# Computer simulations of crystallization kinetics in amorphous silicon under pressure

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With the help of computer simulations we have studied the crystallization kinetics of amorphous silicon in solid phase epitaxial (SPE) and random nucleation growth processes. Our simulations employing classical molecular dynamics and first principles methods suggest qualitatively similar behavior in both processes. Pressure is found to reduce the difference in molar volumes and coordination numbers between the amorphous and crystalline phases, which in turn lowers the energy barrier of crystallization. The activation energy for the SPE growth of four coordinated diamond phase is found to reach a minimum (a maximum in growth rates) close to 10 GPa when its density becomes equal to that of the amorphous phase. The crystallization temperatures of successive high pressure phases of silicon are found to decrease, offering a possible explanation for the pressure induced crystallization reported in this material. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3694735]

## I. INTRODUCTION

Crystallization from an amorphous phase is one of the most fundamental non-equilibrium phenomena universal to a variety of materials. It represents an important area of research not only because of its practical interests in synthesis of advanced materials with novel properties but also because of its significance in understanding the underlying microscopic mechanisms that govern the process. Network forming systems like silicates, chalcogenides, elemental semiconductors, etc., also happen to be good glass formers and have been studied extensively. Silicon, a most widely used electronic material, is a prototypical example of such a network forming covalent solid. Fabrication of silicon based integrated circuits involves several ion implantation steps and regions that receive a sufficiently high implantation dose become amorphous within  $\sim 100$  nm of the free surface. The crystal structure is restored by an interface-mediated crystallization process, which proceeds through layer-by-layer conversion of amorphous to crystalline phase, called solid-phase epitaxial growth (SPEG). Many experiments<sup>1</sup> on SPEG of thin films of Si found the interface velocity (growth rate) to exhibit Arrhenius behavior with activation energy of  $E_a \approx 2.7$  eV. Bulk amorphous samples, not in contact with a crystalline substrate can also undergo crystallization by a process known as random nucleation and growth (RNG)<sup>2-4</sup> resulting in a polycrystalline diamond-like structure with small grains of randomly oriented crystals. Activation energy for RNG was found to be higher than that of SPEG by  $\sim 1.3$  eV and as a consequence it becomes dominant above 1000 K. Theoretically, structure and growth of crystal-amorphous (c/a) interface has been studied using tight binding<sup>5</sup> and several molecular dynamics (MD) simulations.<sup>6,7</sup> With the help of these simulations it has been found that growth velocities are similar along [100] and [110] while it is up to five times lower along the [111] direction<sup>8</sup> and that two distinct temperature regions exists with different activation energies.<sup>9</sup>

Many external and internal parameters are known to enhance the crystallization process of amorphous silicon (a-Si) such as higher annealing temperatures,<sup>4</sup> external force fields,<sup>10</sup> presence of impurities,<sup>11,12</sup> ion beam irradiation,<sup>13</sup> and applied stress.<sup>14,15</sup> Effect of pressure on crystallization process of a-Si has been relatively less explored due to the difficulty in monitoring growth in a diamond cell. In the only experimental study of SPEG under pressure, Lu et al. measured growth velocities of (100) planes of doped and un-doped silicon up to 5 GPa and found it to increase exponentially with pressure.<sup>15</sup> It was explained on the basis of migration of dangling bonds generated at the interface, reconstructing the random network into a crystalline network. Subsequent computer simulations (up to 2 GPa) confirmed the increase in growth velocities with pressure.<sup>16</sup> However, the role of pressure on migration of dangling bonds and activation energy was not clearly understood.

Pressure also induces structural changes within the amorphous phase. For example, similar to glassy water,<sup>17</sup> a-Si undergoes a pseudo-first-order polyamorphous transition from a low density amorphous (LDA) phase to a high density amorphous (HDA) phase close to 14 GPa,<sup>18</sup> which has been rationalized as the nonergodic manifestation of a first-order transition between two liquid phases as in the supercooled regime of water.<sup>19–21</sup> The role of these phase transitions on the crystallization process is also not explored till now.

Normally, crystallization is a prohibitively slow process at room temperatures as the necessary structural relaxations are inhibited by the high viscosity in the amorphous phase. Since external pressure increases density, one would intuitively expect the process to be further suppressed, which is in fact supported by many studies.<sup>22,23</sup> However, an opposite

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effect is observed in many other systems<sup>24,25</sup> including silicon, where applied pressure facilitates crystallization, reducing the crystallization temperature. A notable example is the elemental solid amorphous selenium, which undergoes pressure induced crystallization at ambient temperatures similar to amorphous silicon [12 GPa for a-Se (Ref. 26) and 15 GPa for a-Si (Ref. 27)]. However, unlike in silicon, pressure significantly elevates T<sub>c</sub> in a-Se.<sup>28</sup> In the amorphous alloy Al<sub>89</sub>La<sub>6</sub>Ni<sub>5</sub>, applied pressure resulted in the increase of T<sub>c</sub> after an initial reduction.<sup>29</sup>

In this article, we present results of extensive computer simulations using classical and first principles methods carried out to understand the effect of temperature and pressure on the crystallization of amorphous silicon through SPEG and RNG. We considered crystallization of LDA and HDA phases of a-Si to its crystalline counterparts, namely, four coordinated diamond and six coordinated  $\beta$ -Sn, respectively. Details of the computational methods are given in Sec. II. In Sec. III A, we present the results of MD simulations on the growth of crystalline layers on amorphous layer under pressure. In Sec. III B, we present results for calculations for RNG, parameters for which are derived from classical and first principles simulations.

#### **II. COMPUTATIONAL METHOD**

Simulation of SPEG requires a large supercell containing thousands of atoms and long simulation times spanning several nanoseconds to faithfully represent the structure of the c/a interface and its growth process. Classical molecular dynamics simulations with empirical interaction potentials are ideally suited for this purpose and we have carried out extensive simulations using the DL\_POLY code<sup>30</sup> and interatomic potentials by  $\text{Tersoff}^{31,32}$  that incorporate bond order without complex many body terms. They have been shown to reproduce the structure of crystalline and amorphous silicon as well as recrystallization process in a-Si quite well,<sup>6</sup> even though melting points are somewhat overestimated. Velocity Verlet algorithm is employed to integrate the equations of motion with Berendsen thermostat and barostat keeping temperature and pressure constant. The system is equilibrated for several nanoseconds at each temperature/pressure using a fine time step of 1 fs. The amorphous phase is generated by quenching liquid silicon from 3500 K at a rate 1 K/ps and annealing at 1000 K for several million steps. A fourfold coordinated continuous random network structure with a coordination defect density less than 5% is obtained. The a-Si/(001)Si system is generated by joining the amorphous sample consisting of about 983 atoms to a bulk crystal (in diamond or  $\beta$ -Sn phase) consisting of about 1000 atoms, due to the density difference between amorphous and crystalline silicon. Periodic boundary conditions are employed in all three directions. Extensive annealing at 1000 K allows the interface to relax to a reasonable structure of low energy.

As the formation of nuclei in the amorphous matrix is a thermally activated stochastic process, achieving RNG in computer simulations is a formidable task. However, with the help of modified Stillinger-Weber potentials<sup>33</sup> and long simulation timescales, Nakhmanson *et al.* were able to observe

RNG in classical MD.<sup>7</sup> Since the temperature pressure conditions of interest in the present study are very large, we have instead used analytical expressions derived from classical nucleation theory in conjunction with accurate first principles calculations to study RNG. We employed density functional theory as implemented in Vienna *ab initio* simulation package<sup>34</sup> with generalized gradient approximation<sup>35</sup> and projected augmented wave method<sup>36</sup> to solve Kohn-Sham equations. A Monkhorst-Pack mesh of  $8 \times 8 \times 8$  and a kinetic energy cutoff of 380 eV provided good convergence. The energy-volume characteristics of amorphous phase are calculated using a supercell containing 216 atoms and  $\Gamma$ -centered k-point sampling. Each structure was equilibrated for 0.5 ps at 500 K and subsequently fully relaxed.

### A. Thermodynamic analysis

When an amorphous sample is heated, many tiny crystalline nuclei continuously form as a consequence of thermal fluctuations. Classical nucleation theory predicts the energy of a nucleus to increase with its diameter and reach a maximum at a critical diameter. As a consequence, if a nucleus of diameter larger than the critical value forms spontaneously in the amorphous matrix, it will grow transforming the phase to crystalline phase. The energy required to form this critical nucleus is the nucleation work  $\Delta G^*$  and is related to the growth rate *I* at a temperature *T* according to crystallization kinetics theory as

$$I = I_0 \exp[-(\Delta G^* + Q_n)/kT], \qquad (1)$$

where  $I_0$  is a constant,  $Q_n$  is the activation energy for the transport of an atom across the c/a interface, and k is the Boltzmann constant. For homogenous nucleation,<sup>26</sup> the nucleation work  $\Delta G^*$  can be expressed by

$$\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G^{a\to c}/V^c)^2},\tag{2}$$

where  $\Delta G^{a\to c}$  is the molar free energy change for the transformation from amorphous to crystalline phase,  $\sigma$  is the c/a interfacial energy, and  $V^c$  is the molar volume of the crystalline phase. The thickness of c/a interface is assumed to be infinitely small, which is a valid approximation for crystallization in supercooled region above glass transition temperature. In the case of SPEG, since a crystalline substrate is already available,  $\Delta G^* = 0$  and Eq. (1) can be rewritten in terms of growth velocity v as<sup>15</sup>

$$v(T) = v_0 \exp(-Q_n/kT).$$
(3)

#### **III. RESULTS**

#### A. Crystallization via SPEG

Our simulations of various polymorphs of silicon show that Tersoff potentials can reproduce the structure and energy volume characteristics of the diamond and  $\beta$ -Sn phases quite well (however, it cannot stabilize the simple hexagonal phase probably since the potentials were parameterized for low pressure structures only<sup>32</sup>). Hence, to check the validity of the potentials we simulated the phase diagram of crystalline and amorphous silicon. Melting curve for a-Si is estimated by subjecting the amorphous phase to increasing temperatures and monitoring self diffusion and volume changes to identify the melting point. The crystalline melting curves are identified by heating a cell containing the crystal-liquid interface which moves toward the crystalline region above the melting point.

Figure 1 shows the results of this simulation qualitatively with available experimental data.<sup>37–39</sup> The melting curves for amorphous and crystalline phase of silicon remain almost parallel as a function of pressure. Melting temperatures at ambient pressure obtained from our calculations, for amorphous-Si is  $T_m^g = 2000$  K and for cubic diamond silicon (cd-Si) is  $T_m^c = 2600$  K, in agreement with earlier calculations carried out using the same interaction potentials.<sup>31</sup> Since experimental estimates are 1420 K for amorphous and 1685 K for crystalline silicon<sup>40</sup> our calculations show that Tersoff potentials overestimate the melting temperatures by 40-50%.<sup>6</sup> At ambient pressure the ratio  $T_m^g/T_m^c = 2/2.6$ , which is close to the experimental value of 2/3.<sup>41–43</sup> The simulation correctly reproduces the negative slope of the melting curve under pressure which suggests increased self-diffusion;<sup>44</sup> a common characteristic of negative Clapeyron slope materials where the liquid phase is denser than the solid phase, as in water.<sup>48</sup> This increased diffusion with pressure also results in reduction of the crystallization temperature observed in Si.

Next, following the procedure elucidated in the previous section, we prepare cd/a-Si cell at 0 GPa and  $\beta$ -Sn/a-Si at 15 GPa. These are then equilibrated for about 1 ns at different pressures and subjected to increasing temperatures allowing up to 5 ns at each temperature. The procedure of Mattoni and Colombo<sup>45</sup> based on the calculation of a one dimensional structure factor<sup>41</sup> is used to get the position of the a/c interface during the transition.

Structure of the simulation cell at various temperatures and pressures are given in Fig. 2 which shows the amor-



FIG. 1. Phase diagram for amorphous and crystalline silicon. Solid lines are quadratic fit to simulated melting data.

phous, crystalline, and the interface region clearly. Measuring the densities of different regions at various pressures reveal that at ambient pressure amorphous has lower density (LDA) than the cubic crystalline phase; but has a higher compressibility as consequence of which its density crosses that of diamond close to 10 GPa. Above 15 GPa, a-Si transforms to the higher coordinated HDA phase, in agreement with earlier studies.

To understand the effect of pressure on the growth process better, we define a crystallization temperature  $(T_c^*)$  at which the simulation cell is completely transformed to a crystalline phase at the end of a 5 ns simulation; or in other



FIG. 2. Snapshots of the simulation cell containing c/a interface. Each row shows the beginning (left), intermediate (middle), and final (right) stages of simulation. Structures of the top two rows (P=0 and P=15) correspond crystallization to diamond phase while the bottom row depicts the simulation for transformation to  $\beta$ -Sn phase.

words, at which the growth velocity is 0.25 m/s. The pressure induced variation of this  $T_c^*$  normalized with respect to the value at P = 0 is plotted in Fig. 3.

Under pressure,  $T_c^*$  decreases rapidly indicating that pressure enhances SPEG of diamond silicon in agreement with earlier studies.<sup>14,15</sup> Interestingly, close to 10 GPa, where amorphous and crystalline densities become equal,  $T_c^*$  reaches a minimum. The curve terminates close to a critical pressure  $P_c = 15$  GPa, above which the crystalline cd phase does not grow. This pressure, in fact, marks significant phase changes in silicon. At this pressure, a-Si transforms from LDA to HDA with substantial volume change, as discussed later and shown in Fig. 6. The cd to  $\beta$ -Sn transition has been reported experimentally to be close to 15 GPa. Another important feature of Fig. 3 is the lower transition temperatures of  $\beta$ -Sn which indicates lower activation energies under pressure. SPEG requires rearrangement of many bonds at the c/a interface and in the transition from semiconducting LDA to metallic HDA, the directionality of silicon bonds is lost which facilitates growth. In the case of hydrogenated silicon, it has been observed that Si-Si bonds are weakened by the presence of interstitial hydrogen and crystallization temperature of a-Si with hydrogen impurity is substantially lowered.<sup>12</sup>

The activation energies  $Q_n(P)$  of growth at various pressures can be estimated by measuring the growth velocities v(T, P) at various temperatures and pressures and fitting Eq. (3) to them. In Fig. 4, the logarithm of v(T, P) as a function of inverse temperature has been plotted for the crystallization to cd phase. The straight lines fit using Eq. (3) can be seen to exhibit the expected Arrhenius behavior. The values calculated from the slope,  $Q_n(P)$ , and intercept (velocity prefactor  $v_0$ ) are given in Table I. Calculated  $Q_n(P)$  at ambient pressure is close to the experimentally reported value of 2.7 eV.<sup>1</sup> While  $v_0$  increases monotonously under pressure,  $Q_n(P)$  exhibits a minimum at 10 GPa similar to  $T_c^*$ .

To understand the structural changes that lead to the observed variation in activation energies, we have presented the atomic volume and coordination distribution in the simu-



FIG. 3. Normalized crystallization temperature  $T_c^*$  (at which growth velocity is 0.25 m/s) as a function of external pressure for SPEG of diamond and  $\beta$ -Sn silicon. Solid lines are quadratic fit to simulation data.



FIG. 4. Arrhenius plots of the growth velocity as a function of temperature at various pressures for crystallization to diamond structure. Symbols correspond to simulation data and the straight lines are fit to the data.

lation cell at different pressures. At ambient conditions, in the amorphous region the Voronoi volumes are more spread out and their average higher than the crystalline region (center of simulation box) owing to the lower density and higher distortion in a-Si. The thickness of the a/c interface at 0 GPa is close to 6 Å, as can be seen in Fig. 5(a), in good agreement with earlier estimates.<sup>5</sup> At 10 GPa, although amorphous and crystalline parts have similar average densities ( $\Delta V = 0$ ), the former has a higher coordination of 4.3 [Fig. 5(b)]. The distribution of atomic volumes at this pressure is somewhat narrower, pointing to an increased regularity factor<sup>46</sup> which is a consequence of collapse of open volumes that result in better packing. At 15 GPa, the crystalline phase is a six coordinated  $\beta$ -Sn and the amorphous phase is 5.5 coordinated HDA. The amorphous side boundary is less discernable at this pressure. with the interface gradually changing to HDA.

Below 10 GPa, the LDA phase of Si has a lower density as compared to the cubic diamond phase and, hence, the transformation causes a negative volume change ( $\Delta V = V^c - V^a$ ) during the amorphous to crystalline transition, which favors crystallization. However, under pressure  $\Delta V$  decreases and becomes positive, thereby hindering crystallization. Another factor that affects crystallization is the coordination of silicon in the amorphous region, which increases with pressure (Fig. 5) and the difference in coordination number ( $\Delta C = C^c - C^a$ ) across the interface hinders growth. Thus, under high pressures both factors resist ordering leading to the minimum in  $T_c^*$  versus pressure plot for LDA to cubic diamond transformation. Interestingly, an analogous behavior

TABLE I. Activation energy and velocity prefactor at different pressures calculated from Arrhenius fit to simulation results in Fig. 4.

Pressure (GPa)	$Q_n$ (eV)	$v_0 \ (m/s \times 10^5)$
0	2.33	4.88
5	1.80	7.01
10	1.61	10.24
13	1.72	18.67



FIG. 5. Voronoi volumes and coordination of silicon at 0 GPa and 10 GPa with cd/a-Si interface and at 15 GPa with  $\beta$ -Sn/a-Si interface averaged over 100 samples (Note that simulation box has been shifted to center the crystalline region). Open circles represent Voronoi volumes of individual atoms while the red line is the average of the same data and the lower panel represent Si coordination across the unit cell length.

has been observed in the melting curve of ice II (among many other systems) which exhibits maximum under pressure.<sup>47</sup> Water has lower density and higher compressibility than ice II at lower pressures and at the melting maximum density of the two phases become equal. Thus, we find a common feature in two apparently distinct phenomena: in crystallization minimum and melting maximum, the densities of participating phases become equal.

#### B. Crystal growth via RNG

To understand the nature of crystallization via random nucleation in silicon, we have calculated nucleation work as a function of pressure using Eq. (2). For this, the free energy



FIG. 6. (Color online) Variation of volume and enthalpy as a function of pressure, obtained from first principles simulations. The curve exhibiting abrupt change close to 15 GPa in enthalpy and volume corresponds to the LDA to HDA transition in amorphous phase.

change  $\Delta G^{a \to c}$  and  $V^c$  were calculated using first principles methods. Since change in entropy  $\Delta S^{a \to c}$  has been found to be three orders of magnitude smaller<sup>28</sup> than change in enthalpy  $\Delta H^{a \to c}$ , we have used  $\Delta H^{a \to c}$  in our calculations. The energy volume characteristics under pressure estimated from simulations are depicted in Fig. 6.

The results are in good agreement with earlier reports.<sup>48</sup> Volume of a-Si which is initially higher than that of the diamond phase by about 3%, decreases faster and crosses that of diamond Si close to 10 GPa. This is also similar to the observations in classical MD simulations discussed in the previous section. Also similar is the first order phase transition from LDA to HDA, which is accompanied by a large volume drop of ~16%. Note that, the kink in the LDA-HDA enthalpy curve due to the first order nature of the transition is removed by extending the HDA enthalpy to lower pressures (red dotted line).

Turnbull<sup>49</sup> has shown that for most metals the ratio of liquid-solid  $\sigma$  to the enthalpy of fusion is approximately 0.45 at ambient pressure. Using the melting enthalpy of 40.06 kJ/ mol calculated from a classical simulations for diamond (Fig. 1), we estimate the c/a interface energy to be 0.41 J/m<sup>2</sup> which is close to the value 0.49 J/m<sup>2</sup> determined by Brenstein *et al.* from tight binding calculations.<sup>5</sup> We have used this value for  $\sigma$  for both diamond and  $\beta$ -Sn interfaces while calculating nucleation work as shown in Fig. 7. Since first principles calculations of SPEG, we have also estimated nucleation work for crystallization to high pressure primitive hexagonal (ph) phase<sup>50</sup> as shown in Fig. 7.

Consistent with our simulations on SPEG presented in the previous section, we observe a minimum in the nucleation work for crystallization to cd phase close to 10 GPa. This



FIG. 7. (Color online) Variation of nucleation work with the applied pressure for crystallization of *a*-Si to diamond and  $\beta$ -Sn structures.

shows that underlying microscopic parameters affecting both processes are similar. We also see that  $\Delta G^*$  for crystallization from LDA to  $\beta$ -Sn phase decreases very rapidly as compared to that for crystallization to diamond phase. Beyond 8 GPa  $\Delta G^*$  for  $\beta$ -Sn is lower than that for diamond, as observed earlier (Fig. 3). Calculations show that nucleation work for crystallization from HDA to  $\beta$ -Sn also decreases with pressure. In case of crystallization to ph phase, again  $\Delta G^*$  is found to be decreasing with pressure and lower than that for  $\beta$ -Sn phase. This suggests that thermodynamically, high pressure 'ph' phase is more favorable as compared to the  $\beta$ -Sn phase for homogeneous nucleation. However, given the circumstances where seeds of  $\beta$ -Sn phase are already present in the system for example as was in the case of SPEG, crystallization to  $\beta$ -Sn may also realize. Further, one should note that, though we have used same value of  $\sigma$  for both phases, it can be pressure dependent in principle. Further, the c/a interface, which is otherwise assumed to have infinitely small thickness in present study, may also have finite pressure dependent thickness. Depending on its density, as compared with amorphous and crystalline phases, c/a interface can enhance or reduce nucleation work at high pressures. However, since there are no experiments on amorphous silicon at high pressure high temperature in the stability region of the  $\beta$ -Sn phase the above arguments cannot be verified at this stage. Our results should encourage further experiments and first principles calculations on amorphous Si to settle these subtle issues.

#### **IV. CONCLUSIONS**

Our classical and first principles calculations of crystallization process in amorphous silicon predict that nucleation work and activation energy for growth (and hence respective crystallization temperatures) exhibit minima close to 10 GPa at which densities of amorphous and crystalline phases also become equal. Crystallization temperature for  $\beta$ -Sn phase has been found to be much lower than that of diamond phase under pressure, which has been explained to be a consequence of loss of directionality of covalent bonds upon phase transition. If this trend continues, higher pressure phases like primitive hexagonal will have still lower  $T_c^*$ , approaching room temperatures, which may explain recently reported pressure induced crystallization in a-Si.<sup>27</sup> Calculated melting curves show good agreement with experimental data. Close to 15 GPa, amorphous melting curve also exhibits a minimum, which may be a consequence of structural transition from a "strong" to a "fragile" system.<sup>51</sup>

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