

First-Principles Simulation of Collision Cascades in Si to Test Pair-Potential for Si-Si Interaction at 10 eV – 5 keV

J. Keinonen, A. Kuronen and K. Nordlund

Accelerator Laboratory, University of Helsinki, P.O.BOX 43, FIN-00014 Helsinki, Finland

R. M. Nieminen and A. P. Seitsonen

Laboratory of Physics, Helsinki University of Technology, FIN-02150 Espoo, Finland

Interatomic potentials for Si-Si interaction are tested at energies 10 eV–5 keV for Si ions in ion-beam amorphized Si by simulating range distribution data with the molecular dynamics method. The range profile of 1×10^{16} 10-keV $^{30}\text{Si}^+$ cm^{-2} implanted into originally crystalline silicon were measured using a nuclear reaction technique. An interatomic repulsive potential from first-principles calculations is proposed for the Si-Si interaction. The dependence of the number of vacancies produced in low-energy collision cascades on the potential is demonstrated by simulations of the cascade dynamics.

I. INTRODUCTION

Ion implantation of crystalline silicon (c-Si) is a basic technique in semiconductor technology. Processes that generate damage in c-Si during implantation of keV and MeV ions have been studied extensively, e.g. Refs. [1–7]. Ion-mixing experiments [8–12] and Monte Carlo simulations [13] have shown that the damage production in collision cascades depends predominantly on two-body collisions below 1 keV between silicon atoms. Low-energy ion irradiation used for surface modification, thin film deposition, oxidation and doping of semiconductors [14–16], has further emphasized the need to understand the dynamics of low-energy collision cascades. The first step in evaluating the collision cascades and hence damage production consists in determining the interatomic potential for the Si-Si interaction.

In previous works on atomic collisions [17], the interaction in binary collisions has been considered either for neutral atoms or for charged atoms in metals which are fully screened outside a Wigner-Seitz cell by appropriate numbers of free (conducting) electrons. The interatomic potentials, calculated from overlapping rigid atomic (e.g. Hartree-Fock) charge distributions and using first order perturbation theory and local-density approximation, have been evaluated in several studies [17,18]. The results of different calculations show large scatter between interatomic potentials at radial separation distances larger than 0.5 Å. With this in mind, Ziegler *et al.* [17] (ZBL) suggested a universal interatomic screening function and hence a universal interatomic potential, which has been used in various contexts.

The ZBL potential and other potentials based on overlapping rigid atoms [17,18] have deficiencies due to two physical reasons. Firstly, these potentials do not account for the electronic screening accurately throughout the range of the potential. Secondly, a two-body potential is expected to be valid only in the high-energy, repulsive region where the kinetic energies of the colliding atoms

clearly exceed the interatomic potential energy. For low-energy (< 10 eV) interactions where the directional bonding of silicon atoms can not be neglected, empirical many-body potentials have been constructed [19,20].

In this work we want to demonstrate that with the aid of recent development in theoretical methods in solid state physics and first-principles simulations the experimental results on collision cascades in silicon can be accurately reproduced. The experimental techniques are described in Ch. 2. Dynamic simulations of collision cascades in amorphous silicon (a-Si) are then carried out to test interatomic potentials for the Si-Si interactions in Si at distances 0.2–1.5 Å, i.e. at potential energies 5 keV–10 eV, respectively. The range profiles of 10-keV Si ions in a-Si are calculated in full molecular dynamics (MD) simulations using an *ab-initio* potential based on the density functional formalism [21] and contrasted to those obtained using the ZBL [17] and Molière [22] potentials common in simulation works, e.g. Ref. [23]. The methods used to obtain the *ab-initio* potential are described in Ch. 3. The simulated range profiles are compared in Ch. 4 with the experimental profile measured with a nuclear reaction technique.

In previous MD studies reported in the literature on collision cascades, the dynamic processes in energetic displacement cascades have been studied, e.g. very recently vacancy and interstitial dislocation loops in MD simulations of 25-keV Cu in Cu [24]. We also study the dependence of the vacancy production on the interatomic potential by MD simulations of the collision cascades of 1-keV Si atoms in c-Si. These results are reported in Ch. 4.

II. MEASUREMENTS

For the measurements of the range profiles, samples were prepared at the isotope separator of the Accelerator Laboratory by implanting fluences of 1×10^{16} 10-

keV $^{30}\text{Si}^+$ cm^{-2} into n-type Si(100) slices (Czochralski grown, doped uniformly by P to a resistivity of 2.5–3.5 Ωcm) at room temperature. This dose is above the limit (about 10^{15}cm^{-2}) where the amorphization of the implanted layer occurs [25]. During the implantations the specimen normal ($\langle 100 \rangle$ axis) was aligned 6° from the beam axis. Four sets of samples were produced.

To probe the ^{30}Si range distributions in the samples, the nuclear-resonance-broadening (NRB) technique was used [26], along with the sharp ($\Gamma = 68 \text{ eV}$, Ref. [27]), strong ($S = 5 \text{ eV}$, Ref. [27]), and isolated resonance of the $^{30}\text{Si}(p, \gamma)^{31}\text{P}$ reaction at $E_p = 620 \text{ keV}$. The proton beams of about $1 \mu\text{A}$ were supplied by the 2.5-MV Van de Graaff accelerator of the Accelerator Laboratory. The resolving power of the beam, typically 400 eV, was determined at the 620-keV resonance with an un-implanted c-Si sample containing 3.1 at. % of the isotope ^{30}Si . It corresponds to the depth resolution of about 5 nm at the surface. The beam was focused to a spot of $3 \times 3 \text{ mm}^2$. Effects associated with the probing proton beam were controlled by repeating each measurement twice at each beam spot. The γ radiation was detected in a 12.7-cm-diameter \times 10.2-cm NaI(Tl) crystal shielded against the background radiation by 5 cm of lead.

The measured ^{30}Si distribution is shown in Fig. 1.

FIG. 1. Measured and simulated range distributions of ^{30}Si implanted into silicon. Also shown are the deposited energies due to electronic and nuclear stopping powers. For the comparison with the range profiles the deposited energy distributions have also been convoluted by the experimental resolution of the probing proton beam used in the NRB measurements of the range distributions.

The distribution is contributed to by the range distribution of ^{30}Si implants, the natural width of the resonance, the energy resolution of the proton beam, and the width of the energy-loss distribution for protons after traversing in a-Si. The concentration profiles of doped ^{30}Si atoms were obtained by comparison of the γ -ray yields from the doped ^{30}Si nuclei with those from isotope ^{30}Si in natural silicon. In the calculation of the depth scale, the stopping power of silicon for protons was taken from Ref. [28]. The step in the excitation function arising from the natural ^{30}Si concentration was used in determining

the zero-point of the depth scale.

III. MD SIMULATIONS

A. Range distributions

The experimental range profile illustrated in Fig. 1, was simulated using a MD method based on the computer code used very recently in simulations of slowing down of ultra-low velocity recoils produced in thermal neutron capture reactions [29,30]. A Cray X-MP EA/432 super-computer was employed in the simulations.

In every simulation run the trajectories of about 5000 incident ^{30}Si atoms were followed until they had slowed down to a cut-off energy of 5 eV. Due to the high implantation dose of $1 \times 10^{16} \text{ }^{30}\text{Si}^+ \text{cm}^{-2}$ practically all the implanted ions observable with the NRB method can be assumed to slow down in a-Si [25]. The initial coordinates of the lattice Si atoms in a-Si [31] were based on *ab-initio* MD simulations [32,33]. The starting position of the incident ^{30}Si atom was 5 Å above the surface of the computational cell of a-Si in the z direction, and was chosen randomly in the xy plane. The direction of the initial velocity of the incident ^{30}Si atom was aligned 6° from the normal of the surface of a-Si in the (100) direction. The end position of every incident atom was stored for the calculation of the range distribution. Because the coordinates of the Si atoms were taken from the *ab-initio* calculations it was not necessary to equilibrate the MD cell.

Due to the high kinetic energies involved, periodic boundary conditions can not be applied as was done in the simulations of ultra-low velocity recoils [29,30]. Instead, a slab of undisturbed silicon was generated in front of the incident atom every time it got close to the boundary of the computational cell. Thus the incident atom always moved in an undisturbed simulation cell of 63 or 216 Si atoms.

We construct the interatomic potential as follows. For short inter-nuclear separations ($r < 1.7 \text{ \AA}$), the potential is calculated through an accurate treatment of the interacting Si-Si dimer. The repulsive potential is then matched smoothly with the classical Stillinger-Weber many-atom potential [19], which gives a good description of low-energy cohesion and bonding.

The short range repulsive potential is obtained from a self-consistent total energy calculation using density-functional theory and the local-density approximation (LDA) for electronic exchange and correlation [21]. The Kohn-Sham equations are solved numerically using a basis-set consisting of numerical atomic-type orbitals, and a discrete-variational method for the three-dimensional integrals [34]. The stability of the total energy results with respect to the basis set and the density of integration points was carefully monitored. The total

energy, including both the electronic part and the inter-nuclear Coulomb repulsion, is obtained as a function of the dimer distance, and defines the interatomic potential energy. In practice, we use the DMol package [35] well tested in calculations of energetics and structures of small molecules.

In addition to the DMol potential, the simulations were performed also with the ZBL [17] and Molière [22] (with Firsov screening length) potentials as the short range interaction. As in the case of DMol, the Stillinger-Weber potential was splined with the short range potentials between $r = 1.7$ and 2.0 Å.

FIG. 2. Interatomic Si-Si potentials used in the simulations of the range data for the Si ions.

The potentials are compared in Fig. 2.

The experimentally confirmed electronic stopping power from Ref. [36] was included in the equations of motion of the incident atoms as a frictional force [30].

B. Damage simulations

In implantations and ion irradiations of c-Si and a-Si the damage is produced mainly in secondary low energy (of the order of 100 eV) two-body collisions between silicon atoms. This was investigated by a simulation of the evolution of a collision cascade produced in the slowing down of 1-keV silicon atoms in a simulation cell corresponding to c-Si. The simulation cell of 21600 atoms was large enough to totally include the collision cascade of incident 1-keV ^{30}Si atoms within a simulation time of 200 fs. For the dissipation of the recoil energy from the simulation cell, open boundary conditions were applied in all three dimensions.

IV. RESULTS

A. Range distributions

For the comparison with the measured ^{30}Si distributions, the calculated range profiles were convoluted with the natural width of the resonance, the energy resolution

of the proton beam, and the width of the energy-loss distribution for protons after traversing in Si. In the numerical convolution we used a Gaussian function [8] which approximates well Vavilov's energy straggling distribution [37]. The comparison of the front edges of the simulated and experimental range distributions showed that the energy straggling of protons calculated according to the Bohr model [38] had to be multiplied by 0.9.

The simulated ^{30}Si distributions are shown in Fig. 1. The ZBL potential which is weaker than the DMol potential at the interatomic separations $r < 1.0$ Å, results in a longer range (mean range $\bar{R} = 213$ Å) than the experimental range distribution ($\bar{R} = 188 \pm 5$ Å) well reproduced by the use of the DMol potential ($\bar{R} = 187$ Å). Neither is the shape of the range profile reproduced by the use of the ZBL potential. The Molière potential which is weaker than the DMol potential at distances $r < 0.6$ Å and $r > 1.3$ Å but stronger at distances $0.6 < r < 1.3$ Å, results in a slightly larger range ($\bar{R} = 204$ Å) than the experimental one. The reason behind the small difference is the fact that the slowing down process is dominated by the potential region where the Molière potential is both weaker and stronger than the DMol potential, Fig. 2.

The deposited energies due to the nuclear (F_D^{nuc}) and electronic (F_D^{el}) stopping power are also illustrated in Fig. 1 for the simulations done with the DMol potential. The total deposited nuclear energy is 9.0 keV. This is 3 and 2 % higher than those obtained in the simulations with the ZBL and Molière potentials, respectively, indicating also higher damage.

B. Damage simulations

The number of recoiling atoms having energies higher than 15 eV, which corresponds to the threshold energy for the displacement of one Si atom from its lattice site in c-Si [39,40], is shown in Fig. 3 at different times for the DMol, ZBL, and Molière potentials.

FIG. 3. Average numbers of recoiling Si atoms with energies greater than 15 eV ($\bar{N}_{Si}(E > 15 \text{ eV})$) and vacancy aggregates (\bar{N}_V) at different times produced in the slowing down process of one 1-keV Si atom in c-Si. The numbers are averages calculated from 50 simulation events.

The curves have been obtained as averages from 50 simulations events. The significant difference reflects the strength of the repulsive potentials at $r > 0.5 \text{ \AA}$.

The total number of different types of vacancy aggregates at different times is also shown in Fig. 3. The criteria for vacancy formation was that at each time there were no atoms within a radius of 1.2 \AA (half the nearest-neighbor distance in c-Si) around an original Si lattice site. Cases where one, two, three, four, and five adjacent lattice sites are empty were taken to correspond to mono-, di-, tri-, tetra-, and penta-vacancies, respectively. Note that in a collision cascade where several adjacent atoms are displaced from their lattice sites the energy needed to displace a lattice atom is considerably lower than 15 eV . Despite the differences in the repulsive potentials at $r > 0.5 \text{ \AA}$ and in the number of high energy recoils the repulsive potential does not have a significant effect on the number of vacancy aggregates.

For comparison, we also simulated collision cascades with another form for the attractive potential, the pair-potential used in earlier studies of radiation damage [41,42]. The wider attractive well of this potential (compared to the Stillinger-Weber potential) leads to larger (by a factor of four) numbers of vacancy aggregates. This indicates that in the formation of vacancy aggregates in a collision cascade, the form of the attractive potential and the directional bonding between the lattice atoms are important factors.

V. CONCLUSIONS

Based on the MD simulations of range data an experimentally confirmed repulsive interatomic potential (DMol) is proposed for Si-Si interactions in silicon at distances $0.2\text{--}1.5 \text{ \AA}$. MD simulations of low-energy collision cascades using the DMol, ZBL, and Molière potentials showed that the dependence of the initial vacancy production on the interatomic repulsive potential is not very pronounced.

ACKNOWLEDGEMENTS

This work was supported by the Academy of Finland. Dr. D. A. Drabold is acknowledged for providing the atomic coordinates of a-Si for the authors' use.

[1] S. T. Picraux, F. L. Vook, and H. J. Stein, in: Proceedings of the International conference on Defects and Radiation Effects in Semiconductors, Nice, France, 1978, ed. J. H. Albany, Institute of Physics, Bristol, England, 1979, p. 31.

[2] W. R. Brown, in: Beam-Solid Interactions and Phase Transformations, Proceedings of the Materials Research Society, vol. 51, ed. H. Kurz, G. L. Oesau, and J. M. Poate, MRS, Pittsburgh, 1985, p. 83.

[3] J. S. Williams, in Ref. [2], p. 83.

[4] W. J. Choyke, R. B. Irwin, J. N. McGruer, J. R. Townsend, Q. Xia, N. J. Doyle, B. O. Hall, J. A. Spitznagel, and K. Wood, in: Proceedings of the 13th International Conference on Defects in Semiconductors, Coronado, California, 1984, ed. L. C. Kimerling and J. M. Porse, Jr., American Institute of Metallurgical Engineers, Warrendale, 1984, p. 789.

[5] W. R. Fahrner, J. R. Laschinski, and D. Bräunig, Nucl. Instrum. Methods A **268** (1988) 579.

[6] J. Keinonen, M. Hautala, E. Rauhala, V. Karttunen, A. Kuronen, J. Räisänen, J. Lahtinen, A. Vehanen, E. Punkka, and P. Hautojärvi, Phys. Rev. B **37** (1988) 8269.

[7] J. Mäkinen, E. Punkka, A. Vehanen, P. Hautojärvi, J. Keinonen, M. Hautala, and E. Rauhala, J. Appl. Phys. **67** (1990) 990.

[8] J. Keinonen, M. Hautala, I. Koponen, and M. Erola, Phys. Rev. B **41** (1990) 9907.

[9] S.-J. Kim, M.-A. Nicolet, R. S. Averback, and D. Peak, Phys. Rev. B **37** (1988) 38.

[10] I. A. Fenn-Tye and A. D. Marwick, Nucl. Instrum. Methods Phys. Res. Sect. B **18** (1987) 236.

[11] H. J. Whitlow, J. Keinonen, and M. Hautala, J. Appl. Phys. **58** (1985) 3246.

[12] M. Erola, J. Keinonen, M. Hautala, and M. Uhrmacher, Nucl. Instrum. Methods Phys. Res. Sect. B **34** (1988) 42.

[13] W. Möller, Nucl. Instrum. Methods Phys. Res. Sect. B **15** (1986) 688.

[14] J. Y. Tsao, E. Chason, K. M. Horn, D. K. Brice, and S. T. Picraux, Nucl. Instr. Meth. in Phys. Res. **B39** (1989) 72.

[15] M.-A. Hasan, J. Knall, S. A. Barnett, J.-E. Sundgren, L. C. Market, A. Rackett, and J. E. Greene, J. Appl. Phys. **65** (1989) 172.

[16] B. R. Appleton, S. J. Pennycook, R. A. Zuhr, N. Herbots, and T. S. Noggle, Nucl. Instr. Meth. in Phys. Res. **B19/20** (1987) 975.

[17] J. F. Ziegler, J. P. Biersack, and U. Littmark, in: The Stopping and Range of Ions in Matter, vol. 1, Pergamon, New York, 1985.

[18] W. Eckstein, Computer Simulations of Ion-Solid Interactions, Springer-Verlag, Berlin, 1991, p. 40.

[19] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31** (1985) 5262.

[20] J. Tersoff, Phys. Rev. B **37** (1988) 6991.

[21] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61** (1989) 689.

[22] W. Eckstein, in Ref. [18], eq. (4.4.3) on p. 55.

[23] H. Feil, H. J. W. Zandvliet, M.-H. Tsai, J. D. Dow, and I. S. T. Tsang, Phys. Rev. Lett. **69** (1992) 3076.

[24] T. Diaz de la Rubia and M. W. Guinan, Phys. Rev. Lett. **66** (1991) 2766.

[25] J. R. Dennis and E. B. Hale, J. Appl. Phys. **49** (1977) 1119.

[26] A. Kehrel, J. Keinonen, P. Haussalo, K. P. Lieb, and M. Uhrmacher, Radiat. Eff. and Defs. **118** (1991) 297.

- [27] P. M. Endt and C. van der Leun, Nucl. Phys. **A310** (1978) 1.
- [28] H. H. Andersen and J. F. Ziegler, in: The Stopping and Range of Ions in Matter, vol. 3, Pergamon, New York, 1977.
- [29] J. Keinonen, A. Kuronen, P. Tikkanen, H. G. Börner, J. Jolie, S. Ulbig, E. G. Kessler, R. M. Nieminen, M. J. Puska, and A. P. Seitsonen, Phys. Rev. Lett. **67** (1991) 3692.
- [30] A. Kuronen, J. Keinonen, H. G. Börner, J. Jolie, and S. Ulbig, Nucl. Phys. **A549** (1992) 59.
- [31] D. A. Drabold, private communication.
- [32] D. A. Drabold, P. A. Fedders, O. F. Sankey, and J. D. Dow, Phys. Rev. B **42** (1990) 5135.
- [33] P. A. Fedders, D. A. Drabold, and S. Klemm, Phys. Rev. B **45** (1992) 4048.
- [34] B. Delley, J. Chem. Phys. **92** (1990) 508.
- [35] DMol is a trademark of Bio Sym. Inc., San Diego, California, USA.
- [36] J. Keinonen, K. Arstila, and P. Tikkanen, Appl. Phys. Lett. **60** (1992) 228.
- [37] P. V. Vavilov, Zh. Eksp. Teor. Fiz. **32** (1957) 920, [Sov. Phys.-JETP **5**, 749 (1957)].
- [38] N. Bohr, Mat. Fys. Medd. Dan. Vid. Selsk. **18** (1948), No. 8.
- [39] P. Lucasson, in: Fundamental Aspects of Radiation Damage in Metals, ed. M. T. Robinson and F. N. Young Jr., ORNL, Springfield, 1975, p. 42.
- [40] H. H. Andersen, Appl. Phys. **18** (1979) 131.
- [41] Y. N. Knyzhnikov, Radiat. Eff. **25** (1975) 41.
- [42] A. M. Mazzone, Phil. Mag. Lett. **60** (1989) 131.