High Density Amorphous Form and Polyamorphic Transformations of Silicon

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Polyamorphic transformations of silicon have been investigated by constant-pressure first-principles molecular-dynamics simulations. By pressurizing a normal amorphous Si with tetrahedral coordination, a new high density amorphous (HDA) form that has a strong resemblance to HDA water is obtained. We find that the HDA form can be also obtained through vitrification of liquid Si under pressure. Both HDA and liquid Si contain deformed tetrahedral configurations with interstitial atoms. These findings indicate that HDA Si is directly connected with liquid Si, which is of particular importance in understanding phase relations of polyamorphs of Si.

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Recent investigations have revealed that two or more distinct forms are realized in a wide variety of amorphous and liquid systems [1–3]. This phenomenon is called "polyamorphism," which is prominent especially in substances with tetrahedral coordination [4–7]. Investigations on polyamorphism were triggered by the discovery of a high density amorphous (HDA) form of water in 1984 [4,8]. Since the discovery of HDA water, polyamorphism in water and other substances has been extensively examined [1–10]. Amorphous silicon (Si) has recently attracted significant attention in view of polyamorphism [1,2,6,7]. Because tetrahedral configuration is preserved in amorphous and liquid states, one can expect polyamorphic transformations in Si [1,4]. However, much less is understood about polyamorphism in Si than in water. Here we report first-principles molecular-dynamics (MD) simulations of polyamorphic transformations of Si. It is well recognized that microscopic approaches are of particular importance in clarifying underlying mechanisms of polyamorphism.

Silicon and water have the following common characteristics: (1) locally tetrahedral coordination; (2) denser liquid than its crystalline form; and (3) decrease of the melting temperature with increasing pressure. These are closely related to each other, especially the latter two [(2) and (3)] are directly linked by the Clausius-Clapeyron relation [11]. These characteristics essentially result from the directional bonding that forms an open structure (tetrahedral configuration) at ambient pressure. It has been considered that open atomic configuration could be a key factor of polyamorphic transformations [1]. Silicon therefore has great potential to exhibit polyamorphic transformations. In water, it has been argued that there are two distinct liquid forms with different densities, which are closely related to two distinct amorphous forms, low density amorphous (LDA) and high density amorphous (HDA) water, respectively [4,8]. These distinct liquid forms, low density liquid (LDL) and high density liquid (HDL), are observed only in a computer simulation of supercooled liquid water [12]; not yet in experiments due to spontaneous crystallization below a certain temperature [4]. Silicon may show similar behavior so that computer simulations should be of great use to explore polyamorphs of Si.

Recently, a distinct high density amorphous form of Si with coordination 8-9 is found in a computer simulation [7] (we refer to this as "very high density amorphous (VHDA) form" [13]). However, the relationship between the amorphous form and the HDA form of water is not apparent, and the connection to liquid forms has not been discussed. In this Letter, we have found out a new HDA form of Si with coordination ~5. This is very close to HDA water and is regarded as an intermediate form between LDA (normal amorphous silicon with tetrahedral coordination) and VHDA. We show that the HDA form can be obtained not only by pressuring a LDA form but also by vitrifying a liquid Si (*l*-Si) under pressure. These findings are certainly helpful for understanding the phase relations of polyamorphs of Si.

The Car-Parrinello method [14] incorporating the pressure [15,16] and temperature [17] controlling techniques was employed to perform isothermal-isobaric first-principles MD (FPMD) simulations. The electronic state calculation was based on density functional theory within the local density approximation [18]. The norm-conserving pseudopotential [19] was used to describe the electron-ion interaction. Wave functions were expanded in a plane wave basis with an energy cutoff of 20 Ry [20]. The supercell contained 64 Si atoms with periodic boundary conditions. The pressure was controlled by the uniform volume change of the supercell [16]. It has been demonstrated that the pressure controlling techniques are critical in dealing with structural transformations in MD simulations [10,16,21,22].

A new amorphous form was obtained by pressurizing a LDA form prepared by rapid quenching of a *l*-Si at

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atmospheric pressure. The obtained LDA form agrees with a previously reported amorphous form [23,24] that has locally tetrahedral coordination. During compression, LDA did not show any drastic changes until the external pressure reached 12 GPa. However, the volume suddenly decreased at 12 GPa as shown in Fig. 1, indicating transformation to a HDA form. Figure 2(a) shows the pair correlation functions $g(r)$ for the LDA and the resulting HDA forms. It is apparent that the transformed amorphous form has completely different characteristics from those of LDA. Remarkable changes are found in the first peak and the first minimum. The broadening of the first peak indicates reduction of the covalent bond that forms a locally tetrahedral configuration. The change around the first minimum influences the coordination number N_c that is obtained by integrating $4\pi r^2 g(r)$ up to the first minimum r_m. N_c of LDA is 4.0 reflecting the tetrahedral coordination, whereas that of HDA is calculated as 5.1. To see more insight into the structural differences, the bond-angle distribution function $A(\theta)$ is calculated for LDA and HDA [Fig. 2(b)] [25]. LDA has a single peak around 109.5° which clearly reflects the tetrahedral configuration. In contrast, the main peak in HDA is broadened and the peak position is shifted to ~90°. Detailed analysis shows that the first four neighbors in HDA still form a (slightly deformed) tetrahedral structure, but the fifth neighbor is located at an open space of the tetrahedron. It can be considered that the HDA structure is formed by forcing the fifth neighboring atom, which is outside the first coordination shell in LDA, into the interstitial position. This structure is significantly different from that of VHDA [7]. N_c of VHDA is 8-9, and a distinct peak at ~60° is found in $A(\theta)$ for VHDA [7], indicating more close packed structure than HDA. It is worth mentioning that N_c of LDA, HDA, and VHDA roughly coincide with those of the crystalline forms of Si, viz., the diamond, β-tin, and sh structures, respectively (note that the latter two are high-pressure forms [26] and N_c of diamond, β-tin, and sh is 4, 6, and 8, respectively). It appears that the trend in crystalline forms also persists in amorphous forms, and HDA bridges the gap between LDA and VHDA.

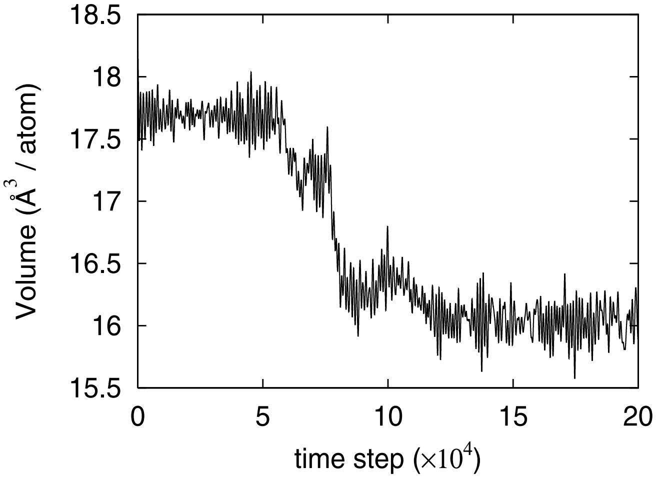

FIG. 1. Time evolution of the volume per atom in the transformation from the LDA to HDA form at 12 GPa. The time step is taken to be 0.126 fs.

Atomic configurations of LDA and HDA are displayed in Fig. 3. The HDA structure of Si is almost the same as that of water. Each water molecule in HDA water is tetrahedrally coordinated as in LDA water, but an interstitial molecule is present in the first coordination shell [27]. We thus consider that the LDA-HDA transformation of Si observed in our simulation has a strong resemblance to that of water.

It is also found that LDA can be recovered by decompression as in amorphous water. Upon decompression at

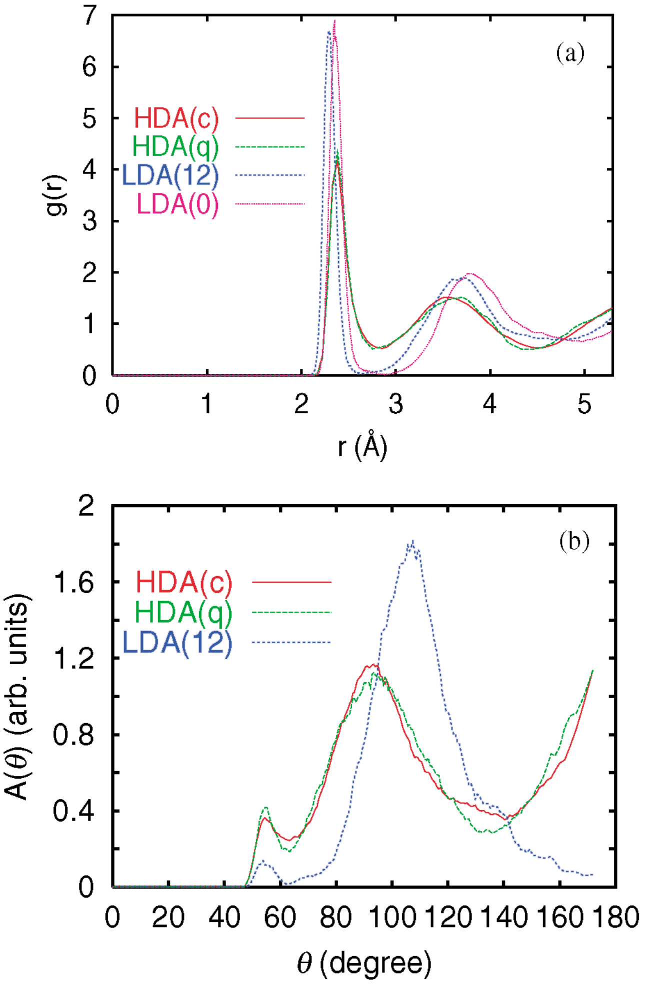

FIG. 2 (color). (a) Pair correlation functions $g(r)$ and (b) bond-angle distribution functions $A(\theta)$ for LDA and HDA. Those for HDA obtained from LDA are labeled by HDA(c) and for HDA obtained from l-Si under pressure are by HDA(q). LDA(12) and LDA(0) denote results of LDA at 12 GPa and 0 GPa, respectively.

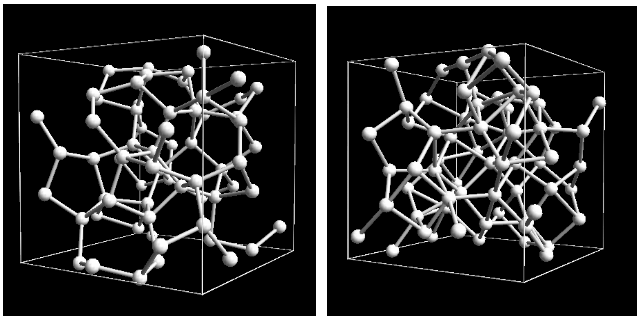

FIG. 3. Representative atomic configurations of the LDA (left) and HDA (right) forms. Thin white lines represent the supercell.

300 K, HDA was still preserved at 0 GPa, but heating up induced transformation to LDA. The reverse transformation was initiated at ~700 K. $g(r)$ for the amorphous form thus obtained has a sharp first peak containing four nearest neighbors and distinct separation between the first and second peaks. It is clearly shown that HDA was reversely transformed to LDA. Note that the reversible LDA-HDA transition in the present simulation is in excellent agreement with recent experimental observations [2,6].

It is worth investigating whether the HDA form is directly related to a liquid form. To clarify this, quenching was performed on l-Si maintaining the external pressure at ~12 GPa. Upon rapid quenching, atomic mobility was gradually reduced and solidification began at 700–800 K. A glassy form was obtained which is almost identical to the HDA form. In Fig. 2 $g(r)$ and $A(\theta)$ for this glassy state are compared with those for HDA obtained from LDA. The coincidence between the two forms is remarkable. The glassy form also contains a deformed tetrahedral structure with an interstitial atom (in average) resulting in N_c of ~5. It is also found that such characteristic structures are already formed in l-Si before vitrification. From these results, we consider that HDA Si is directly connected with supercooled l-Si under high pressure, viz. HDL.

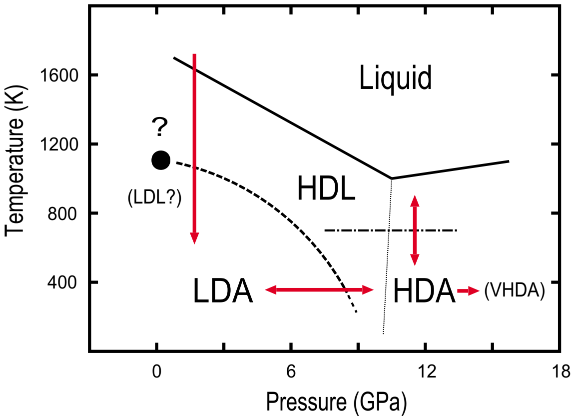

FIG. 4 (color). Schematic phase relations of amorphous and liquid Si based on our simulations and conjecture from the similarity between Si and water. The red arrows represent observed transformation processes in our simulations. The thick solid line is the melting line of crystal Si. The thick dashed line is a speculated boundary between LDA and HDA: the scale of pressure and temperature is uncertain. The thick dash-dotted line denotes the approximate location of the vitrification from HDL to HDA. The thin dotted line is the boundary between the diamond and β-tin structures of crystalline forms [26]. There may exist the hypothesized second critical point (the filled circle) that is believed to exist in water [4].

Figure 4 summarizes our simulation results. It is of particular interest that the relations between amorphous forms (LDA, HDA, and VHDA) resemble those between crystalline forms (the diamond, β-tin, and sh structures). Both HDA and the β-tin structure contain deformed tetrahedra with interstitial atoms resulting in N_c of 5-6. The reported VHDA form partially contains sh-like configurations and N_c is between 8-9 [7]. Thus, it is likely that the VHDA form results from an incomplete crystallization of the sh structure. In fact, we obtained a mixture of the sh crystalline form and the VHDA form by further compression on HDA. It is noteworthy that the third distinct amorphous form with coordination ~9 is recently observed in water (VHDA water) [8,28]. We have also found that structures of HDA and quenched l-Si under pressure are based on the same framework: distorted tetrahedra with interstitial atoms. Considering this structural similarity and the vitrification under pressure, we reach the conclusion that supercooled l-Si under pressure (HDL) is directly connected with HDA. It appears that the reduction of the tetrahedral configuration followed by interstitial atoms plays a key role in Si under pressure. The stability of the tetrahedral configuration may be used as a kind of order parameter to classify disordered states of Si.

The similarity between amorphous Si and water leads to the conjecture that HDA water is also continuously connected with supercooled liquid water under pressure (HDL). Finney *et al.* have pointed out the similarities of local structures between them [27]. Although glassy pure water under pressure has not been directly obtained in experiment, a recent MD study reports a consistent result with the conjecture [29].

A LDL form of Si is recently found at around 1060 K and 0 GPa in a classical MD simulation [30]. In our FPMD simulations, however, LDL has not been observed: lowering the temperature below ~1100 K in l-Si at 0 GPa induced a transition to LDA, instead of to LDL. It appears that the formation of LDL was bypassed by the liquid to LDA transition. Our results do not exclude the possibility of the LDL form, but imply that the stability of LDL strongly depends on the preparation process and LDL could exist only under specific conditions (extremely low temperatures, within a limited time span followed by solidification). In a liquid state we investigated (above 800–1100 K at 0–12 GPa), no discontinuous structural change was observed. It should be also stressed that $g(r)$ for l-Si at 1100 K and 0 GPa is very similar to that for HDA at 0 GPa. We therefore consider that l-Si (at least above ~1100 K) can be primarily characterized by HDL, not by LDL, as shown in Fig. 4. Finally, we note that the liquid to LDA transition at atmospheric pressure is accompanied by large volume jump as in previous MD simulations [24,31]. This strongly indicates that LDA is not directly related to l-Si above ~1100 K.

Our findings imply that disordered phases with tetrahedral coordination such as amorphous Si have common characteristics with respect to polyamorphism. Remarkable similarities between HDA Si and HDA water have been revealed, which improves our understanding of the phase diagram of disordered phases. The discovery of the HDA form has drawn our conclusion that l-Si at 0–12 GPa can be roughly described by the HDA (HDL) form. In contrast, our simulations suggest that LDA is not directly related to a normal l-Si and LDL could be observed only at low temperatures and pressures (or negative pressures). Accordingly, the LDL-HDL transition is expected to occur at a very low temperature, but it may be obscured by crystallization or vitrification.

The calculations were run on the NEC SX-7 and Fujitsu VPP5000 computers at the Research Center for Computational Science, Okazaki National Research Institute. I thank O. Mishima for fruitful discussion, and M. Vaccaro for reading the manuscript carefully.

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