Structural, Dymanical, and Electronic Properties of Amorphous Silicon: An *Ab Initio* Molecular-Dynamics Study

R. Car and M. Parrinello
Scuola Internazionale Superiore di Studi Avanzati, Trieste 34014, Italy

(Received 31 August 1987)

An amorphous silicon structure is obtained with a computer simulation based on a new molecular-dynamics technique in which the interatomic potential is derived from a parameter-free quantum-mechanical method. Our results for the atomic structure, the phonon spectrum, and the electronic properties are in excellent agreement with experiment. In addition we study details of the microscopic dynamics which are not directly accessible to experiment. We find in particular that structural defects are associated with weak bonds. These may give rise to low-frequency vibrational modes.

PACS numbers: 61.40.+b, 63.50.+x, 71.25.Mg

A very important problem in the physics of amorphous semiconductors is the understanding of the way short-range order (SRO) is incorporated in the disordered network.[1] Many of the characteristic properties of amorphous semiconductors depend crucially on SRO. However, despite the very substantial progress made in the field over the last twenty years, our understanding of SRO and of how it affects structural and electronic properties is still largely incomplete. Experimentally, the presence of disorder means that one can measure only averaged properties and an accurate determination of the individual atomic coordinates is impossible. Yet a quantitative characterization of the atomistic disorder, i.e., an accurate microscopic model of the amorphous network, is a prerequisite of any quantitative theoretical approach to the properties of amorphous semiconductors.

Not surprisingly, a large effort has been devoted to the attempt to construct structural models of disordered semiconductors. Some of the more systematic approaches in this area make use of interatomic potentials in conjunction with molecular dynamics (MD)[2] or Monte Carlo[3] techniques that allow simulation of thermal treatments similar to those used in laboratories to prepare glasses. The main difficulty relies on the need for realistic interatomic potentials. So far these have been constructed empirically,[4] trying to model the complex many-body interatomic interactions by means of a few simple potential functions whose parameters are fitted to experimental data. Although very useful, such an approach suffers some basic limitations since (i) it is difficult to assess the range of validity of the empirical potentials, and (ii) the approach does not explicitly display the dependence existing in nature between bonding electronic properties and atomic dynamics. This may be particularly important in covalent semiconductors.

These limitations are overcome in a first-principles MD scheme that we have recently proposed.[5] In this approach the interatomic potential is constructed directly from the electronic ground state, and this is treated with accurate density-functional techniques such as those used in electronic-structure calculations. We have already shown in a preliminary report[6] that both liquid and amorphous silicon can be simulated in this way.

Here we focus on the numerical simulation of amorphous silicon and present results for a number of properties ranging from atomic to electronic structure. Our calculated radial distribution function (RDF) and phonon spectrum are in excellent agreement with experimental neutron-diffraction studies, showing that not only static but also dynamic properties of disordered systems may be obtained in this way. Quite remarkably our calculated electronic density of states reproduces both the metallic character of the liquid and the presence of a gap in the amorphous state. In addition we study coordination defects and topological properties of the computer-generated disordered network. Our findings have a number of consequences concerning both the nature of defects and the low-T and vibrational properties of amorphous silicon.

The theoretical method and the computational details have already been discussed elsewhere[5,6] and will not be further elaborated here. Basically we perform a constant-volume MD simulation for both the particles and the electronic orbitals belonging to a periodically repeated unit cell. As in standard MD simulations of condensed matter systems, this is justified if the unit cell is large compared with the longest relevant length scale of the problem, either electronic or atomic.

The present simulation was started from the liquid silicon data at an average temperature of ≈ 2200 K already described in our earlier report.[6] These were in fair agreement with experiment, even though the theoretical RDF was more structured than the experimental one and, correspondingly, the average coordination number was 5.4 instead of 6.4. The origin of such discrepancies is not yet completely understood. The liquid data were obtained with use of an fcc cell containing 54 atoms in a volume appropriate to liquid silicon at the melting point ($\Omega = 1033$ Å^3). We used an accurate nonlocal pseudopotential[7] and adopted for exchange-correlation effects the parametrized local-density form of Perdew and Zunger.[8] We used a plane-wave expansion of the electronic states at $k=0$ with an energy cutoff of 5.5 Ry. Surface[9] and crystal[10] calculations have shown that such a cutoff, albeit not enough for perfect convergence, is sufficient for a reasonably good description of the bonding properties in silicon. The integration of the generalized MD equations[5] was performed with the Verlet algorithm and a time step of 1.7×10^{-16} s, while the "mass" parameter for the electronic degrees of freedom was set equal to 300 a.u.

An amorphous structure was generated by our quenching from the melt, as in Ref. 6, but starting from a different liquid configuration. This was obtained by our letting the liquid evolve for $\approx 0.7\times10^{-12}$ s after the configuration used in Ref. 6. Each atom in the box moved on average by two bond lengths during such a time interval. The thermal treatment consisted of a quench from ≈ 2200 to ≈ 300 K at a cooling rate $\approx 2\times10^{+15}$ K/s, followed by an annealing cycle in which the temperature was raised to ≈ 1000 K before performance of a final equilibration at a temperature of ≈ 300 K. During the initial quenching, the volume of the cell was gradually increased to the value $\Omega = 1080$ Å^3, which is more appropriate to amorphous silicon.[11] The total thermal treatment took $\approx 2\times10^{-12}$ s during which each atom in the box moved on average by more than one bond length, a substantial distance. The structure so obtained is different from the inherent structure of the liquid.[12] Compared to Ref. 6 this new amorphous structure has been obtained with a more careful annealing and the volume variation in the process of amorphization has also been considered. Even so, the newly generated amorphous structure is remarkably similar to that of our earlier report. The most noticeable difference is a substantial reduction in the number of coordination defects in the new structure as a consequence of the additional relaxation and of the more careful annealing. Accurate structural data on tetravalent amorphous semiconductors are available in real space only for *a*-Ge.[13] Since no RDF of corresponding quality has to our knowledge been reported for *a*-Si, we suitably scale our simulation data and compare them with the experimental *a*-Ge data in Fig. 1. The agreement between theory and experiment is very good. Both data sets reveal the disappearance of the third crystalline coordination shell. The area under the first peak of the RDF gives a local coordination of four in both cases. The main difference between theory and experiment is a slightly broader second peak in the theoretical data, which reflects a broader distribution of bond angles around the tetrahedral angle with an rms deviation of ≈ 14° whereas experiment gives an rms deviation of ≈ 10°. This may be a consequence of the preparation and/or the small size of our unit cell. Because of the size of our MD cell, we cannot study distances that are larger than ≈ 6 Å. Since the experimental RDF suggests that SRO effects are present up to distances of ≈ 10 Å, it would be very interesting to perform simulations with larger cells.

Recently the vibrational spectrum of *a*-Si has been measured by inelastic neutron scattering.[14] In our simulation it is relatively easy to obtain the phonon density of states (PDOS) by taking the Fourier transform of the velocity autocorrelation function: $\langle v(0)v(t)\rangle$. The results are displayed in Fig. 2. Again the agreement between theory and experiment is remarkable. The main difference is an almost rigid shift by ≈ 50 cm^{-1} of the theoretical TA peak toward higher frequencies. This is likely to be a consequence of the small cutoff used for the plane-wave expansion, as suggested by the perfect-

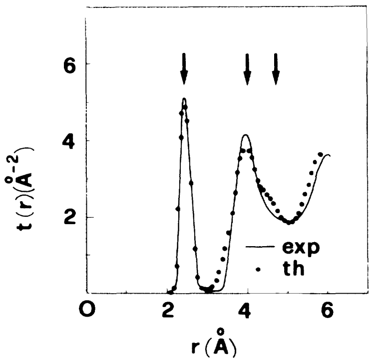

FIG. 1. Plot of $t(r) = 4\pi\rho r g(r)$, where ρ is the average density and $g(r)$ the pair correlation function. Experimental data are for *a*-Ge (see text) (Ref.13) and the theoretical *a*-Si data have been properly scaled. The theoretical curve has been convoluted with the experimental resolution function (Ref.13). Arrows indicate peak positions in the perfect crystalline structure.

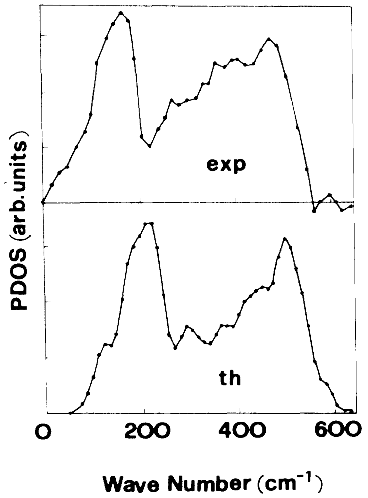

FIG. 2. Theoretical and experimental (Ref.14) phonon density of states. A Gaussian broadening of width 40 cm^{-1} has been used to smooth the theoretical density of states.

crystal phonon calculations by Yin and Cohen.[10] Note that the theoretical PDOS decays to zero more rapidly than the experimental one at low frequencies, because of the low-frequency cutoff set by the finite MD observation time for the velocity autocorrelation function. We observe that the relative strength of the TA and the TO peaks is correctly reproduced in our data, whereas all model calculations assign a larger amplitude to the TO peak.[14,15] It is tempting to relate this to structural defects present both in our simulation and in experiment and which are instead absent in conventional models. These defects can give rise to low-frequency modes which result in a transfer of oscillator strength from higher to lower frequencies. This is indirectly confirmed by the low-frequency shoulder in the TA peak, which is quite prominent in our data and is also present in experiment. An increase in the density of low-frequency vibrational modes with respect to the crystalline case is a common feature of amorphous systems and can be seen, for instance, in low-T measurements of the specific heat.[1]

Trying to discover the structural defects that might be responsible for the above behavior, we have identified two weak bonds which are well separated in space and are associated with coordination defects. The time variation of these two bond lengths r_b is plotted in Fig. 3, and it is seen to undergo large variations on a rather long time scale. If we assign to the first coordination shell all bond distances that are smaller than r_m, where $r_m = 2.75$ Å is the first minimum position in the RDF, we find that in these two stretched bonds the partner atom can have coordination 3 and 4, or 4 and 5, for $r_b > r_m$ or $r_b < r_m$, respectively. Therefore, the ample variations observed in r_b lead to a continuous switching from a threefold coordinated atom (T_3) to a fivefold one (T_5) and vice versa. A recent suggestion[16] that T_5 defects might exist and play an important role in a-Si[16] has attracted considerable interest. Our data confirm that T_3 and T_5 should have comparable formation energies and may be converted into one another via network distortion.[16] However, we find that T_3 dominates on the average, and that the average length of our weak bonds ($\approx 2.8-2.9$ Å is considerably smaller than that expected for an ideal isolated dangling bond pointing into a microvoid or residing on an internal surface. Consequently the wave function associated with such defects will be more delocalized than for a dangling bond. This is quite consistent with the discussion on the localization of the D-center wave function in Ref. 16. However, when comparing our findings with experiment one must be careful. It is very likely that the type and concentration of defects depend on the size of the system and the annealing procedure. Clear evidence is that in the simulation we find an unrealistically high concentration of defects. In addition, intermediate-range order effects, like, e.g., voids occurring on a 100-Å scale, may play an important role in real amorphous systems.[1] Nonetheless, our calculation is highly suggestive of the nature of defects that may be found in real-life a-Si.

In our Md scheme one generates not only a sequence of atomic configurations but also the corresponding electronic self-consistent potentials. These may then be used to study electronic properties. A striking difference between liquid and amorphous silicon is that the former is metallic while the latter has semiconducting character. We were able to reproduce this feature in our simulation. In Fig. 4 the electronic density of states (EDOS) of liquid Si is displayed together with that of our equilibrated a-Si. These EDOS have been calculated as an average over several atomic configurations for both liquid and amorphous silicon. The change in electronic structure that accompanies the change in atomic arrangement as the system becomes amorphous is remarkable, since in

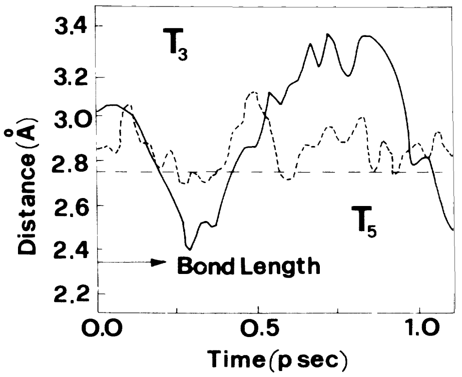

FIG. 3. Weak-bond length as a function of time for the two defects found in the computer simulation. The dash-dotted line is the conventional divide at 2.75 Å between T_3 and T_5 defects. The bond-length distance is also indicated in the picture.

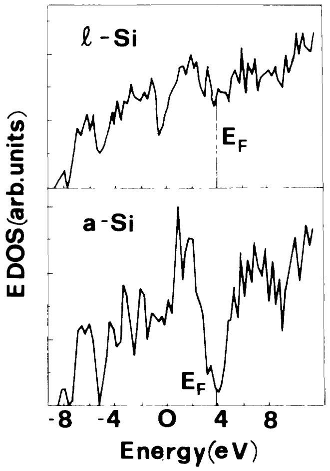

FIG. 4. Electronic density of states for liquid (l-Si) and amorphous silicon. The energy resolution in the histogram is 0.27 eV. The averages have been calculated over 12 and 32 different configurations for l-Si and a-Si, respectively.

a-Si a gap opens at the Fermi level while liquid-Si EDOS exhibits metal-like behavior. A rather similar EDOS for liquid Si has also been calculated by Broughton and Allen[17] using a more conventional approach in which the atomic positions were generated in an MD run that used effective potentials and the electronic levels were subsequently determined with an empirical tight-binding method. Their results are similar to ours, but it must be stressed that in our approach the atomic positions and the electronic states are the result of a single and self-consistent procedure. The formation of a gap in *a*-Si is accompanied by a marked increase in the localization of the wave functions belonging to gap states. This was checked by measurement of the participation ratio.[18] The localized states are absent in the liquid, suggesting that the metallic behavior should be associated with the presence of diffusive motions and the resulting overcoordination. The gap states in our amorphous structure are due to localized defect states induced by the weak bonds discussed above. The rather large concentration of gap states is simply a consequence of the large concentration of defects in our simulated amorphous structure. The poor energy resolution in the EDOS is a consequence of our small unit cell and limited statistics. This does not allow us to say anything conclusive concerning the shape of the EDOS in the lower valence-band region. It has been suggested[19] that experimental x-ray photoemission spectra in that region might provide evidence for the existence of odd-membered rings in the amorphous network in addition to the even-membered rings typical of the diamond structure. Even if we cannot say how odd-membered rings correlate with the EDOS, an analysis of the ring statistics of our amorphous structure has revealed a significant fraction of odd-membered rings with a dominance of fivefold rings.[12]

In conclusion, we have demonstrated that first-principles studies of disordered systems are feasible and may yield valuable information. A distinctive feature of our approach is that it treats simultaneously and in a consistent way both atomic and electronic properties: The agreement with experiment found consistently for several properties either atomic and electronic is therefore particularly encouraging. An analysis of the data obtained with the computer simulation has allowed a first realistic microscopic identification of structural defects that may be responsible for several observed properties of amorphous semiconductors. Extensions to larger cells and to different systems and processes are now underway.

This work has been supported by the Scuola Internazionale Superiore di Studi Avanzati–Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale collaborative project, under the sponsorship of the Italian Ministry for Public Education.

---

[1] See, e.g., N. F. Mott and E. A. Davis, *Electronic Processes in Noncrystalline Materials* (Clarendon, Oxford, 1979), and review articles, e.g., in *Amorphous Semiconductors,* edited by M. H. Brodsky (Springer-Verlag, Berlin, 1985).

[2] K. Ding and H. C. Andersen, Phys. Rev. B **34**, 6987 (1986).

[3] F. Wooten, K. Winer, and D. Weaire, Phys. Rev. Lett. **54**, 1392 (1985).

[4] Empirical potentials for silicon have been recently constructed by F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985); R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001 (1985); J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).

[5] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[6] R. Car and M. Parrinello, in *Proceedings of the Eighteenth International Conference on the Physics of Semiconductors, Stockholm, 1986,* edited by O. Engstrom (World Scientific, Singapore, 1987), pp. 1165–1172.

[7] D. R. Hamann, M. Schlueter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[8] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[9] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 2303 (1981).

[10] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 3259 (1982).

[11] This is the volume appropriate to crystalline silicon. In real amorphous silicon the density is lower because of the presence of microvoids (Ref. 1).

[12] I. Stich, R. Car, and M. Parrinello, to be published.

[13] J. H. Etherington, A. C. Wright, J. T. Wenzel, J. C. Dore, J. H. Clarke, and R. N. Sinclair, J. Non-Cryst. Solids **48**, 265 (1982).

[14] W. A. Kamitakahara, H. R. Shanks, J. F. McClelland, U. Buchenau, F. Gompf, and L. Pintchovius, Phys. Rev. Lett. **52**, 644 (1984).

[15] K. Winer, Phys. Rev. B **35**, 2366 (1987).

[16] S. T. Pantelides, Phys. Rev. Lett. **57**, 2979 (1986).

[17] J. Q. Broughton and P. B. Allen, in *Computer-Based Microscopic Description of the Structure and Properties of Materials,* edited by J. Q. Broughton, W. Krakow, and S. T. Pantalides, MRS Symposium Proceedings Vol. 63 (Materials Research Society, Pittsburgh, 1986).

[18] R. J. Bell and P. Dean, Discuss. Faraday Soc. **50**, 55 (1970).

[19] J. D. Joannopoulos and M. L. Cohen, Phys. Rev. B **7**, 2644 (1973); for a review, see J. D. Joannopoulos and M. L. Cohen in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1976), Vol. 31, pp. 71–148.