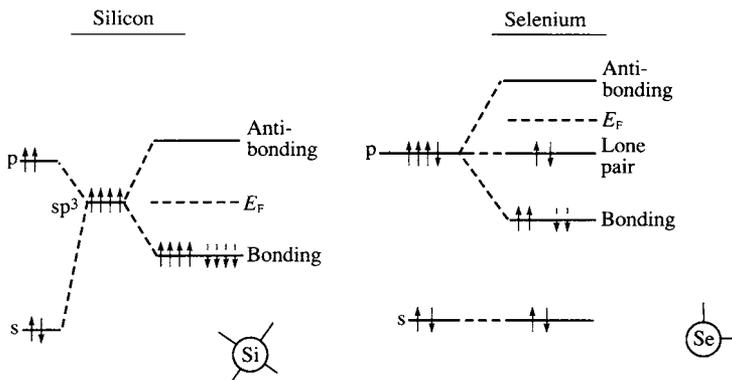
allows an isolated coordination defect, which is not possible in a crystal. The contrasting defects are illustrated in Fig. 1.4, and are discussed further in Chapter 4.

The intrinsic disorder of the continuous network is less easily classified in terms of defects. The network has many different configurations, but provided the atomic coordination is the same, all these structures are equivalent and represent the natural variability of the material. Since there is no correct position of an atom, one cannot say whether a specific structure is a defect or not. Instead the long range disorder is intrinsic to the amorphous material and is described by a randomly varying disorder potential, whose effect on the electronic structure is summarized in Section 1.2.5.

### 1.2.2 Chemical bonding, the 8-N rule and defect reactions

The continuous random network model places emphasis on the local chemical bonding of the atoms. A-Si:H and most other amorphous semiconductors are covalently bonded, with well-defined bonding geometries and coordination. A molecular orbital model for silicon and selenium is illustrated in Fig. 1.5 and this type of diagram is used elsewhere in this book. The electrons of an isolated silicon atom occupy two 3s and two 3p states, in addition to the deeper core states which are not involved in the bonding. When the atoms combine to form a solid, the electron interaction splits the valence states into bonding and anti-bonding levels, as illustrated in Fig. 1.5. Chemical bonding occurs because the bonding state has a lower energy than the

Fig. 1.5. Illustration of the bonding configuration of (a) silicon and (b) selenium atoms constructed from hybridized molecular orbitals. The position of the Fermi energy,  $E_F$ , is indicated.



isolated atomic levels and the material has the lowest total energy when the maximum number of electrons occupy bonding states. Their number is constrained by the Pauli exclusion principle which prevents more than two electrons occupying one state. To optimize the number of bonding states, the atomic wavefunctions combine to form hybrid molecular orbitals, described by,

$$\Phi_{\text{hyb}} = a\Phi(3s) + b\Phi(3p) \quad (1.1)$$

where  $a$  and  $b$  are constants. The four silicon valence electrons combine to give four  $sp^3$  orbitals. Each orbital comprises  $\frac{1}{4}$  of an  $s$  state and  $\frac{3}{4}$  of one of the three equivalent  $p$  states. These four orbitals form bonds to adjacent atoms and since silicon has four valence electrons, all the bonds are occupied by two electrons, one from each atom forming the bond. The hybridization minimizes the total energy by arranging as many electrons as possible in bonding orbitals.

It is not always possible to arrange all the valence electrons in bonding orbitals, because four is the maximum number of orbitals which can be made from  $s$  and  $p$  states. In selenium, which contains six valence electrons,  $sp^3$  hybridization is no longer the lowest energy configuration because this constrains some electrons to occupy the high energy anti-bonding states. Instead there is no hybridization and the  $s$  state and one of the  $p$  states are filled with electron pairs, forming non-bonding states known as lone pairs. The remaining two singly occupied  $p$  states form covalent bonds, splitting into bonding and anti-bonding orbitals, which are then fully occupied by the remaining electrons (Fig. 1.5). The atomic coordination is 2, and the top of the valence band is formed from the lone pair  $p$  state electrons, with the bonding  $p$  states deeper in the valence band.

Similar diagrams can be constructed for other elements. For example, group V elements bond in  $p^3$  configurations, with  $s$  electrons forming the non-bonding pairs. It follows that the optimum number,  $Z$ , of covalent bonds for elements is,

$$Z = 8 - N \quad (\text{for } N \geq 4 \text{ and } Z = N \text{ for } N < 4) \quad (1.2)$$

where  $N$  is the number of valence electrons. This prediction of the atom coordination is known as the '8 -  $N$ ' rule (Mott 1969). The essential point is that chemical bonds are formed such that the maximum number of electrons are paired in bonding orbitals, the remaining electrons are paired in non-bonding states and the anti-bonding states are empty. The continuous random network allows atoms to take their preferred coordination. Thus the network in Fig. 1.3 might be composed of silicon, phosphorus and hydrogen.

The different roles of local chemistry in the amorphous and crystalline networks are highlighted by considering the bonding of an impurity atom. Since every atomic site in a crystal is defined by the lattice, the impurity either substitutes for the host, adapting itself to the chemistry of the host or occupies a position which is not a lattice site, forming a defect. A substitutional impurity such as phosphorus is four-fold coordinated and acts as a donor because one of its electrons is not involved in bonding and is released into the conduction band. An amorphous material has no rigidly defined array of lattice sites, so that an impurity can adapt the local environment to optimize its own bonding configuration, while also remaining a part of the host atomic network. The  $8 - N$  rule suggests that phosphorus in amorphous silicon is three-fold coordinated and therefore inactive as an electronic dopant. Indeed it seems to follow from the  $8 - N$  rule that substitutional doping must be impossible in an amorphous semiconductor. Actually, the chemical bonding does not forbid, but does severely constrain, the doping in a-Si:H, as is explained in Chapter 5.

The  $8 - N$  rule also suggests the importance of electronically induced structural reactions. The excitation of an electron from one state to another changes the occupancy of bonding and anti-bonding states. The  $8 - N$  rule predicts that such an electronic excitation destabilizes the atomic bond and induces a change in coordination. Such reactions are usually prevented in crystalline semiconductors by the long range order of the lattice and the extended electron wavefunction. They are promoted in amorphous materials by the adaptability of the continuous random network and by the localization of electronic carriers. Electronically induced structural changes are an important and fascinating feature of all amorphous semiconductors (see Chapter 6).

### 1.2.3 *Electronic structure*

One of the fundamental properties of a semiconductor or insulator is the presence of a band gap separating the occupied valence band from the empty conduction band states. According to the free electron theory, the band gap is a consequence of the periodicity of the crystalline lattice. In the past, there was considerable debate over the reason that amorphous semiconductors had a band gap at all, let alone one that is similar to that in the corresponding crystal. Subsequent work explained that the band gap is equivalently described by the splitting of the bonding (or lone pair) and anti-bonding states of the covalent bond (Fig. 1.5). The bands are most strongly influenced by the short range order, which is the same in amorphous and crystalline silicon and the absence of periodicity is a small perturbation.

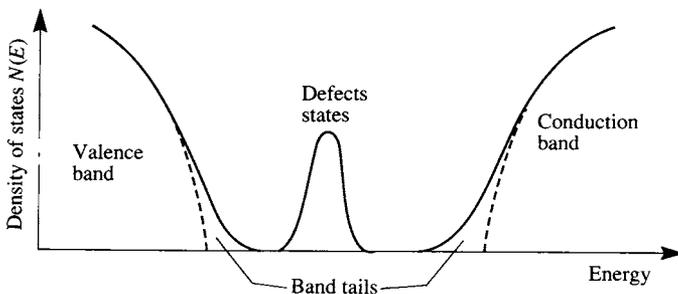
These results were most clearly stated by Weaire and Thorpe (Weaire 1971, Thorpe and Weaire 1971), who described the bonding by a tight binding Hamiltonian of the form

$$H = V_1 \sum_{j \neq j'} |\Phi_{ij}\rangle \langle \Phi_{ij'}| + V_2 \sum_{i \neq i'} |\Phi_{ij}\rangle \langle \Phi_{i'j}|. \quad (1.3)$$

The wavefunctions,  $\Phi$ , are the  $sp^3$  hybrid orbitals of the tetrahedral silicon bonding. The first term in Eq. (1.3) is a sum over interactions for which the two wavefunctions  $\Phi_{ij}$  belong to the same atom and the second term sums pairs of orbitals that belong to the same bond. This Hamiltonian describes the short range bonding information, but contains no information about the long range order, and so applies equally to amorphous and crystalline silicon. Weaire and Thorpe showed that there are ranges of the interaction strength  $V_1/V_2$  for which the conduction and valence bands are separated by a band gap, irrespective of the long range structure.

The three principal features of the structure of amorphous semiconductors are the short range order of the ideal network, the long range disorder and the coordination defects. The preservation of the short range order results in a similar overall electronic structure of an amorphous material compared to the equivalent crystal. Thus, silicon dioxide is an insulator in both its crystalline and amorphous forms and silicon is a semiconductor. The abrupt band edges of a crystal are replaced by a broadened tail of states extending into the forbidden gap, which originates from the deviations of the bond length and angle arising from the long range structural disorder. The band tails are most important despite their relatively small concentration, because electronic transport occurs at the band edge. Electronic states deep within

Fig. 1.6. Schematic density of states distribution for an amorphous semiconductor showing the bands, the band tails, and the defect states in the band gap. The dashed curves are the equivalent density of states in a crystal.



the band gap arise from departures from the ideal network, such as coordination defects. These defects determine many electronic properties by controlling trapping and recombination. The electronic structure of an amorphous semiconductor (see Fig. 1.6) comprises the bands, the band tails and the defect states in the gap and the correspondence between the structure and the electronic properties is summarized in Fig. 1.1.

#### 1.2.4 Electronic properties

The wavefunctions of the electronic states are the solutions to Schrödinger's equation,

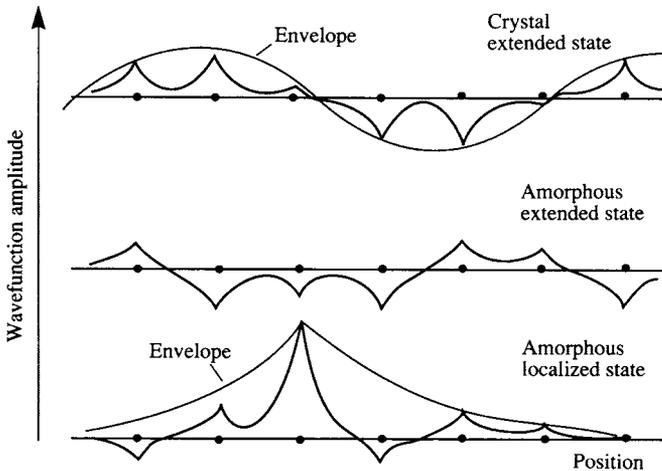
$$-\frac{\hbar^2}{2m}\nabla^2\Phi + V(\mathbf{r})\Phi = E\Phi \quad (1.4)$$

where  $E$  is the electron energy and  $V(\mathbf{r})$  is the potential energy arising from the atomic structure. The periodic potential of the ordered crystal leads to the familiar Bloch solutions for the wavefunction,

$$\Phi(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}) U_{\mathbf{k}}(\mathbf{r}) \quad (1.5)$$

where  $U_{\mathbf{k}}(\mathbf{r})$  is the periodicity of the lattice. There is a constant phase relation between the wavefunction at different lattice sites. The wavefunction has a well-defined momentum,  $k$ , and extends throughout the crystal. The energy bands are described by energy-momentum

Fig. 1.7. Illustration of the wavefunctions of extended and localized states of an amorphous material, compared to the extended states of a crystal.



$(E-k)$  dispersion relations, which, in turn, determine the effective mass, electronic excitations, etc.

These solutions to Schrödinger's equation do not apply to an amorphous semiconductor because the potential  $V(\mathbf{r})$  is not periodic. A weak disorder potential results in only a small perturbation of the wavefunction and has the effect of scattering the electron from one Bloch state to another. The disordering effect of an amorphous semiconductor is strong enough to cause such frequent scattering that the wavefunction loses phase coherence over a distance of one or two atomic spacings. Fig. 1.7 illustrates the wavefunction of extended electron states in crystalline and amorphous semiconductors and shows the rapid change of phase induced by the disorder.

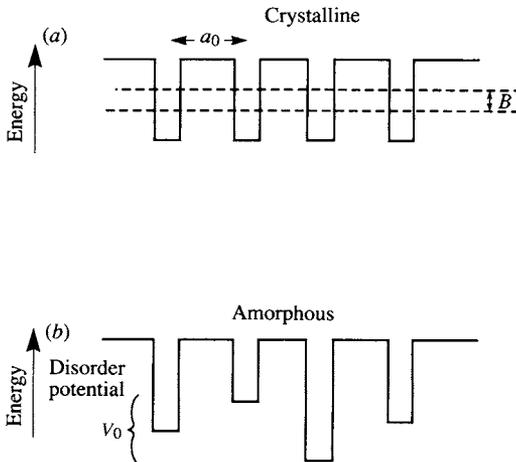
The strong scattering causes a large uncertainty in the electron momentum, through the uncertainty principle,

$$\Delta k = \hbar/\Delta x \approx \hbar/a_0 \approx k \quad (1.6)$$

where  $\Delta x$  is the scattering length and  $a_0$  is the interatomic spacing. The uncertainty in  $k$  is similar to the magnitude of  $k$ , so that momentum is not a good quantum number and is not conserved in electronic transitions.

The loss of  $k$ -conservation is one of the most important results of disorder and changes much of the basic description of the electronic states. There is a greater emphasis on the spatial location of the carrier than on its momentum. Some consequences of the loss of  $k$ -conservation are:

Fig. 1.8. The Anderson model of the potential wells for (a) a crystalline lattice and (b) an amorphous network.  $V_0$  is the disorder potential.



- (1) The energy bands are no longer described by the  $E$ - $\mathbf{k}$  dispersion relations, but instead by a density-of-states distribution  $N(E)$ , illustrated in Fig. 1.6. Also the electron and hole effective masses must be redefined as they are usually expressed as the curvature of  $E(\mathbf{k})$ .
- (2) The conservation of momentum selection rules does not apply to optical transitions in amorphous semiconductors. Consequently, the distinction is lost between a direct and an indirect band gap, the latter being those transitions which are forbidden by momentum conservation. Instead transitions occur between states which overlap in real space. This distinction is most obvious in silicon which has an indirect band gap in its crystalline phase but not in the amorphous phase.
- (3) The disorder reduces the carrier mobility because of frequent scattering and causes the much more profound effect of localizing the wavefunction.

### 1.2.5 *Localization, the mobility edge and conduction*

An increasing disorder potential causes first strong electron scattering and eventually electron localization, in which the wavefunction is confined to a small volume of material rather than being extended. The form of the localized wavefunction is illustrated in Fig. 1.7. Anderson's theory of localization uses the model illustrated in Fig. 1.8 (Anderson 1958). The crystal is described by an array of identical atomic potential wells and the corresponding band of electronic states is broadened to a band width  $B$  by the interaction between atoms. The disordered state is represented by the same array of sites to which a random potential with average amplitude  $V_0$  is added. Anderson showed that when  $V_0/B$  exceeds a critical value, there is zero probability for an electron at any particular site to diffuse away. All of the electron states of the material are localized and there is no electrical conduction at zero temperature.

The critical value of  $V_0/B$  for complete localization is about three. Since the band widths are of order 5 eV, a very large disorder potential is needed to localize all the electronic states. It was apparent from early studies of amorphous semiconductors that the Anderson criterion for localization is not met. Amorphous semiconductors have a smaller disorder potential because the short range order restricts the distortions of the bonds. However, even when the disorder of an amorphous semiconductor is insufficient to meet the Anderson criterion, some of the states are localized and these lie at the band edges. The center of the band comprises extended states at which there is strong scattering and

states at the extreme edges of the bands are localized. The extended and localized states are separated by a mobility edge at energy  $E_C$ , which derives its name because at zero temperature, only electrons above  $E_C$  are mobile and contribute to the conduction. This is the essence of the standard model of amorphous semiconductors proposed by Mott (e.g. Mott and Davis (1979) Chapter 1).

The electronic structure is illustrated in Fig. 1.9. The energy of the mobility edge within the band depends on the degree of disorder and is typically 0.1–0.5 eV from the band edge in all amorphous semiconductors. The properties of states near the mobility edge are actually more complicated than in this simple model of an abrupt mobility edge and are described in more detail in Chapter 7. Nevertheless, the model of Fig. 1.9 provides a good description of amorphous semiconductors.

Fig. 1.9. The density of states distribution near the band edge of an amorphous semiconductor, showing the localized and extended states separated by the mobility edge.

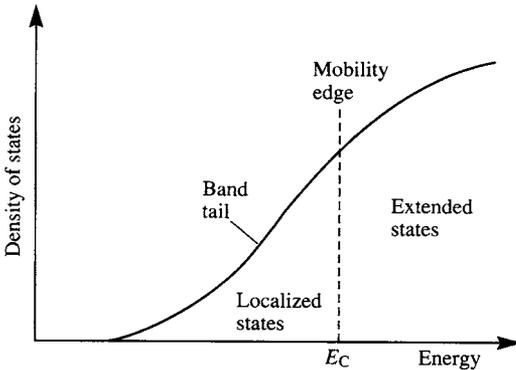


Fig. 1.10. Model showing the tunneling between two localized states separated by distance  $R$  and energy  $E_{12}$ ;  $R_0$  is the localization length.

