Amorphous semiconductors : Structural models

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Abstract. The structure of amorphous semiconductors has become the subject of intense study in recent years. In this paper, the models, that have been constructed and applied to represent the structures, have been briefly reviewed. Details of the construction of continuous random network (CRN) models have been presented and a comparative study of the microcrystallite model and the random network model has been made in the light of their recent applications.

Keywords. Amorphous semiconductors ; structural models ; continuous random network ; microcrystallite model.

1. Introduction

In recent years there has been a great deal of interest in the study of amorphous semiconductors mainly because of their widespread application in electronic devices ; one of their latest applications being in solar cells where amorphous hydrogenated silicon is currently being regarded as the most acceptable candidate for solar cell material. Much work has been done on the structural characteristics of a-semiconductors and in this paper, we shall briefly review the models that have been constructed to represent the structures.

The structure of a system is specified by the spatial distribution of the constituent phases as well as the molecular configurations within each phase. On a microscopic scale, substances are classified as fluids or solids according to the motion of their molecules which give rise to intermolecular collisions. In fluids, these motions are mostly translatory or diffusive, while in solids they are almost entirely oscillatory. Thus the solid structure is characterized by a definite set of positions about which the atoms or molecules oscillate. Solids are again classified under crystalline or amorphous depending on the spatial pattern of these positions. In crystalline solids this spatial pattern exhibits translational symmetry so that by knowing the positions of the atoms in one region of the solid one can specify the positions of all the atoms

throughout the crystal. In other words crystalline solids have long range order. On the other hand, in amorphous solids the spatial pattern of the atomic positions is completely aperiodic and no long range order is present. However, because of the correlations of the oscillatory motions of the atoms or molecules, some kind of order exists over a short range *i.e.* over distances of a few atomic spacings.

An 'ideal' or a 'true' amorphous solid is one in which the arrangement of atoms is continuously random so that neither short range nor long range order is present. However, this is also an idealization since this 'ideal' structure is related to the prepared amorphous material in much the same way as the 'real' crystal with the presence of defects in the actual material.

It is generally believed that the amorphous solid state is a metastable one, slowly relaxing towards some more stable state. Information about the average structural environment around an atom can be obtained from x-ray or electron diffraction studies. The atomic arrangement is deduced from the elastically scattered intensity. The Fourier inversion of this yields the radial distribution function (RDF), which gives the average number of nearest neighbours as well as higher-order neighbours and their average distance from an average atom.

Structural models have been constructed to picturise the three dimensional atomic arrangements in amorphous solids. These models are of use in revealing the ring statistics, dihedral angle distribution and other features of short range order which are not directly revealed by the experimental radial distribution functions.

The models, which are more discussed and applied, are of four kinds : (i) microcrystallite model (Rudee 1972) (ii) amorphous cluster model (Grigorovici and Manaila 1967) (iii) random network model (Polk 1971) and (iv) dense random packed model (Bernal 1964). The most widely accepted model of amorphous semiconductors is the random network model. In this paper, we shall briefly review the construction of these models with a special emphasis on the random network model for amorphous semiconductor materials in the light of recent developments.

2. Brief description of models

2.1 Microcrystallite model

The idea of this kind of model originated from the observation that peaks in polycrystalline diffraction pattern broadened as the size of the grains became smaller. In this kind of arrangement, atoms exist in small regions of crystalline order and the macroscopic solid is an aggregate of these microcrystals oriented at random.

The size of the crystallites must exceed two to three unit cell dimensions (Warren and Biscoe 1938). Since the essential feature in a crystalline structure is a regular repetition, the term 'crystalline' ceases to have any meaning when

applied to volumes of the order of one unit cell. Also, for so small a crystallite size, half of the atoms would lie on the crystallite boundaries and it would be necessary to know the structure and density of the connective tissue required to bond together two separate misoriented crystallites. Rudee (1972) has proposed a random network structure of the sort described by Polk (1971). If this is so, there is a possibility that a microcrystallite structure would degenerate into a continuous random network structure when the crystallite size decreased without limit.

Rudee (1972) and Rudee and Howie (1972) have shown that the microstructure of amorphous germanium and amorphous silicon can be represented by a microcrystallite model with a crystallite diameter of $\sim 14 \text{ \AA}$.

2.2 Amorphous cluster model

In this model it is supposed that a group of atoms (about 100), arranged in a regular but non-periodic manner, has a lower free energy than a cluster with crystallographic configuration. In each of these clusters chemical valence is satisfied and bond lengths and angles are practically unchanged from the crystal. An amorphous solid will have an amorphous cluster structure if it is formed under conditions where energy minimization occurs for such aggregates of atoms with non-crystallographic configurations.

The problem of fitting the clusters together to form the macroscopic solid is the same as in the microcrystallite model.

Tilton (1957) used this model to explain the structure of silica glass, the basic unit of which was called the 'vitron'. The vitron contained SiO_4 tetrahedra arranged to have the external symmetry of clusters of pentagonal dodecahedra.

Grigorovici (1968) applied this model to explain the structure of a-Ge. The basic unit was of the shape of a pentagonal dodecahedra containing 20 atoms and was termed an amorphon.

An amorphous cluster differs from a microcrystallite in that it cannot grow beyond 100 atoms or so without developing defects which probably involve dangling bonds and larger vacancies.

There are no internal dangling bonds and the number of surface dangling bonds per cluster atom is somewhat less than the number for a crystallite containing the same number of atoms. The densities of the clusters apparently are not specified (Paul *et al* 1973).

2.3 Random network model

This model is concerned with atoms which are arranged in a continuous liquid-like random packing without abrupt structural discontinuities. It contains, in principle, no regions with short-range order. Every atom is bonded to the number of nearest-neighbours required to satisfy its chemical valence so that

there are no internal dangling bonds. But the local order is distorted by fluctuations in the bond lengths and angles from their crystalline values.

It was first proposed by Zachariasen (1932) as a general model for glasses. The atoms in this kind of structure form three-dimensional networks which lack the periodicity and symmetry of a crystalline network. Solids possessing such a random network (RN) structure will be isotropic which is a consequence of the absence of symmetry and they will not possess a sharply-defined transition temperature from the solid to the liquid state due to the lack of periodicity. As there is no scheme of repetition in the glass, no two points are exactly identical; in other words no two atoms are structurally equivalent. So the energy required to detach an atom from the network will be different for each individual atom. With increasing temperature we would get an increasing number of detached atoms, so that the breakdown of the network would be a continuous rather than an abrupt phenomenon.

Random network models are constructed according to the following rules (Turnbull and Polk 1972) :

- (a) the number of nearest neighbours (NN) and the average NN spacing are taken to be the same as in the corresponding crystal; a small dispersion of NN spacings about the average is permitted,
- (b) a certain distribution of distortions of bond angles from their ideal crystal values is specified and,
- (c) the density of dangling bonds on the surface is kept constant during the building of the model.

The model was adopted by Ordway (1964), Evans and King (1966) and Bell and Dean (1966, 1972) to describe the structure of amorphous SiO_2 .

Bell and Dean constructed a ball and stick model of SiO_4 tetrahedra arranged according to certain rules and showed that the pair distribution functions obtained therefrom agreed with experiment. Also the configurational entropy calculated from their model agreed well with experiment thereby removing the objection to the RN model which was based on its inability to account for the relatively low configurational entropy of silica glass.

Polk (1971) constructed a 440-unit random network model for a-Ge and a-Si and showed that it yielded a radial distribution function and density in reasonable agreement with experiment. All subsequent model building of tetrahedrally co-ordinated continuous random networks has been essentially a refinement of his work.

2.4 Dense random packed model

It has been used to model the structure of metallic and metallic alloy glasses. Such structures are an arrangement of rigid spheres which are dense in the sense that they contain no internal holes large enough to accommodate another sphere but are random in that there are only weak correlations between positions of spheres separated by five or more sphere diameters and that they apparently contain no recognizable regions of crystalline like order (Cargill 1975).

3. Construction of random network models

Structural modelling for most of the amorphous semiconductors studied is based on the random network model. So, we shall discuss this model in some detail.

A random network model of amorphous semiconductor is generally acceptable if it satisfies the following conditions :

The radial distribution function (RDF) calculated from the model must agree with the experimental RDF. Since the experimental RDF exhibits structure to about $10 \text{ \AA}$, a model RDF should extend at least this far. So the number of units *i.e.* 'atoms' of the model should be such as to produce a cluster of $20 \text{ \AA}$ in radius, thus allowing the RDF of the model to be extended to about $r = 10 \text{ \AA}$ with fair statistics. Most of the models, so far constructed, yield RDF's which fit over a considerable range of experimental data but not the entire range.

The radial distribution function (RDF), defined by $4\pi r^2 \rho(r)$, describes the average number of atom centres between distances r and $r+dr$ from the centre of an average atom. $\rho(r)$ is the number of atoms per unit volume at distance r from any arbitrary origin atom.

Experimentally, the scattered coherent radiation is measured, which is normalized and corrected for background, polarization, multiple scattering and Compton scattering and is denoted by $I(k)$, the interference function.

The reduced intensity function $F(k)$ is given by

$$F(k) = k \left[\frac{I(k)}{f^2} - 1 \right] , \quad (1)$$

where $k = \frac{4\pi \sin \theta}{\lambda}$ = momentum transfer vector, 2θ = scattering angle, λ = wavelength of radiation and f = atomic scattering factor.

The RDF is calculated from $G(r)$, the Fourier transform of $F(k)$

$$\begin{aligned} G(r) &= \frac{2}{\pi} \int_0^{\infty} F(k) \sin kr \, dk \\ &= 4\pi r \left[\rho(r) - \rho_0 \right] \end{aligned} \quad (2)$$

ρ_0 = average atomic density.

$G(r)$ is called the reduced radial distribution function :

The RDF is

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + rG(r). \quad (3)$$

The radial density function $J(r) = 4 \pi r^2 \rho(r) dr$, which is assumed *a priori* to be spherically symmetric, describes the number of atoms in a spherical shell between r and $r + dr$. The number of atoms $CN(i)$ in each co-ordination shell i located at r_i is given by

$$CN(i) = \int_{r_i - \Delta}^{r_i + \Delta} 4 \pi r^2 \rho(r) dr. \quad (4)$$

The broadening of the peaks in $J(r)$ is due to static displacements and thermal vibrations of atoms. $J(r)$ is then represented as

$$J(r) = \sum_{i=1}^{\infty} \frac{C_i}{(2 \pi r_i^2)^{1/2}} \exp \left[-\frac{(r-r_i)^2}{2\sigma_i^2} \right] \quad (5)$$

where C_i is the number of atoms in the i th shell about an arbitrary origin atom, r_i is the distance from the origin to the i th shell and σ_i^2 is the mean square amplitude of vibration plus mean square static displacements.

From the experimental RDF, we can therefore determine, in principle, the co-ordination numbers $CN(i)$, the neighbour distance r_i , static displacements and temperature effects. One can further derive the pair distribution function $\rho(r)/\rho_0$, which is also an useful parameter and gives the number of pairs of atoms as a function of the distance between the atoms that make up the pair.

The experimental $J(r)$, however, contains errors because of inadequate correction of experimental errors in $I(k)$ and termination effects associated with the finite range of k in the integral of equation (2) (Graczyk and Chaudhari 1973). Because of these difficulties, Rudee and Howie (1972) suggested that comparisons between experiment and theory be made *via* the reduced intensity function $F(k)$, which is one step closer to the experimental data.

Graczyk and Chaudhari (1973) have shown that $F(k)$ can be calculated from a random network model by using a Debye intensity function

$$F(K) = \frac{1}{N} \sum_{\substack{n=1 \\ m \neq n}}^N \frac{1}{r_{mn}} (\sin Kr_{mn}) \exp(-2M_{mn}) \quad (6)$$

where the sum is over all atom pairs in a cluster containing N atoms, and r_{mn} = distance between atoms m and n , $\exp(-2M_{mn})$ = Debye-Waller temperature factor.

Even if the model RDF fits with the experimental RDF, it does not make the model unique as different structures may have similar RDF's. In order to approach a unique fit, the distribution of dihedral angles, the ring statistics and correlations of deviations of atomic separations and bond angles from the mean values should be specified.

Figure 1a. Photograph of the CRN model (reproduced from Polk 1971)

The model should also be consistent with other structural properties like atomic density, the heat of crystallization etc., and should provide a plausible explanation of the effects of annealing, the kinetics of annealing and the process of recrystallization ; this may involve the necessity of incorporation of defects into the network.

The model must also explain the results of any experiments such as nuclear magnetic resonance, electron spin resonance or Raman scattering which can give the detailed local atomic configurations. Finally, the phonon energy and electron energy density of states calculable from model co-ordinates must correspond to those measured experimentally (Paul and Connell 1976).

Models may be constructed entirely by hand (Polk 1971) or constructed first by hand with subsequent adjustments of its co-ordinates by computer (Polk and Boudreaux 1973) or constructed entirely by computer simulation (Shevchik and Paul 1972).

Hand-built models use ball and spoke building units. The number of spokes equal the first co-ordination number (valency) and the direction of the spokes reproduces the direction of the covalent bonds. Very rigid spokes do not permit bond length or bond angle variation. To acquire sufficient flexibility, springs have been used (Grigorovici and Belu 1972).

4. CRN models for amorphous tetrahedrally co-ordinated semiconductors

Amorphous germanium and amorphous silicon are the two most extensively studied amorphous semiconductors. Most of the modifications of random network models developed so far have been tested by fitting the model RDF's with that of a-Ge and a-Si.

4.1 Hand-built CRN models

The first random network model of a-Ge and a-Si was constructed by Polk (1971) (figure 1a). The units were made of metal and plastic and consisted of a small central section with four rods emanating from it. The rods representing the bonds could be bent and snapped together so that the tetrahedral bond angle between the rods could be varied and adjoining tetrahedra rotated into configurations other than that found in the crystalline structure. This ensured the noncrystallinity of the model structure.

The core of the structure consisted of a mixture of five and six membered rings. There were no unsatisfied (dangling) bonds in the interior of the model. When an additional unit was connected to other units the dihedral angle was chosen so as to minimize the strain. The strain minimization was found to be operationally equivalent to requiring that the surface density of dangling bonds be kept constant over the entire surface as the model size was increased.

The final model appeared capable of indefinite extension without including dangling bonds and without producing too much strain.

Figure 1b. Comparison of the RDF for the CRN model of Polk (1971) (histogram) with the experimental RDF of Moss and Graczyk (1970). The parabola represents the average density, and the vertical lines and corresponding numbers represent the position and number of neighbours in a crystal with a nearest neighbour separation equal to the mean separation in the model.

The bond angles were distributed with an average deviation of $\pm 10^\circ$ and a maximum deviation of $\pm 20^\circ$ about the ideal tetrahedral angle $109^\circ 28'$. With the average nearest neighbour separation chosen to match that of the corresponding crystal, the density of the structure was $97 \pm 2\%$ of the crystalline value. All the units of the structure were included in 5 or 6-membered rings and the ratios of the numbers of 6 to 5 membered rings was found to be approximately 4 to 1.

The final model consisted of 440 atoms. The RDF was determined by direct measurement from sixteen centrally located atoms. The RDF is shown in figure 1.

In the Polk's model (Polk 1971) since the co-ordinates of the atomic positions were not obtained, the properties of the structure such as its diffraction behaviour, electronic energy levels and vibrational spectra could not be calculated. The physical characteristics of the tetrahedral units used to produce the model caused some of the first neighbour distances to be lengthened when the stresses due to distortions were too great for the connectors to hold together. This combined with the uncertainties in the measurement of the central position produced original data with large fluctuations in the first neighbour distances.

Polk and Boudreaux (1973) refined the original Polk (1971) model to produce equal neighbour distances. The model was extended to 519 atoms and the coordinates of each individual atom was measured with an accurately positioned laser beam.

With the help of a computer all the first neighbour distances were first calculated; then their mean and the two atoms with separations farthest from the mean were identified. These two atoms were then moved an equal distance along the line joining them so that the difference between that distance and

the mean was reduced by 50%. The first neighbour distances affected by the movement were then recalculated and the procedure iterated until the standard deviation of all the interatomic separations was less than a predetermined value (actually about 0.2%) with these refined co-ordinates the RDF, the mean tetrahedral bond angle and its standard deviation, the distribution of dihedral angles and the density were determined. The bond length and bond angle fluctuations were found to be constant throughout the model. The mean bond angle was 109.2° with standard deviation of 9.1° compared with the 10° of the Polk model. Density was found to be 1% less than the diamond cubic structure with a near neighbour distance equal to the mean of that of the random network (In Polk's model the density deficit was $3 \pm 2\%$). The width of the model RDF and that of the experimental RDF fit when the effects of thermal, mathematical and experimental broadening are removed from the latter (figure 2).

As pointed out by Steinhardt *et al* (1974), the drawbacks of the Polk-Boudreaux model is that only bond length deviations are minimized but not bond

Figure 2. Comparison of the $G(r)$ calculated from the Polk-Boudreaux (1973) model (histogram) with the experimental function found for a-Si by Moss and Graczyk (1970) (smooth curve). The calculated histogram is broadened to reduce statistical fluctuations.

angle deviations. The condition of equal bond lengths represents two constraints per atom (less when a surface is present) while there are three degrees of freedom per atom. Thus co-ordinates from the bond length equalization procedure depend to some extent on the elastic properties of the plastic and metal units used to build the model and have rather larger bond angle deviations than necessary.

Steinhardt *et al* (1973) improved the Polk-Boudreaux model by simultaneously relaxing the bond length and bond angle deviations. This was done by minimizing the Keating (1966) expression for elastic energy.

$$V = \frac{3}{16} \frac{\alpha}{d^2} \sum_{l,i} \left(\vec{r}_{li} \cdot \vec{r}_{li} - d^2 \right)^2 + \frac{3}{8} \frac{\beta}{d^2} \sum_{(i,i')} \left(\vec{r}_{li} \cdot \vec{r}_{li'} + \frac{1}{3} d^2 \right)^2 \quad (7)$$

where d is the equilibrium bond length and α and β are the bond stretching and bond bending force constants respectively. The first sum is on all atoms l and their four neighbours specified by i , the second is over all atoms l and all pairs of distinct neighbours i and i' ; r_{li} is the vector from atom l to atom i . These two terms are the first in a power series expansion about the equilibrium positions of a perfect lattice and so the expression may be incorrect for large distortions. Thus, an estimate of the elastic energy from equation (1) and the model co-ordinates may be inaccurate. In addition, the values of α and β to be used are somewhat uncertain. Fortunately, the properties of the models ultimately derived do not seem to depend significantly on the choice of β/α so that one may infer that the structure will be adjusted using the Keating expression in the right sense, even though the absolute adjustment may be in some error (Paul and Connell 1976).

The new co-ordinates of the 519 atom Polk-Boudreaux model were obtained by repositioning each atom separately and sequentially (while keeping the co-ordinates of the other atoms fixed) until it was in equilibrium under the bond stretching and bond bending forces due to its nearest and next-nearest neighbours. The repositioning of each atom in the model was repeated over 50-100 iteration cycles until convergence was achieved.

Using this energy minimization procedure, Steinhardt *et al* (1973) obtained the co-ordinates of another new 201 atom random network. The network was obtained by serially adding atoms to a 21-atom rough measured seed. The added atoms were relaxed from automatically guessed start positions. Thus the connectivity of the network *i.e.* identification of nearest neighbours was determined by the relaxation procedure.

The two models were then analyzed in terms of density, elastic distortion energy, elastic constants, number of five, six and seven-fold rings, distribution of dihedral angles and radial distribution functions. It was found that despite their different origins the models had essentially identical characteristics.

The density of both the models was found to be within 1% of that of the diamond cubic form of crystalline germanium.

In the 201-atom model the root mean square bond length deviation was 0.8% and root mean square angular deviation was 6.66° . The relaxed 519 atom model had rms bond length deviation of 1.04% (which is six times larger than the

Figure 3. Comparison of the RDFs of the CRN model of Steinhardt *et al* (1973) and the measured result for a-Ge (Connell *et al* 1973). The CRN results are corrected for finite size of the model and were Gaussian broadened to allow for thermal, instrumental, and termination broadening. Heavy line is the experiment, dashed line is 519 atom model and thin line is 201 atom model.

Figure 4. $G(r)$ s for the 201-atom model, 519-atom relaxed model (Steinhardt *et al* 1973) and for the unrelaxed 519 atom model of Polk and Boudreaux (1973).

unrelaxed Polk-Boudreaux(PB) model) and an rms angular deviation of 7.1° , smaller than the 9.25° of the PB model. The dihedral angle distribution was the same as in the unrelaxed PB model. Further, the two models had essentially identical ring statistics after correction was made for finite size of the models. With corrections for surface effects the bulk rings per atom for both models were 0.38 five fold/atom, 0.90 six fold/atom and 1.05 seven fold/atom. The radial distribution function was corrected for finite size of the model and is illustrated in figure 3. The agreement between the RDF's for the two different CRN models and experiment is seen to be quite good in the region from 0 to $10 \text{ \AA}$. The second and third prominent peaks which are sharper for the models than for the experimental curve are due to the over-simplified force constant scheme used to relax the models. According to Steinhardt *et al* (1973), the corrections made for termination errors in the experimental RDF may somewhat distort the experimental curve. Consequently the small peak near $4.8 \text{ \AA}$ in the model curves do not correspond precisely to the structure evident in the experimental curve.

The graphs of $G(r)$ for the 201 atom and 519 atom relaxed and unrelaxed 519 atom models is shown in figure 4. It is seen that the $G(r)$'s of the relaxed networks exhibit sharper features because of the decrease in the rms angular deviation.

The relaxation of the 519 atom Polk-Boudreaux (PB) model, by minimizing the Keating expression for elastic energy, was also carried out by Duffy *et al* (1974). Whereas Steinhardt *et al* (1973) randomly perturbed the model and relaxed it, Duffy *et al* (1974) simultaneously moved each atom along the direction of the force on that atom through a distance proportional to the magnitude of the force on them. After each such move, the forces were recalculated and the atoms moved again and the process iterated until the forces and displacements became small. The atoms were moved according to

$$\Delta x_i = -h \Delta_i E, \quad (8)$$

where E is the Keating expression for elastic energy and h is some constant. The choice of h only matters in that a bad choice increases the number of iterations necessary although it need not lead to errors in the final co-ordinate.

This method is similar to the classical method of steepest descent.

There are no significant differences in the result obtained by Duffy *et al* and Steinhardt *et al*, the slight variations being due to the fact that Duffy *et al* used a value of 0.29 for β/α while Steinhardt *et al* used 0.20. But (as pointed out by Duffy *et al*) the relaxed structure of Steinhardt *et al* is closer to the equilibrium than Duffy's because the approximate expression results in some small deviations from equilibrium.

Shevchik and Paul (1973, 1974) have shown experimentally that the RDF's of the amorphous III-V compounds (GaAs, GaP, GaSb, InSb) are similar to that of amorphous germanium, reflecting tetrahedral bonding. Therefore, the structural model, which will fit the data of the III-V compounds, will be a continuous random network (CRN). But existing constructions of such a network contain an appreciable number of five-membered rings which imply bonds between like atoms ('wrong bonds') in a binary compound.

Figure 5. Radial distribution functions of the Connell-Temkin model (dotted curve) and the Polk model (dashed curve) (Polk 1971) compared to experiment (solid curve) (Temkin *et al* 1973).

Figure 6. Comparison of the RDF derived from the model of Chao and Nowak (1976) (histogram) with the experimental RDF of a-Ge (Connell and Temkin 1974b) (dashed curve). The smooth curve represents $4\pi r^2 \rho_0$.

Connell and Temkin (1974a) built tetrahedrally co-ordinated CRN model that has no odd-membered rings and no wrong bonds when the atoms of a binary compound are assigned to the lattice positions so as to avoid such bonds.

The Connell and Temkin model was constructed from 238 plastic tetrahedra interconnected by aluminium rods following the same general procedure as employed by Polk (1971). Whenever a surface configuration occurred that could lead to a five-fold or seven-fold ring, adjacent surface atoms were reorganized to eliminate it. The co-ordinates of each atom were adjusted by computer so that the variance of the bond lengths was equal to that due to static distortions measured experimentally in amorphous Ge. The RDF obtained is shown in figure 5.

In contrast to the Connell and Temkin (CT) model (1974a) which contained no odd membered rings Chao and Nowak (1976) constructed a five-membered ring dominated tetrahedrally bonded CRN of 940 atoms. The model was built starting with a pentagonal dodecahedron and using the criterion of forming

as many planar 5-fold rings as possible without large strains. 99% of the rings were five-fold and a few six-fold, four-fold and non-planar. No attempt was made to relax the atomic positions. The density was 95.5% that of crystalline Ge. The model RDF compared with the experimental RDF of Connell and Temkin (1974b) is shown in figure 6. The matching is seen to be not as good as other CRN models discussed. Chao and Nowak have claimed that their model RDF shows a better correspondence with the experimental RDF of Grigorovici and Manaila (1967).

Thus it is seen that there are several models which have considerable success in matching the radial distribution function obtained from x-ray diffraction data of a-Ge. But there are significant differences between the structures of the models. For example, both the models suggested by Connell and Temkin (1974a) and Steinhardt *et al* (1973) have RDF's fairly close to the experimental ones but there are significant differences in the structure particularly in the ring statistics. According to Beeman and Bobbs (1975) a possible explanation of having two very different models being close matches to experiment but not close enough is that they both differ from the actual structure only in being too far to one or the other from an optimum model in the middle. A suggestion of Connell and Temkin (1974a) that the average of the two model RDF's gives a better match than either led them to restructure by computer the CRN model of Connell and Temkin (1974) (which has no odd-membered rings) by gradually incorporating an increasing number of odd membered rings. All the restructured models were made with energy relaxation and finite size correction. Figure 7 shows a comparison of

Figure 7. RDF of relaxed Connell-Temkin (CT) model (open circles), restructured CT model (dots) and Steinhardt *et al* (1974) model (dashed line) compared to experimental data (solid line) of Temkin *et al* 1973.

the RDF's of the relaxed Connell-Temkin [CT] model, the Steinhardt *et al* model, and a restructured CT model in which the five-membered rings per atom is 0.336, six-fold rings/atom is 1.506 and 7-fold rings/atom is 0.808 with experimental RDF as obtained by Temkin *et al* (1973).

The restructured model shows an improved match to experiment over previous models. This leads to the conclusion that models with a ratio of odd to even-membered rings of bonds slightly reduced from the Polk-Boudreaux network would best fit the data (Bullett and Kelly 1979).

All the above models were built entirely by hand or first built by hand and then co-ordinates adjusted by computer. Now we shall discuss models of tetrahedrally co-ordinated semiconductors built entirely by computer.

4.2 Computer built CRN models of tetrahedrally co-ordinated a-semiconductors

A computer simulation of the atom-by-atom deposition process of a-Ge was carried out by Shevchik (1973) and Shevchik and Paul (1972). First, they specified a set of rules governing the behaviour of an adatom on the surface in becoming a part of the cluster. The rules formed by observing the experimental RDF of a-Ge are the following

- (i) All the bonds of the adatom with the surface atoms must have length $2.45 \text{ \AA}$ (*i.e.* the atoms are hard spheres, $2.45 \text{ \AA}$ in diameter) as the first peak in the experimental RDF is sharp.
- (ii) The adatom can have no other neighbours at a separation from $r = 2.5$ to $r = 3.2 \text{ \AA}$ since in the experimental RDF no atomic distances are observed in the region 2.5 to $3.2 \text{ \AA}$. This condition automatically limits all bond angle distortions to a maximum of 30° .
- (iii) All atoms must have four or fewer nearest neighbours as the experimental RDF shows that the average co-ordination number is very close to four.

Next, an initial seed of 15 atoms was generated by randomly distorting the bonds of each atom within a 20° solid angle about their corresponding undistorted bonding directions. As each additional adatom was added to the cluster it was moved about (while all the other atoms were held fixed) until it found a position where it could best satisfy it and its neighbours bonding requirements. The adatom first tried to make a bond with three existing neighbours while satisfying the above three constraints. This was equivalent to allowing the atom to minimize its energy. If unsuccessful, it attempted a double bond site and if still unsuccessful it attempted to find a place where it could make a single bond that is consistent with the bond angle fluctuation permitted to the atom to which it is joining (parent atom). If this also failed the parent bond was left unsatisfied or dangling and the adatom moved to a new parent bond and likewise attempted to satisfy the new parent bond and any neighbouring bonds.

In this way a cluster of 1000 atoms was generated. But about 5 to 8 % of the bonds were broken and this made the model inadequate for use in calculations

of intrinsic vibrational and electronic properties, since the structure of real materials deposited at room temperature has far fewer than 5 to 8 % broken bonds. Nevertheless, the model is more or less successful in fitting the RDF to experimental data (although the first peak of the model is too narrow). The fitting is shown in figure 8.

The computer model built by Henderson and Herman (1972), using periodic boundary condition, is better suited for calculating vibrational and electronic properties. Their model simulates the combined effects of structural and thermal disorder and has all bonds satisfied. In their model the initial positions of the 64 atoms are taken to be those of the f.c.c. crystal which is equivalent to considering a system of 64 atoms in a cubic box with periodic boundary conditions. Then the crystal structure is disrupted and each atom is moved sequentially and at random 10% of the distance to the centroid of its four nearest neighbours. Then the four nearest neighbours and the twelve next-nearest neighbours are moved radially 10% of the distance to the nearest and next-nearest neighbour distances of the crystal. The process is repeated until a satisfactory RDF is obtained. The comparison of the model RDF to experimental RDF is shown in figure 9. The experimental curve is that of a-Si obtained by Moss and Graczyk (1970).

Alben *et al* (1973) have satisfactorily explained the Raman spectra of amorphous Ge and Si using the random network model of Henderson and Herman.

Duffy *et al* (1974) have constructed entirely by computer fully connected random networks which have their strain energies minimized so that they may represent metastable equilibrium arrangements. The deformation energy of the model was taken to be that given by Keating (1966).

Two models were built — one a 200 atom model and another a 500 atom model. The 200 atom model was built by serially adding atoms to a core using only interatomic distances as the bonding criterion while for the 500 atom model the bonding criterion was based on a combination of the local energy (computed from the Keating expression) and the distances. The first criterion is as follows: if the first estimate of the position of the added atom is within a specified distance of an atom already in the model, the two atoms were bonded to each other. The acceptance distance used is $1.27 d_0$ where d_0 is the equilibrium bond length.

In the second criterion a search is made for possible neighbours of a certain atom n by bonding n to another atom m which is within a distance of $1.4 d_0$ of n and has at least one unsatisfied bond. Then to minimize strain energy a local energy relaxation is performed on n and all its neighbours including m , and the local energy E_1 is calculated. Next another atom p is placed between m and n and bonded to each of them. After relaxation the local energy E_2 is calculated. n and m are bonded when $E_1 < \omega E_2$ where ω is a weighting factor. Both the models are relaxed after the addition of every five new atoms.

The statistics of the two models differ significantly. Though RDF's have been calculated from the models no attempt has been made to compare them with experimental data.

Figure 8. RDF from the computer simulation of the deposition process (Shevchik and Paul 1972) compared with the RDF of sputtered Ge.

Figure 9. Comparison of RDF of Henderson-Herman (1972) model (histogram) with the experimental results of Moss and Graczyk (1970) (lower curve).

Here again the connectivity of the network depends on the accuracy of the Keating expression for elastic distortion energy. For elemental materials additional terms enter which are concerned with the relative rotation of neighbouring tetrahedra and may influence the network topology (Paul and Connell 1976). Further the Keating energy expression does not agree well with experiment for numerical values of the strain energy (Moss *et al* 1973, 1974). However, in spite of these shortcomings, it is found to be sufficiently accurate for defining the atomic positions which give an energy minimum (Beeman and Bobbs 1975).

Guttman (1976) has generated tetrahedrally co-ordinated CRN models by computer in which there are no unsatisfied bonds and which satisfy periodic boundary conditions. The procedure, in brief, consisted in selecting a region of a cubic crystal containing the desired number of atoms and connecting each atom in turn to four others by a quasi-random process, periodic boundary conditions being maintained. By successive modifications of the bond pattern, the energy of the system as calculated at the minimum of the Keating potential for each pattern, was lowered until further changes seemed to be practically unattainable. A particular example was then retained as being realistic if its residual angular distortions were sufficiently small, as determined by comparison with experimental measurement of the width of the second neighbour peak in the RDF. Guttman (1981) used this method to build a model for pure amorphous silicon from which he generated a model for hydrogenated amorphous silicon. This model was constructed by breaking bonds on atoms (of pure a-Si) that were not nearest neighbours. H-atoms were then added to the two sites provided by the dangling bonds. A total of 12 examples were constructed containing 10-13 at % of H-atoms. The atomic co-ordinates were determined by minimizing a valence force potential of the Keating form supplemented by a repulsion between H-atoms other than those that are bonded to each other. The computed neutron scattering was in good agreement with recent diffraction data.

A model structure for hydrogenated amorphous silicon has also been reported by Weaire *et al* (1979). The model was built in much the same way as the model of Polk (1971). Atoms were added in a random manner, consistent with the minimization of strain, the avoidance of dangling bonds and the maintenance of a roughly spherical duster. The hydrogen atoms were grouped in clusters rather than dispersed throughout the structure.

All the above models represent the characteristics of a statistically homogeneous continuous amorphous structure. However, structural investigations using phase contrast transmission electron microscopy and small angle scattering have shown that amorphous germanium films evaporated onto two-dimensional substrates have an inhomogeneous structure consisting of a super-network of low density channels connecting high density islands (Barna *et al* 1974, 1976; Fuhs *et al* 1974; Donovan and Heineman 1971). Thus the structure of a-Ge films cannot be represented by any of the CRN models discussed so far. However, the structure of the high density islands can be approximated by fully co-ordinated CRN generated by hand or computer. Barna *et al* (1978) carried out a computer simulation of the atom-by-atom deposition of Ge on a two-dimensional substrate. They have modelled the

early stage of formation of the film and have compared the actual phase contrast micrograph with a cine film of the computer generated growth of the film. Their model is a qualitative one and is aimed at understanding the formation of the heterogeneous supernetwork structure of the films.

5. Continuous random network models with three fold co-ordination (amorphous arsenic)

A handbuilt CRN model of amorphous arsenic was built by Greaves and Davis (1974). The model consisted of 533 units which were made by soldering thick copper wires to form the three bonds which were preset to 97° , the bond angle of the rhombohedral structure. The dihedral angle was chosen so as to reduce bond angle distortions to a minimum. Although the bond lengths were constrained to be equal no computer relaxation was carried out. A few of the bonds were unsatisfied. The standard deviation of the bond angle distribution was 7.4° . The dihedral angle distribution was similar to the PB and CT model of tetrahedrally co-ordinated semiconductors. However, contrary to the latter the 3-fold CRNs had a large variety of odd and even membered rings. The ring statistics is shown in figure 10a. The four fold CRN's because of their extra co-ordination, constitute a tighter structure and accordingly have a much narrower selection of rings. The main difference from the 4-fold network was the low density. The density was 13% less than that of the crystalline form while both the PB and CT models had densities within 1% that of the crystal.

Figure 10. Ring statistic of (a) Greaves and Davis (1974) [G.D.] model (b) Matthews *et al* (1979) [MDE] model of a-As.

Elliott and Davis (1976) and Davis *et al* (1977) refined the triply co-ordinated network to a constant bond length and relaxed the structure to a minimum energy configuration by computer.

The refinement and relaxation procedure was different from that of the tetrahedral networks and was carried out in the following way : the atom with longest bonds was first repositioned so that all three bonds were equal to the mean of the model. The co-ordinates were recalculated. The atom with the next longest bonds was then shifted in the same way and the process continued until the standard deviation for the bond length for the whole model was suitably small. There was no restraint on the bond angle in the procedure and the final figure was found to be $101^\circ \pm 10^\circ$. The Keating expression for elastic energy was used for energy minimization which resulted in an increase in density.

The RDF of the relaxed model is shown in figure 11 out to 8 Å. The distribution has been broadened to simulate the thermal broadening of the experimental first peak. The experimental RDF of β and γ amorphous As, as obtained by Krebbs and Steffen (1964), are included in the figure for comparison. The agreement between model and experiment is fairly close especially the shape and height of the second peak is accurately produced by the CRN.

An even ring 513 atom model of amorphous arsenic have been constructed by Matthews *et al* (1979) following exactly the same procedure as in constructing the Greaves-Davis (GD) model (1974) except that odd-membered rings of atoms were intentionally avoided. The ring statistics is shown in figure 10b.

Though the RDF of the even ring model provides a fairly good fit to the experimental curve, the vibrational densities of state calculated for both the models and compared with experimental spectra of amorphous, rhombohedral

Figure 11. RDF of relaxed Greaves and Davis model of a-As. (Elliott and Davis 1976) compared to two experimental curves for a-As due to Krebbs and Steffen (1964).

and orthorhombic arsenic shows that the GD model with no constraint on ring order is more appropriate in accounting for the experimentally observed features (Davis *et al* 1979).

6. CRN models with two fold co-ordination (amorphous, selenium and tellurium)

A 539-atom model representing the structure of a-Se and a-Te was constructed by hand by Long *et al* (1976). The model was built following the method of Steinhardt *et al* (1973) for constructing 4-co-ordinated network models. The positions of the atoms were measured by hand and then computer-relaxed under potentials that represent bending and stretching of the covalent bonds within the chains and van der Waals interactions between the chains. The model had no interior broken covalent bonds and no rings—a feature distinguishing it from the four-fold co-ordinated networks. A random distribution of dihedral angles was found to give a better fit to experiment than a model in which the distribution had a maximum at 102° —the dihedral angle of hexagonal selenium being 101.7° .

The density of the model was within 3% of the measured value of $0.0325 \text{ atom/\AA}^3$ for quenched amorphous selenium. The densities of the crystalline forms are 0.0336 for monoclinic and 0.0332 for β monoclinic and 0.0369 for trigonal Se. The fair agreement of the first four peaks in the radial distribution function and the calculated x-ray and neutron scattering intensities with experimental results led the authors to conclude that the structure of a-Te and a-Se may well be approximated by spirals of freely rotating chains of densely packed atoms.

7. Monte-Carlo model

A discussion on structural models of amorphous materials would be incomplete if no mention is made of the Monte-Carlo models developed by Rechlin *et al* (1974). The entire procedure involves two steps. In step I an initial quasi-random configuration of atoms is constructed with the degree of randomness restricted by some assumptions about the nature of the near neighbour arrangement. The parameters to be considered during the random positioning of the atoms are: (i) the range of nearest neighbour correlation distances allowed. The value of this parameter can be obtained from the position of the leading peak edge of the experimental RDF which is a direct measurement of the smallest possible interatomic distance.

(ii) the number of nearest neighbours.

In materials which are covalent or partially ionic the maximum number of nearest neighbours of an atom may be determined on the basis of the valence state in the crystalline material of the same composition. Since the localized bonding character is usually the same in the crystalline and amorphous state this appears to be a reasonable assumption.

(iii) the permissible bond angle distribution for any given atom.

The actual positions of the nearest neighbours about an arbitrarily chosen atom cannot be known with a high degree of certainty as they have only a probability of residing within a volume due to the finite breadth of the first and second correlation peaks of the RDF. Therefore the bond angles associated with the generation of a new atom position must be calculated.

(iv) The type of nearest neighbour atoms allowed about a particular atom species.

This can be determined with the help of Boltzmann probability factor.

In step II the quasi random configuration is altered by picking the atoms at random and moving them an arbitrary distance such that the displacement improves the calculated fit to the RDF. If no improvement is obtained the atom is shifted back to the original position. The magnitude of the maximum allowed displacement is so chosen that it does not allow atoms to pass through intervening atoms. The restrictions in the first stage is also maintained in the second stage.

Figure 12 shows the comparison of the RDF calculated from the Monte-Carlo model of $\text{As}_{24}\text{Se}_{76}$ with the experimental RDF. The fit is seen to be fairly impressive. However an equally impressive fitting can also be obtained from a model based on a starting configuration where atoms are arranged as in a crystalline lattice instead of being randomly positioned (Renninger *et al* 1974). Thus the model constructed is not a unique representation of the structure of the given amorphous material. Construction of unique models will necessarily involve additional experimental data. Another point raised by Long *et al* (1976) is that it is not clear whether chemically unreasonable local configuration can always be avoided in this approach.

Figure 12. Radial distribution function for the Monte-Carlo model (dotted line) and experimental results for $\text{As}_{24}\text{Se}_{76}$ (full line).

8. Discussion

Radial distribution functions play an important role in the testing of a model for its acceptability. But the diffraction techniques (from which the RDF is determined) yield information only about average structural environment around an arbitrarily chosen atom. This limitation has been overcome by transmission electron microscopy which can provide direct information about local atomic arrangement.

From dark field electron microscope studies, Rudee (1972) suggested the structure of a-Ge to be represented by microcrystals of diamond structure with a crystallite size of 14 Å. However the experimental RDF of a-Si (Moss and Graczyk 1970) showed no peak at the distance of the third neighbour spacing of the crystal and also had a relative wide dispersion of the second neighbour spacings. This led to the dismissal of the microcrystallite model with the diamond structure.

Later Rudee and Howie (1972) and Rudee (1972) proposed a wurtzite-structured microcrystallite model with crystalline domains 14 Å in diameter. Howie *et al* (1973) arrived at similar conclusions from interference electron microscopy using tilted illumination.

Chaudhari *et al* (1972) and Shevchik (1973) have found that the dark field observations were not inconsistent with a random network model. Further Chaudhari *et al* (1976) have pointed out that the fringes observed by Howie *et al* (1973) and Rudee and Howie (1972) are associated with aberrations introduced during the tilting of the electron beam and have used untilted beam interference microscopy to study a-Ge film. Their observations provided no evidence for the microcrystallites. Using phase contrast transmission electron microscopy Barna *et al* (1976) have found the structure of a-Ge and a-Si to consist of a coherent supernetwork of low density material in channels connecting rod like high density regions.

Weinstein and Davis (1973) used the microcrystallite model to calculate the diffraction and radial distribution functions for a variety of tetrahedrally co-ordinated crystal structures: diamond, wurtzite, Ge III and Si III — two high pressure polytypes of Ge and Si — and two clathrate structures based on pentagonal and dodecahedral units. Comparison with experimental data showed that the microcrystallite model (MM) is inadequate to fit diffraction data of a-Ge. Reduced intensity function and structure factor calculations carried out by Graczyk and Chaudhari (1973) show diamond and wurtzite structured MM and amorphon model (Grigorovici and Manaila 1967) of a-Ge give a poorer match with experimental data than the random network model of Henderson and Herman (1972). However, a statistical polytype microcrystallite model in which a-Ge and a-Si are supposed to be statistical combinations of 60% Si III and 40% clathrate II provides a good fit to the density and diffraction data (Weinstein 1974). On the other hand, the ability of relaxed GRN models (201 atom Steinhardt *et al* model and 519 atom PB model) to reproduce the scattering properties of real amorphous tetrahedrally co-ordinated materials has been proved by Graczyk and Chaudhari (1975).

For triply co-ordinated amorphous arsenic, MM (Smith *et al* 1975) have failed to provide a satisfactory matching to experimental RDF. Further, Stobbs (1980) using both high resolution bright field and tilted illumination dark field electron microscopy, has demonstrated that the structure of sputtered films of amorphous arsenic is not microcrystalline.

For two fold co-ordinated amorphous selenium, however, the balance tilts somewhat towards the microcrystallite side. Kaplow *et al* (1968) first attempted to reproduce the RDF curve of a-Se with the help of monoclinic and hexagonal MM. Though their attempt was not very successful, later Satow and Uemura (1978) were able to obtain quite an impressive fit to the experimental curve from an RDF calculated by adding two curves from microcrystals of monoclinic and hexagonal Se at the ratio 0.75 : 0.25.

Shiojiri *et al* (1979) have measured the densities of vacuum evaporated amorphous films of Ge, C, SiO, Se and WO₃, using multiple beam interferometry in combination with an oscillating crystal microbalance. The measurements indicated that the amorphous film densities were 23-31% less than the crystalline bulk densities. According to Shiojiri *et al* this density deficit is due to voids, the presence of which can be deduced from microcrystallite models of amorphous films. In this context it may be stated that the network models yield a density deficit of about 1%.

MM and CRN models have also been examined on the basis of vibrational densities of states (DOS), infrared absorption spectrum (IS) and Raman scattering spectra (RS). The Raman spectra of wurtzite diamond, cubic diamond, graphite, wurtzite silicon, Si (2H-4) and Si (FC-2) microcrystallites have been compared with that of amorphous diamond, amorphous graphite and amorphous silicon by Solin and Kobliska (1974). From their observations they have come to the conclusion that MM is not applicable to a-Si, diamond or graphite and is thus not likely to be valid for a-Ge.

Beeman and Alben (1977) have calculated the DOS, IS and RS for random network models of four co-ordinated (germanium like), three co-ordinated (arsenic-like) and two co-ordinated (selenium-like) structures and have compared them, wherever possible, to experimental results. They have found that the Ge and As models are quite compatible in representing the real material while for Se, several important aspects of the experiment are not explained and that the force constants and structure need a better understanding.

Finally, we may conclude that, although the general trend is at present in favour of CRN models, a unique model is still to be created. A number of CRN models with different characteristics give more or less the same fitting to the experimental RDF. To establish a unique model, therefore, structural data alone is not sufficient and information from a wider range of experimental data is very much necessary.

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