PHYSICAL REVIEW B VOLUME 36, NUMBER 8 15 SEPTEMBER 1987-I

Amorphous-silicon formation by rapid quenching: A molecular-dynamics study

Mark D. Kluge and John R. Ray
Kinard Laboratory of Physics, Clemson University, Clemson, South Carolina 29634

Aneesur Rahman
Supercomputer Institute and School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455
(Received 13 April 1987)

We have studied the formation of amorphous silicon by rapid quenching of the melt using the Stillinger-Weber potential to model the interaction between silicon atoms. By quenching the melt at a rate of 3×10^{14} K/s we form amorphous silicon. Excellent agreement with the experimental neutron scattering structure factor is obtained. In our sample of amorphous silicon, approximately 88% of the atoms have a coordination number of 4 while 12% have a coordination number of 5. The distribution in space of the fivefold-coordinated atoms is not uniform.

I. INTRODUCTION

Stillinger and Weber[1] have developed an effective potential-energy function to describe the solid and liquid forms of silicon. The potential-energy function includes both two- and three-body interactions. Stillinger and Weber employed their potential in molecular-dynamics computer-simulation studies of the melting and the inherent structure underlying the liquid phase of silicon.

Other workers have used the Stillinger-Weber potential to study other properties of silicon using molecular-dynamics and Monte Carlo methods. Landman *et al.*[2] studied the faceting at the silicon (100) crystal-melt interface. Abraham and Broughton[3] explored the pulsed melting of silicon (111) and (100) surfaces. Dodson and Taylor[4] studied the stability of coherently strained layers of mismatched silicon. Kluge, Ray, and Rahman[5] have determined the elastic constants at three different temperatures of crystalline silicon.

The Stillinger-Weber potential is a first attempt at constructing a potential for silicon to be used in computer simulation studies of solid and liquid silicon. Biswas and Hamann[6] and Tersoff[7] have presented specific proposals for obtaining a potential which could more accurately model silicon. Other more fundamental work by Car and Parrinello[8,9] combines molecular dynamics and density-functional theory to give a combined quantum description of the electrons and a classical description of the ions.

The Stillinger-Weber potential includes two- and three-body terms which have the form

$$U_2(r_{ab})=A(Br_{ab}^{-p}-r_{ab}^{-q})h_\beta(r_{ab}) , \tag{1}$$

$$U_3(r_{ab},r_{ac},r_{bc})=h_{cab}+h_{abc}+h_{bca} ,$$
$$h_{cab}=\lambda h_\gamma(r_{ab})h_\gamma(r_{ac})(\cos\theta_{cab}+\tfrac{1}{3})^2 , \tag{2}$$

where r_{ab} is the distance between atoms a and b, $h_\delta(r)=e^{\delta(r-a)^{-1}}$ for $r<a$ and vanishes for $r>a$; θ_{cab} is the angle between the vectors $\mathbf{r}_{ab}$ and $\mathbf{r}_{ac}$. In Eqs. (1) and (2) r is expressed in dimensionless units where the unit distance is 2.0951 Å, the energy is expressed in dimensionless units where the unit of energy is 3.4723×10^{-12} ergs. Stillinger and Weber indicated that they carried out a limited search over the parameters in Eqs. (1) and (2) to obtain the values $A=7.049\,56$, $B=0.602\,225$, $p=4$, $q=0$, $\beta=1$, $a=1.8$, $\lambda=21$, and $\gamma=1.2$. Note that the three-body energy Eq. (2) vanishes for the perfect tetrahedral angle $\cos\theta=-\frac{1}{3}$.

II. LIQUID SILICON

The Stillinger-Weber potential provides a method of studying the solid to liquid phase transformation as well as the structure of the liquid. The solid melts at approximately the correct temperature; we find a value of the melting temperature of 1750 K compared with the experimental value 1683 K. The liquid possesses the approximate structure of real liquid silicon as was discussed by Stillinger and Weber.[1] To illustrate this agreement we show in Fig. 1 the comparison of the liquid structure factor as calculated using the Stillinger-Weber potential and the experimental x-ray results of Waseda and Suzuki.[10] While there are discrepancies between the observed and calculated results in Fig. 1 it is difficult to judge their significance since it is not easy to estimate the errors in the experimental structure factor given by Waseda and Suzuki.[10] For example, later neutron measurements of the structure factor of molten silicon have been carried out and reported by Gabathuler and Steeb.[11] There are significant differences between these two sets of measurements of the structure factor. Thus more experimental work seems to be called for in this area before we can assess the importance of the differences in Fig. 1.

III. AMORPHOUS SILICON

In this paper, we are mainly interested in the formation of amorphous silicon. We have recently studied the formation of Stillinger-Weber amorphous silicon by rapid cooling of the melt using molecular dynamics with periodic boundary conditions. We used the same system size of 216 particles as in Ref. 5. We used the Andersen[12]

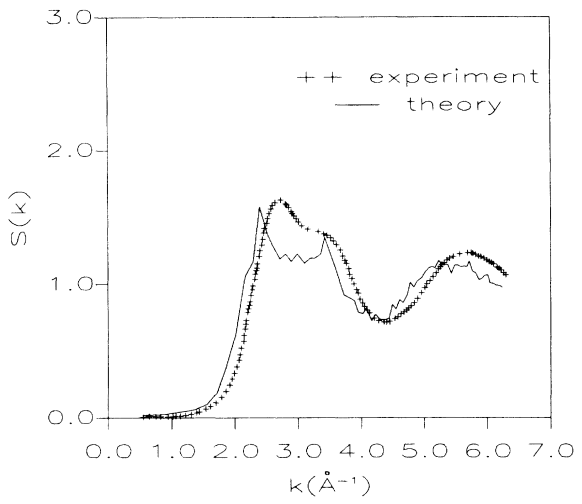

FIG. 1. A comparison of the x-ray-scattering structure factor for melted silicon from Ref. 10 with the Stillinger-Weber result. The temperature of the experimental sample was 1733 K. The temperature of the sample in our calculation was 1850 K.

constant-pressure form of molecular dynamics with a cubic computational cell in the calculations discussed in this paper. We also used the Parrinello-Rahman[13] form of molecular dynamics which allows for a variable shape and size of the computational cell in other calculations; the same general results were obtained in both studies. These calculations were all carried out at zero pressure.

In order to form amorphous silicon using molecular dynamics we first melted crystalline silicon to produce molten silicon at a temperature of 1850 K. Next we equilibrated the melt. We recall that the density of silicon increases by about 10% upon melting due to partial collapse of the rather open tetrahedral structure. The Stillinger-Weber potential predicts a 5% density increase, that is, the density of the crystal was 2.32 g/cm^3 whereas the molten state had a density of 2.44 g/cm^3. The liquid was next cooled to 972 K at a rate of 3×10^{14} K/s to form what we shall refer to as an intermediate state. This intermediate state corresponds to a supercooled liquid. The system in the intermediate state shows gradual changes in time; a slow diffusion and a slow rise in temperature. Note that there are significant differences between the intermediate state and the liquid state since the coordination has changed from the liquid value of 7.7 to a value of 4.7 in the intermediate state. Since the density of amorphous silicon (which is free of voids) is close to the density of crystalline silicon, we expanded the system by the application of negative pressure to reduce the density and thereby hasten transformation to the amorphous state. After equilibration of the system at this lower density, the temperature of the system was reduced to 472 K and the pressure removed. The system at this cooler temperature was then equilibrated at zero pressure and found to have a density of 2.29 g/cm^3 at zero pressure. The density of ideal amorphous silicon without voids has been reported to be 2–10% less than for crystalline silicon.[14] The density of Stillinger-Weber crystalline silicon at 500 K is 2.31 g/cm^3. Therefore we find that our sample of amorphous silicon has a density 1% lower than crystalline silicon at the same temperature. Also the system showed no diffusion. If the application of pressure to the intermediate state is nor carried out then we do not see a decrease in density after cooling from 972 to 472 K; that is, if the above-mentioned intermediate state is cooled to 472 K without the expansion then its density becomes 2.45 gm/cm^3; it therefore remains a supercooled liquid. The expansion of the system is necessary in order for the system to reorganize into the amorphous structure in a reasonable amount of computer time. The structure factor and radial distribution function along with other properties were then determined for this state of the system. We shall refer to the system in this state as amorphous silicon.

A sample was also prepared using the same annealing process except the Parrinello-Rahman variable shape and size molecular dynamics was employed. An amorphous structure with the same general properties was obtained. Also, in order to study the influence of the cooling rate, we reduced the cooling rate by $\frac{1}{20}$ of the previously stated value and performed the same annealing process. At this lower cooling rate of 1.5×10^{13} K/s, we observed the same general behavior of the system during the annealing process. This is not in disagreement with experimental results which show that amorphous silicon is formed by laser glazing[15] at the slower cooling rates of 10^{12} K/s.

One of the most useful quantities to monitor during the above annealing process is the three-body energy. As mentioned previously, the three-body energy vanishes in the perfect diamond structure. In the hot solid at 1450 K the three-body energy has an average value of 9.7 in the units given above. In the molten state the three-body energy has an average value of 138. This large increase in the three-body energy is mainly due to the breakdown of the tetrahedral structure. In the intermediate state the three-body energy has an average value of 101. Finally, in the amorphous structure the three-body energy has an average value of 39.2.

Another way to categorize the changes in the system which give rise to these changes in the three-body energy is to look at the fraction of the particles in the system having four nearest neighbors. In the crystal this is 100%, in the melt 0.5%, in the intermediate state 42%, and in the amorphous solid 88%. In the amorphous solid, we find that 88% of the atoms have a coordination number of 4 while 12% have a coordination number of 5. In particular, we do not find atoms having a coordination number of 3. This should be contrasted with the results in Ref. 9 where the coordination number of 3 is found in a computer-simulation study of amorphous silicon. In our other sample obtained using the variable shape and size molecular dynamics, we found approximately these same percentages for the amorphous state. In order to define the coordination number, one much choose a cutoff distance such that particles closer than this distance are called first nearest neighbors. By a study of the radial distribution, we selected this distance for each of the states of silicon involved in our study. These neighbor

TABLE I. A summary of the properties of the four states of silicon used in the process of forming amorphous silicon. The first-neighbor cutoff distances were determined by a study of the radial distribution function. The fraction of atoms having a coordination number of 4 and the three-body energy are inversely related as expected. The average coordination number is the value of the coordination number out to the first-nearest-neighbor cutoff distance.

State	T (K)	ρ (g/cm^3)	Three-body energy (3.47×10^{-12} ergs)	Range used for calculating neighbors (2.0951 Å)	Number fourfold coordinated atoms (%)	Average coordination No. at neighbor range
Crystalline solid	1450	2.29	9.7	1.30	100	4.0
Melt	1850	2.44	138	1.60	0.5	7.7
Intermediate	972	2.44	101	1.40	42.4	4.7
Amorphous solid	472	2.29	39.2	1.385	88	4.12

distances are shown in Table I along with other relevant data such as the average coordination number at this cutoff distance. We are presently investigating the detailed defect structure of the samples of amorphous silicon obtained in this study.

The structure factor of pure amorphous silicon has been measured by Postal, Falco, Kampwirth, Schuller, and Yelon[16] using neutron scattering. In Fig. 2 we show the comparison between our calculated results and the values measured by these authors. The agreement is quite good and shows that the structural properties, represented by the structure factor, are fit quite well by Stillinger-Weber amorphous silicon. The differences between the two curves at small k are explained by Guttman[17] as caused, in part, by errors in subtracting the scattering by large (>10 Å) defects. This same experimental data has been explained with the same precision as our calculation by Guttman[17] using a random-network model for constructing amorphous silicon. In the random-network model, only atoms having a coordination number of 4 are allowed. Therefore, as is obvious on other grounds, the structure of real amorphous silicon cannot be determined by a study of $S(k)$ alone.

In Fig. 3 we show the radial distribution function calculated for our sample of amorphous silicon. The atoms that have a coordination number of 4 have an average first-nearest-neighbor distance of 2.414 ± 0.005 Å whereas the atoms that have a coordination number of 5 have an average first-neighbor distance of 2.475 ± 0.020 Å. The bond-angle distribution is $108.4°\pm13.6°$. The distribution in space of fivefold coordinated atoms in the system is not uniform. Note that we have not tried to compare our radial distribution function to the various ones that appear in the literature since these are one step removed from the experimentally determined structure factor.

The coordination number of the system is 4.12 as shown in Table I. This number may be understood by looking at the fraction of the particles with four and five neighbors, namely 88% and 12%; $0.88\times4+0.12\times5=4.12$. It is likely that by further annealing one can reduce this number to a value closer to 4.0. For example, in our first sample using a similar annealing procedure we obtained a coordination number of 4.3. By the way we have prepared our sample of amorphous silicon there should be no rem-

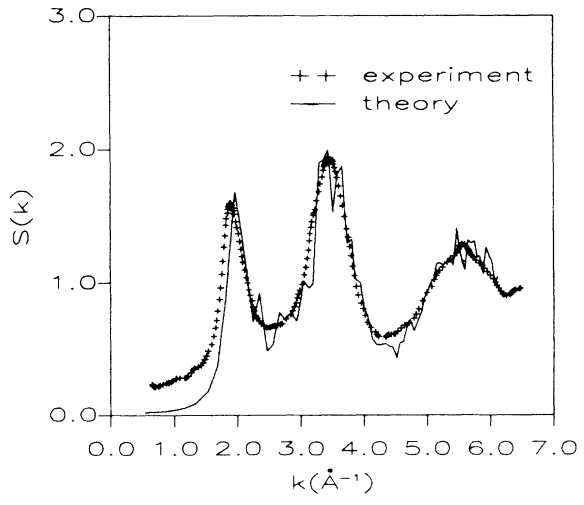

FIG. 2. A comparison of the neutron scattering structure factor for amorphous silicon from Ref. 15 and our calculation using the Stillinger-Weber potential for the system at 472 K.

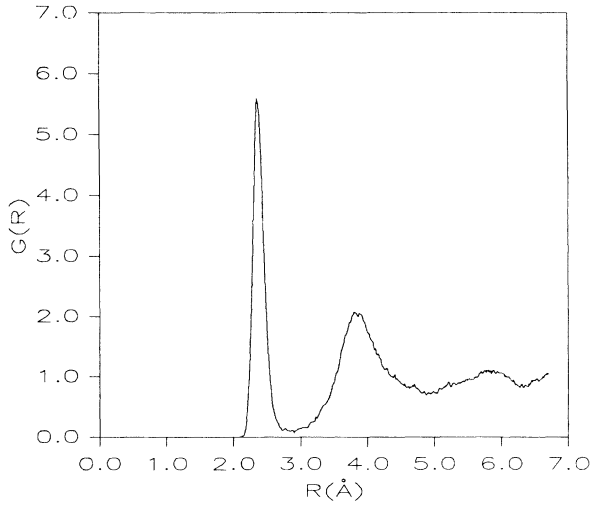

FIG. 3. The radial distribution function for amorphous silicon as calculated using the Stillinger-Weber potential. This system is the same molecular-dynamics system as in Fig. 2.

nant of the crystalline phase; the system was well equilibriated as a liquid before quenching. In order to check on this point we calculated $S(\mathbf{k})$ at the lowest 30 Bragg vectors. Inspection of these values shows no features associated with the crystalline phase.

IV. CONCLUSIONS

In the preparation of amorphous silicon just described there are four different states involved: crystalline solid, hot melt, intermediate state, and amorphous solid. In Table I we present as a summary these four states and some of their properties discussed above. Also, we note that Pantelides[18] also discusses fivefold coordination in amorphous silicon.

Ding and Anderson[19] have also studied the formation of amorphous silicon using the Stillinger-Weber potential. In their calculations the system apparently remains "stuck" in the intermediate state which has a coordination number of 4.6.

In order to study the relative stability of our sample of amorphous silicon, we cooled the system to essentially 0 K and computed the energies of the three states: crystalline, intermediate, and amorphous; these energies are -432, -409, and -412, respectively. This shows that the potential energy is lower for the amorphous state than the intermediate state. In order to show the free-energy is lower would require a more extensive calculation.

ACKNOWLEDGMENTS

M. D. K. would like to thank the R.C. Edwards Endowment for financial support. J. R. R. thanks L. Guttman for helpful discussions. These calculations were carried out using Clemson University computers. We thank Dr. C. J. Duckenfield and his staff for allowing us use of these machines.

[1]F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[2]U. Landman, W. D. Luedka, R. N. Barnett, C. L. Cleveland, M. W. Ribarsky, E. Arnold, S. Ramesh, H. Baumgart, A. Martinez, and B. Kahn, Phys. Rev. Lett. **56**, 155 (1986).
[3]F. F. Abraham and J. Broughton, Phys. Rev. Lett. **56**, 734 (1986).
[4]B. W. Dodson and P. A. Taylor (unpublished).
[5]M. D. Kluge, J. R. Ray, and A. Rahman, J. Chem. Phys. **85**, 4028 (1986).
[6]R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001 (1985).
[7]J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).
[8]R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[9]R. Car and M. Parrinello (unpublished).
[10]Y. Waseda and K. Suzuki, Z. Phys. B **20**, 339 (1975).
[11]J. P. Gabathuler and S. Steeb, Z. Naturforsch. A **34**, 1314 (1979).
[12]H. C. Andersen, J. Chem. Phys. **72**, 2384 (1980).
[13]M. Parrinello and A. Rahman, J. Appl. Phys. **52**, 7182 (1981).
[14]*Pulsed Laser Processing of Semiconductors,* Vol. 23 of *Semiconductors and Semimetals,* edited by R. F. Wood, C. W. White, and R. T. Young (Academic, New York, 1984).
[15]R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).
[16]T. A. Postol, C. M. Falco, R. T. Kampwirth, I. K. Schuller, and Y. B. Yelon, Phys. Rev. Lett. **45**, 648 (1980).
[17]L. Guttman, Phys. Rev. B **23**, 1866 (1981).
[18]S. T. Pantelides, Phys. Rev. Lett. **23**, 2979 (1986).
[19]K. Ding and H. C. Andersen, Phys. Rev. B **34**, 6987 (1986).