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Liquid-liquid phase transition in quasi-two-dimensional supercooled silicon

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Abstract

Anomalies of the local structural order in quasi-two-dimensional liquid silicon upon cooling are investigated. Results show that the appearance of the left subpeak in pair correlation functions is the signature of the liquid-liquid phase transition (LLPT). The structural origin of the LLPT is the formation of a crystal-like ordered structure with a short-range scale, which in turn forms the local well-organized paracrystalline region. Unlike in the bulk liquid silicon, the stages of the LLPT and liquid-solid phase transition (LSPT) in the quasi-two-dimensional liquid silicon do not overlap. The crystal-like ordered structures formed in the LLPT are precursors which are prepared for the subsequent LSPT. Also observed was a strong interconnection between the local well-organized paracrystalline region and the transition from the typical metal to the semimetal in the two-dimensional silicon. This study will aid in better understanding the essential phase change in two-dimensional liquid silicon.

Introduction

Silicon remains the central material of choice in semiconductor technology because of its unique electronic properties. Silicon single crystals are usually prepared from the melt, thus a better understanding of their physical properties and structural transition in liquid and undercooled states is of considerable importance. Much effort has been devoted to the study of the structure of supercooled liquid silicon (l-Si), but the atomic structure and its transition from a metallic structure at high temperature to a semiconducting network at low temperature remain uncertain, due to the limitations of current theoretical understanding [1]. High-temperature, high-pressure X-ray diffraction results have revealed unusual structural properties concerning the pressure [2] and temperature [3] of 1-Si. In fact, one of the most challenging issues involved with the physics of l-Si is the possible existence of a liquid-liquid phase transition (LLPT) hidden deeply in the supercooled region from a high-density liquid (HDL) to a low-density liquid (LDL), a concept which was pointed out by Aptekar [4] based on thermodynamic considerations. Recently, Deb [5] and McMillan [6] observed the existence of a high-coordinated HDL, a tetrahedrally coordinated LDL and a LLPT in supercooled l-Si. Meanwhile, theoretical simulations [7-9] provided further evidence to support the idea of an underlying LLPT implying the existence of a LDL phase and its glass transition to an amorphous solid. High-energy heavy ion irradiation experiments by A. Hedler *et al.* [10] also provided experimental evidence for the existence of the LDL and supported the idea of liquid polymorphism as a general phenomenon in tetrahedral networks. In these studies, the method of evaluating an LLPT is to test an abrupt variation of the structural properties as a function of number density [11-14]. M. Beye *et al.* [15] have used femtosecond x-ray pulses to check the valence electronic structure in order to prove the existence of the LLPT in l-Si. These findings are valuable to well understand whether a HDL phase exists that has a smooth transition to LDL phase. However, as for what forms in the supercooled l-Si during the LLPT, in other word, what is the origin of the LLPT, has not been well tackled. Some researchers [16-18] suggested that the competition between the normal liquid density ordering and bond ordering favoring formation of local structures existing in supercooled l-Si leads to the LLPT. Therefore, the main concern of researchers is whether or not the local crystalline order is the origin of the LLPT in supercooled l-Si. Despite numerous experimental and theoretical attempts to determine the structural nature of LLPT, a satisfactory understanding has yet to be attained, due to the complexity of the liquid structures. This unsatisfactory research state has hindered not only the criterion of the LLPT, but also the clarification of the mechanism of this transition. In particular, most research regarding LLPT has focused on three-dimensional bulk l-Si, and studies covering two-dimensional (2d) l-Si have been even more limited. In fact, it is very difficult for local structural order to monitor in a three-dimensional picture of a continuous random network, many structural techniques, such as diffraction, which are sensitive only to atomic position correlations and not to connectivity, may not be able to detect the topological order at a medium-range length scale (10-35 Ǻ). [19] However, quasi 2d l-Si is believed to be convenient for monitoring the local structural order from the complex random network in the LLPT. On the other hand, research regarding quasi 2d l-Si may provide profound guiding significance for the further understanding of the growth mechanism of silicene, which is regarded as a potential candidate for use in the semiconductor industry. [20-21] Based on these circumstances, this study mainly focuses on the nature of the LLPT in the supercooled region and the internal relation among the local structural order, LLPT and electronic structure in quasi 2d l-Si at the nanoscale.

Methods

Classical MD simulations of l-Si have been performed using the Stillinger-Weber (SW) potential [22] supplied in LAMMPS [23]. A system with 3200 silicon atoms distributed in a 20×20×1 lattice unit box was employed to model the quasi 2d silicon. The simulation is performed with NPT ensemble and the pressure of the system is 1 bar. Periodic control was exerted on the x- and y- dimensions of the box. The lower boundary of the simulation box along the z-direction (not refer to atoms) was fixed just like a physical wall. The physical wall at the lower edge can interact with the interface atoms, the function of which is similar with the substrate. The existence of the physical wall can bound the simulation domain on one of its faces with a flat wall that interacts with the atoms in the group by generating a force on the atom in a direction perpendicular to the wall [23-26]. The initial box lattice was set to 5.42 Å, and the initial positions of the atoms were arranged based on the structure of the diamond. The MD time step was chosen as 1 fs. The temperature was controlled by the Nose-Hoover thermostat [27]. First, the well-equilibrated l-Si was prepared by gradually heating the ideal crystal to 2700 K at a low cooling rate (Q=1 K/ps), then relaxing it for 100 ps. The relaxing time is sufficient to obtain the well-equilibrated state of quasi 2d l-Si at high temperature. Afterwards, the l-Si was quenched to T = 300 K at different cooling rates, varying from 1.08 to 10.8 K/ps. At each given temperature during the quenching process, the configurations were saved in order to further analyze the structural information and electronic properties of the simulated system. The pair correlation functions, the deviation curves and mean-squared displacement are a statistical average of fifty configurations recorded in simulations.

Next, we chose a quarter of the obtained configurations as the initial data for the Car-Parrinello (CP) simulation performed with Quantum Espresso package [28]. In the following CP simulation, the electronic structure was described within the framework of the density-functional theory (DFT) using the generalized gradient approximation (GGA) [29]. We employed norm-conserving pseudopotentials with plane-wave expansion of the Kohn-Sham wave functions and charge densities up to a kinetic energy cutoff of 24 and 96 Ry, respectively. A time step of 0.1 fs was used with the fictitious mass of electron set to 300 a.u. within the suggested range for the accurate CP simulation [30,31]. The Nose-Hoover thermostat on ions and electrons was applied in both liquid and solid silicon [32].

Results and Discussion

In order to showcase the LLPT in the supercooled l-Si, the pair correlation functions (PCFs) with different cooling rates are shown in Figure 1. As shown in Figure 1a-c, the main peak height of the PCFs increases significantly as the temperature decreases, indicating the enhancement of short-range order (SRO) or medium-range order (MRO) in the supercooled l-Si. Unlike the main peak, the shape of the second peak shows a variety of changes at different cooling rates. When the cooling rate is Q1 = 10.8 K/ps, the left subpeak on the second peak of PCF starts to appear as the temperature decreases. In order to check whether the system remains liquid upon cooling and to distinguish from its amorphous state, we have calculated the mean-squared displacement (MSD) of the quasi 2d silicon at different temperature as shown in Figure 2. The MSD of the quasi 2d silicon at 1300 K keeps a high slope upon different cooling rate, indicating that the system remains liquid. Considering that this subpeak appears before the LSPT, it is suggested that the left subpeak may be the signature of the LLPT. When the cooling rate decreases to Q2 = 2.7 K/ps, the second peak splits into the left and right subpeaks. In the case of Q3 =1.08 K/ps, the left subpeak becomes weak but the right subpeak is more apparent, which implies that the length of the ordered structure formed is further extended to a large scale. Actually, the information of the LLPT in bulk l-Silicon is easily hidden by the LSPT unless an appropriate cooling rate is applied, which is proved by N. Jakse and A. Pasturel [8],while the situation in 2d l-Silicon may be different from the 3d one owing to the nature of the quasi-2d materials. Actually, further studies verify that the LLPT can also be observed with the appearance of the short-range structures composed of the ordered bond-types with different physical walls. That is to say, the LLPT may be the natural character of the quasi-2D liquid silicon, which is not affected by the role of the physical wall.

To get a better characterization of LLPT, the distribution of local bond orientated order parameter Q6 is applied. The bond orientated order parameter is usually used to describe the symmetry of bond orientations regardless of the bond lengths [7]. The LLPT and LSPT regions can be defined according the distribution of local bond orientated order parameter Q6. A bond is defined as the vector joining a pair of neighboring atoms. There are two methods to obtain the bond order parameters, one is the “global” average bond order parameter; the other is the “local” bond order parameter of a specified atom according to its nearest neighbors [24]. The changes of the local bond orientational order parameter with temperature at three different cooling rates are supplied in Figure 3. At 1500 K, the distribution of local Q6 has only one flat peak at Q6=0.45. But, when the temperature decreases to the 1300 K, another sharp peak at Q6=0.6 appears which gradually shifts toward higher Q6 as the temperature decreases, indicating a new structural change in the liquid silicon, which corresponds to the above mentioned low-density hexagon frameworks. As for the cooling rate 1.08 K/ps, it can be seen that the main peak at Q6=0.45 decreases with the temperature, and finally at T=1000 K, the main peak nearly disappears. Interestingly, another subpeak at Q6=0.6 becomes more and more apparent with the temperature. At T=1000 K, the subpeak at Q6=0.6 becomes a very sharp peak. Therefore, we suggest that the temperature range to occur the LLPT might be between about 1300 K and 1500 K.

The corresponding atomic evolution snapshots are used to further analyze the LLPT in the 2d supercooled l-Si. In general, high-temperature l-Si is heterogeneous at a short-range scale (less than 5 Å). As shown in Figure 4, at high temperature (T = 2400 K), the l-Si is mainly composed of two distinct regions: one is partially ordered in short range (shown in I), and the other is fully disordered (shown in II). "Partially ordered in short range" region means the region in short range has some covalent atoms, while the "disordered" regions means there is no covalent atom in short range. At the temperature of T =1300 K, the fraction of short-range structures begins to increase, which corresponds to the subpeak formation in the PCFs, indicating the LLPT. Afterwards, these short-range ordered regions convert into some local well-organized regions with crystal-like ordering. It is worth noting that there are two types of local well-organized regions possessing different growth orientations with decreasing temperatures, which is similar to the graphene possessing polycrystallinity.[33,34] It should also be noticed that the cooling rate may significantly affect the length scale of the local well-organized regions. At Q1 = 10.8 K/ps, some hexagon-like structures with lengths of less than 8 Å appear at 1100 K, and finally convert into the short-range ordered regions. When the cooling rate is decreased to Q2 =2.7 K/ps, the case is different with the above mentioned. At 1100 K, the short-range regions with hexagon-like ordering begin to extend to a large-range length scale, then these short- or medium-range ordered regions change into some local paracrystalline regions in a large-scale at 900 K, showing some isolated paracrystallites embedded in a disordered matrix, displayed by the right subpeak formation in the PCFs as shown in Figure 1b. A further decrease in the cooling rate from 2.7 to 1.08 K/ps would lead to an increase in the fraction of the paracrystalline region and its length scale (from 10 to 35 Å). Actually, when the length scale of the paracrystalline regions extends to 35 Å, it would lead to the formation of the distinct right subpeak in PCFs. It is worth mentioning that the origin of the LLPT is the formation of the local crystal-like ordered region with a short- or medium-range scale in the supercooled l-Si.

The above results arouse our interest in further studying the internal structural evolution upon cooling. Bond statistics [35-38] are efficient tool for describing and discerning the concrete bond relation between an atom and its neighbors, which may clearly reflect the atomic packing. In particular, the bond-type Nx (N = 0, 1 2 3) is defined as the bond number of a central atom sharing with its neighboring atoms in the quasi 2d plane. As shown in Figure 5, at 2400 K, only a small fraction of 1x bond-types exists. With the temperature decreasing to 1500 K, the number of 1x and 2x bond-types begins to increase, exhibiting a certain degree of covalent character. Meanwhile, 3x bond-types may also be observed. At 1300 K, the isolated ordered bond-types (1x, 2x and 3x) have connected with each other to form an incomplete hexagon framework with a short- or meidum-range, which corresponds to the LLPT. Further decreasing the temperature would cause some ordered bond-types to join together and create long-periodic hexagon topological frameworks, which corresponds to the length of the ordered structure is extended to a large scale (exceed to 35 Å).

The short-range ordered structure present in the supercooled l-Si should be reflected in the electronic properties of the system. [39,40] Therefore the density of states (DOS) have been calculated for three different configurations at Q = 10.8 K/ps with temperature decreases. Figure 6 shows the DOS obtained from three typical temperatures. In the high-temperature equilibrium liquid states at 2400 K, due to the lack of the crystal-like ordered structure, the DOS does not display a pseudogap at the Fermi energy, indicating that the system shows a typical metallic character. As the temperature decreases, a pseudogap is found in the supercooled l-Si at 1300 K at the Fermi energy, which corresponds to the appearance of the incomplete hexagon-like ordered structures. These structures contain an abundance of isolated ordered bond-types which possess a certain degree of covalence. Therefore, it is confirmed that the appearance of incomplete hexagon frameworks composed of ordered bond-types may be the structural origin of the LLPT, which separates the equilibrium liquid into a high-density metallic liquid and a low-density semimetallic one. At the temperature of T = 900 K, the pseudogap at the Fermi energy becomes more evident. This is a consequence of the length of the ordered structure is extended to a large scale (exceed to 35 Å), which have a more covalent nature than the incomplete ones. The difference in the DOS provides direct evidence for the metal-to-semimetal structural transition of 2d l-Si upon cooling [39]. Ab initio study of the DOS for the silicone [41] showed that its gap is closing at the Fermi energy, while the dispersion around this point is linear, which is similar to graphene. It worth noting that the DOS of quasi 2d silicon is different from those of the silicene and bulk silicon [1,2,7,8,41], which possesses several atom layers along the z-axis and can be viewed as the mixture of the hexagon framework and disordered regions. [23,24] In fact, short- or medium-range ordered regions, visible to different extent in quasi 2d supercooled l-Si, clearly show the existence of the LLPT. These ordered regions result in some changes to the electronic properties and anisotropy. The new short- or medium-range ordered structures formed in the LLPT are key units for the LSPT, which determine its freezing behavior.

It must be pointed out that the LLPT in our study is quite different with the study by Angell et al [7]. Firstly, the LLPT studied by Angell et al appears at a constant temperature with the NPH ensemble. In our study, the LLPT has been detected in a continuous quenching process with the NPT ensemble. The LLPT may be covered up by subsequent LSPT [8]. Secondly, the LLPT in 2d l-Si can be regarded as a structural transition by forming small amount of low-density hexagon frameworks in SRO or MRO, while the situation in 3d l-Si is totally different from the 2d one [8,11-14,42,43]. Theoretically, the LLPT in bulk silicon or water can be viewed as the transitions between liquid and crystal [44-47]. However, in quasi-2d materials, some basic precursors generate for the LSPT during the LLPT, and thus the LSPT is regarded as the result of the further development of the LLPT. From the change of Q6, we suggest that the LLPT should be very important for the freezing process, which is the seedtime of the LSPT. In addition, our results show that the orientation of the crystal becomes more and more complicated with the increase of the thickness. In our opinion, the atomic arrangement in the bulk silicon tends to form the more complex network, which is similar to the structure of cubic diamond. With the decrease of the dimensionality, the quasi 2d l-S is more likely to form the hexagon frameworks along the X-Y plane, which makes the structural network of the LLPT of quasi 2d l-Si is totally different from the bulk one.

Conclusions

In summary, we investigated the atomic evolution of the quasi 2d l-Si upon cooling, which experiences an obvious structural transition from short- to medium-range order. The growth of the subpeak on the left of the second main peak indicates the progress of the LLPT. The incomplete hexagon frameworks composed of the ordered bond-types may be the structural origin of the LLPT and the equilibrate liquid could separate into high-density metallic liquid part and low-density semimetallic liquid part. Metal-to-semimetal transition is a consequence of the increase of hexagon frameworks which forms the local paracrystalline region with a more covalent nature. Our findings have provided physical and dynamic insights into the structural transition in the supercooled l-Si in two-dimension. This study is of great significance to control the structure of the low-dimensional amorphous silicon in order to obtain high performance semiconducting materials.

References

[1] P. Ganesh, M. Widom, *Phys. Rev. Lett.* **102**, 075701 (2009).

[2] N. Funamori, K. Tsuji, *Phys. Rev. Lett.* **88**, 255508 (2002).

[3] T. H. Kim, *et al. Phys. Rev. Lett.* **95**, 085501 (2005).

[4] L. I. Aptekar, *Sov. Phys. Dokl.* **24**, 993-995 (1979).

[5] S. K. Deb, M. Wilding, M. Somayazulu, & P. F. McMillan, *Nature* **414**, 528-530 (2001).

[6] P. F. McMillan, *J. Mater. Chem.* **14**, 1506-1512 (2004).

[7] S. Sastry, C. A. Angell, *Nat. Mater.* **2**, 739-743 (2003).

[8] N. Jakse, A. Pasturel, *Phys. Rev. Lett.* **99**, 205702 (2007).

[9] V. V. Vasisht, S. Saw, S. Sastry, *Nat. Phys.* **7**, 549-553 (2011).

[10] A. Hedler, S. L. Klaumunzer, W. Wesch, *Nat. Mater.* **3**, 804-809 (2004).

[11] G. Makov, E. Yahel, *J. Chem. Phys.* **134**, 204507 (2011).

[12] S. Harrington, R. Zhang, P. H. Poole, F. Sciortino, H. E. Stanley, *Phys. Rev. Lett.* **78**, 2409-2412 (1997).

[13] J. N. Glosli, F. H. Ree, **82**, 4659-4662 (1999).

[14] G. Franzese, G. Malescio, A. Skibinsky, S. V. Buldyrev, H. E. Stanley, *Nature* **409**, 692-695 (2001).

[15] M. Beye, F. Sorgenfrei, W. F. Schlotter, W. Wurth, A. Fohlisch, *P. Natl Acad. Sci. USA* **107**, 16772-16776 (2010).

[16] H. Tanaka, *Phys. Rev. B* **66**, 064202 (2002).

[17] K. B. Borisenko, *et al. Acta. Mater.* **60**, 359-375 (2012).

[18] M. M. J. Treacy, K. B. Borisenko, *Science* **335**, 950-953 (2012).

[19] J. M. Gibson, M. M. J. Treacy, T. Sun, & N. J. Zaluzec, *Phys. Rev. Lett.* **105**, 125504 (2010).

[20] G. G. Guzmani., L. C. Lew. *Phys. Rev. B* **76**, 075131 (2007).

[21] P. Vogt, *et al. Phys. Rev. Lett.* **108**, 155501 (2012).

[22] F. H. Stillinger, T. A. Weber, *Phys. Rev. B* **31**, 5262-5271 (1985).

[23] S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).

[24] F. Ding and A. Rosen, *Appl. Phys. Lett.* **88**, 133110 (2006).

[25] K. Zhang, H. Li, L. Li, and X. F. Bian, *Appl. Phys. Lett.* **102**, 071907 (2013).

[26] K. Zhang, *et al. Europhys. Lett.* **96**, 46005 (2011).

[27] S. Nose, *J. Chem. Phys.* **81**, 511(1984).

[28] P. Giannozzi, *et al. J Phys-Condens. Mat.* **21**, 395502 (2009).

[29] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865-3868 (1996).

[30] J. C. Grossman, E.Schwegler, E. W. Draeger, F. Gygi, & G. Galli, *J Chem. Phys.* **120**, 300-311 (2004).

[31] J. T. Okada, *et al. Phys. Rev. Lett.* **108**, 067402 (2012).

[32] W.G. Hoover,. *Phys. Rev. A* **31**, 1695 (1985).

[33] F. Ding, K. Jiao, M. Wu, & B. I. Yakobson, *Phys. Rev. Lett.* **98**, 075503 (2007).

[34] B. I. Yakobson, F. Ding, *Acs Nano* **6**, 5735-5735 (2012).

[35] Y. J. Lu, P. Entel , *Phys. Rev. B*, **84,** 104203 (2011).

[36] J. Bai, H. Tanaka, X. C. Zeng, *Nano Res*, **3**, 694-700 (2010).

[37] J. D. Honeycutt, H. C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).

[38] Y. C. Lo, J. C. Huang, S. P. Ju, X. H. Du, *Phys. Rev. B* **76**, 024103 (2007).

[39] S. S. Ashwin, U. V. Waghmare, S. Sastry, *Phys. Rev. Lett.* **92**, 175701 (2004).

[40] T. Morishita, *Phys Rev Lett* **97**, 165502 (2006).

[41] S. Lebegue, O. Eriksson, *Phys. Rev. B*, **79**,115409 (2009).

[42] P. Beaucage, N. Mousseau, *J. Phys.: Condens. Mat.* **17**, 2269–2279 (2005).

[43] Y. He, X. Li, H. Li, Y. Jiang and X. Bian, *Nanoscale*, **6**, 4217-4224, (2014)

[44] W. Hujo, B. S. Jabes, V. K. Rana et al. *J Statist. Phys.* **145**, 293-312 (2011).

[45] D. T. Limmer, D.Chandler. *J Chem. Phys.* **135**, 134503 (2011).

[46] D. T. Limmer, D.Chandler. *J Chem. Phys*. **138**, 214504 (2013).

[47] K. Zhang, Y. Jiang, K.S. Li, H. Li, D.B. Yu. *J Alloy Compod.* 611, 386–388 (2014).

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Author information

Competing financial interests

The authors declare no competing financial interests.

Figure captions

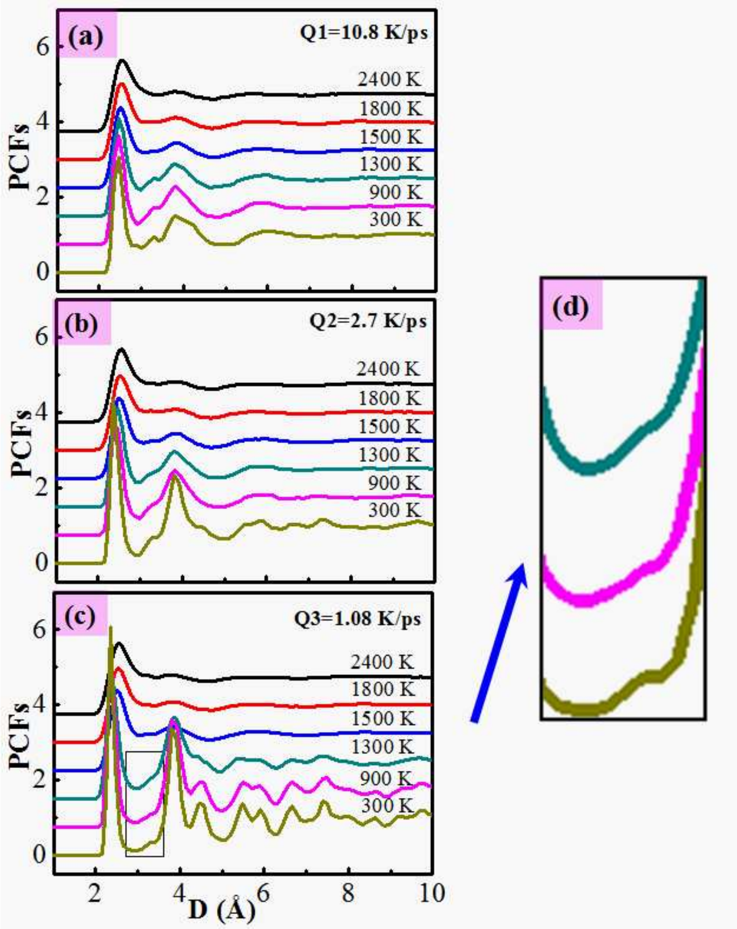

Figure 1 The PCF of the quasi 2d l-Si upon quenching at three different cooling rates: (a) Q1=10.8 K/ps; (b) Q2=2.7 K/ps; (c) Q3=1.08 K/ps; (d) the enlarged local region between the first and second peaks.

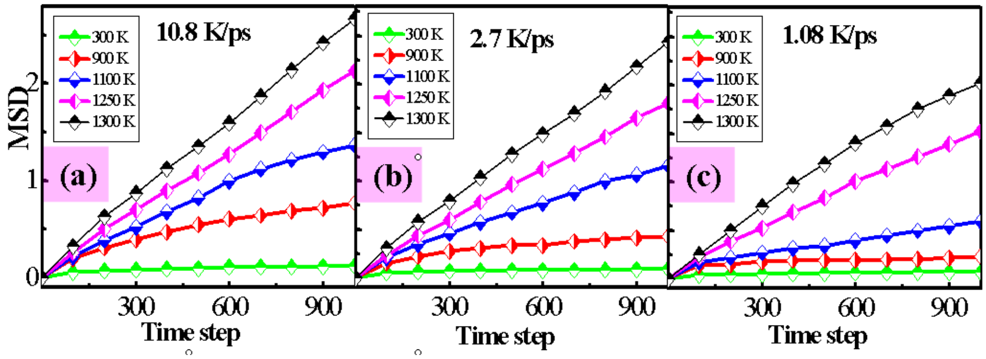

Figure 2 The mean-squared displacement (MSD) curves at different temperatures with three different cooling rates.

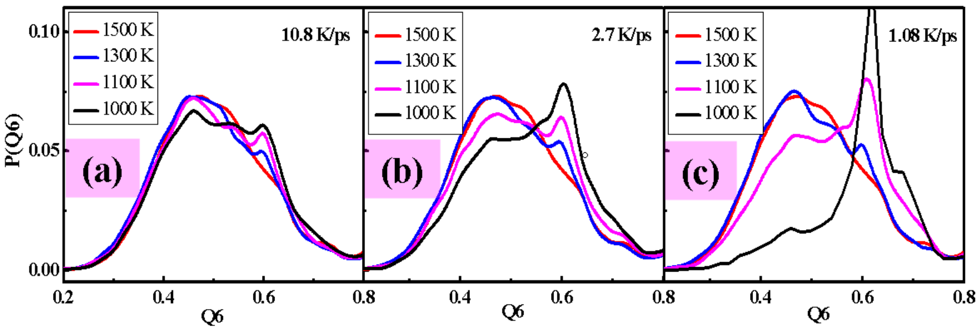

Figure 3 The changes of the local bond orientational order parameter Q6 with temperature at three different cooling rates.

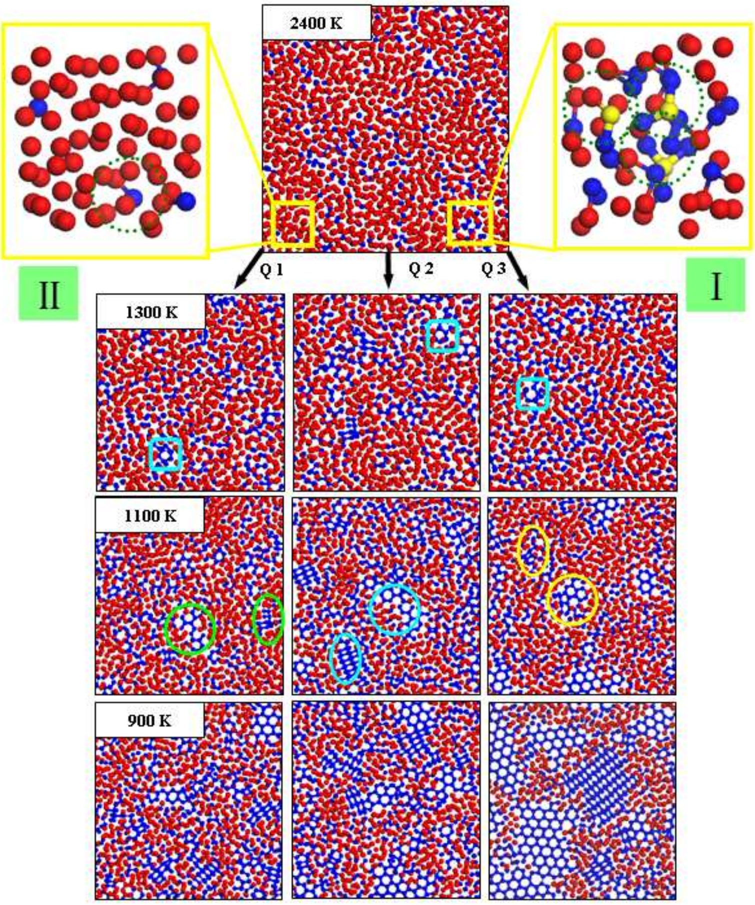

Figure 4 (Top) The top view of atomic configuration of the quasi 2d l-Si at 2400 K (Coloring denotes the local environment of each atom: Blue, atoms in crystal-like order; Red, atoms in disorder). (Bottom) Local atomic arrangement of the quasi 2d silicon with temperature at three cooling rates: (from left to right) Q1 = 10.8 K/ps; Q2 = 2.7 K/ps; Q3 = 1.08 K/ps. The incomplete hexagon framework at 1300 K is labeled with the square. Two primary paracrystallites with different growth orientations at 1100 K are also labeled: RI (circle) and RΠ (ellipse). The yellow atom refers to the central atom of the ordered cluster in short range which is identified by the dotted circle with green line.

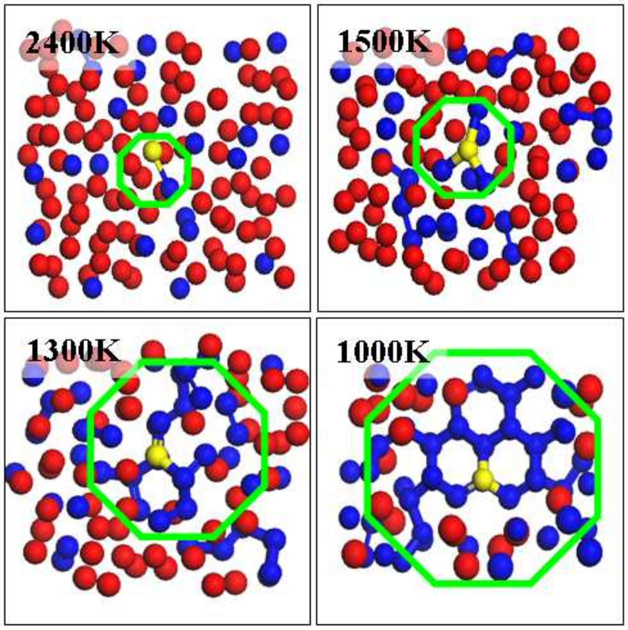

Figure 5 The snapshots of the ordered bond-types which construct hexagon-like structures and then convert into the paracrystalline region with short- or medium-range order.

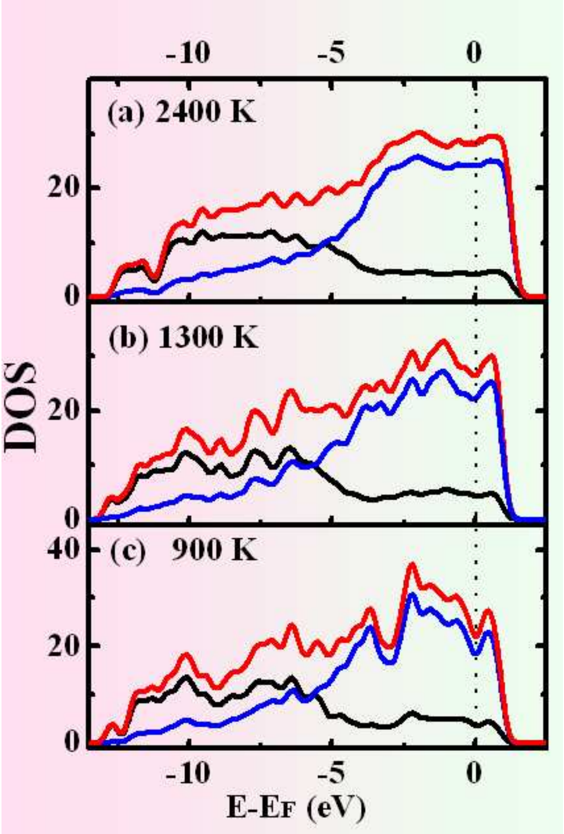

Figure 6 Total and partial DOS curves for different temperatures: (a) 2400 K; (b) 1300 K; (c) 900 K at Q1=10.8 K/ps. Black: s-orbit; blue: p-orbit: red; the total orbit.