

Elastic constants and density of states of a molecular-dynamics model of amorphous silicon

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Recently we formed a model of amorphous silicon by using a molecular-dynamics calculation with the Stillinger-Weber potential to rapidly cool liquid silicon. We report here on the calculation of the elastic constants of this model of amorphous silicon at two temperatures, 294 and 478 K. The Rayleigh surface-wave velocity of our model is lower than the minimum shear velocity in the crystal by 0.4×10^5 cm/s. The observed Rayleigh surface-wave velocity is 0.5×10^5 cm/s lower than the minimum shear velocity. The Young's modulus of our model shows a decrease of 3.5×10^{11} dyn/cm² from the average Young's modulus in the crystal, which is close to the observed decrease. We also exhibit the density of states for our model of amorphous silicon and compare it to the observed density of states. The main discrepancy is a shift of the high-energy peak to higher frequencies. The molecular-dynamics models of amorphous silicon we form can be of any size, satisfy periodic boundary conditions by construction, and show no memory of the crystalline phase. Our models seem to be as good as or better than the random-network models that have been used previously to study the tetrahedral semiconductors.

I. INTRODUCTION

Recently, we have reported on the formation of a model of amorphous silicon which was produced by rapidly ($\approx 10^{13}$ K/s) cooling liquid silicon in a molecular-dynamics computer simulation.¹ Although we shall discuss only one such sample, we have produced several, and are still studying the formation process. The potential employed in this calculation was the Stillinger-Weber potential² which has been used in a number of computer-simulation studies of silicon.³⁻¹² In the present paper we report on various other properties of the sample of amorphous silicon discussed in Ref. 1.

As was explained in Ref. 1, the geometrical structure factor of our sample of amorphous silicon gives very good agreement with the observed structure factor of amorphous silicon as determined by neutron scattering.¹³ Also, a study of the structure factor at Bragg vectors shows that the sample retains no memory of the crystalline phase, as would be expected for a sample of amorphous silicon prepared by rapidly quenching a well-equilibrated liquid. In the present paper the calculated elastic constants and the phonon density of states for a sample of Stillinger-Weber amorphous silicon are compared with experimental results. In both cases we find good agreement. Of particular interest is the excellent agreement for the *change* in elastic properties in going from the crystalline to the amorphous phase.

II. ELASTIC CONSTANTS

A. General discussion

In earlier work⁴ we have determined the elastic constants of crystalline silicon at three different temperatures using the Stillinger-Weber potential. The results of this calculation show that while the values of the elastic con-

stants were different than the observed values by 10–30 %, the softening of the calculated values with increasing temperature is quite similar to the observed behavior. Given the simplicity of the Stillinger-Weber potential, as well as the fact that no mechanical material properties were used in its construction, we consider the agreement of the calculated elastic with the observed values to be good. In Table I we show the experimental and calculated values of the elastic constants of crystalline silicon at room temperature. The experimental values are from the Landolt-Bornstein compilation,¹⁴ whereas the theoretical values are extrapolated to room temperature from our previous calculations.⁴ Also shown in Table I are the average Young's modulus, bulk modulus, and the maximum and minimum shear veloci-

TABLE I. The experimental and theoretical elastic constants of crystalline silicon at room temperature in units of 10^{11} dyn/cm² and the maximum and minimum shear velocities in units of 10^5 cm/s. The average Young's modulus Y_{av} is determined by writing Young's modulus for an arbitrary direction and averaging over the unit sphere. The shear velocity v_{T1} is determined from the shear constant $(C_{11} - C_{12})/2$ and v_{T2} is determined from C_{44} .

	c-Si (Expt.) ^a	c-Si (Theory) ^b
C_{11}	16.6	15.0
C_{12}	6.4	7.6
C_{44}	7.9	6.0
Y_{av}	16.0	12.4
B	9.8	10.1
v_{T1}	4.7	4.0
v_{T2}	5.8	5.1

^aReference 14.

^bReference 4.

ties as determined from the elastic constants. All elastic constants in Table I are in units of 10^{11} dyn/cm², while the shear velocities are in units of 10^5 cm/s. As mentioned above the actual values obtained using the Stillinger-Weber potential are different by up to 30%; however, in the present paper we show that the change in the elastic properties between the amorphous and crystalline phases is very accurately modeled by the Stillinger-Weber potential.

Our method of calculation of the elastic constants makes use of microcanonical ensemble fluctuation formulas which contain the elastic constants. These formulas were evaluated by using the molecular-dynamics method. The theory of this method, for molecular dynamics, was first given by Ray and Rahman,¹⁵ whereas examples showing that the method furnishes an efficient and accurate method of determining elastic constants using molecular dynamics were presented by Ray, Moody, and Rahman.^{16,17} We employed these same formulas and calculational techniques to determine the elastic constants of amorphous silicon reported in this paper. We shall refer the reader to Refs. 15–17 for the relevant formulas.

B. Experimental values

The elastic properties of amorphous silicon have been experimentally studied by Grimsditch, Senn, Winterling, and Brodsky,²⁸ Senn, Winterling, Grimsditch, and Brodsky,¹⁹ and Tan, Berry, and Crowder.²⁰ The Rayleigh surface-wave velocity in amorphous silicon was determined¹⁹ using Brillouin scattering to have the value $v_R = 4.16 \times 10^5$ cm/s. Young's modulus of amorphous silicon was determined²⁰ to have the value $Y = 12.4 \times 10^{11}$ dyn/cm² using vibrating thin reeds. Due to experimental difficulties these are the only known elastic properties of amorphous silicon. In both of these studies the authors reported the density of amorphous silicon to be 95% of the crystalline density or 2.21 g/cm³. There is no way to compare in detail the samples used in these studies of amorphous silicon, since no common properties except the density were reported.

A recent interesting study²¹ contains suggestions that when forming an amorphous phase, a different amorphous phase is produced when irradiating a (111) surface as compared to irradiating a (100) surface.

C. Theoretical values

In Table II we present Young's modulus, shear modulus, and bulk modulus, of our model of amorphous silicon at two different temperatures. These values were calculated using the fluctuation formulas mentioned above. A detailed study of our calculation yields error estimates of about 10% for our calculations of the elastic properties of amorphous silicon. By increasing the length of time over which averages are calculated in the fluctuation method we could decrease the error in the calculated values.

In Table III we show the comparison between the calculated and observed properties of amorphous silicon. The observed Rayleigh surface velocity is 4.2×10^5 cm/s, whereas we obtain 3.6×10^5 cm/s in our calculation. Also shown is the difference between the crystalline shear

TABLE II. The theoretical elastic constants of amorphous silicon at two temperatures for our model. Note the significant softening with increasing temperature. There are no experimental results available at the higher temperature. The density of the system at both temperatures is $0.98\rho_c$ where ρ_c is the crystal density. The elastic constants are in units of 10^{11} dyn/cm².

	<i>a</i> -Si (Theory) 294 K	<i>a</i> -Si (Theory) 478 K
<i>Y</i>	8.9	7.5
μ	3.3	2.7
<i>B</i>	10.6	10.0

velocity v_{T1} and the surface velocity v_R ; the observed difference is 0.5×10^5 cm/s, whereas our calculations using our model of amorphous silicon give a difference of 0.4×10^5 cm/s for this same quantity. The observed Young's modulus is 12.4×10^{11} dyn/cm², whereas our calculated value is 8.9×10^{11} dyn/cm². The difference between the average Young's modulus in the crystal and the value in the amorphous phase is 3.6×10^{11} dyn/cm² observed to 3.5×10^{11} dyn/cm² calculated. Thus, while the absolute values calculated for v_R and *Y* are not so close to the observed values, the changes are very close to the observed changes. Thus, our calculation using the Stillinger-Weber potential yields the correct *softening* of the elastic properties when going from the crystalline to the amorphous phase. This suggests that the softening of the elastic properties depends more strongly on the structure differences between crystalline and amorphous silicon than the details of the potential.

D. Details of the calculations

The formation of amorphous silicon, using molecular dynamics, by rapid cooling of the liquid, is discussed in detail in Ref. 1. The theory of the method of calculating elastic constants using fluctuation formulas is discussed in Refs. 15–17. Our calculations used a system of 216 atoms together with periodic boundary conditions. As shown in Ref. 4, the elastic constants of crystalline silicon were unchanged when we increased the system size to 1728 atoms. Therefore, for the present calculation on amorphous silicon we used 216 atoms.

The use of fluctuation formulas to calculate elastic constants involves estimating ensemble averages of several

TABLE III. The Rayleigh surface wave velocity v_R and Young's modulus *Y* for amorphous silicon compared to our calculated value at 294 K. Also shown are the differences between the crystalline minimum shear velocity from Table I and the Rayleigh velocity, and the difference between the average Young's modulus in the crystal from Table I and Young's modulus of the amorphous material.

	<i>a</i> -Si (Expt.) ^{a,b}	<i>a</i> -Si (Theory)
v_R	4.2	3.6
$v_{T1} - v_R$	0.5	0.4
<i>Y</i>	12.4	8.9
$Y_{av} - Y$	3.6	3.5

^aReference 19.

^bReference 20.

quantities by molecular-dynamics time averages. The molecular-dynamics runs used to calculate the elastic constants in Table II consisted of 80 000 iterations of the equations of motion for the 478-K calculation and 50 000 iterations for the 294-K calculation, with each iteration being equal to 7.66×10^{-16} s for a total time of 61.2 and 38.3 ps, respectively.

For an isotropic system such as an amorphous solid there are two independent elastic constants, say C_{11} and C_{44} . The elastic constant C_{12} is related to these independent components by the relation $C_{12} = C_{11} - 2C_{44}$. In a molecular-dynamics calculation we can easily calculate all (there are, in general, 21 independent elastic constants) of the elastic constants. In the present work we calculated C_{11} , C_{22} , C_{33} , C_{12} , C_{13} , C_{23} , C_{44} , C_{55} , C_{66} , and C_{63} independently. The values found for C_{11} , C_{22} and C_{33} can be used as independent values for C_{11} to calculate a standard deviation for an error estimate in the calculated value of C_{11} . The errors in C_{12} and C_{44} can be estimated in a similar same way. These standard deviations show that the error in all the calculated elastic constants for amorphous silicon are less than $\pm 10\%$.

Also, as a measure of the isotropy of our sample we can use the independently calculated elastic constants to check the isotropy condition $C_{11} - 2C_{44} = C_{12}$. For C_{12} we found the value 8.3×10^{11} dyn/cm² for the 478-K run, and from the values in Table II we may determine $C_{11} - 2C_{44} = 8.0 \times 10^{11}$ dyn/cm². The difference between the values 8.3 and 8.0 is not significant to the accuracy of our calculation; in other words, our system satisfies the elastic constant isotropy condition to the accuracy of our calculation. For the 294-K run these numbers are $C_{12} = 8.3 \times 10^{11}$ dyn/cm², whereas $C_{11} - 2C_{44} = 8.6 \times 10^{11}$ dyn/cm². As another check on our calculations we calculated the elastic constant C_{63} which should be zero by symmetry; the value of C_{63} was zero to the accuracy of our calculation; that is, its value was less than the error determined in the nonzero elastic constants.

E. Other theoretical results

Related theoretical results can be found in the work by Guttman.²² Guttman's calculations make use of random-network models of amorphous silicon that he constructed. These models satisfy periodic boundary conditions. In the random-network method of constructing models of amorphous silicon one starts with a crystal lattice of atoms and follows a specific set of rules for altering bonding of the atoms; this alteration of the system is followed by a relaxation of the lattice by minimizing the potential energy. The Keating potential²³ was used by Guttman. Repeated alterations and relaxations leads in some cases to a lattice that has properties, that one believes, represent a good model for amorphous silicon; some of the properties that one considers are tetrahedral coordination, bond-angle distributions, and nearest-neighbor distance distributions. With such rules one can construct random-network models of amorphous silicon of several hundred atoms, satisfying periodic boundary conditions, although not every attempt will end in a successful model. For further details of such methods we refer the

reader to the references.²⁴

In Ref. 22 Guttman determined the elastic constants of amorphous silicon by homogeneously deforming random-network models and determining the change in the energy for given strains. The models employed by Guttman were composed of 16 and 54 atoms with periodic boundary conditions. The elastic constants were determined from derivatives of the energy with respect to the strain. The parameters in the Keating potential may be chosen so that the elastic constants of crystalline silicon are correct to a few percent. Guttman's results for Young's modulus, shear modulus, and bulk modulus of amorphous silicon are $Y = 0.74(\alpha/r_0)$, $\mu = 0.30(\alpha/r_0)$, and $B = 0.46(\alpha/r_0)$, where α is the bond-stretching force constant in the Keating potential and r_0 is the interatomic distance in the crystal. The Keating-potential bond-bending force constant β was chosen to satisfy $\beta/\alpha = 0.3$, which implies that the elastic constants of crystalline silicon may be fit to about 5%. If we fit the crystalline value of C_{11} ,

$$C_{11} = \sqrt{3}(\alpha/4r_0)(1 + 3\beta/\alpha) = 16.6 \times 10^{11} \text{ dyn/cm}^2,$$

then we find $\alpha/r_0 = 20.2 \times 10^{11}$. Using this value for α/r_0 , we determine the values $Y = 14.9 \times 10^{11}$ dyn/cm², $\mu = 6.05 \times 10^{11}$ dyn/cm², and $B = 9.28 \times 10^{11}$ dyn/cm² for Guttman's model. The Rayleigh surface wave velocity determined from these elastic constants is $v_R = 4.7 \times 10^5$ cm/s. Recall that the observed Young's modulus is 12.4×10^{11} dyn/cm², while the observed Rayleigh velocity is 4.2×10^5 cm/s. Thus, Guttman's calculations give too high a value for both Y and v_R when compared to the observed values. Recall that the Stillinger-Weber calculation gives values too small when compared to experiment. When compared to the average crystalline value Guttman's Young's modulus softens by 1.1×10^{11} dyn/cm², whereas the Rayleigh velocity is the same as the shear velocity v_{T1} in the crystal. Recall that in the Stillinger-Weber calculation one obtains excellent agreement in the changes between crystalline and amorphous values for Y and v_R . Note that the crystalline elastic constants in Guttman's calculations are the observed values.

III. PHONON DENSITY OF STATES

Our model of amorphous silicon was cooled until it reached a temperature near zero. The eigenfrequencies of small vibrations about equilibrium were then determined by finding the eigenvalues of the dynamical matrix $D_{ai,bj}$

$$D_{ai,bj} = \partial^2 U / \partial x_{ai} \partial x_{bj}, \quad (3.1)$$

where a and b denote particle numbers and i and j denote Cartesian components. The eigenvalues of the matrix D, λ are related to the vibrational frequencies ω by $\omega^2 = \lambda$.

We also cooled a crystalline system and calculated the density of states for comparison purposes. Figure 1 shows a plot of the crystalline density of states along with the experimental curve calculated from potentials fitted to the dispersion relations determined from neutron

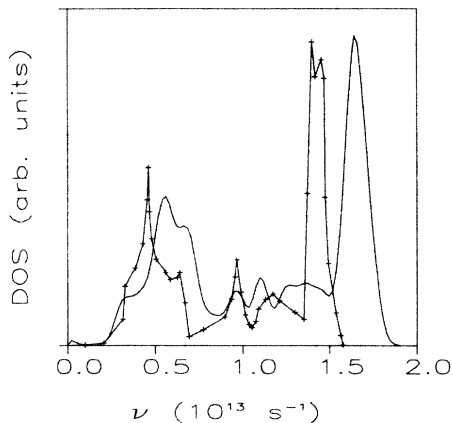


FIG. 1. The experimental and theoretical vibrational density of states (DOS) for crystalline silicon. The experimental curve is distinguished by the + markers. The density of states curves have not been normalized.

scattering.^{25,26} Except for the thermal broadening, which makes the theoretical curve smoother, the high-frequency peak being shifted to higher frequency is the main difference between the curves in Fig. 1. Except for this one feature the theoretical curve agrees well with the experimental results.

The phonon density of states for amorphous silicon is essentially a broadened version of the crystal density of states. In Fig. 2 we show the comparison between the experimental density of states as determined by inelastic neutron scattering²⁷ and our model of amorphous silicon. The agreement shown in Fig. 2 is as good or better than that for the crystal; again the main difference is the shift of the high frequency peak to higher frequencies. In contrast to the elastic constant data there has been a great deal of work on the density of states of amorphous silicon. Most of this work consists of finding the density of states for random-network models of amorphous silicon.

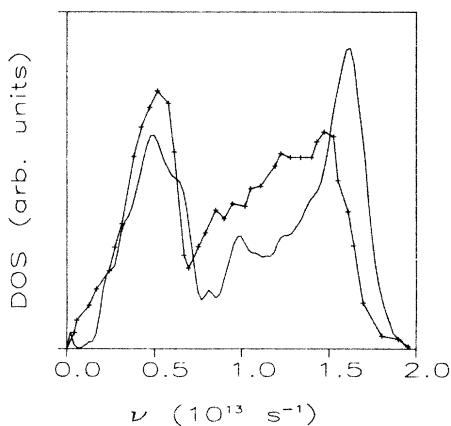


FIG. 2. The experimental and theoretical vibrational density of states for amorphous silicon. The experimental curve is distinguished by the + markers. The density of states curves have not been normalized.

Early work by Guttman²⁴ and Ross, Perlov, Fong, and Guttman²⁸ made use of Guttman's random-network models discussed above. A more-recent discussion of the phonon density of states is contained in a paper of Winer,²⁹ which also contains references to the literature.

IV. CONCLUSIONS

In this paper we have used a model of amorphous silicon which is formed by rapidly quenching the melt. In earlier work¹ models of amorphous silicon produced in this manner gave a good description to the observed static structure factor. By construction our models satisfy periodic boundary conditions and can be made of arbitrary size.

In this paper we have shown that the observed softening of Young's modulus and the lower value for the Rayleigh velocity, as compared to the crystalline shear velocity, in amorphous silicon is very well fit by our model. Also, the phonon density of states is in good agreement with the observations. The agreements between observed and calculated values one obtains using the Stillinger-Weber potential is not of high precision, but given the simplicity of the potential these agreements show that the potential does contain much the physics of the bonding of silicon atoms in crystalline, amorphous, or liquid phases. As a word of caution we mention that other properties calculated using the Stillinger-Weber potential are in poor quantitative agreement with the observed values. As an example we mention the determination of the latent heat of fusion of crystalline silicon to be 932 J/g in Ref. 11, whereas the observed value is 1800 J/g. This makes it clear that the potential needs improvement.

In a recent paper Broughton and Li³⁰ have studied a model of amorphous silicon using the Stillinger-Weber potential. Their model was constructed by taking the coordinates of a random-network model of amorphous silicon and using this configuration as initial conditions in a molecular-dynamics calculation with the Stillinger-Weber potential. The coordinates used by Broughton and Li were obtained from the models discussed by Wooten, Winer, and Weaire.³¹ It has been shown by Wooten and Weaire³² and Winer²⁹ that the models discussed in Ref. 31 retained a memory of the crystalline phase through, for example, their structure factor for Bragg vectors, and are, therefore, not good models of amorphous silicon. These models may be further randomized, by continuing the rules for making these random-network models, in which case they lose the memory of the crystalline phase.³² It is not clear from the paper of Broughton and Li whether they used the original "crystalline" amorphous silicon constructed in Ref. 31 or the "noncrystalline" amorphous silicon discussed in Ref. 32. If the former is true then some of the results in Ref. 30, in particular, phase transformations between amorphous and crystalline silicon, could be due to their sample having a memory of the crystalline phase. Recall that our models of amorphous silicon do not retain a memory of the crystalline phase since they are formed by rapidly cooling a liquid.

Nevertheless, it appears from a study of Ref. 30 that their model of amorphous silicon has some properties

similar to the models we have formed by rapidly cooling the liquid. The phonon density of states given by Broughton and Li is very similar to the Stillinger-Weber result shown in Fig. 2. Also, they state that the zero-temperature energy per atom of their model is -1.9022 , whereas we find an energy of -1.9074 for the amorphous system discussed in this paper; the crystal energy is -2.0000 . Also, in their simulation they found 86.6% of the atoms had fourfold coordination while 11.8% had fivefold coordination and 1.2% had threefold coordination. In the simulation that we used to determine the elastic constants of amorphous silicon at 478 K we found 86.1% of the atoms had fourfold coordination, 13.1% had fivefold coordination, 0.5% had sixfold coordination, and 0.3% had threefold coordination; for a precise definition of our coordination number see Ref. 1; the same numbers were found for the 294-K calculation.

The results of this paper along with Ref. 1 make it clear that molecular dynamics may be used to construct

models of amorphous silicon, of arbitrary size, satisfying periodic boundary conditions, and having no memory of the crystalline phase. These model show excellent agreement with the observed static structure factor, give good agreement with the phonon density of states, and show the correct changes in elastic properties from the crystalline to the amorphous state.

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