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Measuring radiation damage dynamics by pulsed ion beam irradiation: 2015 Annual Progress Report for DOE/NE/NEET

S. O. Kucheyev

March 7, 2016

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1 Cover page data

1.1 Federal Agency and Organization Element to Which Report is Submitted

U.S. Department of Energy, Office of Nuclear Energy, NEET-Reactor Materials.

1.2 Federal Grant or Other Identifying Number Assigned by Agency

PICS:NE Workpackage #: CA-13-CA-LL-0403-06. Work authorization number NT/0114/14/AL/50.

1.3 Project Title

Measuring radiation damage dynamics by pulsed ion beam irradiation.

1.4 PI Name, Title, and Contact Information

Sergei Kucheyev, physicist, kucheyev@llnl.gov, phone: (925) 422-5866.

1.5 Name of Submitting Official, if other than PD/PI

See Sec. 1.4.

1.6 Submission Date

December 30, 2015.

1.7 DUNS Number

785627931.

1.8 Recipient Organization (Name and Address)

Lawrence Livermore National Laboratory, 7000 East Ave, Livermore, California 94550.

1.9 Project/Grant Period (Start Date, End Date)

Start date: January 1, 2014. End date: December 31, 2016.

1.10 Reporting Period End Date

December 30, 2015.

1.11 Report Term or Frequency (annual, semi-annual, quarterly, other)

Annual.

1.12 Signature of Submitting Official

Sergei Kucheyev

2 Accomplishments

2.1 Major goals of the project

The major goal of this project is to develop and demonstrate a novel experimental approach to access the dynamic regime of radiation damage formation processes in nuclear materials. In particular, the project exploits a pulsed-ion-beam method in order to gain insight into defect interaction dynamics by measuring effective defect interaction time constants and defect diffusion lengths. For Year 2, this project had the following two major milestones: (i) measurement of the temperature dependence of defect dynamics in SiC and (ii) the evaluation of the robustness of the pulsed beam method from studies of the defect generation rate. As we describe below, both of these milestones have been met.

2.2 Specific accomplishments for the reporting period

Major activities. This was the second year of the project. Major activities consisted of (i) ion bombardment of Si and SiC single crystals under well controlled pulsed-ion-irradiation conditions, (ii) advanced characterization of irradiated targets by ion channeling, transmission electron microscopy (TEM), and Raman spectroscopy, and (iii) dissemination of results by documenting our findings in peer-review publications. We have performed pulsed ion beam experiments with both SiC (a prototypical nuclear ceramic material) and Si (the best studied and arguably the simplest material) targets. By doing it, we investigated radiation damage dynamics in SiC and tested the robustness of the pulsed ion beam method (with both Si and SiC targets).

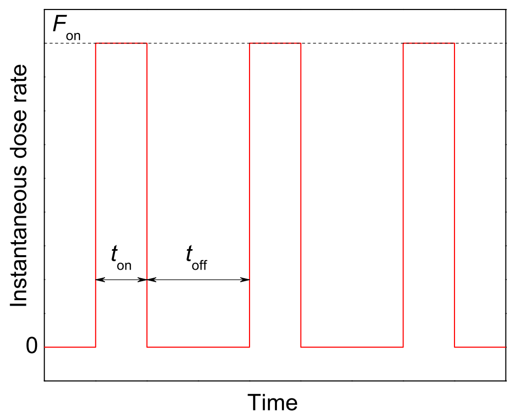

Figure 1: Schematic of the time dependence of the dose rate, defining t_{on}, t_{off}, and F_{on} (the maximum instantaneous dose rate).

During Year 2 of the project, we executed a successful series of pulsed ion beam irradiation experiments that demonstrated the robustness of the pulsed ion beam method for studying radiation defect interaction dynamics. Our pulsed ion beam experiments allowed us to measure effective time and length constants of defect interaction processes. The defect interaction time constant τ was measured directly by studying the dependence of lattice disorder on the passive part of the beam duty cycle, t_{off}, while the effective defect diffusion length L_{d} was estimated from the dependence of damage on the active part of beam cycle, t_{on}. Such additional pulsed-beam-related irradiation parameters (t_{on}, t_{off}, and also F_{on}, which is the maximum instantaneous dose rate) are defined in Fig. 1, which shows a schematic of the time dependence of the dose rate during pulsed ion beam irradiation. In such pulsed-beam experiments, the total ion dose was split into a number of equal square pulses. These experiments involved ion irradiation of a series of specimens to the same total dose with all except one of the irradiation parameters fixed. Irradiation was followed by measurements of the level of stable disorder in the crystal bulk and at the surface with ion channeling spectrometry, TEM, or Raman scattering.

Specific objectives. During Year 2, the project had the following specific objectives:

- Study of radiation damage buildup in 3C-SiC under continuous (not pulsed) beam irradiation in the temperature range of interest ($25 - 250$ °C). Such a study of the damage buildup under continuous ion irradiation was a prerequisite for understanding the dynamic aspects of radiation damage in subsequent pulsed ion beam experiments. Results of this study are documented in the following publication:

  1. J. B. Wallace, L. B. Bayu Aji, T. T. Li, L. Shao, and S. O. Kucheyev, "Damage buildup in Ar-ion-irradiated 3C-SiC at elevated temperatures," J. Appl. Phys. **118**, 105705 (2015).

- The demonstration of the applicability of the pulsed-ion-beam method for studies of radiation defect dynamics in SiC. Results of this study are documented in the following publication:

  2. J. B. Wallace, L. B. Bayu Aji, T. T. Li, L. Shao, and S. O. Kucheyev, "Time constant of defect relaxation in ion-irradiated 3C-SiC," Appl. Phys. Lett. **106**, 202102 (2015).

- Study of effects of the collision cascade density, the instantaneous dose rate, the total dose, and the dopant concentration on the parameters of radiation defect dynamics (τ and L_{d}) in Si at room temperature. This study has demonstrated the robustness of the pulsed ion beam method for studying radiation defect interaction dynamics. Results of this study are documented in the following publication:

  3. J. B. Wallace, L. B. Bayu Aji, L. Shao, and S. O. Kucheyev, "Radiation defect dynamics in Si at room temperature studied by pulsed ion beams," J. Appl. Phys. **118**, 135709 (2015).

- Measurement of the temperature dependence of defect dynamics in SiC and Si. Results of this study remain unpublished, with the following three journal manuscripts currently under review:

  4. L. B. Bayu Aji, J. B. Wallace, L. Shao, and S. O. Kucheyev, "Non-monotonic temperature dependence of radiation defect dynamics in silicon carbide."

  5. L. B. Bayu Aji, J. B. Wallace, L. Shao, and S. O. Kucheyev, "Effective defect diffusion lengths in Ar-ion bombarded 3C-SiC."

  6. J. B. Wallace, L. B. Bayu Aji, A. A. Martin, S. J. Shin, L. Shao, and S.O. Kucheyev, "Evidence for the dominant role of vacancy and interstitial diffusion in dynamic annealing in ion-irradiated Si."

Significant results. During Year 2 of the project, we have done pulsed ion beam irradiation experiments that demonstrated the robustness of the pulsed ion beam method for studying radiation defect interaction dynamics and revealed the temperature dependence of defect dynamics in SiC. By doing this, we have fully met the two major milestones set for Year 2. Details can be found in the 6 manuscripts listed above. Here, we will not reproduce such details. Instead, we give a summary of the most significant results in the same order as that of the list of specific objectives given above.

- Study of radiation damage buildup in 3C-SiC under continuous beam irradiation.

  We have used a combination of ion channeling and TEM to study damage buildup up to amorphization in 3C-SiC irradiated with 500 keV Ar ions with a constant dose rate of 1.9×10^{13} cm^{-2} s^{-1} in the temperature range of $25 - 250$ °C. We have found that, starting at 200 °C, the shape of damage–depth profiles becomes anomalous, with the damage peak narrowing and moving to larger depths and an additional shoulder forming close to the ion end of range. Such an anomalous behavior has been attributed to nucleation-limited amorphization and quantitatively described by a phenomenological model based on an assumption of a linear dependence of the effective amorphization cross section on ion dose. We have demonstrated that $3C$-SiC can be amorphized by irradiation with 500 keV Ar ions even at 250 °C, which is larger than the critical amorphization temperature estimated previously from experiments with lower displacement generation rates. This reflects a dominant role of defect interaction dynamics at elevated temperatures and calls for further systematic studies of radiation defect dynamics in SiC.

- The demonstration of the pulsed-ion-beam method for studies of radiation defect dynamics in SiC.

  We have used the pulsed-ion-beam method for quantitative measurements of the dynamic annealing time constant (τ) in $3C$-SiC. A τ of $\sim$ 3 ms or $\sim$ 5 ms (with assumptions of the second or first order kinetic decay, respectively) and a dynamic annealing efficiency of $\sim$ 40% have been measured for defects in both the Si and C sublattices of $3C$-SiC irradiated at 100 °C with 500 keV Ar ions (Fig. 2). This has demonstrated the applicability of the pulsed-ion-beam technique for studies of radiation defect dynamics in materials other than Si. Furthermore, statistically indistinguishable radiation dynamics parameters for C and Si sublattices have demonstrated a close temporal and spatial coupling of damage accumulation between the two sublattices of SiC (Fig. 2).

- Evaluation of the robustness of the pulsed ion beam method for studying radiation defect interaction dynamics.

  We have studied effects of the collision cascade density, the instantaneous dose rate, the total dose, and the dopant concentration on the parameters of radiation defect dynamics (τ and L_{d}) in Si at room temperature. A second order defect relaxation kinetics has been found for all the cases studied, with a defect relaxation time constant τ in the range of $4-13$ ms and a diffusion length L_d of $\sim 15-50$ nm at room temperature. Both τ and L_d are essentially independent of the maximum instantaneous dose rate, total ion dose, and dopant concentration within the ranges studied. Both τ and L_d, however, increase with increasing ion mass (Fig. 3), demonstrating that collision cascade density influences the parameters of radiation defect dynamics in Si. This work emphasizes the importance of dynamic annealing effects in ion-irradiated Si and demonstrates the strengths and limitations of the pulsed-ion beam method to assess the defect dynamics.

- Measurement of the temperature dependence of defect dynamics in SiC and Si.

  We have used the pulsed beam technique to measure the temperature (T) dependence of the effective time constant of dynamic annealing in Si bombarded in the T range from -20 to 140 °C with 500 keV Ar ions. For SiC, we have studied the T range of $20-250$ °C. Results for Si have revealed two well-defined Arrhenius regimes described by activation energies of $\sim$ 73 and $\sim$ 420 meV, below and above 60 °C, respectively (Fig. 4). These activation energies suggest that, for the irradiation conditions studied, inter-cascade defect interaction is dominated by migrating self-interstitials or vacancies. For SiC, results have revealed a non-monotonic T-dependence of τ with a maximum at 100 °C, indicating a change in the dominant dynamic annealing mechanism at $\sim$ 100 °C (Fig. 5). We have also used the pulsed ion beam method to measure the effective defect diffusion length (L_d) in $3C$-SiC bombarded in the T range of $25-200$ °C with 500 keV Ar ions to relatively large relative bulk disorder levels of $>$ 20 %. Our results have revealed that the L_d slightly increases from $\sim$ 9 nm to $\sim$ 13 nm with increasing T (Fig. 6), suggesting a weak T dependence of the effective concentration of defect traps. The knowledge of the L_d is important not only for understanding the basic mechanisms of radiation damage but also for designing novel radiation-tolerant materials via controlled interaction of mobile defects with surfaces and interfaces since the L_d determines the maximum dimensions of radiation-resistant nanostructures.

2.3 Opportunities for training and professional development

Training. One graduate student (Joseph Wallace) and two postdocs (Bimo Aji and Aiden Martin) are working full time on this project. The project has provided opportunities of one-on-one work (training) of the PI (Kucheyev) with the graduate student and the postdocs.

Professional development. Wallace, Bayu Aji, and Kucheyev participated in the 2015 Spring MRS Meeting held in San Francisco, April 6 − 10, 2015. Kucheyev (PI) gave an oral presentations based on results of this project at Symposium XX: Multiscale Modeling and Experiments on Microstructural Evolution in Nuclear Materials.

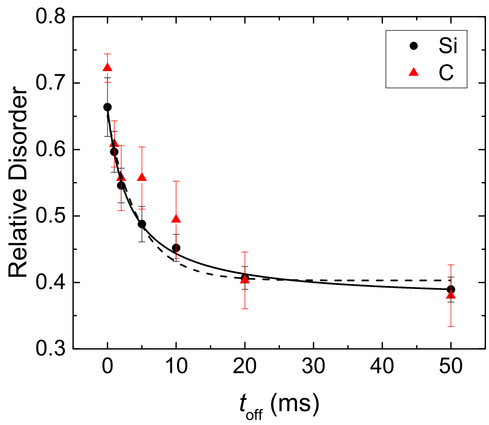

Figure 2: Relative bulk disorder in Si and C sublattices (as indicated in the legend) of $3C$-SiC bombarded at 100 °C with a pulsed beam of 500 keV Ar ions as a function of the passive portion of the beam cycle (t_{off}). Fitting curves of the data for the Si sublattice with the first and second order rate equations are shown by dashed and solid lines, respectively.

2.4 Dissemination of results

The major focus of the second year of this project was on obtaining and documenting results. Results have been disseminated at the international conference listed in the preceding paragraph, in the 6 manuscripts listed under "Specific objectives" above.

2.5 Plan to accomplish the goals of the next reporting period

For Year 3, we plan the following activities:

- Complete measurements of the effect of the collision cascade density (determined by ion mass and energy) on the temperature dependence of the defect interaction time constant (τ) in 3C-SiC and Si.
- Measure the dependence of τ (for Si and SiC) on the level and type of pre-existing disorder.
- Compare defect interaction dynamics in different major polymorphs of SiC ($3C$, $4H$, and $6H$).
- Demonstrate alternative characterization techniques to study defect dynamics by pulsed ion beams.
- Document our results in peer-review journal articles.

3 Participants and other collaborating organizations

3.1 Individuals who have worked on the project

The following five individuals have worked on the project:

Sergei Kucheyev

- Name: Sergei Kucheyev
- Project Role: PI
- Nearest person month worked: 3
- Contribution to Project: Sergei has led the project and participated in all activities of this project
- Funding Support: Funding only from this award
- Collaborated with individual in foreign country: No
- Country(ies) of foreign collaborator: None
- Traveled to foreign country: Yes
- If traveled to foreign country(ies), duration of stay: None

Joseph Wallace

- Name: Joseph Wallace
- Project Role: graduate student
- Nearest person month worked: 12
- Contribution to Project: Joseph has performed pulsed ion beam irradiation and ion beam analysis experiments
- Funding Support: Joseph's salary in Year 2 was paid by the Livermore Graduate Scholar Program (LGSP)
- Collaborated with individual in foreign country: No
- Country(ies) of foreign collaborator: None
- Traveled to foreign country: No
- If traveled to foreign country(ies), duration of stay: None

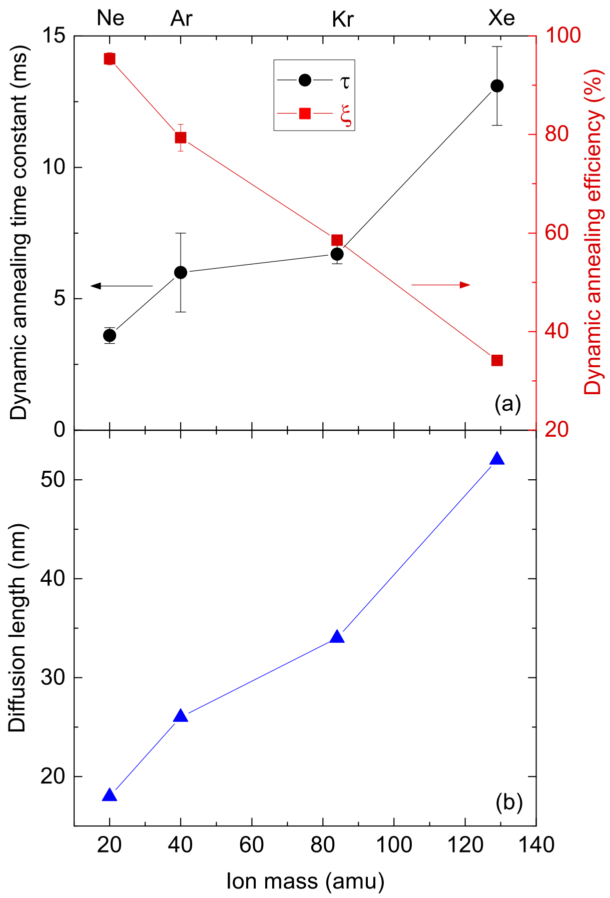

Figure 3: Dependence of [(a), left axis] the dynamic annealing time constant (τ), [(a), right axis] the dynamic annealing efficiency (ξ), and (b) defect diffusion length (L_d) on ion mass for FZ-Si bombarded at room temperature with pulsed beams of 500 keV Ne, Ar, Kr and Xe ions with $t_{on} = 1$ ms and F_{on} values of 2.9, 1.2, 0.5, and 0.3×10^{13} cm^{-2} s^{-1}, respectively.

Bimo Aji

- Name: Bimo Aji (full name: Leonardus Bimo Bayu Aji)
- Project Role: postdoc
- Nearest person month worked: 12
- Contribution to Project: Bimo has performed pulsed ion beam irradiation and ion beam analysis experiments
- Funding Support: Funding only from this award
- Collaborated with individual in foreign country: No
- Country(ies) of foreign collaborator: None
- Traveled to foreign country: No
- If traveled to foreign country(ies), duration of stay: None

Aiden Martin

- Name: Aiden Martin
- Project Role: postdoc
- Nearest person month worked: 6
- Contribution to Project: Aiden has performed irradiation, ion beam analysis, and Raman experiments and rate theory simulations
- Funding Support: Funding only from this award
- Collaborated with individual in foreign country: No
- Country(ies) of foreign collaborator: None
- Traveled to foreign country: No
- If traveled to foreign country(ies), duration of stay: None

Swanee Shin

- Name: Swanee Shin
- Project Role: electron microscopist
- Nearest person month worked: 1
- Contribution to Project: Swanee performed TEM analysis
- Funding Support: Funding only from this award
- Collaborated with individual in foreign country: No
- Country(ies) of foreign collaborator: None
- Traveled to foreign country: No
- If traveled to foreign country(ies), duration of stay: None

3.2 Other organizations that have been involved as partners

Texas A&M University (TAMU)

- Organization Name: Texas A&M University (TAMU)
- Location of Organization: TAMU, College Station, Texas
- Partners contribution to the project: Work of Joseph Wallace (a graduate student from TAMU) at LLNL and advice of Prof. Lin Shao (Joseph's graduate student adviser) from TAMU.
- Financial support: None
- In-kind support: Supervisory guidance of graduate student (Joseph Wallace) by Prof. Lin Shao from TAMU
- Facilities: None in 2015
- Collaborative research: None in 2015
- Personnel exchanges: Joseph Wallace (a student from TAMU) works full time at LLNL in Livermore while being financially supported by the Livermore Graduate Scholar Program (LGSP).
- More detail on partner and contribution (foreign or domestic): LLNL offers a highly competitive fellowship (LGSP) to employ graduate students who are willing to perform full time research at LLNL toward a degree from their degree-granting institution. The salary of Joseph Wallace was fully supported by the LGSP in 2015. Sergei Kucheyev is the LLNL mentor of Joseph Wallace, who worked in 2015 on this NEET pulsed beam project. Since Prof. Lin Shao from TAMU is the graduate adviser of Joseph Wallace, Prof. Shao is also involved in the project although with zero costs to the project.
- Have other collaborators or contacts been involved? No.

4 Impact

4.1 Impact on the development of the principal discipline of the project

This project offers an excellent opportunity to pioneer a new direction of advanced reactor materials characterization techniques and tools. It could establish the pulsed ion beam method as the primary approach to study defect interaction dynamics in nuclear materials. Understanding radiation defect dynamics is vital to the development of new materials for service in advanced nuclear reactors. It is critical if we want to extend our laboratory findings to nuclear material lifetimes and to time scales of geological storage of nuclear waste.

Experimental data on defect interaction dynamics is essential for building realistic and physically sound models to describe the formation of stable radiation defects. Indeed, the level of sophistication of a physical model of damage accumulation increases dramatically if this model is benchmarked against defect dynamics dataset measured in this project (instead of against damage buildup curves). The development of truly predictive tools requires both general understanding of radiation damage processes gained from experiments and specific experimental data to guide such theoretical efforts. This project is both developing a novel experiment approach to gain such understanding of dynamic defect processes and providing benchmark experimental data needed to link theory and modeling to experiments and critically assess radiation damage models.

Moreover, for several decades, many laboratories have been using ion beams to simulate neutron-induced radiation damage in nuclear materials. Such ion beam irradiation experiments inevitably use rastered ion beams, resulting in an effectively pulsed beam operation for any given location on the sample. The shape of the pulse and the pulsed-beam parameters of typical raster irradiation experiments are, however, difficult to control since they depend on the focused beam shape (determining the instantaneous dose rate) and specific rastering conditions. The fundamental understanding of defect dynamics revealed in this project could be used to guide future ion irradiation experiments with rastered ion beams for, at least, first order estimates of the importance of instantaneous and average dose rates.

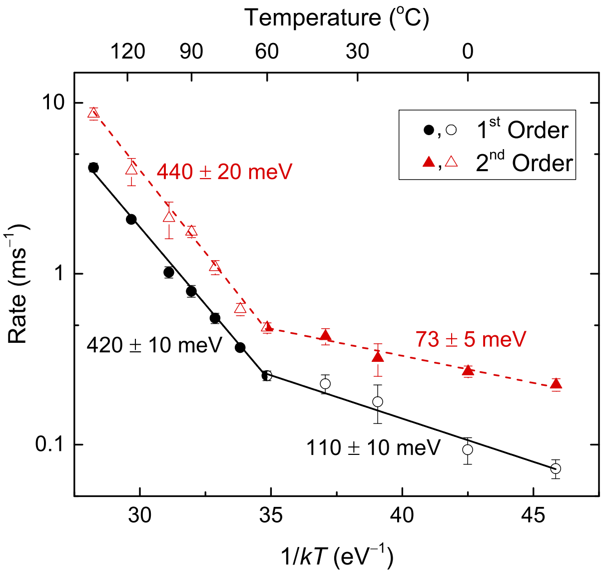

Figure 4: Arrhenius plot of the dynamic annealing rate. Solid symbols are results of the best fit to experimental dependence of the disorder level on t_{off}, which is the second order decay below 60 °C and the first order decay above 60 °C. Straight lines show results of linear fitting, revealing activation energies of 420 (440) meV and 73 (110) meV for the first (second) order fitting above and below 60 °C, respectively.

4.2 Impact on other disciplines

The method developed in this project could be used to study implantation damage effects in semiconductors where ion irradiation is extensively used for doping the material and for dry etching. It could also be used to understand radiation effects in the field of astrophysics.

4.3 Impact on the development of human resources

This project has provided a research opportunity and challenge for Joseph Wallace, a graduate student for TAMU.

4.4 Impact on physical, institutional, and information resources that form infrastructure

This project has resulted in the development and implementation of a variable temperature holder for high-dose pulsed-ion-beam irradiation experiments with accurate dosimetry.

4.5 Impact on technology transfer

Nothing to report.

4.6 Impact on society beyond science and technology

Nothing to report.

4.7 Dollar amount of the awards budget spent in foreign country(ies)

None.

5 Changes/Problems

5.1 Changes in approach and reasons for change

There were no changes in the objectives, scope, or approach during the reporting period.

5.2 Actual or anticipated problems or delays and actions or plans to resolve them

During Year 2, the project encountered no notable delays.

5.3 Changes that have a significant impact on expenditures

The delay with re-hiring a postdoc during Year 1, described in detail in the 2014 Annual Progress Report, has resulted in a significantly lower level of expenditures during Year 1. Expenditures were further reduced by the full time involvement of Joseph Wallace, who is a graduate student with the salary fully paid by the Livermore Graduate Scholar Program (LGSP). See Sec. 3.1 for additional details. The remaining Year 3 of the project will have an increased effort, within the budget, to ensure that the project objectives are met.

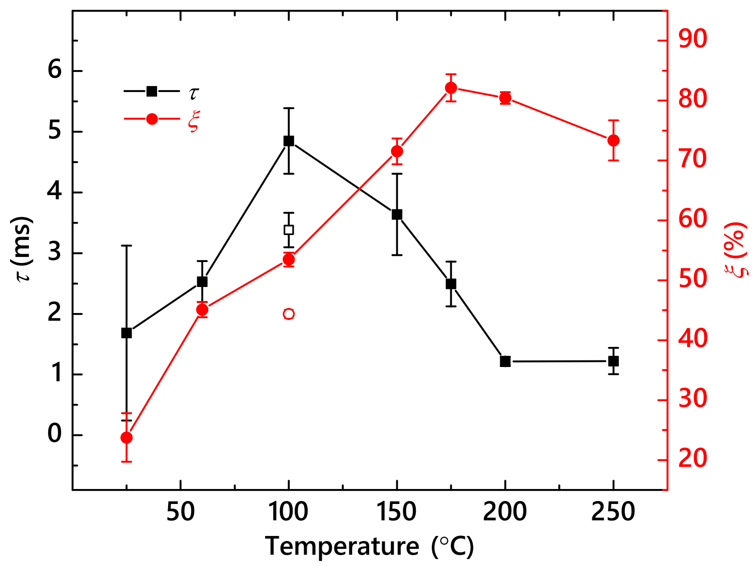

Figure 5: Temperature dependencies of the effective time constant of dynamic annealing (τ) and the dynamic annealing efficiency (ξ) for 4H-SiC bombarded with 500 keV Ar ions with $F_{on} = 1.7 \times 10^{13}$ cm^{-2} s^{-1} and $t_{on} = 1$ ms.

5.4 Significant changes in use or care of human subjects, vertebrate animals, and/or Biohazards

Nothing to report.

5.5 Change of primary performance site location from that originally proposed

Nothing to report.

6 Budgetary information

As of the reporting period end date (December 30, 2015), the total reported costs of the project are $505k.

7 LLNL auspice statement

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

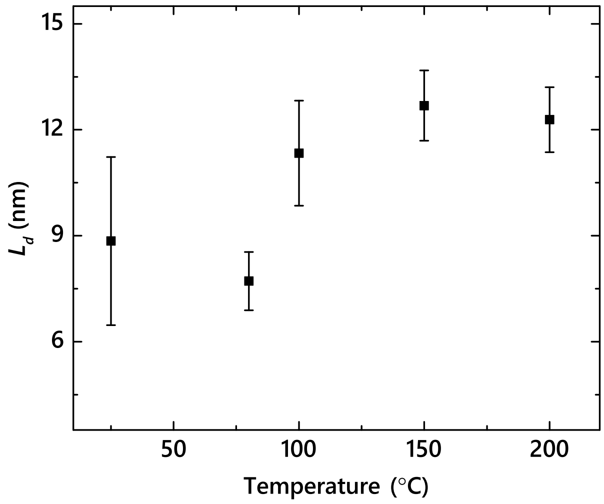

Figure 6: Temperature dependence of the effective defect diffusion length (L_d) in 3C-SiC bombarded with 500 keV Ar ions.