Appendix A: Recombination rate in mean concentration fields

Starting from uniform distributions of vacancies and self-interstitial atoms (SIAs), their concentrations can be represented by spatially independent $c_0^i$ and $c_0^v$. The probability of having an SIA (vacancy) at a lattice site is therefore given by $c_0^i$ ($c_0^v$). To derive the recombination rate, we first consider the recombination of a mobile SIA in a uniform field of vacancies. This gives the recombination rate induced by SIA diffusion. The recombination caused by vacancy diffusion can be treated symmetrically, and the summation of both gives the total recombination rate. Two possible assumptions can be used for the derivation. The first assumes that the background vacancy concentration is static without evolving. Following this, the recombination probability for the SIA to revisit a site is zero. The accumulated recombination probability is thus proportional to the total volume the SIA visits [1]. The second assumes a constant vacancy concentration, but the field is dynamically evolving, e.g., by defect production, diffusion and annihilation. Following this, the SIA has the same probability to be recombined every time it visits a site. The accumulated recombination probability is proportional to the number of hops the SIA performs. In this work, we follow the second assumption. As will be shown in the Appendix C, these two assumptions give different expressions of recombination rates when SIA performs one-dimensional (1D) diffusion. In bcc metals such as Mo and W, SIAs diffuse much faster than vacancies. At the first glance, this seems suggest that vacancies should be treated as being static when SIAs are diffusing. However, due to its much higher diffusivity, the SIA concentration is usually much lower than that of vacancy when defect sinks exist. When the system is approaching steady state, $c_i D_i \approx c_v D_v$; $D_i$ and $D_v$ are the SIA and vacancy diffusivities, respectively. As the evolving rates of defect fields due to diffusion depend on both the concentrations and the diffusivities, it is reasonable to think that under irradiation the vacancy field is dynamically evolving with a rate similar to that for the SIA field, rather than being static. As an attempt to justify the assumption, several atomic kinetic Monte Carlo (AKMC) simulations are carried out with $c_i D_i = c_v D_v$.

In such a condition, the second assumption is found to be more suitable for formulating recombination.

Considering an SIA with a recombination radius $R_{rec}$, within which there are $N_{rec}$ neighboring sites around the SIA. After hopping for one atomic jump, there will be $N_{new}$ atomic sites entering its new recombination sphere in 3D (or circle in 2D, as shown in Fig. S1 as a schematic). In the dilute concentration regime, the probability of this SIA being annihilated by recombination after one atomic hop is just the probability of having one vacancy entering its recombination sphere, given by:

$$p = N_{new} c_0^v$$  \hspace{1cm} (A1)

The probability of the SIA to survive after one hop is $q = 1 - p$. Accordingly, the probability for this SIA to be recombined after the second hop will be $qp$, and that after the $n^{th}$ hopping is $q^{n-1}p$. Note that with the assumption used here, the probability of being recombined is the same for an SIA to hop to a new site or to hop back to its

FIG. S1: (Color online) 2D schematic of the recombination radius of an SIA. The position of the SIA is represented by the red circle, and its neighboring sites by blue squares. The solid symbols are neighbors of the original site, and the open ones after one atomic hop. In this case, $N_{rec} = 4$ and $N_{new} = 3$. 

previous site. The mean free life of an SIA (defined as the mean number of hops of a SIA before being recombined) subject to recombination (without considering sink absorption) can be derived as:

\[ t^I = \lim_{n \to \infty} (p \sum_{j=1}^{n} (jq^{-1})) = 1/p = 1/(N_{new}c^0_v) \]  

(A2)

This corresponds to a mean free path of \( \sqrt{1/p\lambda_0} \), which is the average distance an SIA diffuses before being recombined, with \( \lambda_0 \) being the length of each atomic hop. Symmetrically, \( t^I = 1/(N_{new}c^0_i) \). Recall that the probability of having an SIA at an atomic site is \( c^0_i \). The average recombination rate caused by SIA diffusion can then be derived as:

\[ K_{iv}^i c^0_i c^0_v = c^0_i / (t^I + dt) = N_{new}c^0_i c^0_v \omega_i \]  

(A3)

Where \( dt \) is the hopping time for each hop, and \( dt = 1/\omega_i \) with \( \omega_i \) being the hopping frequency of SIA. The total recombination rate with both SIA and vacancy diffusion is:

\[ K_{iv}^i c^0_i c^0_v = (K_{iv}^i + K_{iv}^v)c^0_i c^0_v = N_{new}c^0_i c^0_v (\omega_i + \omega_v) \]  

(A4)

With the assumption used here, Eqs.A3&A4 hold for both 1D and 3D SIA diffusion. Vacancies are assumed to have 3D diffusion. For 3D SIA diffusion, \( D_i = \omega_i \lambda^2_0 / 6 \), and Eq.A3 gives \( K_{iv}^i = 6N_{new}D_i / \lambda^2_0 \). This is consistent with the recombination rate given in the book [2] (Eq. 5.58 on page 210), \( K_{iv}^i = Z_v \Omega D_i / \lambda^2_0 \). \( Z_v \) is the prefactor and it is dependent on the crystal structure. Note that in Was et al. [2] the atomic volume \( \Omega \) needs to be included because the concentration has a unit of per volume there. Minor differences may exist in the prefactor. While for 1D SIA diffusion, a different expression, \( K_{iv}^i \sim D_i c^0_i / \lambda^2_0 \), has been used in the literature [3]. This follows the expression derived for the annihilation of 1D diffusing SIA clusters by static traps [4]. As will be shown in the Appendix C, the assumption that the vacancy field is dynamically evolving seems more suitable for the case under irradiation.

Appendix B: Recombination probability with small perturbation and SIA diffusion anisotropy

Now consider spatially dependent concentrations. Again, we will consider the recombination caused by SIA diffusion only. With position dependency, the probability of having an SIA at the atomic site \( r \) is now \( c_i(r) \). After one atomic hop with a hopping vector \( \lambda_1 \), its position becomes \( r + \lambda_1 \). The recombination probability after one hop is then:

\[ p_1(r) = N_{new}c_i(r)c_v(r + \lambda_1) \]  

(B1)

with a survival probability of \( q_1 \). Note that now the probability of having an SIA at site \( r \) is already included. Accordingly, the probability of the SIA to survive \( j - 1 \) hops is \( \prod_{m=1}^{j-1} q_m \), and the probability of it being recombined after the \( j^{th} \) hop is:

\[ p_j(r) = N_{new}c_i(r)c_v(r + \lambda_j) \prod_{m=1}^{j-1} q_m \]  

(B2)

Here \( \lambda_j \) represents the location of the SIA after \( j \) hops in reference to its original position \( r \). \( q_m \) represents the probability of the SIA surviving the \( m^{th} \) hop without being recombined, and

\[ q_m = 1 - N_{new}c_i(r)c_v(r + \lambda_m) \]  

(B3)

Therefore the accumulated recombination probability from the first to the \( j^{th} \) hop is

\[ P_j(r) = \sum_{l=1}^{j} p_l = \sum_{l=1}^{j} N_{new}c_i(r)c_v(r + \lambda_l) \prod_{m=1}^{l-1} q_m \]  

(B4)
Now consider a small perturbation in a mean-field vacancy concentration \(c_0^i\) expressed as \(\delta_i \exp(i k \cdot r)\). Due to the nature of mutual recombination, this will induce a simultaneous anti-phase perturbation in the SIA concentration \(c_0^i\), which can be denoted as \(-\delta_i \exp(i k \cdot r)\) (i.e. \(\delta_i \exp(i (k \cdot r + \pi))\)). Here \(k\) is the wave vector for the perturbation. \(\delta_i\) and \(\delta_v\) are the amplitudes of the perturbations on top of \(c_0^i\) and \(c_0^v\), respectively. Therefore, the recombination probability at the \(j\)th hop (Eq. B2) becomes:

\[
p_j(r) = N_{\text{new}}(c_0^i - \delta_i \exp(i k \cdot r))(c_0^v + \delta_v \exp(i k \cdot (r + \lambda_j))) \prod_{m=1}^{j-1} q_m
\]

\[
= N_{\text{new}}(c_0^i c_0^v + \delta_i \delta_v \exp(i k \cdot (r + \lambda_j)) - c_0^i \delta_i \exp(i k \cdot r) - \delta_i \delta_v \exp(i k \cdot r) \times \exp(i k \cdot (r + \lambda_j))) \prod_{m=1}^{j-1} q_m \quad \text{(B5)}
\]

The expected recombination probability at the \(j\)th hop in the entire domain (averaged over \(r\)) is then

\[
< p_j > = < N_{\text{new}} \prod_{m=1}^{j-1} q_m > < c_0^i c_0^v + \delta_i \delta_v \exp(i k \cdot (r + \lambda_j)) - c_0^i \delta_i \exp(i k \cdot r) - \delta_i \delta_v \exp(i k \cdot r) \times \exp(i k \cdot (r + \lambda_j)) >. \quad \text{(B6)}
\]

To obtain Eq.B6 it is assumed that each hopping step is independent of others. When the domain size is much larger than the wave length, we have

\[
< c_0^i \delta_v \exp(i k \cdot (r + \lambda_j)) >, = < c_0^i \delta_i \exp(i k \cdot r) >, = 0 \quad \text{(B7)}
\]

and

\[
< \delta_i \delta_v \exp(i k \cdot r) \times \exp(i k \cdot (r + \lambda_j)) >, = \frac{1}{2} \delta_i \delta_v < \exp(i k \cdot (2r + \lambda_j)) + \exp(i k \cdot \lambda_j) >, = \frac{1}{2} \delta_i \delta_v < \exp(i k \cdot \lambda_j) >. \quad \text{(B8)}
\]

This gives

\[
< p_j > = < N_{\text{new}} \prod_{m=1}^{j-1} q_m > < c_0^i c_0^v - \frac{1}{2} \delta_i \delta_v \exp(i k \cdot \lambda_j) >. \quad \text{(B9)}
\]

Again, since the recombination probability at each hop is independent of others, we have

\[
< p_j > = N_{\text{new}} \prod_{m=1}^{j-1} < q_m > < c_0^i c_0^v > < \exp(i k \cdot \lambda_j) > = N_{\text{new}} q_0^{j-1} (c_0^i c_0^v - \frac{1}{2} \delta_i \delta_v < \exp(i k \cdot \lambda_j) >) \quad \text{(B10)}
\]

Where \(q_0 = < q_m >\) is the average surviving probability at each step, and it is \(1 - (N_{\text{new}} c_0^i)^{-1}\). As shown in Eq.B10, now the recombination probability is independent of \(r\). On the other hand, it is dependent on both SIA diffusion properties via \(\lambda_j\) and the perturbation wave vector \(k\). Without perturbation, the second term in the parenthesis in Eq.B10 vanishes and the equation converges to the mean field consideration. For the stochastic nature of SIA diffusion, another averaging procedure is needed over \(\lambda_j\):

\[
< p_j > = N_{\text{new}} q_0^{j-1} (c_0^i c_0^v - \frac{1}{2} \delta_i \delta_v < \exp(i k \cdot \lambda_j) >) \quad \text{(B11)}
\]

In this case of 3D random walk, \(\lambda_j\) is spherically symmetrical, so that the expected value of < \(\exp(i k \cdot \lambda_j) >\lambda_j\) depends only on the length of \(k\), and it approaches zero when \(|k \cdot \lambda_j| >> 1\) with non-zero \(k\). When SIA performs anisotropic diffusion, \(p_j\) can now be dependent on both the length and direction of \(k\) via the term < \(\exp(i k \cdot \lambda_j) >\lambda_j\). For 1D and 2D SIA diffusion, evident minimums exist for wave vectors that satisfies \(i k \cdot \lambda_j = 0\) for all \(\lambda_j\). For example, when SIA performs 1D diffusion along \([1 \ 0]\) in a 2D domain, perturbation waves with wave vectors along \([0 \ 1]\) are subject to the lowest recombination flux, and are thus favored to grow over other waves with the same wave numbers, as shown in Fig.2 in the main text.
For arbitrary diffusion anisotropy, numerical calculations can be carried out to explore the existence of favorable wave directions. From Eq.B4, the accumulated recombination probability can be defined as:

$$P_j = \sum_{m=1}^{j} N_{new} q_0^{m-1} (c_i^0 c_v^0 - \frac{1}{2} \delta_i \delta_v < \exp(ik \cdot \lambda_m) >_{\lambda_m})$$  \hspace{1cm} (B12)$$

An average recombination rate can be derived using the expected diffusion time for $j$ hops, $\Delta t = \sum_{m=1}^{j} q_0^{m-1} / \omega_i$, as:

$$< K^i_{iv} c_ic_v > = N_{new} c_i^0 c_v^0 \omega_i - \frac{1}{2} N_{new} \omega_i \delta_i \delta_v \sum_{m=1}^{j} q_0^{m-1} < \exp(ik \cdot \lambda_m) >_{\lambda_m} / \sum_{m=1}^{j} q_0^{m-1}$$  \hspace{1cm} (B13)$$

This represents the average recombination rate when $j$ approaches the mean free life. As only the anisotropy is of interest and it is contained only in the second term, only the second term in Eq.B13 is calculated and normalized as:

$$-\sigma_{k\lambda} = - \sum_{m=1}^{j} q_0^{m-1} < \exp(ik \cdot \lambda_m) >_{\lambda_m} / \sum_{m=1}^{j} q_0^{m-1}$$  \hspace{1cm} (B14)$$

which has a minimum of -1 when $ik \cdot \lambda_j = 0$ is satisfied for all $\lambda_j$. Because of the stochastic nature of atomic hopping, we have

$$< \exp(ik \cdot \lambda_m) >_{\lambda_m} = \sum_{n=1}^{m} q_0^n \exp(ik \cdot \lambda_n)$$  \hspace{1cm} (B15)$$

Here $q_0^m$ is the probability that an SIA is located at $\lambda_m$ from its original position after $m$ hops. For average, $j$ is chosen as the mean free life defined in Eq.A2. The Eq.B14 can be calculated for a group of $k$ with a given wave number but varying wave directions. The results can be plotted on a unit sphere to show the anisotropy. The calculation can be repeated for a range of wave numbers and then averaged when the preferred wave number is unknown. In summary, the calculation takes the below steps:

1) Choose a crystal type, a recombination radius $R_{rec}$ and a vacancy concentration $c_v^0$ to calculate the SIA mean free life $l_i$ (via Eq.A2) and $q_0$. We note that an accurate estimate of $l_i$ is not needed to show the anisotropy. The same anisotropy holds as long as $l_i$ is larger than the recombination radius;

2) Compute Eq.B14 for each $m$ from 1 to $l_i$ based on the diffusion property with given wavelength and wave direction;

3) When averaging is needed, repeat the calculation for different wavelength followed by normalization;

4) Plot the result as a function of wave direction to elucidate the anisotropy.

Appendix C: Calculating the recombination rate from atomic kinetic Monte Carlo simulations

AKMC simulations are carried out to testify the assumption used in the above derivation of recombination rate. In the simulations, Frenkel pairs are produced with varying production rates $G$ from 0.98 to 980 dpa/s, with dpa being displacement per atom. To be consistent with the assumption, no sink absorption is considered. In such a situation, $c_i = c_v = c$, all following:

$$\frac{\partial c}{\partial t} = G - k_{iv} c^2$$  \hspace{1cm} (C1)$$

To further simplify the analysis, the same migration barrier, 0.5 eV is used for both vacancy and SIA. This automatically satisfies the condition $c_i D_i = c_v D_v$. We note that this is different from the cases in bcc Mo and W, in which the SIA migration barrier is much smaller than that for vacancies. Without existing sinks, a much lower SIA diffusion barrier will lead to $c_i D_i >> c_v D_v$ because $c_v = c_i$ and $D_c << D_i$. The temperature in the simulations is 673 K. A cubic simulation cell with 1,024,000 atoms in the bcc crystal structure is used in all simulations. The
recombination radius is set to be the first nearest neighbor cutoff, so that $N_{\text{new}} = 7$. For comparison, two different cases are considered with 3D SIA diffusion and 1D SIA diffusion along the ⟨111⟩ directions, respectively. The simulations are performed until the steady states are reached, as shown in Fig.S2. As can be seen in the figure, using 1D SIA diffusion seems to result in a higher steady state vacancy concentration $c_v$ (and $c_i$). The reason will be given in the following text.

![Figure S2: (Color online) Evolution of vacancy concentration $c_v$ as a function of dose from AKMC simulations with 1D and 3D SIA diffusion. The dose rate used in the simulations is 98 dpa/s.](image)

When $k_{iv}$ is constant and independent of $c_v$ and $c_i$, with $\frac{\partial c}{\partial t} = 0$, the steady state solution is simply $c = (G/k_{iv})^{1/2}$. When $k_{iv}$ is proportional to $c$, e.g., $k_{iv} = k_0 c$, as suggested in Amino et al. [3], the solution will be $c = (G/k_0)^{1/3}$. To compare with these theoretical solutions, the steady state vacancy concentration $c_v$ is obtained by averaging the AKMC results after the steady state is reached. As shown in Fig.S3, for both 1D and 3D SIA diffusion, $c_v$ is proportional to $G^{1/2}$, indicating that $k_{iv}$ is independent of $c_i$ and $c_v$. This justifies the validity of Eq.A4 for both 1D and 3D SIA diffusion. In the literature, it has been shown that when the traps are allowed to move, as in the case of SIA clustering during annealing, the reaction rate constant depends only weakly on instead of being proportional to the concentration $c_i$ for 1D SIA diffusion [3]. This indicates that different assumptions should be used for different conditions, e.g., under irradiation vs. annealing.

Some further clarification is needed to understand the different results for 1D and 3D SIA diffusion. The slopes obtained from linear fitting in Fig.S3 are $1.338 \times 10^{-5}$ and $1.043 \times 10^{-5}$ for 1D and 3D SIA diffusion, respectively. This difference comes from the difference in the attempt rates. For 3D SIA diffusion, there are 8 symmetrical paths in a bcc crystal, so that $\omega_i = 8\nu_i$, with $\nu_i$ being the attempt rate for each individual path. For 1D SIA diffusion, there are only two paths, and $\omega_i = 2\nu_i$. With the same diffusion barriers used, we have $\omega_v = 8\nu_i = 8\nu_t$ as well. Therefore, for 3D SIA diffusion, $\omega_i + \omega_v = 16\nu_t$, and for 1D, $\omega_i + \omega_v = 10\nu_t$. This gives a factor of $(16/10)^{1/2} = 1.26$, which is very close to the ratio of the slopes calculated from Fig.S3, $1.338/1.043 = 1.28$. This is regarded as a good agreement considering the stochasticity of AKMC simulations, indicating that the difference in the steady state $c_v$ is caused by the difference in the attempt rates, i.e., the diffusivity. For the same reason, at the same condition, the steady state $c_v$ is higher with 1D SIA diffusion than that with 3D SIA diffusion, as shown in Fig.S2. This further confirms that Eq.A4 holds for both 1D and 3D SIA diffusion.

It should also be pointed out that by assuming the same recombination probability for an SIA to visit a new site and to return to its previous site, there is some overestimate in the recombination rate. By using the slopes fitted in Fig.S3, the prefactor ($n_{\text{new}}$) is estimated to be about 3 instead of 7, but remains as a constant for both 1D and 3D SIA diffusion and for all dose rates simulated here. This indicates that Eq.A4 can be used for the current analysis
because the prefactor is canceled out during the normalization in Eq.B14. Also, this leads to some underestimate of the mean free life $l_i$ as in Eq.A2. As pointed out in Appendix B, an accurate estimate of $l_i$ is not needed to show the anisotropy in the recombination rate. However, Eq.A4, as well as the expressions given in the literature [2], need to be re-looked at for accurate calculations of recombination rate at different conditions.

FIG. S3: (Color online) Steady state vacancy concentration $c_v$ as a function of the square root of dose rate $G^{1/2}$. The symbols are the averages of steady state $c_v$ from AKMC simulations, and the lines are from linear fitting.

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