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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 diameters 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 toward in-depth understanding of radiation response of functional oxide nanowires for electronic device applications in extreme environments.

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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 {1 1 1} and {1 1 0} planes, with Burgers vector along ⟨1 1 0⟩ 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 1010–1380 °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 $Ca_2Nd(SiO_4)_6O_2$ [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

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helium-implanted $Ni_{73}P_{27}$ 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 nuclear reactors.

Here, by using the *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 the 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, assisting their applications in electronic devices in extreme radiation environment.

2. Methodologies

2.1. Material 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 (25 eV) and O (28 eV) were used in the calculation.

2.2. 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) is 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]:

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

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

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

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

Physical meanings of the variables in the above equations are listed in Table 1. The first two equations represent the time evolution of the concentration of interstitials (C_i) and vacancies (C_v), respectively, the third equation is for the concentration of interstitial loops (C_L), and the fourth is for the concentration of interstitials in loops (C_{iL}). 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

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
ν_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

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