Resilient ZnO nanowires in an irradiation environment: an *in situ* study

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Abstract:

ZnO nanowires (NWs) have been extensively studied for various device applications. Although these nanowires are often suspected to be impractical and highly unstable under hostile radiation environments, to date little is known on their radiation tolerance. Here, we show outstanding resilience of ZnO NWs by using *in situ* Kr ion irradiation at room temperature inside a transmission electron microscope. Our studies show that ZnO nanowires with certain diameter become nearly immune to radiation damage due to the existence of dislocation loop denuded zones. A remarkable size effect also holds: the smaller the nanowire diameter, the lower the defect density. Rate theory modeling suggests that the size effect arises from fast interstitial migration and a limit in size to which interstitial loops can grow. *In situ* studies also revealed a surprising phenomenon: the pristine prismatic loops can prevail over the strongest known defect sinks, free surfaces, to trap radiation-induced defect clusters. This study comprises the first critical step towards in-depth understanding of radiation response of functional oxide nanowires for electronic device applications in extreme environments.

Keywords: ZnO nanowires, radiation damage, extreme environments, defect denuded zone

1. Introduction

Nuclear energy provides more than 10% of electricity internationally and is increasingly used in developing countries. Development of next generation nuclear reactors requires radiation tolerant ceramics for various applications, including electronic devices, sensors, immobilization forms for radioactive wastes, cladding materials for gas-cooled fission reactors and structural components for fusion reactors [1-3]. Under heavy ion irradiation, the primary damage in ceramics is the displacement of atoms/ions and the consequent formation of Frenkel (interstitial-vacancy) pairs and defect clusters. The formation and migration of defect clusters in irradiated ceramics are complicated due to the presence of multiple sublattices, prominent bond orientation effects, electrostatic effects and greater importance of chemical and ionization effects [4].

Dislocation loops and voids are two major types of defect clusters formed in irradiated ceramics. In Zr^+ ion irradiated MgAl_2O_4 at 650°C , interstitial loops formed on $\{11\bar{1}\}$ and $\{110\}$ planes, with Burgers vector along $\langle 110 \rangle$ direction [5]. Certain oxides, such as magnesia (MgO) and alumina (Al_2O_3), are susceptible to formation of voids [4, 6]. Defect denuded zones (DDZs) in the vicinity of defect sinks are typically observed after radiation at high temperature. For instance, DDZs along grain boundaries (GBs) were reported in SiC after neutron irradiation at $1010\text{-}1380^\circ\text{C}$ [7]. Under light or heavy ion irradiation at 650°C , DDZs formed near the surface or adjacent to GBs in MgAl_2O_4 and Al_2O_3 [5]. Volumetric swelling due to accumulation of point defects, defect clusters (dislocation loops, voids, etc.), or amorphization [2, 8, 9] has been frequently reported in various irradiated ceramic materials [10-13]. Unit-cell volume expansion was reported in Ar^+ ion irradiated polycrystalline $\text{Ca}_2\text{Nd}(\text{SiO}_4)_6\text{O}_2$ [8]. Macroscopic volumetric swelling reached 18.4% in zircon (ZrSiO_4) under alpha decay and was attributed to radiation-induced amorphization [14].

Strategies that introduce defect sinks, such as GBs [15-17], phase boundaries [18, 19], twin boundaries [20] and immiscible layer interfaces[21], have been applied to suppress the formation of defect clusters in metals and ceramics. Free surfaces are the strongest known defect sinks and nanoporous metals have shown superior radiation tolerance [22, 23]. A recent research showed helium-implanted $\text{Ni}_{73}\text{P}_{27}$ metallic glass nanocylinders exhibit enhanced ductility without sacrifice in yield and ultimate tensile strength [24]. ZnO NWs have been extensively investigated for electronic device applications [25-27] and could be a representative device candidate for in nuclear reactors.

Here, by using *in situ* Kr ion irradiation technique inside a transmission electron microscope, we show that ZnO NWs have remarkable radiation tolerance, manifested by the existence of radiation immune NWs with small diameters, due to the formation of DDZs even at room temperature. Kinetic rate modeling was performed to understand the size dependent migration of defect clusters and variation of defect density in existence of abundant free surfaces. Our study suggests that radiation tolerance of functional oxide NWs has prominent size dependence and the NWs with certain diameters can be potentially immune to radiation, assist their applications in electronic devices in extreme radiation environment.

2. Methodologies

2.1 Materials synthesis and *in situ* Kr ion irradiation

ZnO nanowires were synthesized from Zn powders (Fisher Scientific, purity 99.3 %). Before heating up, the powders were placed in a quartz tube furnace, in which ~50 sccm oxygen flowed for one minute in order to remove air and other residues. Subsequently, the furnace was heated up to 850 °C at a rate of ~ 85 °C/min and kept for 30 min with a continuous ~5 sccm O_2

flow throughout the entire synthesis process. At the end of the annealing, the furnace was naturally cooled at a rate of approximately 10 °C/min above ~200 °C and approximately 1 °C/min below ~200 °C [28]. ZnO NWs were lifted directly onto carbon-coated grids for transmission electron microscopy (TEM) studies. The microstructure of as-synthesized ZnO NWs was examined with a Quanta 600 field emission scanning electron microscope and JOEL 2010 transmission electron microscope.

In situ Kr⁺⁺ ion irradiation at an energy of 1 MeV was performed for ZnO NWs at room temperature in the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory, where an ion accelerator was attached to a HITACHI H-9000NAR microscope [29]. The microscope was operated at 200 keV and kept on during radiation in order to record the microstructural evolution. The average dose rate was 2×10^{-3} dpa/s. A CCD camera was used to record the microstructure evolution during ion irradiation at a rate of 15 frames/s. The stopping and range of ions in matter (SRIM) [30] computer program was used to estimate the damage level under ion irradiation. The displacement energies of Zn (25eV) and O (28eV) were used in the calculation.

2.3 Rate theory modeling

The rate theory model is a rather standard model of defect evolution in irradiated materials [31-33]. Our model assumes that the production of interstitials (I) and vacancies (V) are at rates similar to those expected in the experiment, as described below. These defects can diffuse and either annihilate through an $I+V \rightarrow 0$ reaction or interstitials can aggregate to form loops ($I+I \rightarrow L$) or interact with existing loops to cause them to grow. Di-interstitial clusters are assumed to be the nucleus of interstitial loops. The surfaces of the wire are assumed to be perfect

sinks for defects such that all defect concentrations at the surfaces are identically zero. Even though ZnO is a binary compound and thus there are two types of interstitials and two types of vacancies, the rate theory model only accounts for one type of each species, which is reasonable as the two types of defects behave similarly, especially as predicted by empirical potentials. The expressions governing the evolution of defects in the material are [34]:

$$\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + P(1 - C_v)(1 - ZC_v) - R_{iv}C_iC_v - 2R_{ii}C_iC_i - \Theta(\alpha)ZD_i\sqrt{C_{iL}C_L}C_i \quad (1)$$

$$\frac{\partial C_v}{\partial t} = D_v \frac{\partial^2 C_v}{\partial x^2} + P(1 - C_v)(1 - ZC_v) - R_{iv}C_iC_v - ZD_v\sqrt{C_{iL}C_L}C_v \quad (2)$$

$$\frac{\partial C_L}{\partial t} = R_{ii}C_iC_i \quad (3)$$

$$\frac{\partial C_{iL}}{\partial t} = \Theta(\alpha)ZD_i\sqrt{C_{iL}C_L}C_i - ZD_v\sqrt{C_{iL}C_L}C_v + A_{iL} \frac{\partial C_L}{\partial t} \quad (4)$$

Physical meanings of the variables in the above equations were listed in Table 1. The first two equations represent the time evolution of the concentration of interstitials and vacancies, respectively, the third equation is for the concentration of interstitial loops, and the fourth is for the concentration of interstitials in loops. All concentrations are a function of time and distance (x) across the wire. As mentioned, we explicitly consider only one type of interstitial and vacancy defect. Other parameters defining the model include R_{iv} and R_{ii} , which are the reaction coefficients for interstitials with vacancies and interstitials with interstitials, and are defined as $R_{iv}=Z(D_i+D_v)$, $R_{ii}=Z(D_i+D_i)$. Z is the recombination volume, taken to be $24a$ [34], with $a=0.321$ nm, and D is the diffusivity of each defect defined by [35]

$$D = \frac{1}{6}a^2\nu_0 e^{\frac{-E_m}{k_B T}} \quad (5)$$

where $\nu_0=10^{13}/s$ is the rate prefactor, E_m is the migration energy, T is the temperature, and k_B is the Boltzmann constant. The migration energy of interstitials, E_{mi} , is the primary quantity varied in our simulations. The average loop size at any given time and position, measured as the

average number of interstitials per loop, is defined as $\langle N_i \rangle = C_{iL}/C_L$. α is then defined as $N_{max} - \langle N_i \rangle$ and thus $\Theta(\alpha)$, where Θ is the step function, turns off the growth of loops due to the arrival of interstitials for loops containing N_{max} or more interstitials. In one scenario, N_{max} is effectively set to infinity, while in the second scenario, labeled as “arrested,” interstitial interaction with the existing loops is suppressed in regions of the wire where the average loop size exceeds a predefined value, estimated from the experiments. This maximum (arrest) value is estimated from the fact that the largest loop size in the experiments is roughly 6 nm in diameter. If one assumes that all of the interstitials in the loop are in one plane, this corresponds to roughly $N_{max}=600$ atoms. Finally, P is determined from the damage rate estimated by SRIM calculations. The estimated damage rate is 2×10^{-3} dpa/s. This is the number of displacements per atom per second in the material. Given the density of ZnO is 83.9 atoms/nm^3 , this gives a displacement rate of 1.678×10^{-1} displacements/ nm^3s . This final value is converted to actual defects produced by recognizing that not all displacements lead to a defect. After Katoh et al.[33], we use a factor of about 0.2 to convert displacements to damage, giving a final value for $P=0.03356$ defects/ nm^3s . Rate theory modeling will be applied to investigate size dependent radiation damage in ZnO nanowires in this study.

3. Results

3.1 Experimental

As-received ZnO NWs had a hexagonal shaped cross section as shown in Fig. 1a. TEM micrograph and selected area diffraction (SAD) pattern in Fig. 1b-c revealed that a majority of these NWs were single crystals with Wurtzite phase. ZnO NWs with different diameters (30-250 nm) were subjected to Kr ion irradiation at room temperature to a dose of 5 displacements-per-

atom (dpa). Radiation-induced damage was examined by TEM using two-beam conditions with diffraction vector $g=[\bar{1}2\ 0]$. It is evident in Fig. 2 that a large number of dislocation loops were generated after radiation of a NW with an average diameter (D) of 250 nm. Furthermore DDZs with a width of ~ 25 nm were observed near surface of the NW. Dislocation-loop DZs were also apparent in irradiated ZnO NWs with an average D ranging from 70 to 100 nm (Fig. 2b-c). When $D = 30$ nm (Fig. 2d), no dislocation loops were observed, NWs of such small diameters were nearly free of observable radiation-induced defects. The high resolution TEM (HRTEM) image in Fig. 2e shows some typical dislocation loops located on $\{0001\}$ planes in irradiated ZnO NW ($D = 70$ nm). In comparison, the HRTEM image of irradiated 30 nm ZnO NWs in Fig. 2f shows a nearly perfect NW with no evidence of dislocation loops.

Statistical analysis on distribution of dislocation loop density across the NWs (in Fig. 3) shows interesting parabolic trends for NWs with D of 70 - 250 nm. The peak density of dislocation loops occurs in the center of the wires, and the loop density in 30 nm ZnO NW is essentially zero. The peak density of dislocation loops scales linearly with D as shown in Fig. 3b. Meanwhile the distribution of dislocation loop size in irradiated NWs with different diameters (in Fig. 4) shows that by reducing D from 250 to 70 nm, the average dimension of defect clusters d_{loop} decreased from ~ 6 to ~ 4 nm. Furthermore radiation-induced dislocation segments with an average length of 18 nm were observed, while they were absent in NWs when $D = 70$ nm.

Radiation-induced swelling and the interaction between preexisting prismatic loops (L1-L3 in Fig. 5a) and radiation-induced loops were analyzed. Under irradiation, these preexisting large dislocation loops migrated along the prismatic plane of the NW at a velocity of ~ 2 nm/s in the early stage and slowed down to be eventually stationary (see supplementary video). By 1.5 dpa, as shown in Fig. 5b, these preexisting dislocation loops were pinned by the high-density

radiation-induced small dislocation loops. Swelling of the ZnO NWs along the radial direction was observed during irradiation. For instance the diameter of a wire that was initially 168 nm (Fig. 5a) increased to 180 nm by 1.5 dpa (Fig. 5b). Radiation-induced radial strain (ϵ) was calculated by using $\epsilon = (d - d_0)/d_0$, where d_0 and d are the wire diameter before and after radiation. Comparison of the variation of radial strain for various NWs in Fig. 5c shows that (1) the radial strain increased monotonically for wires with D of ~60 nm or greater; (2) the magnitude of strain decreased for wires of smaller diameter subjected to the same magnitude of radiation dose; (3) the rate of increase in strain during the early stage of irradiation is also lower for wires of smaller diameter. Radial strain was not detectable for wires with D of 30 nm or smaller. A magnified region of Fig.5b, shown in Fig. 5d, illustrates that a high density of small radiation-induced dislocation loops were trapped by the preexisting large dislocation loops, leading to the formation of dumbbell-shape distribution of defect clusters, accompanied by the surface DZs with width of 25 nm or less. Fig. 6 illustrates the uniform DDZs in the regions without pristine dislocation loops (in Fig. 6a) and dumbbell-shape distribution of defect clusters due to the attraction of preexisting dislocation loops (in Fig. 6b).

3.2 Modeling

Vacancy migration is generally slow in ZnO with migration energy in excess of 1 eV. The values of the migration energy of interstitials in ZnO vary significantly (0.1-0.6 eV) in the literature [36, 37]. Values from empirical potentials [37] tend to be higher than those derived using density functional theory (DFT) [36, 38], which are sensitive to the charge state. Here a two-dimensional rate theory model was used to understand size dependent defect evolution in irradiated ZnO NWs. Fig. 7a shows the crystallographic structure of defect in our modeling

studies: a di-interstitial cluster (I2) in Wurtzite-structured ZnO. Fig. 7b compares the simulated loop density profiles across the wire as a function of NW diameter when the migration energy of interstitials $E_m = 0.15$ eV. These simulated profiles are similar to experimental observations in that they clearly show a parabolic distribution of loop density and smaller wires lead to much fewer dislocation loops. Furthermore, limiting the maximum size of loops (indicated as “arrested” for 100 nm NW) also increases the loop density (comparing to unarrested state) as more interstitials are free to nucleate loops. However, as Fig. 8a reveals, as E_m is increased beyond 0.15 eV, the dependence of loop density on wire diameter diminishes. When E_m is unrealistically large, ≥ 0.4 eV, all wires exhibit similar loop densities in the center of wires. Meanwhile the simulated loop density increases with greater E_m because interstitials cannot diffuse very far and loop nucleation is dominated not by interstitial diffusion to existing loops but by the creation of a high concentration of interstitials during the damage events such that the clustering probability of less mobile interstitials significantly increases. Fig. 8b illustrates that as the migration energy of interstitials increases, the average loop size in the center of the wires decreases. That is, as the number of loops increases, the average size decreases. Conversely, when the migration energy is small, the average loop size predicted by the model becomes quite large, almost 100 nm in diameter, unless the maximum size of interstitial loops is limited (as indicated by "arrested") to be comparable to the experimental observations. In MgAl_2O_4 , interstitial loops are found to grow only to a maximum size as they are faulted loops and the fault energy results in an energetic penalty for further growth [39].

To assess the sensitivity of the predicted results on our model, we considered two other variants of the model. Simulations using empirical potentials show that interstitial clusters in ZnO can have very high mobility, just as we found in MgO [40]. We thus constructed a model in

which we explicitly tracked di-interstitial clusters and considered a loop to be nucleated with clusters of sizes greater than 2 formed. The basic qualitative behavior did not change, as the loop distributions were governed by the slower moving species. That is, if clusters diffuse much quicker than mono-interstitials, they quickly find mono-interstitials (as at these radiation conditions there is always a large number of interstitials being produced) and nucleate a loop.

The second variant explicitly tracked Zn defects separately from O defects. In this model, the mobility of each type of interstitial could be changed independently, in accordance with theoretical results[36-38]. Again, as for the cluster model above, the behavior was dominated by the slower moving species. The results from this two-interstitial model and the original one-interstitial model are very similar if the mobility of the slowest interstitial was the same in both cases. That is, the behavior of this two-interstitial model can be captured in the one-interstitial model by setting the migration energy of the single interstitial to that of the slower interstitial in the two-interstitial model. We thus conclude that these variants, while maybe slightly changing the predicted loop densities and distributions, do not change the qualitative behavior, at least for the range of mobilities considered here.

4. Discussion

4.1 Defect denuded zones (DDZs) and swelling in NWs

The formation of DDZs in ZnO NWs is the result of the abundant defect sinks, free surface in particular. The width of the DDZs is strongly coupled to the migration energy (E_m) of interstitials. Our modeling shows that, for there to be a strong size (wire diameter) dependent loop density at room temperature, interstitials must diffuse quickly with a low E_m (~0.15 eV). Slow migration leads to essentially homogeneous loop distributions across the wire. The small value of E_m is in

agreement with DFT calculations[36]. However, the absolute magnitude of loop densities simulated in our model is smaller than the experimental observations. A number of factors may contribute to this disparity. First, *in situ* studies show that the preexisting loops trap radiation-induced loops and balance the sink effect from free surface, resulting in drastic increase of loop density locally. Second, electrostatic interactions between interstitials and loops may be significantly weaker than those between two interstitials, increasing the rate of $I+I \rightarrow L$ loop reactions over $I+L$ reactions (where L stands for loop), which is not accounted for in the model. Third, the rate of annihilation ($I+V \rightarrow 0$) recombinations might also be reduced if vacancies are allowed to form small clusters that do not interact with interstitials as strongly via electrostatics as monovacancies do. Finally, the actual Frenkel pair production rate may be higher in the experiments than estimated in the model or loops may essentially nucleate within the cascade. Both of these would tend to increase the loop density as interstitials and loop nuclei would be produced in higher quantities. Accounting for all of these factors that would lead to full agreement between the model and experiment is challenging, but the qualitative agreement reveals that both the dependence of the loop density on wire diameter and the DDZs observed near the surface of the wires is a direct consequence of the high mobility of interstitials.

Swelling of ZnO NWs along the radial direction observed under irradiation at room temperature mainly originates from the formation of interstitials clusters. The swelling rate of NW with diameter of 168 nm (Fig. 5c) has probably undergone an initial primary stage at high swelling rate, followed by a secondary stage at much lower rate. In comparison, as the wire diameter decreased, the primary swelling rate declined, implying an enhanced swelling resistance in wires of smaller diameters. Alleviation of swelling in ZnO NWs of smaller

diameters is a direct consequence of size dependent reduction of defect density due to the existence of free surface.

4.2 Dumbbell-shape distribution of dislocation loops in NWs

Free surface has hitherto known to be the strongest defect sinks. Without the influence of pristine loops, a uniform defect DDZ typically forms in ZnO NWs with a width of ~ 25 nm, as illustrated in Fig. 2a-c. However, in presence of pristine loops, we observed the dumbbell-shape distribution of dislocation loops (Fig. 5d). Such a surprising observation indicates that the stress field from these large loops (with size comparable to wire diameter) counteracts the image forces arising from image dislocations in close proximity to the free surfaces (as shown schematically in Fig. 6b) and fetters the radiation-induced small loops from escaping to the free surface.

Next we attempt to compare the stress field from the large loops and free surface. Khraishi et al. [41] calculated the stress field of a circular Volterra dislocation loop normal to the plane of a loop. Using the geometry of a pristine loop, shown schematically in Fig. 9a-b, we calculate the relevant stress field components (σ_{xx} and σ_{yy}) of the large pristine loop by using:

$$\begin{aligned} \sigma_{xx} = & \frac{x^2}{\rho^2} \left(-\frac{Gb_z}{\pi} [C_1 \mathbf{E}(k) + C_2 \mathbf{K}(k)] - \frac{Gb_z}{2\pi(1-\nu)} [C_3 \mathbf{E}(k) + C_4 \mathbf{K}(k)] \right) \\ & + \frac{y^2}{\rho^2} \left(-\frac{Gb_z}{\pi} [C_5 \mathbf{E}(k) + C_6 \mathbf{K}(k)] - \frac{Gb_z}{2\pi(1-\nu)} [C_7 \mathbf{E}(k) + C_8 \mathbf{K}(k)] \right) \end{aligned} \quad (6)$$

where the shear modulus $G = 44$ GPa, and Poisson's ratio $\nu = 0.35$. $\mathbf{K}(k)$ and $\mathbf{E}(k)$ are complete elliptic integrals of the first and second kinds respectively, where k is the modulus of these integrals or functions. $b_z = 0.520$ nm is the magnitude of Burgers vector along z -axis. Coefficients C_1 to C_8 are related to the spatial coordinates (x, y, z) and the loop radius, R . The resultant of stresses, $\sigma_{xx}^{\text{loop}}$ and $\sigma_{yy}^{\text{loop}}$, are calculated as a function of distance from the preexisting

large loops. It is evident that the magnitude of the stress decreases at locations farther away from the center of the two preexisting large loops. Meanwhile the free surface imposes two competing image stresses $\sigma_{xx}^{\text{image}}$ and $\sigma_{yy}^{\text{image}}$, calculated by using similar method for dislocation loops with a diameter of 6 nm. Comparisons of the stress field resulted from the large loops and the image force are illustrated in Fig. 9c. The image stress imposed on the small loops in the middle plane ($z=0$) at 25 nm from the free surface is calculated to be ~ 35 MPa, which is nearly identical to $\sigma_{xx}^{\text{loop}}$ and $\sigma_{yy}^{\text{loop}}$ arising from the pristine large loops. Within the dumbbell region the pristine loops exert more stress on the small loops, whereas the image stress prevails in the regions outside the dumbbell region. Foregoing discussions confirm that the attractive stress field from the pristine large loops can compete with the image stress or prevail in certain cases, leading to the observation of high density of dislocation loops in irradiated large NWs.

5. Conclusions

In situ Kr ion irradiations of ZnO NWs at room temperature show the existence of DDZs with a width of ~ 25 nm near free surfaces. The parabolic distribution of defect density in the wires, the size-dependent reduction of defect density and swelling are due to the surface defect sinks and low interstitial migration energy (~ 0.15 eV). NWs with sufficiently small wire diameters are nearly immune to radiation, manifested by the absence of interstitial loops and diminished radiation-induced swelling and creep. Preexisting dislocation loops show surprisingly large drag force that can compete with free surface. This study implies that nanowires of certain diameters may significantly enhance the radiation tolerance of oxides in general for device applications in extreme radiation environment.

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Table 1 List of parameters in the rate theory modeling.

Parameter	Physical Meaning	Value
P	Defect production rate	0.03356 defects/nm ³ s
t	Simulation time	2500 s
T	Temperature	300 K
d	Width of nanowire	variable
a	Nearest neighbor anion-anion distance	0.321 nm
v_0	Rate prefactor	10 ¹³ /s
E_{mi}	Interstitial migration energy	variable
E_{mv}	Vacancy migration energy	1.44 eV
Z	Reaction volume	7.704 nm
N_{max}	Maximum loop size	variable
A_{iL}	Number of interstitials in loop nucleus	2 interstitials

Fig.1. Microstructure of as-fabricated ZnO nanowires with different diameters. (a) SEM micrograph of as-received ZnO nanowires. The cross-section of the nanowire shows hexagonal shape. (b) Bright field (BF) TEM micrograph of a typical single crystal ZnO nanowire grew along $\langle 0001 \rangle$ direction. (c) Selected area diffraction (SAD) pattern confirm the formation of single crystal $\langle 0002 \rangle$ ZnO nanowire.

Fig.2. Defect denuded zone (DDZ) in ZnO nanowires with different diameters revealed by *in situ* Kr ion irradiations up to 5 dpa. (a) TEM micrograph showing a DDZ with a width of ~ 25 nm for a ZnO nanowire with an average diameter D of ~ 250 nm. A similar width of DDZ was also displayed in nanowires with D of 100 nm (b) and 70 nm (c). Meanwhile the density of defect clusters appeared to reduce with decreasing wire diameter. (d) When $D = 30$ nm, no clear evidence of dislocation loop can be observed, that is the wire of this diameter is immune to radiation induced damage. (e) High resolution TEM (HRTEM) image showing dislocation loops in irradiated nanowire with D of 70 nm. The dislocation loops, with ~ 5 nm in diameter, were located on $\{0001\}$ plane. (f) HRTEM image of irradiated nanowire ($D = 30$ nm) showing the absence of dislocation loops.

Fig.3. Quantitative analyses of size dependent enhancement of radiation tolerance in ZnO nanowires. (a) Defect cluster density as a function of distance to the center of wires for Kr ion irradiated ZnO nanowires with diameters of 30-250 nm. Parabolic distribution of defect density was observed in most cases, that is, defect density in central region is greater than that close to surfaces. (b) Wire size dependent peak dislocation loop density. The peak defect density is substantially higher in wires of larger diameters. When the wire diameter reduces to 30 nm, the ZnO nanowire is basically free from visible dislocation loops.

Fig.4. Comparison of statistical distribution of defect size in wires of 250 nm (a) and 70 nm (b) in diameter show that the average diameter of dislocation loops (d_{loop}) reduced with decreasing wire diameter. The dislocation segments formed in the wire with D of 250 nm were absent in the wire with D of 100 nm or less.

Fig.5. Radiation-induced swelling and interaction of large preexisting pristine dislocation loops with radiation-induced small defect clusters. (a) Bright field TEM image of several preexisting dislocation loops (L1-L3) in ZnO nanowire prior to irradiation. (b) After Kr ion irradiation up to 1.5 dpa, a high density of defect clusters was observed near an array of hexagonal shaped preexisting dislocation loops (L1- L3). The wire diameter (measured from the same location) swelled from 168 to 180 nm, and the dash arrows show the reference position for the measurements. Notice that another loop (L4) migrated upward along wire axial direction during radiation. (c) Comparison of radiation induced swelling (radial strain) in wires of various diameters shows that wires of larger diameter ($D = 168$ nm) swelled rapidly to $\sim 9.0\%$ by 5 dpa. In contrast, wires of smaller initial diameter, 61 nm, swelled gradually and moderately to $\sim 3.6\%$. (d) Magnified TEM micrograph of the loops L1 and L2 in Fig. 5b shows that a large number of small dislocation loops were trapped by pristine dislocation loops, and consequently a dumbbell distribution of small loops was observed.

Fig.6. (a) Schematic illustration of uniform DDZs in the region without pristine dislocation loops. (b) With preexisting dislocation loops, the attraction of radiation-induced loops by preexisting loops results in the dumbbell-shape distribution of defect clusters and non-uniform DDZs.

Fig.7. (a) Structure of the di-interstitial cluster (I₂) in wurtzite-structured ZnO. The interstitial atoms are highlighted (light colored larger spheres). Essentially, this structure has two split interstitials, one O and one Zn, next to each other. (b) Distribution of dislocation loop density vs. the distance to the center of the wires of various diameters. The interstitial migration energy E_m is 0.15 eV. “Arrested” indicates that the maximum loop size was limited.

Fig.8. (a) Loop density in the center of the wire as a function of wire diameter and interstitial migration energy (E_m). When E_m is in the range of 0.15-0.2 eV, a clear size dependent reduction of defect density is visible. (b) The average loop size in the center of the wire varies as a function of E_m , and in general depends little on wire diameter. When $E_m^{\text{arrest}} = 0.15\text{-}0.2\text{eV}$, the estimated loop diameter is consistent with experimental studies.

Fig.9. (a) Top view and (b) cross-section view of the geometry of two pristine dislocation loops that generate stress fields. The radius of loops is 90 nm and two loops were separated by 200 nm , following the geometry in Fig. 5d. (c) Bisectional view of a nanowire with 90 nm in radius showing stress values at numerous points between two preexisting large loops. The stress field from the preexisting large loops is compared to that of image stress for a dislocation loop with diameter of 6 nm .