Defect-Induced Shifts in the Elastic Constants of Silicon

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ABSTRACT

As MEMS devices become ever more sensitive, even slight shifts in materials properties can be detrimental to device performance. Radiation-induced defects can change both the dimensions and mechanical properties of MEMS materials, which will be of concern to designers of MEMS for applications involving radiation exposure, such as those in a reactor environment or in space. We have performed atomistic simulations of the effect that defects and amorphous regions, such as could be produced by radiation damage, have on the elastic constants of silicon. We have then applied the results of the elastic constant shift calculations to a hypothetical MEMS device, and calculated the difference that would be generated by this effect.

INTRODUCTION

It is well known that environmental factors such as temperature can adversely impact the performance of MEMS devices. In this study, we will demonstrate that radiation is also a potential source of performance degradation for sensitive devices through the alteration of mechanical properties of common MEMS materials. Space-based electronic devices are notoriously susceptible to degradation due to radiation, since the electrical properties of materials can be dramatically altered by relatively low radiation doses. Mechanical properties such as density and elasticity can also be altered by radiation damage. While these changes are slight, they can be of critical importance to a MEMS device operating in space or in a reactor environment.

We assume a reactor environment involving fast (1 MeV equivalent) and thermal neutron fluxes, as well as gamma flux. Gamma radiation will be present in space, but protons, rather than neutrons, will be of primary concern in terms of ballistic collision displacement damage. It is convenient for the present analysis to examine the neutron case, since the mean free path of a 1 MeV neutron in Si is about 4.5 cm. This is a long mean free path on the MEMS scale, and will result in recoil ions that are uniformly distributed in silicon MEMS components. By contrast, a 1 MeV proton was shown in a SRIM-2003 [1] simulation to penetrate to only about 17 μm, which would complicate the analysis of elastic effects in MEMS parts due to the sharp gradient in damage with depth from the surface. With neutrons, we will also not have to account for the electronic stopping that is so important for protons.

Fast neutrons cause damage by displacing atoms from their lattice sites through collisions with atomic nuclei. A 1 MeV neutron has an elastic scattering cross-section [2] of about 4.5
barns ($10^{-24}$ cm), with no non-elastic cross section of any importance to our analysis. The energy spectrum of Si recoils that scatter such neutrons is approximately flat. [3] The maximum recoil energy for an Si atom is

$$T_n = \frac{4M_1M_2}{(M_1 + M_2)^2}E,$$

where $M_1$ and $M_2$ are the mass of the neutron and the recoil nucleus, and $E$ is the initial energy of the neutron. We therefore assume equal probability for recoil atoms in Si to have energies from 0 eV to $T_n = 133$ keV. Calculations were made using SRIM-2003 of such a recoil spectrum in Si, and it was determined that on average, a primary knock-on atom (PKA) creates about 1077 vacant lattice sites through its collisions and the ensuing sub-cascades. To calculate the probability of an effluent neutron creating a PKA within a Si thickness $x$, one can use:

$$P(x) = 1 - e^{-\Sigma x},$$

where $\Sigma$ is the macroscopic scattering cross section $\sigma\text{N}$, with $\sigma$ being the microscopic cross-section (4.5 barns) and $N$ being the number density [4] of Si ($4.99 \times 10^{22}$ n/cm$^3$).

For a given neutron fluence and a thin piece of silicon, then, we can estimate the number of initial displacements in the silicon. How these displacements translate into damage will depend on temperature, dose rate, and total dose. [5,6,7] Damage can be categorized into isolated defects and amorphous 'pockets.' At high temperatures, more of the vacancy-interstitial pairs will anneal out shortly after forming. At high dose rates, amorphization becomes more probable, since regions of high defect concentration are more likely to get hit by another cascade before annealing has had a chance to happen.

Since computational studies of damage cascades are limited in the time scales they can address, the actual damage profile is hard to specify for low neutron fluences. We therefore take the approach of characterizing the effects of such damage by examining the two extreme cases: 1) the displaced atoms all form isolated defects and 2) the displaced atoms are all in amorphous pockets. We will briefly summarize results that are detailed elsewhere, [8] then apply these cases to a simple vibrating silicon beam.

**COMPUTATIONAL MODELING**

**Point Defects**

The environment dependent interatomic potential (EDIP) [9,10,11] was used to create defected samples and calculate their elastic effects on Si. Two examples of point defects that cause elastic property changes are shown in Figure 1. The monovacency and dumbbell interstitial shown are two relatively low energy configurations according to EDIP. Depending on the potential/a $ab\ initio$ method used, other relaxed configurations around a vacancy or interstitial can be lower energy. To test the effects of random initial positions for interstitials and vacancies, we constructed 45 samples of 1728 atoms (in a simulation cell using periodic boundary conditions), into which we randomly placed defects, then allowed atomic positions to relax. Annealing using the DL_POLY [12] molecular dynamics code (with EDIP as the force algorithm) was performed at room temperature. Ten different configurations for interstitials, di-interstitials, and di-vacancies resulted, with the two pictured defects occurring for the vast majority of cases.
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\[ \text{Figure 1. Two point defects referred to the unit cell in Si. A vacancy is shown at left, with darkened neighbors. A <110> split dumbell is shown at right with the two atoms darkened that result from the "splitting" of one.} \]

\[ \text{To obtain the elastic constants for the defected samples, we imposed strains on the} \]

\[ \text{simulation cell and recorded the energy. The second derivative of a polynomial fit to a plot of} \]

\[ \text{energy vs. strain yields the elastic constants. The traditional three independent elastic constants} \]

\[ \text{of C}_{11}, C_{12}, \text{and } C_{44} \text{ were obtained in this way. The results for the 45 randomly arranged} \]

\[ \text{defected samples are shown in Figure 2. It can be seen that the trend at even these unphysically} \]

\[ \text{high defect concentrations is linear. One can therefore deduce that the effects of each point} \]

\[ \text{defect are fairly independent. Additionally, the effects of each type of point defect are fairly} \]

\[ \text{similar. We verified this by constructing 1728-atom cells containing a single isolated defect and} \]

\[ \text{measuring its elastic constants for each defect type, and found that on a per atom basis (some of} \]

\[ \text{the point defects are two-atom complexes) the net result of each was to reduce } E_{<100>} \text{ by an} \]

\[ \text{amount between 0.25 and 0.41 percent for the cell. It is important to note that both vacancies} \]

\[ \text{and interstitials reduce Young's modulus and to a similar degree. Volume was found to linearly} \]

\[ \text{expand for the defected samples, being dominated by the monovacancy and dumbell defects} \]

\[ \text{which had formation volumes of 28.8 } \AA^3 \text{ and 8.7 } \AA^3, \text{ respectively.} \]

\[ \text{Amorphous Si} \]

\[ \text{We prepared amorphous simulation cells by quenching from the liquid,} \]

\[ \text{[8] then calculated} \]

\[ \text{elastic constants using EDIP as for the point defected samples. The two largest (1728-atom) samples} \]

\[ \text{were found to have a Young's modulus of 70.5 GPa and 71.4 Gpa, with a 3.1 % and 3.3} \]

\[ \text{% volume expansion, respectively. The modulus found by EDIP is significantly different from} \]

\[ \text{that of experiment, which varies from 118 GPa [13] to 125 GPa [14] according to measurements} \]

\[ \text{of surface acoustic wave velocities in surface layers amorphized by ion bombardment. These} \]

\[ \text{differences may be due to an artifact of the potential we used, or they may have to do with the} \]

\[ \text{different method of sample preparation (liquid quench computationally vs. ion bombardment} \]

\[ \text{experimentally). Since the only experimental samples of amorphous silicon have been thin films} \]

\[ \text{on crystalline substrates, there is also the question of whether or not these thin films are} \]

\[ \text{representative of the bulk material, or more appropriate to our problem, small pockets of} \]

\[ \text{amorphous material embedded in a crystalline matrix.} \]

\[ \text{We can bracket the changes to overall elastic modulus } E_C \text{ in terms of the volume fraction} \]

\[ \text{of amorphous material } V_A \text{ and the elastic moduli of the matrix } E_2 \text{ and the embedded amorphous} \]

\[ \text{regions by using:} \]

\[ [15,16] \]
Figure 2. Young's modulus along <100> as a function of point defect content. Diamond represent samples with interstitials only, triangles vacancies, and squares Frenkel pairs. Each point is the average of three samples, each of which is averaged over all three spatial directions.

\[
\left[ \frac{V_1}{E_1} + \frac{(1-V_1)}{E_2} \right]^{-1} < E_C < V_1E_1 + (1-V_1)E_2 . \quad (3)
\]

The difficulty of estimating the volume fraction of amorphous material is somewhat tricky, caused partly by the lack of an easy definition of an 'amorphous' atom. Molecular dynamics simulations [17] have shown that heavy ions (As) will cause defects that occur mostly in disordered (amorphous) zones in Si, and that light ions (B) will cause damage wherein isolated defects predominate. Comparing to the SRIM results for these simulations and interpolating to the Si mass, we determine that the total number of defects (vacancies + interstitials) for a recoil in the MD simulations is a constant factor of that predicted by SRIM for a given recoil mass. Interpolating between the masses of As and B to obtain such factor for Si, we estimate that MD simulations such as these would predict about 660 atoms occupying amorphous zones for an average PKA recoiling from a 1 MeV neutron collision.

MEMS EXAMPLE

As an illustration of the effect that point defects and amorphous zones created by radiation damage will have on MEMS performance, we consider a simple vibrating silicon beam, 50 μm thick by 10 μm wide by 1000 μm long. It is suspended above a glass substrate to which the ends are anodically bonded. Many MEMS devices are fabricated using silicon anodically bonded to a Pyrex substrate, so this is a very typical example. Proton fluences (1 MeV equivalent) accumulated in space would be about 1×10^{14} n/cm² over one year. We will take, for
the reasons discussed above, a benchmark dose of neutrons to be the same. Typical gamma dose for a year in space is 1 MRad.

The dependence of the frequency $f$ of a double-supported vibrating beam on the elastic modulus $E$ is:

$$\frac{df}{f} = \frac{1}{2 \frac{dE}{E}}.$$  \hspace{1cm} (4)

The benchmark neutron fluence will cause $2.24 \times 10^{13} \text{ PKA/cm}^3$, each of which will cause about 1785 point defects (vacancies + interstitials), per the SRIM/Caturla et al. [17] analysis described above. If these are not isolated, but occur only in amorphous zones, then this number reduces to about 660 atoms occupying an amorphous region. Using the slopes from Figure 2, we predict that the shift of Young's modulus would be about -5 parts per million (ppm) for the case of 1785 isolated defects per cascade. For the other extreme case of the 660 atoms in amorphous zones per cascade, Eq. 3 brackets the shift in Young's modulus to be between -145 and -280 parts per billion (ppb). The corresponding relative frequency shift for the beam for any of these cases would be simply half the relative change in $E$.

We mention in passing that damage to the silicon is only half the story for the vibrating MEMS beam we described. Borosilicate glass such as Pyrex is susceptible to compaction from cascade damage (protons and neutrons) and from gamma exposure, whereas silicon is very resistant to ionizing radiation such as gamma and electrons. [18] The Pyrex compaction from neutron the neutron fluence considered here would be around -600 ppb strain. Extrapolations from experiment to this neutron fluence predict that silicon would expand by about 25 ppb (strain). [19] Such differential compaction would put the hypothetical beam under compression, causing even more dramatic changes to its frequency. Additionally, extrapolation predicts that a gamma dose of 1 MRad will cause an additional -470 ppb compaction of the Pyrex. [20,21] Clearly, borosilicate glass is the weak link for radiation hardness for MEMS. For a discussion of neutron damage experiments in borosilicate glass, see Allred et al. [22]

**CONCLUSIONS**

We have shown that MEMS devices are susceptible to performance degradation due to material mechanical property changes from radiation damage. By computational atomistic simulation of point defect effects on elasticity, we have characterized the response of Young's modulus to radiation-produced defects in the low dose, linear response range. We have bracketed the range of response to amorphous pockets from radiation cascade damage, though these numbers are highly dependent on the estimation of amorphous fraction. Neutron- and proton-induced cascades in silicon are likely to lie between the two extremes considered here, based on the literature which shows that As ions (heavier than Si) produce mostly amorphous regions and B ions (lighter than Si) produce mostly isolated defects.

The views expressed in this article are those of the author and do not reflect the official policy or position of the United States Air Force, the Department of Defense, or the United States government.

**REFERENCES**

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