Ab initio generation of amorphous semiconducting structures. The case of a-Si

Fernando Alvarez, Ariel A. Valladares *

Instituto de Investigaciones en Materiales-UNAM, Apartado Postal 70-360, México, DF 04510, Mexico

Abstract

Using a new thermal process and an ab initio molecular dynamics method based on the Harris functional on originally crystalline, periodically continued 64-atom diamond-like cells, we generate amorphous silicon (a-Si) with a 10.0 fs time step. We obtain radial and angular distribution functions and analyze the topology of the models. The radial distribution function (RDF) obtained shows four characteristic experimental peaks and agrees with *all* known experimental results reported up to date. The bond-angle and dihedral distributions are also obtained, as well as the number of n-atom rings. The structures generated have fewer bond defects than those produced from the melt. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Car–Parrinello molecular dynamics and quenching from the melt of 64-atom periodically continued supercells have been a standard procedure to generate amorphous structures of semiconductors. These have the generic shortcomings of radial distribution functions (RDFs) that reproduce, at best, the first two peaks of the experimental results and that only agrees with some of them, an excess of defects, both dangling and floating bonds, and the non-existence of electronic and/or optical gaps, just to mention the most relevant. The pioneering ab initio work of Car and Parinello, no doubt, has permeated all efforts during

the last 15 years, to the point that their annealing processes have been used frequently, almost without questioning.

These methods were applied first to a-Si, a semiconductor that has been studied intensively for the last three decades, both experimentally and theoretically. The scientific and technological relevance of a-Si, pure and hydrogenated, is well known and needs not be emphasized here; early work on the atomic structure of the pure amorphous material started more than four decades ago, both experimentally and theoretically. Experimentally, work on the amorphous phases of pure germanium and silicon evolved in parallel, beginning with the electrolytic approach of Szekely [1] in 1951 and the pioneering efforts of Richter and Breitling [2] in 1958. Theoretically, the first atomic models of both a-Si and a-Ge appeared in the literature over 30 years ago. Grigorovici and

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* Corresponding author.

E-mail address: valla-dar@servidor.unam.mx (A.A. Valladares).

Manaila [3] and Coleman and Thomas [4] in 1968 suggested structures based on arrangements of closely packed simplified Voronoi polyhedra that have the shape of truncated tetrahedra both eclipsed and staggered by 60° about their common bond, leading to rings of five atoms and to boat-like rings of six atoms, as in the carbon and silicon amorphous clusters that we have recently studied [5]. As is well known, fivefold symmetry is non-crystallographic and therefore yields an amorphous-like diffraction pattern with broad maxima. The eclipsed configuration with a fivefold symmetry structure is energetically unfavorable in the crystalline phases but occurs in the amorphous form, since atomic arrangements with a large internal energy can appear in such frozen structures [6].

Several experimental RDFs have been obtained for pure a-Si using a variety of techniques from X-ray to neutron diffraction, in order to comprehend better their atomic structure. A consistent picture has emerged for the atomic structure of a-Si. The experimental works of [7–13] are considered in this paper.

On the theoretical side, there have been ab initio calculations described in Refs. [14–18] for a-Si and they approach the structural problem by generating amorphous cells using first-principles quantum methods. A considerable amount of work, both with classical and quantum techniques, has been done to simulate the atomic structure of a-Si. A knowledge of its atomic topology leads to better and more realistic calculations of the electronic structure of this system. The ab initio methods attempt to answer all the questions from first principles and are generally applicable without adjustable parameters, but are very demanding in computer resources and so are limited to handling relatively small amorphous cells. The question is, how generally can an ab initio method that uses a reasonably sized supercell be applied, and how accurate can one expect the results to be? The present work addresses these issues for a-Si.

2. Method

In this work, we report the generation of a-Si using a new approach that leads to a structure with an RDF in agreement with experiment and with a minimum of coordination defects. We use *Fast-Structure* [19], a DFT code based on the Harris functional [20], and optimization techniques based on a fast force generator to allow simulated annealing/molecular dynamics studies with quantum force calculations [21]. We use the LDA parameterization due to Vosko, Wilk and Nusair [22] (VWN). The core is taken as full which means that an all-electron calculation is carried out, and for the amorphization process a minimal basis set of atomic orbitals was chosen with a cutoff radius of 5 Å (compared to values of ≈ 2.6 Å used by Sankey and coworkers, see e.g. [23]), a compromise between cost and accuracy. For the optimization process, a cutoff radius of 3 Å was utilized. The physical mass of silicon is used throughout and the default time step is given by $(m_{min}/5)^{1/2}$, where m_{min} is the value of the smallest mass in the system, i.e., 2.44 fs. However, in order to simulate better the dynamical processes that occur in the amorphization, a time step of 10 fs was used. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional, as discussed by Lin and Harris [24]. The evaluation of the 3-center integrals that contribute to the matrix elements in the one-particle Schrodinger equation is the time-limiting feature of *FastStructure* and each is performed using the weight-function method of Delley [25].

Since it is clear that quenching from a melt or from partially melted samples generates undesirable structures, we took a different path. Our process is not designed to reproduce the way an amorphous material is grown, but has the objective of generating an amorphous sample that would represent adequately the ones obtained experimentally. We amorphized the crystalline diamond structure with 64 silicon atoms in the cell (a crystalline density of 2.33 g/cm³) by slowly heating it from 300 to 1680 K, well above the glass-transition temperature and just below the melting point, in 100 steps of 10 fs, and immediately cooling it down to 0 K in 122 steps of 10 fs. The heating/cooling rate was 1.38×10^{15} K/s. The atoms were allowed to move freely within each cell of volume $(10.8614 \text{ Å})^3$ with periodic boundary conditions. Once this first stage was completed,

we subjected each cell to annealing cycles at 300 K (below microcrystallization) with intermediate quenching processes. Finally a geometry optimization was carried out to find the local energy minimum of the amorphous structure.

3. Results

The RDF obtained from our simulation agrees very well with experiment from 0 to 10 Å, Fig. 1 (cell length = 10.8614 Å). We Fourier-smoothed the RDF to have adequate curves to allow comparison with experiment, since the number of atoms in the cell leads to statistical fluctuations that are not representative of the bulk. In Fig. 1 we present a direct comparison of our results with the upper and lower experimental bounds from [8–14] and, considering that not all experimental results cover the range 0–10 Å, the agreement is excellent, including the existence and position of the third and the fourth amorphous peaks. The evolution of the crystalline peaks can also be observed and the first crystalline peak remains as the most prominent feature in the amorphous material. The sec-

ond crystalline peak also remains but is widened and highly diminished since it contributes to filling in the first and second crystalline valleys. The third crystalline peak disappears to contribute to the valleys between the second and third and the third and fourth crystalline peaks, and the fourth crystalline peak disappears to contribute to filling in the valleys between the third and fifth crystalline peaks. The fifth crystalline peak generates a third amorphous peak slightly displaced to smaller distances, etc.

Fig. 2 is a representation of the number of bond angles for values of the angles from 60° to 180°. It should be remembered that the crystalline bond angle is 109.47° and there are two prominent peaks between 90° and 110°. The 90° contributions are due in part to the existence of 4-atom rings. We have studied the bond angles for over and under coordinated atoms, and these values are shown in the figure.

The dihedral-angle distribution is shown in Fig. 3 where it can be observed that for this sample the distribution is practically constant, with some peaks around 70° reminiscent of the 60° crystalline dihedral angle.
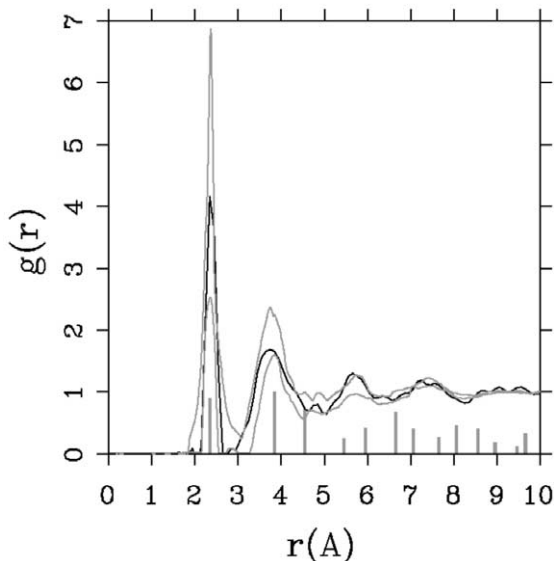

Fig. 1. RDF for a-Si. The lighter lines are the experimental upper and lower bounds [27] and the dark line is our simulation. Crystalline peaks are also included.
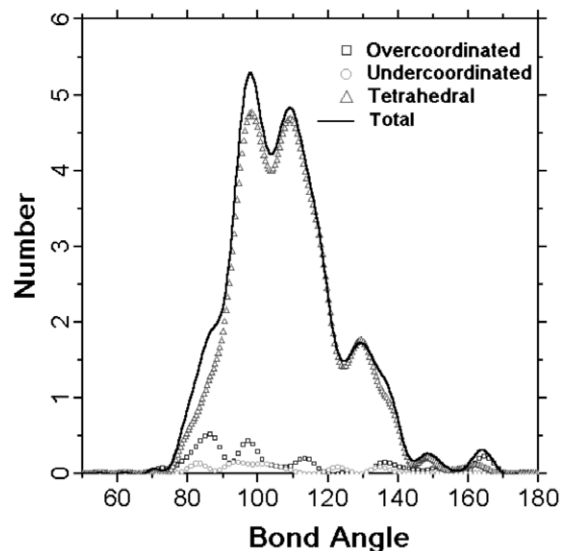

Fig. 2. Bond-angle distribution. Three peaks due to tetrahedral bonds are clearly observed. The contribution due to over-coordinated atoms can also be observed.
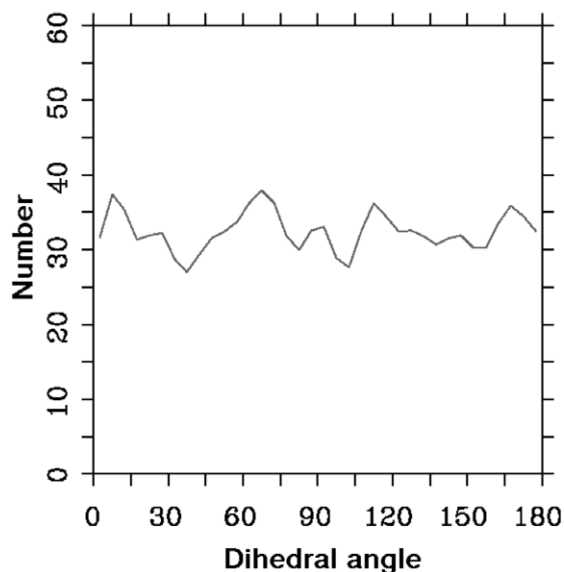
Fig. 3. Dihedral-angle distribution. A subtle peak at about 60°
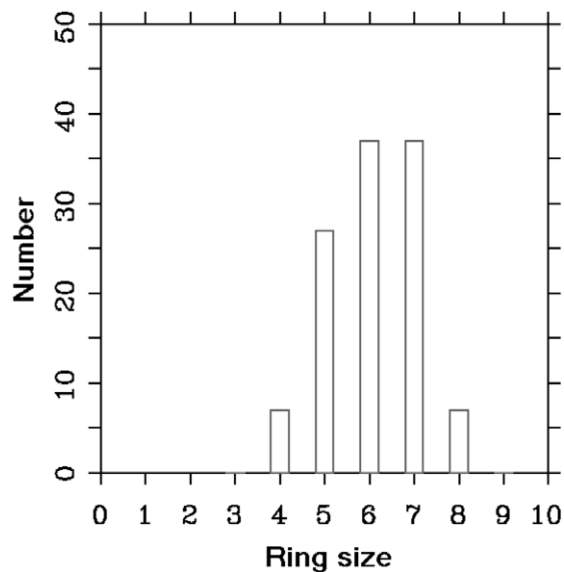can be observed, a remnant of the crystalline structure.

Fig. 4. Number of rings as a function of ring size. The number
of 6- and 7-atom rings is practically the same, whereas the 5-
atom rings are also prominent in the structure. 4- and 8-atom
rings are also present.

This sample contains rings that are formed by a
number of atoms different from 6, the crystalline
value. Fig. 4 gives the number of simple rings in
the sample; there are only 4, 5, 6, 7 and 8 atom
rings in this structure. It can be observed that the
6- and 7-atom rings are the most prominent and
are practically the same; the 5-atom rings are next
in relevance.

4. Discussion

Generating a clean gap in 64-atom cells is dif-
ficult since bonding defects always appear in the
simulations; the most one can hope for is to min-
imize the number of these defects to obtain a
reasonably clean electronic gap. Now, defining a
dangling or a floating bond is to some extent ar-
bitrary since one has to choose some representa-
tive interatomic distance; Drabold et al. [15]
chose an interatomic distance of 2.7 Å, although
no clear justification is given. Lee and Chang [18]
use the distance at which the minimum between the
first and second peaks of the RDF occurs, 2.73 Å,
which leads to an average number of nearest
neighbors in the amorphous cell of 3.9. Were one
to use the minimum value of the RDF of Fedders

et al. [17], $\approx 1.2 \times 2.35 = 2.82$ Å, it is certain that
the number of defects reported by Drabold and
coworkers would have changed significantly. An
analysis of structural defects versus spectral de-
fects was performed by these authors who con-
cluded that dangling bonds give rise to defects
within the gap, that some strained tetrahedral
structures may also generate gap states, and that it
seems that floating bonds do not create gap states.
Recent work, however, indicates that floating
bonds may also generate gap states [26,27].

Our amorphous cell has 3 dangling bonds and 3
floating bonds for a cutoff radius of 2.56 Å; up to
this distance the average number of nearest neigh-
bors, the area under the first amorphous peak, is
equal to 4.

The bond-angle distribution, Fig. 2, presents
two major peaks and one intermediate due to tet-
rahedrally bonded atoms, and minor peaks due
to overcoordinated atoms, or atoms with floating
bonds. The contributions of undercoordinated
atoms, or atoms with dangling bonds, are more or
less evenly distributed and do not possess a well-
defined peak for any angle.

The fact that the dihedral-angle distribution is more or less constant indicates that the probability of any angle is practically the same; in other words, no clearly preferred dihedral angle is observed for this structure. It is well known that for crystalline materials, with boat-like rings, the dihedral angle is 60°.

Finally, the existence of a large, comparable number of 6- and 7-atom rings and the clear presence of 5-atom rings in this structure clearly indicates a departure from crystallinity. a-Si does possess clathrate-like atomic structures, unlike amorphous carbon, for example.

5. Conclusions

Dealing theoretically with a covalent amorphous material in bulk is difficult because there are many possible structures for a given RDF. Classical and semiempirical random-network models have achieved considerable success in generating a-Si structures but these models are not easily generalized to other glassy materials or systems with different species of atoms. For that reason the simulation of any covalent amorphous semiconductor in the bulk, both pure and alloyed, has encountered serious obstacles. In the present work, we have been able to perform an ab initio simulation of the atomic structure of a-Si and of its atomic RDF that reproduce many experimental features. In particular, our RDF agrees very well with the corresponding experimental distributions up to the third and fourth peaks, as can be seen in the direct comparisons made in Fig. 1.

The procedure that we used to generate the structure is different from the ones found in the literature and leads to amorphous samples with fewer dangling and floating bonds. It consists of heating a crystalline sample of 64 atoms of silicon just below its melting temperature and then cooling it down to 0 K with subsequent annealing and quenching cycles at temperatures dictated by experiment. At the end, a geometry optimization is performed to find the local energy minimum.

We believe that our procedure can be generalized to other monatomic or diatomic amorphous semiconducting materials and therefore allows our

process, and ab initio technique, to be used in other areas to provide more representative structures and a more complete description of their atomic characteristics than is possible with parameterized methods. Furthermore, ab initio simulations can be used to provide the parameters needed in non-ab initio techniques to be able to handle larger amorphous cells.

Acknowledgements

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