Fundamental aspects of radiation damage of nonmetallic materials:
Microstructural evolution

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IAEA/ICTP School on Physics of Radiation Effects and its Simulation for Non-metallic Condensed Matter

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Outline

• Temperature dependence of microstructural evolution
  • Important regimes include onset temperatures for interstitial and vacancy defects

• Dose dependence of microstructural evolution

• Effect of irradiation spectrum
  • Primary knock-on atom effects
  • Ionizing radiation effects
  • Swift heavy ion effects (brief introduction)
Electrical resistivity defect recovery stages in copper after electron irradiation at 4 K

Overview of Defect Microstructures in Irradiated Materials

- Dislocation loops
- Voids, precipitates, solute segregation
- Grain boundary helium cavities
- Amorphization

Irradiation Temperature ($T/T_M$)

- Stage I: 0.1
- Stage III: 0.2
- Stage V: 0.3

- 0.4
- 0.5
- 0.6
Microstructure of MgAl$_2$O$_4$ following 4 MeV Ar ion irradiation to 5 dpa at 200 K

Quantification of dislocation loops in irradiated materials

Habit plane determination

Displacement vector evaluation
Defect concentration at four depths in ZnO irradiated with 200 keV Ar ions at 15K (Rutherford Backscattering Spectrometry)

Note: defect saturation achieved for a dose <0.05 dpa at low $T_{irr}$ (immobile defects)

Overview of swelling regimes in Al₂O₃

- 3 distinct swelling regimes are observed in irradiated Al₂O₃

- Activation Energies:
  - Al vacancy: 1.8-2.1 eV
  - O vacancy: 1.8-2 eV
  - Al, O interstitial: 0.2-0.8 eV

Clinard, 1982

Amorphous Point defect swelling Void swelling
Irradiation-induced swelling in SiC

Amorphous Regime → Saturable Regime → Non-Saturable Regime

<table>
<thead>
<tr>
<th>Amorphous Regime</th>
<th>Saturable Regime</th>
<th>Non-Saturable Regime</th>
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Stage I Stage III

800°C, 40 dpa
Katoh ICFRM14

8.5 dpa
5 dpa
1.75 dpa

Swelling (%) vs Irradiation Temperature (°C)
Comparison of point defect swelling behavior in irradiated metals and ceramics

- Large variation in magnitude of point defect swelling in materials
  - Metals typically have point defect swelling values near 0.1% (Al, Cu, Ag, Au), compared to 1-5% for ceramics
    - Implies shorter point defect recombination radii or reduced barriers for recombination in metals versus ceramics

Keilholtz et al. 1966
Snead & Katoh, 2008
Zinkle & Singh, unpubl.
Berger et al. 1964
One strategy for radiation resistance: Immobile defects

- Defect accumulation is limited if one or more defect types are immobile
  - Utilize materials with negligible point defect mobility at desired operating temperatures
  - A key potential consequence (particularly in ordered alloys and ceramics) is amorphization, with accompanying significant volumetric and property changes

*Regime with intrinsically high point defect recombination typically occurs at too low of temperatures for power generation applications (except SiC and possibly Al$_2$O$_3$, W, Re)*

*after S.J. Zinkle, Chpt. 3 in Comprehensive Nuclear Materials (Elsevier, 2012)*
Effect of fission neutron irradiation near 75°C on the lattice parameters of BeO

Amorphization occurs by several mechanisms or pathways
Direct-Impact Amorphization in Ceramics

Amorphization Along 800 keV Kr⁺ Ion Track in Ca₂La₈(SiO₄)₆O₂

W.J. Weber et al.
Calculated depth-dependent damage energy and implanted ion profiles for 2 MeV Al ion irradiated MgAl$_2$O$_4$

Colloidal metal nanoclusters can be created in MgAl_2O_4

Energy loss (eV)

Intensity (counts)

Matrix plasmon peak

colloid peak

Energy-filtered TEM used to quantify colloid distribution
Implanted ion stabilized amorphous band in Si$_3$N$_4$ after 3.6 MeV Fe ion irradiation at 300 K

0.22x10$^{20}$ Fe/m$^2$
1.3 dpa, 0.1 at.% Fe at peak

1.1x10$^{20}$ Fe/m$^2$
7 dpa, 0.4 at.% Fe at peak; 5 dpa at 1.5 μm

Defect clusters in AlN after 2 MeV Si ion irradiation to $4 \times 10^{20}$/m$^2$ at 78 K

~5 dpa
Defect-free zones are predicted next to sinks (e.g., grain boundaries) due to reduced point defect concentration.

- Solve steady state rate eqns:

\[
\begin{align*}
D_i \frac{d^2 C_i}{dx^2} - \alpha C_i C_v - D_i C_i C_s + P &= 0 \\
D_v \frac{d^2 C_v}{dx^2} - \alpha C_i C_v - D_v C_v C_s + P &= 0
\end{align*}
\]


Distance

cf. R. Sizmann (1978), etc.
Depth dependent microstructure of MgAl$_2$O$_4$ irradiated with 2 MeV Al ions to a fluence of 4.6x10$^{20}$/m$^2$ at 650°C

Determination of interstitial migration energies in ceramics

Defect-free zones in ion-irradiated MgAl₂O₄

- Solve steady state rate eqns:
  \[ D_i \frac{d^2 C_i}{dx^2} - \alpha C_i C_v - D_i C_i C_s + P = 0 \]
  \[ D_v \frac{d^2 C_v}{dx^2} - \alpha C_i C_v - D_v C_v C_s + P = 0 \]

- For sink-dominant conditions \((C_v > 10^{14}/m^2)\), the defect-free zone width is related to the diffusivity \((D_i)\) and damage rate \((P)\) by:
  \[ D_i = \frac{L P}{C_{i,\text{crit}} \sqrt{C_s}} \]
Weighted average recoil atom energy for 1 MeV particles in copper as a function of recoil energy (T)

Comparison of molecular dynamics simulations of 1-50 keV PKA displacement cascades in iron
Displacement cascades in ceramics such as SiC are much less compact than in medium-Z metals.


Time dependence and spatial distribution of defect production in a 50 keV Si cascade

F Gao & WJ Weber
Defects & Amorphous Atoms for 30 keV U in Zircon

- 1.1 million atom simulation
- Zr, Si and O are shown
- Core is Si rich; periphery is Zr rich

SiC Amorphization

3 recovery substages are observed below 320 K

Analysis of flux dependence shows recovery substages are not associated with long range point defect migration (F<0.5 up to 380 K)

Implies that both vacancies and interstitials are immobile in SiC up to 100°C (interstitials are mobile in many other ceramics at room temperature)
Effect of irradiating particle (PKA energy) on the temperature-dependent dose for amorphization


Note: there are also numerous cases where PKA energy has a weak effect on amorphization dose (degree of sensitivity is linked to amorphization mechanisms).
ZrSiO$_4$: Temperature Dependence

Good Agreement Between Heavy-Ion (Pb and Bi) Data and $^{238}$Pu Data

(T$_c$ is Independent of Irradiating Ion Mass → Thermal Recovery Process)

W.J. Weber et al.
Cross-section microstructure of $\text{Al}_2\text{O}_3$ irradiated with 2 MeV Al ions at 650 C to a fluence of $9 \times 10^{20}/\text{m}^2$

Cross-section microstructure of Al$_2$O$_3$ irradiated with 3 MeV C ions at 420 C to 18 dpa

Cross-section microstructure of Al₂O₃ irradiated with 1 MeV He ions at 650 C to a fluence of 1x10²²/m²

Cross-section microstructure of $\text{Al}_2\text{O}_3$ irradiated with 1 MeV H ions at 650 C to a fluence of $1.7 \times 10^{22}/\text{m}^2$

3 dpa, 60at.%H at peak; 0.03 dpa at 0.5 $\mu$m

Cross-section TEM microstructure of 1 MeV He ion irradiated MgAl$_2$O$_4$ at 650°C (1x10$^{21}$ He/m$^2$)

Investigation of ionization-induced diffusion in ceramics

Large interstitial loops in MgAl$_2$O$_4$ ion-irradiated at 25°C for regions with >100 eln.-hole pairs per dpa


Aligned cavities in Al$_2$O$_3$ ion-irradiated at 25°C (Al/O/He ion irradiation, >500 eln.-hole pairs per dpa)
Ionizing Radiation can induce myriad effects in ceramics

• Defect annealing and coalescence (ionization-induced diffusion)
  – Athermal defect migration is possible in some materials

• Defect production
  – Radiolysis (SiO$_2$, alkali halides)
  – Ion track damage (“swift heavy ions”)

Ionizing Radiation can induce recrystallization in amorphous ceramics

- 120 keV electron (subthreshold displacement energy) illumination of MgAl$_2$O$_4$ (amorphized by swift heavy ion irradiation)

Max energy transfer = 11 eV (Al), 12 eV (Mg), 18 eV (O)
Swift heavy ions ($S_e > 1-10$ keV/nm) can introduce new physical phenomena in metals compared to conventional particle irradiations.

Fig. 1. Electronic and nuclear stopping powers of xenon ions in an iron target as a function of the incident ion energy.
Swift heavy ions ($S_e > 1-10$ keV/nm) can introduce new radiation effects phenomena.

**Electronic Stopping Powers in Alumina**

- **72 MeV $I^+$** $\rightarrow$ $\text{MgAl}_2\text{O}_4$
- **710 MeV $\text{Bi}$** $\rightarrow$ $\text{Al}_2\text{O}_3$

Zinkle et al., NIMB 91 (2002) 758

Amorphization for $S_e > 7.5$ keV/nm

Skuratov et al., Rad. Meas. 34 (2001) 571

Zinkle et al., MRS symp proc 540 (1999) p. 299
The high electronic stopping powers associated with fission fragment recoil ions can produce pronounced effects

- \( \text{MgAl}_2\text{O}_4 \) irradiated with 72 MeV \( \text{I}^+ \) ions experiences a crystalline phase change and then amorphization when \( \frac{dE}{dx})_e > 8 \text{ keV/nm} \)
  - Volumetric expansion \( \Delta V/V \sim 35\% \) due to amorphization will cause severe stresses and cracking
  - Amorphization occurs readily up to 500 \( ^\circ \text{C} \)

The threshold $dE/dx$ value for Si$_3$N$_4$ track formation is $\sim 15$ keV/nm.

710 MeV Bi $\rightarrow$ Si$_3$N$_4$
## Summary of threshold ionizing radiation levels for defect production in ceramics

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal conductivity (W/m-K)</th>
<th>Threshold dE/dx)_e for ion track damage</th>
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</thead>
<tbody>
<tr>
<td>MgAl_2O_4</td>
<td>20</td>
<td>8 keV/nm</td>
</tr>
<tr>
<td>β-Si_3N_4</td>
<td>29</td>
<td>15 keV/nm</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>32</td>
<td>~20 keV/nm</td>
</tr>
<tr>
<td>AlN</td>
<td>177</td>
<td>&gt;34 keV/nm</td>
</tr>
<tr>
<td>SiC</td>
<td>350</td>
<td>&gt;34 keV/nm</td>
</tr>
<tr>
<td>U_3Si</td>
<td></td>
<td>19 keV/nm [Hou 2003]</td>
</tr>
<tr>
<td>UO_2</td>
<td></td>
<td>22-29 keV/nm [Matzke 2000]</td>
</tr>
</tbody>
</table>

- Velocity effects also need to be considered (low velocity ions are more effective at inducing damage for a given dE/dx)_e)

- Threshold dE/dx)_e is higher than the ionizing radiation fields anticipated in fission or fusion reactors

- Studies on effect of radiation-induced thermal conductivity degradation on threshold dE/dx for track formation are in progress

  - Radiation-induced degradation of K_th may cause reduction in threshold dE/dx)_e
Conclusions

• Irradiation temperature has a pronounced effect on microstructural evolution
  • Important regimes include onset temperatures for interstitial and vacancy defects

• Dose dependence of microstructural evolution is generally more complex at elevated temperatures
  • Saturation often occurs at 0.1-0.5 dpa at low temperatures

• Implanted ions can exert significant influence on the microstructural evolution (e.g., amorphization, precipitation)

• Effect of irradiation spectrum can be complex
  • Primary knock-on atom effects
  • Ionizing radiation effects
  • Swift heavy ion effects (brief introduction)
Radiation Damage can Produce Large Changes in Ceramic Materials

- Amorphization and disordering (<0.2 $T_M$, >0.1 dpa)

- Thermal conductivity degradation and defect cluster swelling (<0.35 $T_M$, >0.01 dpa)

- Phase instabilities from radiation-induced precipitation (0.3-0.6 $T_M$, >10 dpa)

- Irradiation creep (<0.45 $T_M$, >10 dpa)

- Volumetric swelling from void formation (0.3-0.6 $T_M$, >10 dpa)

after S.J. Zinkle, Chpt. 3 in Comprehensive Nuclear Materials (Elsevier, 2012)
Depth dependent microstructure of MgAl$_2$O$_4$ irradiated with 2 MeV Al ions to a fluence of $3.7 \times 10^{21}/\text{m}^2$ at 650$^\circ\text{C}$

101 dpa at peak damage;
30 dpa at 0.5 $\mu\text{m}$