Investigating the fast cooling process of silicene by MD simulation

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Abstract. This paper presents the results of two-dimensional silicene cooling studies by MD simulation with a sample of 6400 atoms. Silicene after melting to 3500K, it is cooled at a rate of $10^{13}$K/s to a temperature of 300K. Investigation of the dependence of energy on temperature shows a jump in the average total energy of molten silicene at the temperature $T = 1772$K. Investigations on the radial distribution function $g(r)$, coordinate number distribution, ring distribution, and angular distribution all show that the freezing temperature of silicene is about 1772K. When cooled to 300K, silicene is in crystalline form, but the ratio of the defects is quite high and approximately 37.5%.

Keywords: silicene, structure, and properties of silicene, molecular dynamics simulation of silicene

1. Introduction

Following the discovery of graphene, a new 2-dimensional form of carbon (C) by Russian physicists Andrei Geim and Konstantin Sergeevich Novoselov, the scientists started investigating related two-dimensional forms of materials to Si 2D, Ge 2D, ... Owing to the promise of new technologies, they are very desirable. While three-dimensional silicon has long been used in physics for important applications in electronic engineering, two-dimensional silicon content has not been extensively studied. The presence of 2-dimensional silicon theoretically predicted in 1994 [1], and in 2007, Guzman-Verri et al. rediscovered and named silicene [2]. Compared to its two-dimensional carbon counterpart graphene [3,4], silicene has a similar but buckled honeycomb structure, which means that the atoms are not strictly in sp2 hybridized states. Silicene exhibits properties similar to those of graphene according to theoretical investigations [5, 6]. In addition, the puckered structure implemented in highly symmetrical configurations can be exploited in some electronic applications [7]. Similar to graphene, silicene also has many potential applications in photoelectric and photoelectronic equipment [8], solar cell production [9], and hydrogen storage [10], for example. One advantage of silicene over other 2D materials is that it blends easily with nanomaterials based on silicone. Polycrystalline silicone experiments have also recently been conducted by the authors [11], suggesting great potential for the use of silicene. Bocchetti et al. [12] simulated the melting of silicene with the original and improved versions of the Tersoff voltage parameter (called ARK) for the
silicon atom using the Monte Carlo method. The results show that the temperatures of the phase transition are 3600K and 1750K, respectively. Using a reactive force field, Berdiyorov et al. [13] simulated the effect of defects by MD simulation and found that pure silicene remained stable up to 1500K. Tjun Kit Min et al. [14] also investigated the melting process of silicene via MD simulation and obtained the phase transition temperature with an optimized 1500K Stillinger-Weber potential. Vo Van Hoang et al. have also carried out some studies on two-dimensional silicene materials and at around 1775K obtained the phase transition temperature from molten to solid silicene [15]; amorphous silicene (a-silicene) approximately 1350K [16], approximately 1950K for crystallization transition temperature and approximately 1350K for glass transition temperature with tetra-silicene [17], approximately 1620 K for P-silicene [18]. We also studied fast-melting silicene by MD simulation at a rate of $10^{13}$ K/s and obtained a phase transition temperature of about 1772K [19]. How does the heating rate affect the phase transition temperature in silicene from a liquid-state to a solid-state? This research presents the results of the silicene cooling process at a rate of $10^{13}$ K/s by the MD simulation. The paper is organized as follows: calculations and simulation results are presented in Part 2; the conclusion is presented in Part 3.

2. Calculations and simulation results

The simulation process is designed as follows: the model includes 6400 Si atoms, which are cooled according to the NPT mode and periodic boundary. First, the model after being melted to 3500K, it was relaxed in $5 \times 10^4$ simulation steps and the results obtained show that such a model is stable because the volume and temperature are stable. Then, the Si liquid was cooled from 3500K down to 300K with a rate of $10^{13}$K/s, including 320 thousand simulation steps. This cooling rate is relatively fast and we expect to also obtain crystalline Si. The potential of Stillinger-Weber (SW) type is used in the simulation process, it consists of the 2-particle term and 3-particle term with a dimensionless parameter $\lambda$ controls the relative strength between them as follows [20],

$$U = \sum_i \sum_{j>i} U_2(r_{ij}) + \lambda \sum_i \sum_{j>i} \sum_{k>j} U_3(r_{ij}, r_{ik}, \theta_{jk})$$

The first term consists of a repulsion force at a very short distance and an attractive force at a short distance,

$$U_2(r) = A\varepsilon[B\left(\frac{\sigma}{r}\right)^p - (\frac{\sigma}{r})^q]\exp\left(\frac{\sigma}{r - \alpha\sigma}\right)$$

The second term is the sum of all triples of three-form interaction,

$$U_3(r_{ij}, r_{ik}, \theta_{jk}) = \varepsilon[\cos \theta_{jk} - \cos \theta_0]^2 \exp\left(\frac{\gamma_1\sigma}{r_{ij} - \alpha\sigma}\right)\exp\left(\frac{\gamma_2\sigma}{r_{ik} - \alpha\sigma}\right)$$

LAMMPS software is used to run the MD simulations, ISAACS software to calculate the ring and angular distribution, the VMD software to display the atomic configuration image.
2.1 Investigate the correlation between the average total energy per atom and the temperature
Figure 1 shows the dependence of total energy on temperature when cooling silicene in molecular dynamic simulation at rate $10^{13}$K/s.

![Figure 1. Temperature dependence of total energy when melting 2-dimensional Silicene model](image)

From Figure 1, we can see that at a temperature of 2264K, the curve deviates from the tangent. At 1279K, the curve also deviates from the tangent, the phase transition temperature is the average of these two temperatures, to be 1772K. The temperature of this phase transition is only slightly different from that of the silicene phase transition when cooled at a rate of $10^{10}$ K/s by the team of Vo Van Hoang to be 1775K [9].

2.2 Radial distribution function
The graph in Figure 2 shows the radial distribution function (RDF) at different temperatures during silicene cooling.
Figure 2. Temperature dependence of radial distribution functions when cooling silicene model, bold lines are for $T = 1700K$ and $T = 1780K$ which are closed to $T = 1772K$

From the graph, we can see that in the temperature range from 3500K to below 1780K appeared another atomic distribution peak. At a temperature of 1770K (close to the phase transition temperature), there appear many peaks in the $g(r)$ function, indicating the appearance of crystal formation. This result reinforces the above results showing that the phase transition temperature is about 1772K. From the transition temperature onward, the peaks form more and more clearly. At 300K, the plot has discrete pointed peaks, indicating that crystalline silicene has formed in the model.

2.3 Coordination number distribution function

The graphs in Figure 3 show the distribution of coordination number at different temperatures of 3500K, 1770K, and 300K.
At temperature $T = 3500K$, there are no coordinate numbers greater than 8. The coordinate numbers 2, 3, 4, 5, 6, 7 have an uneven distribution. The coordinate number percentages of 3 and 4 are 38.92% and 46.69% respectively. Besides, the 2, 5, 6 coordinate number percentages are small proportions of 1.55%, 11.91%, and 0.812% respectively. At the temperature close to the transition temperature of $T = 1770K$, the coordination number of 4 tends to decrease and reaching 31.57%, on the contrary, the number coordination of 3 continues to increase and reaching 65.01%. At 300K, the number coordination of 4 decreases to 4.87%, the 3-coordinate increases continuously, and reaching 94%, the 2-coordinate is of small value, about 1.14%, the remaining coordinates disappear.

Figure 3. Coordination number distribution (a) 3500K, (b) 1770K (c) 300K
2.4 Ring distribution function

The graphs in Figure 4 show the ring distribution at different temperatures of 3500K; 1770K and 300K.

At temperature 3500K, the value of ring 3 dominates with a ratio of 39.04%. Percentages of rings 4, 5, 6 are 24.09%, 23.05%, 10.27% respectively. Percentages of rings 7, 8, 9, 12 are very small, insignificant.

At temperature T = 1770K, ring 3 tends to decrease gradually and reaches 8.86%, ring 6 increases rapidly and reaches 26.89% at the phase transition temperature. At temperature T = 300K, rings of 3, 4, 5 continue to decrease, ring 6 increases and dominates, reaching the ratio of 62.50%.
2.5 Mean ring distribution

Figure 5 shows the change of the average ring distribution on the temperature. The graph is plotted for 20 different temperatures.

![Figure 5](image)

**Figure 5.** Temperature dependence of mean ring size

The mean ring size values distribute in the range of 4.15 before the phase transition temperature. At phase transition temperature, the mean ring size changes soared. After the transition temperature, the mean ring size did not change much, having a value in the range of 5.41. The mean ring size values tend to increase with decreasing temperature from 3500K to 300K. The mean ring size reaches 6 when the temperature is close to 300K.

2.6 The angle distribution function

The graphs in Figure 6 show the distribution of the bonding angle at different temperatures of 3500K; 1770K and 300K.
Figure 6. Bond - angles distributions (a) 3500 K, (b) 1770 K (c) 300 K

At 3500K, the Si - Si - Si bond-angle distributes mainly in the 53º-168º range. The curve has a continuous variation. The ratio of Si-Si - Si angle value increases and decreases continuously, it concentrates mostly at the value 108.5º, with a ratio of 1.10%, but the peak is not formed. From the value of angle 121º, the angles tend to decrease steadily as the temperature decreases; the peak of the curve is more visible. At temperatures close to the phase transition temperature, 1770K, the peak of the curve is more pointed, reaching a maximum at 116.52º with a ratio of 1.68%. At temperature 300K, the value of the bonding angle narrows in the range 51.47º to 179.63º, reaching the highest ratio at the bonding angle of 119.46º with a ratio of 3.87%. The peak of the curve has a change of magnitude and percentage; it tends to shift to the right as the temperature decreases.
2.7 Interatomic distance distributions
The graphs in Figure 7 show the interatomic distance distributions at different temperatures of 3500K, 1770K, and 300K.

The interatomic distance change at pre-phase transition temperatures from 3500K to 1770K is not clear. At 300K, the interatomic distance varies from 0.1-0.2 (Å).

Figure 7. The interatomic distance distribution (a) 3500 K, (b) 1770 K (c) 300 K
2.8 The distribution function of mean angle
The graph in Figure 8 shows the dependence of the mean bond-angle distribution on the temperature.

![Graph showing the distribution function of mean angle](image)

**Figure 8.** Temperature dependence of the mean bond angle distribution.

The values of the average bond angle ranged around 110.67º before the phase transition temperature. After the phase transition, this value is about 117.25º. When reducing the temperature from 3500K to 300K, the average bond angle tends to increase intermittently.

2.9 Visualization 2D of the crystalline silicene model
The visual image of the silicene model at a temperature of 300K is shown in Figure 9 below. It can be seen that at a cooling rate of $10^{13}$ K/s, silicene forms two-dimensional crystals with the majority of rings 6, with a ratio of 62.5%. Structural defects form rings 5, 7, 8, which have a pretty high ratio. The defects of the ring-merging type also appear such as merging 2 rings, 3 rings. These will significantly increase the electrical and thermal conductivity of silicene. This result is significantly different from the result obtained by the Vo Van Hoang group [15], they also cooled silicene from 3500K to 300K but the lattice structure defects ratio is less than 3%. This is because the cooling rate in the study of the Vo Van Hoang group is $2.10^{10}$ K/s which is much lower than $10^{13}$ K/s in our study.
3. Conclusion
The paper presents the results of the study of cooling silicene liquids at a rapid cooling rate of $10^{13}$ K/s. Simulation results show that the phase transition temperature from liquid to crystal is about 1772K. Investigations of the ring distribution, the coordination number distribution, the distribution of the angles, the distance distribution also showed phase transition at this temperature. As the temperature decreases, silicene gradually forms a crystal structure with the majority of Si atoms distributed in the lattice. The crystal has a nearly symmetrical structure, with lattice failure with a large percentage, about 37.5%. This failure of the lattice causes the electrical and thermal conductivity of silicene to increase significantly compared to perfect silicene.

4. References

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