Molecular Dynamics Simulation of Nanoindentation on Ion-induced Damage of Silicon Surface

S Satake 1, S Yamashina 1, K Ando 1, M Shibahara 2, J Taniguchi 1 and S Momota 3

1 Department of Applied Electronics, Tokyo University of Science, 2641 Yamazaki, Noda, 278-8510 Chiba, Japan
2 Department of Mech Eng, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan
3 Department of Intelligent Mechanical Systems Engineering, Kochi University of Technology, 185 Miyanokuchi, Tosayamada, Kami, Kochi 782-8502, Japan
satake@te.noda.tus.ac.jp

Abstract. Nanoindentation on ion-induced damage of silicon surface was performed using molecular dynamics. The simulation revealed interaction between a ion-induced damage substrate and a indentation. Two types of silicon substrates are used. One is silicon crystal, and another is amorphous silicon which damaged by argon ion bombardment. The initial velocity of the ion bombardment was $3.807 \times 10^5$ m/sec at 30 keV. The computation volume (8.00 nm $\times$ 8.00 nm $\times$ 17.24 nm) consisted of 57600 Si atoms with Si (100) surface. Each silicon substrate was pressed by the indentation and the force acting on the indentation head were investigated. The force of the ion-induced substrate is smaller than that of the crystalline substrate. Consequently, it turned out that the internal structure of silicon with ion-induced damage can be examined by the force distribution of the indentation.

1. Introduction
Ion beam lithography (IBL) has being rapidly developed as one of nanotechnologies for a semiconductor. Following the development, a superior analytical method is essential now. And the probe of scanning probe microscopes (SPM) such as scanning tunneling microscope (STM) or atomic force microscope (AFM) was introduced and has contributed to development of high accurate analysis for years. Especially nanoindentation test is widely used in field of nanotechnology.

The method introduced by Pharr and Oliver [1] is valid to study material properties in detail. A nanoindentation test needs high accurate control and measurement but is easily put into practice without particular circumstances. Even if measure is quite small, it reveals mechanical properties such as surface, hardness, modulus from just only load-unloading data. Recently, the enhancement of an irradiation effect on the nanohardness on a Si crystal was observed [2], and this enhancement suggests
increased defect production in Si crystal by highly-charged ion beams. However, it is difficult to elucidate the mechanism by the experiment because the phenomena caused at the atomic scale order. On the other hand, a molecular dynamics (MD) simulation can solve such as the problem because it can track each ion and atom dynamically. MD simulations about nanoindentation were made by some studies, for instance, a dislocation emission in single crystalline aluminum [3] and phase transformations in silicon monocrystals [4] were presented. In this paper, a crystalline silicon substrate and an ion-induced damaged one were pressed by the indenter. And force acting on the indenter head has been recorded as mathematical values through simulations. The purpose is to investigate each property of the substrates and examine an effect of ion bombardment.

2. The numerical method and the model systems
We performed MD simulations to investigate indentation load-unloading on a Si target. We have previously found an optimal combination of potential functions for the target material and the indentation. The optimal potential combination is found for Silicon, Argon and Carbon: Tersoff potential [5] for the target material and the indenter, Ziegler, Biersack and Litmark (ZBL) potential [6] and Lennard and Jones potential. We used our previous MD code [7]. In the present MD calculations, the Verlet algorithm was used for time integration. Table 1 shows combinations for each potential.

| Potential function | Pattern          |
|-------------------|-----------------|
| Tersoff           | Si-Si,C-C       |
| ZBL               | Si-Ar,Ar-Ar     |
| Lennard-Jones     | Si-C,Ar-C       |

2.1. Potential function
For the simulation with a Si target, the Tersoff potential function [5] was employed:

\[
\phi = \frac{1}{2} \sum_i \sum_{j \neq i} f_c(r_{ij}) \left( f_R(r_{ij}) + b_y f_A(r_{ij}) \right)
\]

\[
f_R(r) = A \exp(-\lambda r)
\]

\[
f_A(r) = -B \exp(-\mu r)
\]

\[
f_c(r) = \begin{cases} 
1, & r < R \\
\frac{1}{2} + \frac{1}{2} \cos \left( \frac{\pi (r-R)}{S-R} \right), & R < r < S \\
0, & r > S
\end{cases}
\]

\[
b_y = \left( 1 + \beta^n \xi_y^n \right)^{-1/2n}, \quad \xi_y = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}), \quad g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2}
\]

Here \( i, j, \) and \( k \) label the atoms of the system, \( r_{ij} \) is the length of the \( ij \) bond, and \( \theta_{ijk} \) is the bond angle between bounds \( ij \) and \( jk \). The Tersoff potential is also used for Carbon as the indenter. The parameters in Eq. (1) are summarized in Table 2.
### Table 2. Tersoff potential parameters for C, Si.[8]

| Parameter          | C                  | Si                  |
|--------------------|--------------------|--------------------|
| \(A[\text{eV}]\)  | \(1.3936 \times 10^3\) | \(1.830 \times 10^3\) |
| \(B[\text{eV}]\)  | \(3.467 \times 10^2\)  | \(4.7118 \times 10^2\) |
| \(\lambda [\text{Å}^{-1}]\) | 3.4879 | 2.4799 |
| \(\mu [\text{Å}^{-1}]\) | 2.2119 | 1.7322 |
| \(\beta\)         | 1.5724 \times 10^{-7}\) | 1.1000 \times 10^{-6}\) |
| \(\eta\)          | 7.2751 \times 10^{-1}\) | 7.8734 \times 10^{-1}\) |
| \(c\)             | 3.8049 \times 10^4\)  | 1.0039 \times 10^5\)  |
| \(d\)             | 4.384               | 16.217             |
| \(h\)             | -0.57058            | -0.59825           |
| \(R(1)[\text{Å}]\) | 1.8                 | 2.7                |
| \(R(2)[\text{Å}]\) | 2.1                 | 3.0                |

2.2. Ziegler, Biersack and Littmark (ZBL) potential.
The Ar ion potential is represented by the Ziegler, Biersack and Littmark (ZBL) potential [6]:

\[
\phi(r) = \frac{Z_i Z_j e^3}{4 \pi \varepsilon_0 r_{ij}} \Phi(r)
\]

\[
\Phi(r) = \sum_{k=1}^{4} c_k \exp \left( -d_k \frac{r_{ij}}{a_u} \right) a_u = \frac{0.8854 a_u}{Z_i^{0.23} + Z_j^{0.23}}, a_u = 0.529 \text{ Å}
\]

Here \(Z_1\) and \(Z_2\) are atomic numbers. The detailed parameters are shown in Table 3.

### Table 3. ZBL potential parameters.

| \(c_i\) | \(d_i\) |
|---------|---------|
| 0.028171 | 0.20162 |
| 0.28022  | 0.4029  |
| 0.50986  | 0.94299 |
| 0.18175  | 3.1998  |

2.3. Lennard and Jones (L-J) potential
Force on Si-C, Ar-C are described in Van der Waals' force by

\[
\phi(r) = 4 \varepsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} \left( \frac{\sigma}{r_{ij}} \right)^{6}
\]

(3)
where \( r_{ij} \) is the separation distance between two particles \( i \) and \( j \), \( \varepsilon \) is the potential depth for a parameter of energy, \( \sigma \) is the diameter of an atom. The parameters are shown in Table 4.

**Table 4.** Lennard-Jones potential parameters.

| Combination | \( \varepsilon [eV] \) | \( \sigma [\text{Å}] \) |
|-------------|-----------------|-----------------|
| Si-C        | 2.461           | 3.555           |
| Ar-C        | 4.998           | 3.38            |

3. Computational parameters

![Simulation model](image)

Figure 1. Simulation model.

Computational domain is shown in figure 1. The targets domain was 8.00 nm × 8.00 nm × 17.24 nm, consisting of 56,700 Si atoms. Except for the targets domain, the free boundary conditions were applied in the \( x \), \( y \), and \( z \) directions. In the targets domain, bottom and all of lateral consist of a fixed heating bath: Langevin layer. The bottom surface is fixed to \( z \)-direction. This layer keeps a substrate temperature of 300K. In this simulation two substrates were used. One was single crystalline, the other was amorphous due to Ar ion bombardment with \( 3.807 \times 10^5 \) m/sec initial speed at 30keV. These collisions were carried out ten times toward a 4.07 nm × 4.07 nm region and incident position is at random and a dose amount was \( 0.6036 \times 10^{14} \) ion/cm\(^2\). The computational domain of the substrates was divided into sixteen parallel partitions from the surface to the bottom of the Si target, referred to as regions. A spherical indenter was used and has in total 1269 carbon atoms. The radius was 1.95 nm. The indenter moved at a constant velocity of 100 m/s. A loading phase continued until the indenter is completely into the substrates, and its move was stopped for 10 ps following the previous phase. Then, the indenter was pulled out at the same velocity.
4. Result and discussion

The result of the simulation about indent load histories is shown in Fig. 3. The force acting on the tip is integrated by the z-components of force acting on the individual atoms during load-unloading process. Figure 3 shows that loads acting on the tip for the crystalline substrate are stronger. In contrast, the histories of the ion-induced substrate are below that of the crystalline one. As a result of the comparison, forces generated on ion-induced state are less than those on crystalline state.

Figure 4 shows load-displacement curves of the ion-induced and crystalline substrate. These curves show that differences between the ion-induced and crystalline substrate are gradually increased as a depth is deeper. Hence it turned out that the ion irradiation affected on the load values.
Moreover, hardness of the substrates was determined with $F/A$. $F$ is value of repulsive forces during the loading. And the $A$ corresponds to contact area of the indenter. Figure 5 shows calculated results for hardness. The curves of hardness are exponentially decaying as depth is deeper. Both curves have an extreme value around surface. That of the crystalline substrate is broadly flat around 2GPa in 0.2-1.2nm depth. By contrast, that of the amorphous rises slightly in the same range. This phenomenon can be caused by dislocation emission beneath an indenter in a report by Shibutani [9]. In Experimental studies, silicon beneath an indenter transforms from diamond cubic structure to beta-silicon structure at pressure about 8GPa. Amorphous silicon also transforms into beta-silicon structure at 12GPa [10]. In other words, beta-silicon structure is harder than amorphous structure. So the transformation from beta-silicon structure to amorphous structure results in increase of microhardness. In this simulation, the irradiation area is probably on amorphous state in ion collisions. Thus, the hardness of the ion-induced substrate is lower than that of the crystalline. Therefore it has presented that ion-induced substrate is softer than crystalline one.

5. Conclusions

Molecular dynamics simulation was carried out for the nanoindentation on ion-induced damage of silicon surface. The simulation revealed interaction between ion-induced damage and the indentation. Two types of silicon substrates were used. Each silicon substrate was pressed by the indentation and the force acting on the indentation head were investigated. The force of the amorphous substrate is smaller than that of the crystalline substrate. Thus, the ion irradiation affects load and hardness of a substrate. In addition for ion irradiation effect, hardness of large irradiation is softer in that of small irradiation. Consequently, it turned out that the internal structure of silicon with ion-induced damage can be examined by the force distribution of the indentation.

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