

Molecular dynamics simulation of the local inherent structure of liquid silicon at different temperatures

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(Received 5 January 1999; revised manuscript received 19 March 1999)

Constant-volume and constant-temperature molecular dynamics simulations have been performed to study the inherent structural properties of liquid silicon (*l*-Si) at different temperatures by using Tersoff potential. Our results first show that the 50°–60° peak in bond angle distributions decomposes into two peaks, which are located 52° and 60°, and a new peak at 75° appears; the 52° peak disappears with a small cutoff distance. The bond length of bonds contributing to 52° peak is much greater than the cutoff distance of covalent bond. The height of 52° peak at first increases and then decreases with temperature, and has a maximum at a certain temperature. The probability of the covalent bonds whose bond angle is greater than 67° shows an anomalous decrease at a certain temperature. These anomalous features may play an important role on the anomalous behavior of some physical properties in *l*-Si such as electrical resistivity. The height of 60° and 75° peaks increases with temperature. [S0163-1829(99)04229-0]

I. INTRODUCTION

Most silicon (Si) single crystals are grown from melts. Recent technological demands for Si devices require upgrading of the quality and scaling up of the size of crystals. Dislocation-free single crystals are obtained only by restricting the condition in a temperature range near the melting point. It has recently been pointed out that the fundamental physical properties including the atomic-scale structure of liquid silicon (*l*-Si) are required for understanding and control of the crystallization mechanism.¹

l-Si has several intriguing and poorly understood properties. Upon melting, the density of Si increases by ~10%,² and its structure goes from an open structure with coordination number equal to 4 to a more compact liquid structure characterized by a coordination number exceeding 6.^{3,4} *l*-Si is metallic; in contrast, the crystal and the amorphous phase are semiconducting. The experimentally determined atomic structure factor of *l*-Si exhibits peculiar features,^{3,4} and its static structure factor strongly differs from that characteristic of simple liquid metals. The low coordination of *l*-Si indicates a persistence of covalent bonding in the liquid.

Recently, anomalous temperature dependence of the physical properties of *l*-Si have been observed in the temperature range just above the melting point of Si by Kimura and co-workers, such as the density,⁵ the surface tension,⁶ the viscosity,⁷ and the electrical resistivity.⁸ For temperatures lower than about 1430 °C, the density and the viscosity show a steep increase. Above 1425 °C, the surface tension increases with decreasing temperature with the temperature coefficient being negative, however, the temperature coefficient of the surface tension becomes positive at about 1425 °C and returns to a negative value just above the melting point. The temperature coefficient of the resistivity is negative near the melting point of Si and positive for higher temperature, the resistivity of molten Si shows a local minimum in the range from 1450–1500 °C. They suggest that changes in the melted

structure, such as interatomic distance, coordination number, and local ordering, lead to this anomalous behavior. A thorough understanding of this anomalous behavior is technologically important because the anomalous range is involved in the crystal growth from molten Si. However, to our knowledge, the detailed analysis of the anomalous behavior has not been performed.

Molecular dynamics (MD) simulations provide a useful technique to analyze atomic structure of the liquid phase. Several empirical interatomic potential for Si have been proposed by many investigators.⁹ Recently, the potential presented by Tersoff¹⁰ have been used to investigate the validity of this potential for *l*-Si,^{11,12} and it is found that this potential is very useful for the structural analysis of *l*-Si (Ref. 10) though the Tersoff potential overestimates greatly the melting temperature. The results of bond angle distributions are in good agreement with those obtained by *ab initio* calculations¹³ and tight-binding MD simulations.¹⁴ A peak appears around 60° in the bond angle distributions of *l*-Si and increases slightly with temperature, which leads to a conclusion that a possible structure model is simple hexagonal (SH) structure.¹² From these results and the static structure factors of *l*-Si recently measured by Waseda *et al.*¹⁵ (a characteristic shoulder on the high-wave number side of the first peak has been found to become slightly obscure as temperature increase), the authors in Ref. 12 suggest that the *l*-Si network may consist of not only the white-tin structural units but also configurations with the closed-packed layer such as SH structure and believe that structural fluctuations between the white-tin and SH structure can be attributed to anomalous behavior of physical properties in *l*-Si near melting temperature. However, it should be noted that the 60° peak in bond angle distribution in Ref. 14 (where it was considered to be around 50°) was attributed to abundant floating bonds in *l*-Si.

An insightful approach to study the local structure of liquid and amorphous states of matter is through the classifica-

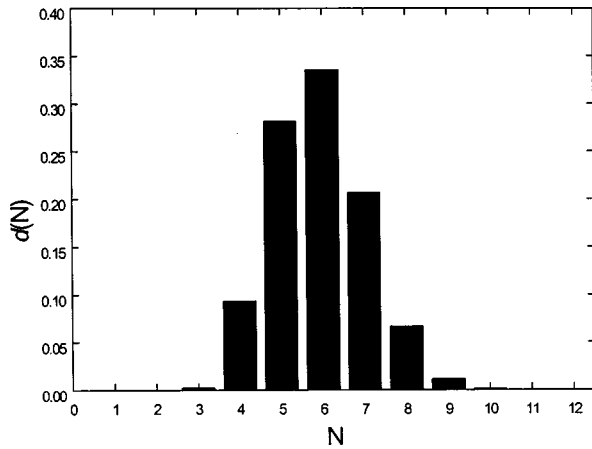


FIG. 1. Distribution $d(N)$ of local coordination in l -Si obtained near melting temperature. The coordination shell is defined by the cutoff distance 3.1 Å.

tion of atomic configurations, according to multidimensional potential-energy minima, that can be reached by steepest descent paths in computer simulation of these systems.¹⁶ The “inherent structure” formalism is a way to partition the configuration space for the vibrations of a n -body system into various regions. Within each region there is one local minimum of the potential-energy surface that can be reached by a minimization algorithm. This process is the basis for the partitioning of configuration space and the structure at local minimum is the inherent structure of the corresponding region. The idea of resolving observable order in liquid and amorphous materials into the vibrational and the inherent structural parts offers a way to classify their microstructure and to discover the kind of the short-range order in these materials.

In this work, we present results of a microstructural study of l -Si using MD simulations and a conjugate gradient energy minimization method to find its inherent structures of the multidimensional potential-energy surface given by the Tersoff potential. The main goal of this work is to investigate the local inherent structural properties of l -Si at different temperatures and attempts to obtain some information on the

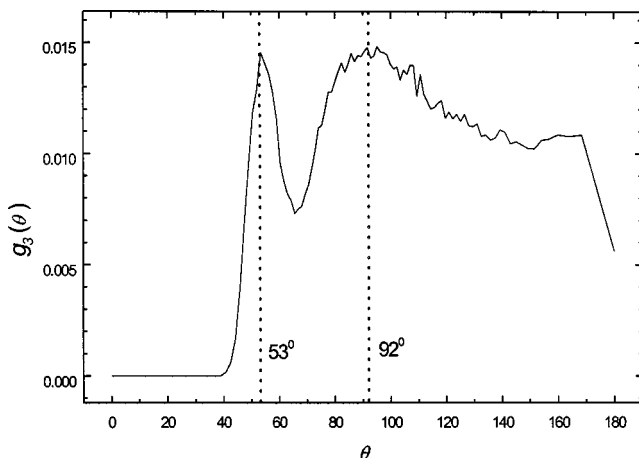


FIG. 2. Bond angle distribution function $g_3(\theta)$ at 3000 K. The cutoff distance is 3.1 Å. The two dotted lines denote the location of two peaks.

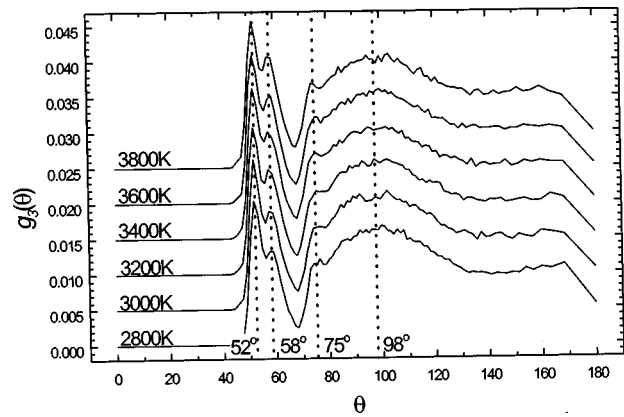


FIG. 3. Bond angle distribution function $g_3(\theta)$ at six different temperatures. The cutoff distance is 3.1 Å. The four dotted lines denote the location of four peaks.

above anomalous temperature dependence of the physical properties of l -Si. In Sec. II we present the computational methods. Section III contains the results and discussion. A brief summary and the conclusion of this work are given in Sec. IV.

II. COMPUTATIONAL METHODS

In the present work, the Tersoff potential¹⁰ is employed to model the Si atomic interaction. Tersoff has developed a different type of empirical interatomic potential for covalent solids. This potential is written as a Morse pairwise potential, but its attractive term depends on the local environment of a specific atomic pair which effectively includes many-body interactions. Although the Tersoff potential does not fit any liquid-phase data, the qualitative feature of static properties in the Tersoff liquid are in good agreement with those obtained the experiments and *ab initio* MD simulations.^{11,12}

The MD calculations were performed under constant volume and constant temperature conditions. The system consisting of 512 atoms subjects to periodic boundary conditions. The density of MD cell was fixed at 2.57 g/cm³, which agree with the density of l -Si. The Newtonian equations of motion were integrated using a velocity-Verlet algorithm with a time step $\Delta t = 2 \times 10^{-3}$ ps. First, the atoms were placed on the diamond lattice sites and their initial velocities were randomly given. Then, the system was heated up to a desired temperature by rescaling the velocities of the particles. The system is run for 30 000 time steps to guarantee an equilibrium liquid state. Another run of 12 000 time steps at the given temperature is performed to obtain 60 configurations for analyzing the microstructural quantities. The temperatures investigated were 2800, 3000, 3200, 3400, 3600, and 3800 K. In the present study structural properties of l -Si are analyzed by two different methods. (1) By directly using the obtained configurations, we calculate the structural properties in order to compare our results with those in Refs. 12–14. (2) Following Stillinger,¹⁶ we first relax the system to its closest local minimum by a conjugate gradient energy minimization and then analyze the inherent structure. Our results are obtained by averaging 60 configurations.

III. RESULTS AND DISCUSSION

The distribution of the number of nearest-neighbor atoms in l -Si at 3000 K (the melting temperature is about 2750 K

by the Tersoff potential) is shown in Fig. 1. Our results indicate the presence of a broad distribution of local coordination dominated by the sixfold one, and this is consistent with the experimental result³ and that in Ref. 12. *l*-Si is rather loosely packed as compared with most liquid metals which are more closely packed with a coordination ~ 12 . This indicates a persistence of covalent bonding in the liquid, though the electronic properties of *l*-Si are metallic.

Additional information on the local short-range order in *l*-Si can be obtained from higher-order correlation functions. The triplet correlations are particularly important since the system retains some covalent bonding effects and has directional forces. This is conveniently measured by the bond angle distribution $g_3(\theta)$. Here θ is the angle between two vectors that join a central particle with two nearest neigh-

bors. Our $g_3(\theta)$ with the cutoff distance of 3.1 Å at 3000 K, shown in Fig. 2, is rather broad with maxima centered at $\theta \sim 53^\circ$ and 92° , which are denoted as P_1 and P_2 , respectively. This is in good agreement with that obtained by *ab initio* calculations¹³ and tight-binding MD simulations,¹⁴ and the same as that in Ref. 12. We have also calculated bond angle distributions for atoms with various coordination numbers, which are the same as Fig. 6 in Ref. 12.

Based on the above results, we can see that the Tersoff potential is very useful for the structural analysis of *l*-Si. In the following, we study the local inherent structural information of *l*-Si at different temperatures by a conjugate gradient energy minimization.

We have calculated the bond angle distribution functions from the inherent structures at six different temperatures with

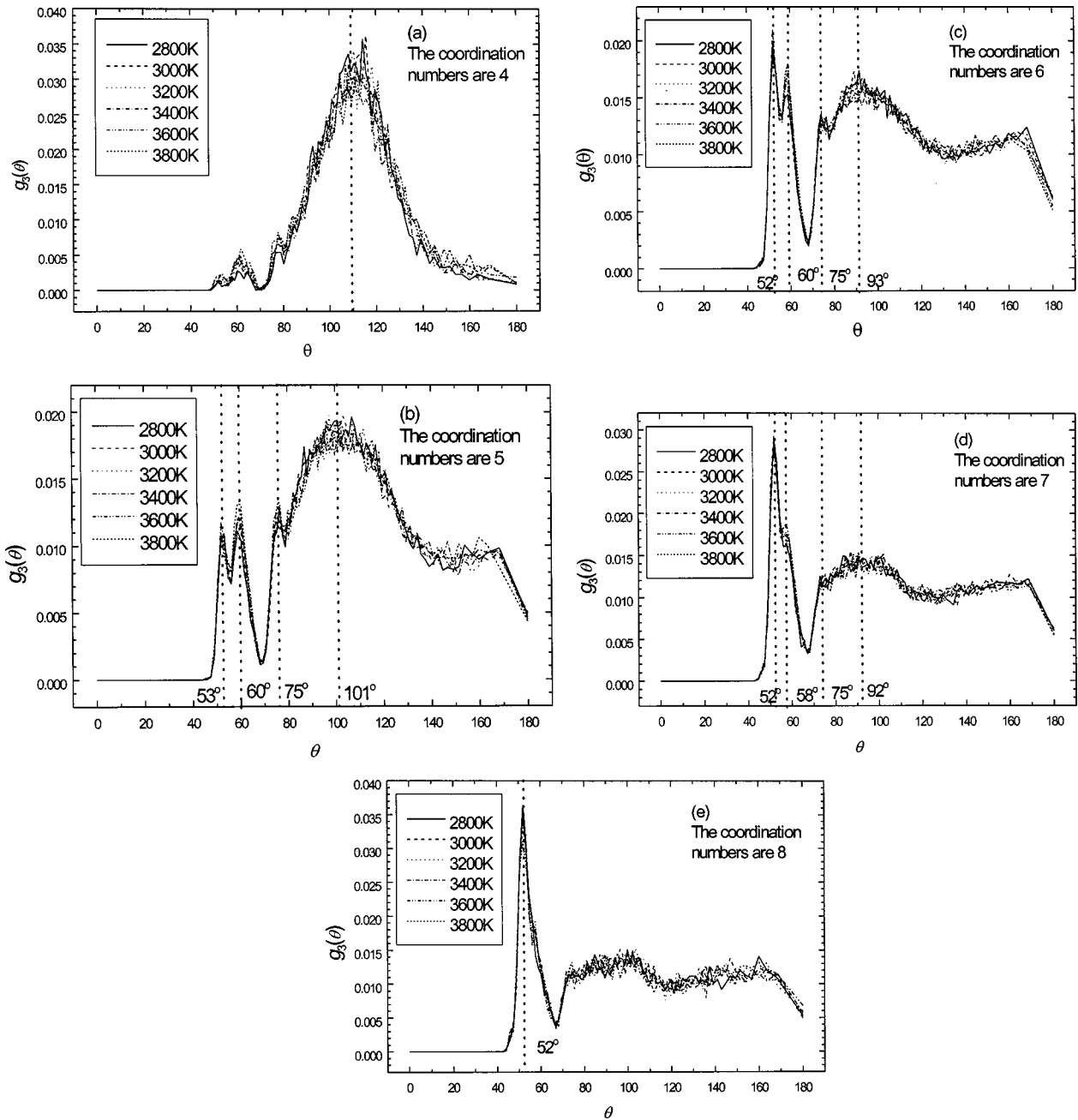


FIG. 4. Bond angle distribution functions $g_3(\theta)$ for atoms with various coordination numbers at six different temperatures. The cutoff distance is 3.1 Å. The dotted lines denote the location of peaks.

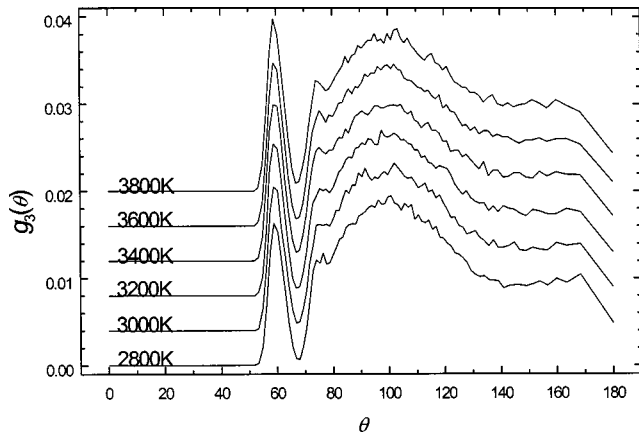


FIG. 5. Bond angle distribution function $g_3(\theta)$ at six different temperatures. The cutoff distance is 2.9 Å.

the cutoff distance 3.1 Å, as shown in Fig. 3. Our results indicate that P_1 decomposes into two peaks, one locates at 52° (P_{1a}) and another at 58° (P_{1b}). The location of P_2 shifts to a high angle (98°) and a new peak (P_{2a}) located around 75° appears. With increasing temperature, P_{1a} , P_{1b} , and P_{2a} show an observably increasing trend. In order to study the origin of these results, we further investigate some bond angle distributions for atoms with coordination numbers 4, 5, 6, 7, and 8, which are respectively presented in Figs. 4(a)–(e).

For the fourfold coordination, the bond angles are broadly distributed around the tetrahedral angle, suggesting the existence of the atomic clusters constructed by sp^3 bonding even in the liquid state. The average bond length of atoms with coordination numbers 4 is ~ 2.4 Å, which is quite close to the bond length (2.35 Å) in crystal Si, and the largest bond length is ~ 2.6 Å. These results are in good agreement with the *ab initio* results.¹³ These structural properties are insensitive to temperature. A similar bond angle distribution is found in amorphous Si. The presence in the *l*-Si of local tetrahedron may play an important role in explaining why Si is able to reconstruct easily a tetrahedral network upon cooling. For the fivefold coordination, the main peak in bond angle distribution locates around 101° , and the three peaks P_{1a} , P_{1b} , and P_{2a} also appear, but the height of these three peaks is lower than the main peak. The height and width of the main peak is independent on the temperature, whereas

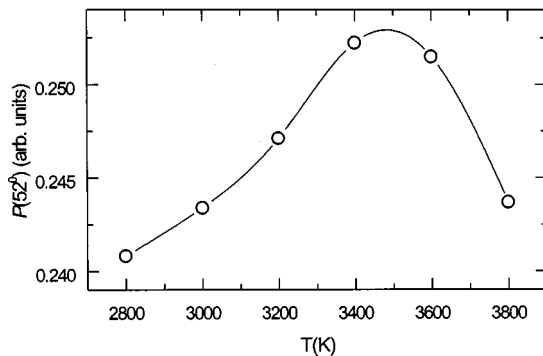


FIG. 6. The relative probability $P(52^\circ)$ of bond angle $52^\circ (\pm 3^\circ)$ found in the system at six different temperatures.

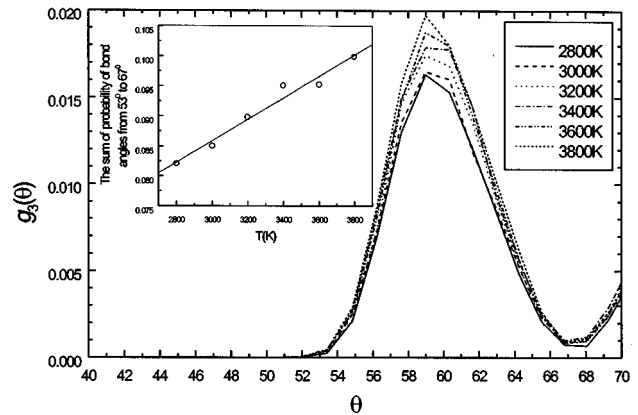


FIG. 7. The enlargement of the 60° peak of Fig. 5. Inset: the sum of the probability of bond angles between 53° and 67° at six different temperatures.

the height of P_{1a} , P_{1b} , and P_{2a} shows a weak relation to the temperature. For the sixfold coordination, the case is similar as the fivefold coordination, but the relative height of P_{1a} and P_{1b} significantly increase, particularly for P_{1a} . For seven- and eightfold coordination, the P_{2a} disappears and P_{1a} becomes very high.

Thus P_{1a} and P_{1b} become prominent as the coordination number increases, whereas P_{2a} mainly comes from five- and sixfold coordination, the positions of these three peaks do not depend on the coordination numbers. Some investigators^{17,18} have proposed the existence of the white-tin structure (which is sixfold coordinated and metallic) in *l*-Si in order to reproduce the shoulder of the first peak in the static structure factor. The white-tin structure is composed of the four nearest neighbors and two next-nearest neighbors, and the bond angles associated with these six neighbors are 74.6° , 94.0° , 105.4° , 149.3° , and 180° . The position of P_{2a} is $\sim 75^\circ$, which gives a position proof, but the appearance in fivefold coordination gives a negative answer. To the origin of the P_1 ($P_{1a} + P_{1b}$), Kin and Lee¹⁴ think it attributes to the abundant floating bonds in *l*-Si, while Ishimaru *et al.*¹² think it attributes to SH structure existed in *l*-Si. About these we will also discuss in the following.

It is interesting to note that, with the choice of cutoff distance 2.9 Å, the P_{1a} disappears in the bond angle distribution, which are presented in Fig. 5. From this figure, we can see that P_{1b} and P_{2a} also appear in the bond angle dis-

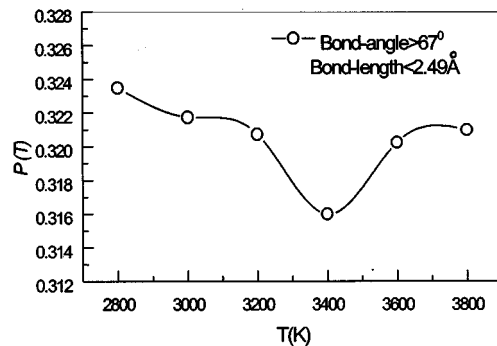


FIG. 8. The relative probability of bond length less than 2.49 Å found in the system at six different temperatures.

tribution, and the positions of these two peaks are 60° and 75° , respectively. Our results of Figs. 3 and 5 indicate that the P_{1a} can be attributed to the floating bonds with bond length between 2.9 and 3.1 Å. We turn back to calculate the relative probability of bond angle $52^\circ (\pm 3^\circ)$ found in the system at six different temperatures with the choice of cutoff distance 3.1 Å, as shown in Fig. 6. Figure 6 illustrates the change trend with the temperature of the relative probability of bond angle 52° or the floating bonds with bond length 2.9~3.1 Å, which at first increases, then decreases and has a maximum at a certain temperature.

An enlargement of the 60° peak of Fig. 5 is shown in Fig. 7. From this figure, we clearly see that the height of this peak increases with temperature. While from the inset in Fig. 5, we cannot see an anomalous temperature dependence of the 60° peak. Therefore the anomalous physical properties of *l*-Si near the melting point may not be attributed to the structure with $\sim 60^\circ$ bond angles. We also calculate bond angle distribution for atoms with various coordination numbers. The results indicate that the 60° peak clearly appears in particles with 5, 6, 7, and 8 nearest neighbors. A similar feature of the 75° peak has been observed, so their origin should be further studied in the future.

Based our present results, we now turn to the anomalous temperature dependence of some properties. In the present work, we will focus on the electrical property. The conductivity of metallic *l*-Si have been discussed in Refs. 13 and 19. In the melt Si, the current is carried both by electrons and charged ionic cores. The ionic contribution to the electric current is negligible.¹³ Thus the current is mainly carried by electrons. In Ref. 13, the authors studied the evolution of the valence electron density that accompanies atomic motion. Their analysis showed that covalent bonds almost always form between pairs separated by a distance less than ~ 2.49 Å in *l*-Si. According to our results, the bond length of floating bonds contributing to 52° peak is much greater than 2.49 Å. Hence these bonds are not covalent and show some characteristics of metallic bond. Therefore the greater the probabilities of these bonds, the more conduction electrons there are, and the smaller the electrical resistivity is.

We have further calculated the relative probability of covalent bonds whose bond angle is greater than 67° and bond length is less than 2.49 Å at different temperatures, shown in Fig. 8. From this figure, we can see that the relation between the relative probability of covalent bonds and temperature shows an anomalous decrease at 3400 K. We have also calculated the bond angle distributions with the choice of cutoff distance 2.49 Å, which is in agreement with Fig. 3 in Ref. 13 and Fig. 2(a) in Ref. 14. The electrons forming a covalent bond tend to be partly localized in the region between the

two atoms joined by the bond. Hence the less the probability of these bonds, the more conduction electrons there are, and the smaller the electrical resistivity. It should be pointed out that this anomalous point is in agreement with that in the 52° peak.

Thus we can see that there are two different types of bonds which show different anomalous behavior. The one is covalent bonds; the other is the floating bonds contributing to 52° peak, whose bond length is much greater than the cutoff distance for covalent bonds. The former shows an anomalous decrease at 3400 K and the latter shows an anomalous increase at 3400 K. According to the properties of these two types of bonds discussed above, the less the first type of bonds and the more the second type of bonds are, the smaller the electrical resistivity is. Therefore the experimental results,⁸ the temperature coefficient of the electrical resistivity at first is negative and then positive with increasing temperatures, the electrical resistivity of molten Si shows a local minimum in the temperature range from 1450–1500 °C, may be reasonably explained by the temperature curves of these two types of bonds.

IV. CONCLUSIONS

We have presented an extensive MD study of the inherent structure properties of *l*-Si at different temperatures. The results are encouraging. The 50° – 60° peak in bond angle distributions decomposes into two peaks, which are located at 52° and 60° , and a new peak at 75° appears; the 52° peak disappears with a small cutoff distance. The height of the 52° peak shows an anomalous temperature dependence, at first increases and then decreases with increasing temperature, while the height of 60° and 75° peaks show a monotonous temperature dependence, that is, they increase with temperature. The probability of those covalent bonds whose bond angle is greater than 67° , shows an anomalous decrease at a certain temperature. The anomalous characteristics of the height of the 52° peak and the probability of those covalent bonds may play an important role on the anomalous behavior of some physical properties in *l*-Si such as electrical resistivity near the melting point. The origin of 60° and 75° may not simply attribute to SH and white-tin structure, and deserves more extensive study.

ACKNOWLEDGMENTS

We are greatly indebted to Professor Q. F. Fang for valuable discussions. This work was supported by the National Natural Science Foundation of China (Grant No. 19874067) and the Foundation of Chinese Academy of Sciences (Grant No. KJ952-J1-412).

¹S. Kimura, J. Crystallogr. Soc. Jpn. **17**, 264 (1990).

²Y. Waseda, *The Structure of Non-Crystalline Materials; Liquid and Amorphous Solids* (McGraw-Hill, New York, 1980).

³Y. Waseda and K. Suziki, Z. Phys. B **20**, 339 (1975).

⁴J. P. Gabathuler and S. Steeb, Z. Naturforsch. A **34**, 1314 (1979).

⁵H. Sasaki, E. Tokizaki, K. Terashima, and S. Kimura, Jpn. J.

Appl. Phys., Part 1 **33**, 3803 (1994); **33**, 6078 (1994); H. Sasaki, E. Tokizaki, S. Takeda, K. Terashima, and S. Kimura, *ibid.* **34**, 482 (1995).

⁶H. Sasaki, Y. Anzai, X. Huang, K. Terashima, and S. Kimura, Jpn. J. Appl. Phys., Part 1 **34**, 414 (1995).

⁷H. Sasaki, E. Tokizaki, X. Huang, K. Terashima, and S. Kimura,

- Jpn. J. Appl. Phys., Part 1 **34**, 3432 (1995).
- ⁸H. Sasaki, A. Ikari, K. Terashima, and S. Kimura, Jpn. J. Appl. Phys., Part 1 **34**, 3426 (1995).
- ⁹H. Balamane, T. Halicioglu, and W. A. Tiller, Phys. Rev. B **46**, 2250 (1992), and references therein.
- ¹⁰J. Tersoff, Phys. Rev. B **38**, 9902 (1988); **39**, 5566 (1989).
- ¹¹M. Ishimaru, K. Yoshida, and T. Motooka, Phys. Rev. B **53**, 7176 (1996).
- ¹²M. Ishimaru, K. Yoshida, T. Kumamoto, and T. Motooka, Phys. Rev. B **54**, 4638 (1996).
- ¹³I. Stich, R. Car, and M. Parrinello, Phys. Rev. B **44**, 4262 (1991).
- ¹⁴E. Kim and Y. H. Lee, Phys. Rev. B **49**, 1743 (1994).
- ¹⁵Y. Waseda, K. Shinoda, K. Sugiyama, S. Takeda, K. Terashima, and J. M. Toguri, Jpn. J. Appl. Phys., Part 1 **34**, 4124 (1995).
- ¹⁶F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982); **28**, 2408 (1983); F. H. Stillinger, Science **267**, 1935 (1995); S. Sastry, P. G. Debenedetti, and F. H. Stillinger, Nature (London) **393**, 554 (1998).
- ¹⁷J. P. Gaspard, P. Lambin, C. Mouttet, and J. P. Vigneron, Philos. Mag. B **50**, 103 (1984).
- ¹⁸V. Petkov and G. Yunchov, J. Phys.: Condens. Matter **6**, 10 885 (1994).
- ¹⁹P. B. Allen and J. Q. Broughton, J. Phys. Chem. **91**, 4964 (1987).