LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

LLNL-JRNL-677429

Temperature dependence of radiation defect dynamics in 4H-SiC

L. B. Bayu Aji, J. B. Wallace, L. Shao, S. O. Kucheyev

September 22, 2015

Scientific Reports

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed 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 Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Temperature dependence of radiation defect dynamics in 4H-SiC

L. B. Bayu Aji*
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

J. B. Wallace
Lawrence Livermore National Laboratory, Livermore, California 94550, USA and Department of Nuclear Engineering, Texas A&M University, College Station, Texas 77843, USA

L. Shao
Department of Nuclear Engineering, Texas A&M University, College Station, Texas 77843, USA

S. O. Kucheyev
Lawrence Livermore National Laboratory, Livermore, California 94550, USA
(Dated: September 21, 2015)

The formation of stable radiation defects in SiC at room temperature and above is dominated by dynamic annealing (DA), whose mechanisms remain poorly understood. Here, we use a pulsed beam method to study DA in 4H-SiC bombarded with 500 keV Ar ions in the temperature range of $25-250$ °C. Results reveal that the DA efficiency monotonically increases with temperature. In contrast, the defect relaxation time constant (and, hence, the DA rate) exhibits a non-monotonic temperature dependence with a maximum of ~ 5 ms at ~ 100 °C, indicating a change in the dominant defect interaction mechanism at this temperature. For the $\sim 150-250$ °C range, the dominant DA process has an activation energy of 0.25 ± 0.05 eV.

Silicon carbide (SiC) is an important material for electronics[1] and nuclear materials technologies.[2] For both of these applications, a fundamental understanding of radiation damage processes is desirable, particularly for practically-relevant irradiation at room temperature and above. For such irradiation conditions, all three main polymorphs of SiC (3C, 4H, and 6H) exhibit pronounced dynamic annealing (DA),[3–13] which refers to migration, recombination, and clustering of radiation-generated point defects *during* irradiation. The degree of DA increases with increasing sample temperature (T). This is evidenced as a reduction in the level of stable post-irradiation disorder with increasing T (with all the other irradiation conditions kept constant) or as an increase in the ion dose required to reach a certain level of disorder with increasing T.[3–6,8,10,13] The DA also manifests as a dose rate dependence of damage (with all the other irradiation conditions being constant).[9,11–13] However, mechanisms of DA in SiC remain elusive. Indeed, physically very different models of point defect interaction can describe the same experimental T-dependencies of the amorphization dose.[14] More sophisticated measurements of radiation defect dynamics are needed to unravel the underlying mechanisms.

We have recently demonstrated[9,16,17,23] that details of DA can be accessed in pulsed beam experiments when ion dose is delivered as a train of equal square pulses with a duration of t_{on} and an instantaneous dose rate of F_{on} separated by a passive portion of the beam duty cycle of t_{off} (see the inset in Fig. 1). In particular, the dependence of the amount of stable post-irradiation disorder on t_{off} reveals the characteristic time constant of DA (τ)[16] and, hence, the DA rate. We have successfully applied such a pulsed-beam method to measure τ in Si at room temperature and in 3C-SiC at 100 °C.[9,16,23] Here, we use pulsed beams to study the $\tau(T)$ dependence in 4H-SiC bombarded with 500 keV Ar ions in the T range of $25-250$ °C. Interestingly, results reveal a non-monotonic $\tau(T)$ dependence with a maximum at ~ 100 °C, reflecting a change in the dominant DA mechanism at ~ 100 °C.

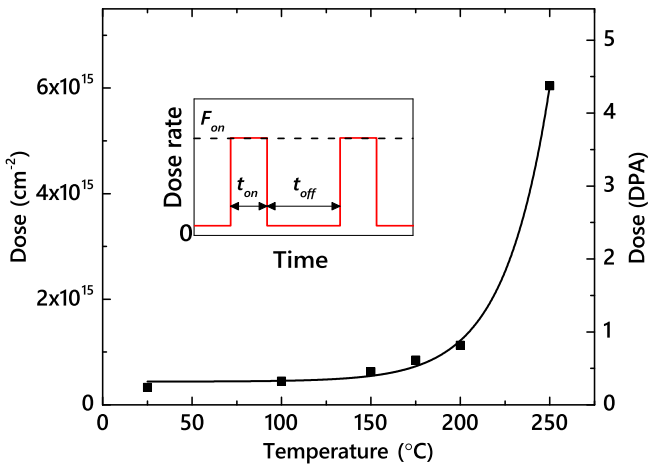

FIG. 1: (Color online) Temperature dependence of the ion dose required to reach a damage level of 0.7 in 4H-SiC bombarded with a continuous beam (i.e., $t_{off} = 0$) of 500 keV Ar ions with a dose rate of 1.7×10^{13} cm^{-2} s^{-1}. The solid line is an exponential fit to the data. The inset is a schematic of the time dependence of the instantaneous dose rate for pulsed beam irradiation, defining t_{on}, t_{off}, and F_{on}.

High purity semi-insulating (0001) 4H-SiC single crystals (with a resistivity of $\gtrsim 10^5$ Ω cm), obtained from

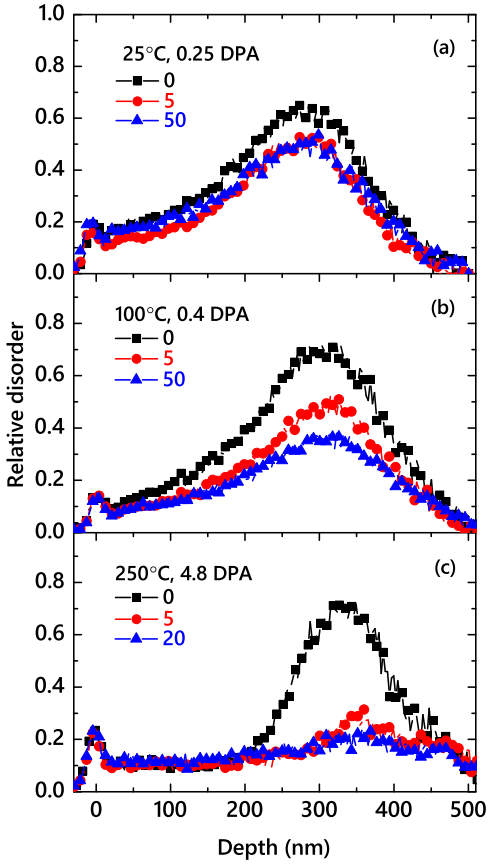

FIG. 2: (Color online) Selected depth profiles of relative disorder in 4H-SiC bombarded with a pulsed beam of 500 keV Ar ions with $F_{on} = 1.7 \times 10^{13}$ cm^{-2} s^{-1}, $t_{on} = 1$ ms, and different t_{off} values, given in legends (in units of ms), at different temperatures and total doses, also shown in legends. For clarity, only every 5th experimental point is depicted.

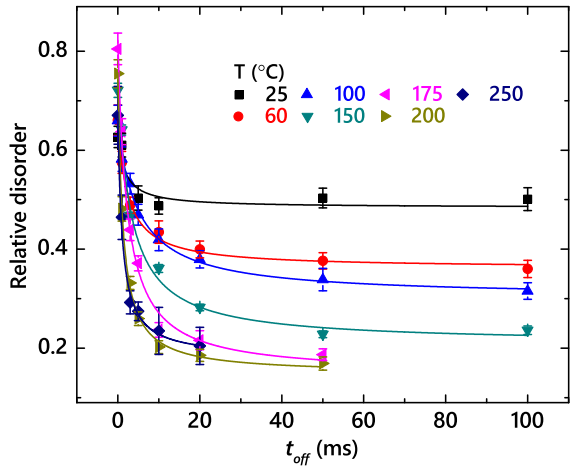

FIG. 3: (Color online) Relative bulk disorder in 4H-SiC bombarded with a pulsed beam of 500 keV Ar ions with $F_{on} = 1.7 \times 10^{13}$ cm^{-2} s^{-1} and $t_{on} = 1$ ms as a function of the passive portion of the beam duty cycle (t_{off}) at different temperatures given in the legend (in units of °C). Fitting curves of the data with the second order decay equation are shown by solid lines.

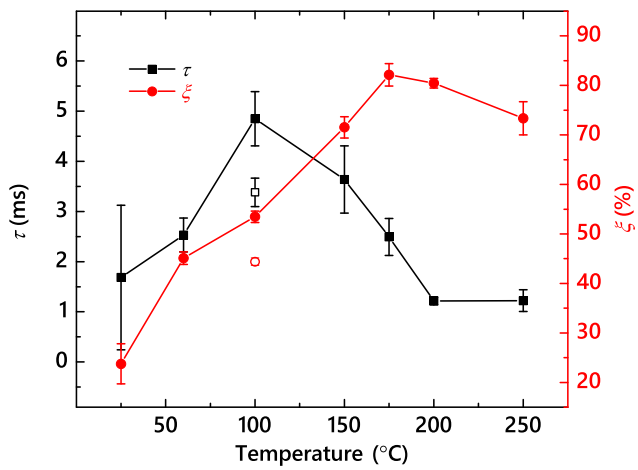

FIG. 4: (Color online) Closed symbols: temperature dependencies of the effective time constant of DA (τ) and (b) the DA efficiency (ξ) for 4H-SiC bombarded with 500 keV Ar ions with $F_{on} = 1.7 \times 10^{13}$ cm^{-2} s^{-1} and $t_{on} = 1$ ms. Open symbols show data points for 3C-SiC irradiated at 100 °C with 500 keV Ar ions with $F_{on} = 1.9 \times 10^{13}$ cm^{-2} s^{-1} and $t_{on} = 1$ ms, taken from Ref. 9.

Cree, Inc., were bombarded with 500 keV Ar ions at 7° off the [0001] direction in the T range of 25 − 250 °C.[18] To improve thermal contact, the samples were attached to the Ni sample holder with conductive Ag paste. The sample holder temperature was monitored with a chromel/alumel thermocouple (with an accuracy of ±1 °C). All irradiations were performed in a broad beam mode.[16] Ion beam pulsing was achieved by applying high voltage pulses to a pair of parallel plates deflecting the beam in the vertical direction off the final beam defining aperture so that the total dose was split into a train of equal pulses each with an F_{on} of $\sim (1.7 \pm 0.05) \times 10^{13}$ cm^{-2} s^{-1} and duration $t_{on} = 1$ ms. The adjacent pulses were separated by time t_{off}, which was varied between 1 and 100 ms. A more detailed description of the experimental arrangement can be found elsewhere.[9,16,17,23]

The dependence of lattice damage on t_{off} was studied *ex-situ* at room temperature by ion channeling. Depth profiles of lattice disorder in the Si sublattice were measured with 2 MeV ^{4}He$^+$ ions incident along the [0001] direction and backscattered into a detector at 164° relative to the incident beam direction. Spectra were analyzed with one of the conventional algorithms[19] for extracting the effective number of scattering centers (referred to below as "relative disorder"). Values of averaged bulk disorder (n) were obtained by averaging depth profiles of relative disorder over 10 channels (∼25 nm) centered on the bulk damage peak maximum. Error bars of n are standard deviations.

Figure 1 shows an exponential T dependence of the dose required to achieve $n = 0.7$ for continuous beam

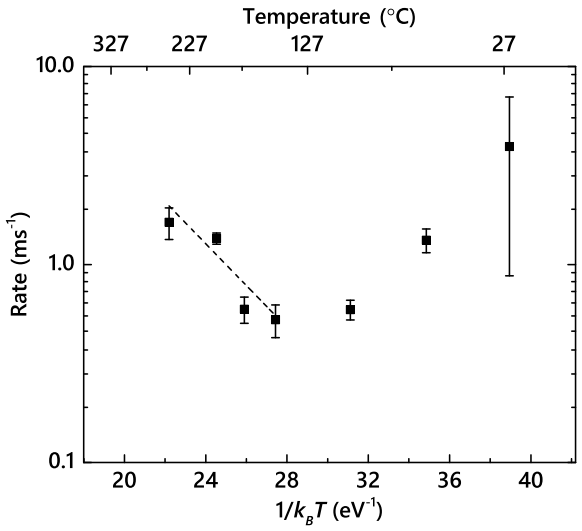

FIG. 5: (Color online) Arrhenius plot of the DA rate defined as $1/(\tau(n(0) - n_{inf}))$ for a second order decay process. The straight line shows results of linear fitting, revealing an activation energy of 0.25 eV for temperatures above 100 °C.

irradiation (i.e., $t_{off} = 0$). Such a dose increases from 0.2 to 4.3 displacements per atom (DPA)[20–22] when T is increased from 25 to 250 °C, reflecting the thermally activated nature of DA processes. An increase in the dose required to reach a certain disorder level with increasing T is expected since, at higher Ts, point defects have higher diffusivity, resulting in a higher rate of vacancy-interstitial recombination. The exponential T dependence is consistent with a number of previous damage buildup studies of 3C-SiC, 6H-SiC, and 4H-SiC.[3–8,10,13,15] Based on damage buildup data such as shown in Fig. 1, we have chosen ion doses for pulsed beam experiments at different Ts so that, for $t_{off} = 0$ (i.e., continuous beam irradiation), n is in the range of $0.6 - 0.8$.

Figure 2 shows representative depth profiles of relative disorder for bombardment of 4H-SiC with continuous and pulsed beams at Ts of 25, 100, and 250 °C. It is seen that, for all three Ts shown, depth profiles are bimodal, with the first small peak at the sample surface and the second major peak in the crystal bulk. The bulk peak (with a height of n) is centered on $\sim$ 300 nm, which corresponds to the maximum of the nuclear energy loss profile for 500 keV Ar ions.[20] It is also seen from Fig. 2 that n decreases with increasing t_{off} for all three Ts. We have found such a reduction in n with increasing t_{off} in all our measurements at different Ts, which is also consistent with our previous pulsed beam studies of Si and 3C-SiC.[9,16] Figure 2 further shows that the degree of reduction in n with increasing t_{off} increases dramatically with increasing T. For example, for $T = 250$ °C [Fig. 2(c)], an increase of t_{off} from 0 to 5 ms results in an $\sim$ 2.5-fold reduction in n. In contrast, the damage level at the sample surface is independent of t_{off}, which is consistent with previous findings for Si and 3C-SiC.[9,16]

Figure 3 summarizes $n(t_{off})$ dependencies for all the Ts of this study ($25 - 250$ °C). It reveals that n monotonically decreases with increasing t_{off}. Solid lines in Fig. 3 are fits of the data via the Marquardt-Levenberg algorithm with second order decay equation ($n(t_{off}) = n_\infty + \frac{n(0)-n_\infty}{1+\frac{t_{off}}{\tau}}$). Here, n_∞ is relative disorder for $t_{off} >> \tau$. We have found that all the $n(t_{off})$ dependencies from Fig. 3 obey the second order decay better than the first order decay.

The $\tau(T)$ dependence is shown in Fig. 4, revealing a non-monotonic behavior, when τ first increases with T, reaches a maximum at 100 °C, followed by a monotonic decrease for $T \gtrsim 100$ °C. Also plotted in Fig. 4 is the T dependence of the DA efficiency (ξ), which we define as before:[16] $\xi = \frac{n(0)-n_\infty}{n(0)}$. As discussed in detail recently,[23] for our choice of F_{on} and t_{on}, ξ is the magnitude of the dose rate effect; i.e., the difference between n for continuous beam irradiation with dose rates of $F = F_{on}$ and $F \to 0$. It is seen from Fig. 4 that, in contrast to the $\tau(T)$ dependence, ξ increases monotonically with T. Above $\sim$ 175 °C, ξ saturates at $\sim$ 80%. Hence, both $\tau(T)$ and $\xi(T)$ dependencies of Fig. 4 are non-trivial, reflecting the details and the complexity of defect interaction processes.

Values of τ revealed by Fig. 4 are in the range of $\sim 1-5$ ms. These are orders of magnitude larger than the predictions of molecular dynamics (MD) and kinetic Monte Carlo simulations discussed in our recent report,[9] highlighting the well-known limitations of MD to model long-time defect evolution and the currently limited understanding of radiation defect dynamics in SiC. Interestingly, Fig. 4 also shows one data point available for 3C-SiC at 100 °C (taken from our recent work[9]), revealing a larger τ for 4H-SiC than for 3C-SiC. This finding is not unexpected, given that DA processes depend on the type and properties of lattice-structure-specific point and extended defects.[9,10] Further systematic studies of the $\tau(T)$ dependencies for 3C-SiC and 6H-SiC will be interesting and could reveal the similarities and differences in DA of the three main SiC polymorphs.

Figure 4 unambiguously shows that qualitatively different defect relaxation processes are operative above and below a transition temperature (T_r) of $\sim$ 100 °C. Such a T_r of 100 °C is not evident from the T dependence of the damage buildup (as shown in Fig. 1 and in numerous previous studies[3–6,8,10,13]). Neither it is evident from the $\xi(T)$ dependence that, as mentioned above, reflects the T dependence of the dose rate effect, also studied previously in traditional continuous (or unintentionally scanned due to beam rastering) beam measurements of the dose rate effect.[11,13] A special role of $T \sim 100$ °C has, however, been noted in a number of previous studies of all the three main polymorphs of SiC: 4H-SiC,[12] 6H-SiC,[24–27] and 3C-SiC,[28–31] evidenced either as the onset of post-irradiation defect annealing,[24–26,28–30] as a rapid decrease in the cross-section of damage production,[27] as a qual-

itative change in the radiation resistance of nanocrystalline SiC,[31] or as a maximum of the concentration of open-volume defects monitored by positron annihilation spectroscopy.[12]

The increase in τ, and a corresponding decrease in the DA rate, for $T \lesssim 100$ °C suggests the dominance of a thermally activated process of defect clustering (responsible for the formation of stable lattice defects). At $T \gtrsim 100$ °C, a thermally activated process of defect recombination appears to dominate. In order to better understand the mechanism of DA for Ts above the $T_r \sim 100$ °C, in Fig. 5, we replot the $\tau(T)$ dependence from Fig. 4 in Arrhenius coordinates, with the DA rate defined as $\frac{1}{\tau(n(0)-n_\infty)}$,[32] and with kT having the usual meaning. An Arrhenius regime is seen in Fig. 5 for the temperature range of $150-250$ °C. Linear fitting of the data gives an activation energy (E_a) and a pre-exponential factor of 0.25 ± 0.05 eV and $(5.23 \pm 0.62) \times 10^2$ Hz, respectively. This E_a value is much smaller than an E_a of 1.3 eV obtained by Kuznetsov et al.[11] by the analysis of the T-dependence of the dose rate effect in the T range of $20-225$ °C based on the method proposed by Schultz and co-workers.[33] This is equivalent to the analysis of the $\xi(T)$ dependence of Fig. 4. Such an apparent inconsistency in E_a could be attributed to limitations of the method of Schultz et al.[33] Indeed, ξ (i.e., the magnitude of the dose rate effect) reflects the fraction of ballistically-generated Frenkel defects that participate in DA processes for any given F_{on} rather than the *rate* of defect interaction. Our E_a of ~ 0.25 eV is consistent with E_a values for $6H$-SiC reported by Weber et al.[5,34] from the analysis of the T dependence of the amorphization dose based on the empirical model of Morehead-Crowder.[35] Future theoretical studies of point defect migration and interaction processes in $4H$-SiC are currently needed for better understanding DA mechanisms in SiC.

In conclusion, we have used the pulsed beam method to measure the temperature dependence of the effective time constant of DA in $4H$-SiC bombarded with 500 keV Ar ions in the temperature range of $25-250$ °C. Results have revealed a non-monotonic T-dependence of τ with a maximum at 100 °C, indicating a change in the dominant DA mechanism at ~ 100 °C. The Arrhenius regime in the T range of $150-250$ °C is described by an activation energy of ~ 0.25 eV.

This work was performed under the auspices of the US DOE by LLNL under contract DE-AC52-07NA27344. L.S. thanks the support from NSF Grant No. 0846835, and J.B.W. acknowledges the LLNL Lawrence Scholar Program for funding.

---

* Electronic address: bayuaji1@llnl.gov

[1] A. Fissel, Phys. Rep. **379**, 149 (2003).

[2] L. L. Snead, T. Nozawa, Y. Katoh, T. S. Byun, S. Kondo, and D. A. Petti, J. Nucl. Mater. **371**, 329 (2007).

[3] H. Inui, H. Mori, H. Fujita, Philos. Mag. B **61**, 107 (1990).

[4] H. Inui, H. Mori, A. Suzuki, and H. Fujita, Philos. Mag. B **65**, 1 (1992).

[5] W. J. Weber, L. M. Wang, N. Yu, N. J. Hess, Mater. Sci. Eng. A **253**, 62 (1998).

[6] S. J. Zinkle and L. L. Snead, Nucl. Instr. and Meth. B **116**, 92 (1996).

[7] E. Wendler, T. Bierschenk, W. Wesch, E. Friedland, and J. B. Malherbe, Nucl. Instr. and Meth. B **268**, 2996 (2010).

[8] A. Matsunaga, C. Kinoshita, K. Nakai, and Y. Tomokiyo, J. Nucl. Mater. **179-181**, 457 (1991).

[9] J. B. Wallace, L. B. Bayu Aji, L. Shao, and S. O. Kucheyev, Appl. Phys. Lett. **106**, 202102 (2015).

[10] J. B. Wallace, L. B. Bayu Aji, T. T. Li, L. Shao, and S. O. Kucheyev, J. Appl. Phys. **118**, 105705 (2015).

[11] A. Y. Kuznetsov, J. Wong-Leung, A. Hallen, C. Jagadish, and B. G. Svensson, J. Appl. Phys. **94**, 7112 (2003).

[12] J. Slotte, K. Saarinen, M. S. Janson, A. Hallen, A. Y. Kuznetsov, B. G. Svensson, J. Wong-Leung, and C. Jagadish, J. Appl. Phys. **97**, 033513 (2005).

[13] Y. Zhang, W. J. Weber, W. Jiang, C. M. Wang, V. Shutthanandan, and A. Hallen, J. Appl. Phys. **93**, 1954 (2003).

[14] N. Swaminathan, D. Morgan, and I. Szlufarska, J. Nucl. Mater. **414**, 431 (2011).

[15] We, however, note that the critical amorphization temperature, revealed by Fig. 1, is larger than those reported in the previous studies of SiC (Refs. 3–8,13) due to a larger dose rate used in the present work. As we discussed in detail in our recent systematic study of the damage buildup in $3C$-SiC,[10] this highlights the dominant role of DA in the formation of stable post-irradiation damage in SiC at elevated Ts.

[16] M. T. Myers, S. Charnvanichborikarn, L. Shao, and S. O. Kucheyev, Phys. Rev. Lett. **109**, 095502 (2012).

[17] S. Charnvanichborikarn, M. T. Myers, L. Shao, and S. O. Kucheyev, J. Phys. Condens. Matter **25**, 162203 (2013).

[18] 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.

[19] K. Schmid, Radiat. Eff. **17**, 201 (1973).

[20] The depth profile of vacancies was calculated with the TRIM code (version SRIM-2013.00, full cascade calculations)[21] with an atomic concentration of SiC of 9.64×10^{22} atoms cm^{-3} (Ref. 2) and threshold energies for atomic displacements of 20 and 35 eV for C and Si sublattices, respectively.[22] To convert to DPAs (at the depth corresponding to the maximum of the nuclear energy loss profile), ion doses in 10^{14} Ar ions cm^{-2} are multiplied by 0.0898.

[21] J. F. Ziegler, M. D. Ziegler, and J. P. Biersack, Nucl. Instr. and Meth. B **268**, 1818 (2010).

[22] R. Devanathan, W. J. Weber, and F. Gao, J. Appl. Phys. **90**, 2303 (2001).

[23] J. B. Wallace, S. Charnvanichborikarn, L. B. Bayu Aji, M. T. Myers, L. Shao, and S. O. Kucheyev, Unpublished.

[24] R.C. Barklie, M. Collins, B. Holm, Y. Pacaud, and W. Skorupa, J. Electron. Mater. **26**, 137 (1997).

[25] S. Dannefaer, and D. Kerr, Diam. Relat. Mater. **13**, 157 (2004).

[26] A. A. Rempel, H. -E. Schaefer, Appl. Phys. A **61**, 51 (1995).
[27] W. Jiang, Y. Zhang, and W. J. Weber, Phys. Rev. B **70**, 165208 (2004).
[28] H. Itoh, N. Hayakawa, I. Nashiyama, and E. Sakuma, J. Appl. Phys. **66**, 4529 (1989).
[29] H. Itoh, M. Yoshikawa, I. Nashiyama, H. Okumura, S. Misawa, and S. Yoshida, J. Appl. Phys. **77**, 837 (1995).
[30] A. Hallen, M. S Janson, A. Yu Kuznetsov, D. Aberg, M. K Linnarsson, B. G Svensson, P. O Persson, F. H. C Carlsson, L. Storasta, J. P Bergman, S. G Sridhara, Y. Zhang, Nucl. Instr. and Meth. B **186**, 186 (2002).
[31] L. Jamison, K. Sridharan, S. Shannon, and I. Szlufarska, J. Mater. Res. **29**, 2871 (2014).
[32] For the second order decay process ($\frac{d(n-n_\infty)}{dt} = -R(n - n_\infty)^2$), the decay time constant (τ) depends on the initial concentration of mobile defects, and the decay rate is $R = \frac{1}{\tau(n(0)-n_\infty)}$.
[33] P. J. Schultz, C. Jagadish, M. C. Ridgway, R. E. Elliman, and J. S. Williams, Phys. Rev. B **44**, 9118 (1991).
[34] W. J. Weber, W. Jiang, S. Thevuthasan, Nucl. Instr. and Meth. B **166**, 410 (2000).
[35] F. F. Morehead, and B. L. Crowder, Radiat. Eff. **6**, 27 (1970).