Russian Research Center” Kurchatov Institute”

Qualification of behavior of new structural composite materials - SiC under neutron and charged particle irradiation

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Joint ICTP/IAEA Advanced Workshop on Development of Radiation Resistant Materials

20-24 April 2009, Trieste, Italy

Fabrication of SiC

SiC *was first synthesized in 1891 by Acheson:*

(E.G.Acheson, Chem.News 68 (1893) 179).

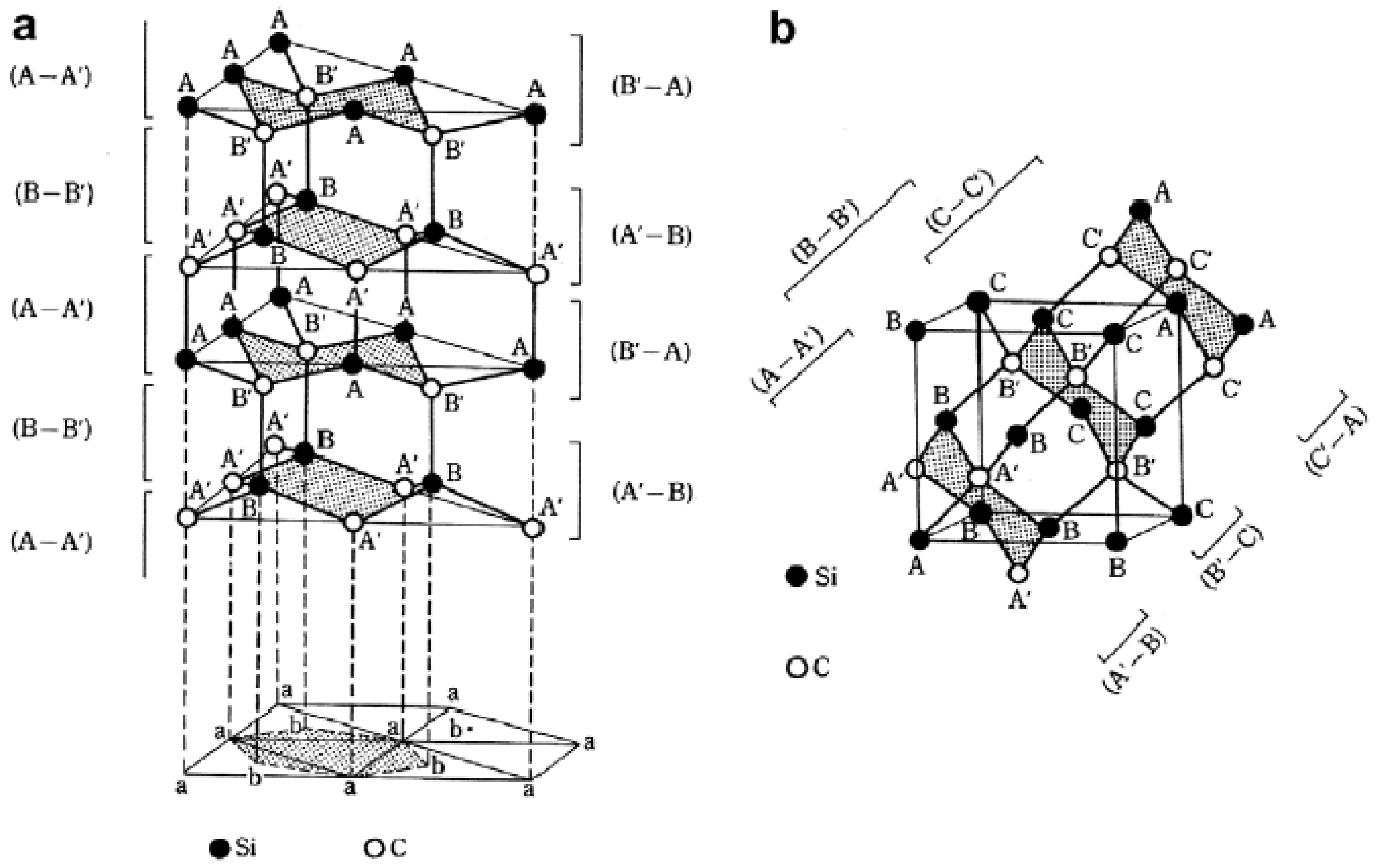
By electrochemical reaction in an electric furnace:

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

α-SiC formed at T = 2373 K and

β-SiC formed at T = 1273 – 1873 K

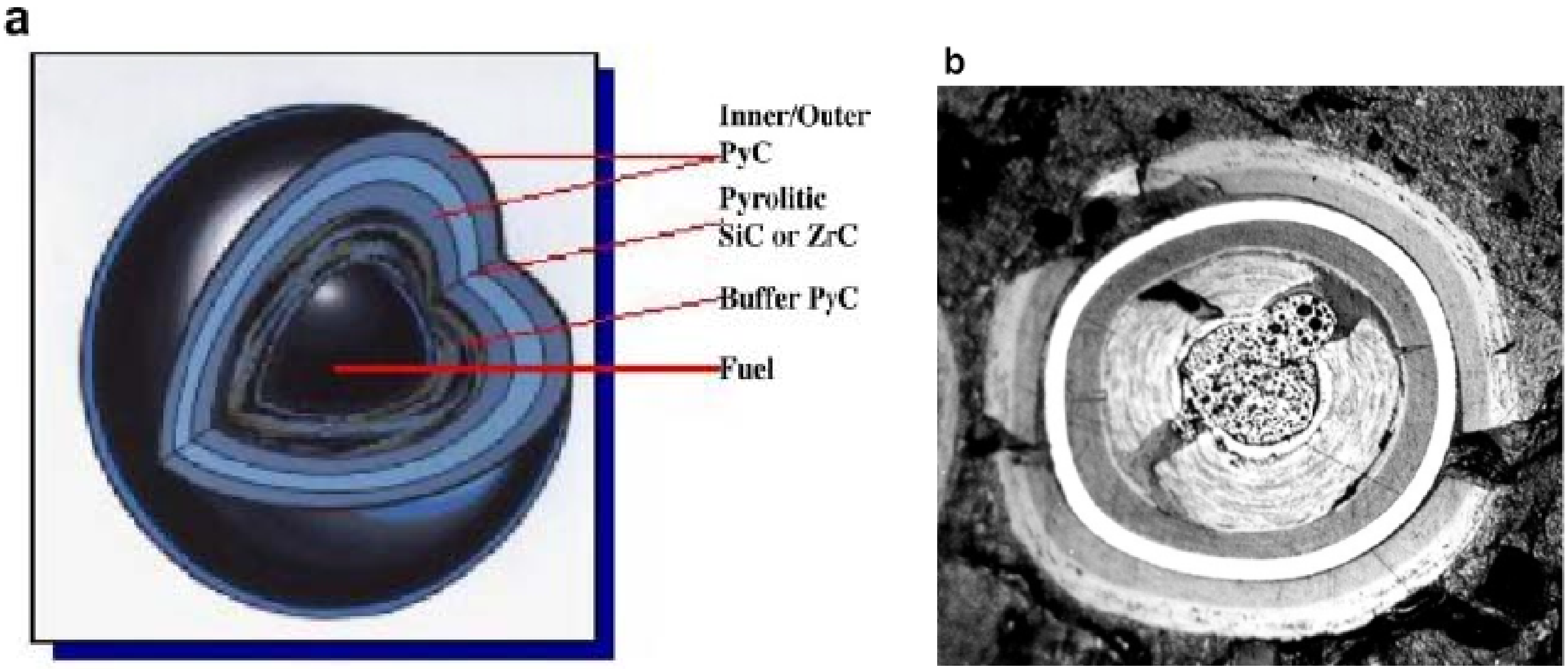
Crystal structures of (a) α-SiC and (b) β-SiC



Possibility for using of SiC materials in nuclear energy systems:

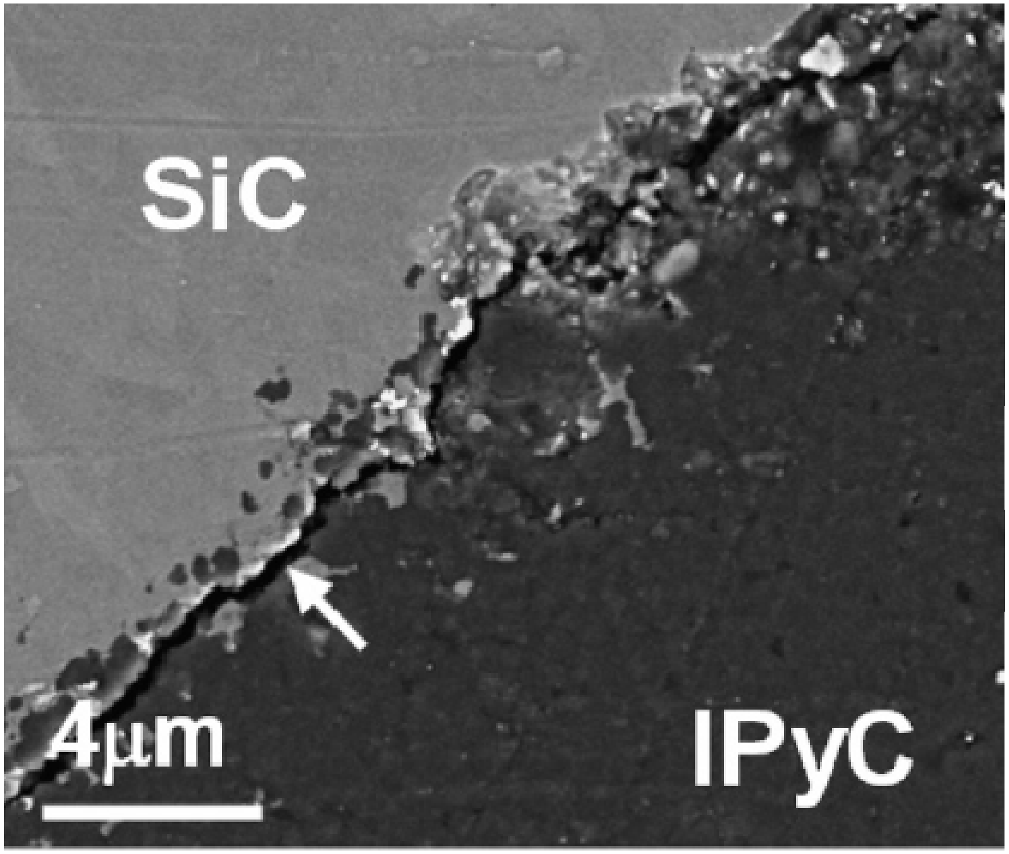
- fuel element in high temperature gas-cooled reactor (HTGR)
- fuel blocks for the gas fast reactors (GFR)
- guide tubes materials in very high temperature reactors (VHTR)
- test blanket module designs for the ITER

Schematic illustration of fuel elements: nonirradiated (a) and irradiated (b)



L. Snead, ORNL

Crack propagation at the inner Py/SiC interface



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Background and Objective

Silicon Carbide - Superior Performance for advanced Energy systems

Under the irradiation environment

- Potential irradiation resistance
- Low induced activity, Low after-heat

At the elevated Temperature

- High strength, Chemical stability

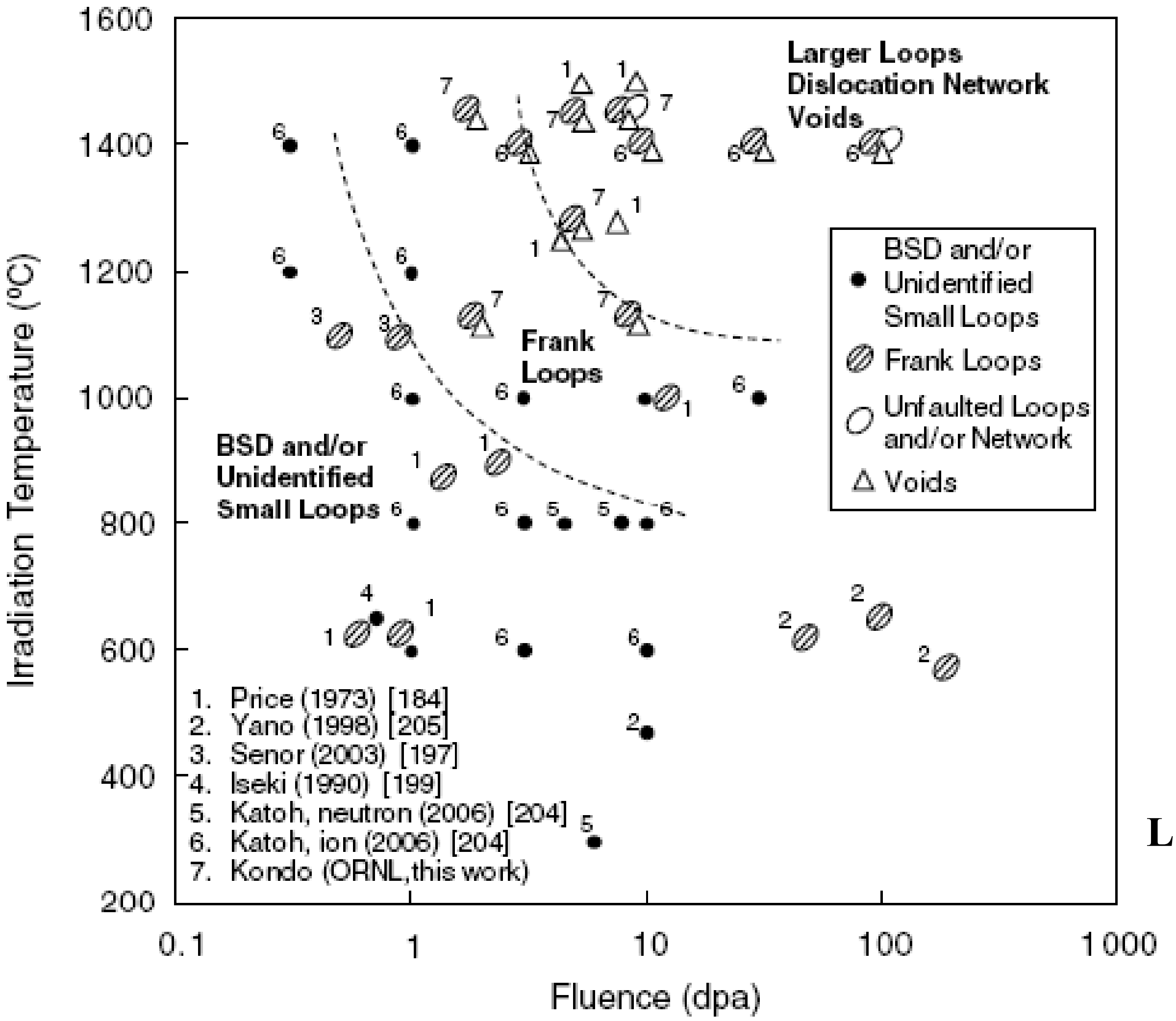
Issues under irradiation environment

- Irradiation induced volume expansion (swelling)
- Effects of helium production through (n, α) nuclear reaction (in fusion)

Objective

- Determine the effects of irradiation conditions on swelling in SiC
- Investigation of the synergistic effects of displacement damage and helium production

Microstructural development in cubic SiC during neutron and ion irradiations



L. Snead, Y. Katoh, ORNL

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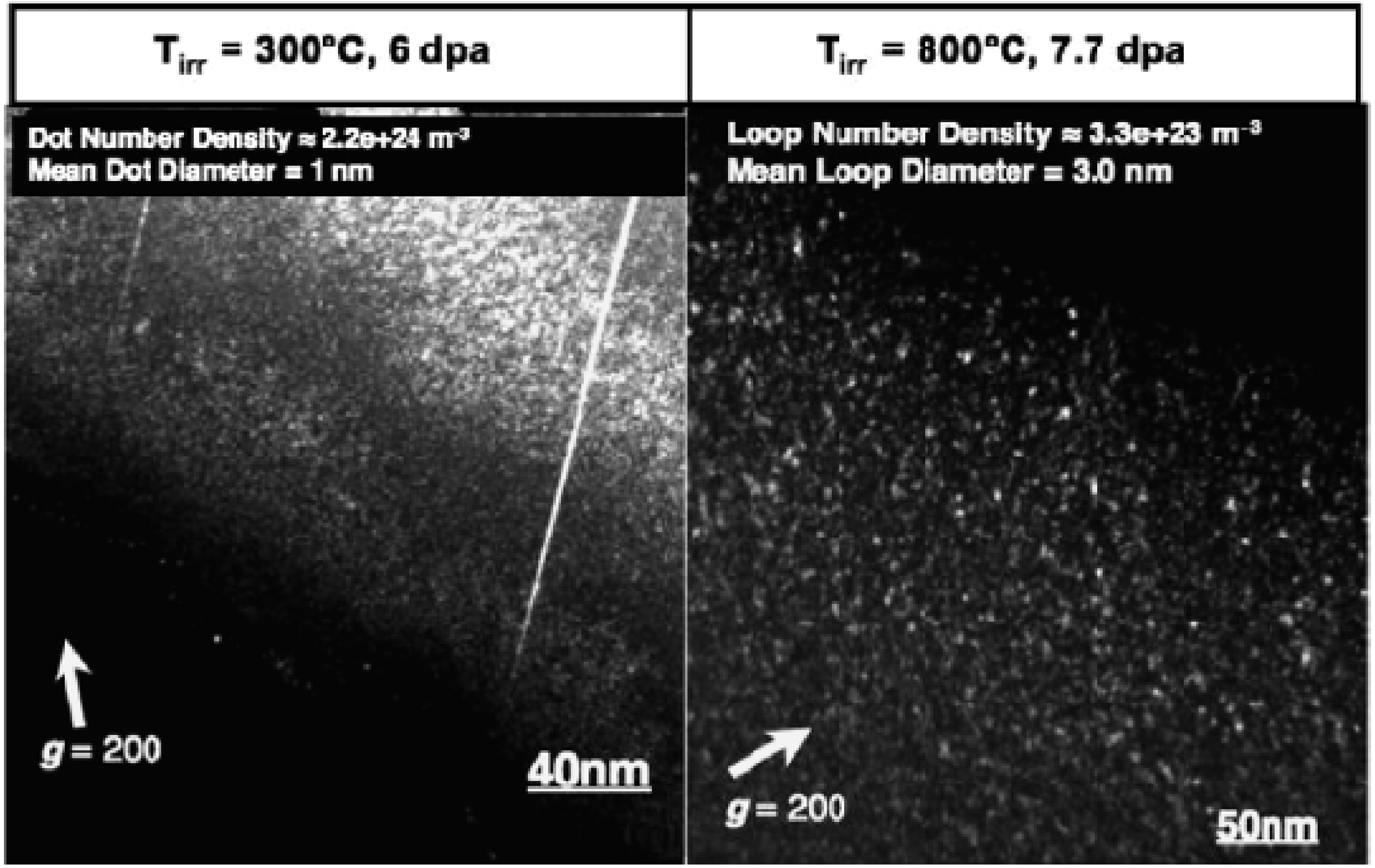
Saturated microstructure for CVD SiC neutron irradiated at 573 K and 1073K



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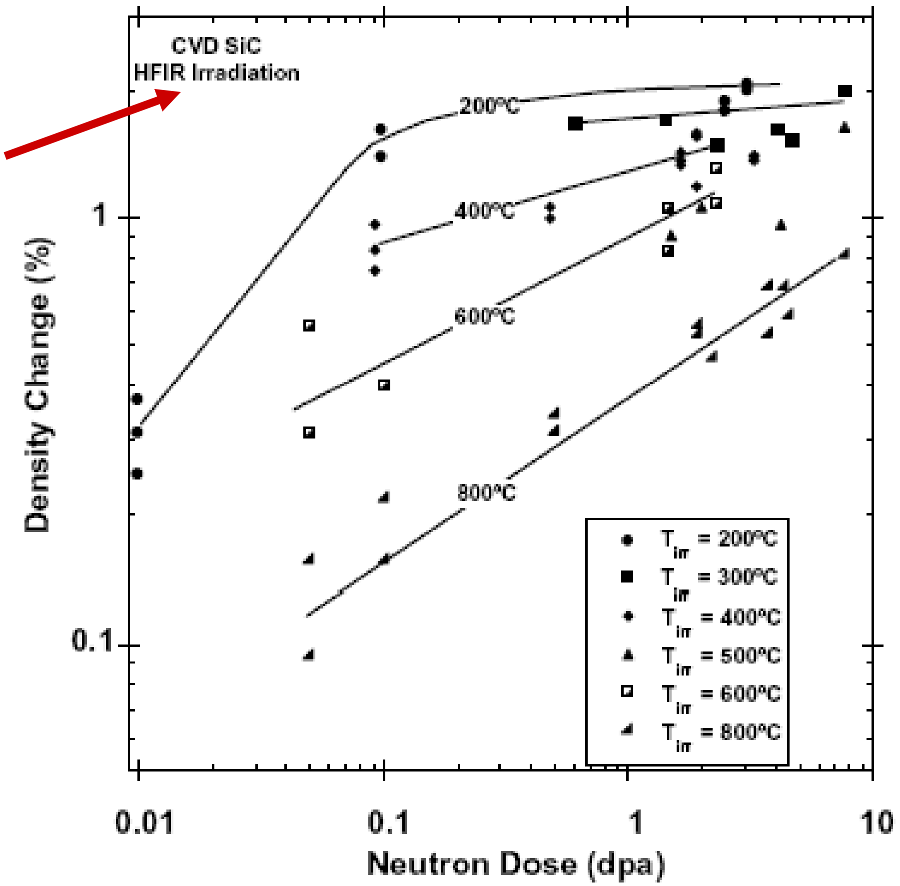
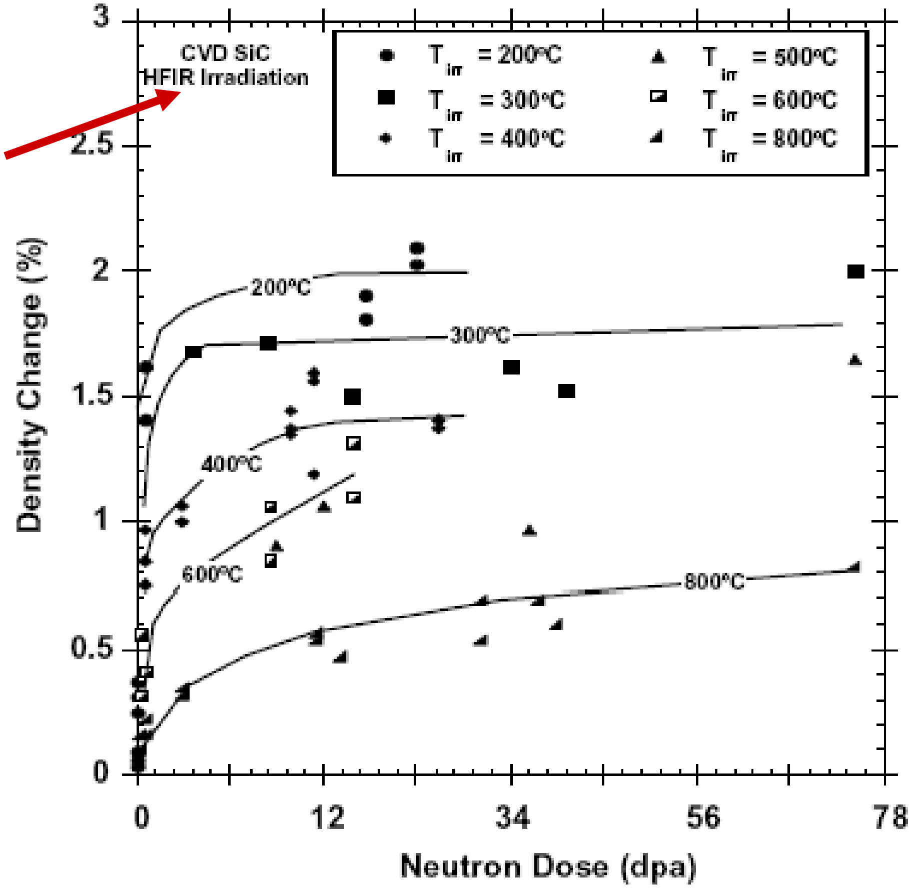
Swelling regime of CVD SiC at different irradiation doses and temperatures.





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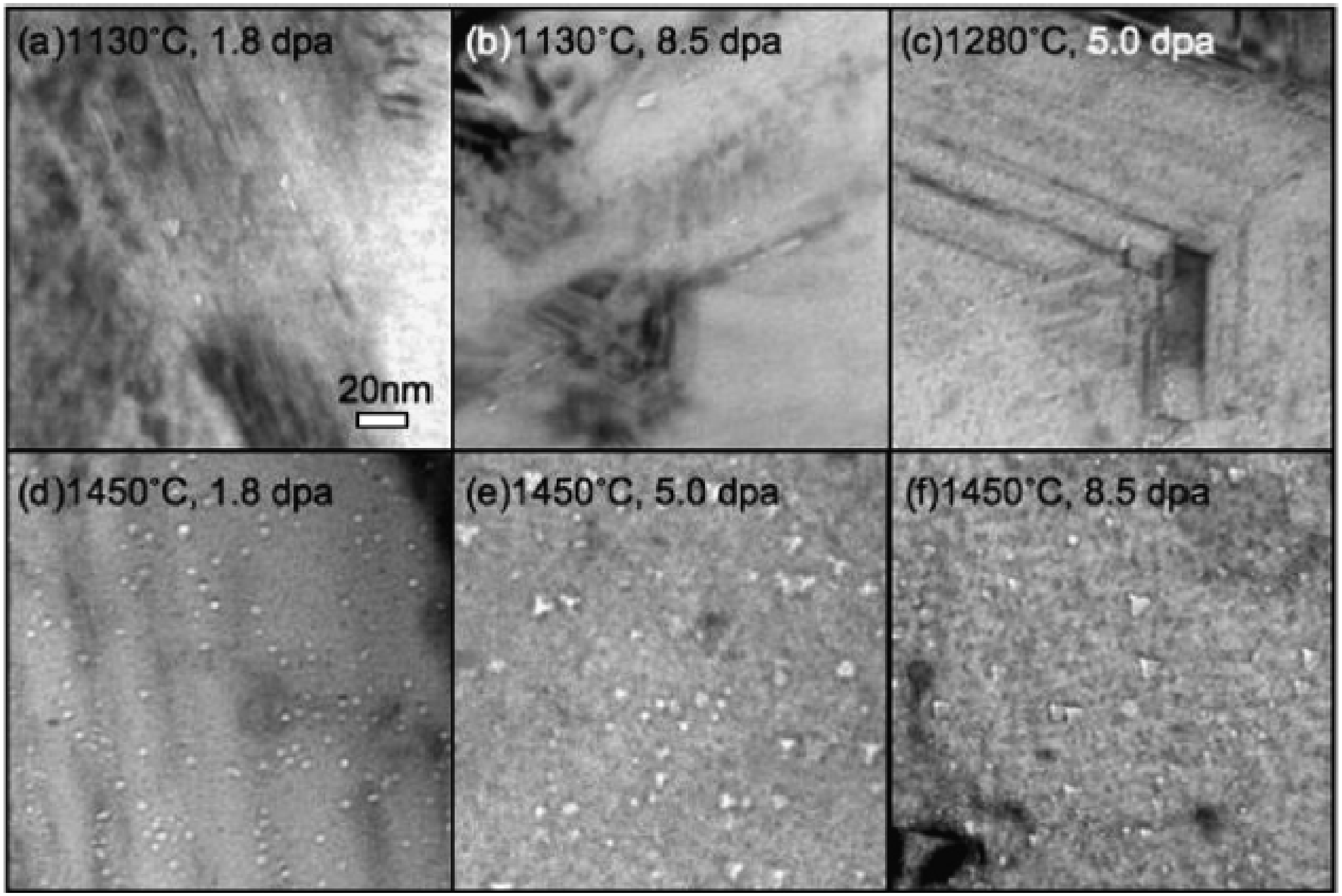
Evolution of voids in high temperature irradiated CVD SiC



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Experimental

Materials: *Morton CVD-SiC (Polycrystalline β-SiC)*

Specimen geometry: $3.0\text{mm}^{f} \times 0.25\text{mm}^{t}$

Ion beam irradiation:

Specimens are covered with molybdenum meshes

Facility: *HIT facility, University of Tokyo*

Ions: *4MeV Ni*

4MeV Ni + 1MeV He (degraded)

Temperature: *T= 333K, 473K, 673K, 873 K*

Dose rate: *f = $1\text{x}10^{-5}$ - $1\text{x}10^{-3}$ dpa/s (nominal)*

Dose: *0.005-100dpa (nominal)*

He/dpa ratio: *60 appm He/dpa (nominal)*

Swelling characterization :

Surface profilometry by the optical interferometry

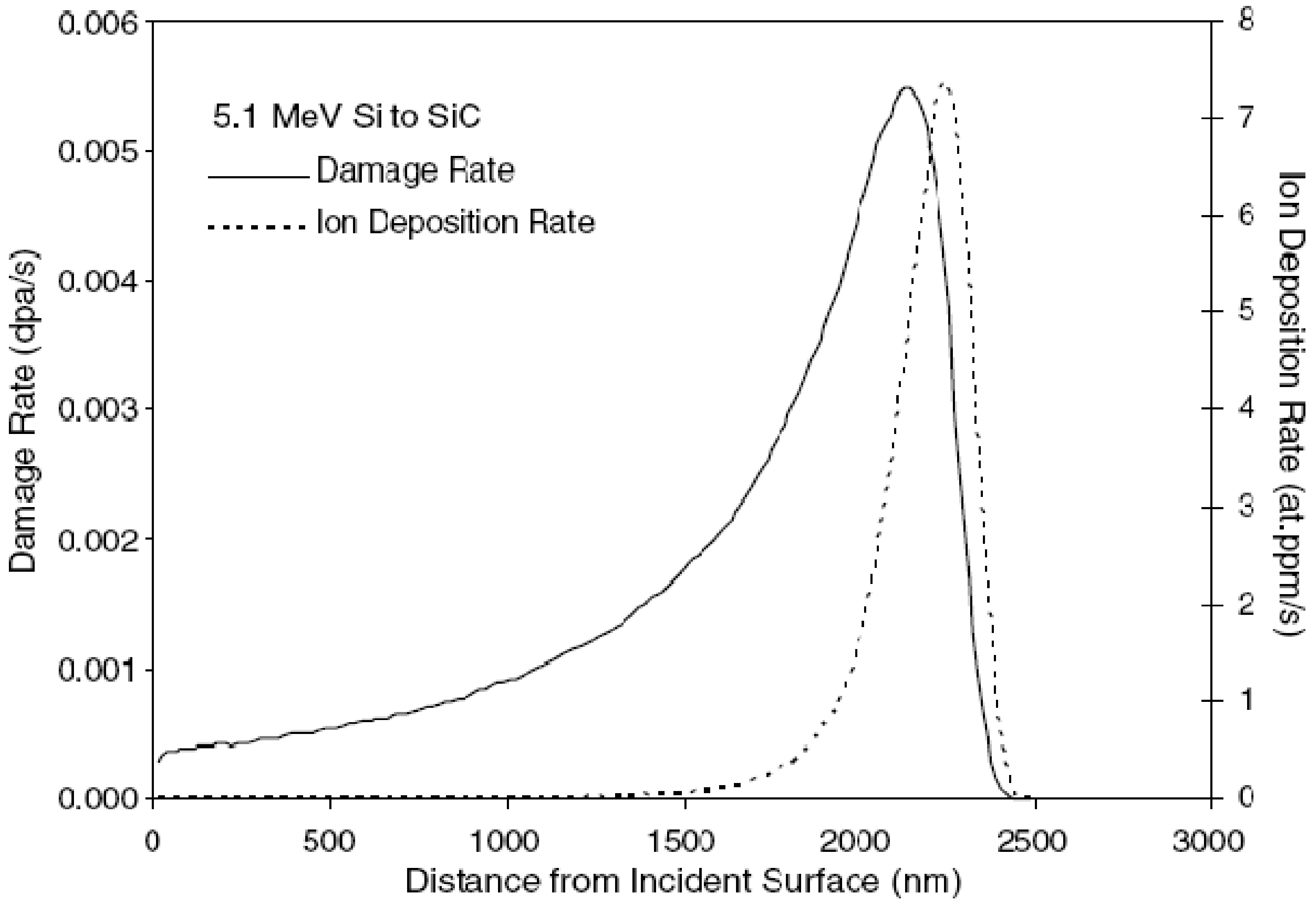
Thin film Processing :

Performed by Focused ion beam (FIB) devise

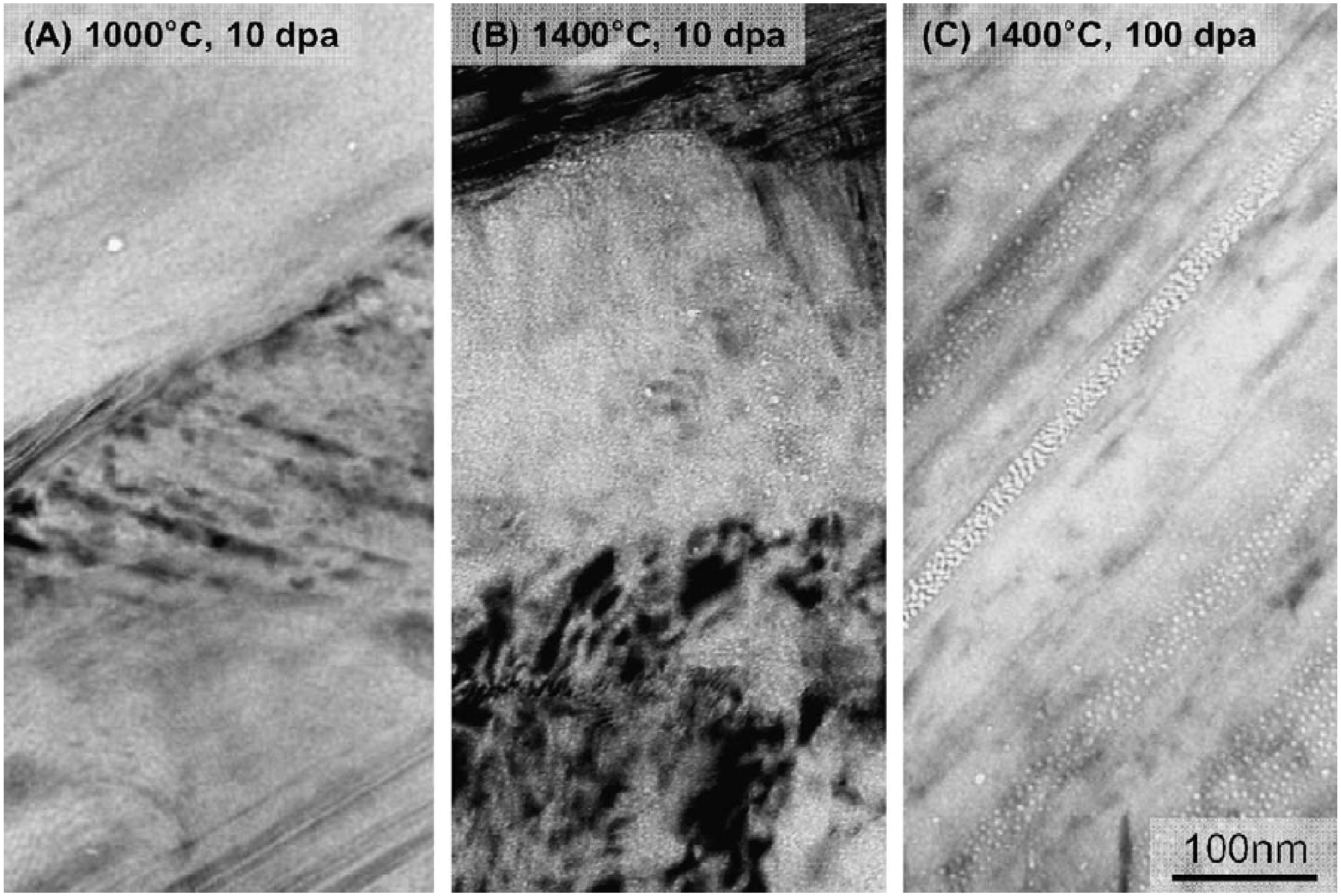
/JEOL/Micrion JFIB-2100

TEM observation : */JEOL JEM-2010 (200kV)*

Displacement damage and ion deposited rate profiles in SiC irradiated by 5.1 MeV Si ions

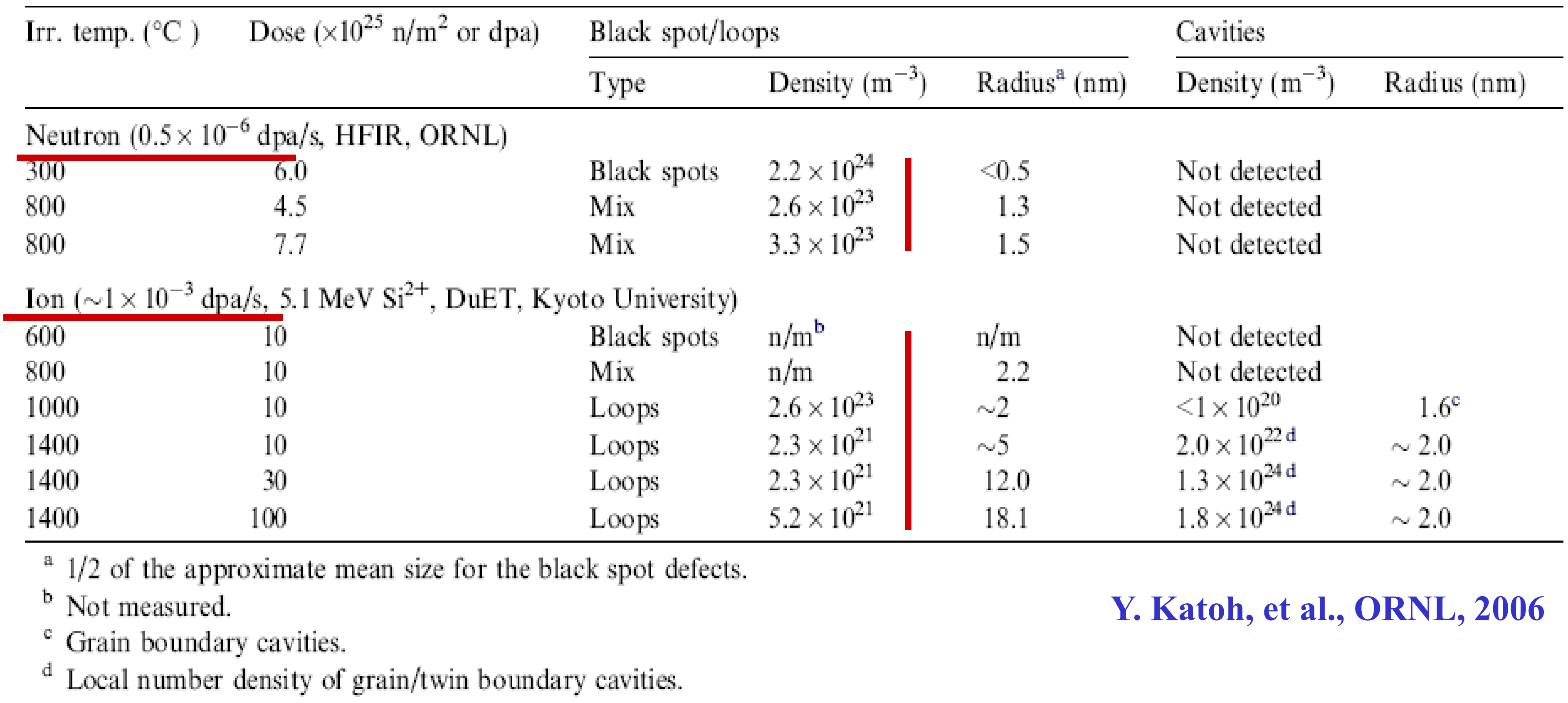


Cavity microstructure in cubic SiC irradiated by 5.1 MeV Si ions



Y. Katoh, ORNL

Microstructural data for irradiated cubic SiC



Irr. temp. (°C)	Dose ($\times 10^{25}$ n/m^2 or dpa)	Black spot/loops			Cavities	
		Type	Density (m^{-3})	Radius[a] (nm)	Density (m^{-3})	Radius (nm)
Neutron (0.5×10^{-6} dpa/s, HFIR, ORNL)						
300	6.0	Black spots	2.2×10^{24}	<0.5	Not detected	
800	4.5	Mix	2.6×10^{23}	1.3	Not detected	
800	7.7	Mix	3.3×10^{23}	1.5	Not detected	
Ion ($\sim1\times10^{-3}$ dpa/s, 5.1 MeV Si^{2+}, DuET, Kyoto University)						
600	10	Black spots	n/m[b]	n/m	Not detected	
800	10	Mix	n/m	2.2	Not detected	
1000	10	Loops	2.6×10^{23}	~2	$<1\times10^{20}$	1.6[c]
1400	10	Loops	2.3×10^{21}	~5	2.0×10^{22} [d]	~ 2.0
1400	30	Loops	2.3×10^{21}	12.0	1.3×10^{24} [d]	~ 2.0
1400	100	Loops	5.2×10^{21}	18.1	1.8×10^{24} [d]	~ 2.0

[a] 1/2 of the approximate mean size for the black spot defects.

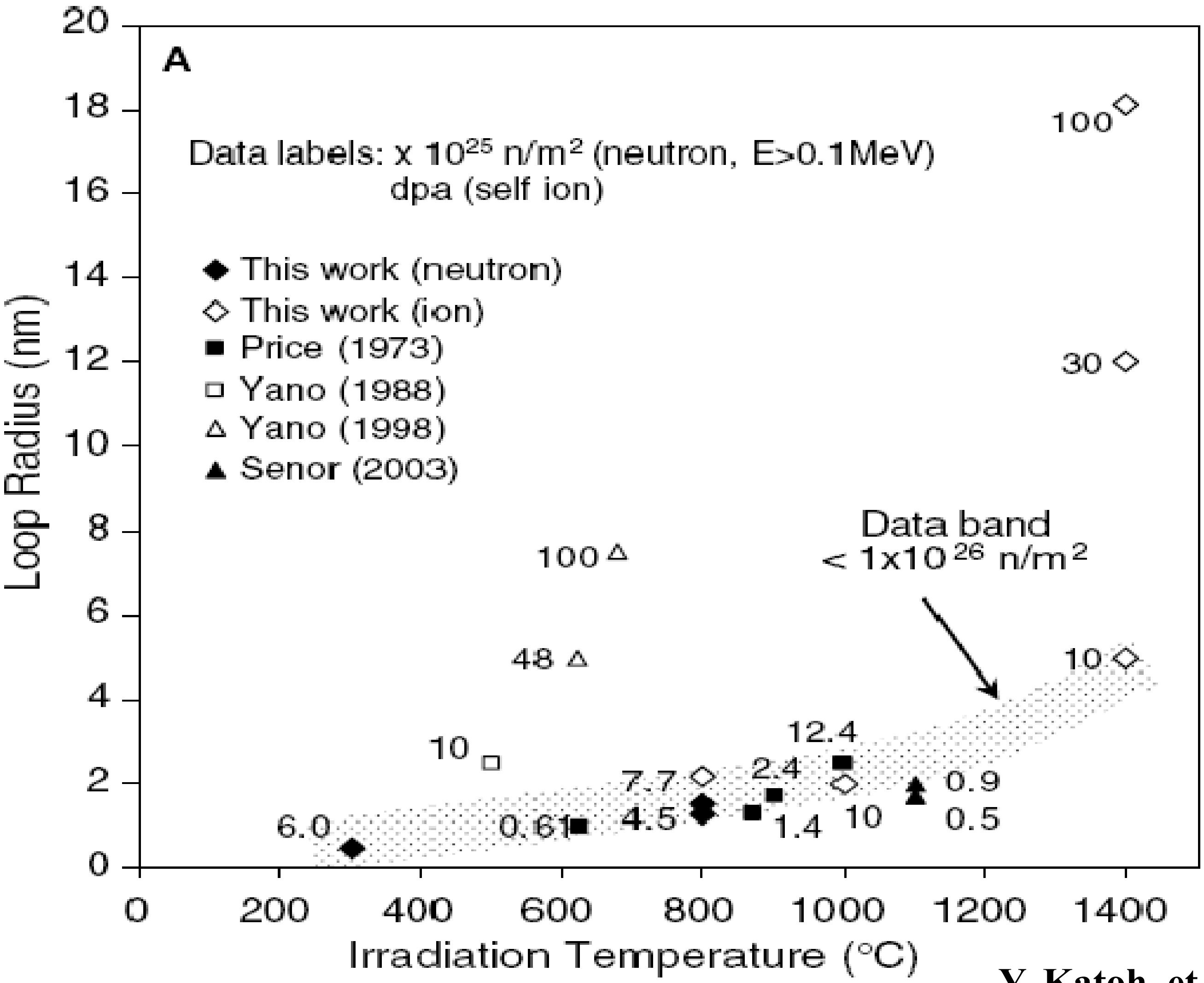
[b] Not measured.

[c] Grain boundary cavities.

[d] Local number density of grain/twin boundary cavities.

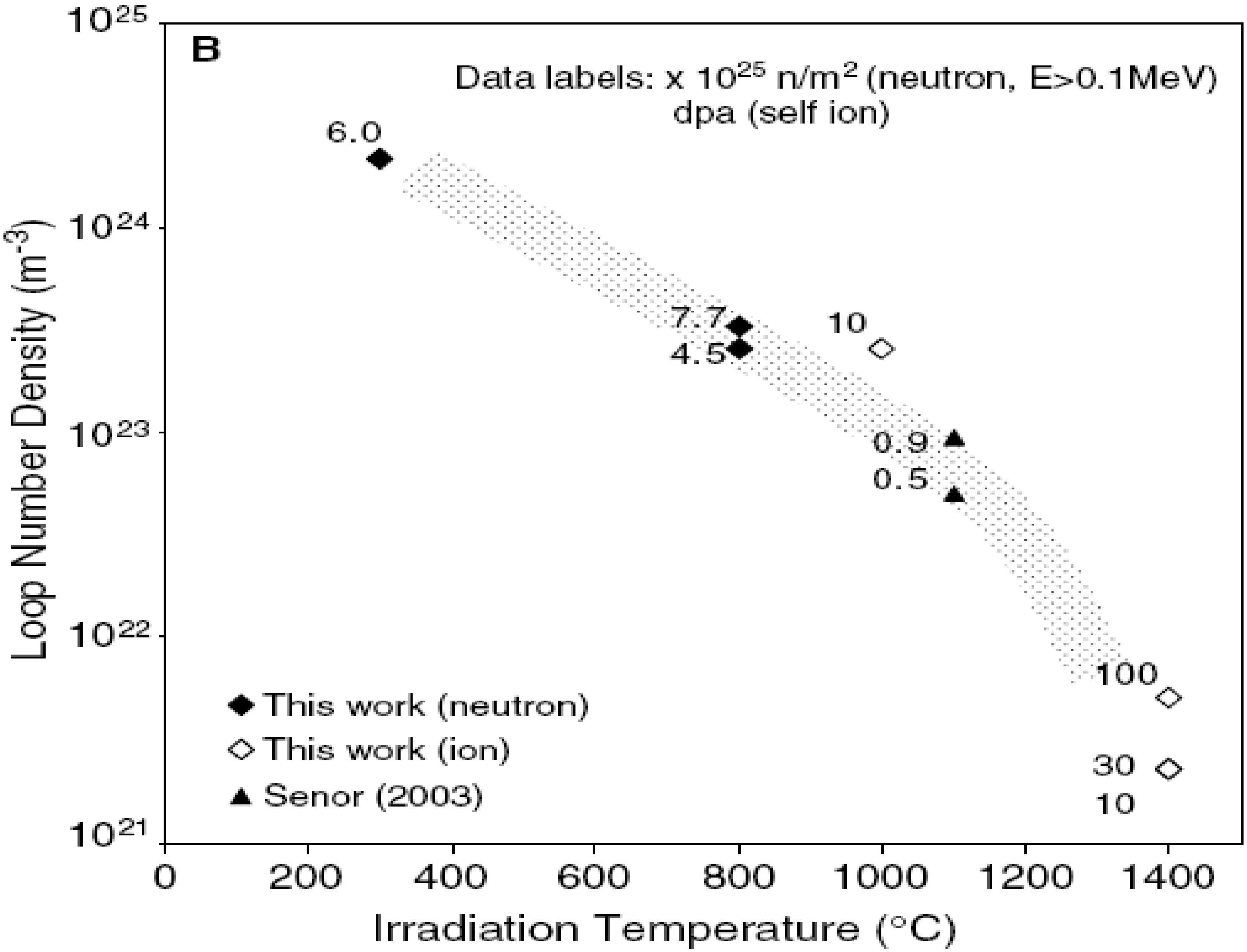
Y. Katoh, et al., ORNL, 2006

Temperature dependence of dislocation loop growth



Y. Katoh, et al., ORNL, 2006

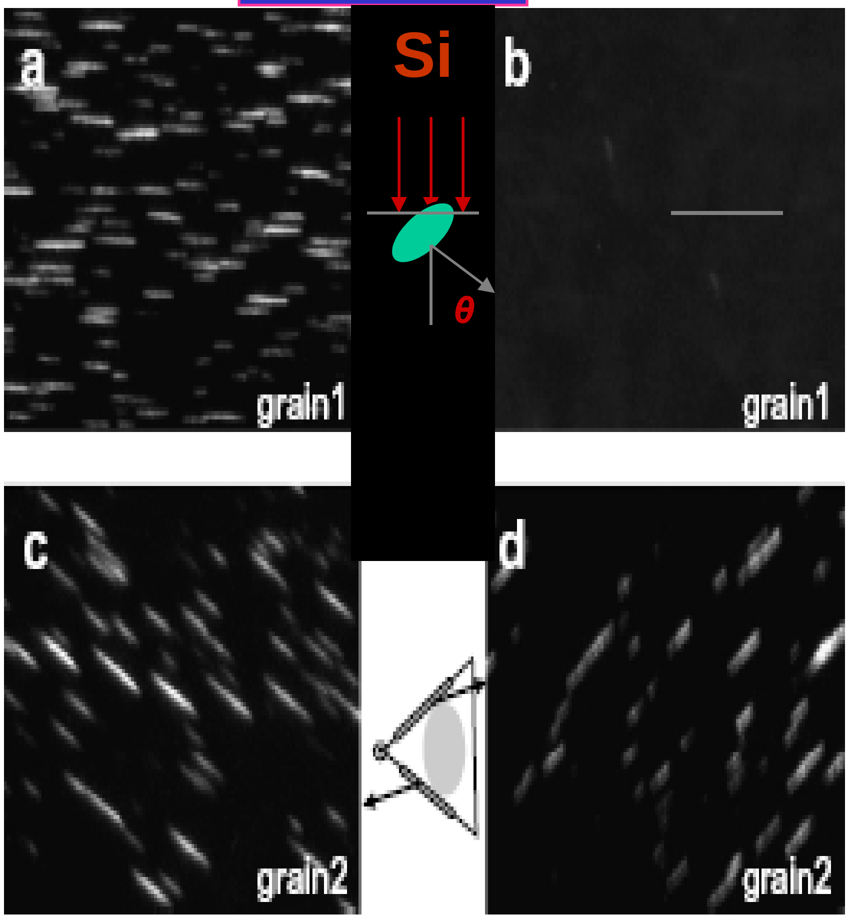
Temperature dependence of dislocation loop density

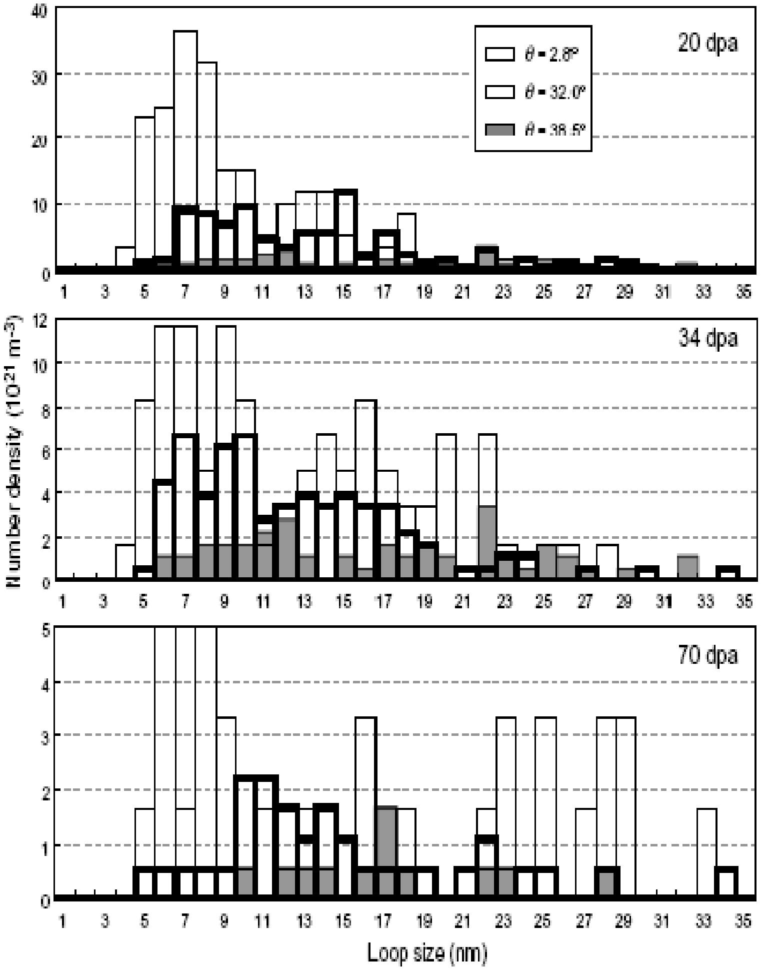


Y. Katoh, et al., ORNL, 2006

TEM images of Frank loops in SiC under 5.1 MeV Si ion irradiation at 1400 C

Dose~34 dpa

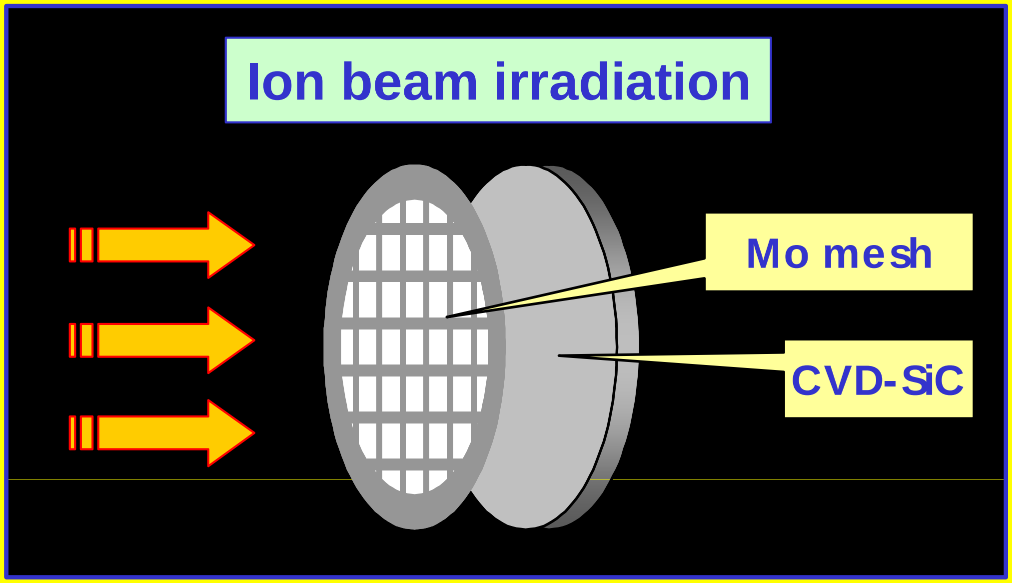




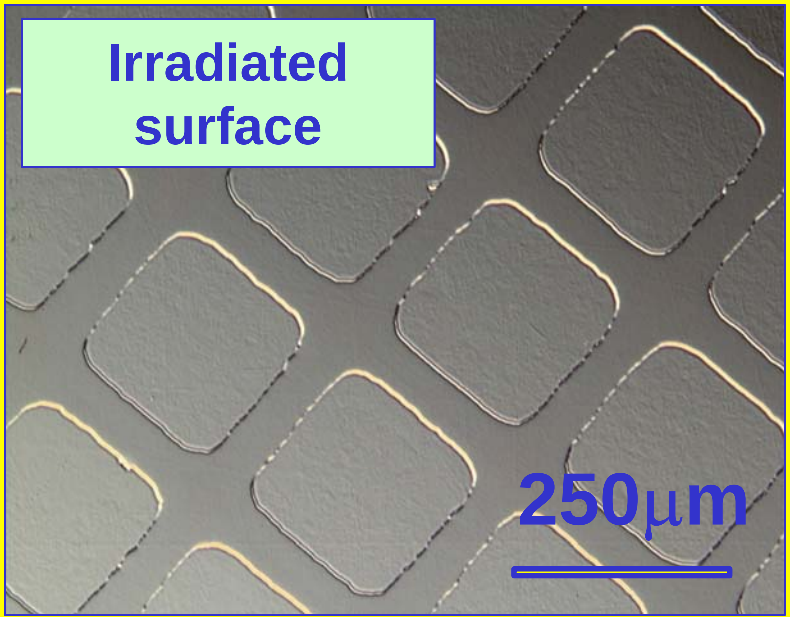
(A.Kohyama et al.,2007)

Ion beam irradiation and Surface profile characterization

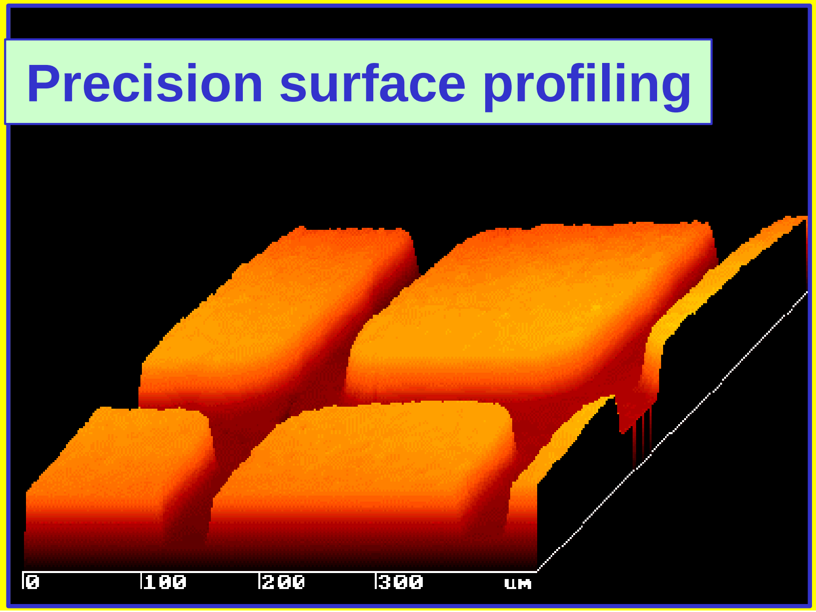
Ion beam irradiation



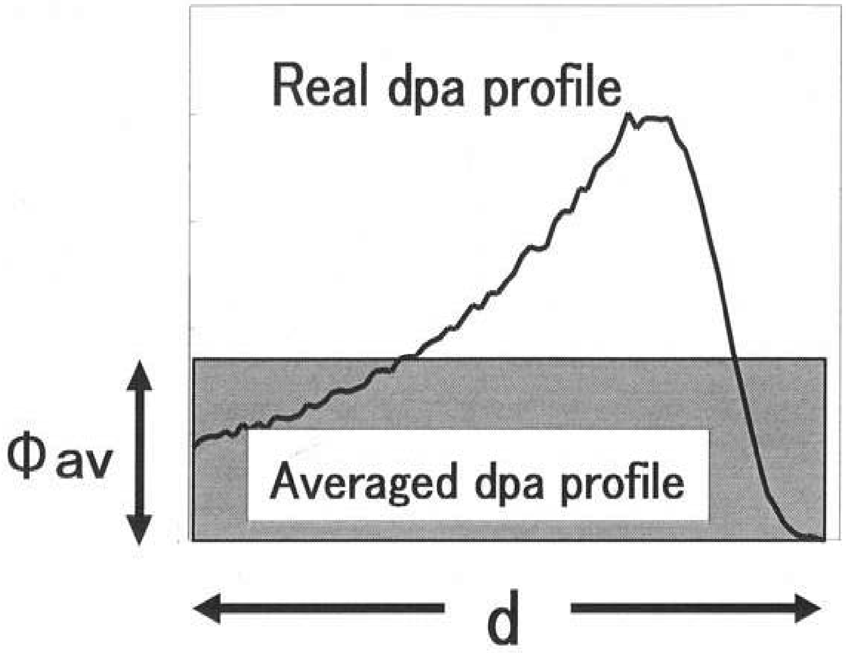
Irradiated surface

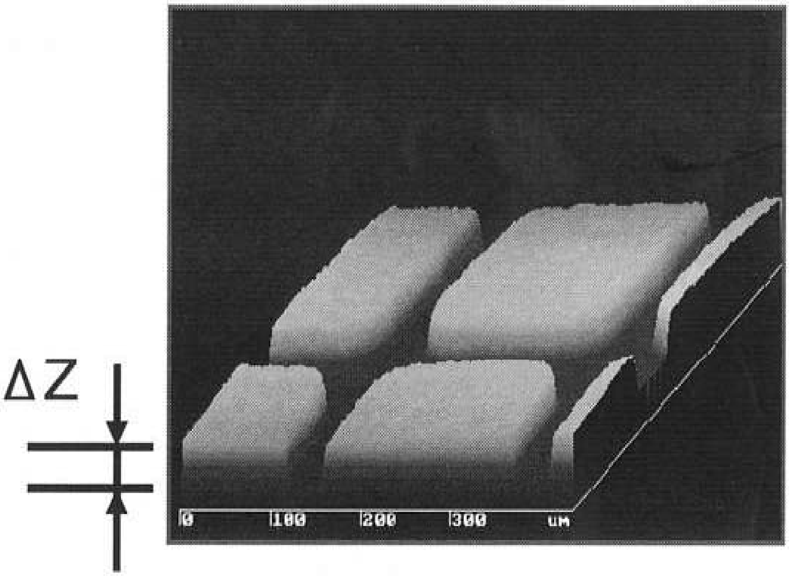


Precision surface profiling



Experimental Measurement of Radiation Swelling





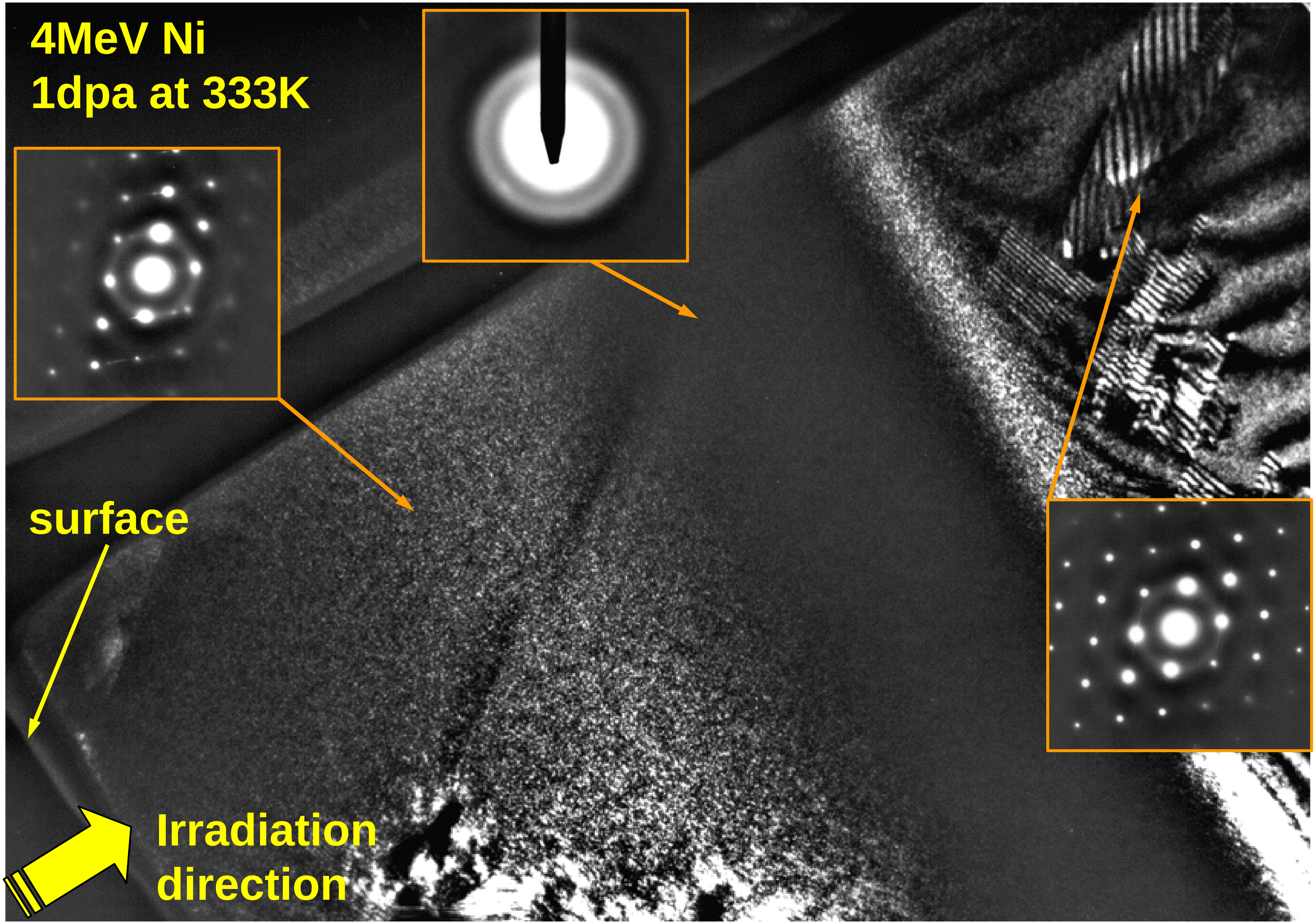
$$\Delta V/V\ (\Phi_{av}) \cong \Delta Z/d$$

Φ_{av} – Averaged dpa profile,

ΔZ - Height of step between irradiated and no irradiated area,

d - Penetration depth of irradiated sample.

Cross-sectional TEM of ion-irradiated CVD-SiC

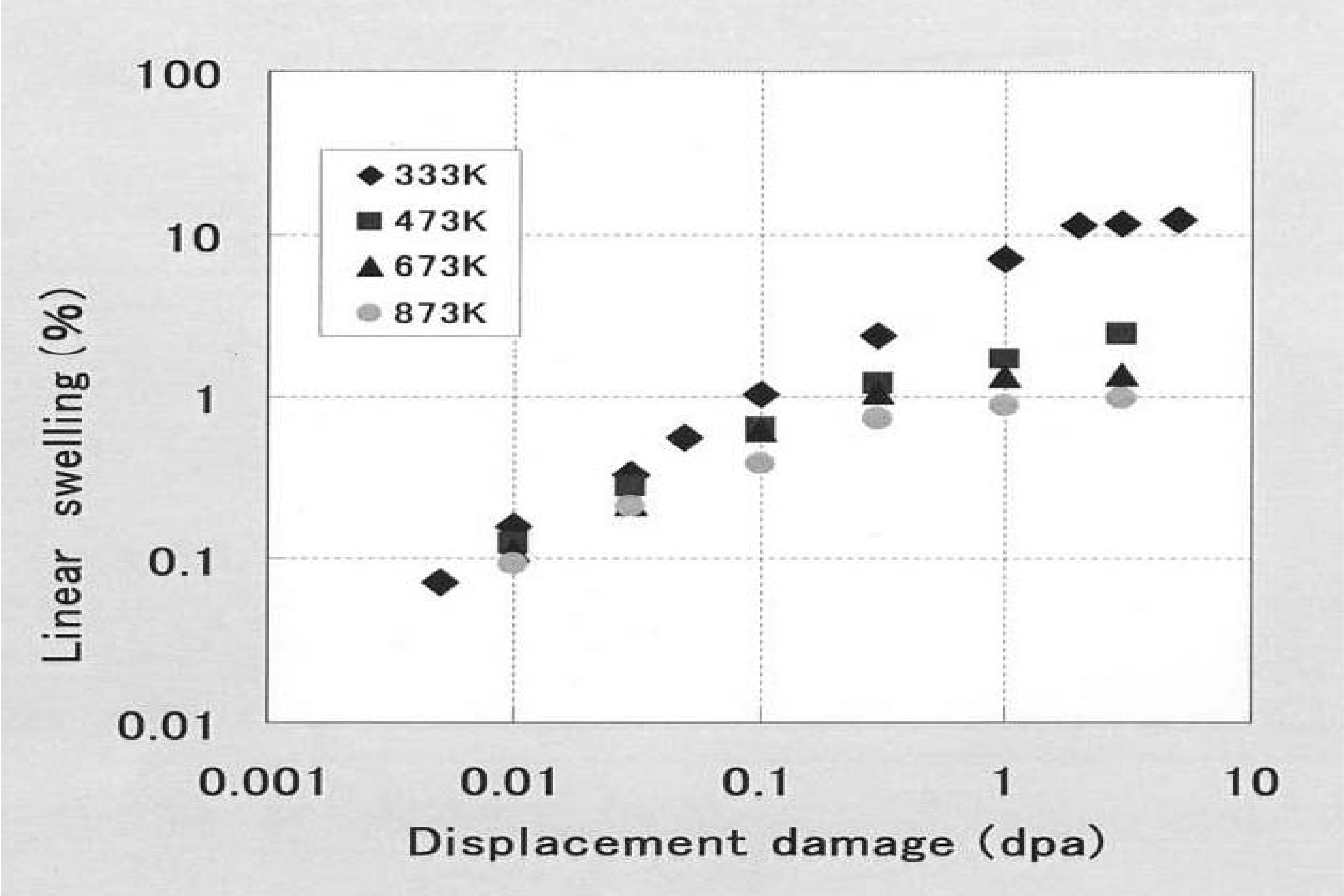


4MeV Ni
1dpa at 333K

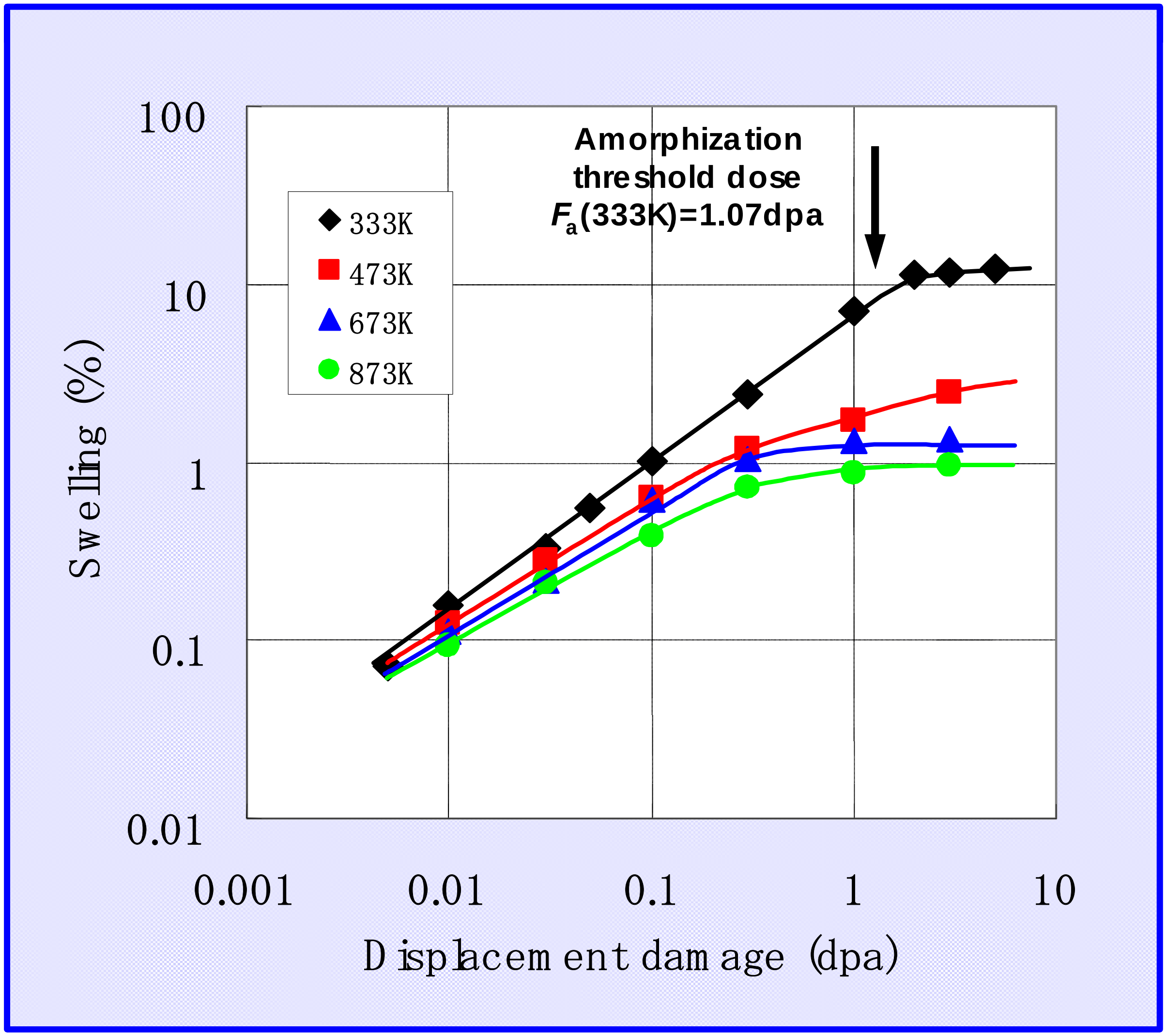
surface

Irradiation direction

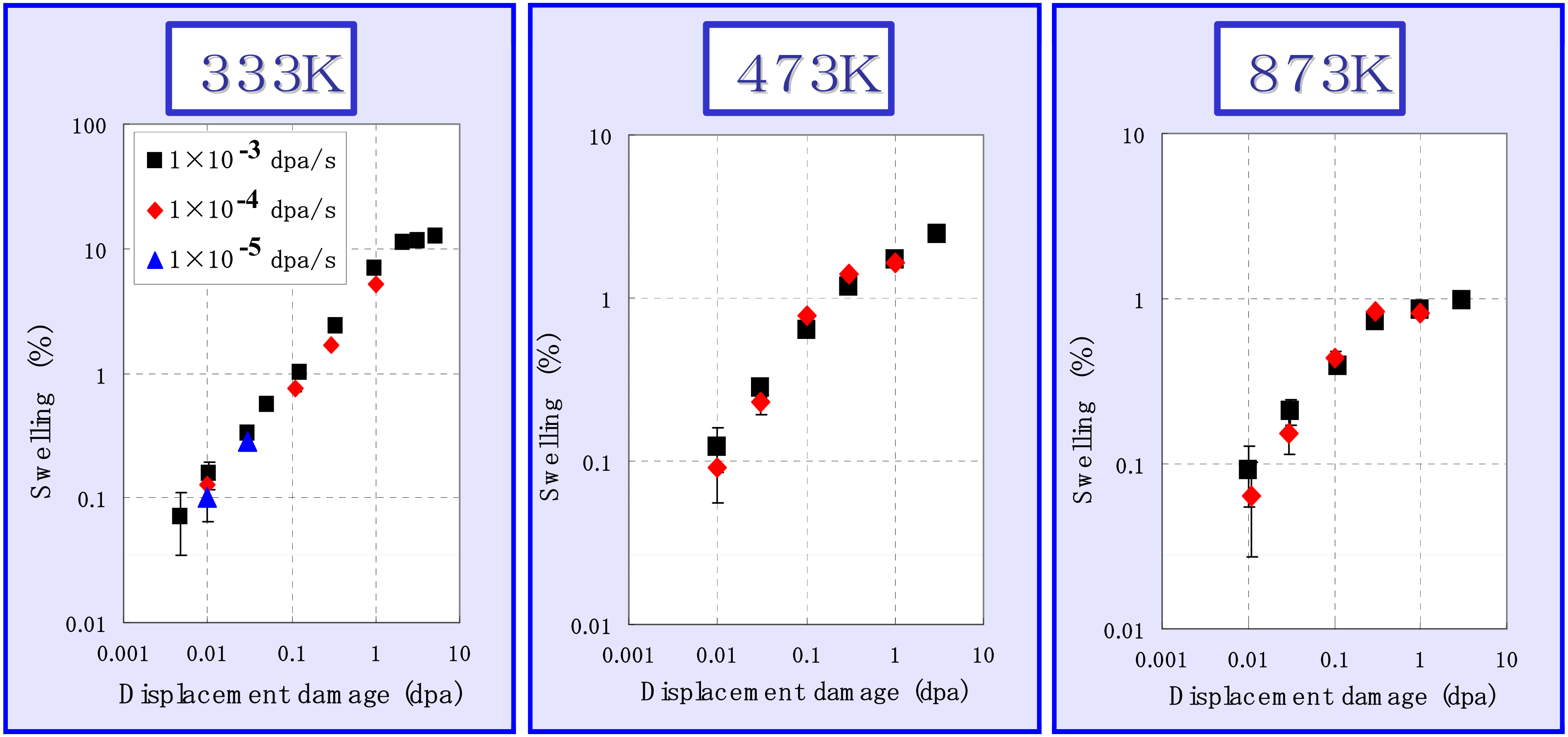
Dose dependence of radiation swelling in SiC



Temperature dependence of Ion-induced swelling in CVD-SiC

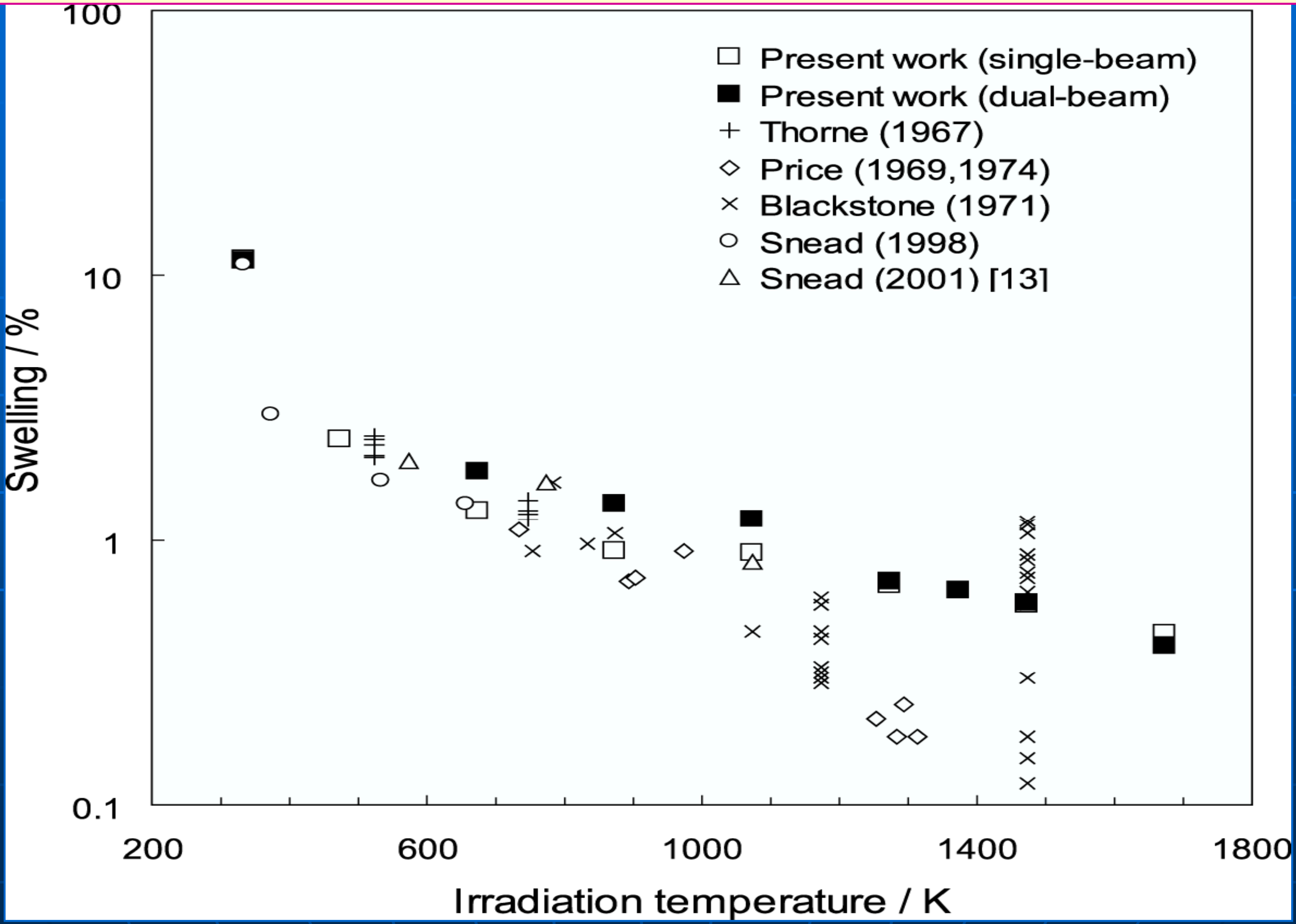


Dose rate dependence of Ion-induced swelling in CVD-SiC

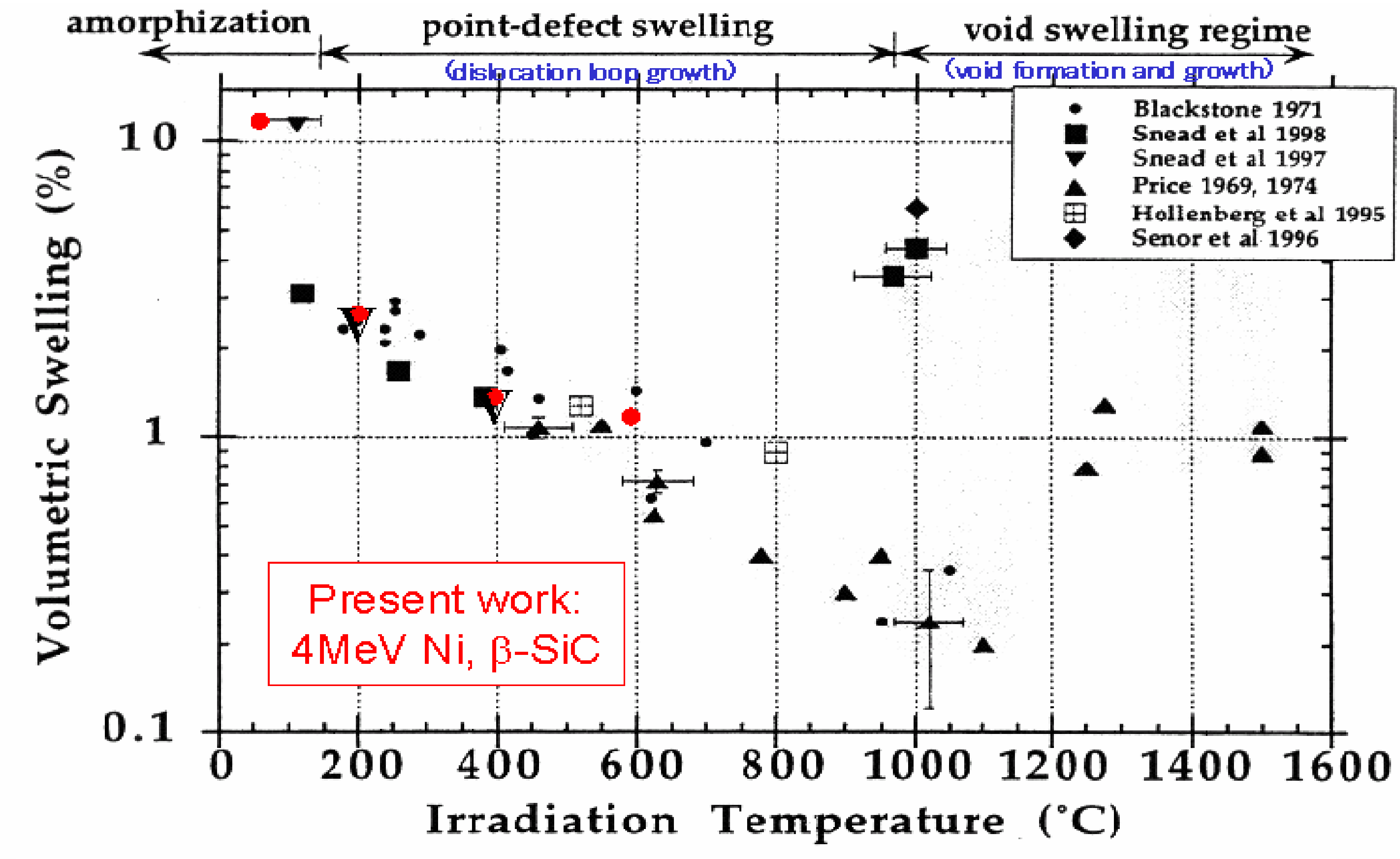


The displacement damage rates were 1×10^{-4} and 1×10^{-3} dpa/s at 333K-873K and 1×10^{-5} dpa/s at 333K with single-beam irradiation. The error bars represent the 96% confidence limits for the Gaussian distribution.

Temperature dependence of swelling of SiC



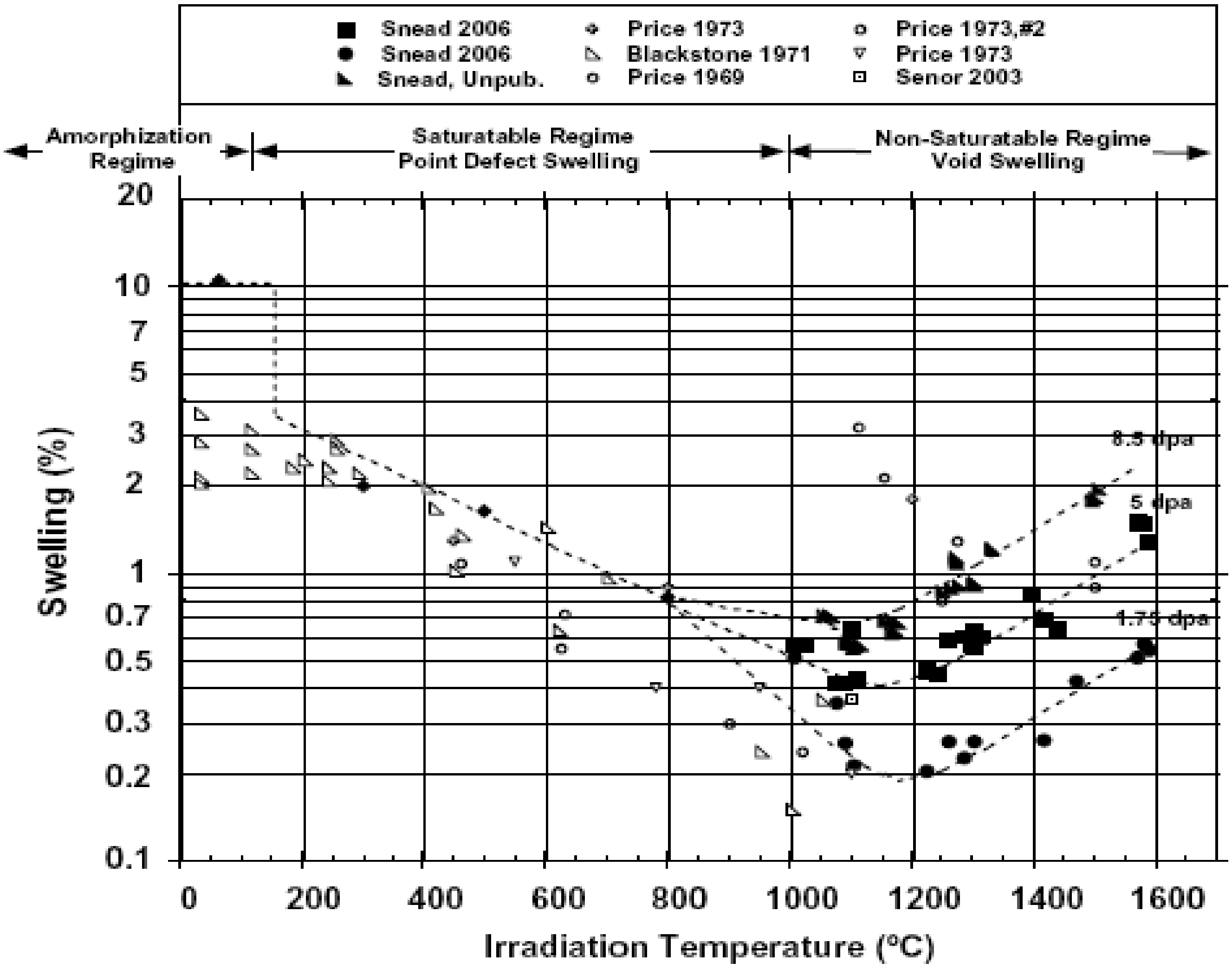
Temperature dependence of swelling of SiC



Present work:
4MeV Ni, β-SiC

S.J.Zinkle and L.L.Snead, DOE/ER-0313/24 (1998) 93-114.

Temperature dependence of irradiation-induced swelling of SiC



L. Snead, ORNL

Difference between metals and dielectrics

Metals:

- Point defects are neutral
- Electric field does not exist in the matrix

Dielectrics (Ceramic Materials):

- Point defects can have effective charge
- Electric field exists in the matrix under the influence of an applied electric field
- Driving force due to an electric field can have a strong effect on diffusivity of charged point defects

Development of theoretical models for the calculations of radiation swelling in SiC materials.

Physical Processes:

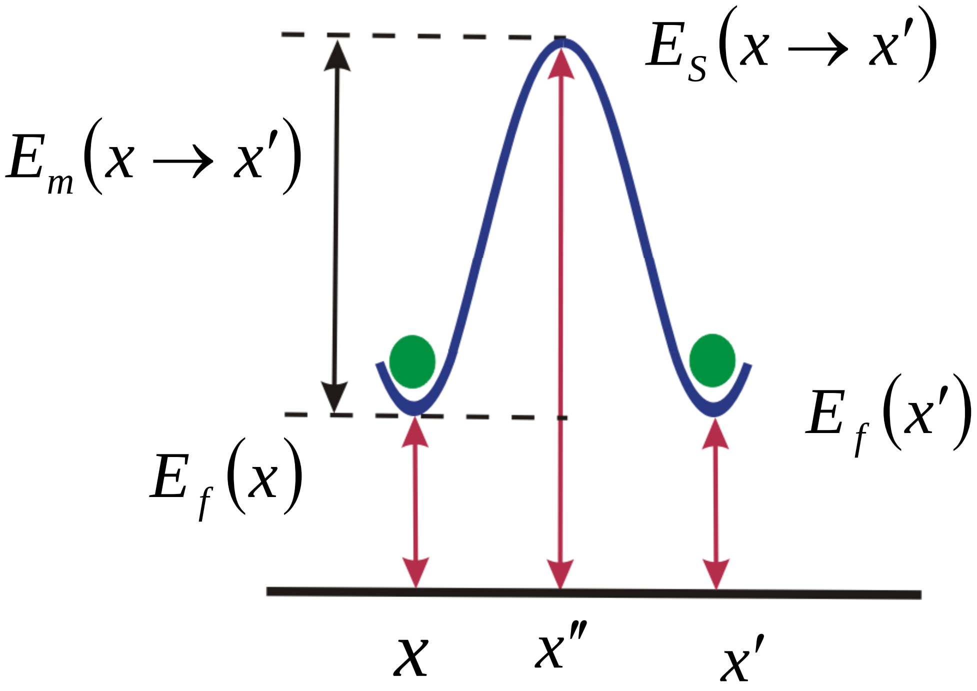
- Generation of Point Defects
- Recombination of Point Defects
- Nucleation of Dislocation Loop
- Growth of Dislocation Loops
- Radiation Swelling

Metals $(\mathbf{E}_0 = 0)$

● Interstitial

● Vacancy

$$q_I = q_V = 0$$



$$W_\alpha(x \rightarrow x') \sim e^{-\frac{E_S(x \rightarrow x') - E_f(x)}{kT}},$$

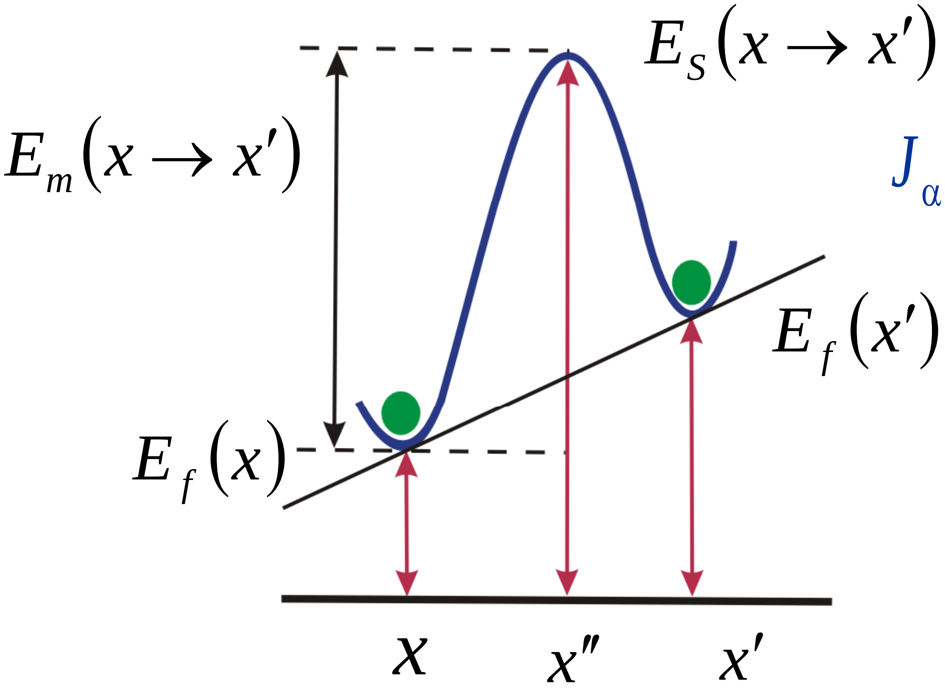
$$(\alpha = I, V)$$

$$J_\alpha(x) = C_\alpha(x) W_\alpha(x \rightarrow x') - C_\alpha(x') W_\alpha(x' \rightarrow x)$$

$$\mathbf{J}_\alpha = -D_\alpha \nabla C_\alpha, \quad (\alpha = I, V)$$

Dielectrics $(\mathbf{E}_0 \neq 0)$

● **Interstitial** q_I ● **Vacancy** q_V



$$J_\alpha(x) = C_\alpha(x) W_\alpha(x \to x') - C_\alpha(x') W_\alpha(x' \to x)$$

$$W_\alpha(x \to x') \sim e^{-\frac{E_S(x \to x') - E_f(x)}{kT}},$$

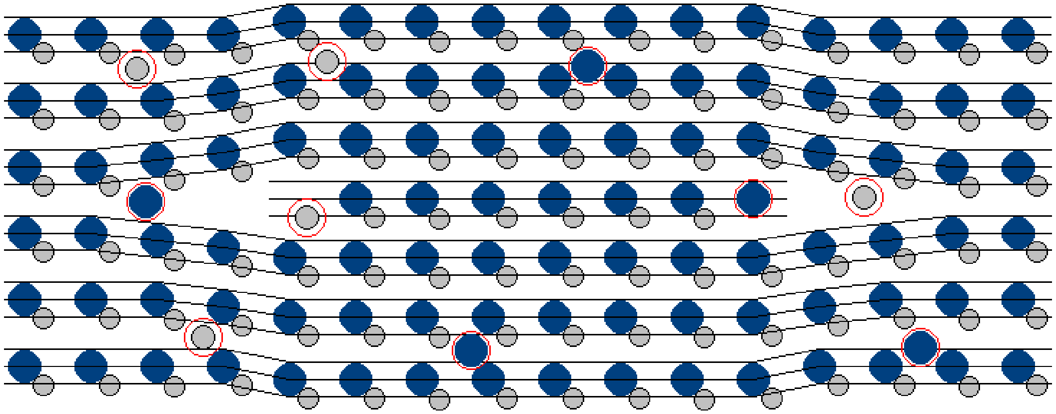
$$(\alpha = I, V)$$

$$E_{S\alpha}(x \to x') = E^0_{S\alpha} + q_\alpha \varphi(x) + q_\alpha (\mathbf{x}'' - \mathbf{x}) \nabla \varphi(x)$$

$$E_{f\alpha}(x) = E^0_{f\alpha} + q_\alpha \varphi(x)$$

$$\mathbf{J}_\alpha = -D_\alpha \nabla C_\alpha - \frac{q_\alpha}{kT} D_\alpha C_\alpha \nabla \varphi, \quad (\alpha = I, V)$$

Dislocation Loop in Dielectrics



System of Equations

$$D_m \Delta C_m + \frac{q\nu_m}{kT} D_m \nabla\left(C_m \nabla\varphi\right) = 0$$

$$\Delta\varphi = -\frac{4\pi}{\varepsilon\omega}\left(\sum_m q\nu_m C_m + \rho\right)$$

Boundary Conditions

$$C_m\Big|_S = 0 \qquad C_m\left(r \to \infty\right) = C_{m0}$$

$$\varphi\left(r \to \infty\right) = 0 \qquad \sum_m \left(q\nu_m \mathbf{j}_m, \mathbf{n}\right)\Big|_S = 0$$

Theoretical model of radiation swelling in SiC

Radiation swelling (S_{tot}) is determined in ceramic materials by the following relation

$$S_{tot} = \sum_{K=1}^{2} C_{IK} e_{IK} + \sum_{K=1}^{2} C_{VK} e_{VK} + \omega \sum_{S,K} (n_{IK}^{S} e_{IK} + n_{VK}^{S} e_{VK})$$

e_α is the dilatation of point defect type α (α = I for interstitial atoms, α = V for vacancies and α = He for helium atoms), ω is the atomic volume, $n_{\alpha k}^{S}$ is the total number of point defects of the type α absorbed by sinks of the type *s* (loops, voids) in an unit volume,

$C_{\alpha k}$ is the concentration of point defects for the two components: k=1=Si , k=2=C in SiC

$$\frac{dC_{VK}}{dt} = G_{VK} - j_{VK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK}$$

$$\frac{dC_{IK}}{dt} = G_{IK} - j_{IK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK} - \mu\left(D_{I1} + D_{I2}\right) C_{I1} C_{I2}$$

G_{VK}, G_{IK} are the generation rates of vacancies and interstitial atoms *k*-th components,

D_{IK}, D_{VK} are the diffusion coefficients of interstitial atoms and vacancies *k*-th component,

ρ_d is the dislocation density, ρ_L is the dislocation loop density ($\rho_L = 2\pi R_L N_L$).

The dislocation loop density is determined from the following relation

$$\omega \frac{dN_L}{dt} = \mu \left(D_{I1} + D_{I2} \right) C_{I1} C_{I2}$$

The growth rate of dislocation loop with loop radius *R* in ceramic materials taking into account the absorption of two types of interstitial atoms and vacancies and remaining of stoichiometric of two components in dislocation loop is given by the following relation

$$\frac{dR_L}{dt} = \frac{\pi r_0}{b} \sum_K \left(j_{IK}^n - j_{VK}^n \right) = \frac{4\pi}{b \ln\left(\frac{8R}{r_0} \right)} \frac{D_{I1}C_{I1}D_{I2}C_{I2} - D_{V1}C_{V1}D_{V2}C_{V2}}{D_{I1}C_{I1} + D_{I2}C_{I2} + D_{V1}C_{V1} + D_{V2}C_{V2}}$$

The initial conditions (at t = 0):

$$C_{IK}(t=0) = 0 \qquad C_{VK}(t=0) = 0 \qquad R_L(t=0) = a$$

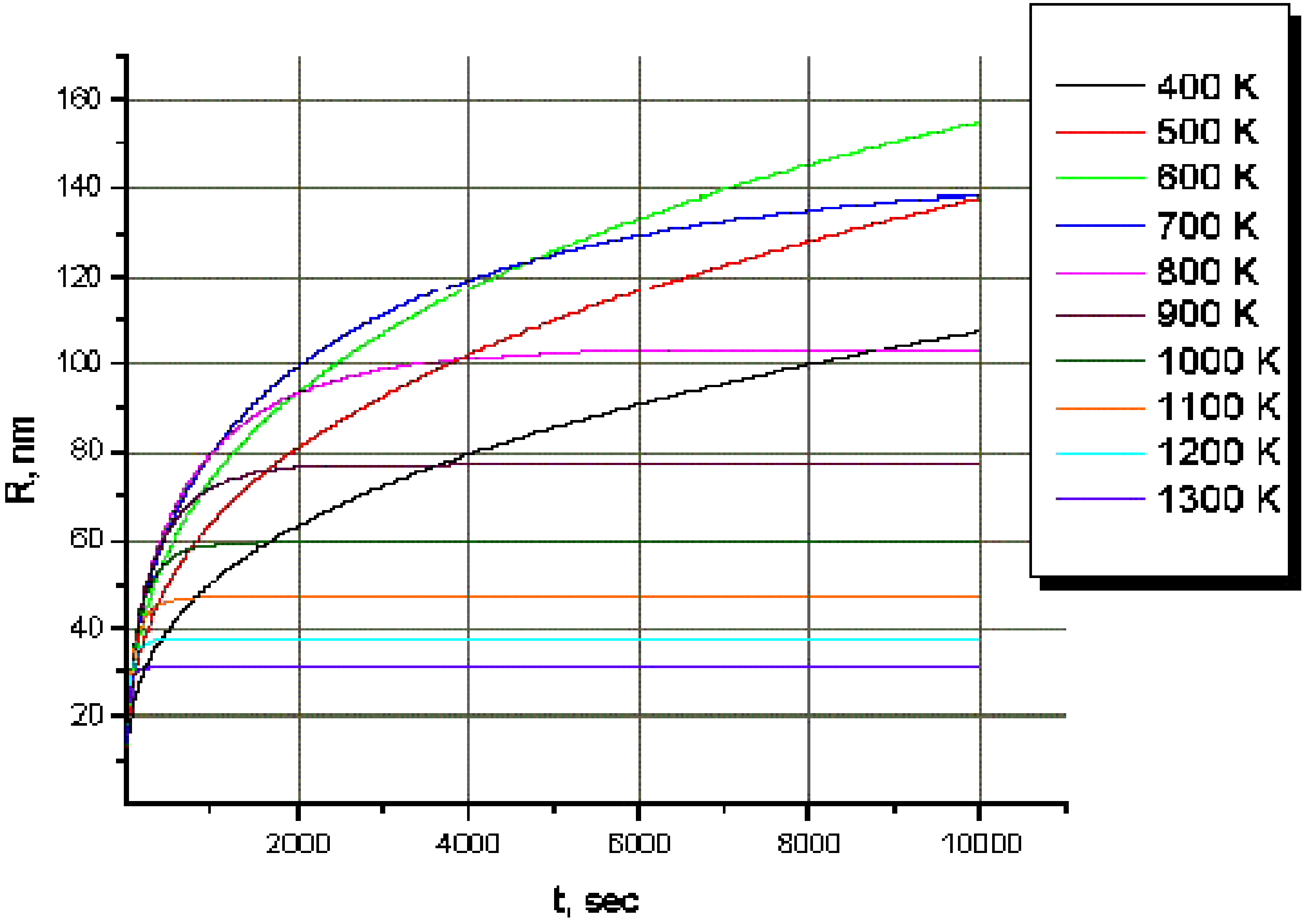
Main parameter values used for numerical calculations of radiation swelling in SiC

$G_1 = G_{Si}$	Point defect generation rate of Si atoms	3.10^{-3} dpa/s
$G_2 = G_C$	Point defect generation rate of C atoms	1.10^{-3} dpa/s
E^{Si}_{mV}	Silicon vacancy migration energy	2.3 eV
E^{C}_{mV}	Carbon vacancy migration energy	2.0 eV
E^{Si}_{mI}	Silicon interstitial migration energy	0.4 eV
E^{C}_{mI}	Carbon interstitial migration energy	0.3 eV
E^{Si}_{FV}	Silicon vacancy formation energy	2.5 eV
E^{C}_{FV}	Carbon vacancy formation energy	2.4 eV
ρ_D	Network dislocation density	10^{10} cm $^{-2}$
$e_{V1} = e_{V2}$	Vacancy dilatation	-0.1
a	Lattice parameter	5.14×10^{-8} cm

$D_{VK} = D^{O}_{VK} \exp(-E^{K}_{mV} / T)$,(where $D^{O}_{V1} = D^{C}_{V2} = 10^{-2} cm^{-2}$),

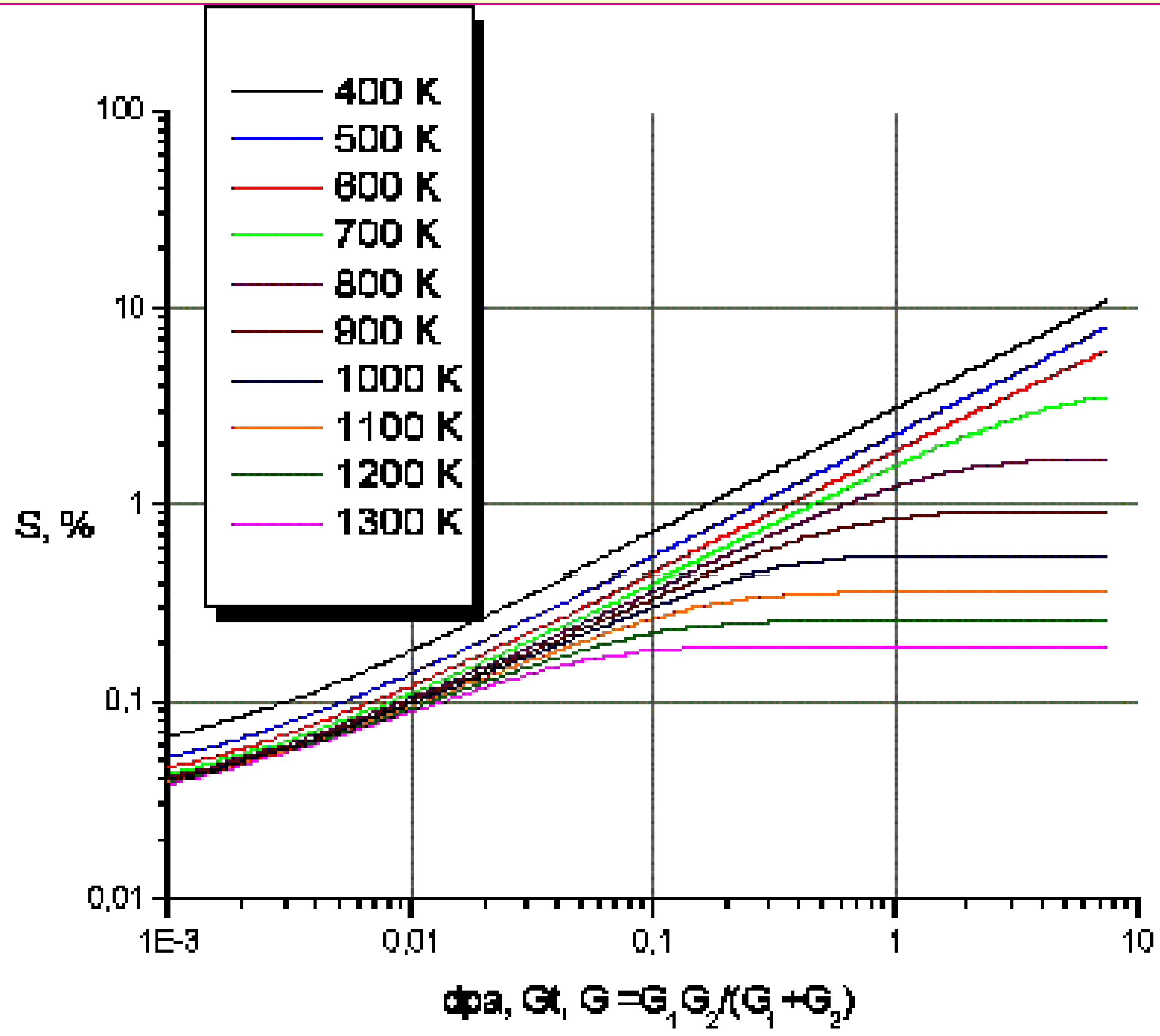
$N_L = N^{O}_{L}[\exp(E^{1}_{m1} / T) + \exp(E^{2}_{ml} / T)]^{1/2}$, (where $N^{O}_{L} = 3.10^{'2} cm^{-3}$).

The time dependence of dislocation loop growth at different irradiation temperatures



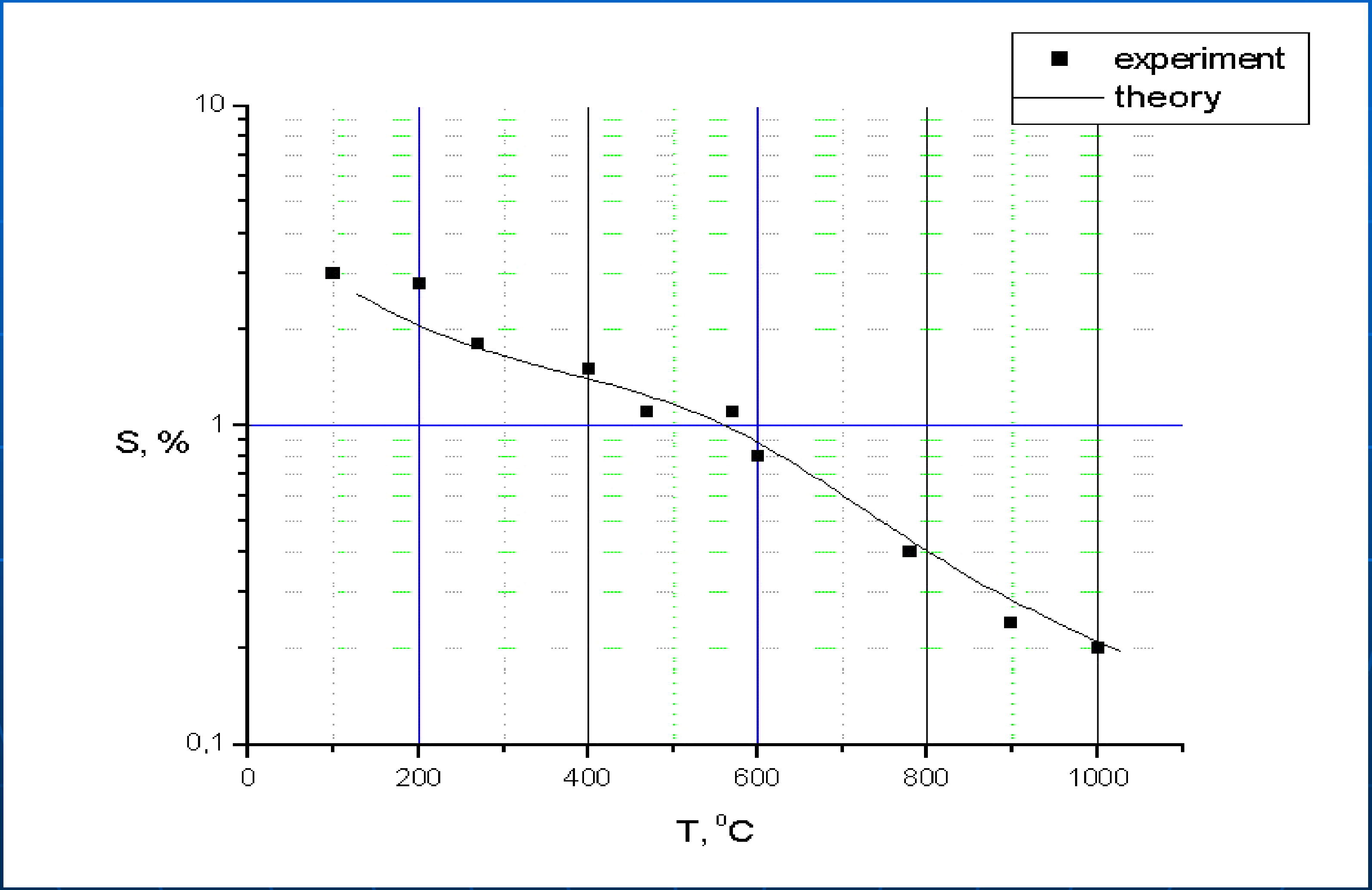
A.Ryazanov, A.Kohyama, 2002

Dose dependence of radiation swelling in SiC at different irradiation temperatures



A.Ryazanov, A.Kohyama, 2002

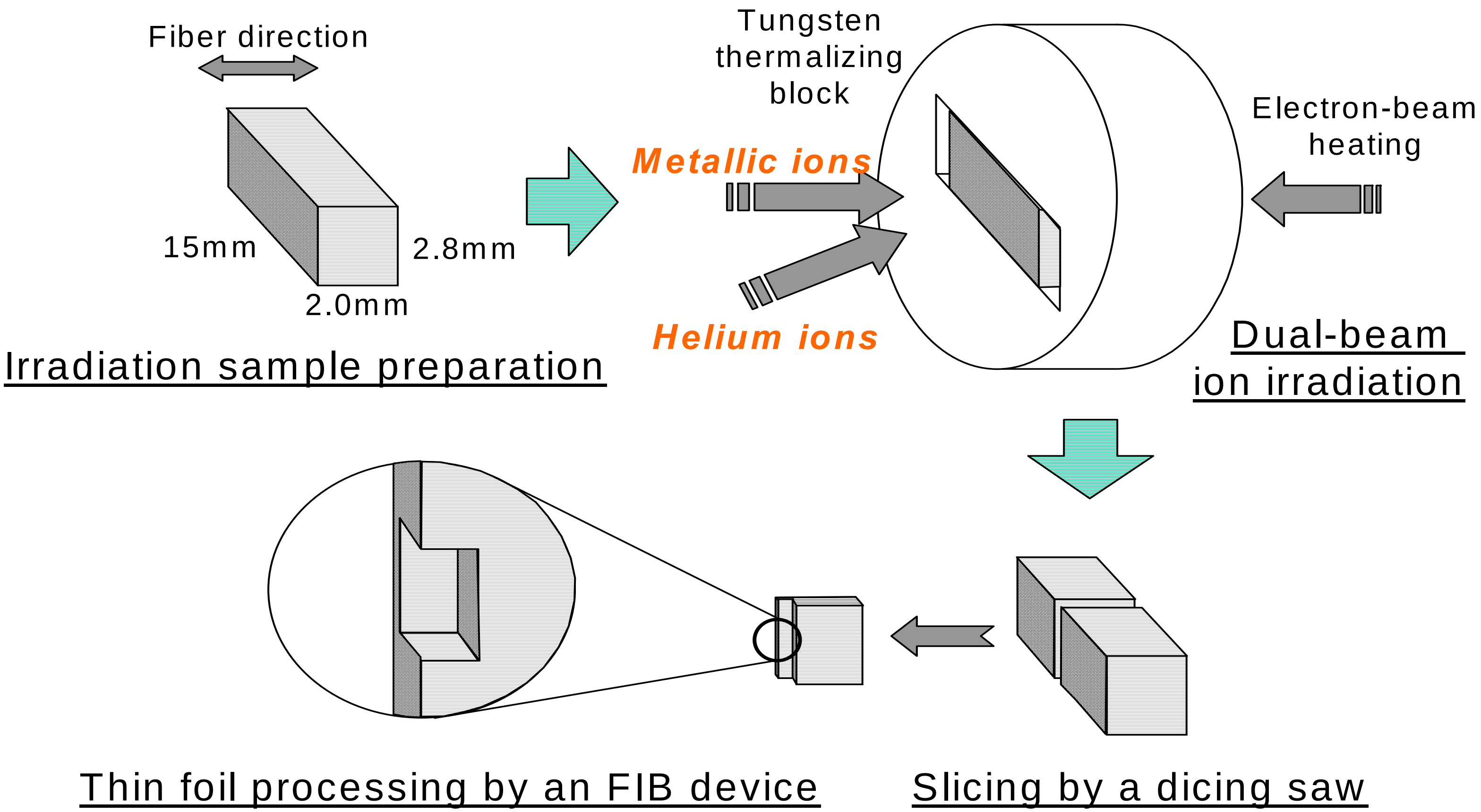
The comparison of experimental and theoretical temperature dependencies of radiation swelling in SiC.



A.Ryazanov, A.Kohyama, 2002

Helium Effect on Radiation Swelling of SiC

Experimental procedure illustrated



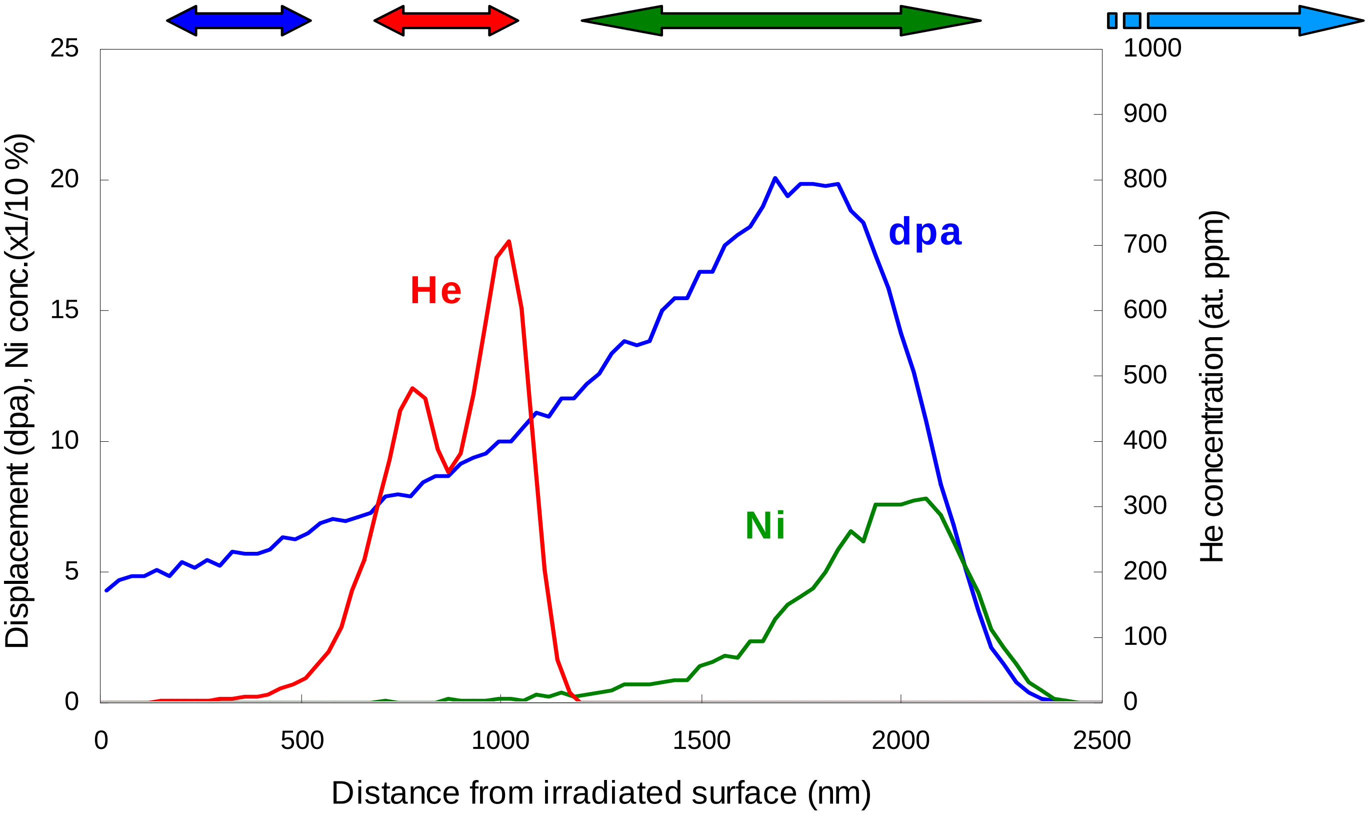
Profiles of displacement damage and deposited Ni in irradiated monolithic SiC. Calculated by TRIM-92 assuming Ed=35eV, ρ=3.21g/cm^3.

<Single-beam> Effect of displacement damage

<Dual-beam> Synergistic effect of displacement and helium

Potential (undesirable) effect of deposited nickel

<Unirradiated> Free from irradiation effects



Depth-profiles of atomic displacement damage, deposited He and Ni ions in dual-beam irradiated randomly oriented micro-crystalline SiC calculated by TRIM-92 assuming target mass density of 3.21g/cm^3 and average displacement threshold energy of 35eV.

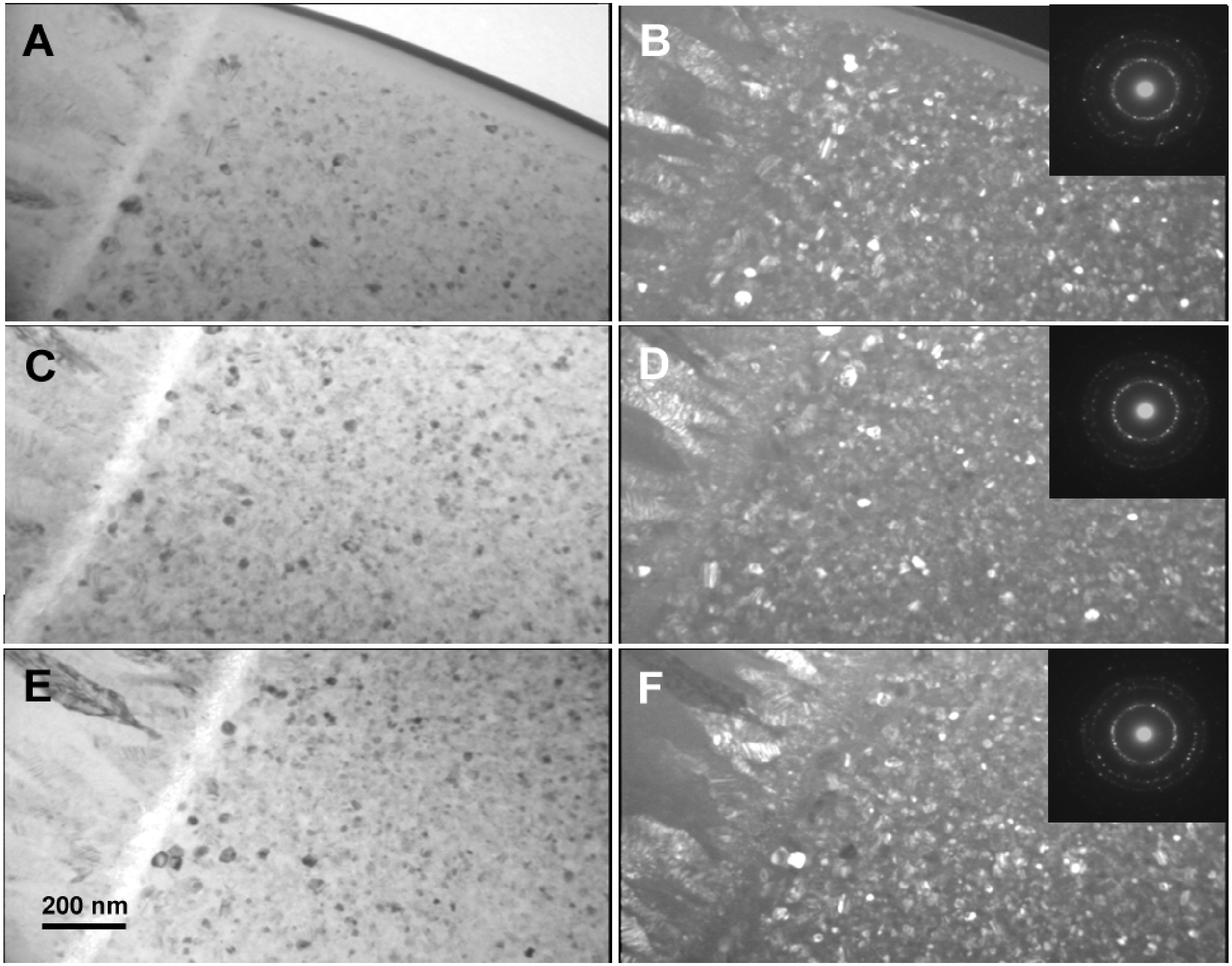
TEM images and SAD patterns for single-beam (A,B), dual-beam (C,D) and unirradiated (E,F) regions of Hi-Nicalon® Type-S/C/SiC composite

Single-beam
10 dpa
873 K

1x10^{-3}dpa/s

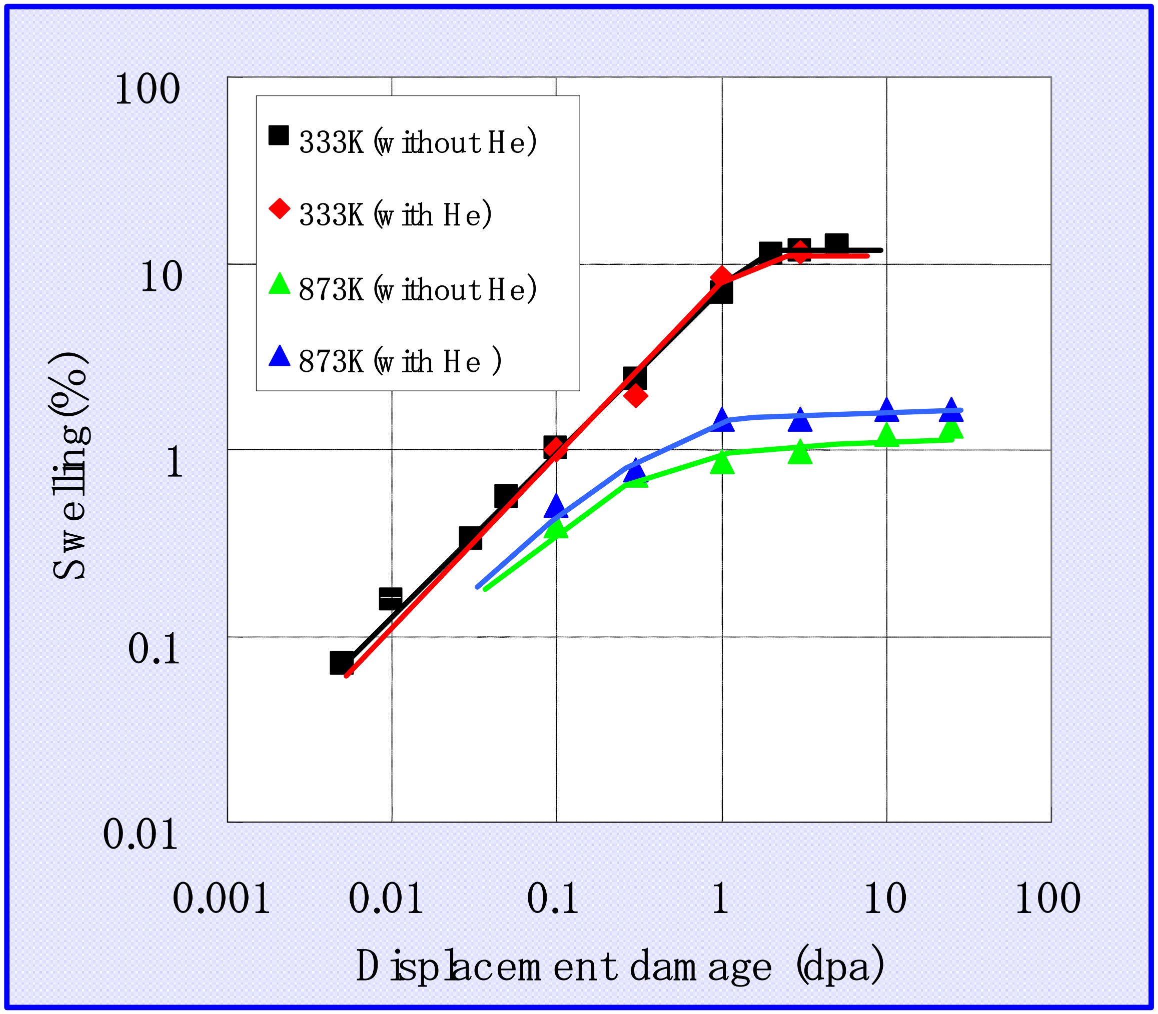
Dual-beam
10 dpa
873 K
1x10^{-3}dpa/s
60appm-He/dpa

Unirradiated
Dark field images from SiC <111> diffraction rings.

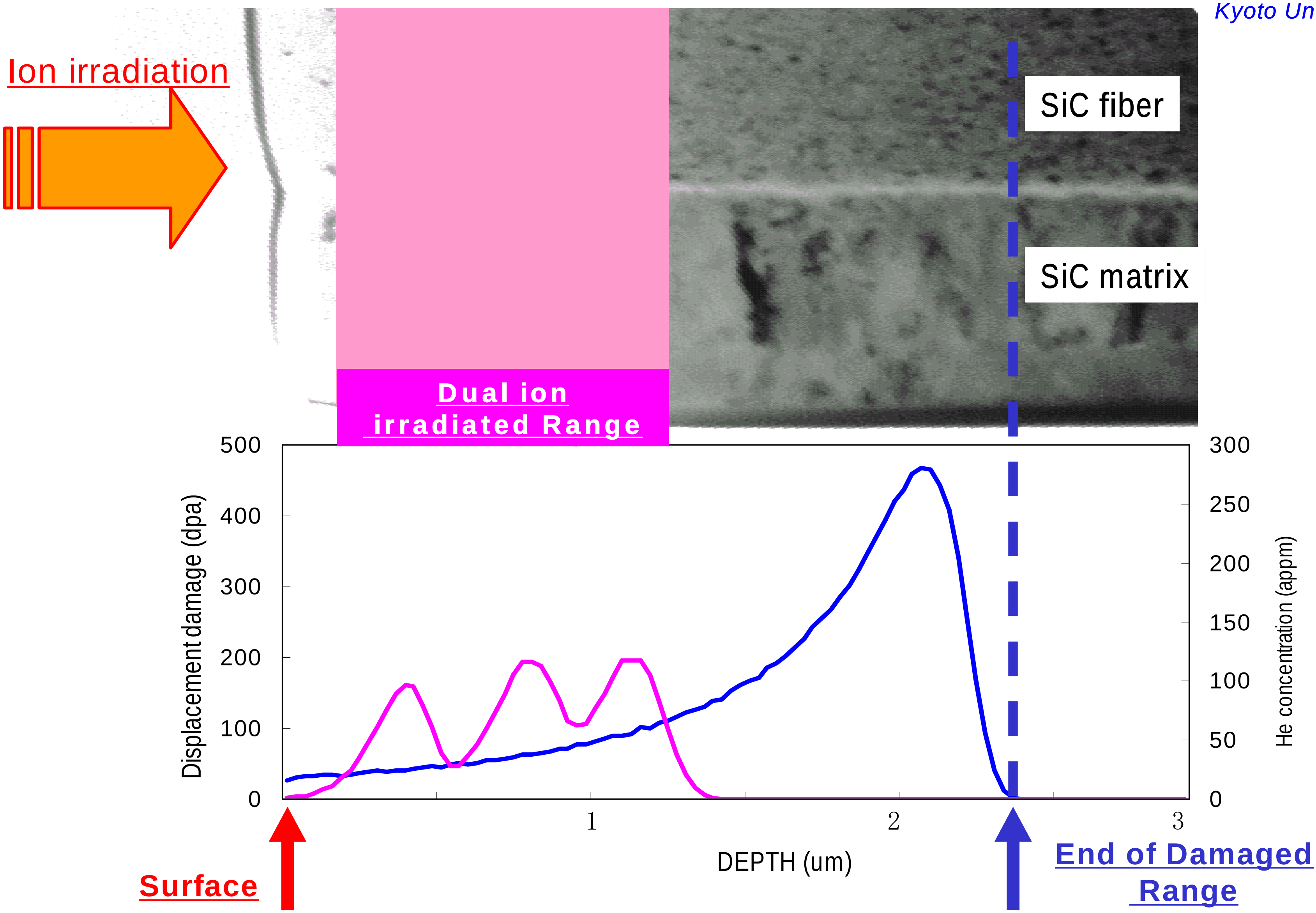


20-24 April 2009, Trieste, Italy

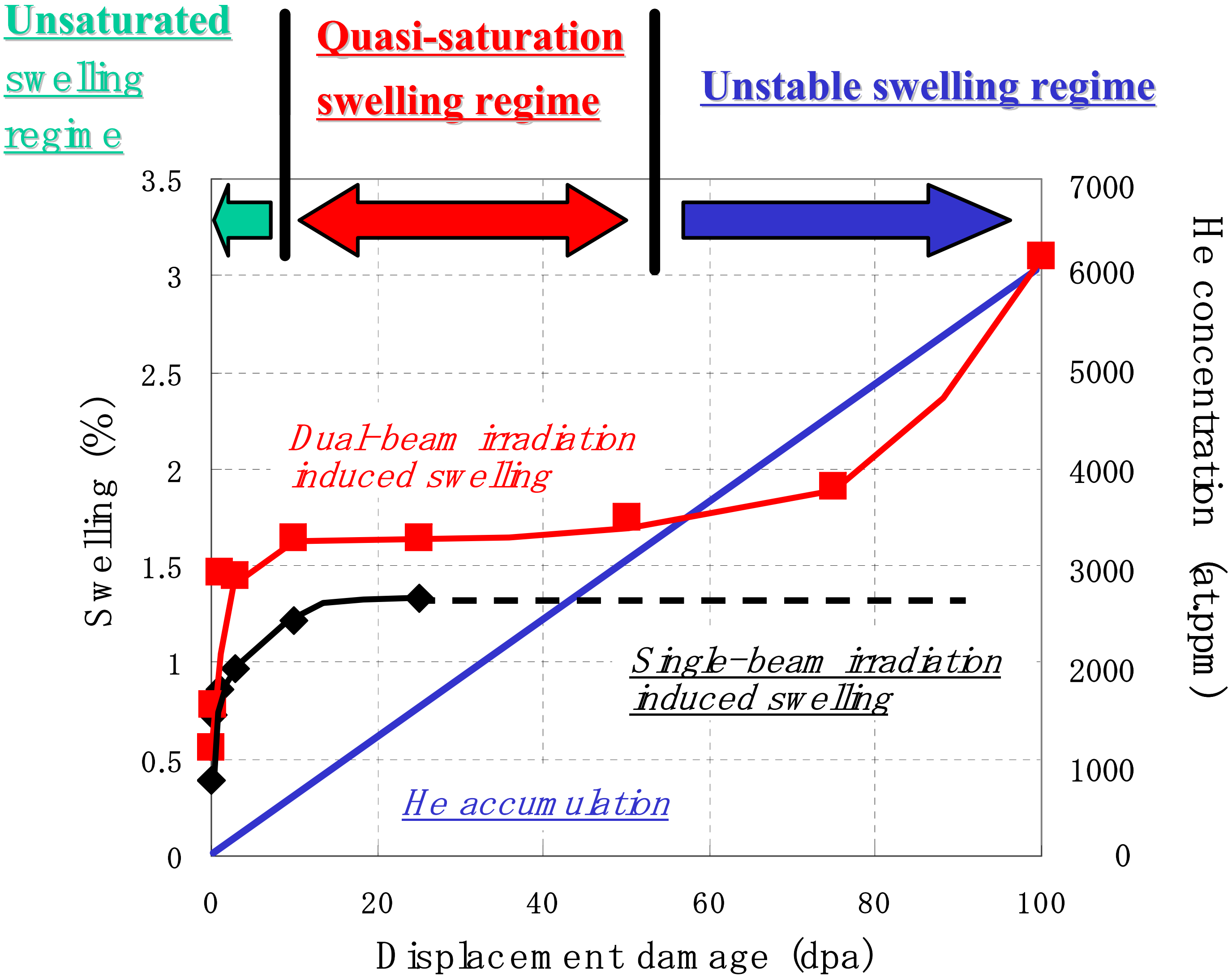
Dual ion beam irradiation-induced swelling in CVD-SiC



Profiles of irradiation induced displacement damage by 5.1 MeV Si^{2+} ion in SiC. SRIM Calculated by SRIM-98 assuming Ed=35eV, $\rho=3.21 g/cm^3$.



He accumulation and irradiation-induced swelling in dual- and single-ion irradiated CVD-SiC at 873K



Unsaturated swelling regime

Quasi-saturation swelling regime

Unstable swelling regime

Theoretical model of helium influence on radiation swelling in SiC

Radiation swelling (S_{tot}) is determined in ceramic materials by the following relation

$$S_{tot} = \sum_{K=1}^{2} C_{IK} e_{IK} + \sum_{K=1}^{2} C_{VK} e_{VK} + C_{He} e_{He} + \sum_{K=1}^{2} C_{HeV\,K}\, e_{HeVK} + \omega \sum_{S,K} (n_{IK}^{S} e_{IK} + n_{VK}^{S} e_{VK})$$

e_{α} **is the dilatation of point defect type α (α = I for interstitial atoms, α = V for vacancies and α = He for helium atoms), ω is the atomic volume.**

$C_{\alpha k}$ **is the concentration of point defects for the two components: k=1=Si , k=2=C in SiC**

C_{He} **is the concentration of helium atoms.**

$$\frac{dC_{VK}}{dt} = G_{VK} - j_{VK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK} - \nu D_{He} C_{He} C_{VK}$$

$$\frac{dC_{IK}}{dt} = G_{IK} - j_{IK}(\rho_D + \rho_L) - \alpha D_{IK} C_{IK} C_{VK} - \mu\left(D_{I1} + D_{I2}\right) C_{I1} C_{I2} - \gamma\left(D_{IK} + D_{He}\right) C_{IK} C_{He}$$

$$\frac{dC_{He}}{dt} = G_{He} - \nu D_{He} C_{He} C_{V1} - \nu D_{He} C_{He} C_{V2} - \gamma\left(D_{I1} + D_{He}\right) C_{I1} C_{He} - \gamma\left(D_{I2} + D_{He}\right) C_{I2} C_{He}$$

G_{VK}, G_{IK}, G_{He} **are the generation rates of vacancies, interstitial atoms *k*-th components and helium atoms respectively, D_{IK} D_{VK} are the diffusion coefficients of interstitial atoms and vacancies *k*-th component respectively**

$$\omega\frac{dN_L}{dt} = \mu(D_{I1} + D_{I2})C_{I1}C_{I2} + \gamma(D_{I1} + D_{He})C_{I1}C_{He} + \gamma(D_{I2} + D_{He})C_{I2}C_{He}$$

The growth rate of dislocation loop with loop radius *R* in ceramic materials taking into account the absorption of two types of interstitial atoms and vacancies and remaining of stoichiometric of two components in dislocation loop is given by the following relation

$$\frac{dR_L}{dt} = \frac{\pi r_0}{b}\sum_K\left(j_{IK}^n - j_{VK}^n\right) = \frac{4\pi}{b\ln\left(\frac{8R}{r_0}\right)}\frac{D_{I1}C_{I1}D_{I2}C_{I2} - D_{V1}C_{V1}D_{V2}C_{V2}}{D_{I1}C_{I1} + D_{I2}C_{I2} + D_{V1}C_{V1} + D_{V2}C_{V2}}$$

The initial conditions (at t = 0):

$$C_{IK}(t=0) = 0 \qquad C_{VK}(t=0) = 0 \qquad R_L(t=0) = a \quad C_{He}(t=0) = 0$$

The concentration of vacancy-helium atom compounds is determined by solving the following equation

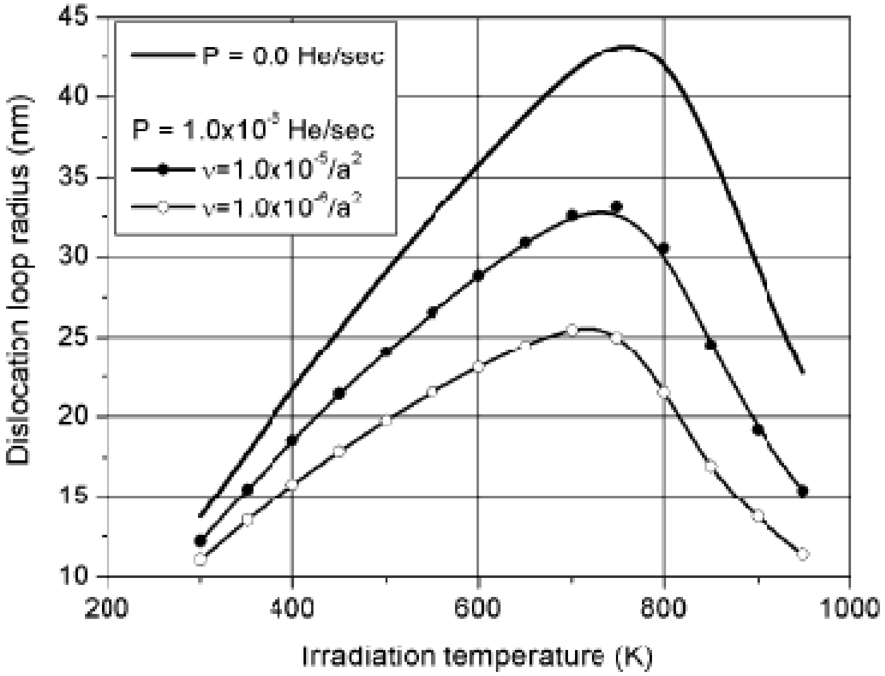
$$\frac{dC_{HeV1}}{dt} = \nu D_{He}C_{He}C_{V1}, \quad \frac{dC_{HeV2}}{dt} = \nu D_{He}C_{He}C_{V2}$$

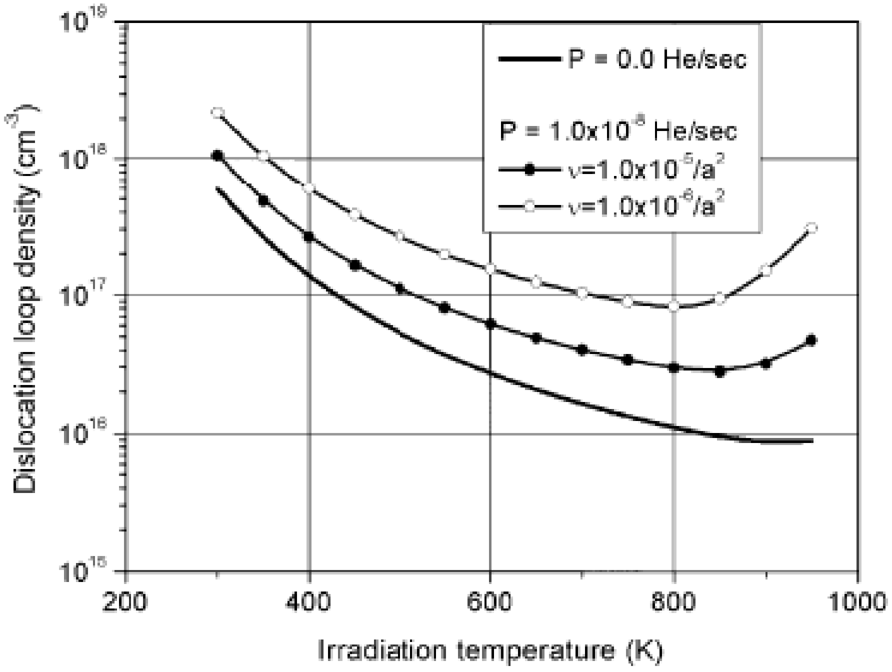
Main parameter values used for numerical calculations of radiation swelling in SiC

$G_1 = G_{Si}$	Point defect generation rate of Si atoms	1.0×10^{-3} dpa/s
$G_2 = G_C$	Point defect generation rate of C atoms	2.5×10^{-3} dpa/s
G_{He}	Helium atom generation rate	6.0×10^{-8} He/s
E_{mV}^{Si}	Silicon vacancy migration energy	2.9 eV
E_{mV}^{C}	Carbon vacancy migration energy	2.4 eV
E_{mI}^{Si}	Silicon interstitial migration energy	0.8 eV
E_{mI}^{C}	Carbon interstitial migration energy	0.7 eV
E_{m}^{He}	Helium atom migration energy	0.3 eV
$e_{I1} = e_{I2}$	Interstitial dilatation	1.2
$e_{V1} = e_{V2}$	Vacancy dilatation	-0.1
e_{He}	Helium atom dilatation	1.2
$e_{HeV1} = e_{HeV2}$	Helium atom–vacancy complex dilatation	1.1
ρ_D	Network dislocation density	10^{-10} cm^{-2}
a	Lattice parameter	3.0×10^{-8} cm

$$D_{\alpha K} = D_{\alpha K}^{O} \exp(-E_{m\alpha}^{K} / T)\text{, (where } D_{\alpha K}^{O} = 1\ cm^{-2}\text{)}$$

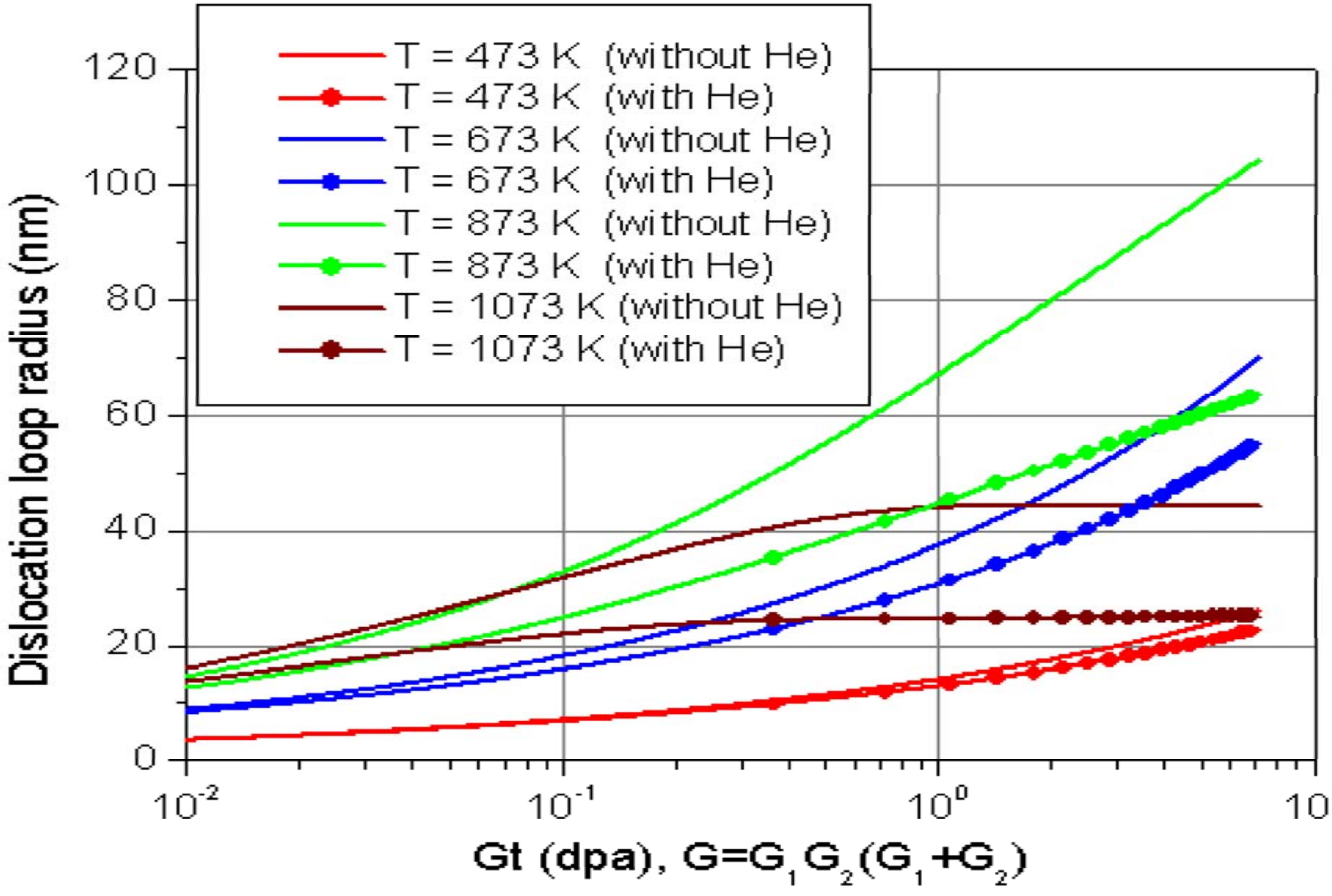
Temperature dependencies of dislocation loop radius and density



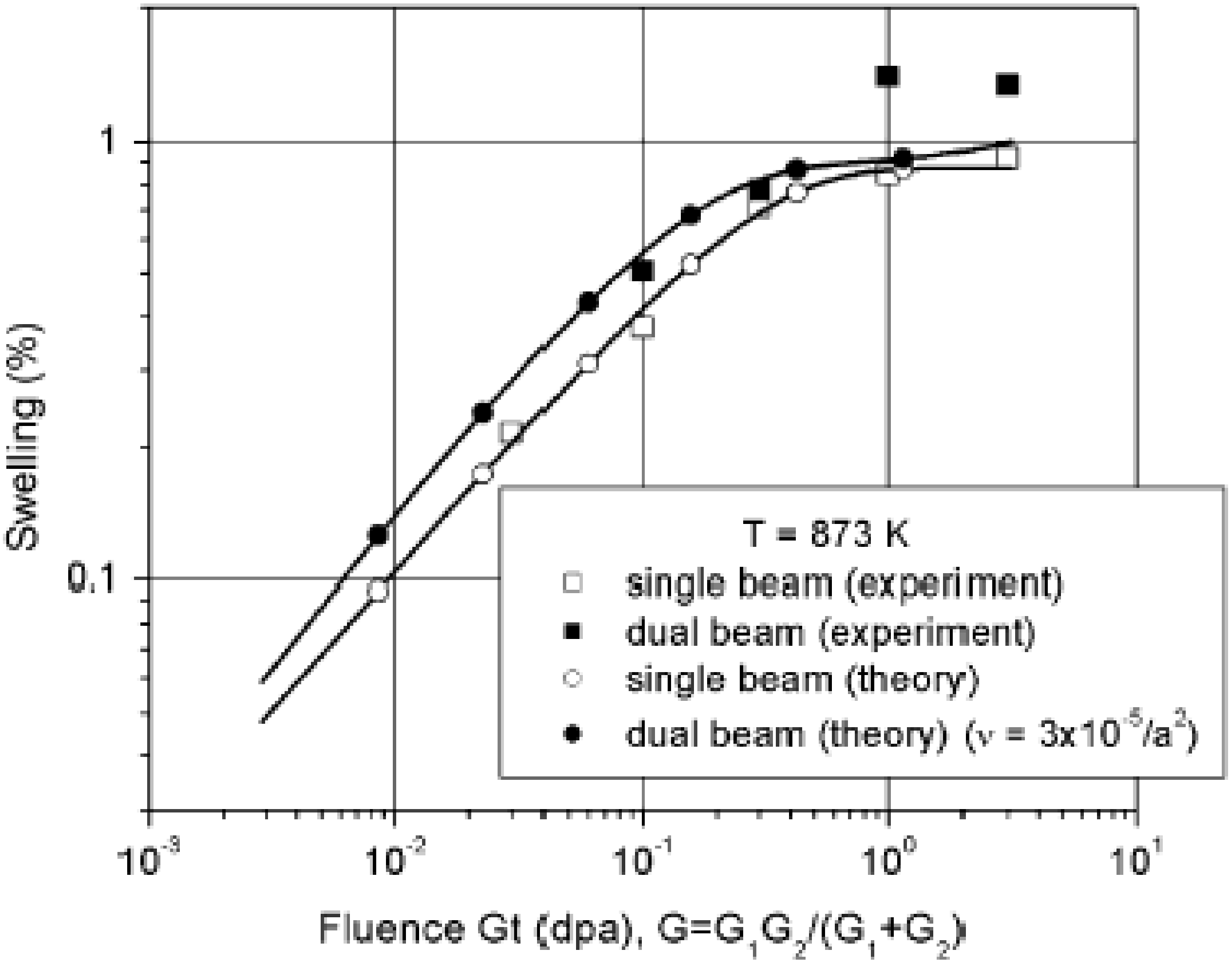


A.Ryazanov, A.Kohyama,Y.Katoh, 2004

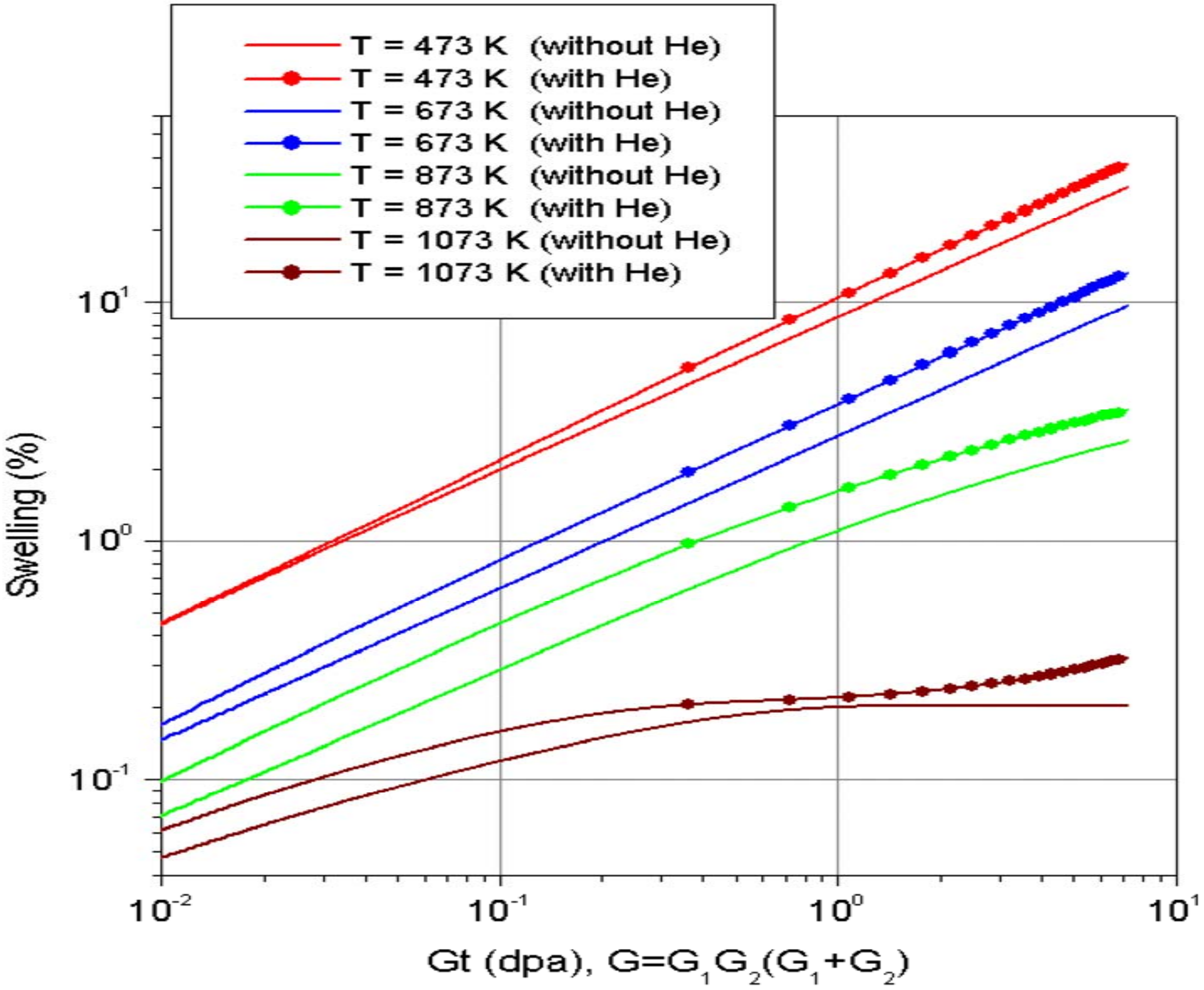
Dose dependence of dislocation loop growth in SiC with helium effect (theory)



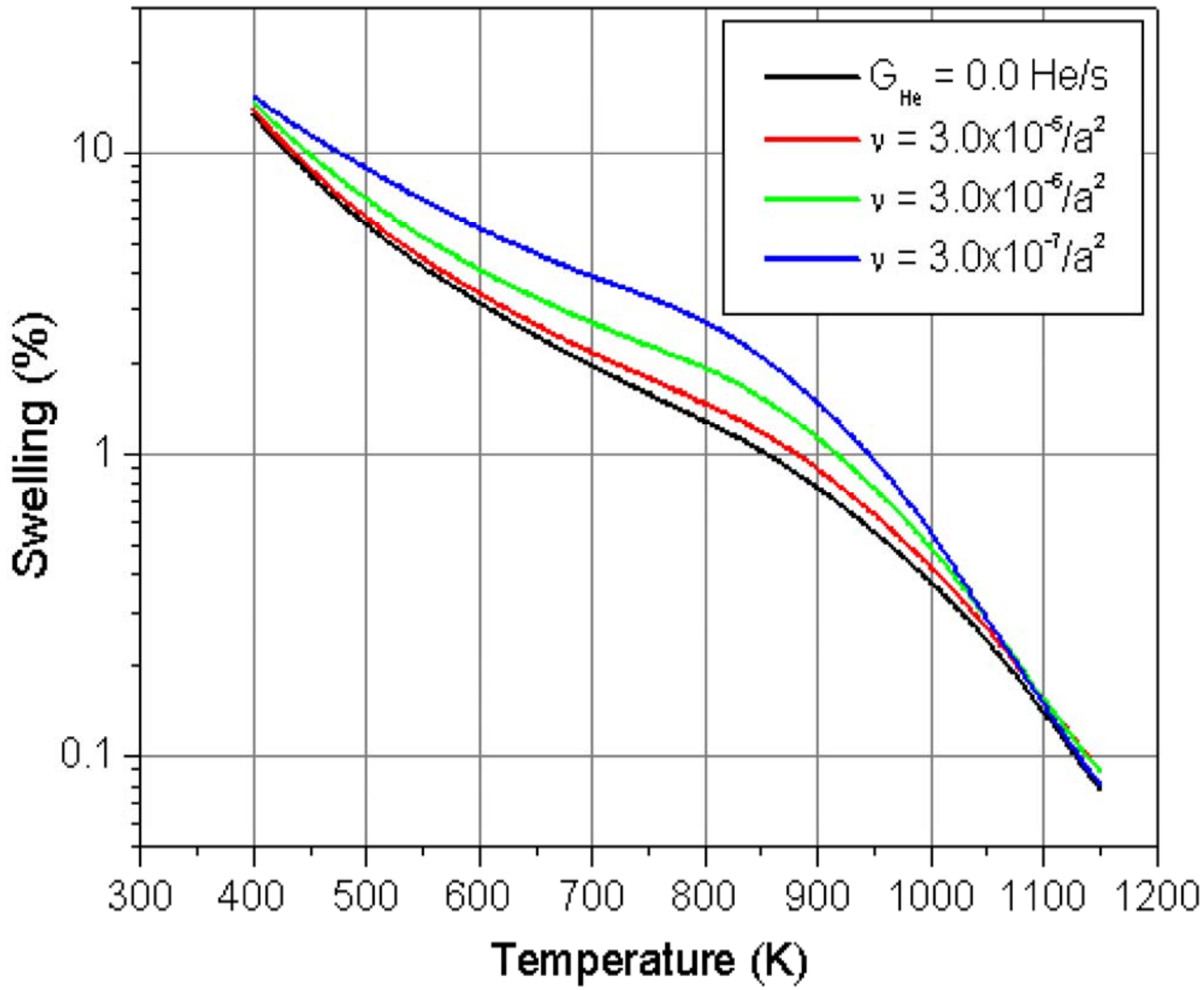
Dose dependence of radiation swelling in SiC under ion irradiatiation



Dose dependence of radiation swelling in SiC at different temperatures with the helium effect



Temperature dependence of radiation swelling in SiC at 0.7 dpa and at different coefficient of helium atom capture by vacancy



A.Ryazanov, A.Kohyama,Y.Katoh, 2004

Summary

- Low temperature swelling in SiC due to point defect accumulation in matrix exceeding 1% at temperatures below 673K, which is supported both by experiment and theoretical model.
- Low temperature swelling in SiC saturates in helium free conditions. Saturation behavior is highly predictable using the suggested theoretical model. Saturation of radiation swelling in SiC is determined based on the growth rate saturation of interstitial dislocation loops.
- The recent experimental data clearly demonstrate the strong monotonic decrease of radiation swelling in SiC up to 1000C. The theoretical calculations give the same temperature dependence for decreasing of radiation swelling in SiC with temperature increase.

- **Helium atoms increase the nucleation of interstitial dislocation loops and decrease an average radius of them. Helium atoms increase radiation swelling in temperature interval from 400 to 1000 K.**

- **The recent experimental data on dual-beam clearly demonstrate the strong temperature decrease of radiation swelling in SiC with helium up to 1000C.**

- **The theoretical calculations give the same temperature dependence for radiation swelling in SiC with temperature increase.**