LA-UR 97-5136

Approved for public release;
distribution is unlimited.

Title: FIRST-PRINCIPLES STUDY OF POINT-DEFECT
PRODUCTION

CONF-971201-

RECEIVED

APR 06 1998

OSTI

Author(s): Wolfgang Windl
Thomas J. Lenosky
Joel D. Kress
Arthur F. Voter

Submitted to: Materials Research Society - Fall '97

DTIC QUALITY INSPECTED 4

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ph*

MASTER

19980504 038

Los Alamos
NATIONAL LABORATORY

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by the University of California for the U.S. Department of Energy under contract W-7405-ENG-36. By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. The Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

FIRST-PRINCIPLES STUDY OF
POINT-DEFECT PRODUCTION IN Si AND SiC

W. WINDL*, T. J. LENOSKY**, J. D. KRESS, A. F. VOTER

Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545

ABSTRACT

We have calculated the displacement-threshold energy E_d for point-defect production in Si and SiC using empirical potentials, tight-binding, and first-principles methods. We show that—depending on the knock-on direction—64-atom simulation cells can be sufficient to allow a nearly finite-size-effect-free calculation, thus making the use of first-principles methods possible. We use molecular dynamics (MD) techniques and propose the use of a sudden approximation which agrees reasonably well with the MD results for selected directions and which allows estimates of E_d without employing an MD simulation and the use of computationally demanding first-principles methods. Comparing our results with experiment, we find the full self-consistent first-principles method in conjunction with the sudden approximation to be a reliable and easy method to predict E_d . Furthermore, we have examined the temperature dependence of E_d for C in SiC and found it to be negligible.

INTRODUCTION

Elastic collisions are one of the most important interactions during the creation of radiation damage. There, the irradiating particle transfers a recoil energy to a lattice atom, the so-called primary knock-on atom (PKA). If this recoil energy exceeds a material dependent displacement-threshold energy E_d , the PKA leaves its original site, thereby creating a Frenkel pair (FP). E_d is a central quantity as an input for simulation codes or analytical formulas.¹ To date, E_d has been calculated mostly by classical molecular-dynamics (MD) simulations using empirical potentials such as—in the case of semiconductors—the Stillinger-Weber,² the Tersoff,³⁻⁵ or the Pearson potential.⁶ In these simulations, one assigns a certain initial momentum to the PKA and examines after a sufficiently long time if the PKA returned to its initial position or not. Although some of the previous studies have looked at the temperature dependence of E_d in a qualitative manner, we are not aware of any work that examined the temperature dependence of E_d in a systematic manner.

In the present work, we want to study the model as well as the temperature dependence of E_d in semiconductors to ascertain the essential ingredients for an accurate determination of displacement-thresholds. We first compare the existing classical results with those of first-principles calculations. Second, we examine the temperature-dependence of E_d using the Tersoff model and compare its influence on E_d with the model dependence. We choose to perform our calculations on two semiconductors, Si and β -SiC (zincblende), for two reasons. First, these materials can be well treated by first-principles methods, and a large amount of expertise is available from existing work. Second, there is significant interest in understanding their radiation behavior. Low-energy ions are used extensively in the manufacturing of Si semiconductor devices (e.g., dopant implantation).⁷ SiC, on the other hand, is one of the materials of choice for radiation-hard environments such as first walls of proposed fusion reactors or coating for radioactive waste.⁸

METHOD

For our first-principles MD simulations, we used the simplified self-consistent local-orbital local-density approximation "FIREBALL96" method by Sankey *et al.* which uses a minimal sp^3 basis set of truncated pseudo-atomic orbitals ("fireballs") and employs other approximations to evaluate the matrix elements.⁹ It has been shown previously that this method is well suited for radiation-damage problems in Si since it accurately describes point defects; to a lesser degree, this is true for SiC where considerable charge transfer sets limits to its accuracy.¹⁰ The approximations employed (including Γ -point sampling) allow very fast and efficient total-energy and force calculations and therefore enable one to perform quantum MD simulations

for moderately large systems from first principles. For comparison, we also determine E_d in Si with a high-quality tight-binding (TB) model¹¹ and with a full plane-wave (PW) LDA¹² pseudopotential¹³ method with a cutoff energy of 15 (35) eV for Si (SiC) and 4 k-points for integration in the 64-atom cell. Since it is not clear when an atom in a semiconductor is permanently displaced and definitely will not return to its initial position,³ we decided to consider an atom permanently displaced in an MD simulation once it has left its nearest-neighbor tetrahedron and does not return within the next 1.5 ps. This allows also a fair comparison to other existing empirical calculations. We used a time step of 1 fs for Si and 0.4 fs for SiC, which we have found to be sufficiently small. For benchmarking the different methods, we use an initial temperature of zero.

RESULTS

Cell size

Since the FIREBALL96 method is still much more computationally demanding than classical MD simulations, we first had to determine what cell size would be sufficient to minimize finite-size effects. We found, in a preliminary study using a Tersoff potential,¹⁴ that E_d in the [111] direction in Si is independent of the cell size for all cells that we tried in the range between 64 and 1000 atoms. The reason for this is that a PKA with energy E_d passes the point-of-no-return towards permanent displacement after 70 fs, whereas the fastest sound wave emitted by the energized PKA crosses a 64-atom cell in 120 fs and therefore cannot interact with the displacement process itself through the periodic-boundary conditions. In both Si and SiC, we found the sound wave to be slower than the displacement event for PKA's in all principal directions. Therefore, we used 64-atom cells for all simulations except for the [100] direction where we used a 128-atom cell in order to avoid self-interactions of the PKA.¹⁰ The 64-atom cell was large enough that for the examined knock-on energies no melting occurred. Since the cell-size is less crucial for the computationally faster TB and classical methods, we used a 216-atom cell throughout for all TB and Tersoff simulations.

Displacement-threshold energies at zero temperature

Our MD values for E_d in the high-symmetry directions in Si are summarized in Table I, together with our TB and Tersoff results (the latter ones nearly identical to the values of Ref. 3), and Stillinger-Weber (SW) values of Ref. 2. The final [111] FP's of the displacement process for the different methods are basically identical [Fig. 1(a), position D]. The displacement takes place by the PKA going through the H interstitial in the nearest hexagonal ring in the knock-on direction to a final T interstitial site [Fig. 1(a)]. Whereas the Tersoff (SW) result is 16% (80%) higher than the FIREBALL96 value, TB finds an E_d which is 23% lower.

We find from our different MD simulations that the effect of a [111] PKA on the other atoms is rather small. The major effect is felt while overcoming the barrier where the circumference (sum of the bond lengths) of the six-fold ring [in Fig. 1(a) between B and C]

TABLE I. Displacement energies for the main-symmetry impact directions in Si (eV). PW stands for plane-wave LDA, TB for tight-binding, T for Tersoff, SW for Stillinger-Weber,² and SA for sudden approximation. FIREBALL96 (FB) MD results have errorbars of ± 0.25 , SW of 2.5 eV, and the others of ± 0.1 eV.

direction	FB-MD	FB-SA	PW-SA	TB-MD	TB-SA	T-MD	T-SA	SW-MD
[111]	9.75	8.7	8.2	7.5	7.4	11.3	12.3	17.5
[100] (near)	9.75	7.4	6.5	unstable	6.7	10.0	11.6	
[100] (far)	17.25			14.6		17.4		22.5
[110]	15.25			11.1		24.0		42.5

Fig. 1. (a) Minimum-energy [111] displacement event. The PKA is displaced from its original site (A) through a hexagonal ring (created by the atoms represented by the dark small spheres between B and C) to its final position (D). (b) Same event, described by the sudden approximation. Shown is the total energy for different positions of the PKA which is moved from A to D while all other atoms are kept fixed. Solid line: FIREBALL96. Long-dashed line: tight-binding. Short-dashed line: Tersoff. Diamond: plane-wave LDA.

is widened by approximately 10% in order to allow the PKA to pass. Therefore, we tried an alternative determination of E_d along [111], which is equivalent to the sudden approximation (SA).¹⁵ There, we move the PKA along the [111] direction while all other atoms are kept fixed and calculate the total energy for each position [Fig. 1(b)]. The difference between the highest energy maximum (somewhere between B and C) before achieving the nominal FP position (D) and the energy of the undisturbed crystal represents E_d in this approximation. Note that this method allows one to estimate E_d *without* any MD simulation, using only a few static total-energy calculations. If we apply the SA to the [111] direction of Si, we find good agreement between the corresponding MD and SA results (Table I). The full PW value is also given in Table I in order to benchmark the other more approximate methods. It is in the same regime as the electronic structure SA values (6% lower than FIREBALL96 and 11% higher than TB), but 50% lower than Tersoff. Note that the dynamical interactions which are neglected in the SA can increase or decrease E_d as discussed elsewhere.¹⁶

For the [100] direction, we find excellent agreement for the E_d results of the FIREBALL96 and the Tersoff MD simulations (Table I). They both find the same FP with a FP separation of $d_{FP} < a/2$ ("near"), where a is the lattice constant. With TB and SW,² the FP is not stable until it reaches a FP separation of $d_{FP} \sim a$ ("far"), a defect which can also be produced with the other two methods using a higher knock-on energy. The SA results for [100] PKA's (Table I) agree less well with the MD results than do those in the [111] direction, +16% (−24%) for Tersoff (FIREBALL96). For our TB model, we find with the SA a saddle with a height of 6.7 eV and a minimum around $d_{FP} < a/2$, even if the corresponding FP was not stable with TB-MD. Therefore, we have to conclude that the SA works somewhat worse than in the [111] case, especially since it does not answer the question about stability of the FP which is not trivial in the [100] direction.¹⁶ The benchmark PW-SA calculation is again in the regime of the electronic structure SA results [12% (3%) smaller than FIREBALL96 (TB)], but considerably smaller (44%) than the Tersoff SA value.

For the [110] direction, the MD results of the different methods vary greatly. The reason for these strong differences is that the [110] PKA does not follow a straight path as in the previous cases, but gets strongly deflected shortly after the start of the simulation by one of its nearest neighbors. Small differences between the different methods that barely influenced the [111] and [100] simulations are magnified by this deflection for [110]. This suggests that for non-high-symmetry directions approximate methods work less well than for high-symmetry directions since the differences to an "exact" method get magnified. Since for the [110] direction there is no simple, straight path for the PKA from its original site to the final defect site, we did not employ the SA in that case.

E_d for C atoms along the high-symmetry directions in SiC is given together with classical Pearson⁶ and Tersoff results^{5,17} in Table II. FIREBALL96 produces for C PKA's nearly identical E_d 's as the Tersoff parametrization of Ref. 5 (T2), which are considerably higher than our Tersoff values (T1), which in turn are several eV larger than the results calculated by the Pearson potential. Si PKA's in SiC have been examined elsewhere.¹⁰ Also for SiC, the SA

works rather well, with differences between the corresponding MD and SA results of 10% or less. The PW-SA result for a [111] C PKA is 43% (30%) smaller than the FIREBALL96 (T1) SA values, but is very similar to the Pearson value. That the PW-SA is significantly smaller than the Tersoff-SA is consistent with what we found for Si. The very strong discrepancy between PW-SA and FIREBALL96-SA, however, was not observed in the case of Si. We think this strong discrepancy is due to the approximate self-consistency mechanism in FIREBALL96 where the charge for all three p orbitals is assumed to be the same. Even if this procedure works well for SiC bulk properties,¹⁸ it seems to be inadequate for the description of, e.g., a vacancy with an extremely non-symmetrical charge distribution in a strongly ionic crystal like SiC.¹⁰ Therefore, we expect the "true" theoretical value for the [111]- E_d to be in the regime of the PW-SA result (~ 15 eV), considerably smaller than the FIREBALL96 value.

For Si, the experimental E_d values are divided into two groups (around 13 eV¹⁹ and around 20 eV²⁰). Three interpretations are possible: (a) the different values are a consequence of anisotropy (low value along [111], high value along [100] where the near defect has only a very short lifetime¹⁶ and should not be observed in experiment) which seems not likely since some high values were measured along [111], (b) the low- E_d displacement cannot be seen in certain experiments (because of forced recombination, etc.), or (c) the interpretation of (some of) the experiments is problematic. Since the [111] displacement with its low value for E_d seems to have a sufficient lifetime to be observed in experiment,¹⁶ further investigations are required to answer this question.

For C PKA's in SiC, the situation is different. Most of the experimental values fall in a range between 17 and 22 eV.²¹ Here, the SA shows its full power since the very reliable full PW SA calculation showed that the FIREBALL96 values should be much too high and that the "true" theoretical value—provided that the [111] displacement is the responsible process—should be more around 15 eV. Hints that the FP described in Fig. 1(a) is indeed present in radiation damaged SiC have been known from ESR measurements.²²

TABLE II. Displacement energies for the main-symmetry impact directions in SiC for a C-PKA (eV). P are Pearson MD results from Ref. 6, T1 our Tersoff values, and T2 Tersoff results from Ref. 5 using different parameters. All MD errorbars are ± 0.5 eV (except T1 [111] ± 0.1 and T2 ± 1 eV). The rest of the notation is the same as in Table I.

direction	FB-MD	FB-SA	PW-SA	P-MD	T1-MD	T1-SA	T2-MD
C [111]	27.5	25.6	14.6	14	21.9	20.9	28
C [100] (near)	unstable	14.3		12	13.5	12.2	
C [100] (far)	28.5				23.5		31
C [110]	38.5			14	30.5		38

Temperature dependence of the [111] displacement-threshold energy for C in SiC

In order to study the temperature dependence of E_d , we chose the [111] displacement of the C atom in SiC. With the Tersoff potential, we first heat a 64-atom simulation cell to a certain temperature (we chose 300, 650, 1000, and 1350 K). Then we give one C atom a certain kinetic energy along the [111] direction (away from its nearest neighbor) and determine after 1.5 ps if the atom is displaced or not. This is repeated $N = 100$ times, and the fraction f of successful events for this energy is noted. We repeat this whole procedure for 25 kinetic energies centered about (± 5 eV) the zero temperature value for E_d of 21.9 eV. The statistical error in the success fraction for our measured points is 5% (at the center of the distribution) or less for 100 runs for every energy value. The distribution of the success rate *vs.* energy can be well fit by an error function of the form $f(E) = 0.5 + 0.5 \operatorname{erf}[(E - E_d^0)/(\sqrt{2}\sigma)]$, where E_d^0 is the center and σ the standard deviation of the underlying Gaussian.

From some simple statistical considerations,¹⁶ we expect the temperature dependence of $E_d(T)$ to be of the form $E_d(T) = E_d^0 - \alpha T$. Furthermore, we expect the second moment, $\sigma^2 = \langle (E - \langle E \rangle)^2 \rangle$, to be directly proportional to T . In Fig. 3, we show our fitted values of E_d and σ^2 as a function of temperature. Indeed, a linear dependence of the data from temperature fits our data reasonably well with $E_d(T) = 21.9 \text{ eV} - 5.7 k_B T$ and $\sigma^2(T) = 1.8 E_d^0 k_B T$. The overall temperature dependence (which is similar for other directions¹⁶) is rather small as compared to the model dependence that we found in the previous section. Therefore, we conclude that temperature effects can be neglected, and the major efforts should rather be aimed towards an accurate description of the system.

Fig. 2. Temperature dependence of E_d . Shown are the two central quantities that describe the sigmoidal threshold function as a function of temperature, (a) the center of the sigmoid, $E_d(T)$, and (b) its standard deviation, σ . We show here σ^2 rather than σ in order to examine an expected linear dependence of σ^2 from temperature.

CONCLUSIONS

In conclusion, we showed that the determination of displacement-threshold energies is accessible to first-principles methods, especially since small cells and the sudden approximation can be used to simplify the calculations considerably. Furthermore, we found a very strong model-dependence of E_d in Si and SiC which suggests that one should use the most accurate method possible for any radiation-damage problem. Fast, approximate schemes may give rise to very large errors in E_d even if other properties are very well described by the method. In the case of Si all examined methods—except Stillinger-Weber with 17.5 eV²—give similar values for E_d around 10 eV, whereas experiment is split in two groups (one with $E_d \sim 13$ eV, the other with $E_d \sim 20$ eV). For SiC, the different calculation methods show more variation (15–28 eV) compared to experiment (17–22 eV). Our best calculation (full *ab initio* in conjunction with the sudden approximation, $E_d \sim 15$ eV) favors here, like in Si, the lower end of the experimental E_d values. Temperature effects, on the other hand, seem to be negligible as compared to the strong model dependence.

ACKNOWLEDGMENTS

We would like to thank Kurt Sickafus, Mike Nastasi, Don Parkin, and Yok Chen for very useful discussions. This work was sponsored by the Division of the Materials Science, Office of the Basic Energy Sciences, U.S. Department of Energy.

REFERENCES

- * Current address: Motorola Computational Materials Group, Los Alamos National Laboratory, M.S. B268, Los Alamos, NM 87545, windl@lanl.sps.mot.com
- ** Current address: Department of Physics, Arizona State University, Tempe, AZ 85287-1504
- ¹ For recent reviews on theoretical treatment of radiation damage, see, e.g., F.W. Clinard, Jr., *Mater. Res. Soc. Bull.* **22** (4), 11 (1997); T. Díaz de la Rubia, *Annu. Rev. Mater. Sci.* **26**, 613 (1996); I.M. Albertson, R.S. Averback, D.K. Tappin, and L.E. Rehn, *Fundamentals of Radiation Damage* (North-Holland, Amsterdam, 1994); W.J. Weber, L.K. Mansur, F.W. Clinard, Jr., and D.M. Parkin, *J. Nucl. Mater.* **184**, 1 (1991).

- ² M.J. Caturla, T. Díaz de la Rubia, and G.H. Gilmer in Materials synthesis and processing using ion beams, edited by R.J. Culbertson *et al.* (Mater. Res. Soc. Proc. **316**, Pittsburgh, PA, 1994), p. 111.
- ³ L.A. Miller, D.K. Brice, A.K. Prinja, and S.T. Picraux, Phys. Rev. B **49**, 16 953 (1994); Radiation Effects and Defects in Solids **129**, 127 (1994).
- ⁴ J. Wong, T. Díaz de la Rubia, M.W. Guinan, M. Tobin, J.M. Perlado, A.S. Perez, and J. Sanz, J. Nucl. Mater. **212**, 143 (1994).
- ⁵ R. Devanathan, T. Díaz de la Rubia, and W.J. Weber, Nucl. Inst. and Meth. in Phys. Res. B (in print).
- ⁶ A. El-Azab and N.M. Ghoniem, J. Nucl. Mater. **191-194**, 1110 (1992).
- ⁷ J.F. Ziegler, Handbook of Ion Implantation Technology (North-Holland, Amsterdam, 1992).
- ⁸ G.R. Hopkins and J. Chin, J. Nucl. Mater. **141-143**, 148 (1986).
- ⁹ A.A. Demkov, J. Ortega, O.F. Sankey, and M.P. Grumbach, Phys. Rev. B **52**, 1618 (1995); O.F. Sankey, A.A. Demkov, W. Windl, J.H. Fritsch, J.P. Lewis, and M. Fuentes-Cabrera, Int. J. Quantum Chem. (in print).
- ¹⁰ W. Windl, T. J. Lenosky, J. D. Kress, and A. F. Voter, Nucl. Inst. and Meth. in Phys. Res. B (in print).
- ¹¹ T.J. Lenosky, J.D. Kress, I. Kwon, A.F. Voter, B. Edwards, D.F. Richards, S. Yang, and J.B. Adams, Phys. Rev. B **55**, 1528 (1997).
- ¹² J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
- ¹³ N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- ¹⁴ J. Tersoff, Phys. Rev. B **38**, 9902 (1988); **39**, 5566 (1989).
- ¹⁵ R.D. Levine and R.B. Bernstein, Molecular Reaction Dynamics (Oxford University Press, New York, 1974).
- ¹⁶ W. Windl, T.J. Lenosky, J.D. Kress, and A.F. Voter (to be published).
- ¹⁷ Our Tersoff results for SiC are different from the ones previously calculated in Ref. 4, where the same potential was employed, for reasons we do not yet understand.
- ¹⁸ W. Windl, O. F. Sankey, and J. Menéndez, Phys. Rev. B (in print).
- ¹⁹ J.J. Loferski and P. Rappaport, Phys. Rev. **111**, 432 (1958); P. Sigmund, Appl. Phys. Lett. **14**, 114 (1969).
- ²⁰ P.L.F. Hemment and P.R.C Stevens in Atomic Collision Phenomena in Solids, edited by D.W. Palmer, M.W. Thompson, and P.D. Townsend (North-Holland, Amsterdam 1970), pp. 217-231; P.C. Banbury and I.N. Haddad, Phil. Mag. **14**, 841 (1966); B.T. Kelly, Irradiation Damage to Solids (Pergamon, New York, 1966), p. 4.
- ²¹ R.R. Hart, H.L. Dunlap, and O.J. Marsh, radiation effects **9**, 261 (1971); S.J. Zinkle and C. Kinoshita, J. Nucl. Mater. (in print) and references therein.
- ²² J.H.N. Loubser, J.A. de sousa Balona, and W.P. van Ryneveld, Mat. Res. Bull. **4**, 249 (1969).

M98004372

Report Number (14) LA-4R--97-5136

CONF-971201--

Publ. Date (11) 199803

Sponsor Code (18) DOE/ER, XF

UC Category (19) UC-411, DOE/ER

DOE