Computer Simulation of Silicon Nanoscratch Test

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By the molecular dynamics method, a computer simulation of a scratch test with a nanometer scale was performed. The specimen was composed of 1008 silicon atoms with a diamond single-crystal structure. The indenter was assumed to be a perfect rigid body, and the Morse potential was utilized as the interaction between the indenter and a silicon atom. Two types of potential, *i.e.*, Stillinger-Weber and Tersoff potentials, were examined as the interaction between silicon atoms. The present simulation clarified that the standard deviation of the friction constant increased with decreasing scratch depth and became maximum when the indenter just began to scratch the specimen surface at critical load. The friction coefficient, indentation hardness and scratch hardness at critical load were estimated to be 1.2–1.6, 80–90 GPa and 8.5–9.4 GPa, respectively.

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1. Introduction

In recent years, the structure of function materials has become ultrafine and/or ultrathin with a nanometer scale, and it is essential to analyze the material behavior at the atomic or molecular level. To examine mechanical properties, the nanoindenter and the nanoscratch tester have been developed, enabling us to study the mechanical behavior at the nanometer-order scale experimentally.¹⁾ However, it is difficult to interpret the experimental results by continuum mechanics, which can be adopted only for macroscale phenomenon. Therefore, it is important to clarify the dynamic behavior of the atoms and molecules under nano-indentation or nanoscratching by computer simulation.

The studies of nanoindentation by the molecular dynamics (MD) method began in 1990. Landman *et al.* performed computer experiments in which a nickel indenter was pushed into a gold specimen using the embedded atom method (EAM).²⁾ They observed first the jump-to-contact, which is a kind of aggregation phenomenon of a nanoscale, when the indenter approached the surface of a specimen. A similar MD simulation was performed for the contact of Pb-Pb crystals³⁾ and NaCl-NaCl crystals.⁴⁾ Recently, MD simulation of the indentation of a nanocrystal was also performed for gold,⁵⁾ copper⁶⁾ and cobalt⁷⁾ systems.

Recent developments in scratch simulation are that the potential function has become sophisticated and the system huge. Komanduri *et al.* simulated a scratch test of single-crystal aluminum, of which the interaction potential was assumed to be the Morse type, along the [100] direction.⁸⁾ Ye *et al.* performed a simulation of nano-order cutting for single-crystal copper where the blade was composed of copper atoms.⁹⁾ The atomic interaction of the copper specimen was assumed to be EAM potential. Mulliah *et al.* performed an MD simulation of a silver (100) nanoscratch test and examined the correlations among the friction constant, hardness and orientation of the pyramidal indenter.^{10,11)} The indenter is composed of C atoms in the diamond

structure and Brenner-type potential was assumed as the C–C interaction. The EAM potential was adopted for the Ag–Ag interaction and the ZBL-type repulsive potential for the Ag-indenter interaction. Jun *et al.* simulated nanoscratching of single-crystal Al, of which the atomic interaction was calculated by EAM.¹²⁾ The system was composed of 6 million Al atoms, the largest system treated at that time. The interaction between Al and the indenter was represented by the repulsive potential. It was clarified that the slip pattern of the Shockley partial dislocation is dependent on scratch direction and that the indenter shape affects facet creation at the scratch groove.

In addition to metallic systems, actual experiments of nanoindentation were performed for silicon, an important material for semiconductor devices, and the structural transition from crystalline to amorphous was observed in the region around the indenter.¹³⁾ In addition, for the Ih ice crystal, of which the oxygen arrangement is similar to that of diamond, the structural transition to amorphous was also observed in both actual experiment¹⁴⁾ and in Monte Carlo simulation.¹⁵⁾ The pressure-induced amorphization has attracted much attention from both theorists and experimentalists. However, simulations of such dynamical structural change are still rare. In the present study, computer simulation of the scratch test on a nanometer scale was performed by the molecular dynamics method, and the movements of silicon atoms during scratch testing were analyzed in detail.

2. Methods of Calculation

2.1 Potential functions and MD calculation

Stillinger-Weber¹⁶⁾ and Tersoff¹⁷⁾ potentials were utilized for the Si–Si atomic interaction in the present study. Since silicon is an element which undergoes tetragonal bonding, the interaction potential should include the effects of surrounding atoms, *i.e.*, coordination number, and bonding angles. Empirical potential models for such elements can be classified into two types, Stillinger-Weber and Tersoff. The Stillinger-Weber (SW) potential is mainly focused on the energy increment of the structures perturbed from the most

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stable diamond structure, while the Tersoff potential represents the effects of the surrounding atoms on the interaction between the two atoms of interest, and as a result, the diamond structure becomes the most stable.

The functional form and the parameters of Tersoff potential were determined to reproduce both the dependences of bonding energy on coordination number and of total energies of various bulk structures on volume, obtained by the theoretical calculation using local density approximation (LDF).¹⁷⁾ In contrast, it is pointed out that SW potential cannot reproduce these properties so well.¹⁸⁾ In addition, it is reported experimentally that the structural transition from diamond to β -Sn structure, which is a high-pressure phase, occurs during indentation.¹⁹⁾ This phenomenon can be attributed to pressure induced phase transition. The calculation with Tersoff potential succeeded to produce β -Sn structure during indentation,²⁰⁾ while that with SW potential predicted the direct structural transition from crystalline to amorphous or liquid-like disordered structure.^{21,22)} From these facts, we concluded that Tersoff potential provides more reliable results than SW potential in the simulation of indentation and scratch experiments. It should be noted, however, that SW potential can describe the properties of silicon with diamond, liquid and amorphous structures better than Tersoff potential.²³⁾ For example, the melting point of silicon crystal was overestimated to be 2547 K by Tersoff potential, while 1691 K by SW potential and 1683 K by experiment. Therefore the results obtained by SW potential cannot be abandoned immediately. At the present stage, the both results obtained by Tersoff and SW potentials are worth to be considered.

The most time-consuming part of the MD simulation is the calculation of forces acting on individual atoms, using the potential function. Therefore the neighbor list method was utilized to save time in the force calculation process. The neighbor list method constructs directories of the particles within the interaction region around the atom of interest, and the use of these directories significantly reduces the force calculation time.²⁴⁾ The cut-off length was 1.1 times the nearest-neighbor distance, and the neighbor list was updated every 20 MD steps. The Verlet velocity form was utilized to integrate Newton's equation of motion.²⁵⁾ The system temperature was controlled to be 298 K using an ad hoc velocity scaling.

2.2 Setting indenter

For the computer simulation of hardness and scratch tests, it is desirable to calculate the motion of the individual atoms that constitute the indenter, which is made of a very hard material such as diamond. However, such calculation requires huge computing time. Therefore the indenter is assumed to be a perfect rigid body of conical shape to save calculation time. Although this assumption is fictitious, the main features of the nanoscratch phenomenon can be achieved. Figure 1 shows the shape of the indenter used in the present study. The side of the indenter is a cone with an apex angle of 60 deg and the top is spherical with a diameter of 0.5 nm.

As the interaction between the specimen atom and the indenter, Morse potential,

Fig. 1 Geometry of the top of the indenter.

$$\phi(r) = D[\exp\{-2\alpha(r - r_0)\} - 2\exp\{-\alpha(r - r_0)\}], \quad (1)$$

was assumed in the present study, where D , r_0 and α are the parameters that can be related to binding energy, equilibrium distance and stiffness, respectively, and r is the nearest distance between a specimen atom and the surface of the indenter. The values of the potential parameters are

$$\begin{aligned} D(\text{eV}) &= 0.435, \quad \alpha(\text{nm}^{-1}) = 46.487, \\ r_0(\text{nm}) &= 0.19475, \end{aligned} \quad (2)$$

which were taken from Ref. 26).

For the equation of motion for the indenter, a damping mechanism was assumed.²⁷⁾ The velocity of the indenter v was derived from

$$v = \frac{F_{\text{external}} - F_{\text{atom}}}{\zeta}, \quad (3)$$

where F_{external} , F_{atom} and ζ are the loading force acting on the indenter, the total force acting on the indenter from the specimen atoms, and the friction constant, respectively. Setting the value of ζ is a subtle problem. If ζ is too large, the velocity of the indenter becomes too low for the system to become stationary within a reasonable time. While the value of ζ is too small, the movement of the indenter fluctuates greatly and an unphysical result occurs. In the present study, preliminary calculations were performed by varying the value of ζ , and $\zeta = 200$ was found to be the most appropriate for obtaining physically reasonable results; this value was used hereafter.

The scratch depth is defined as the distance between the top of the indenter and the surface of the specimen. It should be noted that the sign of the depth is plus when the vertical position of the top of the indenter is below the specimen surface.

The indentation hardness is defined as

(vertical load)

/(contact area between the indenter
and the specimen at maximum scratch depth),

and the scratch hardness as

(vertical load)

/(section area of the indenter cut
by the specimen surface at maximum scratch depth).

Fig. 2 Changes of atomic arrangement during nanoscratch test simulated with Tersoff potential. Lateral and vertical loads are 0.3 nN and 10 nN, respectively. Durations are (a) 0 fs, (b) 2340 fs, (c) 4500 fs and (d) 6480 fs.

These definitions are consistent with those of engineering.

The dynamical friction constant of the specimen was calculated as

$$\mu = \frac{F_y}{F_z}, \quad (4)$$

where F_y and F_z are the forces along the scratch direction and the loading vertical direction, respectively.

2.3 Specimen

As a specimen, 1008 Si atoms were set on diamond lattice sites. The dimensions of the sample along x [100], y [010] and z [001] directions are 1.63 nm, 7.60 nm and 1.63 nm, respectively. The indenter was applied load along the vertical z direction and pushed into the sample. Then the load along the horizontal y direction was additionally applied to the indenter to scratch the sample surface. This procedure mimics the scratch test in an actual experiment. The fixed boundary condition was set along the horizontal x and y directions, while the free boundary was along the vertical z direction. The fixed atoms in the silicon single-crystal structure were

positioned in the peripheral region of the sample to achieve the fixed boundary condition.

3. Results and Discussion

In the present study, the load along the y direction was kept constant at 0.3 nN, while the load along the z direction was varied as 10 nN, 3 nN and 0.35 nN. Using the Tersoff and Stillinger-Weber potentials to calculate forces, the nanoscale scratch test was simulated. Figure 2 represents the change of atomic arrangements for vertical load of 10 nN and Tersoff potential during the scratch simulation. As the indenter moves along the y direction, the atomic arrangement around the indenter becomes disordered. Figure 3 shows the position in the y direction of the indenter during the simulation. It can be seen from the figure that the load along z direction was applied for 0–2000 fs, and then the load along the y direction was additionally applied to the indenter for 2000–6000 fs, leading to the movement of the indenter along the y direction at a constant velocity.

The atomic configuration after the scratch test and the

Fig. 3 Time change of indenter position along the scratch direction. Experimental condition is the same as in the case of Fig. 2.

Fig. 5 Same as Fig. 4 but with vertical load of 3 nN.

Fig. 4 (a)&(b) The final atomic arrangements and (c) time change of indentation depth for nanoscratch test with vertical load of 10 nN. (a) Tersoff potential and (b) Stillinger-Weber potential were used for simulation.

change of indentation/scratch depth during the test are shown in Figs. 4–6. As shown in Fig. 4, for the vertical load 10 nN, the indenter scratched the sample more deeply than in the other cases shown in Figs. 5 and 6, under lighter vertical load conditions. The hardness of the system calculated using the Tersoff potential was greater than that of the system calculated using the Stillinger-Weber potential, since the indentation depth in the case of Tersoff potential is smaller than that in the case of Stillinger-Weber potential. As shown in Fig. 5, with the vertical load of 3 nN, the indenter scratched only the topmost atomic layer and it can be considered that this load is the critical load for scratching to occur. In the case of the vertical load of 0.35 nN, as can be seen in Fig. 6, the indenter only slipped over the surface of the specimen, so scratching does not occur at this load.

Fig. 6 Same as Fig. 4 but with vertical load of 0.35 nN.

The radial distribution function (RDF) after the scratch test is represented in Fig. 7. For the vertical load of 10 nN, the fourth and fifth peaks disappeared, which suggests that the atomic arrangement of the scratched region of the sample is disordered. In contrast, for the vertical loads of 3 nN and 0.35 nN, the atomic arrangement maintains the crystalline long-range order. According to the previous simulation study on the structure of bulk silicon,²³⁾ the third peak of the RDF in diamond structure disappears perfectly in amorphous struc-

Fig. 7 Radial distribution functions calculated for the final atomic arrangements. The potential used and applied vertical load are (a) Tersoff, 10 nN, (b) Tersoff, 3 nN, (c) Tersoff, 0.35 nN, (a') Stillinger-Weber, 10 nN, (b') Stillinger-Weber, 3 nN, and (c') Stillinger-Weber, 0.35 nN.

ture. In the present simulation, the third peak still remains even for the largest vertical load 10 nN. Therefore it can be considered that the resultant structure of the scratched surface is not amorphous, but the disordered structure with short-range order up to the third neighbor distance. It should be noted, however, that the data shown in Fig. 7 were calculated for the whole surface region affected by the indenter after the scratch test. As described below, the resultant structure of the scratched surface can be separated into two types, *i.e.*, the disordered structure with short-range order of the crystalline and amorphous.

For the case of vertical load 10 nN and Tersoff potential, the specimen surface is equally divided into 5 regions and the time change of RDF was calculated for these regions separately. Figure 8 shows the change of RDF for the center

region and its left side region. The forth and fifth peaks of the RDF of the center region disappeared at 3.87 ps, reflecting the structural disordering by the onset of scratching (see also Fig. 2). The third peak still remains in the RDF, therefore the structure of this region is not amorphous, but the disordered structure with short-range order up to the third neighbor distance. In the RDF at 7.74 ps, after the completion of the scratch test, the structure can be considered to be amorphous because the third peak disappeared. On the other hand, the left region is scratched earlier than the center region but the scratch depth is too shallow in this region to cause structural transition to amorphous. Therefore the structure of this region is the disordered structure but with short-range order of the crystalline up to the third nearest neighbor.

Tables 1, 2 and 3 show average values of the friction

Fig. 8 Change of radial distribution functions for the center (gray lines) and the left (black lines) regions of the surface of the specimen. The potential model and vertical load are Tersoff and 10 nN, respectively.

Table 1 Average values of friction coefficient for the Tersoff and Stillinger-Weber (SW) potential models.

Load [nN]	Tersoff	SW
10	0.980	1.737
3	1.198	1.637
0.35	0.873	0.602

Table 2 Indentation hardness for the Tersoff and Stillinger-Weber (SW) potential models.

Load [nN]	Tersoff [GPa]	SW [GPa]
10	61.35	31.66
3	89.98	77.49
0.35	—	—

Table 3 Average values of scratch hardness for the Tersoff and Stillinger-Weber (SW) potential models.

Load [nN]	Tersoff [GPa]	SW [GPa]
10	19.34	13.19
3	8.52	9.40
0.35	—	—

Fig. 9 Standard deviation of friction coefficient as a function of vertical load. (a) Tersoff and (b) Stillinger-Weber potential models. The solid lines are only for guide eye.

coefficient, indentation hardness, and scratch hardness, respectively. The friction coefficient, indentation hardness and scratch hardness at the critical load of 3 nN were estimated to be 1.2–1.6, 80–90 GPa and 8.5–9.4 GPa, respectively. The values of the indentation hardness are about ten times larger than that for bulk silicon, about 8 GPa. The reason is that the indentation depth is as small as the order of one atomic layer. From Table 2, it can be seen that the indentation hardness decreases significantly as the indentation load increases from 3 nN to 10 nN. According to the results of the previous computer simulation performed by the authors, the indentation depth reached 2.8 nm and the indentation hardness reached 5.85 GPa when the indentation load was set to be 100 nN.²²⁾

The dynamic friction constant μ varies with time around the average value because the forces F_y and F_z fluctuate with time, reflecting the dynamic change of the atomic arrangement around the indenter. The standard deviation of $\mu(t)$, σ , is calculated and plotted as a function of vertical load in Fig. 9. From the figure it is clear that the standard deviation of the friction constant increases with decreasing scratch depth and becomes maximum at the critical load at which the indenter just begins to scratch the surface. This is confirmed by both the Stillinger-Weber and Tersoff potential models. In addition, the Fourier analysis was performed for $\mu(t)$, as shown in Fig. 10, and it was clarified that the variation of the

Fig. 10 Fourier analysis of dynamic friction coefficient $\mu(t)$. The potential used and applied vertical load are (a) Tersoff, 10 nN, (b) Tersoff, 3 nN, (c) Tersoff, 0.35 nN, (a') Stillinger-Weber, 10 nN, (b') Stillinger-Weber, 3 nN, and (c') Stillinger-Weber, 0.35 nN.

frequency amplitude is smallest at the critical load of 3 nN along the vertical z direction than in the other cases of vertical load. As stated above, the critical load at which the thin film is broken by scratching can be evaluated precisely by statistical analysis and Fourier analysis of the dynamic friction constant $\mu(t)$.

Recently, machining process with nanometer scale has been extensively studied. Sasaki *et al.* performed ultra-fine machining of (100) surface of single crystalline silicon by friction force microscopy (FFM) with the cantilever especially designed for this experiment.²⁸⁾ The vertical load was about 800 μN and the depth of the digged region was about 30 nm. Since the spatial scale of this experiment is about 60 times larger than that of the present simulation, the direct comparison between the experiment and simulation results is impossible at present. In the near future, however, the spatial scale of experiment will become smaller and that of

simulation larger, the direct comparison will be realized. The authors have begun to develop the parallel code of the present simulation for a massive parallel machine to treat larger specimen.

4. Conclusion

By the molecular dynamics method, a computer simulation of a scratch test with a nanometer scale was performed. The specimen was composed of 1008 silicon atoms with a diamond single-crystal structure. The indenter was assumed to be a perfect rigid body, and the Morse potential was utilized as the interaction between the indenter and a silicon atom. Two potential models, *i.e.*, Stillinger-Weber and Tersoff potential models, were examined as the interaction between silicon atoms. The obtained results can be summarized as follows.

- (1) The standard deviation of the friction constant increased with decreasing scratch depth and became maximum when the indenter just began to scratch the specimen surface at the critical load of 3 nN.
- (2) The friction coefficient, indentation hardness and scratch hardness at critical load were estimated to be 1.2–1.6, 80–90 GPa and 8.5–9.4 GPa, respectively.
- (3) Analysis of the radial distribution function revealed that the structure of the scratched region changed from crystalline to the disordered structure with short-range order of crystalline and amorphous.
- (4) The Fourier analysis for $\mu(t)$ clarified that the variation of frequency amplitude is smallest at the critical load of 3 nN along vertical z direction than in the other cases of vertical load.

The present study revealed that the critical load at which the thin film is broken by scratching could be evaluated precisely by the statistical analysis and Fourier analysis of the dynamic friction constant $\mu(t)$.

The computer simulation of the nanoscratch test for various metals on silicon substrates is now being carried out by the authors, and the mechanics of the breakage of the films and the strategy for the improvement of adhesion between heterogeneous interfaces will be clarified in the near future.

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