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Radiation defect dynamics studied by pulsed ion beams

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ABSTRACT

The formation of stable radiation damage in solids often proceeds via complex dynamic annealing processes, involving migration and interaction of ballistically-generated point defects. Our current understanding of the underlying physics is still not sufficient for predicting radiation damage even for Si, which is arguably the simplest and most extensively studied material. The complexity of radiation damage is closely related to radiation defect dynamics. Here, we demonstrate how defect interaction dynamics can be studied by pulsed beam irradiation when the total ion fluence is split into a train of equal square pulses. By varying the passive portion of the beam duty cycle, we measure a characteristic time constant of dynamic annealing and, hence, the defect relaxation rate. Measurements of stable lattice disorder as a function of the active portion of the beam duty cycle give an effective defect diffusion length. We illustrate the pulsed beam method with examples for Si bombarded at 100 °C with 500 keV Ar ions.

1. Introduction

The formation of stable radiation damage in materials is a dynamic phenomenon. For most irradiation environments relevant to nuclear technologies and radiation-assisted processing of electronic materials, the damage buildup proceeds via complex dynamic annealing (DA) processes (see, for example, reviews in [1–3]). The DA involves migration and interaction of ballistically-generated point defects after the thermalization of collision cascades, over time scales $\gtrsim 1$ ps. Such DA leads to point defect annihilation or, in turn, to clustering and the growth of various extended lattice defects, such as dislocations, stacking faults, planar defects, non-stoichiometric inclusions, amorphous zones, bubbles, and voids. As a result, lattice disorder experimentally observed after irradiation can significantly depart from predictions based only on collisional processes [1–3]. The DA manifests as a non-trivial dependence of radiation damage on irradiation conditions. This currently precludes the prediction and ultimately control of radiation damage.

Most previous studies of DA have focused on the measurements of the dependencies of damage on the beam flux (i.e., the dose rate) and on the density of collision cascades, determined by ion mass and energy for a given target material [1–6]. The flux effect is caused by the interaction of mobile defects originating in different collision cascades created in close proximity of each other. This involves a convolution of both spatial (such as the defect diffusion length, L_d) and temporal (i.e., the lifetime of mobile point defects, τ) parameters of DA. Attempts to understand DA from flux effect data have been somewhat cumbersome [3,5,7] since serious assumptions are required to extract the τ and L_d from experimental data by modeling defect interaction processes.

Here, we describe the development of a pulsed beam method (PBM) for accessing the dynamic regime of defect accumulation and measuring both τ and L_d [3,8–13]. The inset in Fig. 1 shows a schematic of the time dependence of the beam flux during pulsed beam irradiation, defining the additional PBM parameters (t_{on}, t_{off}, and F_{on}). In such experiments, the total ion fluence is split into a train of equal pulses. These PBM experiments involve ion irradiation of a series of specimens with all except one of the irradiation parameters fixed (either t_{off} or t_{on}). Irradiation is followed by the measurement of the level of stable disorder by, for example, ion channeling. Parameters τ and L_d are evaluated based on the analysis of experimental dependencies of the level of stable disorder on t_{off} and t_{on}, respectively [3,8–13].

2. Experimental

Float-zone grown (100) Si single crystals (with a resistivity of $\sim 5\ \Omega$ cm) were bombarded at 100 °C with 500 keV $^{40}Ar^+$ ions at 7° off the [100] direction. To improve thermal contact, the samples were attached to the Cu sample holder with Ag paste. All irradiations were performed in a broad beam mode [8]. In each irradiation

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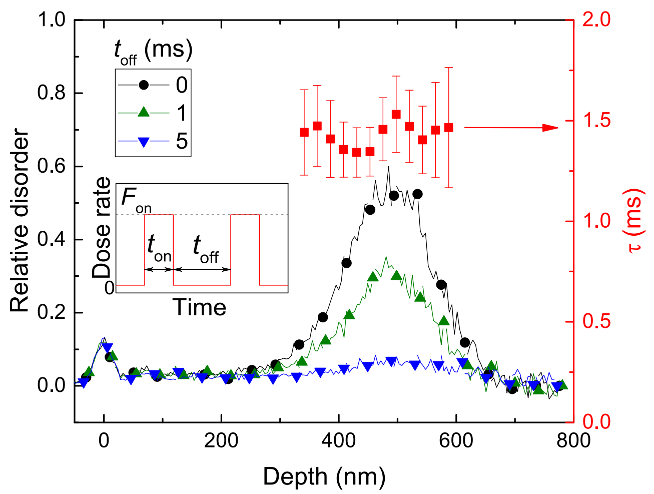

Fig. 1. Left axis: selected depth profiles of relative disorder in Si bombarded at 100 °C with a pulsed beam of 500 keV Ar ions with $F_{on} = 1.8 \times 10^{13}$ cm^{-2} s^{-1}, $t_{on} = 1$ ms, a total ion fluence of 8.75×10^{14} cm^{-2}, and different t_{off} values given in the legend. For clarity, only every 10th experimental point is depicted. Right axis: the depth dependence of the dynamic annealing time constant (τ) measured as described in the text. The inset is a schematic of the time dependence of the instantaneous beam flux for pulsed beam irradiation, defining t_{on}, t_{off}, and F_{on}.

run, the total ion fluence was split into a train of square pulses, each with an instantaneous beam flux F_{on} and a fluence per pulse of $F_{on}t_{on}$ (see the inset in Fig. 1). For τ measurements [3,8,10,11,13], $F_{on} = 1.8 \times 10^{13}$ cm^{-2} s^{-1}, $t_{on} = 1$ ms, the total fluence was 8.8×10^{14} cm^{-2}, and adjacent pulses were separated by time t_{off}, which was varied between 0.2 and 10 ms. For L_d measurements [3,9,12], $F_{on} = 10^{14}$ cm^{-2} s^{-1}, the total fluence was 1.2×10^{15} cm^{-2}, t_{on} was varied between 0.1 and 3 ms, and each pulse was separated by $t_{off} = 20$ ms, which, as will be shown below, was much greater than the τ value.

The dependence of stable lattice damage on t_{off} and t_{on} was studied *ex-situ* at room temperature by ion channeling. Depth profiles of lattice disorder were measured with 2 MeV $^4He^+$ ions incident along the [1 0 0] direction and backscattered into a detector at 164° relative to the incident beam direction. Raw channeling spectra were analyzed with one of the conventional algorithms [14] for extracting depth profiles of relative disorder. Values of average relative bulk disorder (n) were obtained by averaging depth profiles of relative disorder over 20 channels (~ 38 nm) centered on the bulk damage peak maximum. Error bars of n are standard deviations. The total ion fluence was chosen such that, for continuous beam irradiation (i.e., $t_{off} = 0$), n was ~ 0.6 (with $n = 1$ corresponding to full amorphization). The 4 MV ion accelerator (National Electrostatics Corporation, model 4UH) at Lawrence Livermore National Laboratory was used for both ion irradiation and ion beam analysis. A more detailed description of the experimental arrangement can be found elsewhere [3,8–13]. The choice of the pulsing parameters for measurements of τ and L_d was discussed in detail in [3].

3. Results and discussion

3.1. Measurement of τ

The measurement of either τ or L_d for any given combination of the target material, temperature, ion mass, energy, and F_{on} starts with the selection of the total ion fluence resulting in the damage level of interest. Hence, in the absence of previous experimental data or predictive models, the first experiment in the PBM is the measurement of the traditional damage buildup curve. This is shown in Fig. 2 for Si bombarded at 100 °C with a continuous beam of 500 keV Ar ions with $F_{on} = 1.8 \times 10^{13}$ cm^{-2} s^{-1}. The damage buildup revealed by Fig. 2 is highly sigmoidal. Data can be readily fitted with a phenomenological defect stimulated and direct amorphization model [15] (with fitting parameters $\sigma_a = 4.4 \times 10^{-14}$ cm^{-2} and $\sigma_s = 9.6 \times 10^{-15}$ cm^{-2}) and Gibbons overlap model [16] (with fitting parameters $k = 20$, $A = 2.6 \times 10^{-14}$ cm^{-2}). The Gibbons overlap model required 20 overlaps of disordered regions to fit the data, which suggests that the physics of stable damage formation for these irradiation conditions is beyond what this model is capable of describing.

Fig. 1 (left axis) shows representative depth profiles of relative disorder in Si bombarded with Ar ions with three different t_{off} values (given in the legend) and all the other parameters kept constant. It is seen that, with increasing t_{off}, while the damage level in the first ~ 250 nm from the sample surface remains unchanged, the intensity of the bulk disorder peak (n) dramatically decreases. This observation suggests different dynamic mechanisms of bulk and surface disordering. It is consistent with our previous depth-resolved studies of defect interaction dynamics in Si [3,8,9,13].

Fig. 3 (bottom axis) shows the $n(t_{off})$ dependence for Si under Ar ion bombardment. The monotonic $n(t_{off})$ decay, revealed by Fig. 3 (bottom axis) is related to the interaction of defects generated in different pulses (and, hence, in different cascades). As the beam is pulsed off the target, the concentration of mobile defects decreases via DA with a characteristic time constant τ. For irradiation with $t_{off} \gg \tau$, DA processes have essentially decayed in time intervals between individual ion pulses.

The time constant of the dominant DA process (τ) can be quantitatively evaluated by analyzing such experimental $n(t_{off})$ dependencies. For example, τ can be obtained by fitting $n(t_{off})$ dependencies with either the first order $(n(t_{off}) = n_\infty + (n(0) - n_\infty)\exp(-t_{off}/\tau_1))$ or the second order $\left(n(t_{off}) = n_\infty + \frac{n(0)-n_\infty}{1+\frac{t_{off}}{\tau_2}}\right)$ decay equations. Here, n_∞ is relative disorder for $t_{off} \gg \tau_{1,2}$. The "1" and "2" subscripts refer to whether the

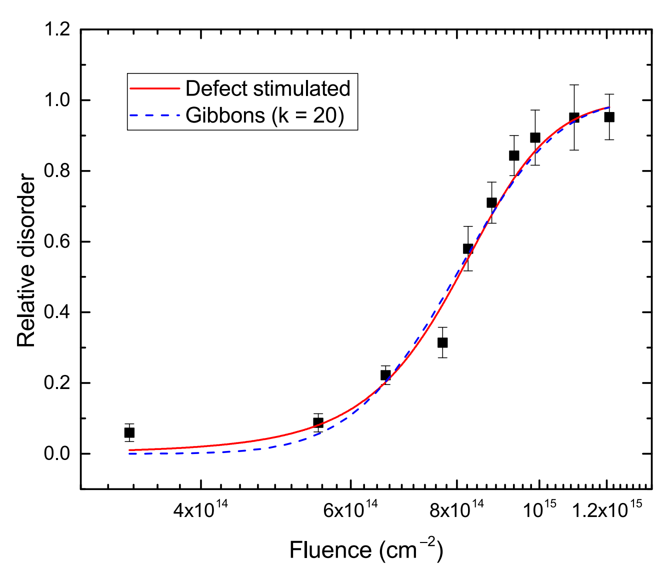

Fig. 2. Dose dependence of relative disorder at the maximum of the bulk defect peak for Si bombarded at 100 °C with a continuous beam of 500 keV Ar ions with a beam flux of 1.8×10^{13} cm^{-2} s^{-1}. Results of fitting the data with the defect stimulated amorphization model [15] and the Gibbons overlap model [16] with $k = 20$ are shown by solid and dashed lines, respectively.

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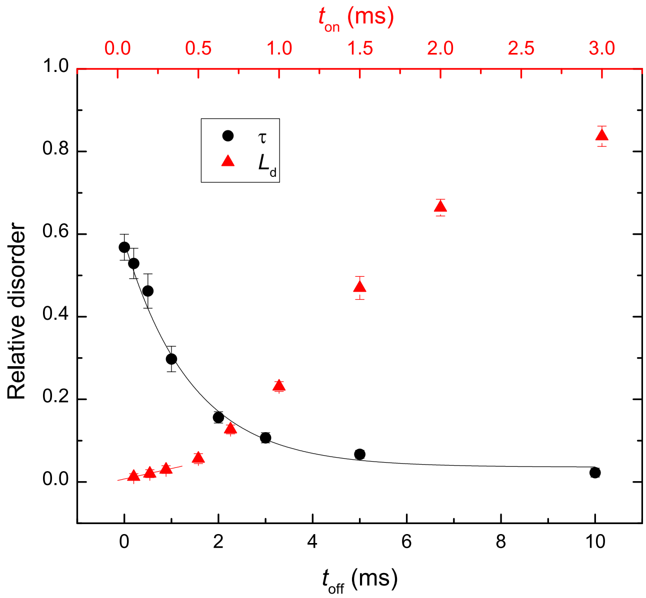

Fig. 3. Relative bulk disorder in Si bombarded with a pulsed beam of 500 keV Ar ions (bottom axis) as a function of t_{off} with a fixed $t_{on} = 1$ ms and $F_{on} = 1.8 \times 10^{13}$ cm^{-2} s^{-1} and (top axis) as a function of t_{on} with a fixed $t_{off} = 20$ ms and $F_{on} = 10^{14}$ cm^{-2} s^{-1}. Fitting curves (bottom axis) with the first order (i.e., exponential) decay and (top axis) with linear equations are shown by solid lines.

fitting was done with the first or second order decay equation, respectively. We have found that $n(t_{off})$ data from Fig. 3 is best fitted with the first order decay equation. Fig. 1 (right axis) gives an example of depth-resolved τ_1 measurements. It shows that the τ_1 is essentially independent of depth in the ion end of range region.

3.2. Measurement of L_d

The L_d is evaluated based on the experimental $n(t_{on})$ dependence, with all the other irradiation parameters kept constant and with $t_{off} \gg \tau$ in order to suppress the interaction of mobile defects generated in different pulses [3,9]. The L_d is evaluated by analyzing $n(t_{on})$ data for low t_{on} values (i.e., low ion fluence increments per pulse) when the average lateral distance between neighboring ion impacts in each pulse is larger than L_d. This corresponds to the onset of the interaction of mobile defects generated in adjacent (sub) cascades within each pulse. With increasing $F_{on}t_{on}$, the average distance between individual collision cascades for each pulse decreases, resulting in more efficient interaction of mobile defects generated in different cascades. Such a measurement of the $n(t_{on})$ dependence is illustrated in Fig. 3 (top axis) for the case of Si. In this L_d measurement, the complexity of cascade formation and subsequent DA is approximated by the following scenario. At any given depth in the plane perpendicular to the sample surface, each ion creates a damage zone with a circular area (A) with a radius $L_d + R_{ballistic}$, where $R_{ballistic}$ is the radius of the ballistic cascade, which can be estimated with a binary collision code. Recent measurements [3] have shown that $L_d \gg R_{ballistic}$. Ion impacts obey Poisson statistics as they are random and uncorrelated. Hence, there is a finite probability (with a Poisson parameter of $AF_{on}t_{on}$) of multiple ion impacts into L_d-defined areas. If, for low t_{on} values, the efficiency of the stable damage formation scales with the displacement density, $n \propto 1 + 4L_d^2F_{on}t_{on}$. This linear equation is used to fit the initial (linear) portion of the $n(t_{on})$ dependence, with the L_d as a fitting parameter. Fitting the data from Fig. 3 (top axis) gives $L_d = 78 \pm 14$ nm.

3.3. Implications and future work

With the PBM, we have recently successfully measured both L_d and τ for Si and SiC in the temperature range up to 250 °C [3,8–13]. These results have tremendously clarified previous estimates of τ, ranging over the astonishing 12 orders of magnitude! Moreover, the robustness of the PBM has recently been demonstrated in a systematic study [3] of the dependence of τ and L_d in Si at room temperature on the doping level, ion dose, the instantaneous defect generation rate (defined by F_{on}), t_{on}, and the average density of collision cascades. We have found that the average density of collision cascades influences not only the efficiency of damage accumulation and annealing but also defect interaction dynamics. Recent experiments [3] have revealed a nontrivial dependence of τ on the choice of parameters of the active part of the beam duty cycle (i.e., F_{on} and t_{on}). This observation suggest an important role of the instantaneous concentrations of mobile defects in defect dynamics and warrants further studies.

Understanding radiation defect dynamics is not just academic curiosity. Experimental data on defect interaction dynamics is essential for benchmarking models of radiation damage buildup. Such an understanding is critical if we want to extend our laboratory findings to nuclear material lifetimes and to time scales of geological storage of nuclear waste. Furthermore, the knowledge of DA parameters measured by the PBM has direct implications for understanding the difference between rastered and broad-beam irradiation, which is a topic of current interest in the nuclear materials community [17]. Indeed, bombardment with rastered beams results in an effectively pulsed beam irradiation for any given location on the target. Moreover, PBM measurements of the L_d could help design materials with improved radiation-resistance via controlled interaction of mobile defects with interfaces (see, for example, [18,19]). In this case, the L_d determines the required dimensions of "radiation-resistant" nanostructures.

4. Summary

In summary, we have described how defect interaction dynamics can be accessed by irradiation with pulsed ion beams. Our pulsed-beam method (i) separates spatial (L_d) and temporal (τ) information, (ii) does not require assumptions about explicit defect interaction processes for measurements of τ and L_d, (iii) averages data over multiple ion cascades and pulses, and (iv) is not limited to any particular defect characterization technique such as ion channeling. Examples have been given for the case of Si crystals bombarded at 100 °C with 500 keV Ar ions. Results have revealed a defect interaction time constant of 1.5 ms (for the first order, exponential, decay). Within error bars, τ is independent of depth (and, hence, the stable damage level) in the ion end of range region. An L_d of ~ 78 nm has been estimated for a bulk damage level of $\sim 1\%$. Future pulsed-beam experiments could further contribute to our understanding of radiation defect dynamics in solids.

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References

[1] J.S. Williams, Rep. Prog. Phys. 49 (1986) 491.
[2] M.T. Robinson, J. Nucl. Mater. 216 (1994) 1.

[3] J.B. Wallace, S. Charnvanichborikarn, L.B. Bayu Aji, M.T. Myers, L. Shao, S.O. Kucheyev, J. Appl. Phys. 118 (2015) 135709.
[4] D.A. Thompson, Radiat. Eff. 56 (1981) 105.
[5] A.I. Titov, A.Y. Azarov, L.M. Nikulina, S.O. Kucheyev, Phys. Rev. B 73 (2006) 064111.
[6] B.G. Svensson, C. Jagadish, J.S. Williams, Phys. Rev. Lett. 71 (1993) 1860.
[7] G. Carter, J. Appl. Phys. 79 (1996) 8285.
[8] M.T. Myers, S. Charnvanichborikarn, L. Shao, S.O. Kucheyev, Phys. Rev. Lett. 109 (2012) 095502.
[9] S. Charnvanichborikarn, M.T. Myers, L. Shao, S.O. Kucheyev, J. Phys. Condens. Matter 25 (2013) 162203.
[10] J.B. Wallace, L.B. Bayu Aji, L. Shao, S.O. Kucheyev, Appl. Phys. Lett. 106 (2015) 202102.
[11] L.B. Bayu Aji, J.B. Wallace, L. Shao, S.O. Kucheyev, Sci. Rep. 6 (2016) 30931.
[12] L.B. Bayu Aji, J.B. Wallace, L. Shao, S.O. Kucheyev, J. Phys. D 49 (2016) 19LT01.
[13] J.B. Wallace, L.B. Bayu Aji, A.A. Martin, S.J. Shin, L. Shao, S.O. Kucheyev, Sci. Rep. 7 (2017) 39754.
[14] K. Schmid, Radiat. Eff. 17 (1973) 201.
[15] N. Hecking, K.F. Heidemann, E. Te Kaat, Nucl. Instr. Meth. B 15 (1986) 760.
[16] J.F. Gibbons, Proc. IEEE 60 (1972) 1062.
[17] G.S. Was, J. Nucl. Mater. 30 (2015) 1158.
[18] X.-M. Bai, A.F. Voter, R.G. Hoagland, M. Nastasi, B.P. Uberuaga, Science 327 (2010) 1631.
[19] S. Charnvanichborikarn, M.T. Myers, L. Shao, S.O. Kucheyev, Scr. Mater. 67 (2012) 205.

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