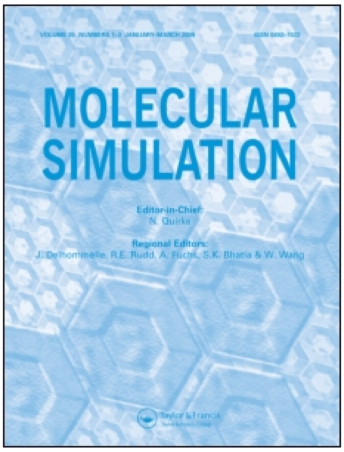

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Stillinger-Weber Type Potentials in Monte Carlo Simulation of Amorphous Silicon

Gülay Dereli[a]
[a] Department of Physics, Middle East Technical University, Ankara, Turkey

To cite this Article Dereli, Gülay(1992) 'Stillinger-Weber Type Potentials in Monte Carlo Simulation of Amorphous Silicon', Molecular Simulation, 8: 6, 351 — 360

To link to this Article: DOI: 10.1080/08927029208022490

URL: http://dx.doi.org/10.1080/08927029208022490

Molecular Simulation, 1992, Vol. 8, pp. 351–360
Reprints available directly from the publisher
Photocopying permitted by license only

STILLINGER-WEBER TYPE POTENTIALS IN MONTE CARLO SIMULATION OF AMORPHOUS SILICON

GÜLAY DERELI

Department of Physics, Middle East Technical University, 06531 Ankara, Turkey

(*Received March 1991, accepted August 1991*)

The growth of amorphous silicon on a substrate of a two-layer slab of crystalline silicon with various surface indices is simulated with Stillinger-Weber type interatomic potentials. The growth is realized by means of a continuum Monte Carlo method and the radial distribution functions are evaluated for various cases.

KEY WORDS: Stillinger–Weber potentials, amorphous silicon

1 INTRODUCTION

It is a well known fact that amorphous materials do not possess long range order of their constituent atoms, but they are not completely disordered on the atomic scale [1]. Any attempt at a quantitative discussion of amorphous structure must start with the determination of the short range order (SRO), that is the local atomic arrangement about a reference atom. In disordered systems short range order is maintained in the sense that the coordination number of each atom remains the same as in the case of a corresponding ordered crystal, although bond lengths and bond angles fluctuate from their corresponding crystalline values. Presently the most convenient probe of the short range order is provided by means of the radial distribution function (RDF) that is defined as the number of atoms contained within a spherical shell of radius r, centered at a reference atom. The experimental RDF for amorphous silicon shows that the basic tetrahedral arrangement of the diamond structure is preserved [2]. The width of the first peak corresponds to the spread in nearest neighbor spacings. The width of the second peak occuring at second nearest neighbor distance in RDF gives bond angle distortions. Moreover, both the area and the shape of the third peak are measures of the fluctuations in the dihedral angles. In Figure 1 the comparison of the experimental RDF's for cystalline and amorphous silicon are shown as functions of the interatomic distance r [2, 3]. The first peak appearing at the nearest neighbor distance, 2.35 Å, is almost the same for both structures. The fluctuations in the interatomic distances show up already in the shape of the first peak. There is a second peak at the next nearest neighbor distance 3.84 Å. The width of the second peak after corrections for thermal broadening, gives bond angle distortions of about $\pm 20°$ (rms) off the normal tetrahedral angle of $109° 28'$. In crystalline silicon, we observe another peak at 4.50 Å, which is the third nearest neighbor distance. This peak is lost in experimental RDF's for amorphous silicon. On the other hand a peak around 5.43 Å can be seen that corresponds to the fourth nearest neighbor distance. The absence of

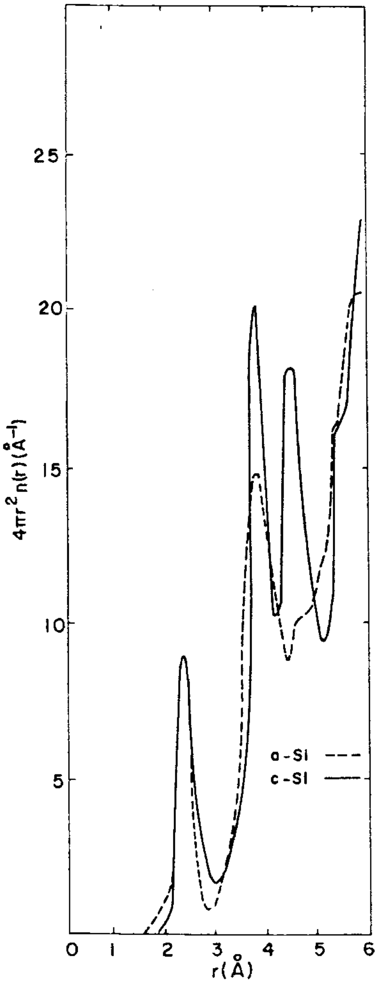

Figure 1 Experimental RDF's for crystalline and amorphous silicon.

long range order shows itself in the fact that peaks in RDF rarely occur beyond third or fourth nearest neighbors. Thus the analysis of successive peaks in the RDF yields more than one dimensional information concerning amorphous structure. It should be noted, however, that there is not a one to one correspondence between SRO and RDF. Therefore the only way to describe the three dimensional SRO is to construct structural models.

There are several types of structural models such as continuous random network models (CRN), microcrystalline models or swiss cheese models that are used in understanding the amorphous structure of silicon [4]. Unfortunately, the model building procedures have not yet been evolved into a standard one as one would have expected. The models mentioned above all have some deficiences although they are useful in their own ways in picturing the structure of amorphous silicon.

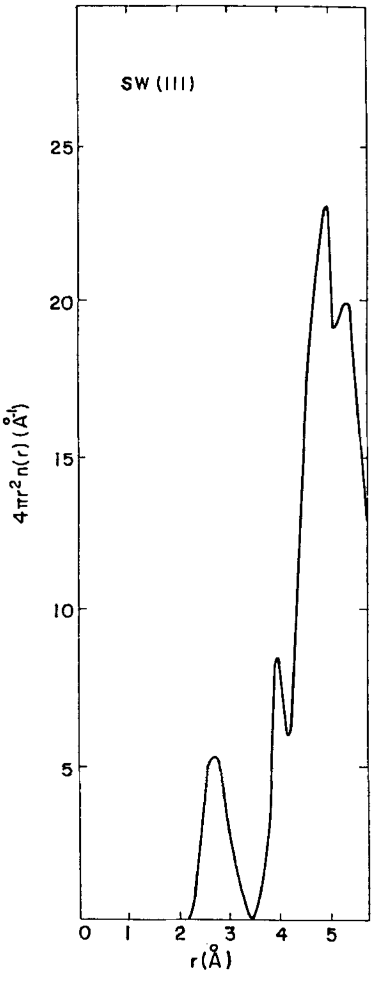

Figure 2 RDF of 93 atom structure grown on Si(111) substrate.

The most direct approach to the problem seems to exploit the speed and power of the computers to investigate the dynamics of simple models. Computer simulation experiments in this sense can be very useful and may point out the way to more intiutive structural models. One way of constructing structural models through computer simulations is with the use of molecular dynamics (MD) subject to pair potential approximation for the interaction among constituent atoms and molecules [5]. Appropriate pair potentials should be chosen on the basis of physical considerations concerning the motion of atoms that is simulated. There are other models based on Monte Carlo techniques (MC) to computer generate amorphous structures [6]. The Monte Carlo techniques are expected to give faster approach to equilibrium for a given configuration of atoms in comparison to molecular dynamics analyses. In practice the specific needs of a problem may require the development of new simulation models. It is in this way we started some time ago a computer simulation experiment

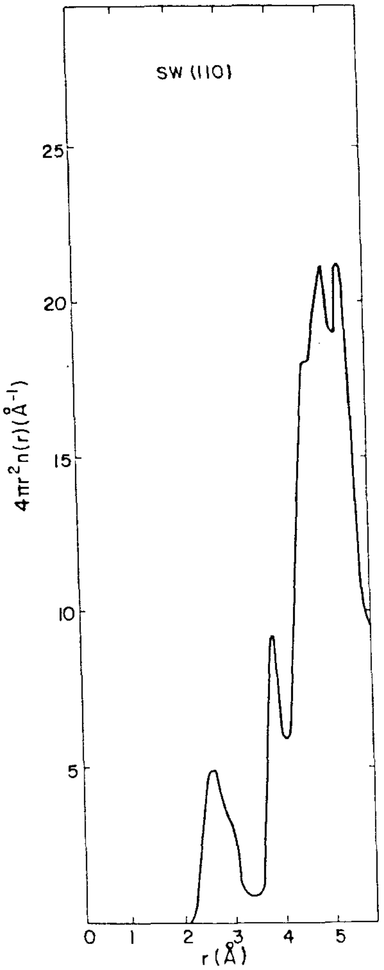

Figure 3 RDF of 97 atom structure grown on Si(110) substrate.

based on a continuum Monte Carlo technique [7] of the growth of amorphous silicon on a crystalline substrate surface [8]. It is known that the epitaxial growth of amorphous materials in the laboratory is done either by quenching from a liquid at constant volume or by atomic deposition onto a surface. It is not unexpected if the amorphous structures obtained by these two methods are found not to be the same. Therefore a study of the growth of amorphous silicon on a crystalline substrate by an independent simulation method will be interesting. The continuum Monte Carlo method we developed simulates the deposition of silicon atoms one by one on a substrate surface to form amorphous silicon structure. This method requires the specification of the interatomic forces, including the 2-body and 3-body interactions, among the atoms of the system. We first choose a substrate surface by specifying the initial positions of a number of silicon atoms. Then we bring down an additional silicon atom along a vertical line onto the substrate thus distorting the initial substrate configuration

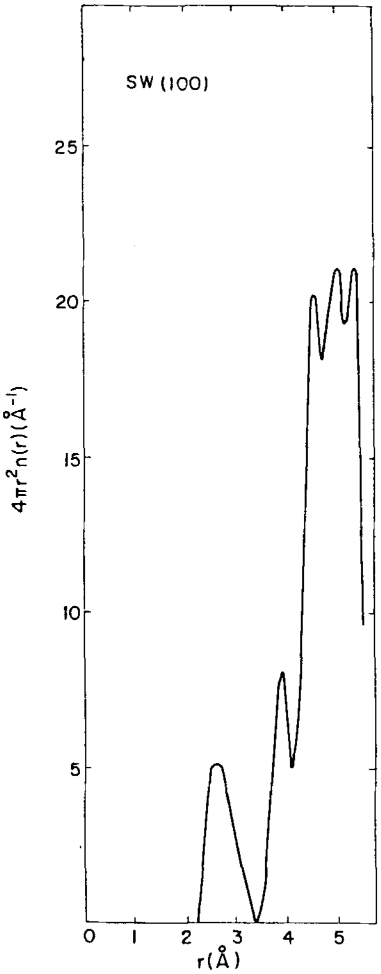

Figure 4 RDF of 97 atom structure grown on Si(100) substrate.

through the interatomic forces between the additional atom and the substrate atoms. After the extra atom is deposited onto the substrate surface a succession of moves of all the atoms is performed in order to take the system towards thermodynamic equilibrium. The final substrate configuration is recorded and used as initial data when the process is repeated for the next additional atom. When a cluster of silicon atoms which is sufficiently large to be statistically analyzed is obtained, the corresponding RDF with respect to a reference atom is evaluated and compared with experimental and other theoretical curves. The effects of ambient temperature and/or the growth rate may be explored in this model by varying certain parameters of the simulation.

In the following we consider the growth of amorphous silicon structure on (100), (110) and (111) crystalline silicon symmetry planes by using Stillinger–Weber type interatomic potentials [9] and discuss the resulting RDF's.

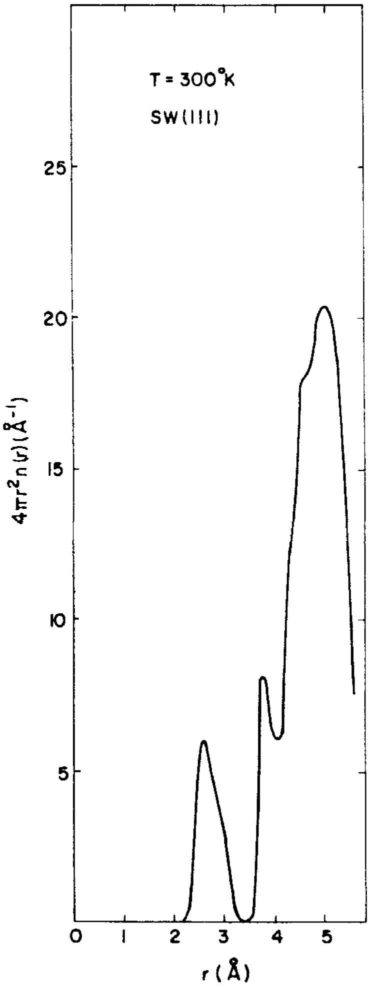

Figure 5 RDF of 85 atom structure grown on Si(111) substrate at 300 K.

2 INTERATOMIC POTENTIALS

The Stillinger–Weber interaction potentials are defined from the power series expansion

$$\phi = \frac{1}{2!}\sum_{i}^{N}\sum_{j\neq i}^{N} U_2(\mathbf{r}_i, \mathbf{r}_j) + \frac{1}{3!}\sum_{i}^{N}\sum_{j\neq i}^{N}\sum_{k\neq i,j}^{N} U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) \tag{1}$$

by the following 2-body and 3-body potentials

$$U_2(\mathbf{r}_i, \mathbf{r}_j) = U(|\mathbf{r}_i - \mathbf{r}_j|) = \varepsilon f_2\left(\frac{r_{ij}}{r_0}\right), \tag{2}$$

$$U_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \varepsilon f_3\left(\frac{\mathbf{r}_i}{r_0}, \frac{\mathbf{r}_j}{r_0}, \frac{\mathbf{r}_k}{r_0}\right). \tag{3}$$

which depend on the interatomic distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The vector $\mathbf{r}_i$ denotes the position of the i-th particle. The energy parameter ε is chosen so as to give the potential function a depth of -1, and r_0 is chosen to make $f_2(2^{1/6}) = 0$. We assume that the function f_2 depends only on the distance between a pair of atoms and f_3 has full transitional and rotational symmetry. The following form of the reduced 2-body potential is used:

$$f_2(r) = \begin{cases} A\left(B\left(\dfrac{r}{r_0}\right)^{-p} - \left(\dfrac{r}{r_0}\right)^{-q}\right) e^{r_0/r-\rho} & \text{for} \quad r < \rho \\ 0 \quad \text{otherwise,} & \end{cases} \tag{4}$$

where A, B, p and ρ are positive constants. This generic form has a cut-off at $r = \rho$ without having discontinuities in any r derivatives. The reduced 3-body potential has the form

$$f_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = h(r_{ij}, r_{ik}, \theta_{jik}) + h(r_{ji}, r_{jk}, \theta_{ijk}) + h(r_{ki}, r_{kj}, \theta_{ikj}) \tag{5}$$

where θ_{jik} is the angle subtended at the vertex i between the vectors $\mathbf{r}_j$ and $\mathbf{r}_k$. The 3-body interactions are going to be specified by a 2-parameter family of functions

$$h(r_{ij}, r_{ik}, \theta_{jik}) = \lambda\, e^{\gamma/(r_{ij}-\rho)}\, e^{\gamma/(r_{ik}-\rho)}(\cos\theta_{jik} + \tfrac{1}{3})^2 \tag{6}$$

provided both r_{ij} and r_{ik} are less than the previously introduced cut-off ρ, and h vanishes identically otherwise. We have the same cut-off as in 2-body interactions, and here again it does not introduce discontinuties in any r derivatives. The parameters λ and γ are both positive. We note that for the ideal tetrahedral structure $\cos\theta = -\frac{1}{3}$. Therefore the angular part of the above expression discriminates in favour of the pair of bonds emanating from the i^{th} vertex with the tetrahedral geometry. We used in our work, the values of the parameter set as given by Stillinger and Weber:

$$A = 7.049\,556\,277.$$
$$B = 0.602\,224\,558\,4.$$
$$p = 4,\ q = 0,\ \rho = 1.80,$$
$$\lambda = 21.0,\ \gamma = 1.20.$$

The energy parameter $\varepsilon = 3.4723$ eV/atomic pair and the 2-body structure parameter $r_0 = 2.0951$ Å were found by considering the observed lattice spacing and atomization energy of the silicon at 0° K.

3 MONTE CARLO SIMULATION

The essential points of our computer modelling of the growth of amorphous structure on a chosen substrate of atoms is explained in following steps.

(i) The first step consists of choosing a suitable 2-dimensional substrate of silicon atoms. The initial configuration is supplied in terms of the Cartesian components of the lattice points of a symmetry plane of the silicon crystal.

(ii) Next a succession of random moves of atoms, one at a time, is carried out. Each move is designed to take the structure closer to thermal equilibrium. This is achieved as follows: Suppose the configuration of N atoms at the positions $\mathbf{r}_1$,

$\mathbf{r}_2, \ldots, \mathbf{r}_N$ is reached at some certain time. Then a random number generator chooses one of these atoms and a new coordinate is generated for this i-th atom: $\mathbf{r}_i \rightarrow \mathbf{r}_i + \boldsymbol{\delta}$. The ν component of the displacement vector is given by

$$\delta_\nu = \frac{2k_B T}{F_\nu} \ln\left(\frac{1}{\alpha} + \left(\alpha - \frac{1}{\alpha}\right)R\right) \tag{7}$$

with $\alpha = \exp(|(\varepsilon F_\nu/2k_B T|)$ where F_ν is the ν component of the force acting on the atom, k_B is the Boltzmann constant, T is the temperature, and R is a random number in the interval [0, 1]. ε fixes the length scale. The following can be verified from the above expression

$$|\delta_\nu| \leqslant \varepsilon \tag{8}$$

$$\lim_{\gamma \to \pm\infty} \delta_\nu = \pm\varepsilon \tag{9}$$

$$\lim_{\gamma \to 0} \delta_\nu = (1 - 2R)\varepsilon \tag{10}$$

where $\gamma = |(\varepsilon F_\nu/2k_B T)|$. Consequently, the atom moves in any direction the maximum distance ε. The move is random at high temperatures and small values of the force on the atom, while it is in the direction of the force at low temperatures and large values of the force on the atom. In addition the probability density function for δ_ν has an exponential shape within the range of values from $-\varepsilon$ to ε, Therefore, provided ε is chosen sufficiently small so that the component of force does not change over the distance ε, the ratio of the mutual transition probabilities of an atom between two points separated by a distance less than ε is equal to $\exp(-\Delta\phi/k_B T)$. Here $\Delta\phi$ shows the change in energy of the system due to the transition under consideration. Consequently such transitions satisfv the detalied balance condition and the procedure generates ensembles of atoms whose energies are distributed as $\exp(-\phi/k_B T)$.

(iii) The above procedure is repeated a chosen number of times per atom. Then a random point on the surface is selected and a new atom is brought down along the vertical axis at that point. A succession of moves of the new atom under the influence of all other atoms (as carried out in the second step above) is performed before the new atom is included in the substrate. Thus one now has a substrate with one more atom than before. The procedure can be repeated all over again with this new substrate.

(iv) We repeat the steps (i)–(iii) as many times as desired, thus adding atoms on the substrate one by one. When the size of the cluster of silicon atoms becomes large enough to be statistically analyzed, the corresponding RDF's can be evaluated.

In this way the deposition of silicon atoms on a surface to form an amorphous silicon structure is simulated. The effects of temperature and growth rate can be controlled by varying the parameters of the simulation. The accuracy of Monte Carlo simulation depends on the number of times the atoms are moved. We employed 10 moves per atom and checked the RDF's obtained with 20–30 moves per atom.

4 RESULTS AND DISCUSSION

In the present work, we took the initial substrate configuration to be the lattice points of a symmetry plane of crystalline silicon. In particular we tried (111), (110), (100) planes. Then additional atoms are brought on to the substrate surface one by one. Every new atom is moved 10 times before it is included in the substrate. The whole system of atoms is also moved 20–30 times per atom before a new atom is added. The number of Monte Carlo trials on the substrate atoms before a new atom is introduced is a parameter that controls the rate of growth. When a cluster of silicon atoms large enough to be statistically analysed is obtained, we determined the corresponding RDF's which provide a direct comparison between the model and experiment. The growth temperature corresponds to 600° K.

In Figure 2, the RDF for a 93 atoms structure, grown on a two-layer Si(111) substrate of 21 atoms is given. The first two peaks occur at 2.58 Å and 3.86 Å.

Figure 3 shows the RDF for a cluster of 97 atoms grown on the Si(110) surface. The main peaks occur at 2.58 Å and 3.81 Å.

Figure 4 shows another 97 atom structure grown this time on a Si(100) substrate. The main peaks are at 2.58 Å and 3.81 Å.

The general appearance of these curves are similar. In general the first peak position is slightly shifted to the right, while the second peak is where it should be. The height of the peaks would grow as the number of atoms deposited increases. The wide gap in the experimental RDF that corresponds to the characteristic third neighbor peak in the crystalline RDF at 4.50 Å is not prominent in the simulated RDF's. This shouldn't be a surprise because larger variations in the dihedral angle would have removed to a greater extend the characteristic third neighbor spacing while the computer algorithms have no control on the variations of the dihedral angle. The last peak we see in the simulated RDF's is bifurcated and the average peak position is pushed beyond 5.00 Å. These bifurcations correspond to the bumps one sees in the experimental RDF as the fourth nearest neighbor peak is approached. These bifurcations tend to be smoothed out as the number of atoms deposited increases.

In order to discuss the effect of temperature on growth, we present in Figure 5 the RDF for a cluster of 85 atoms grown on the Si(111) 21 atom substrate at temperature $T = 300°$ K with the main peaks occuring at 2.58 Å, 3.81 Å, and 4.54 Å. We haven't been able to detect any outstanding effect on RDF's when the ambient temperature is varied within a physically meaningful range. This is essentially due to the fact that interatomic forces considered here are too strong. The temperature values that would have given observable effects on RDF's cannot be studied without taking phase changes into account. Much for the same reasons we could find no other effect of the growth rate on the RDF's except that the sharper peaks occur for faster growth rates [10].

Next we wish to compare the above results with those in our previously published paper that reports on a similar computer experiment where the 2-body interactions were prescribed by Lennard–Jones potentials while 3-body interactions by Pearson–Takai–Halicioğlu–Teller (PTHT) potentials [10]. It should be noted that in all three cases given above the peak positions are shifted slightly to the right and the peaks are broadened in comparison with the RDF's drawn using the PTHT type potentials. In order to understand this behaviour, a comparison of the r and θ dependences of the PTHT and SW potentials is useful [8]. The SW potential has an absolute minimum at $r = 2.35$ Å whereas the absolute minimum of PTHT potential occurs at $r = 2.30$. This difference may be responsible for the shift occuring in the first peak position in RDF's. Furthermore, the peaks in the SW potential case are borader compared with the PTHT potentional. The reason for this may be seen by a comparison of the

θ-dependence of the corresponding forces. The SW force is non-symmetric in θ while PTHT force is symmetric.

Finally there are a few worthy remarks: Stillinger–Weber interatomic potentials are used in a recent paper on molecular dynamics study of amorphous germanium with results similar to those found by us [11]. There exists in the literature new classical potentials for more accurate simulation of atomic processes in silicon [12]. We have just become aware of a Monte Carlo simulation study of the growth of amorphous silicon which is similar to ours in some respects, though with an emphasis on surface diffusion effects [13].

To conclude, the results presented in this paper together with the results presented in a previous paper [10] provide direct evidence that both the shapes and the positions of the peaks in RDF in the continuum Monte Carlo simulation of the growth of amorphous silicon on a crystalline substrate depend critically on the choice of the interatomic potentials used.

Acknowledgement

I would like to thank the members of the Middle East Technical University Computer Center for their cooperation.

References

[1] R. Zallen, The Physics of Amorphous Solids, Wiley (1983).

[2] N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials, Clarendon Press, p. 323 (1979).

[3] S.C. Moss and J.F. Graczyk, "Evidence of voids within the As-deposited structure of glassy silicon", *Phys. Rev. Lett.*, **23**, 1167 (1969).

[4] cf. e.g. J.M. Ziman, Models of Disorder, Cambridge U.P, (1979).

[5] R.D. Biswas and D.R. Hamann, "Interatomic potentials for silicon structural energies", *Phys. Rev. Lett.*, **55**, 2001 (1985).

[6] F. Wooten, K. Winer and D. Wearie, "Computer generation of structural models of amorphous Si and Ge", *Phys. Rev. Lett.*, **54**, 1392 (1985).

[7] K. Binder (ED.), Monte Carlo Methods in Statistical Physics, Springer, (1986).

[8] G. Dereli, Ph. D. thesis submitted to Middle East Technical University (1987).

[9] F.H. Stillinger and T.A. Weber, "Computer simulation of local order in condensed phases of silicon", *Phys. Rev.* **B31**, 5262 (1985).

[10] G. Dereli, M.C. Yalabık and S. Ellialtıoğlu, "A computer simulation of amorphous silicon", *Phys. Scr.*, **40**, 117 (1989).

[11] K. Ding and H.C. Andersen, "Molecular-dynamics simulation of amorphous germanium", *Phys. Rev.*, **B34**, 6987 (1986).

[12] E. Kaxiras and K.C. Pandey, "New classical potential for accurate generation of atomic processes in Si", *Phys. Rev.*, **B38**, 12736 (1988).

[13] J. Wang and A. Rocket, "Simulating diffusion on Si(001) 2 × 1 surfaces using a modified interatomic potential", *Phys. Rev.*, **B43**, 12571 (1991).