PHYSICAL REVIEW B **86**, 134105 (2012)

Sensitivity of the threshold displacement energy to temperature and time

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(Received 20 August 2012; published 5 October 2012)

The impact of temperature and time scale on the threshold displacement energy (E_d) has been investigated using molecular dynamics simulation. Employing a systematic approach to simulating low energy displacement cascades, defect formation probability has been quantified and precise values of E_d have been calculated at temperatures of 50, 300, 750, and 1200 K. In application to rutile TiO_2, the thermal activation of Frenkel pairs at elevated temperatures is found to significantly reduce defect formation probability and cause an increase in the oxygen value of E_d. Relating the high-temperature, picosecond simulations to experimental measurement conditions, we find that thermally activated processes are responsible for discrepancies in values of E_d reported by various techniques. This work establishes that E_d is not an intrinsic material property but depends on the conditions in which it is measured and the context in which it is to be used.

DOI: 10.1103/PhysRevB.86.134105 PACS number(s): 61.72.Cc, 61.82.Ms, 61.80.Az, 31.15.xv

I. INTRODUCTION

Developing a fundamental understanding of radiation damage is key to the development of current and future materials for nuclear applications. The response of a given material to irradiation is dependent on a multitude of atomic processes occurring on the nanoscale. The coalescence of these processes produce macroscopic changes in structural and chemical properties impacting the intended functionality of the material.

One of the fundamental quantities that helps define a materials radiation tolerance is the threshold displacement energy E_d. As the minimum kinetic energy required to displace an atom from its site, it is an important parameter in various models that estimate defect production during radiation events.[1,2] One such model is SRIM,[3] a widely used computer simulation package in which damage is estimated using a Monte Carlo algorithm based upon the binary collision approximation. SRIM is used in a variety of fields and is commonly utilized in research involving ion implantation.[4,5]

Despite the importance of E_d its exact definition is surprisingly unclear. Defining what constitutes a displacement or a stable defect may vary dependent on the technique used for its determination. Additionally, and perhaps more significantly, the sensitivity of E_d to the measurement conditions is relatively unexplored. Presently, E_d is considered as a material property that remains constant with differences observed either experimentally or via simulation attributed to errors in the approach. However, the dynamics of the atomic processes that are responsible for the value of E_d are dependent on external factors such as temperature and time. This suggests values of E_d depend on the conditions in which it is measured experimentally, calculated via simulation or employed in a theoretical model.

A reliable methodology of determining precise values is a necessity. Using experimental techniques, difficulties arise when accessing the length and time scales required to capture the exact onset of defect formation. This results in a wide range of values of E_d for a given material, and typically results in values higher than the actual threshold. As an alternative to experiments, computer simulation is able to capture the atomic-level dynamics responsible for the evolution of radiation damage. Molecular dynamics (MD) is particularly attractive for such studies as it captures all atomic processes, thereby avoiding approximations implicit in phenomenological treatments of radiation-induced defects.[6]

In the precursor to this study,[7] extensive MD simulations were carried out in a systematic approach to calculating E_d in rutile at 300 K. This study emphasized the importance of rigorous sampling when extracting quantities such as E_d from simulations of radiation events. The high level of statistical accuracy achieved enabled the calculation of defect formation probability as a function of primary knock-on atom (PKA) energy and values of E_d were extracted with great precision. Although the value of E_d for Ti agreed well with experiment, the value of E_d for oxygen at 19 eV was found to be significantly lower than the value reported experimentally for rutile and other oxides at around 40 eV.[8,9] The suggested cause of this discrepancy was the longer time scales inherent in experimental methods. This would allow for thermally activated Frenkel pair recombination which effectively increased the observed value of E_d. The motivation for the study presented in this paper stems from this hypothesis.

In this work, we determine the effect of temperature and time scale on the threshold displacement energy E_d. We employ the previously developed methodology based upon a systematic and statistically significant approach to studying low energy cascades.[7] By extending the previous work into rutile at 300 K to include temperatures of 50, 750, and 1200 K we present the effect of temperature on defect formation probability and quantify changes in E_d. Rate theory is used to relate the picosecond simulations carried out at elevated temperatures to the time scales of experiments. As a result, we achieve excellent agreement with experimental values establishing that E_d and defect formation probability are dependent on measurement temperature and time scale.

II. BACKGROUND

In the review of defect production in ceramics by Zinkle[10] in 1997, a myriad of values of E_d were reported for a range of oxide and carbon-based materials. The report highlighted the degree in which E_d varies between experimental technique, indicating the difficulty in capturing the onset of defect formation. Consolidating results for each material, the report concludes with recommended values of E_d with values for oxygen in ceramics at between 20 and 70 eV. Although the review reports low interstitial migration barriers for the oxides under scrutiny, no direct relation between temperature and defect production was stated. Specifically, the possibility that E_d could be dependent on temperature was not discussed.

One of the earliest studies into the effect of temperature on E_d was carried out in MgO by Pells.[11] A high voltage electron microscope (HVEM) was used to cause displacements at increasing voltages until damage was observed. This work reports a fluctuating dependency of E_d on temperature, the magnitude of which was dependent on crystal orientation. A value of E_d for O between 44 and 64 eV was reported, however, these values are extracted from the point at which observable defect structures, such as dislocations, are formed which is certainly past the threshold for point defect formation.

In the work of Gao *et al.*,[12] MD computer simulation was used to study defect production and disordering in the Ni_3Al alloy at a range of temperatures. A decrease in the number of residual Frenkel pairs (FPs) was observed as temperature increased and this was correlated with an increase in the degree of defect clustering. These trends were attributed to an increased lifetime of the thermal spike phase of the collision cascade, which allowed recombination and reordering. In contrast to the work of Gao *et al.*, MD cascade simulations carried out by Stoller[13] in iron at temperatures between 100 and 900 K found negligible differences in defect production. This work is supported by simulations into vanadium by Zepeda-Ruiz *et al.*[14] where E_d was found to be independent of temperatures up to 900 K.

In the work of Hartmann *et al.*,[15] Xe ion beam irradiation was used to study the build up of defects in rutile. Although this work did not involve determination of E_d, irradiation of samples at 160 and 300 K indicated the accumulation of defects greatly depended on temperature. At 160 K a significantly lower ion beam fluence was required to render the rutile structure amorphous whereas samples at 300 K remained crystalline at fluences an order of magnitude greater. This observation was attributed to thermally activated point defect mobility in rutile increasing the rate of defect recombination as temperature is increased.

One of the first experimental studies into determining E_d for rutile was carried out by Buck.[8] This study was motivated by the development of Synroc[16] and the new-found interest of titanates to the nuclear community. The experimental procedure employed HVEM and TEM to study the effects of electron irradiation on defect formation. Observations of damage development related to an E_d value of between 45 and 50 eV for Ti. Although damage was observed which would correspond to an O value of around 33 eV, the damage could not be solely attributed to O displacements. This work also indicated that the radiation response of rutile was consistent with that of similar covalent metal oxides.

One of the latest techniques for determining anion values of E_d experimentally is time-resolved cathodoluminescence spectroscopy (TRCS). In TRCS, a beam of fast electrons is used to simultaneously cause atomic displacements and excite the electrons trapped in the resulting vacancies. The decay of the associated excited states emits a characteristic photon which can then be attributed to a displacement. The work of Smith *et al.*[9,17,18] used TRCS to determine E_d for O for a range of zirconates and titanates, including rutile. Values of E_d were determined at 300 K of between 45 and 50 eV for the majority of the oxides studied, with rutile marginally lower at 39 eV.

The work of Thomas *et al.*[19] used MD to determine E_d for rutile at 160 K. Defining defect formation probability, two values were reported relating to probabilities of 10 and 50%. For oxygen, values of 45 and 60 eV were determined with values of 105 and 130 eV reported for titanium. The lower values of E_d reported for oxygen correlated well with early MD simulations of Richardson,[20] who reported oxygen values as low as 10 eV. Both studies highlighted the difficulty in defining E_d precisely and emphasized the requirement for good statistics.

In the recent studies by Xiao *et al.*,[21,22] density functional theory molecular dynamics (DFT-MD) was used to determine E_d in $Y_2Ti_2O_7$, ThO_2, CeO_2, and ZrO_2 at 100 K on the picosecond time scale. The study reported similar values for O for each oxide at between 14 and 20 eV, inline with the value derived in our previous study in rutile at 19 eV.[7] This suggested that at low temperature or short time scales significantly lower values of E_d can be determined. However, it is important to note the restrictions inherent to simulations of dynamics using first principle methods. The limitations on simulation cell size may cause unphysical behavior such as the self-interaction of a displacement cascade when periodic boundary conditions are employed. In addition, controlling the simulation temperature of small systems whilst maintaining the correct dynamics of the simulated cascade event is difficult. Also the significant increase in computational cost inhibits the acquisition of statistically reliable results, and values of E_d have to be drawn from only a few simulations.

III. METHODOLOGY

The methodology employed in this work expands on a scheme we recently developed for precisely determining E_d and the onset of defect formation.[7] This approach involves sampling PKA directions evenly distributed on the surface of a sphere and initiating collision cascades at energies finely spaced between 5 and 200 eV. To account for variations in thermal motion, simulations are carried out using 10 lattices that have been thermally equilibrated for varying times between 20 and 30 ps. Carrying out the above sampling for both PKA species results in a significant number of simulations, over 70,000 for each temperature of interest. This degree of sampling is a requirement due to the probabilistic nature of defect production at low PKA energies. The large computational requirement is made possible through the distribution to thousands of processors on a supercomputer. As communication is limited between each job, the implementation of the parallelization is straightforward.

The simulations are carried out using the DL_POLY3 MD code[23] using a variable time step. Equilibrium interactions are based on the Matsui-Akaogi pair potential,[24] which is smoothly joined to the Ziegler-Biersack-Littmark pair potential[25] to model the highly repulsive nuclei-nuclei interactions. As found in the previous work, a cell of 4608 atoms is sufficiently large to accommodate up to 200 eV cascades, with no differences observed in comparison with a 9000 atom cell. The lattices are equilibrated using the Nosé-Hoover thermostat,[26] and a 3.5 Å layer surrounding the cell remains under the control of the thermostat during simulations to dissipate energy from the cascades. Periodic boundary conditions are utilized in all cartesian directions.

To determine the effect of temperature on defect production, the algorithm outlined above was carried out at simulation temperatures (T_{sim}) of 50, 750, and 1200 K. These results were collated with the previous simulations at 300 K. All collision cascade simulations were carried out for a maximum time of 10 ps.

IV. RESULTS

A. Defect formation probability

The average defect formation probability (DFP) for the Ti and O PKAs as a function of temperature and PKA energy are shown in Fig. 1. Each data point is an average across all PKA directions and the 10 equilibrated lattices, representing 1000 MD simulations. The error bars indicate a 95% confidence interval using the standard error in the mean. As found in the previous study at 300 K, the smoothness of each curve highlights the precision achieved by the extensive sampling employed in the methodology.

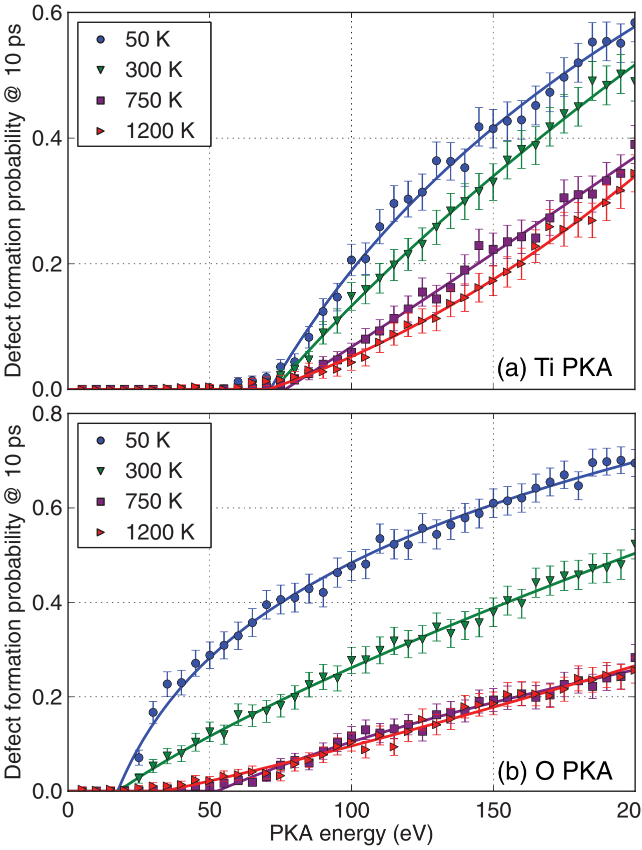

FIG. 1. (Color online) The probability of defect formation for the (a) Ti PKA and (b) O PKA after 10 ps as a function of PKA energy and temperature. The lines in represent the fits to Eq. (1).

Following the procedure in our previous work,[7] we fit the DFP as a function of PKA energy using the following equation:

$$DFP(E) = \begin{cases} 0 & \text{if } E \leqslant E_d \\ \frac{1}{\beta}\left[E^{\alpha} - (E_d)^{\alpha}\right] & \text{if } E > E_d \end{cases}, \tag{1}$$

where α and β are fitting parameters and E is the energy of the PKA. As discussed in the initial study, a multitude of functional forms were tested and this definition was found to give the best fit to data from each PKA species across the complete PKA energy range. In addition, defining a piecewise function in this manner allows simple extraction E_d as it gives a discrete intercept on the energy axis. The resultant fits are shown as solid lines in Fig. 1. To quantify the dependency of the DFP on PKA energies past the threshold, we define a new value E_{50} which represents the energy required to achieve a 50% probability of defect formation; this value can be extracted by rearranging Eq. (1). The values of E_{50}, along with fitted values of E_d at each temperature, are listed in Table I. The errors reported in the fitted values represent a 95% confidence interval calculated using the standard error in each parameter.

The calculated DFP as a function of temperature indicates a contrasting response from each PKA species. For the Ti PKA there are marginal differences in the value of E_d, with an average value of around 72 ± 10 eV. Although there is little experimental data regarding the Ti value of E_d, this is inline with the work of Buck[8] and follows the trend of other oxides with a higher value for the cation species. In comparison with other simulation work, Thomas *et al.*[19] reported energies of 105 and 130 eV for DFPs of 10 and 50%. The value at 10% DFP agrees well with this work with a value of 93 ± 1 eV, however, E_{50} is found to be significantly higher at 195 ± 2 eV.

Although there is no significant dependency of the Ti value of E_d on temperature, the values of E_{50} increase from 174 ± 2 at 50 K to 240 ± 5 eV at 1200 K. Figure 1(a) indicates the differences in E_{50} stem from the immediate decrease in DFP at energies higher than E_d. At temperatures between 50 and 750 K, the reduction in DFP follow similar trends as suggested by the shape of the curves in Fig. 1(a) and the well-defined intercept on the energy axis. At 1200 K however, as well as the reduction in the DFP observed at 750 K, there is an additional variation as PKA energy increases which results in a less distinct intersect on the energy axis. As a result, the extrapolated value of E_{50} is similar to that found at 750 K. We attribute this behavior at 1200 K to the large increases in thermal vibrations, altering the defect production mechanisms.

TABLE I. Values of E_d and E_{50} (50% DFP) for Ti and O as a function of simulation temperature (T_{sim}) after 10 ps. Values are determined using the fit shown in Eq. (1). Errors represent a 95% confidence interval calculated using the standard error in each quantity.

	Ti		O	
T_{sim} (K)	E_d (eV)	E_{50}(eV)	E_d(eV)	E_{50}(eV)
50	73 ± 2	174 ± 2	17 ± 2	105 ± 2
300	73 ± 2	195 ± 2	18 ± 3	198 ± 4
750	77 ± 4	242 ± 8	53 ± 5	437 ± 84
1200	68 ± 6	240 ± 5	34 ± 9	324 ± 27

In contrast to the values determined for the Ti PKA, both E_d and E_{50} for O vary significantly over the temperature range studied. The value of E_d at 50 K supports the value reported in our previous work at 300 K at around 18 eV which is lower than the experimental value for O in rutile and other oxide ceramics at around 40–50 eV.[9,10] However, the lower value is in line with the first principles simulations in $Y_2Ti_2O_7$ at 100 K calculated by Xiao *et al.*[21] Significantly, at 750 K there is a marked increase in E_d to 53 ± 5 eV, which supports the experimentally derived values. As with the Ti PKA, the values of E_{50} show a significant increase between 50 and 750 K, highlighting the higher energies required to achieve a 50% probability of defect formation. At the highest simulated temperature of 1200 K there is a decrease in E_d and E_{50} suggesting an additional process that enhances defect production is occurring. Again we suggest this process relates to the increase in the magnitude of the thermal vibrations present at 1200 K.

It should be noted that the degree in which O DFP is reduced at the higher temperatures has a significant effect on the certainty in the extrapolated values of E_{50} and to some extent the value of E_d at 1200 K. This is due to a reduction in the rate at which DFP increases with respect to PKA energy resulting in a low value of 30% DFP at the end of the PKA energy range. This generates an error of around 20% in the value of E_{50} at 750 K and an error of 25% in E_d at 1200 K as shown in Table I.

B. The probability of atomic displacement

To investigate an alternative definition of E_d and to begin to understand how temperature is effecting the dynamics in the simulations, the probability of an atomic displacement has been calculated and is shown in Fig. 2. This probability captures both defect formation and atomic replacement events and as expected converges to unity much faster than the DFP. In contrast to the DFP, there is a smaller variation in displacement probability as temperature is increased with the general trend suggesting an increased likelihood of displacement at higher temperatures.

For the Ti PKA, there is a marginal increase in displacement probability at higher temperatures, particularly between 60 and 90 eV, which suggests the thermal vibrations are becoming large enough to significantly effect the displacement mechanisms. Correlating this with the changes observed in the DFP suggest that an increase in displacement probability from the Ti PKAs results in a decrease in DFP. This can be attributed to the enhancement of replacement mechanisms by the increase in temperature which aids defect recombination.

The atomic displacement probability calculated for the O PKA shows significantly less variation in comparison with results from the Ti PKA. Across the complete PKA energy range studied, the likelihood of causing atomic displacements from O PKAs is independent of temperature. As found in the precursor to this work,[7] it is important to note the general differences between the DFP and displacement probability, which are particularly distinct for the O PKA. For example, at PKA energies of around 100 eV the simulations at 750 K suggest that although there is a 90% probability of causing a displacement there is only around a 20% chance of defect formation.

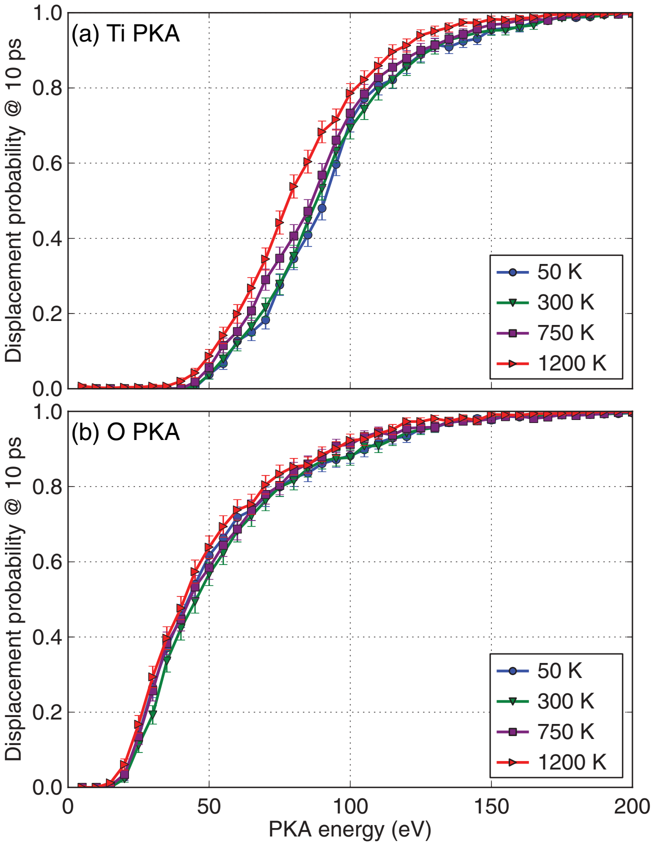

FIG. 2. (Color online) The probability of atomic displacement from (a) Ti PKAs and (b) O PKAs after 10 ps as a function of PKA energy and temperature. This probability accounts for replacement events in addition to defect formation.

C. The impact of thermally activated recombination of Frenkel pairs

With changes in DFP quantified at different temperatures, it is important to determine whether this is due to differences in the collision dynamics within the first few ps of the simulations or if thermally activated recombination of Frenkel pairs (FPs) is the main contributing factor. To extract this information, the DFP was calculated at 1 ps for a subset of simulations at 50 and 750 K. These simulations represent a snapshot immediately after the ballistic phase of the collisions where the defects created have had no time for recombination. This isolates any effects of temperature on the displacement mechanisms.

The resultant DFP calculated at 1 ps is shown in Fig. 3. In contrast to the marked temperature dependency of the DFP at 10 ps (Fig. 1), the DFP calculated at 1 ps is coincident at the simulated temperatures of 50 and 750 K. This indicates changes in temperature have negligible effect on the defect production during the ballistic phase. Therefore, the reduction in DFP observed at elevated temperatures after 10 ps and in particular the shift in the O value of E_d, must be solely attributed to thermally activated recombination.

To determine the energy barriers associated with the thermally activated recombination processes, the Arrenhuis

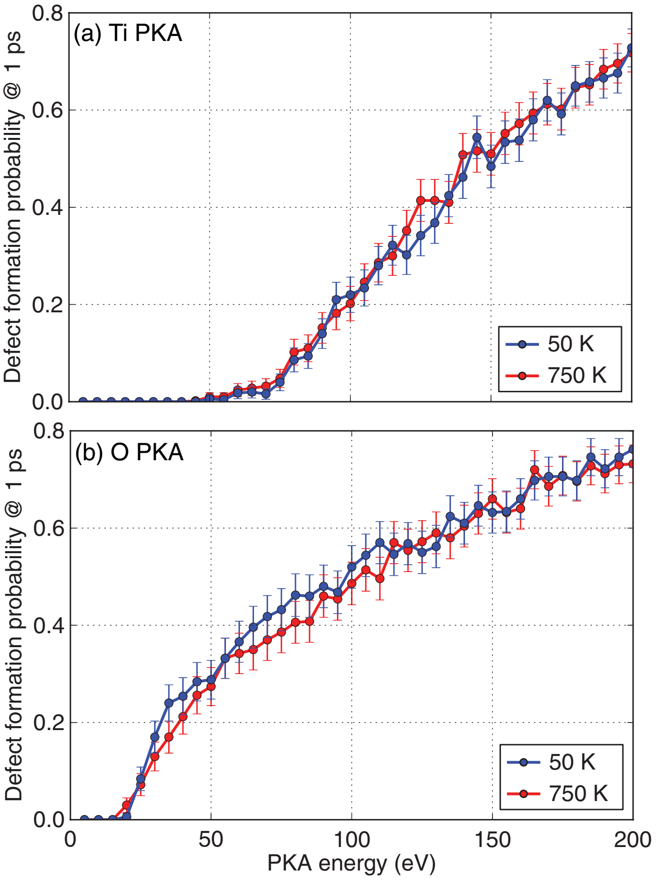

FIG. 3. (Color online) Defect formation probability at 1 ps for the (a) Ti PKA and (b) O PKA as a function of PKA energy at 50 and 750 K.

equation can be used,

$$1/t_{\mathrm{act}} = A\exp\left(-\frac{E_a}{k_B T_{\mathrm{sim}}}\right), \tag{2}$$

where t_{act}, A, and E_a are the activation time, attempt frequency, and the energy barrier for the process of interest, respectively, k_B is Boltzmann's constant and T_{sim} is the simulated temperature. The activation time t_{act} during the simulations is taken as the time between the end of the ballistic phase and the end of the simulation which is around 9 ps. For the estimations of E_a we assume changes in E_d are caused by a single, critical process. In all calculations concerning the Arrenhuis equation, a fixed attempt frequency of 10^{13} s^{-1} is used.

As there is no change in the value of E_d for the Ti PKA, defects produced at low PKA energies at 50 K must remain at the elevated temperatures. From our previous work at 300 K (Ref. 7), it was found that the displacements from the Ti PKA produce both Ti and O defects. Building from this, the constant value of E_d may be caused by a disparity in the activation energy barriers associated with the recombination of defects on each sublattice. At energies around E_d defects are formed on both sublattices and if all defects on one sublattice recombine, residual defects on the alternate sublattice will ensure no change in E_d. As defects remain after 10 ps at the highest temperature of 1200 K, it is possible to determine the minimum barrier associated with the critical recombination transition that has remained unactivated. Assuming rate theory applies, the Arrenhius relation [Eq. (2)] can be used to calculate this minimum energy barrier. Using a temperature of 1200 K and an activation time of 9 ps results in an minimum energy barrier of 0.47 eV. This represents the barrier which would need to be overcome to observe a decrease in the value of E_d for Ti.

At energies above E_d, there is a significant decrease in the DFP from the Ti PKA at each increment of temperature. Using the idea put forward previously that there is a significant difference between the recombination barriers associated with each sublattice, then a decrease in the number of defects of a particular atomic species would be expected. However, examination of the defect proportions indicated that equal numbers of Ti and O defects still remain across the complete temperature and PKA energy range. Therefore, the decrease in the DFP relates to a reduction in both the number of Ti and O defects. As we are assigning changes in DFP to thermally activated processes, then this suggests that there is a recombination mechanism that leads to annihilation of both Ti and O FPs. The barrier associated with this mechanism will be significantly lower than that required to shift the value of E_d and may related to cooperative or assisted migration of defects. Currently the exact mechanism and energy barrier remains unknown.

The most significant result regarding the simulations from the O PKA is the shift in E_d between 300 and 750 K, shown clearly in Fig. 1(b). As stated previously, the higher value of E_d at 53 ± 5 eV correlates well with experimental results carried out at 300 K.[9,10] Again, assuming that the thermal activation of a critical FP recombination transition is responsible for the increase in E_d, then we can derive the associated energy barrier using the Arrhenius equation. The maximum activation energies (E_a) at each simulation temperature (T_{sim}) during the 9 ps activation time are listed in Table II along with the calculated values of E_d. The Table shows that between $T_{\mathrm{sim}} = 300$ and 750 K, where E_d increases from 18 to 53 eV, the maximum barrier for the critical FP recombination lies between 0.12 and 0.29 eV.

Whilst the reduction in the DFP between 300 and 750 K can be attributed to activation of the same FP recombination mechanism that shifts E_d, there is also a general reduction in DFP between 50 and 300 K. From Table II, this suggests that there are recombination transitions with energy barriers of 0.12 eV or less. Although these are not the critical mechanisms that alter the value of E_d they contribute significantly in the lowering of the DFP and may also be responsible for the reduction in the DFP observed for the Ti PKA. This suggests that there are a range of FP recombination transitions with energy barriers less than 0.29 eV that contribute to the

TABLE II. Values of E_d for the O PKA with the associated maximum energy barriers, E_a accessible for each simulated temperature T_{sim} during 9 ps activation time, t_{act}.

T_{sim} (K)	Maximum E_a (eV)	E_d (eV)
300	0.12	18 ± 3
750	0.29	53 ± 5

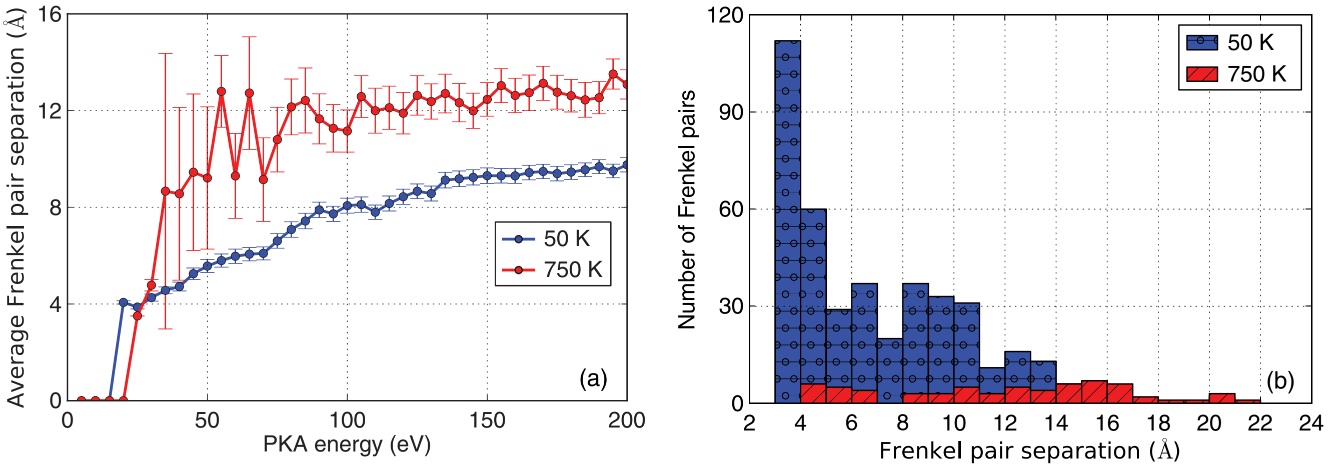

FIG. 4. (Color online) Frenkel pair analysis for the O PKA. (a) Average Frenkel pair separations as a function of PKA energy. (b) Histogram of all Frenkel pair separations at 10 ps at a O PKA energy of 80 eV.

temperature dependence of both E_d and defect production in general. Furthermore, as we previously reported that only O defects are created from O displacements,[7] we can specifically state that these recombination mechanisms relate to O defects. Relating this again to the results from the Ti PKA suggest that the reduction in the number of Ti and O defects may be a result of O-assisted recombination, where the low energy barriers associated with O recombination aid local Ti migration.

In the knowledge that there are O recombination barriers of maximum height 0.29 eV, further analysis allows us to understand the length scale associated with these transitions. This is achieved by calculating the differences in FP separations between 50 K, where the defects are frozen after the ballistic phase and 750 K, where recombination has occurred. Fig 4(c) shows the average FP separations as a function of PKA energy and highlights a marked increase for $T_{\mathrm{sim}} = 750$ K. Combining this trend with the distinct reduction in the DFP at 750 K suggests that the localized FPs have recombined. This reasoning is supported by Fig. 4(c) which shows a histogram of FP separations at $T_{\mathrm{sim}} = 50$ and 750 K at a PKA energy of 80 eV. This figure indicates complete annihilation of FPs separated by 3–4 Å at 750 K which were prevalent at 50 K. Therefore, recombination transitions relating to these FPs can be associated with a maximum energy barrier of 0.29 eV and contribute to the increase in E_d. In addition to the recombination of localized FPs, Fig. 4(c) highlights a marked reduction in FPs with separations from 4 to 14 Å. This suggests that there are multiple recombination mechanisms on the O sublattice spanning great distances that have low energy barriers of the order 0.29 eV. These transitions are responsible for changes in E_d and the overall reduction in the DFP. This result is in line with the experimental work of Hartmann *et al.*[15] who attributed the change in resistance to radiation as temperature increased to the activation of recombination mechanisms.

The multitude of resultant defect clusters created from the large number of simulations provides a valuable catalog of the damage expected at each PKA energy. Analysis of these defects along with the changes observed at the different simulation temperatures will provide insight into the FP recombinations responsible for the changes in DFP and values of E_d. This, along with the calculation of the associated migration energy barriers and the determination of the recombination pathways, is the next stage of this investigation.

D. Implications for experimental methods of determining E_d for oxygen

In determining the maximum energy barriers responsible for the shift in the O value of E_d between 300 and 750 K, it is possible to extrapolate which values of E_d are expected for a given measurement temperature and time scale. Using the two activation energies of 0.12 and 0.29 eV, the Arrenhius equation can be plotted as a function of temperature and time to form bounds for the different values of E_d, as shown in Fig. 5. This figure highlights three regimes dependent on measurement conditions. At short time scales or low temperatures defect mobility is reduced and the low value of E_d at 18 eV is expected. At longer time scales or high temperatures defect recombination will occur causing a higher value of E_d at 53 eV. In between these regions is a range of temperatures and time scales in which the expected value of E_d falls between 18 and 53 eV. The existence of this region is a result of not knowing the exact energy barrier for the critical recombination mechanism.

From Fig. 5 we can extract the time scale required to achieve the lower value of 18 eV at a typical experimental temperature of 300 K. At around 10 ns, this time scale is beyond the capabilities of even the latest experimental technique for determining E_d. For a direct connection with experimental results, the work of Smith *et al.*[9] carried out time-resolved cathodoluminescence spectroscopy (TRCS) in rutile and determined the value of E_d for O to be 39 eV at 300 K. Significantly, the technique involved a 25 ns time delay between displacement of the O atoms and the optical measurement of vacancies, which can be seen as a dashed line in Fig. 5. At 25 ns and 300 K, Fig. 5 indicates the expected value of E_d is indeed the higher value of 53 eV.

The dependency of E_d on measurement conditions illustrated in Fig. 5 can be tested through modifications or extensions to *in situ* techniques such as TRCS. The most

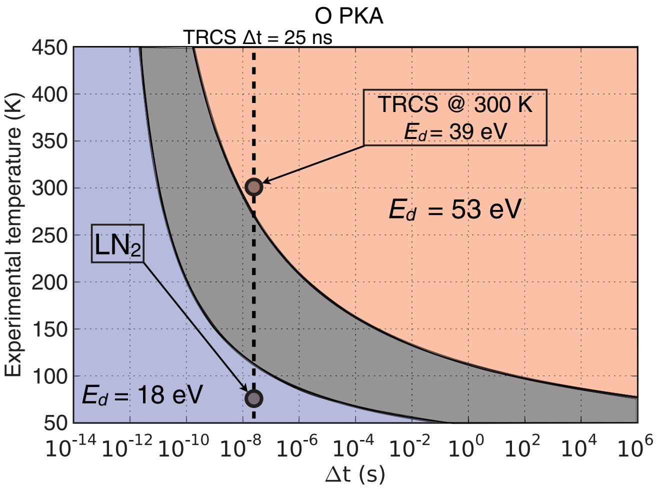

FIG. 5. (Color online) The dependency of E_d for oxygen on temperature (T_{exp}) and time scale (Δt) between displacement and measurement of defects. The dashed line represents the 25 ns time scale in the TRCS experimental technique used by Smith *et al.*[9] who reported a value of 39 eV for oxygen at 300 K. The point at liquid nitrogen temperature highlights the expected lower value of E_d from TRCS experiments. The dark gray region represents the time scales and temperatures in which the value of E_d will fall between 18 and 53 eV.

obvious alteration to experiments at 300 K is reducing the time delay between displacement and measurement of defects to below 10 ns. This will capture Frenkel pairs that have yet to recombine. If this extension is beyond the capabilities of the experimental techniques then an alternative approach is to lower the temperature at which the experiment is carried out. Effectively freezing the Frenkel pairs extends the time frame for recombination. A convenient temperature to use would be 77 K, the temperature of liquid nitrogen. From Fig. 5, to achieve a value of E_d at 18 eV at 77 K requires the time scale between displacement and measurement to be below 100 ns. This is within the capabilities of methods such as TRCS, and therefore should result in the lower value of E_d.

Illustrating that E_d is dependent on the measurement temperature and time scale also has implications for models of radiation damage. In models where E_d is a critical input parameter, the simulation conditions must be taken into account when selecting a value of E_d. Additionally, if successive atomic collisions are to be accurately modeled, the time between collisions may effectively alter the required value of E_d. If collisions within the same volume are infrequent then the activation of thermal recombination will result in the restoration of the perfect crystal lattice and higher energy collisions will be required to produce permanent defects. Conversely, if successive collisions are rapid then there is limited time for recombination and the build up of defects can occur from lower energy collisions.

V. CONCLUSIONS

The effect of thermally activated Frenkel pair (FP) recombination on the threshold displacement energy (E_d) has been determined in rutile. Using a computational approach developed previously,[7] defect formation probability (DFP) has been defined as a function of primary knock-on atom (PKA) energy for a range of simulation temperatures. A contrasting response was observed from each PKA species. For Ti, the value of E_d remained consistent across the complete temperature range at 72 ± 10 eV. The value of E_d for O was found to increase between 300 and 750 K from 18 ± 3 to 53 ± 5 eV. This increase is consistent with experimental work and is a result of O FP recombination mechanisms that are activated at 750 K, increasing the PKA energy required to form stable defects. The maximum activation barrier for this mechanism is around 0.29 eV and the recombination can occur over large separations. Using rate theory and an activation energy of 0.29 eV, the simulation temperatures were related to experimental time scales. It was found that experimental methods of determining E_d for O at 300 K are unable to capture the O FPs observed during simulation which are found to recombine within 10 ns. This provides an explanation for the higher value of E_d for O reported by experiment and indicates that E_d is dependent on the conditions in which it is measured.

At PKA energies higher than E_d, there was a distinct reduction in the DFP from both PKA species. For the O PKA, this can be solely attributed to the recombination of O FPs, but for the Ti PKA a reduction in both O and Ti defects was observed. This may be a result of oxygen-assisted recombination of Ti FPs which will be associated with significantly lower energy barriers than isolated Ti FP recombination mechanisms.

In line with our previous investigation,[7] this study indicates the importance of extensive sampling when extracting quantities such as E_d from dynamic simulations of radiation events. Specifically, the importance of sampling a range of temperatures when determining E_d is highlighted in this work. By monitoring changes in E_d as a function of temperature it is possible to gain an understanding of the critical FP recombination transitions and the associated energy barriers. The degree of which E_d varies with temperature gives us an immediate understanding of a material's radiation tolerance. Experimental techniques that are capable of calculating E_d at a range of temperatures would prove valuable in both supporting the calculations provided in this work and giving a broader understanding of radiation response.

ACKNOWLEDGMENTS

This work was supported by computing resources at the iVEC facility located at Murdoch University.

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