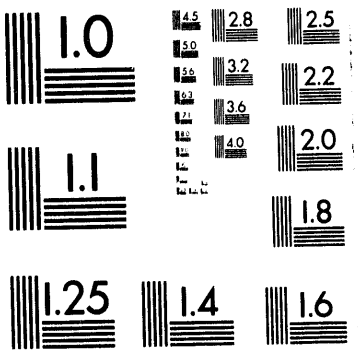
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M.-J. Caturla
T. Diaz de la Rubia
G. H. Gilmer

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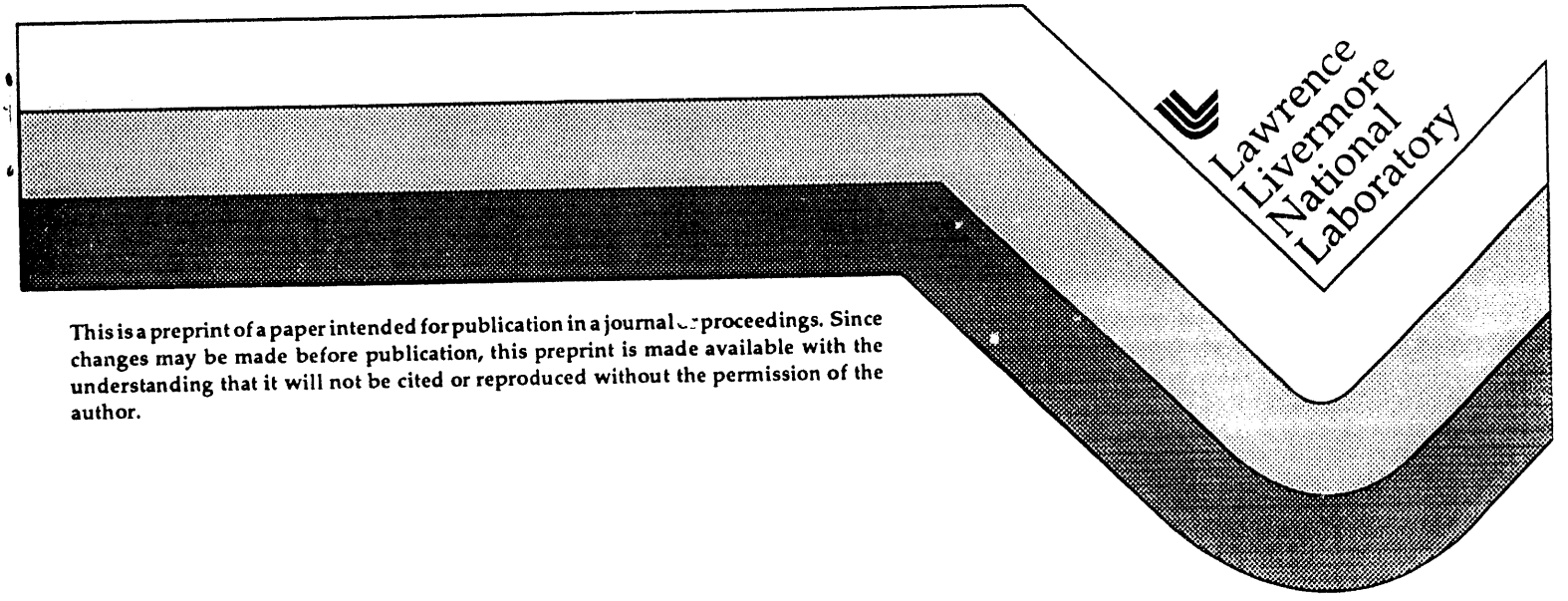

DISCLAIMER

POINT DEFECT PRODUCTION, GEOMETRY AND STABILITY IN SILICON: A MOLECULAR DYNAMICS SIMULATION STUDY

M.-J. CATURLA*#, T. DIAZ DE LA RUBIA*, AND G.H. GILMER**
* Chemistry and Materials Science Department, L-268, Lawrence Livermore National Laboratory, Livermore, CA 94450
# Permanent address: Dep. Fisica Aplicada, Ap. 99, Universitat d'Alacant, E-03080, Alacant, Spain.
** AT&T Bell Laboratories, Room 1E332, 600 Mountain Ave, Murray Hill, NJ 07974

ABSTRACT

We present results of molecular dynamics computer simulation studies of the threshold energy for point defect production in silicon. We employ computational cells with 8000 atoms at ambient temperature of 10 K that interact via the Stillinger-Weber potential. Our simulations address the orientation dependence of the defect production threshold as well as the structure and stability of the resulting vacancy-interstitial pairs. Near the <111> directions, a vacancy–tetrahedral-interstitial pair is produced for 25 eV recoils. However, at 30 eV recoil energy, the resulting interstitial is found to be the <110> split dumbbell configuration. This Frenkel pair configuration is lower in energy than the former by 1.2 eV. Moreover, upon warming of the sample from 10 K the tetrahedral interstitial converts to a <110> split before finally recombining with the vacancy. Along <100> directions, a vacancy-<110> split interstitial configuration is found at the threshold energy of 22 eV. Near <110> directions, a wide variety of closed replacement chains are found to occur for recoil energies up to 45 eV. At 45 eV, the low energy vacancy-<110> split configuration is found. At 300 K, the results are similar. We provide details on the atomic structure and relaxations near these defects as well as on their mobilities.

INTRODUCTION

To develop a better understanding of ion implantation and transient enhanced diffusion in silicon, knowledge of the average value of the threshold energy for defect production under irradiation, E_d, is required. E_d is used in analytical and Monte Carlo calculations of damage, where the number of displacements per atom for a given set of irradiation conditions is given by $\upsilon=0.8E_D/2E_d$ [1]. Here E_D is the damage energy deposited in elastic collisions by the irradiating beam. In addition to E_d, the geometry, stability against recombination, and the mobility of irradiation induced defects are important quantities necessary to obtain a complete understanding of irradiation phenomena.

Despite the many efforts dedicated over the years to the study of the value and orientation dependence of E_d in silicon, controversy over these quantities still remains [2]. Although values of the minimum value of the threshold energy $E_{d,m}$≈13-15 eV [3] are often used in the literature, many experiments indicate $E_{d,m} \approx$ 20-25 eV depending on orientation, with the defect introduction rate being highest along <111> and lowest along <110> [4-6]. A recent study for bulk Si with Tersoff's interatomic potential gave values of E_d=11 eV for recoils near [100] and E_d=13 eV for recoils near [111], [7].

In contrast to studies in metals, electron irradiation investigations of silicon have been unable to establish the value of the migration energy and the geometrical properties of the self-interstitial. Low temperature electron irradiation experiments have long suggested that the self interstitial is mobile in silicon below 4 K [8]. Although these results do not provide a quantitative value of the interstitial diffusivity, they point towards the validity of the Bourgoin-Corbett mechanism of athermal interstitial migration via successive changes in charge state [9]. Ab-initio MD studies by Car et al. [10] have shown that the equilibrium self-interstitial configuration is the <110> dumbbell, an extended defect which, interestingly, has no states in the gap.

For vacancies, migration enthalpies have been measured by tracking the annealing kinetics after low temperature electron irradiation. These results lead unambiguously to values of $H_m \approx 0.3$ eV for the neutral vacancy [11]. Car et al [10] have recently shown that the vacancy migration enthalpy is 0.3 eV in excellent agreement with experimental results.

MD is a valuable tool to study the threshold energy for defect production and its orientation dependence. Also, the properties of the resulting defect structures such as their migration and formation enthalpies and entropies are easily accessible to this type of simulations. Gibson et al. performed the first detailed study of the threshold energy for defect production; albeit in copper [12]. In silicon, the form of the interatomic potential is complicated by the covalent bonding and not as many classical MD studies of radiation effects have been performed to date as in metals [13]. Recent results [14] with the Stillinger-Weber potential [15] for defect formation energies are in good agreement with the *ab-initio* MD studies [10].

In this communication we present results of MD studies of the threshold energy for defect production in silicon for a variety of recoil directions. Because of the importance of melting and amorphization processes in particle-solid interaction phenomena, we employ the Stillinger-Weber (SW) potential [15]. Our results indicate a value of $E_{d,m} \approx 18$ eV, with the damage rate highest along <111> and lowest along <110> directions, in good quantitative agreement with experimental results [4]. In addition, the form of the produced interstitial is the <110> dumbbell, in excellent agreement with *ab-initio* MD studies [10].

MODEL

Our MD simulation employs cubic crystal cells with 8000 atoms which at the start of the simulation occupy perfect diamond cubic lattice sites. The cell had periodic boundary conditions in the X and Y directions. The bottom (001) plane was held fixed and a free unreconstructed (001) crystal-vacuum interface was present. The atoms were allowed to interact via the Stillinger-Weber potential for silicon [15]. The simulations were performed with our MOLDYCASK code and require 7×10^{-5} s/atom–time-step on a Cray YMP C90. The substrate ambient temperature was set at either 10 K or 300 K. Recoil atoms were imparted the appropriate kinetic energy in the direction of interest after equilibration of the crystal at the desired temperature. The equations of motion were then integrated with a fourth order predictor-corrector algorithm and the temperature was kept constant by applying an isokinetic constraint to atoms in the bottom 2 (001) atomic planes of the cell. The time step in the simulations was allowed to vary as the value of the maximum kinetic energy in the cell decreased. The minimum and maximum time steps were 0.05 femtoseconds (fs) and 1 fs, respectively. The simulations were run for times up to 3 picoseconds (ps) at which point no additional thermal diffusion jumps were expected.

In addition to this dynamical runs, quenching of the kinetic energy of the crystal to search for lowest energy defect configurations was also carried out. This was achieved by periodically setting to zero the velocities of those atoms with opposite signs of the velocity and the acceleration. In this manner, only those atoms that are moving toward their equilibrium positions are allowed to move in a given time step while the rest are held fixed. Following this method, quenching rates $\approx 10^{-14}$ K/s were achieved.

RESULTS

We present results for defect production in silicon along the [110], [100], [111], $[\bar{1}\,\bar{1}\,\bar{1}]$, and [221] directions as well a for a variety of additional recoil trajectories. Most of the simulations were done at 10 K with a few of the cases at 300 K for comparison. These results are summarized in Figure 1.

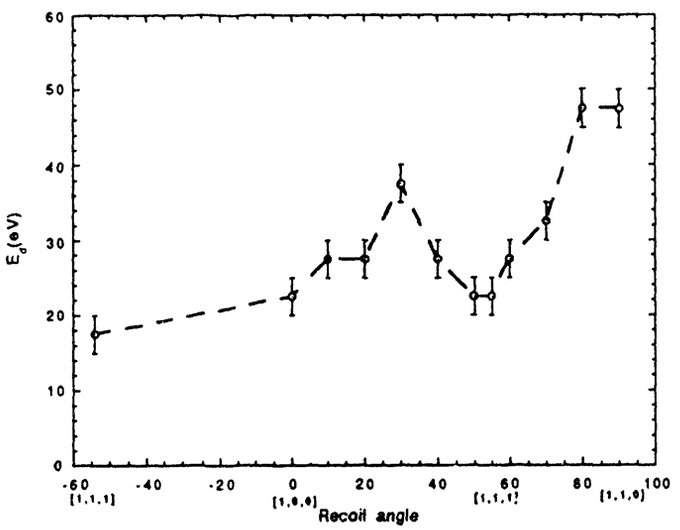

Fig.1 Defect production in Si, E_d(eV), for different recoil directions.

Along the [111] direction, the threshold energy (E_d) was found to be 22.5 eV, while along $[\bar{1}\,\bar{1}\,\bar{1}]$ E_d=17.5 eV. This asymmetry is possibly due to the different geometry along these two directions. While along [111] the recoil atom must displace its first neighbor into the tetrahedral position (or beyond if imparted with sufficient energy), along $[\bar{1}\,\bar{1}\,\bar{1}]$ the recoil moves a distance $d=(3^{1/2}/4)a_0$, where a_0 is the equilibrium lattice parameter, without having to transfer a large amount of kinetic energy. The secondary recoil can then induce a displacement of its neighbor along $[\bar{1}\,\bar{1}\,\bar{1}]$ and this results in a permanent displacement in the lattice at lower threshold energy than in the [111] case. At a primary knock-on atom (PKA) energy of 25 eV along [111], the resulting interstitial was found in a tetrahedral position with the vacancy in the corner of its unit cell. At 30 eV PKA energy however, the resulting interstitial had the low energy <110> dumbbell configuration with the vacancy left at the site of the PKA. The dumbbell is composed of two atoms that share the same lattice site. The length of the dumbbell was found to be $0.57a_0$. The atoms around the vacancy site relaxed towards the vacancy. Upon quenching of the kinetic energy of the system, the potential energy of the crystallite was found to exceed that of the perfect crystal by 6.37 eV. This is in contrast to the 25 eV case where the vacancy-tetrahedral interstitial pair was found to raise the crystal potential energy by 7.68 eV. This results are in excellent agreement with ab-initio MD studies of Car et al [10] which show the <110> dumbbell to be the stable interstitial configuration in silicon. As mentioned above, this interstitial has no states in the gap, a fact that may help explain why the interstitial has never been directly identified in silicon. Table I gives the initial and final coordinates (in lattice parameter units) of the atoms in and around the dumbbell.

Table I. Initial and final positions of atoms in and around the dumbbell.

Atom #	Initial positions			final positions		
1864	-1.50	-2.00	-0.50	-1.29	-2.00	-0.29
1664	-2.00	-2.00	-1.00	-1.70	-2.00	-0.70
4864	-1.75	-1.75	-0.75	-1.65	-1.65	-0.65
6864	-1.25	-1.75	-0.25	-1.35	-1.65	-0.35
6854	-1.75	-2.25	-0.25	-1.74	-2.23	-0.26
4854	-1.25	-2.25	-0.75	-1.24	-2.23	-0.74

Annealing of these configurations at elevated temperatures reveals that the tetrahedral interstitial is not stable and readily recombines with its own vacancy. After 15 ps at 500 K, the interstitial reconfigured into the lower energy <110> dumbbell configuration. Then, because of its close proximity to the vacancy, the pair recombined after 7 ps at 750 K.

Along the <100> directions, the threshold energy was found to be between 20 and 25eV. Figure 2a shows the components of the displacement vector for the 20 eV primary knock-on atom (PKA) as a function of time. The atom moves along [100] but falls back to its original position after 0.5 ps. At E_{pka}=25 eV however, figure 2b shows that the X coordinate of the PKA increases as the atoms moves along [100]. In contrast to the 20 eV case, the PKA remains stable at a distance $\approx 0.95a_0$ from its original position. The atom in the replacement position then formed a self interstitial with one of its nearest neighbors. The vacancy-interstitial pair so produced appeared stable against recombination at 10 K after 4 ps. The interstitial was a <011> split interstitial with the length of the dumbbell $\approx 0.6a_0$ in good agreement with the results of the [111] recoil events. No evidence for multiple vacancies was found.

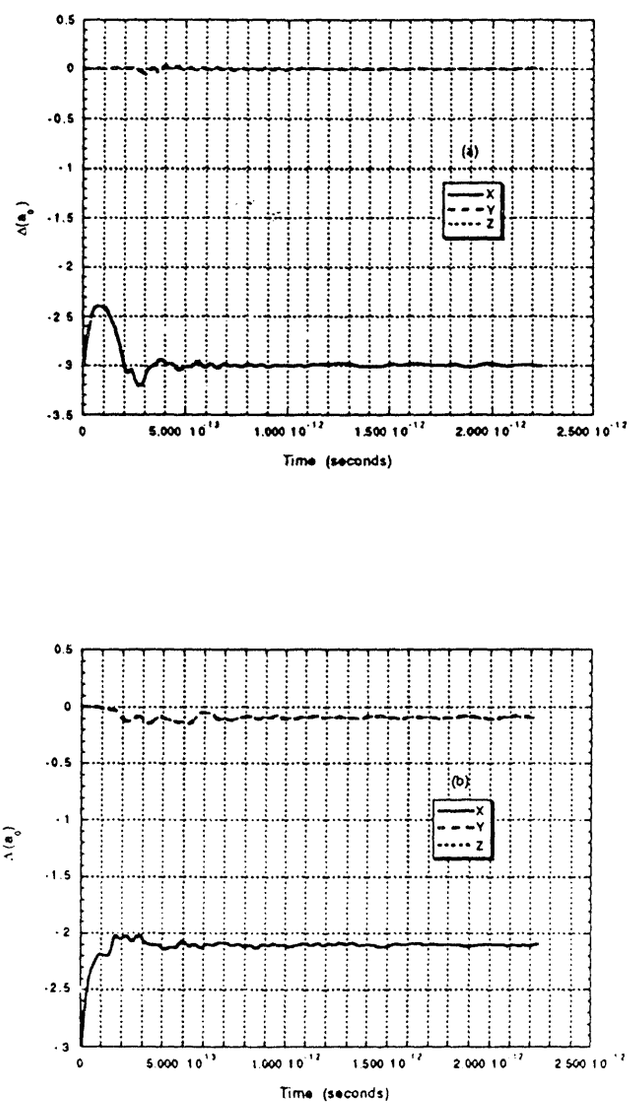

Fig.2 Components of the displacement vector as a function of time, (a) PKA energy 20 eV, no defect production, (b) PKA energy 25 eV, stable vacancy-interstitial formation.

Near [110], the results are more complex. We find E_d between 40 eV and 45 eV, a much higher value than near either [100] or [111]. In addition to this, for recoil events at $E_{pka} \leq 40$ eV, closed replacement chains with no defect production were observed. For example, for a recoil 2° off the exact [110] direction and $E_{pka}=35$ eV , a closed chain of three replacements going back to the original PKA site was observed. This is illustrated in Figure 3 where the atoms that participated in the closed replacement chain are indicated by arrows. Such closed chains have been previously observed in MD studies of defect production in copper [16] and are very efficient at inducing atomic mixing. At $E_{pka}=45$ eV, a vacancy is left at the PKA site and a <110> split dumbbell interstitial is produced centered at the site 2 atomic jump distances away along [110]. It is interesting to note, that these results are very sensitive to the exact direction of the PKA. A simple 2° change in the azimuthal angle of the PKA towards the [110] direction at $E_{pka}=35$ eV results in the absence of closed replacement chains with the PKA returning to its original site. The same results were found at for simulations in lattices at 300 K ambient temperature.

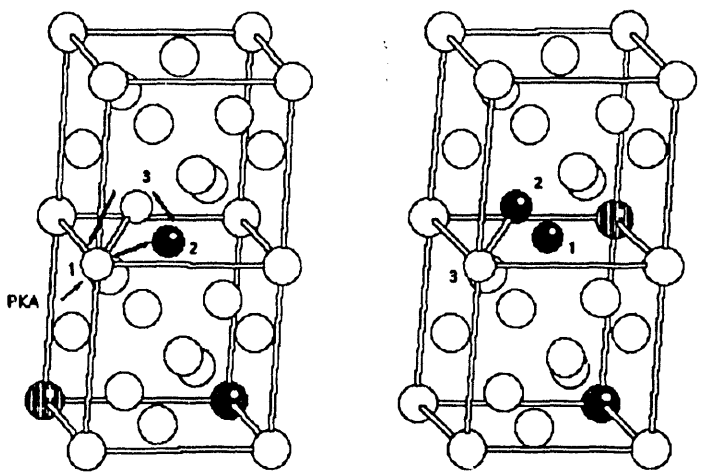

Fig. 3 Replacement loop. Atoms 1-2-3 interchange their positions when atom 1 is the PKA with E=35 eV and direction $\theta=89^o$, $\phi=43^o$.

For recoils directed between the low index crystallographic directions, our results (c.f. Fig 1) are in good qualitative agreement with the data of Hemment and Stevens [4] for irradiation of silicon at 80 K with 400 keV electrons. The damage rate is lowest near <100> and <111>, goes through a local maximum between these two directions and increases as the recoil direction approaches the <110> axis.

SUMMARY

In summary, we have employed the Stillinger-Weber potential to study the directional dependence of the threshold energy for defect production in silicon via molecular dynamics. The potential adequately predicts the minimum value of E_d and gives results that are in good agreement with experimental studies regarding its orientation dependence. Along the <110> directions, the threshold is high, ≈ 45 eV, and closed loops of replacements that do not produce point defects are common at lower energies. Along <111> and <100>, stable vacancy-interstitial pairs are produced for ≈ 25 eV primary recoils and along $[\bar{1}\,\bar{1}\,\bar{1}]$ $E_d \approx 20$ eV. The interstitial defect consist of two atoms that share a common lattice site in the shape of a <110> dumbbell. The <110> orientation of the self-interstitial in silicon is also predicted by *ab-initio* MD studies. The orientation of the interstitial dumbbell prevents it from recombining with the vacancy even when both are separated by as little as $1.25a_0$. On the other hand, the <110> orientation results in a high threshold for producing Frenkel pairs along this orientation as the interstitial strain field intersects the vacancy and the pair easily recombines.

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REFERENCES

[1] M.J. Norgett, M.T. Robinson, I.M. Torrens, Nucl. Eng. Design **33**, 50 (1975).
[2] J.W. Corbett and J.C. Bourgoin, in Point Defects in Solids, edited by J.H. Crowford, Jr., and L.M. Slifkin (Plenum Press, New York, 1975) p. 96.
[3] V.S. Vavilov, V.M. Patskevich, B.Ya. Yurkov, and P.Y. Glazunov, Soviet Phys. - Solid State **2**, 1301 (1961).
[4] 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), p.217.
[5] J.J. Lofersski and P. Rappaport, Phys. Rev. **98**, 1861 (1955).
[6] T.I. Kolmenskaya, S.M. Razumovskii, S.E. Vitovkin, Soviet Phys. – Semicond. **1**, 652 (1967).
[7] L.A. Miller, D.K. Brice, A.K. Prinja, and S.T. Picraux, in Defects in Materials, edited by P.D. Bristow, J.E. Epperson, J.E. Griffith, and Z.Liliental-Weber (Mater. Res. Soc. Proc. **209**, Pittsburgh, PA, 1991) pp. 171-176.
[8] G.D. Watkins, in Lattice Defects in Semiconductors, edited by F.A. Huntley (Inst. of Physics, London, 1975) p.1
[9] J.C. Bougoin, J.W. Corbett, and H.L. Frisch, J. Chem. Phys. **59**, 4042 (1973).
[10] R. Car, P. Blochl, E. Samrgiassi, Mater. Sci. Forum **83-87**, 433 (1992).
[11] J.L. Newton, A. P. Chaterjee, R.D. Harris, and G.D. Watkins, Physica **116B**, 219 (1983).
[12] J.B. Gibson, A.N. Goland, M. Milgram, and G.H. Vineyard, Phys. Rev. **120**, 1229 (1960).
[13] R. Smith and R.P. Webb, Nucl. Instr. Methods **B67**, 373 (1992).
[14] G.H. Gilmer and T. Diaz de la Rubia, Unpublished
[15] F.H. Stillinger and T.A Weber, Phys. Rev. B **31**, 5262 (1985).
[16] W.E. King and R. Benedek, J. Nucl. Mater. **117**, 26 (1983), and Phys. Rev. B **23**, 6335 (1981).

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