Sci. Rep. RITU A44 (1997) pp. 77-81
No. 1, March 1997

# Surface Reconstruction of Si (001) by Genetic Algorithm and Simulated Annealing Method *

Rong-Tang Fu,[a,b] Keivan Esfarjani,[a] Yuichi Hashi,[a,c] Jian Wu,[d] Xun Sun[b] and Yoshiyuki Kawazoe[a]

[a] *Institute for Materials Research, Tohoku University, Sendai 980-77, Japan*
[b] *Department of Physics, Fudan University, Shanghai 200433, P.R. China*
[c] *Research and Development Center, Hitachi Tohoku Software Ltd., Sendai 980, Japan*
[d] *Department of Physics, Tsinghua University, Beijing 100084, P.R. China*

(Received January 21, 1997)

The Genetic Algorithm (GA) is one of the most recently developed techniques to find the "Global" minimum of an energy functional. This technique combined with conjugated gradient or molecular dynamics has been demonstrated to be efficient for the ground-state configuration search in materials research, *e.g.* fullerene formation. In this paper, based on the generalized tight-binding molecular dynamics, we apply the GA to study the surface reconstruction of Silicon (001) for the first time. Up to 65 generations, the "Global" minimum or the ground-state configuration for the surface reconstruction of Si (001) was detected efficiently in our GA simulation. In our tight-binding model, a perfect symmetry-dimer structure was found to be the most energetic while some defect asymmetry-dimer structure could coexist in the lists of candidate structures due to the thermal defect or charge transfer which was described with the smearing parameter empirically. We also perform the more traditional Simulated Annealing (SA) technique to deal with the same problem. The results in terms of efficiency, accuracy of the ground-state reconstructed surface and CPU time are compared.

KEYWORDS: Genetic Algorithm, simulated annealing, surface reconstruction

## 1. Introduction

Advances in computer technology have made molecular dynamics simulations more and more popular in studying the behavior of large and complex systems. Even with modern-day computers, however, there are still two main limitations facing atomistic simulations: system size and simulation time. While recent developments in parallel computer design and algorithms have made considerable progress in enlarging the system size that can be accessed using atomistic simulations, methods for shortening the simulation time still remain relatively unexpected. Generally, it seems urgent and important to develop more efficient algorithms.

More practically and typically, in materials research, the 'Global' geometry optimization or the search of the ground-state configuration is always a challenging problem in computational chemistry and physics. This task becomes more difficult as the number of dimensions and, hence, the number of local minima, grows. Within the past decade, complementary optimization methods have been developed, such as simulated annealing[1-3], quantum annealing[4], potential deformation[5], hierarchical searches[6], interval analysis[7] and genetic algorithms[8-17]. All of the aforementioned methods have advantages and disadvantages which depend on the particular optimization task. In general, optimization methods can be categorized as either deterministic or stochastic. For geometry optimization, deterministic methods produce new conformations from previous conformations in a deterministic fashion, *e.g.* gradient procedures and the Nelder-Mead simplex method[18]. Convergence to the minimum depends on the location of the initial starting configuration. There is no guarantee that a global minimum will be found. Stochastic methods generate conformations in a probabilistic fashion, *e.g.* the most well-known Simulated Annealing (SA) which will always find the global minimum theoretically if the cooling schedule is slow and trajectory infinitely long.

Within the past ten years, genetic algorithms (GA) have been one of the most prominent and widely used representatives of evolutionary algorithms (EA); and a class of stochastic search algorithms are based on the genetic learning process of biological species[19]. The Darwinian theory[23] of evolution, with the survival of the fittest in a changing environment seems to be generally accepted, at least on grounds of accumulated evidence so far on the earth. For materials research, application of the standard GA (S-GA) for geometry optimization of cluster, as described by Goldberg[20], shows to be a powerful technique[21-22]. Besides the computational efficiency, it is also well-adapted to be programmed on parallel machine.

In this paper, we describe the application of such an algorithm to the surface reconstruction of Si(001) by incorporating the information of molecular dynamics into the optimization procedure. Details of a modification of the standard GA method and results and discussions are given in the following context. Parallel to GA, we also performed more traditional Simulated Annealing (SA) technique to deal with the same problem. The results in

*IMR, Report No. 2080

terms of efficiency, accuracy of the ground-state reconstructed surface and CPU time are compared.

## 2. Genetic Algorithm and Surface Reconstruction of Si (001)

The standard genetic algorithm (S-GA) is described by Goldberg[20]. Briefly, GA is an iterative procedure which maintains a constant population size and works as follows. An initial population of a few individuals is generated at random or heuristically. During each iteration step, called a *generation*, the individuals in the current population are evaluated and given a fitness value. To form a new population, individuals are selected with a probability proportional to their relative fitness. This ensures that the expected number of times an individual is chosen is approximately proportional to its relative performance in the population, so that good individuals have more chances of being reproduced. This selection procedure alone cannot generate any new point in the search space. GA traditionally uses two *genetic operators*: *crossover* and *mutation* for generating new individuals and new search points. Crossover is the most important recombination operator: it takes two individuals called *parents* and produces two new individuals called *offsprings* by swapping substrings after a randomly selected crossover point. Through crossover, the search is biased towards promising regions of the search space. The second operator, mutation, is essentially background noise that is introduced to prevent premature convergence to local optimization by randomly sampling new points in the search space. To bit strings, mutation is applied by flipping bits at random in a string with a certain probability called the mutation rate. Similar to other techniques, GAs are also stochastic iterative algorithms without any guarantee of convergence. Termination may be triggered by reaching a maximum number of generations or by finding an acceptable solution.

In the above description, genetic algorithm is just an evolutionary program which adapts itself to environmental changes. The link between an actual optimization problem and the GA is the individual. Each individual represents a feasible solution in some problem space through a suitable mapping depending on a certain subject. Commonly, the mapping from problem space to individuals and the reverse mapping have historically been done through strings of binary digits.

For surface reconstruction of Si (001), our approach is based on the standard genetic algorithm (S-GA) as mentioned above. Moreover, "the generalized tight-binding molecular dynamics" (TBMD) scheme interacts with an optimization strategy inspired by the Darwinian evolution process[23].

## 3. Simulated Annealing technique

This method is based on ideas in statistical mechanics to search the phase space. As is well-known, at higher temperatures, because of the large kinetic energy, the system has a better chance of probing the phase space. This allows a less restricted search for the global minimum as with the large available kinetic energy, the system can pass high energy barriers. Put in terms of the Boltzmann distribution function, the term $e^{-E_i/T}$ gets larger as the temperature $T$ is increased; it has the effect of smoothening the energy landscape by pulling down all the high energy barriers. All the art of SA resides then in the annealing schedule to make the search as effectively as possible without missing any energy valleys and without spending too much time wandering around!

To this end, we have used a recent developed algorithm of Adaptive Simulated Annealing[26]. Usual SA programs, use a linear or exponential annealing schedule. These schemes work reasonably well if the total number of steps is guessed correctly (usually by trial and error since they are size-dependent). But in the adaptive algorithm, the temperature evolves according to:

$$\frac{dT}{dt} = -\frac{v}{\epsilon\sqrt{C}}T \tag{1}$$

where $v$ is the thermodynamic speed (taken as a constant), $\epsilon$ is the relaxation time coming from the second eigenvalue of the transition matrix, and $C$ is the heat capacity of the system indicating the fluctuations in the energy. In our algorithm, we update the temperature at every 500 steps during which the thermodynamical properties of the system are collected and calculated ($C$ and $\epsilon$). This algorithm is also well-suited for parallel implementation, since one usually starts with a few samples evolving independently and the thermodynamic data are then collected from these samples followed by the computation of the averages. Similar to GAs, the evolution of the system is done by using the TBMD code, even though one could also move the particles at random.

## 4. Tight-binding molecular-dynamics (TBMD) scheme in silicon

There has been several studies of Si(001) surface reconstruction. The one performed with the TB method was first done by Chadi[24]. Recently, a transferable tight-binding potential for silicon was provided by Kwon *et al.*[25] to overcome both the heavy computations in *ab* initio methods, and the rude accuracy of empirical models. This method has been successful in describing the energetics of silicon systems over a wide range of environments; in particular the diamond and amorphous structures. This approach includes the effects of directional covalent bonding through the underlying electronic structure described by a generalized tight-binding Hamiltonian. Such a scheme allows the quantum mechanical nature of the covalent bonding to enter the potential in a natural way rather than through the addition of *ad hoc* angular terms in a classical potential. Because of its cheap computational cost and good results for silicon systems, applications in molecular-dynamics studies of silicon systems are very attractive and reasonable. In the model mentioned in Ref.25, the total energy of

the silicon system for a given configuration of N atoms $\{\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}\}$ is written as

$$E_{tot}(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}) = E_{bs}(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}) + E_{rep}(\mathbf{r_1}, \mathbf{r_2}, \cdots, \mathbf{r_N}), \quad (2)$$

where $E_{bs}$ is the sum of electronic eigenvalues over all occupied electronic states, and $E_{rep}$ is a short-ranged repulsive energy. The electronic eigenvalues are obtained by solving the Slater-Koster empirical tight-binding Hamiltonian in which the off-diagonal elements of $\hat{H}_{TB}$ are described by a set of orthogonal $sp^3$ two-centre hopping parameters, $V_{sp\sigma}$, $V_{sp\sigma}$, $V_{pp\sigma}$, $V_{pp\pi}$, scaled with the interatomic separation $r$ . The on-site diagonal terms are the atomic orbital energies of the corresponding atom. The short-ranged repulsive term $E_{rep}$ reads

$$E_{rep} = \sum_i f(\sum_j \phi(r_{ij})), \quad (3)$$

where $\phi(r_{ij})$ is a pairwise potential between atoms $i$ and $j$, and $f$ is a functional expressed as a 4th-order polynomial with argument $\phi(r_{ij})$. For a detailed description of this approach and parameter set, refer to [24]. The force used in the molecular dynamics run is expressed as a sum of two-body forces of the type $(d\phi/dr_{ij})\hat{\mathbf{r}_{ij}}$ and a contribution coming from the energy eigenvalues of $E_{bs}$. In the generalized tight-binding scheme, Hellmann-Feynman forces are easy to retain, especially since a two-center approximation for the tight-binding integrals is applied.

## 5. Construction of candidate structures for the Silicon (001) surface

### 5.1. By the GA method

For the Genetic Algorithm method, we consider a (4×4) surface geometry (001). The slab consists of three silicon layers of 16 atoms each, and a 32 hydrogen atom layer at the bottom, for dangling-bond termination. Except for the first top silicon layer, all atoms in the slab are held fixed since a significant reconfiguration of surface is caused by this layer. Moreover, we save much computational cost for the simulations. Periodic boundary conditions were only imposed along the $X$ and $Y$ directions.

Since only the first layer is relevant to the genetic algorithm, we only considered the latter as candidate structures of evolutionary algorithms. In the present work, we present a candidate structure by the list of 16 atomic Cartesian coordinates $\vec{x}_i$ in arbitrary order,

$$G = \{\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_{16}\}, \quad (4)$$

A common choice is to first map the candidate structure onto a binary number string, then use string recombination as a mating procedure. When a mating procedure occurs, two parent geometries $G$ and $G'$ produce a child $G''$. In our calculation, as the standard GA requires[20], the micro-GA technique[26] with uniform crossover is applied to five candidate structures. We preferentially select parents with low energy from $\{G\}$. The probability

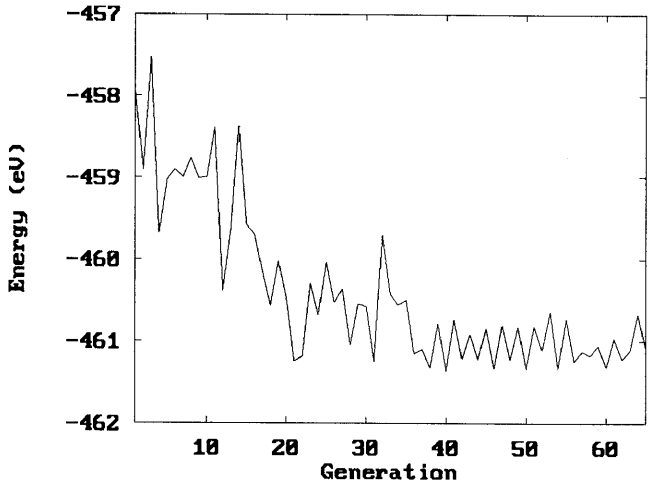


Figure 1. Evolutionary candidate structures with the standard genetic algorithm.

$p(G)$ of an individual candidate $G$ to be selected for mating is given by the Boltzmann distribution:

$$p(G) = A\exp[-E(G)/T_m], \quad (5)$$

where $E(G)$ is the energy of the candidate $G$, and the mating "temperature" $T_m$ is chosen to be roughly equal to the difference between local minima. Here we choose $T_m = 1.0eV$.

Relaxation to the nearest local minimum is performed with molecular dynamics quenching. In carbon clusters, this performance is very impressive since carbon clusters are bound by strong directional bonds which result in large energy barriers between different isomers[22]. Typically, about 30 molecular dynamics steps were applied, in the case of carbon, to a new geometry before a decision is made as to whether or not warrant further optimization. For silicon surface reconstruction, however, much more molecular dynamics steps (about 1 ps=1000 time steps) are needed to relax from the free ideal surface to the reconstructed surface. In this case, the barriers between different surface states are so small that the multi-tunneling between these states is very serious if thermal disorder or charge transfer is considered. In the present work, we select 600 molecular dynamics steps (0.6 ps) and velocity scaling of 99% per MD step. Especially, as is well known, surface states are easily to destroy or change so much by thermal disorder or charge transfer because of the narrow gap. Smearing parameter[27] (0.2eV) is applied to our simulation as we illustrate empirically the effect of the thermal defect or charge transfer to some extent.

### 5.2. By the SA method

In the SA case, since there is total relaxation, and energy differences are sensitive to the number of included layers, we first considered a (2×2) surface of 4 atoms with 10 free layers ended by a layer of 8 hydrogen atoms to saturate the dangling bonds. Like in the GA case, we adopt periodic boundary conditions along the $X$ and $Y$ directions. We first minimized the total energy with

respect to the periodic cell. Then for the optimum cell size, we fixed the lowest layer of silicon atoms and allowed all the rest to move during the MD simulation. The temperature started from 1.2 eV and was updated at every 500 time steps. We found two minima in the process: one in which the buckled dimers are parallel to each other, and one where they are anti-parallel buckled dimers with a higher energy surface (Table 1).

Table 1
Energies per dimer of the two different configurations in the (2×2) simulation cell. The energy of the free unrelaxed diamond structure surface is taken as reference.

| parallel buckled dimers | anti-parallel buckled dimers |
|---|---|
| -1.7911 eV | -1.7051 eV |

## 6. Results and discussion

Figure 1 illustrates several generic features of the algorithms. During the initial few generations, the energy of candidate structures drops rather quickly. As discussed above, because the barriers between local surface states are so small and molecular dynamics steps (0.6 ps) are not enough to reach the fully relaxed structures, the energy oscillation of candidate structures seems to be reasonable. After the 21st generation, one best candidate structure is found. That is a perfect reconstructed surface with all parallel buckled dimers ( Figure 2 ). From 30 generations up to 65 generations, two best candidate structures appear alternatively. The lowest-energy one keeps parallel buckled dimer surface reconstruction (Figure 2). The other, with slightly higher energy, is a reconstructed surface with some anti-parallel buckled dimer defects which seems to be an amorphous surface structure ( Figure 3 ). Up to 65 generations, the parallel buckled dimer structure was the least energetic while some anti-parallel buckled dimer structures could coexist in the lists of candidate structures. But in our ongoing simulation, one question arises: Is the latter configuration more energetic than the perfectly reconstructed surface with parallel buckled dimers or not, when our S-GA program will run with the following improvements ?

(a). Molecular dynamics step used in our simulation (0.6 ps) is so short that much better anti-parallel buckled dimer structures may not have enough time to be formed. After 65 generations, we double the molecular dynamics steps to 1.2 ps.

(b). Up to 65 generations, the thermal disorder due to the smearing parameter set to 0.2 eV is held constant. We believe that this is a main reason to prevent much better anti-parallel buckled dimer structure from the lists of candidate structures. In our next step, we will consider the effect of thermal disorder on the surface reconstruction by decreasing the smearing parameter during the run.

(c). The standard GAs are also stochastic iterative algorithms without guarantee on convergence: the fewer the number of final generations, the more acceptable the 'Global' minimum.

As for the Simulated Annealing method, similar to the GA technique, larger number of layers is necessary for computing a good formation energy for different types of dimers, as well as their mutual interaction. For the (2×2) geometry considered, we can summarize our results in the following table:

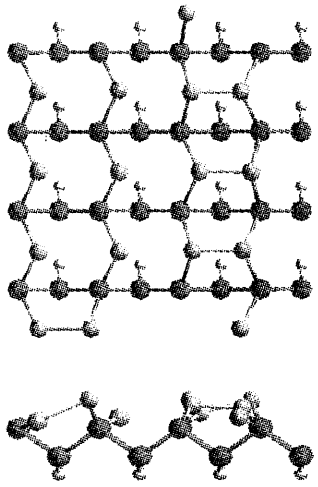

Figure 2. Perfect reconstructed silicon surface (001) with all parallel buckled dimers, topview and sideview.

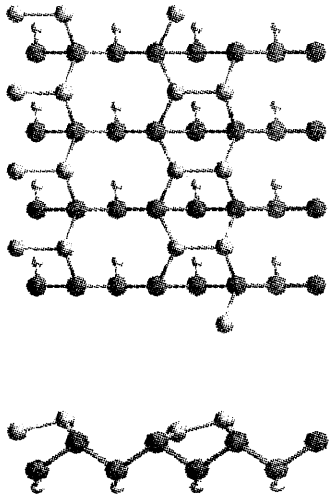

Figure 3. Silicon reconstructed surface (001) with anti-parallel buckled dimer defects, topview and sideview.

## 7. Conclusion

Using both GA and SA techniques, we found that the symmetric buckled dimer structure is the lowest energy reconstructed Si(001) surface. In terms of their efficiency, the genetic algorithm was successful to find the global minimum in 21 generations compared to the SA algorithm. But these numbers must be renormalized to the number of total and moving atoms. GA is very effective in identifying different candidates for the global minimum, where as SA simulations are more realistic in that all atoms are allowed to move and relax. These methods are powerful tools for the search of ground state geometries. Especially GA is very effective to identify structures of complicated topology and geometry, as one can see from its success in finding the icosahedral fullerene as the ground state of $C_{60}$ , and also the bowl shape $C_{20}$ corranulene, and the present study of dimer formation after 21 generations only.

## Acknowledgement

Many valuable suggestions and discussions from Dr. Z.Q. Li are gratefully acknowledged. This work has been partly supported by the National Nature Science Foundation of China. The authors are thankful to the continuous support of the HITAC S-3800/380 supercomputing system by the Information Science Group, IMR, Tohoku University.

1) K. S. Kirkpatrick, C. D. Gelatt, and M. P. Vecchi, Science **220**, 671 (1983).
2) K. S. Kirkpatrick, J. Stat. Phys. **34**, 975 (1984).
3) P. J. M. van Laaarhoven and E. H. L. Aarts, *Simulated Annealing: Theroy and Applications* (Reidel, Dordrecht, 1987).
4) A. B. Finnila, M. A. Gomez, C. Sebenik, C. Stenson, and J. D. Doll, Chem. Phys. Lett. **219**, 343 (1994).
5) L. Piela, J. Kostrowicki, and H. A. Scheraga, J. Phys. Chem. **93**, 339 (1989).
6) L. S. Reid and J. M. Thornton, Proteins **5**, 170 (1989).
7) E. R. Hansen, Numer. Math. **34**, 247 (1980).
8) P. Tuffery, C. Etchebest, S. Hazout, and R. Lavery, J. Biomol. Struct. Dynam. **8**, 1267 (1991).
9) R. S. Judson, M. E. Colvin, J. C. Meza, A. Huffer, and D. Gutierrez, Int. J. Quantum Chem. **44**, 227 (1992).
10) R. Smith, Comp. Phys. Comm. **71**, 134 (1992).
11) W. Linert, P. Margl, and I. Lukovits, Comp. Chem. **16**, 61 (1992).
12) B. Hartke, J. Phys. Chem. **97**, 9973 (1993).
13) R. S. Judson, E. P. Jaeger, A. M. Treasurywala, and M. L. Peterson, J. Comp. Chem. **14**, 1407 (1993).
14) D. B. McCarrah, and R. S. Judson, J. Comp. Chem. **14**, 1385 (1993).
15) Y. Xiao and D. E. Williams, Chem. Phys. Lett. **215**, 17 (1993).
16) S. Forrest, Science **261**, 872 (1993).
17) J. Mestres and G. E. Scuseria, J. Comp. Chem. **16**, 729 (1995).
18) J. A. Nelder and R. Mead, Comp. J. **8**, 308 (1965).
19) T. Back and H.-P. Schwefel, Evol. Comp. **1**, 1 (1993).
20) D. E. Goldberg, *Genetic Algorithms in Search, Optimization, and Machine Learning* (Addison-Wesley, Reading, MA, 1989).
21) S. K. Gregurick, M. H. Alexander, and B. Hartke, J. Chem. Phys. **104**, 2684 (1996).
22) D. M. Deaven and K. M. Ho, Phys. Rev. Lett. **75**, 288 (1995).
23) J. H. Holland, *Adaptation in Natural and Artificial Systems* (The University of Michigan Press, Ann Arbor, 1975).
24) D. J. Chadi, J. Vac. Sci. Technol. **16** 1290 (1979).
25) I. Kwon, R. Biswas, C. Z. Wang, K. M. Ho, and C. M. Soukoulis, Phys. Rev. B **49**, 7242 (1994).
26) The micro-GA technique implements a simple search for an adjacent watershed in the potential hypersurface. When almost all the candidate structures come to the same potential hypersurface, the candidate structures are reset randomly except for the best one. In some cases, it is necessary to apply this technique to the candidate structures because members of the population are limited.
27) B. Andersen, J. M. Gordon, On constant thermodynamic speed for minimizing entropy production in thermodynamic processes and simulated annealing; Phys. Rev. E **50**, 4346 (1994) (and references therein).