

High-pressure phases of amorphous and crystalline silicon

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We study pressure-induced phase transitions in amorphous silicon and crystalline diamond silicon from Gibbs free energies considerations using *ab initio* total energy calculations. We predict a pressure-induced crystallization of the amorphous network at 2.5 GPa and a first order amorphous to amorphous phase transition at 9 GPa. Furthermore, we find a pressure-induced high density amorphization of crystalline diamond silicon around 15 GPa.

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I. INTRODUCTION

Pressure-induced phase transitions have long been studied for ordered (crystalline) materials. A considerable understanding of the physics of these transformations has been obtained.¹ Where amorphous materials are concerned, the situation is far less clear. Only in the last few years has the concept of polyamorphism (the possibility of many distinct amorphous conformations for a given material) been considered.^{2,3} In analogy with pressure-induced polymorphism in crystals, we consider the effects of pressure on the structure of amorphous Si. We also discuss amorphization of crystalline Si and an amorphous to crystalline (β -Sn) transformation.

Experiments⁴ have reported that *a*-Si and *a*-Ge transform to an amorphous metallic phase with a sharp drop in the resistivity and optical gap around 10 and 6 GPa, respectively, and it appears that these transitions are first order. An amorphous to crystal phase transition in *a*-Si and *a*-Ge has been observed in other experiments.^{5,6} In porous silicon,⁷ a transition from the diamond phase to a high density amorphous (HDA) phase is reported while nanocrystalline silicon⁸ undergoes a direct transition from diamond to a simple hexagonal structure. In both porous and nanocrystalline silicon, the samples transform to a low density amorphous structure upon decompression.

Current computational methods have successfully *predicted* high pressure phases of materials using total energy calculations with the thermodynamic criterion of equal free energies. One such prediction was a kinetically hindered first order amorphous to amorphous phase transition in SiO₂.⁹ Recently an experiment confirmed such a first order amorphous to amorphous phase transition.¹⁰ Such calculations obviously require candidate structures which may be obtained from constant pressure simulations and sometimes experiments.

In earlier work, we found that *a*-Si exhibited a first order phase change from a low density amorphous phase to a high density amorphous (HDA) metallic phase using a constant pressure relaxation technique.¹¹ Kelires¹² confirmed an amorphous to amorphous phase transition in *a*-Si and *a*-Ge using Tersoff and EDIP potentials. Although he finds that the transition in both structures proceeds gradually, the free energy

calculation indicated a first order transition in *a*-Si at 9.8 (7.8) GPa for Tersoff (EDIP) potential.¹²

In this paper, we study the pressure-induced phase transitions in *a*-Si and in diamond silicon (*c*-Si) using *ab initio* calculations. We find that *c*-Si undergoes a first order phase transition into β -Sn structure at 9 GPa in agreement with theoretical and experimental studies. An amorphous to β -Sn transformation occurs at 2.5 GPa. Furthermore an amorphous to amorphous phase transition is predicted at 9 GPa consistent with experimental result of 10 GPa.⁴ We also find that pressure-induced amorphization of crystalline diamond silicon near 15 GPa, i.e., a first order phase change from the crystalline diamond to the HDA phase consistent with a recent experiment of porous silicon.⁷

II. METHODOLOGY

We use a local orbital first principles quantum molecular dynamics method of Sankey and Niklewski.¹³ The essential approximations are (1) nonlocal norm-conserving pseudopotentials, (2) slightly excited local-orbital basis set of four orbitals per site, and (3) the Harris functional implementation of the local density approximation. This method has been successfully applied in a wide variety of silicon systems; *c*-Si including high pressure phases,¹³ expanded volume phases of silicon (“zeolites without oxygen”),¹⁴ silicon clusters,^{15,16} and *a*-Si.^{17,18} The Parrinello-Rahman method¹⁹ used conjunction with this *ab initio* technique successfully predicts a first order amorphous to amorphous phase transition in silicon,¹¹ high pressure phases of *c*-Si (Ref. 11) and GaAs,²⁰ and a continuous amorphous to amorphous phase change in GeSe₂.²¹

We employ a starting model of *a*-Si due to Djordjevic *et al.* which is in uniform agreement with structural, vibrational and optical measurements.²² The high pressure phase is determined from starting with Djordjevic *et al.* model and using the method of the preceding paragraph. All the calculations used solely the Γ point to sample the Brillouin zone, which is reasonable for cells with 216 atoms.

III. RESULTS AND DISCUSSION

The calculated the minimum structural energy per atom E_{\min} and corresponding atomic volume V_{\min} for diamond,

TABLE I. The minimum energies E_{\min} , the relative energy difference $\Delta E (= E^i - E^{\text{diamond}})$, the corresponding minimum volume per atom V_{\min} , and its ratio $V_{\min}^r = V_{\min}^i / V_{\min}^{\text{diamond}}$, where i is diamond, β -Sn, a -Si, and HDA phases.

Structure	Diamond	β -Sn	a -Si	HDA
E_{\min} (eV/atom)	-108.006	-107.717	-107.807	-107.53
ΔE_{\min} (eV/atom)	0	0.289	0.199	0.476
V_{\min} (\AA^3 /atom)	20.76	15.42	21.26	15.87
V_{\min}^r	1.0	0.74	1.02	0.76

β -Sn, a -Si and HDA phases are listed in Table I. For diamond and β -Sn structure, the relative total energy difference per atom ($\Delta E_{\min} = E_{\min}^{\beta\text{-Sn}} - E_{\min}^{\text{diamond}}$) and the ratio of the equilibrium volume of β -Sn to diamond ($V_{\min}^r = V_{\min}^{\beta\text{-Sn}} / V_{\min}^{\text{diamond}}$) are found to be 0.289 eV/atom and 0.74, respectively. These values agree with 0.27 eV/atom and 0.77 reported in accurate self-consistent calculations.²³

In a -Si, the energy difference $\Delta E_{\min} (= E_{\min}^{\text{amorphous}} - E_{\min}^{\text{diamond}})$ is 0.199 eV/atom in good agreement with a non-orthogonal tight-binding model.²⁴ However, the difference is a factor of 2 higher than an experimental result 0.0977 eV, as extrapolated to 0 K from the measurement at 960 K using the specific heat listed in that work.²⁵ The density of a -Si is slightly less than the crystal density in agreement with experiment.

The relative stability of the phases can be determined for given pressure by a simple comparison of their Gibbs free energies $G = E_{\text{tot}} + PV$ at zero temperature. The crossing of two curves indices a pressure-induced phase transition between the two phases. The calculated Gibbs free energies of the silicon phases are plotted as a function of pressure in Fig. 1. The curves of diamond and β -Sn phase cross around 9 GPa, which is in good agreement with 9.5–15.4 GPa of experimental observation and previous first principles calculations.²⁶ The corresponding transition volume of dia-

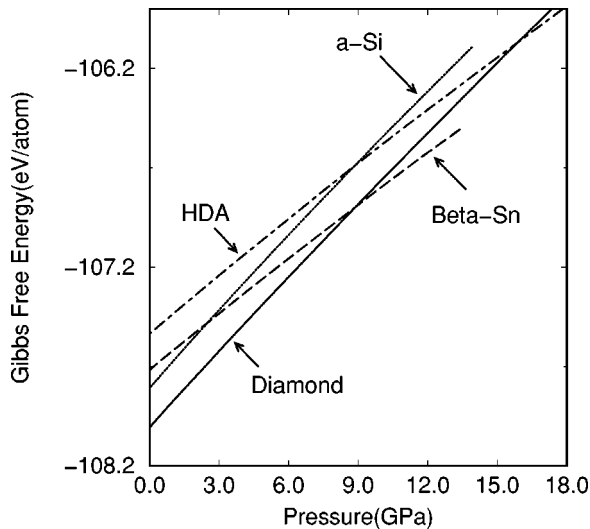


FIG. 1. The calculated Gibbs free energy for diamond, β -Sn, a -Si, and the HDA phases.

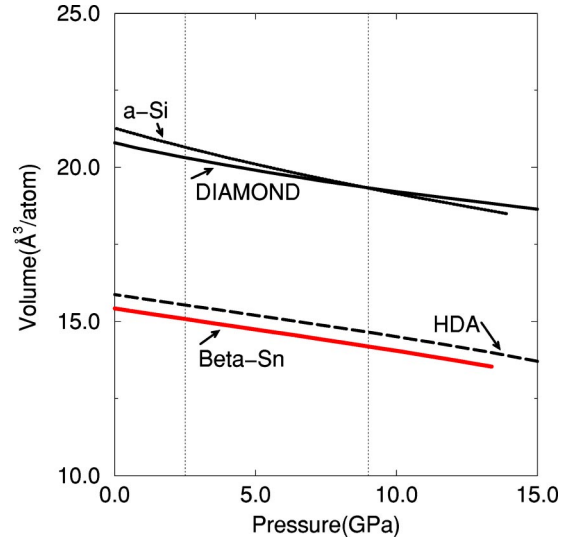


FIG. 2. The pressure dependence of the volume per atom.

mond $V_i(\text{diamond})$ and β -Sn $V_i(\beta\text{-Sn})$ are found to be 0.924 and 0.684 (Fig. 2), respectively. These values are also consistent with experiment and theoretical results of 0.89–0.928 and 0.70–0.719.²⁶

Amorphous materials are thermodynamically unstable. Upon thermal annealing or pressurizing, they can be crystallized into stable or metastable phases. It appears that the pressure-induced crystallization is sensitive to sample properties as well as temperature and pressurizing conditions such as loading rate.⁶ The transition from a -Si to β -Sn phase occurs at a lower pressure of 2.5 GPa from consideration of Gibbs-free energies. The critical pressure in this transition is about one quarter of the diamond to β -Sn transformation. The transition volume $V_i(\text{amorphous})$ is 0.96 while $V_i(\beta\text{-Sn})$ is 0.70 (relative to zero-pressure a -Si volume). The transition volume of β -Sn is 0.72 when it is normalized to the zero-pressure volume of diamond. This is a bit larger than 0.684 obtained in the diamond to β -Sn transition.

The transition predicted between a -Si and β -Sn agrees with experiments. Yet the theoretical crystallization pressure (2.5 GPa) is much less than the experimental observation of 8 GPa. We mentioned above that the relative energy difference between diamond and a -Si is much larger than the experimental value. This means that the a -Si network has a higher structural energy, and the energy difference between the equation state of a -Si and β -Sn is small. Such a lower energy difference yields a lower transition pressure if the slope of common tangent line is considered in the energy volume curve. Therefore, we conclude that the predicted lower transition pressure is due to the higher structural energy of a -Si. However, we should note that in the calculation, we consider that the amorphous network completely transforms into a perfect β -Sn. Indeed, an amorphous phase cannot completely transform into a perfect high-density crystalline structure but partially transforms into a structure that may contain low- and high-density amorphous and crystalline portions as seen in amorphous germanium.⁶ Therefore consideration of such a partial transformation would be more realistic and comparable with experiments.

The crystallization of a -Si requires to bond breaking and large displacement of some atoms. These structural rearrangements are hindered at low-temperature and need more thermal activation. We believe that the crystallization of a -Si was kinetically hindered in the constant pressure simulations,¹¹ and hence a -Si persists until it reaches a metastability limit in which it undergoes a first order phase transition from a low-density amorphous phase to a HDA phase. The calculated transition pressure from the Gibbs free energies is 9 GPa (Fig. 1), which is in agreement with the experimental result of 10 GPa (Refs. 4,27) and theoretical result of 9.8(7.8) GPa.¹² We find $V_i(\text{amorphous})$ and $V_i(\text{HDA})$ are 0.90 and 0.68 relative to the zero-pressure a -Si.

Another observation of interest is that there is no phase transition between β -Sn and the HDA phase but, a phase transition between crystalline diamond silicon and the HDA phase at 15 GPa, which may indicate a pressure-induced high density amorphization of crystalline diamond silicon. In this phase transformation we find that the transition volume of $V_i(\text{diamond})$ and $V_i(\text{HDA})$ is 0.89 and 0.65 relative to the zero-pressured diamond structure. There is no experimental evidence of pressure-induced amorphization of diamond silicon with the application of pressure. Recently Deb *et al.*⁷ have shown the pressure-induced amorphization of diamond silicon at 15–16 GPa in porous silicon. That is, the crystalline portion of the porous silicon transforms to a HDA phase upon compression which is attributed to the sample proper-

ties and transformation mechanisms to the high-density phases. In addition, the extrapolated negative melting slope in the temperature-pressure diagrams of diamond silicon (see Fig. 3 of Ref. 7) yields a pressure-induced amorphization near 14 GPa at 300 K. On the pressure release, it is shown that this HDA phase transforms to a low density amorphous phase.⁷ Both transitions reported in this experiment⁷ confirm the predicted transition in the present study.

IV. CONCLUSIONS

We have studied pressure-induced phase transitions in c -Si and a -Si using an *ab initio* technique. c -Si transforms from diamond structure to β -Sn structure at 9 GPa in agreement with experiments. Furthermore, a pressure-induced amorphization of crystalline diamond silicon is predicted near 15 GPa. We find that pressure-induced crystallization of a -Si at 2.5 GPa and argue that the crystallization pressure strongly depends on structural properties. At 9 GPa, a -Si undergoes a first order phase transition from a low density amorphous phase to a HDA phase.

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