# Use of graphics to study structural models of amorphous semiconductors

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*The molecular graphics program Atomlll is applied to the study of structural models of a-Si. The graphics are used to illustrate a novel CRN model-building process and to demonstrate, for the first time, a nonrandom character to the structure of realistic models.*

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Amorphous semiconductors have been the subject of numerous experimental and theoretical investigations in recent years. Amorphous silicon (a-Si) has received particular attention since it is the simplest covalently bonded amorphous solid and serves as an important prototype for investigating the disordered solid state. Any meaningful attempt to interpret the properties of a-Si must be based on a detailed knowledge of its structure. The main approach to the interpretation of structural data (derived from diffraction experiments) has been the use of models, both hand-built and computer-generated[1].

Continuous random network (CRN) models are used in the study of electronic and vibrational states of amorphous materials in part because they agree with experimental structural data better than microcrystalline models. However, few CRN models accurately reproduce more than the first or second peak in the experimental correlation function. Moreover, existing CRN models tend to have much larger angular distortions than experiment would suggest[1]. The lack of a systematic method of model construction has made it difficult to evaluate the effects of structural changes on electronic and vibrational states. In an attempt to improve this situation, a simple, practical and systematic process has been developed for the generation of CRN models of a-Si[2,3]. The models have periodic boundary conditions and, because they are computer-generated, They do not contain the inherent bias found in hand-built models. The process yields structures that are in substantial agreement with experiment and allows ensembles of topologically different models to be produced.

In this paper the model building process is illustrated with pictures generated by the molecular graphics program Atomlll[4]. These pictures provide some insight into the structure of amorphous silicon.

## PICTURE GENERATION WITH ATOMLLL

ATOMLLL is a 5000 line FORTRAN program written for the Cray computer that requires as input a file containing the atom coordinates and colours (white, red, blue, green, yellow, orange, cyan and magenta), sizes for the atoms and bonds and a bonding table. The program generates outlines of the atoms and bonds which can be displayed on a graphics monitor and/or written to tape for further processing into colour prints. Each 216 atom frame required about 45 s of CPU time on the Cray. Atomlll is not an interactive graphics program; however, by stacking input files, one can view a set of frames that represents, say, a rotation of a group of atoms that can approach real-time response for a small number of atoms.

Colour prints or slides can be produced from the output of Atomlll using the program DNI which is run on a Vax 11-750 computer. DNI further interpolates atom and bond boundaries and adds quadratic shading and colour. The Vax is connected to a Dicomed D48-C film recorder that generates an optical image from the DNI output. The image can then be recorded on a variety of output media. The time required for this image processing is about 5 min per 216 atom frame. Both Atomlll and DNI reside in the public domain and are available from the National Energy Software Center, Argonne, IL.

## MODEL GENERATION

The starting point in a 216-atom cubic cell of silicon in the diamond structure, as shown in colour plate 1. The number of atoms in the model is limited only by the available computing time. Through a process of bond-switching[2,3], the structure is 'scrambled' until the calculated correlation function indicates that all traces of the diamond structure have disappeared. In colour plate 2, two bonds have been switched. In colour plate 3 there are ten pairs of bond-switches. After each pair of bonds has been switched, the structure is relaxed using Keating-type interactions[5]. Once an amorphous structure has been obtained, the bond-switching process continues, but with one change. Now only bond-switches that lower the total energy are allowed,

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except for inclusion of a Maxwell–Boltzmann factor, $\exp(-E/KT)$, which occasionally lifts the structure out of a metastable configuration and allows it a chance to find a lower energy state. The model may either return to the diamond structure or remain amorphous. When an amorphous structure is obtained whose correlation function is in good agreement with experiment, the structure is relaxed with Weber's bond charge interactions[6,7] to its minimum energy configuration. The results of such a process are shown in Colour Plates 4 and 5.

This model-building process is well suited for study by computer graphic techniques. Many models can be generated from the same amorphous 'seed', each with a different topology and different structural features. This allows the comparative study of several related models and visual inspection of sets of models is a useful technique for gaining insights into their structure. Apart from a general feeling for the amorphous state, one can gain specific information regarding the structure that may be difficult to obtain by other means.

## STRUCTURAL FEATURES

The preservation of short-range order and the lack of long-range order are characteristic of the amorphous solid state in covalently bonded solids. In amorphous silicon, short-range order means fourfold atomic coordination and the approximate preservation of chemical bond lengths and tetrahedral bond angles. Strains and angular distortions tend to be distributed uniformly in CRN models. This is the case for the models presented in Colour Plates 4 and 5.

The 1D correlation function, which can be derived from neutron diffraction data, provides the most detailed quantitative structural information available experimentally. Structural models generated by the prescription described in the previous section are automatically in good agreement with experiment since this is the sole criterion used in terminating the model construction process.

Other structural measures of CRN models such as the dihedral angle distribution and ring statistics provide quantitiative structural information about the model, but cannot be directly compared with experiment. This information is useful in making quantitative comparisons between different structural models.

Visual inspection does not allow quantitative comparisons with experiment. Even comparisons between different structural models can only be of a highly qualitative nature. Nonetheless, there are some aspects of the structure that can be usefully evaluated by visual inspection.

An analysis of optical and electronic data from a-Si indicates that some residual phase coherence exists between electronic Eigenstates[8]. This is thought to manifest itself through intermediate-range structural coherence between groups of atoms. If such intermediate-range order is present, open channels should exist in the structure[8]. This possibility can be ascertained easily by visual inspection of the model. If the channels are present, a more quantitative analysis can then determine their significance.

In Colour Plates 4 and 5 there are several channels devoid of atoms. They would extend throughout the material as hollow tubes as a result of the periodicity and small size of the unit cell. The possibility that these channels represent intermediate-range order is presently being investigated.

If one constructs a structural model by destroying long-range order while preserving short-range order, it should not be too surprising that some residual intermediate-range order reminiscent of the perfect crystal persists. The preservation of short-range order acts as a constraint on the possible topology of the model which may allow certain symmetries to remain. The largest channels present in the diamond structure are along the [110] direction (see Colour Plate 1 (right)). Since the cubic cell is maintained in the model-building process, one might expect to find similar channels in the amorphous models as well. This is the case for the model presented in Colour Plate 5. The presence of features characteristic of the diamond structure is striking. Hexagonal channels similar to those found in the diamond structure are clearly visible in the [110] direction (see Colour Plate 5 (right)). Some ordering of groups of atoms can also be detected. Elements of diamond-structure-like channels can also be seen in the [100] direction (Colour Plate 5 (left)). The situation is quite different for the model presented in Colour Plate 4, where there is no clear indication of diamond-structure character present.

Although the models in Colour Plates 4 and 5 do have some common features, they differ in one important aspect. Only the model in Colour Plate 5 was topologically relaxed with the Maxwell–Boltzmann factor. This results in the model being significantly better at reproducing the experimental correlation function as well as having a much lower *rms* angular deviation than that of Colour Plate 4.

The structure of CRN models is usually considered to be more or less random. However, it has been shown that completely random structures are in poor agreement with experiment[2]. Similarly, microcrystalline models have reasonable bond length and angle deviations, but again have correlation functions in poor agreement with experiment. Without the inclusion of a Maxwell–Boltzmann factor, structures get stuck in metastable states that are too highly strained. The Maxwell–Boltzmann factor allows structures to find one of the lowest-energy metastable states available and thus is necessary for the construction of models in good agreement with experiment.

The lowest-energy metastable states are, in a sense, on the verge of crystallization. This is clear from the appearance of diamond structure features in Colour Plate 5. If one were to increase the temperature and continue the topological relaxation process for this model, it would soon become the perfect crystal structure by continuing to build upon the elements of diamond structure order already present.

One would think that the presence of any diamond structure character in a model would show up in its correlation function, particularly since the difference between a good and a fair model is often a matter of changing the positions of only a few atoms. However, the correlation function for the model in Colour Plate 5 is closer to experiment than that of any previous model[3].

The regularity in the structure evident in Colour Plate 5 is similar to the observations of Chaudhari *et al*[9]. They concluded that the scattering properties of

amorphous germanium films were adequately described by hand-built CRN models and that the phase coherence of the scattering for the models was associated with the approximate alignment of the atoms into planes. It is now clear that realistic CRN models cannot be completely random.


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