Computer Generation of Structural Models of Amorphous Si and Ge

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We have developed and applied a computer algorithm that generates realistic random-network models of *a*-Si with periodic boundary conditions. These are the first models to have correlation functions that show no serious discrepancy with experiment. The algorithm provides a much-needed systematic approach to model construction that can be used to generate models of a large class of amorphous materials.

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Amorphous materials represent a large and important emerging area of materials science.[1] It is an area not amenable to most of the conventional theoretical techniques of solid-state physics—there is no periodicity to simplify the mathematics! This lack of periodicity means that one cannot even determine the structure in the sense that one determines a crystal structure from x-ray diffraction. There are limitless possible structures, but no experimental techniques that provide atomic resolution comparable to crystallography.[2] The best one can do is to determine a one-dimensional radial distribution function (RDF).[3] The main approach to the interpretation of the RDF is the use of models, either hand built or computer generated.[1,3] Thus the importance of a systematic procedure for the generation of an ensemble of realistic models can hardly be overestimated.

Amorphous silicon (*a*-Si) is a particularly interesting and important amorphous material. It is the prototypical covalently bonded amorphous semiconductor and it is the most promising material for a wide range of applications of solar energy conversion. As such, it has been the subject of considerable effort devoted to measurement of its optical, electrical, and vibrational properties.[4–6] Much less has been devoted to the central problem of the nature of its structure.

The experimentally determined RDF's for *a*-Si[7] and *a*-Ge[8] are striking. One might have expected the RDF's to be simply broadened versions of the crystalline RDF's. Indeed, the first and second peaks in the crystalline RDF do appear in the amorphous material as broadened peaks, and the fourth and fifth peaks are broadened and merged into a single peak. But the third peak, which is prominent in the crystalline phase, is missing! Thus, modeling the structure of *a*-Si presents an intriguing problem in space filling.

Numerous attempts have been made to model the structure of *a*-Si. Of the earliest models built, that of Polk,[9] later enlarged by Polk and Boudreaux,[10] seems satisfactory in its main features but, being a finite cluster, suffers from the awkward problems posed by free surfaces. The method of construction also suffers from the bias inherent in any hand-built model. The Henderson model[11] avoids surface problems by including periodic boundary conditions, but it was also hand built. Guttman[12,13] has devised a method for the computer generation of models with periodic boundary conditions, but the approach has apparently not yet produced models of reasonable size (> 200 atoms) having RDF's in good agreement with experiment. The methods of construction of most other models have been discussed or reviewed elsewhere.[1,3] One might have thought that the building procedure would have evolved into a standard one by now, but it is not so. A standard and systematic procedure for model construction is still needed.

Three aspects of the structure of *a*-Si demand attention: the homogeneous structure thought to be typical of the bulk material, the isolated defects it contains, and any gross inhomogeneities due to voids or columnar growth. We have been making an attack on all three aspects of the structure. We describe here a significant step forward in modeling the first of these, the homogeneous structure which is generally believed to be a continuous random network.[1,3]

Continuous random-network structures preserve local order, but bond angles and bond lengths are somewhat distorted. Also, the topology includes fivefold

and sevenfold rings in addition to the sixfold and eightfold rings characteristic of the diamond structure. Models of such structures should contain at least several hundred atoms. Practical experience suggests that this is the minimum size at which useful information on the properties of an infinite network can be obtained. The models should also conform to periodic boundary conditions to avoid the awkward problems posed by free surfaces. With these requirements in mind, we have developed and refined an algorithm that provides a systematic method for the computer generation of realistic models of *a*-Si or *a*-Ge.

Our method differs from earlier approaches in its conceptual simplicity and in the inclusion of a Maxwell-Boltzmann factor which is essential for the construction of models of reasonable size that agree with experiment. Our approach is to start from the diamond structure with periodic boundary conditions build in from the start. We then repeatedly rearrange the structure by the elementary process illustrated in Fig. 1, in which tetrahedral bonding is preserved and five- and sevenfold rings are introduced. Progressive alteration of the diamond structure by random rearrangements of this kind generates a sequence of increasingly distorted models. However, if the process is pursued far enough to destroy all identifiable features of the diamond cubic structure, the result is a grossly distorted network with an rms bond angle deviation of about 22°—about twice what is required.[14]

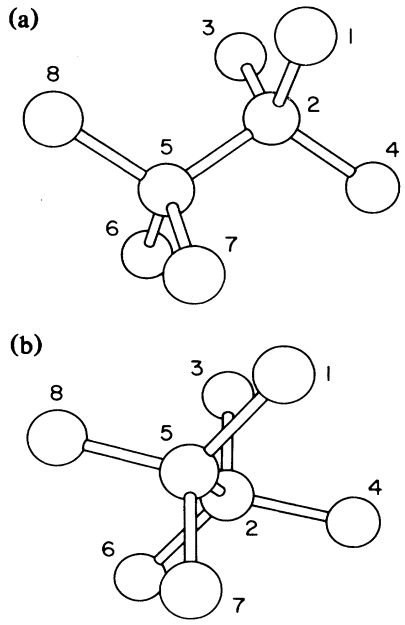

FIG. 1. Local rearrangement of bonds used to generate random networks from the diamond cubic structure. (a) Configuration of bonds in the diamond cubic structure. (b) Relaxed configuration of atoms for a single pair defect.

The first step in the obtaining of a realistic amorphous structure lies in making further rearrangements which lower the energy. Such topological relaxations can reduce the rms angular deviation to near the required value.[15]

In the present study, supercells of 216 atoms were constructed in the diamond cubic structure. After each bond rearrangement, the structure was partially relaxed by use of the Keating potential,[14,16] with a ratio of $\beta/\alpha = 0.285$ for the ratio of bond-bending to bond-stretching force constants.[17]

If the structure is not sufficiently randomized, the imposition of the requirement that all further rearrangements must lower the energy will result in a return to the perfect diamond structure. In rare cases, even an apparently thoroughly randomized structure will return to the perfect diamond structure. Usually, though, it will find its way to a metastable structure whose RDF is remarkably similar to that obtained from experiment for *a*-Si. In such a metastable state, there is no bond switching of the type illustrated in Fig. 1 that will further lower the energy.

The difficulty at this stage is that although the structure is apparently close to that of *a*-Si, it usually has an rms angle deviation of 13° or more, a few degrees greater than experiment suggests. The probability of "cooling" directly to an amorphous structure in good agreement with experiment is very small. We were unsuccessful in several hundred such attempts. Clearly, any method that does not provide a mechanism for the structure to escape from a too highly strained metastable state to a lower-energy state cannot yield models in agreement with experiment.

The solution to further progress is to include a Maxwell-Boltzmann factor $\exp(-E/kT)$, which occasionally lifts the structure out of a metastable state and allows it to find a lower-energy amorphous state. We have found $kT = 0.40$ eV to be a good choice until the structure is approaching agreement with experiment. We then lower kT to 0.25 eV (0.16 eV in the Weber model below). That seems to be the lowest useful nonzero temperature to use.

We have described a procedure for producing structural models by means of a series of well-defined steps. However, these steps need not be disconnected. One could start with the perfect crystal and go directly to the last step in the procedure outlined, namely, the inclusion of the Maxwell-Boltzmann factor. Then, with the choice of a sufficiently high temperature, the structure would first be randomized, much like in melting or ion bombardment. It could then be cooled down and annealed to a stable structure. This approach provides a simple physical picture for the process. It is then much like the Metropolis algorithm[18] applied to optimization by simulated annealing.[19,20] This is a technique that provides a powerful approach

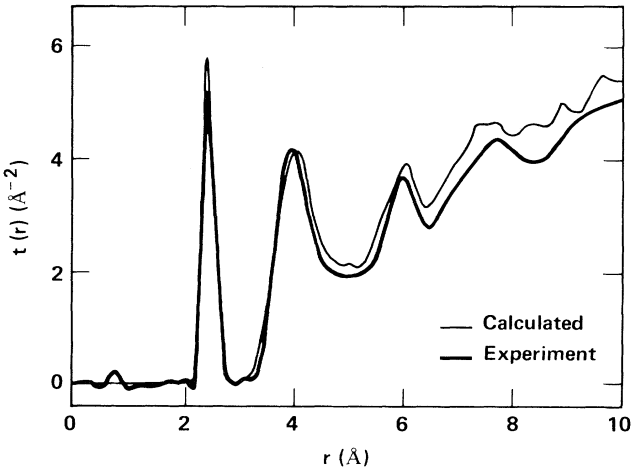

FIG. 2. Comparison of correlation functions for a-Ge (experimental) and a-Si (model scaled to Ge).

to the solution of a wide variety of problems, ranging from statistical mechanics to wiring problems and the design of computers. Here we can apply a variant of that procedure to the modeling of a-Si. However, as a practical matter, in order not to use an excessive amount of computer time, the steps we have outlined provide a more efficient method.

The Keating potential includes only short-range interactions. To explore the effects of long-range interactions, we have relaxed the final structure using a generalization of Weber's adiabatic bond-charge model.[21,22] Here, we see another advantage of periodic boundary conditions, for it would be awkward to include long-range interactions properly in finite clusters without periodic boundary conditions.

The bond-charge model introduces an extra degree of freedom. Since the bond charge need not be directly between the ions (indeed, it cannot be for amorphous structures), the bonds will be "bent" at the positions of the bond charges. This extra degree of freedom permits a narrower deviation in bond lengths with only a small increase in angular distortion—smaller than might have been expected just on the basis of including long-range forces.[14]

The simplest and most direct measure of agreement between models and experiment is a comparison of RDF's. An experimental RDF in the form of the correlation function for a-Ge[3] is shown in Fig. 2. Since the essential difference between a-Ge and a-Si is simply a scaling factor, we also show in Fig. 2 our calculated results for a-Si scaled to model a-Ge. We have included a Gaussian line broadening corresponding to a full width of 0.23 Å at half maximum in order to facilitate comparison with experiment.[3] The resulting correlation function shows no serious discrepancy with experiment apart from the systematic deviation at high r. We believe that the discrepancy is related to inhomogeneities in real a-Si films,[23,24] particularly voids on a scale of, say, 100 Å. We are currently examining this and related experimental questions. Some other characteristics of the model are shown in Table I.

TABLE I. Comparison of model characteristics.

	Keating potential	Weber bond-charge potential
Density relative to crystalline silicon	1.04	1.03
rms angle deviation from tetrahedral	10.9°	11.4°
rms bond-length deviation from crystalline value	2.7%	1.9%

We have described a systematic approach to model building that is applicable to a large class of amorphous materials. It is currently being applied to a-SiO_2 by Thorpe and de Leuuw[25] to study Coulomb effects on the phonon spectrum of glasses. By providing a simple method for the construction of an ensemble of models, it will also provide an objective basis for the investigation of recent conjectures concerning structural anomalies in glass,[26] as well as a number of other issues concerning the structural properties of amorphous materials.

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