Cavity Formation in SiC/SiC Composites during Multi-ion-beam Irradiation at Elevated Temperatures

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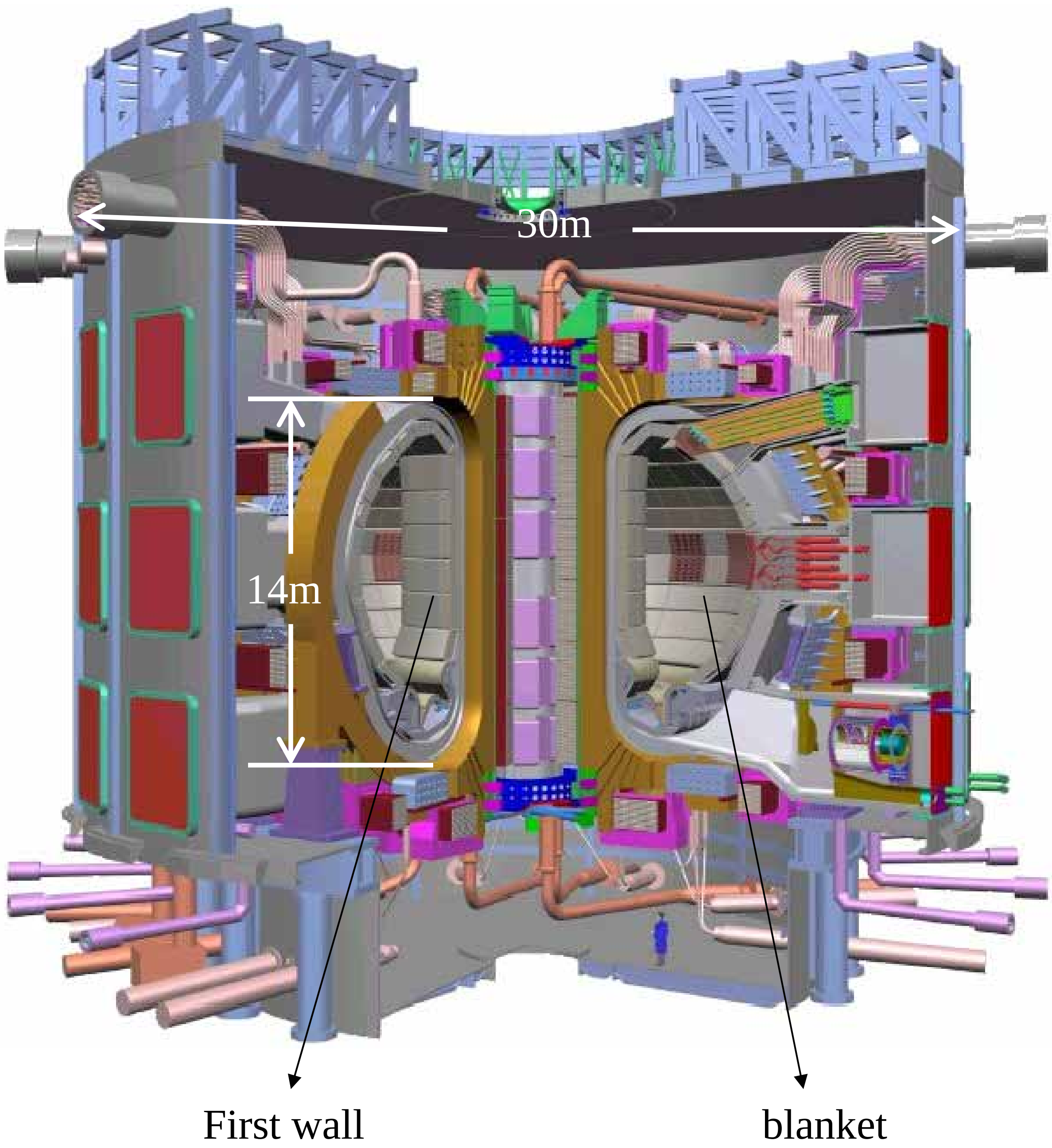
Present at the EUROMAT 2005, September 7, Prague, Czech

- ITER conceptual design is using stainless steels as the first wall and blanket structures.

- SiC/SiC is one of the major candidate materials for future fusion power reactors as the first wall and blanket structures. (T>1000º C, η_{th} = 70%)
- Also can be used for hydrogen production from water.

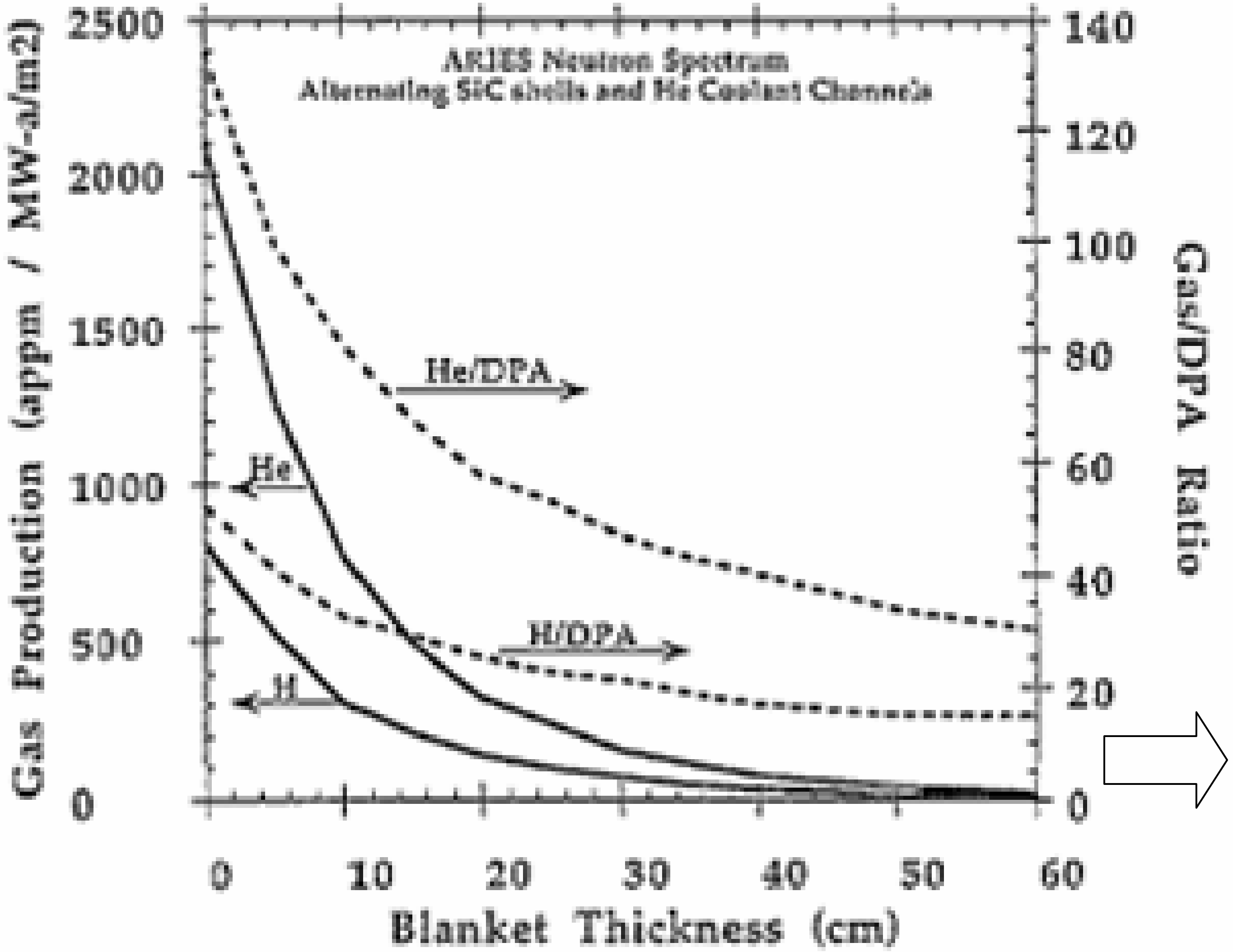


http://www-fusion-magnetique.cea.fr/iter/iter_coupe01.jpg

Background

- SiC/SiC composites are the major candidates as the advanced structural materials for fusion reactors due to its low induced radioactivity, high specific strength, high thermal conductivity and high temperature strength.
- In a fusion reactor, the first wall and blanket will receive not only high level of radiation damage from the high energy neutrons but also contains large amount of deuterium and helium atoms. The stability of the microstructures of the SiC/SiC composites under the fusion environments is a major interest.
- We are using triple-ion-beam irradiation facility to simulate the fusion environments to study the microstructural evolution of the SiC/SiC composites.

The relationship of damage level (dpa) to the amount of He and H gas atoms (appm)

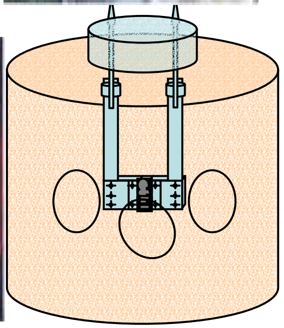


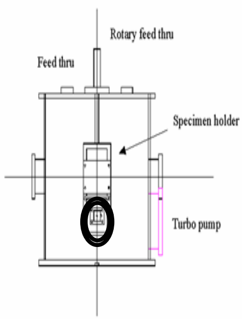
He = 150 appm/dpa

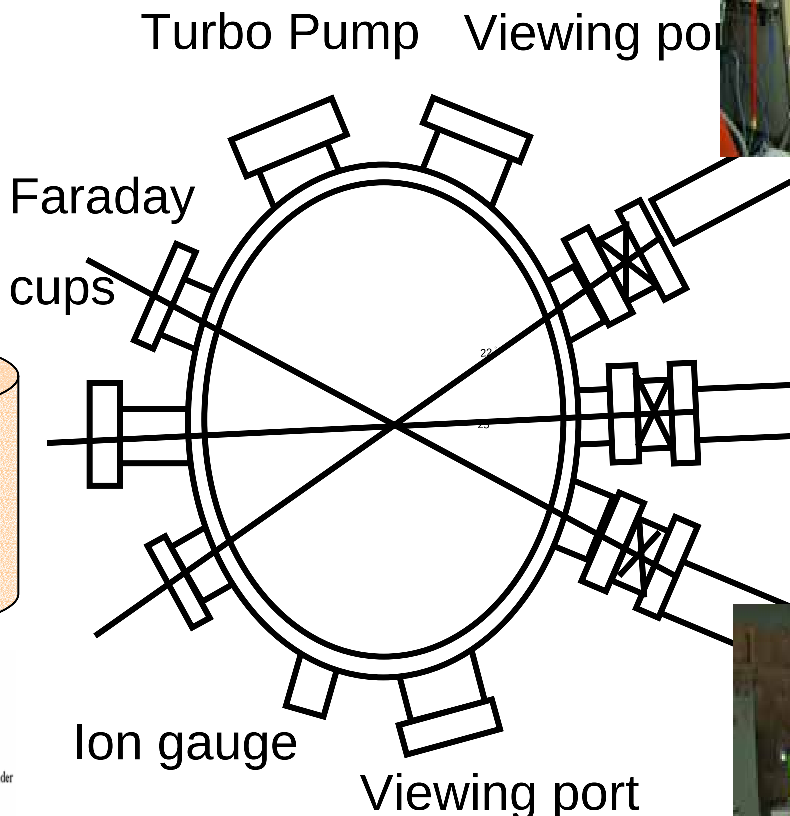
H = 60 appm/dpa

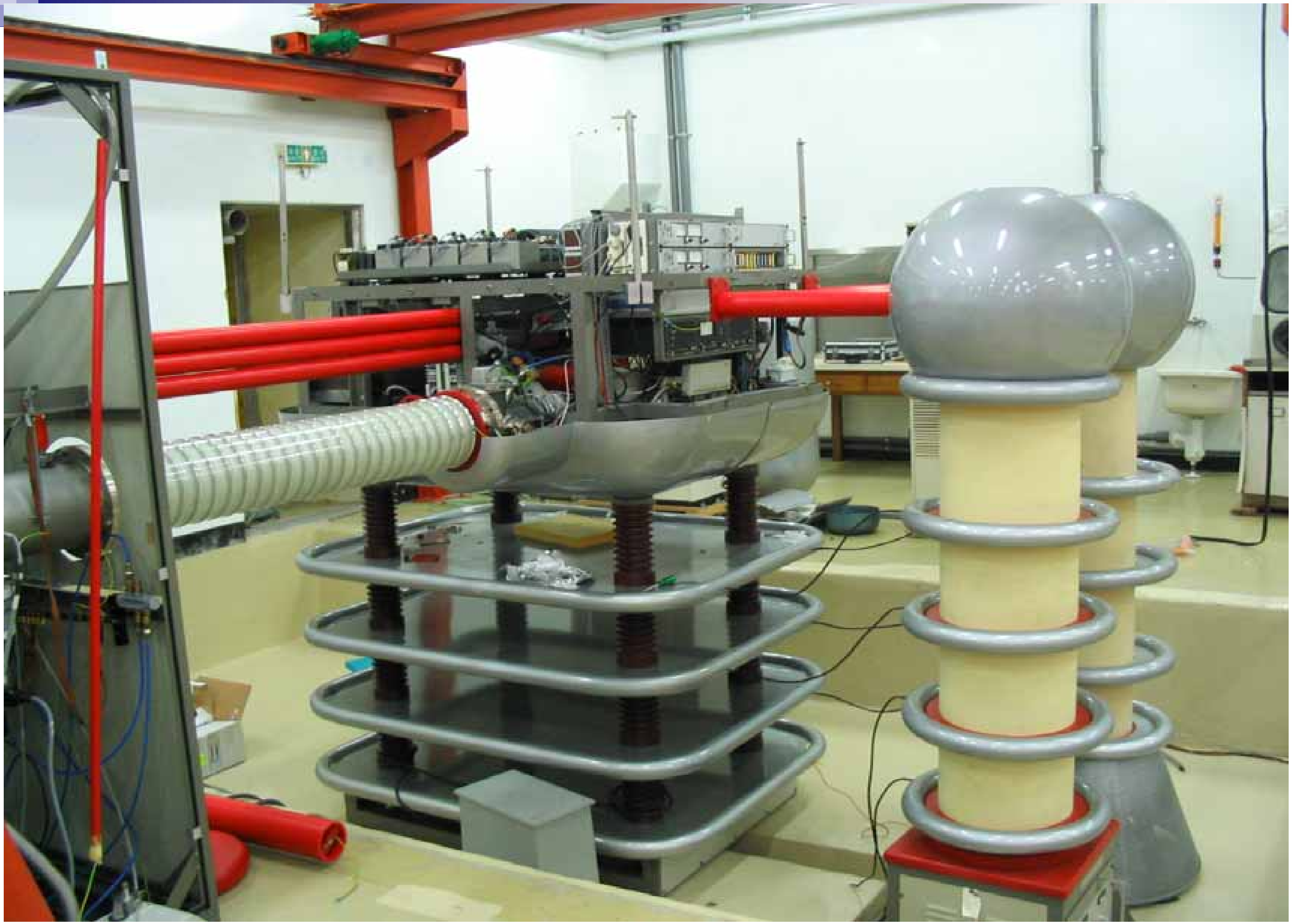
G.R. Hopkins, R.J. Price, Nucl. Eng. Des. 2(1984) 1

Irradiation facility









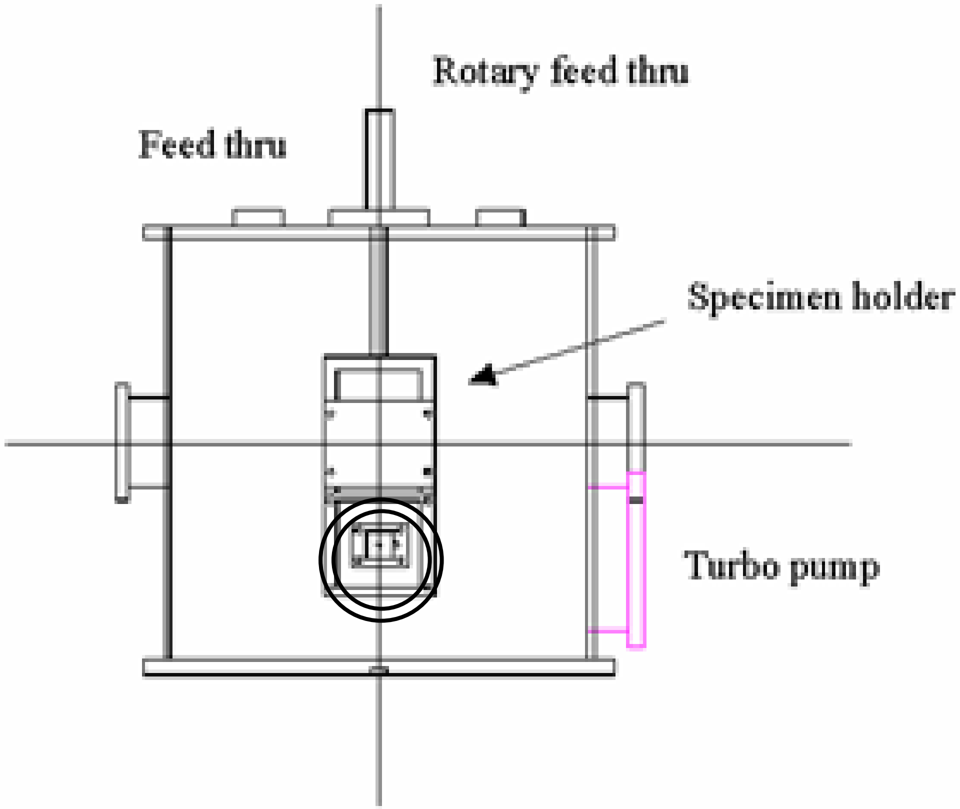
500 keV Ion-Implanter

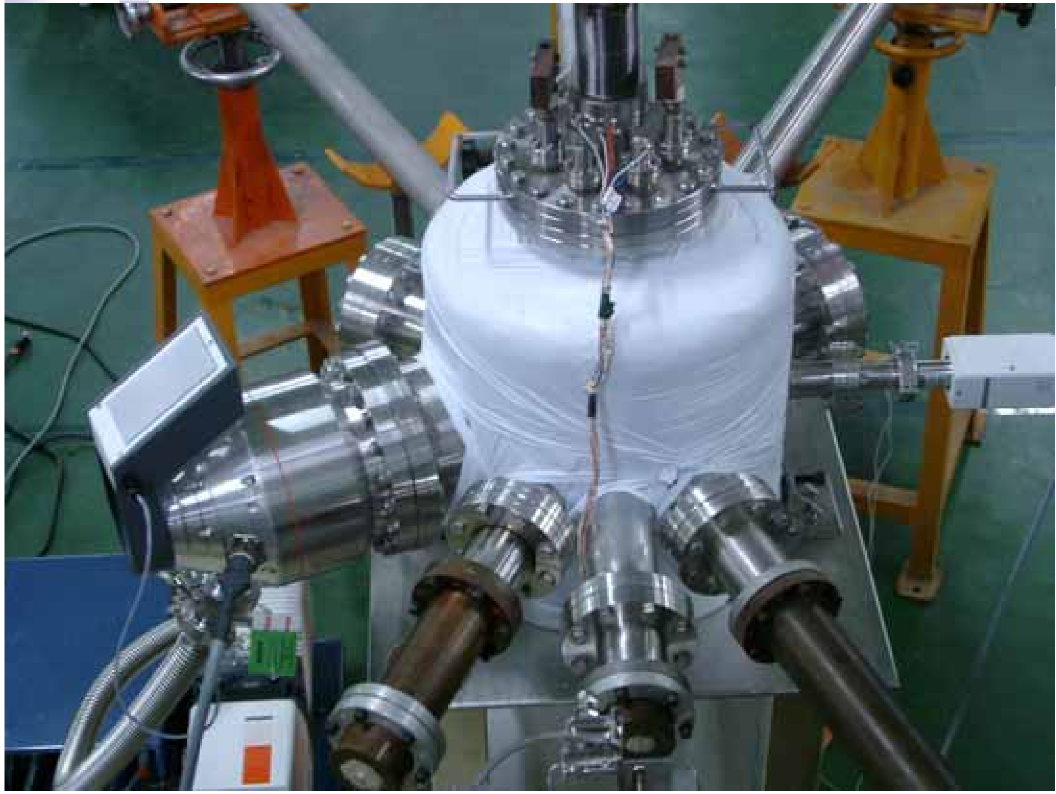
NEC 9SDH-2 3MV Tandem Accelerator

KN 3 MV van der Graaff Accelerator

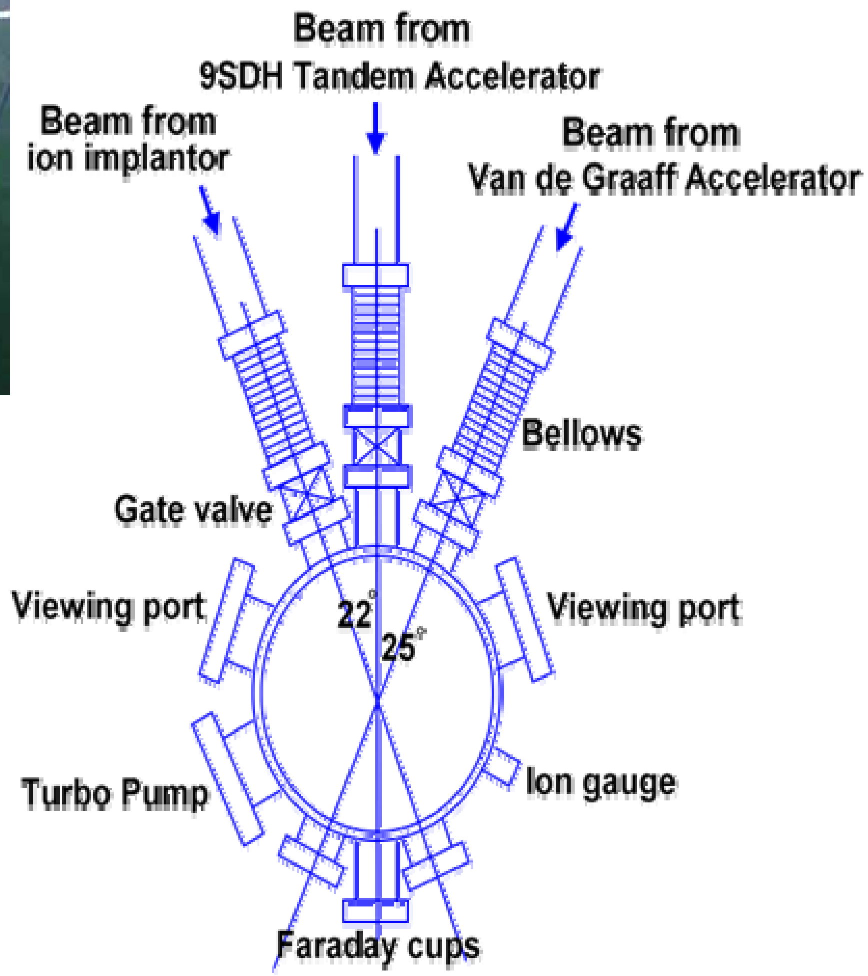
Triple-ion-beam Irradiation Chamber

Specimen Holders





Irradiation angles between the beams



Materials

- Uni-directional SiC/SiC composites with Tyranno-SA fibers and the matrix was fabricated using CVI method.
- Uni-directional SiC/SiC composites with Hi-Nicalon Type-S fibers and the matrix was also fabricated using CVI method.

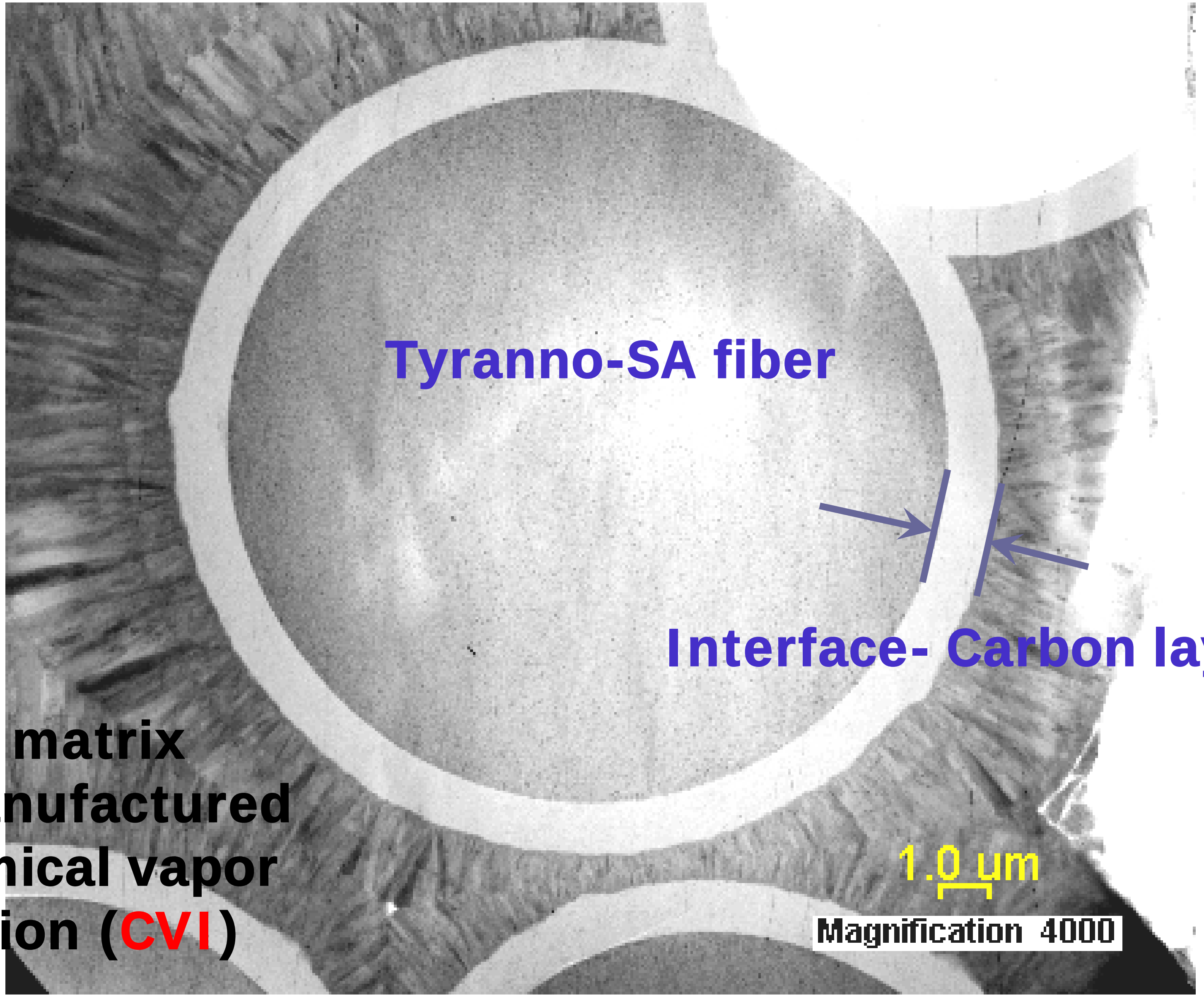
Experiments

unirradiated
- Unirradiated microstructures
- Annealed at 1000°C for 67 hours

Dual-beam irradiations
- Si^{3+}+He^{+} ,600°C and 800°C,10dpa/1500appm
- Si^{3+}+He^{+},800°C and 1000°C,100dpa/15000appm
- H^{+}+He^{+},800°C and 1000°C,6000appm/15000appm

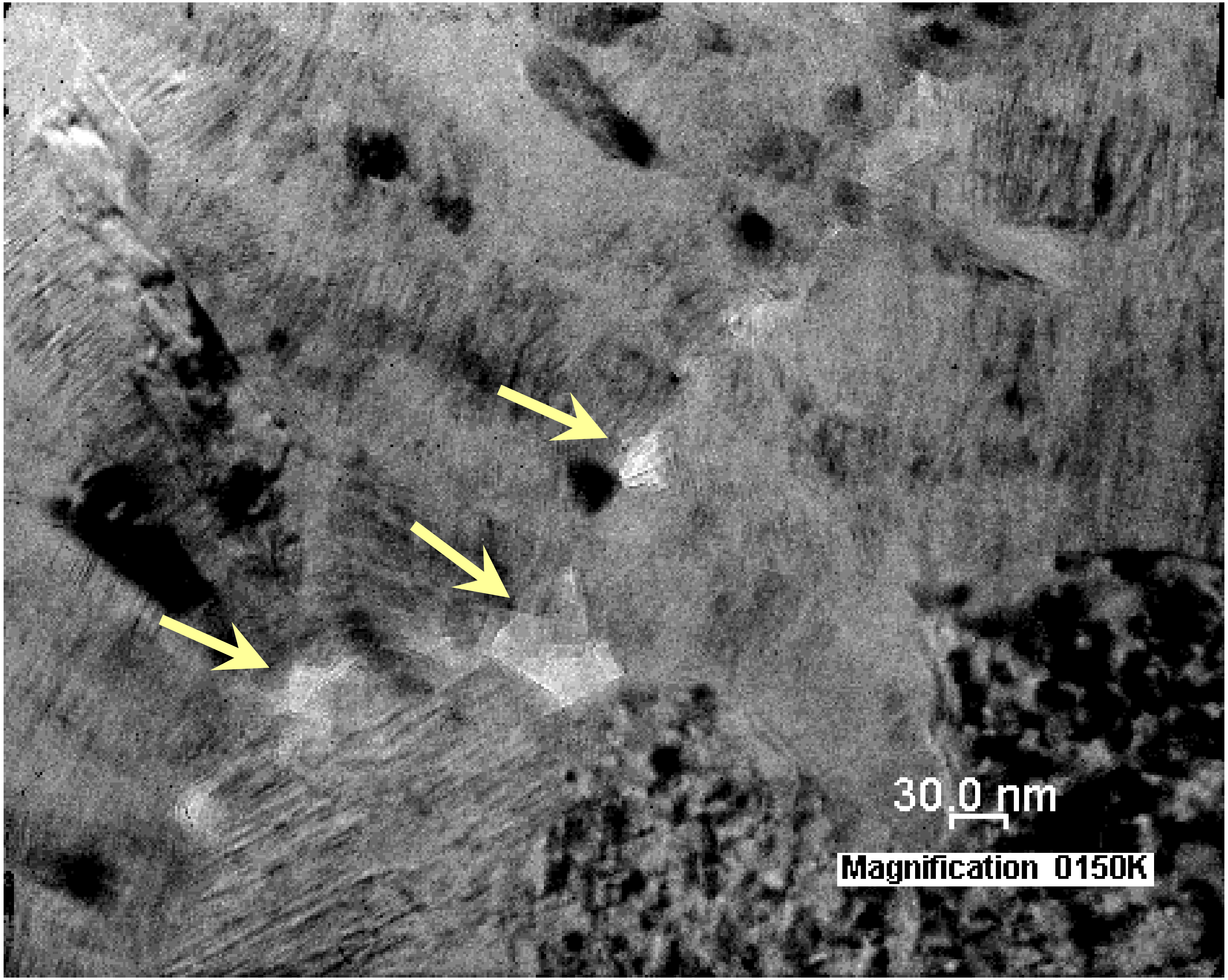
Triple-beam irradiation → He^{+}+H^{+}+Si^{3+} ,800°C/1500appm/600appm/10dpa

Tyranno-SA/PyC/SiC

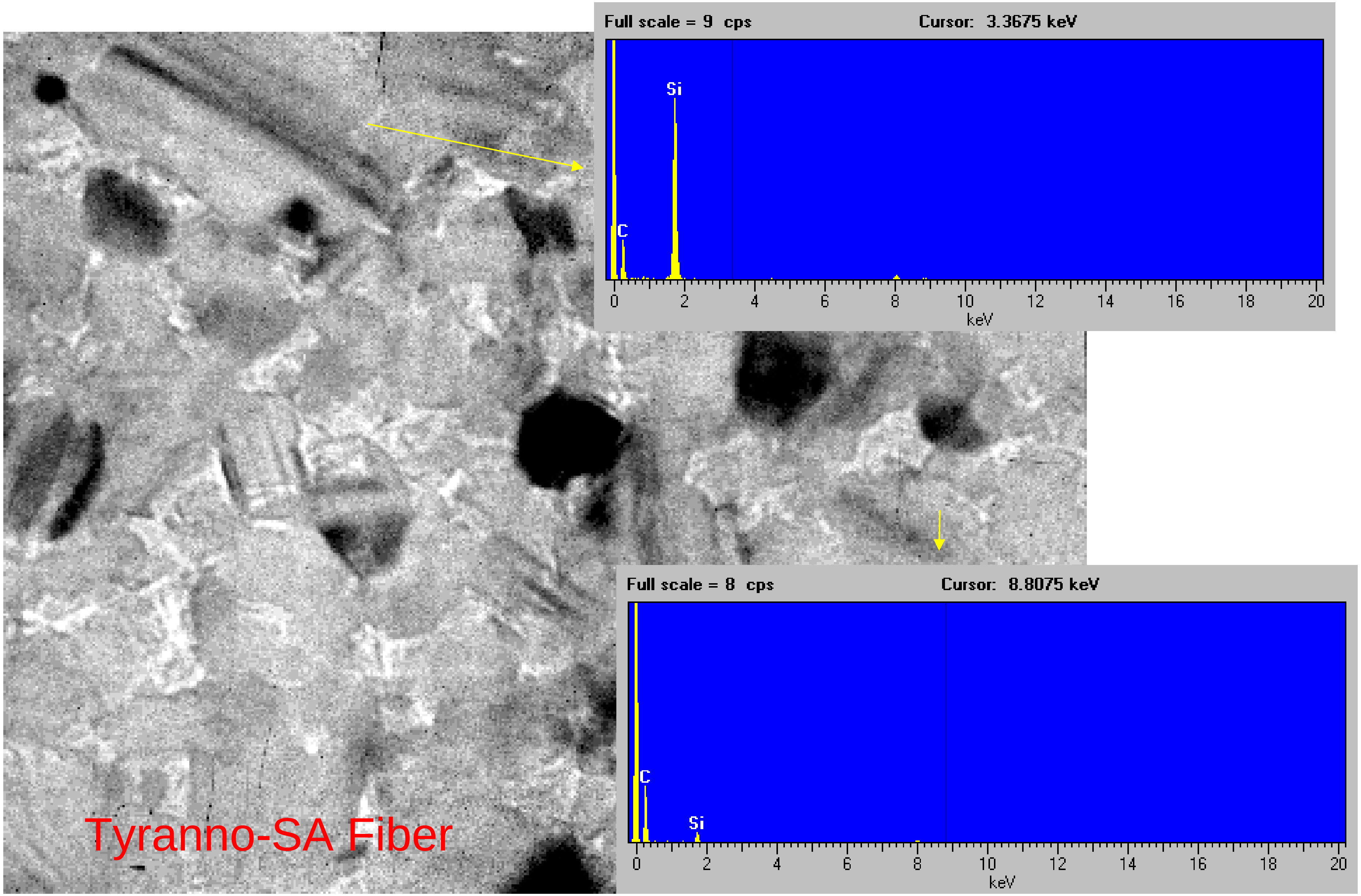


The SiC matrix was manufactured by chemical vapor infiltration (CVI)

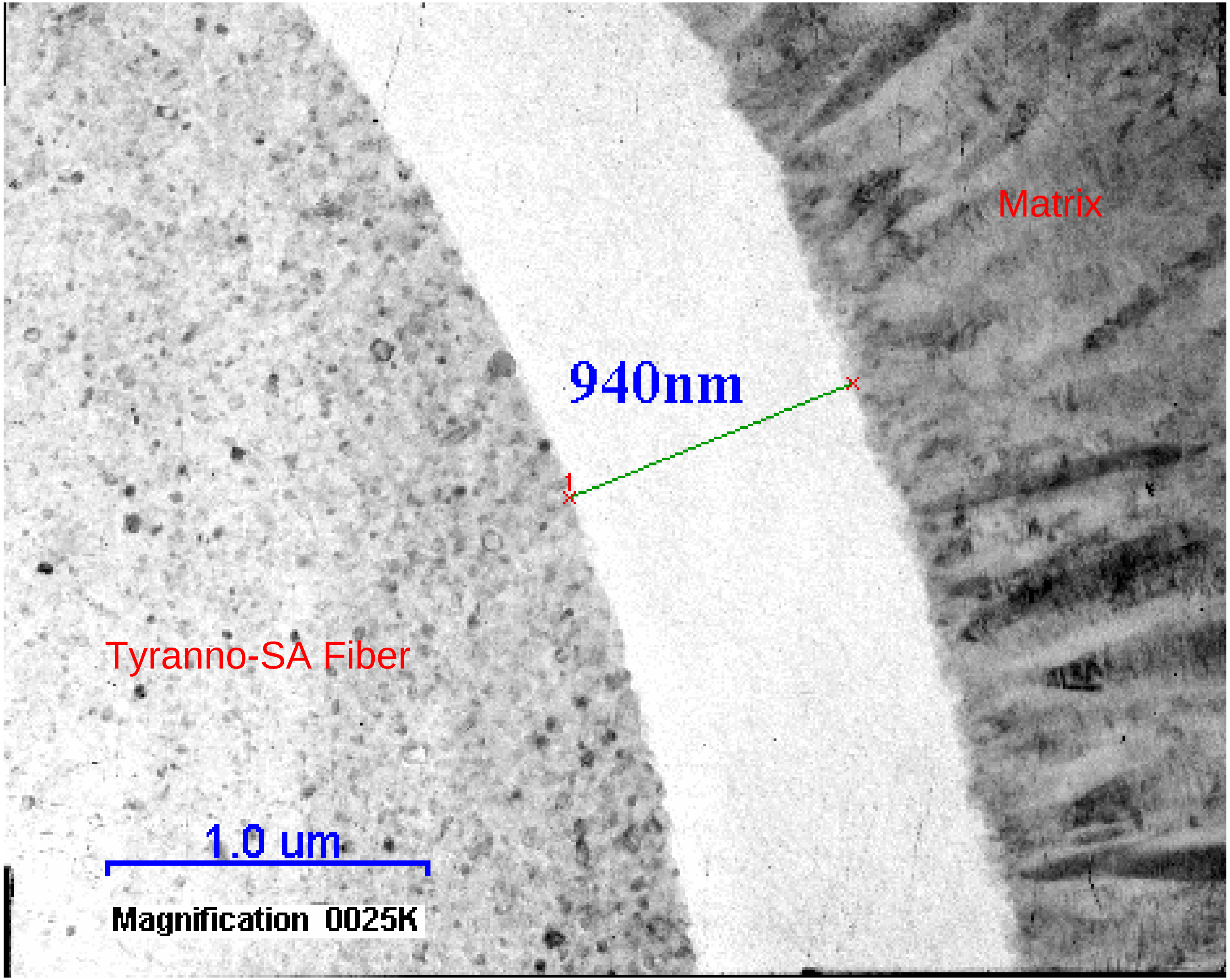
The holes between the layers in the SiC matrix



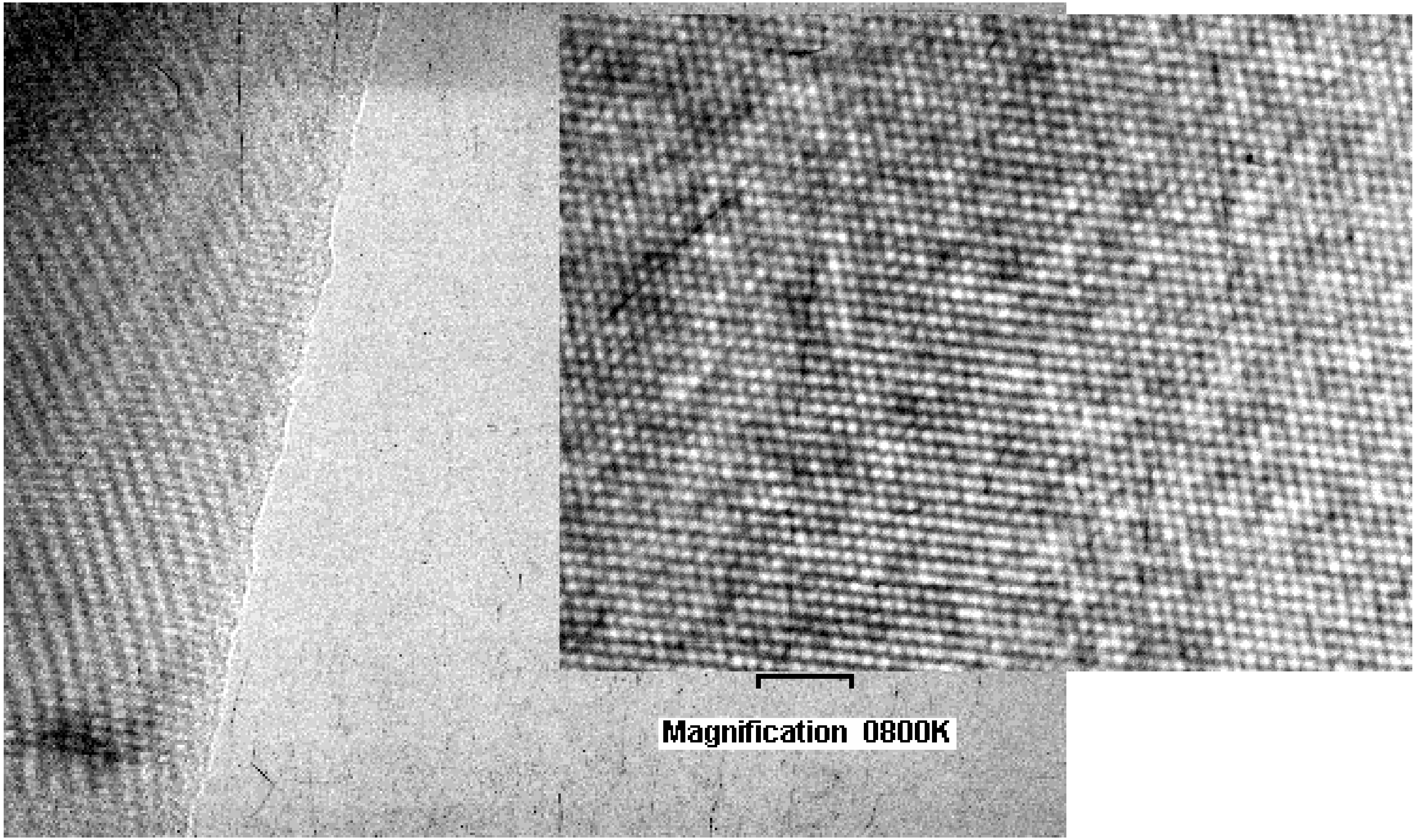
Grains size of the fiber is between 50～100 nm



Interface and Carbon layer

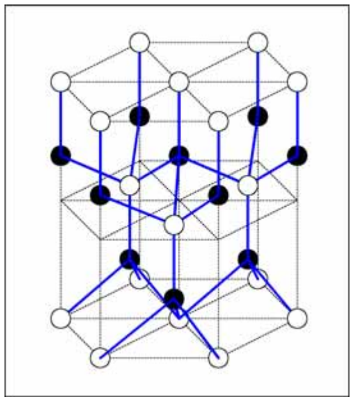


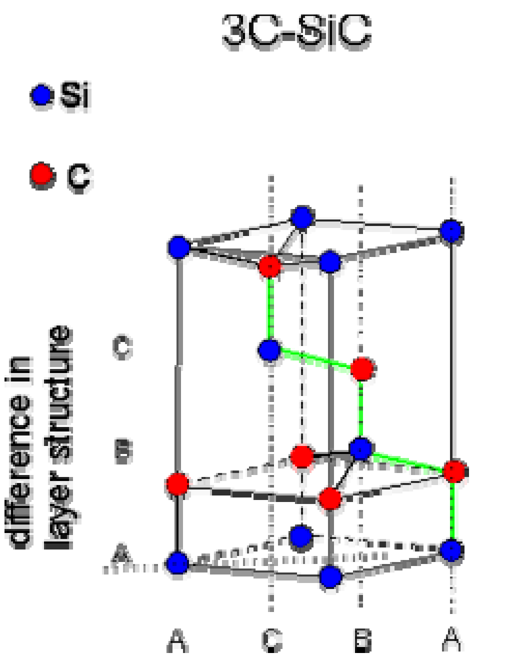
3C β-SiC nano-grain

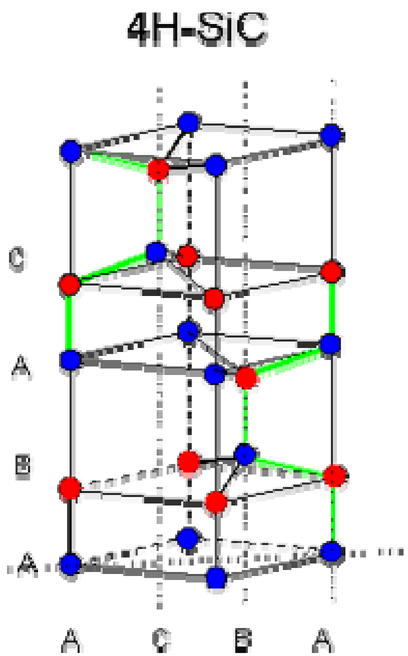


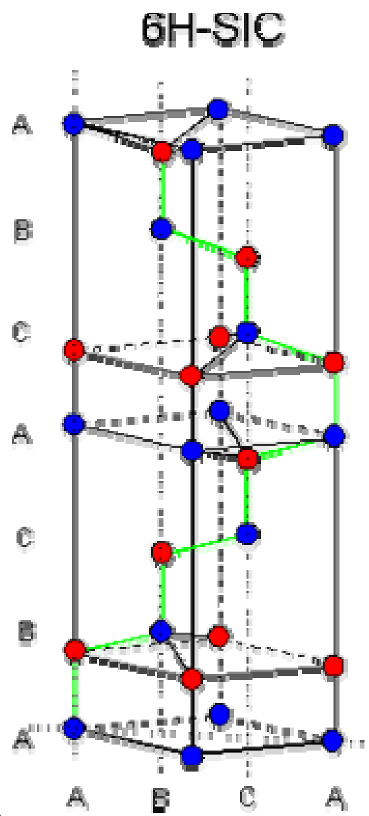
	2H-SiC α-phase	3C-SiC β-phase	4H-SiC α-phase	6H-SiC α-phase
structure	Hexagonal structure (Wurtzite)	Cubic (Zincblende)	Hexagonal structure (Wurtzite)	Hexagonal structure (Wurtzite)

2H-SiC









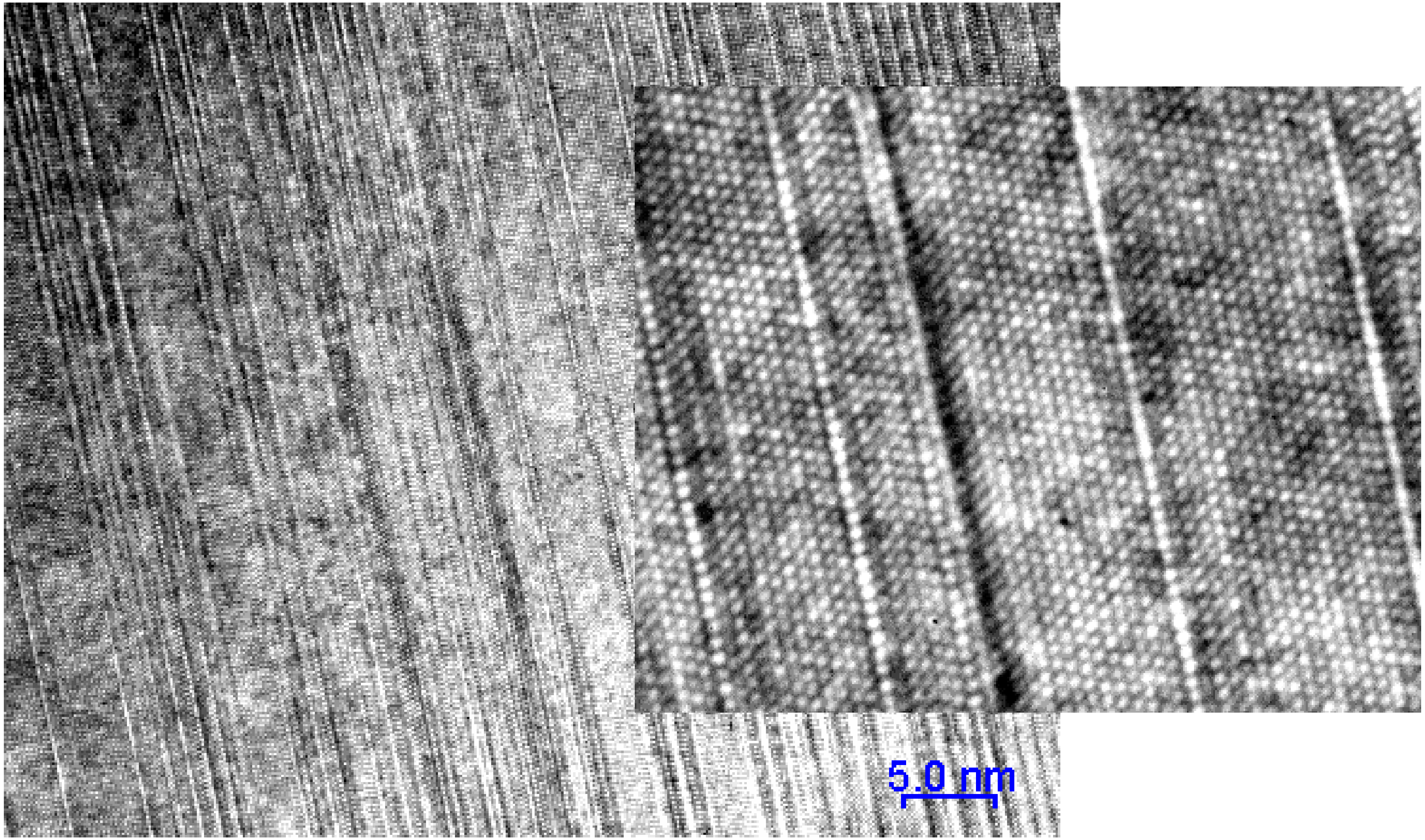
***2H*-SiC** *a*=5.8125 Å

***3C*-SiC** *a*=4.3596 Å

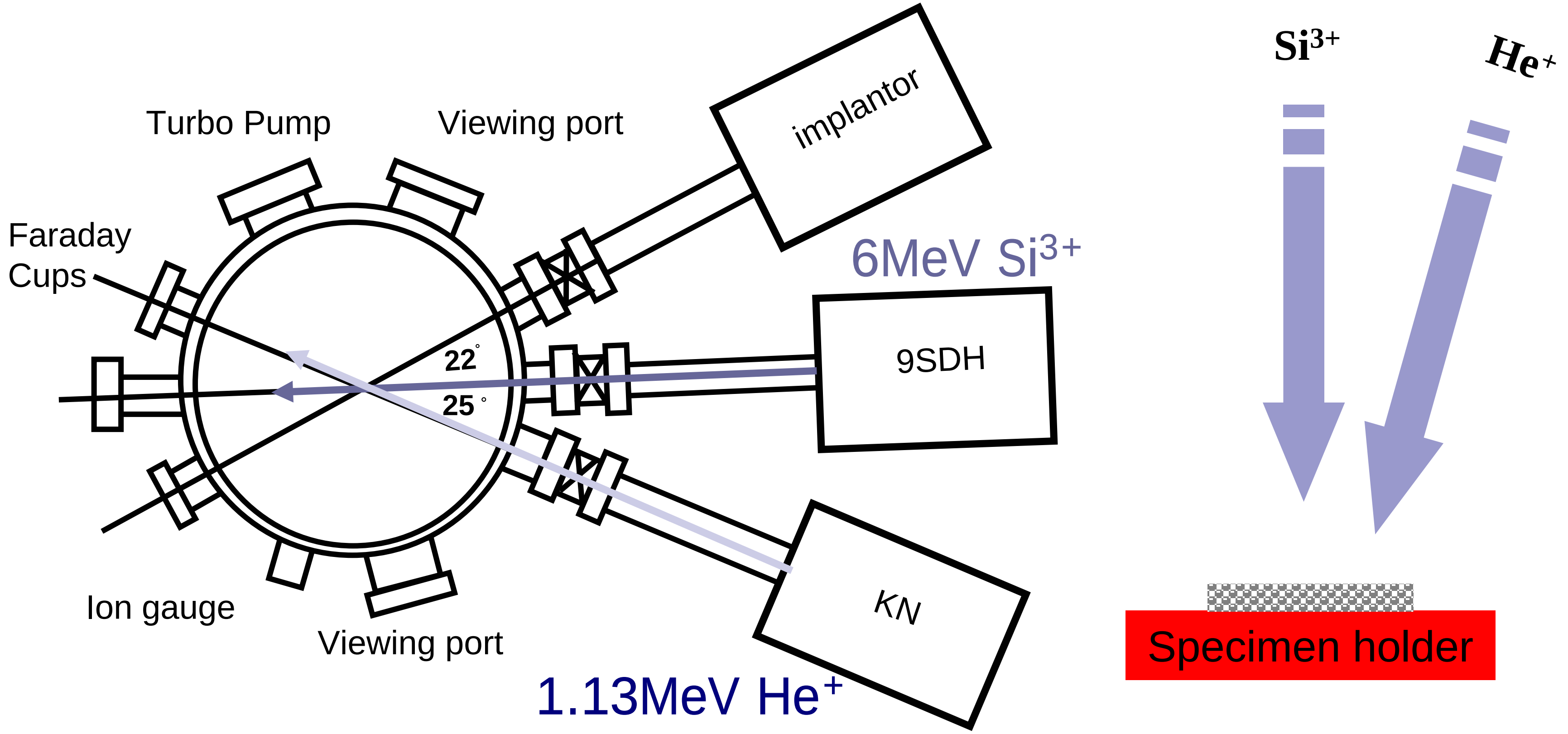
***4H*-SiC** *a* = 3.0730 Å
b = 10.053 Å

6H*-SiCa* = 3.0730A
b = 10.053A

2H, 4H, 6H intermixing microstructures

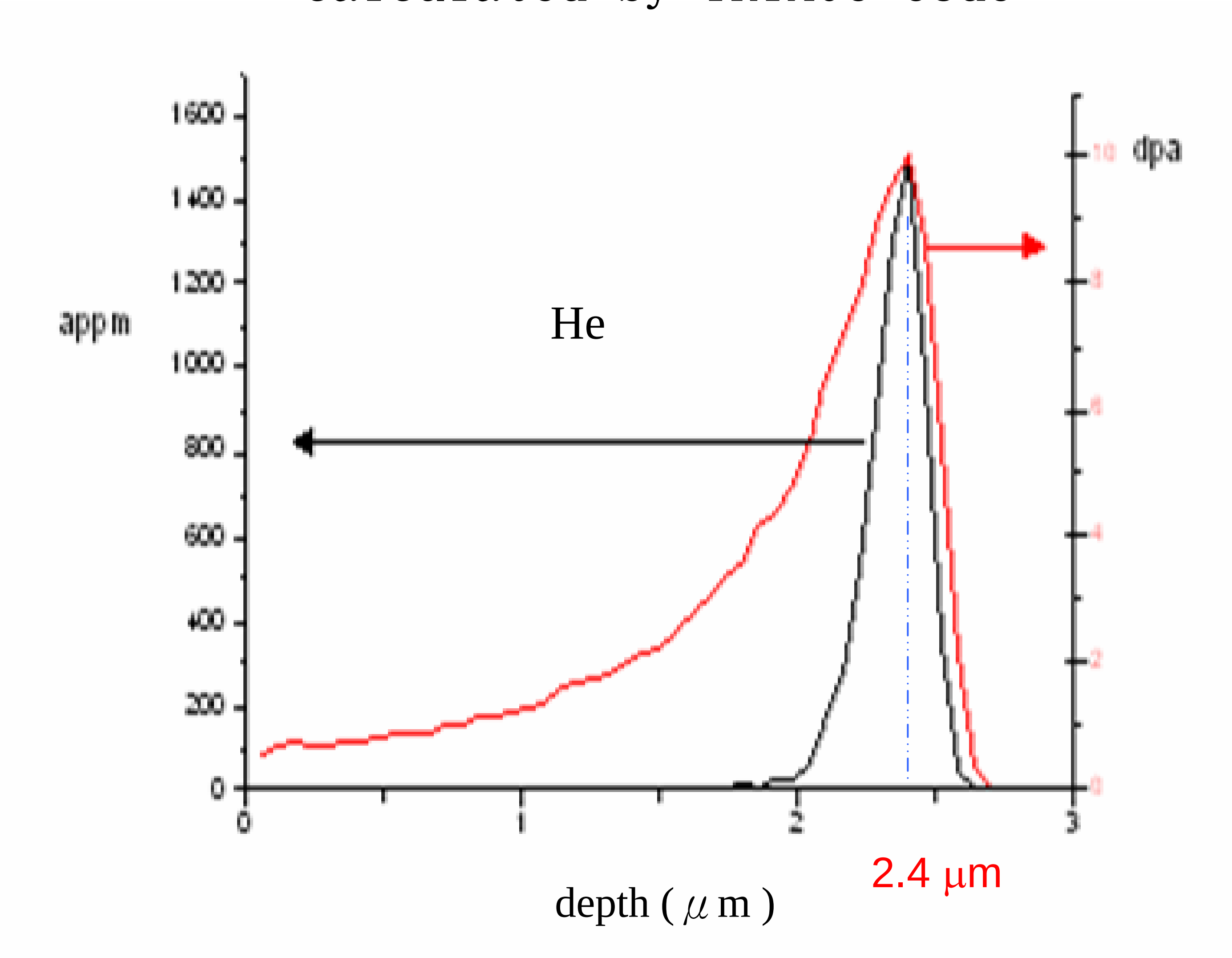


Si/He Dual-beam Irradiation

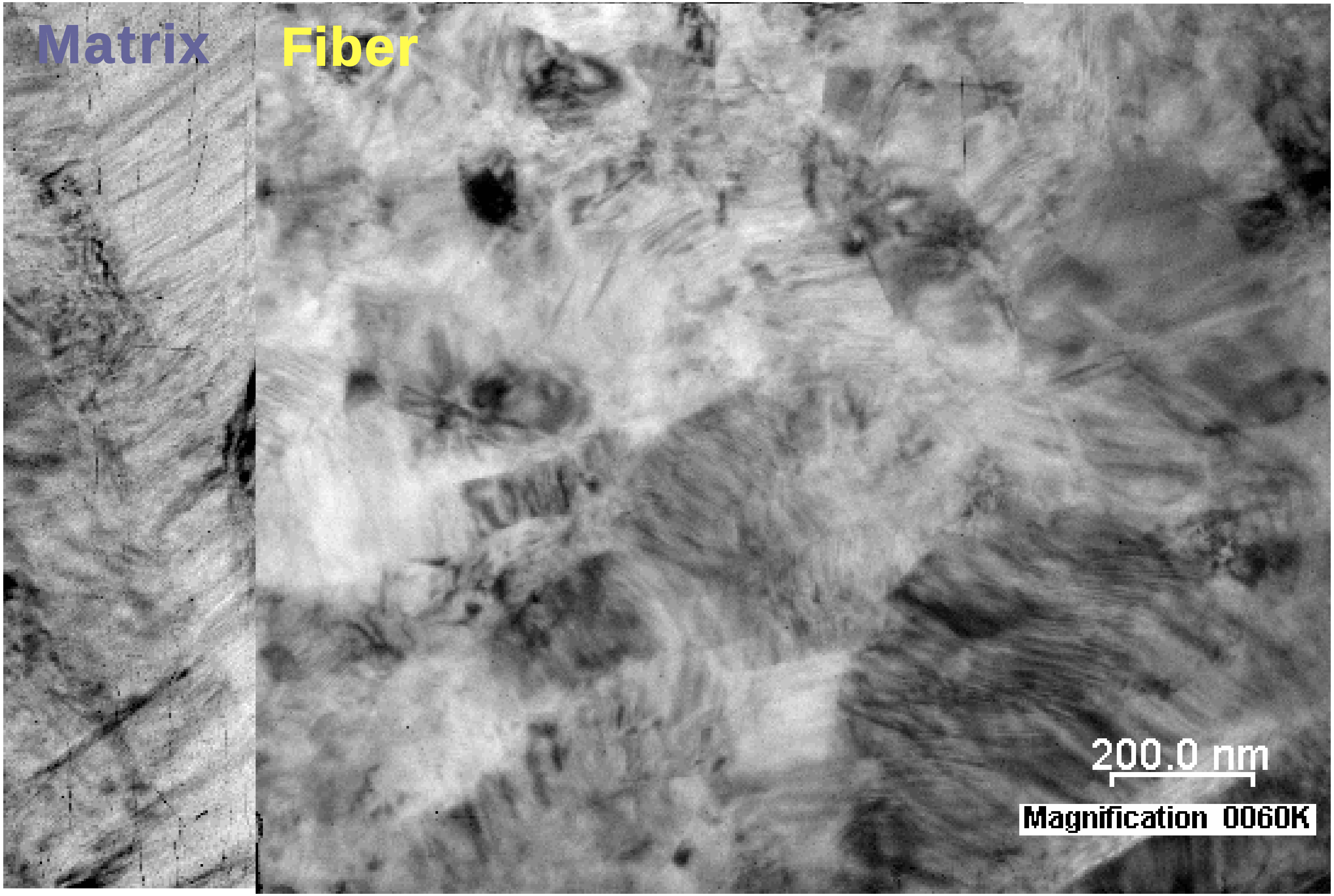


Schematics of the Triple-beam Irradiation Facility

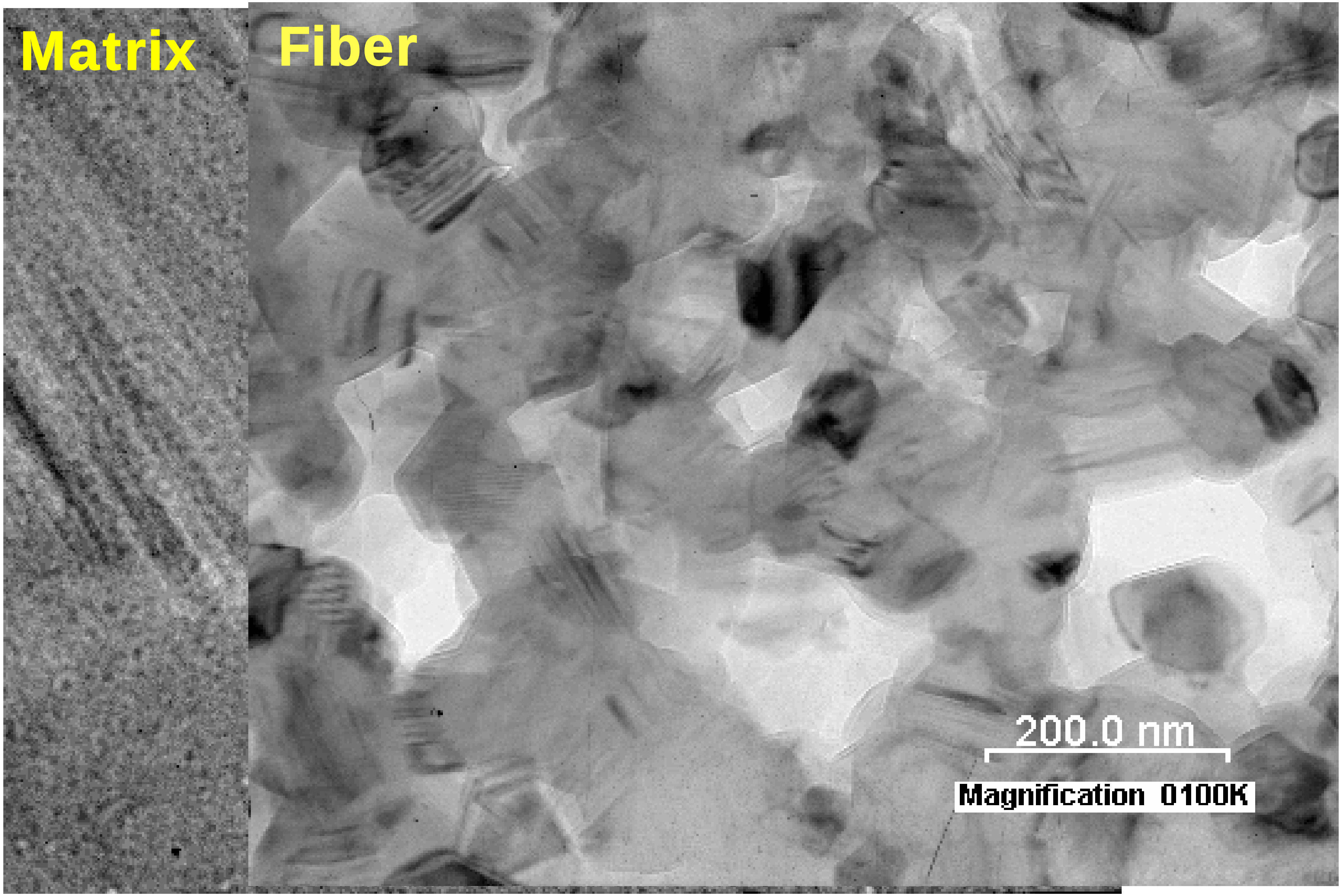
Si-He Dual-beam irradiation calculated by TRIM98 Code



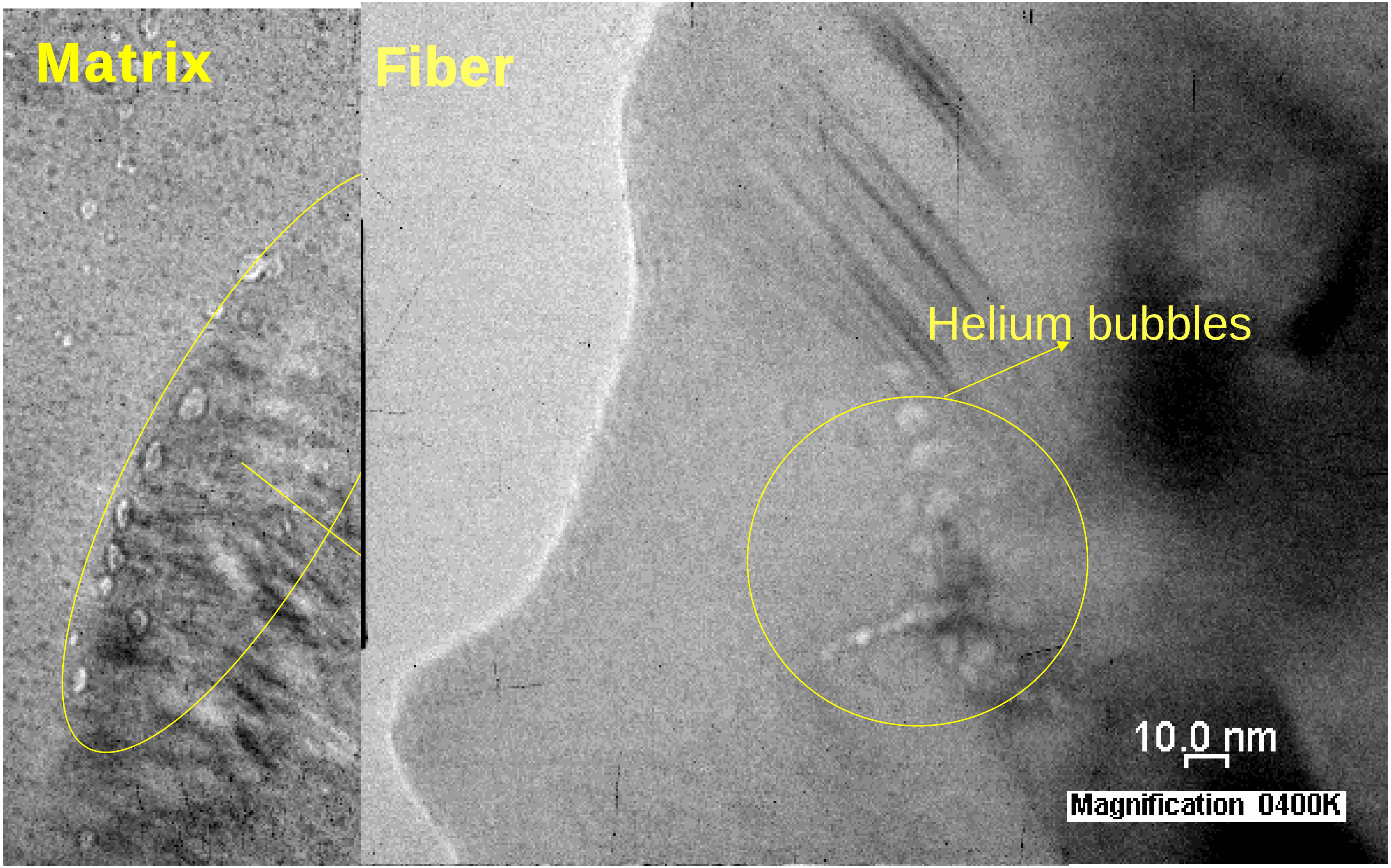
Dual beams implant (Si^{3+} and He^{+}) @600°C, 10dpa/1500appm



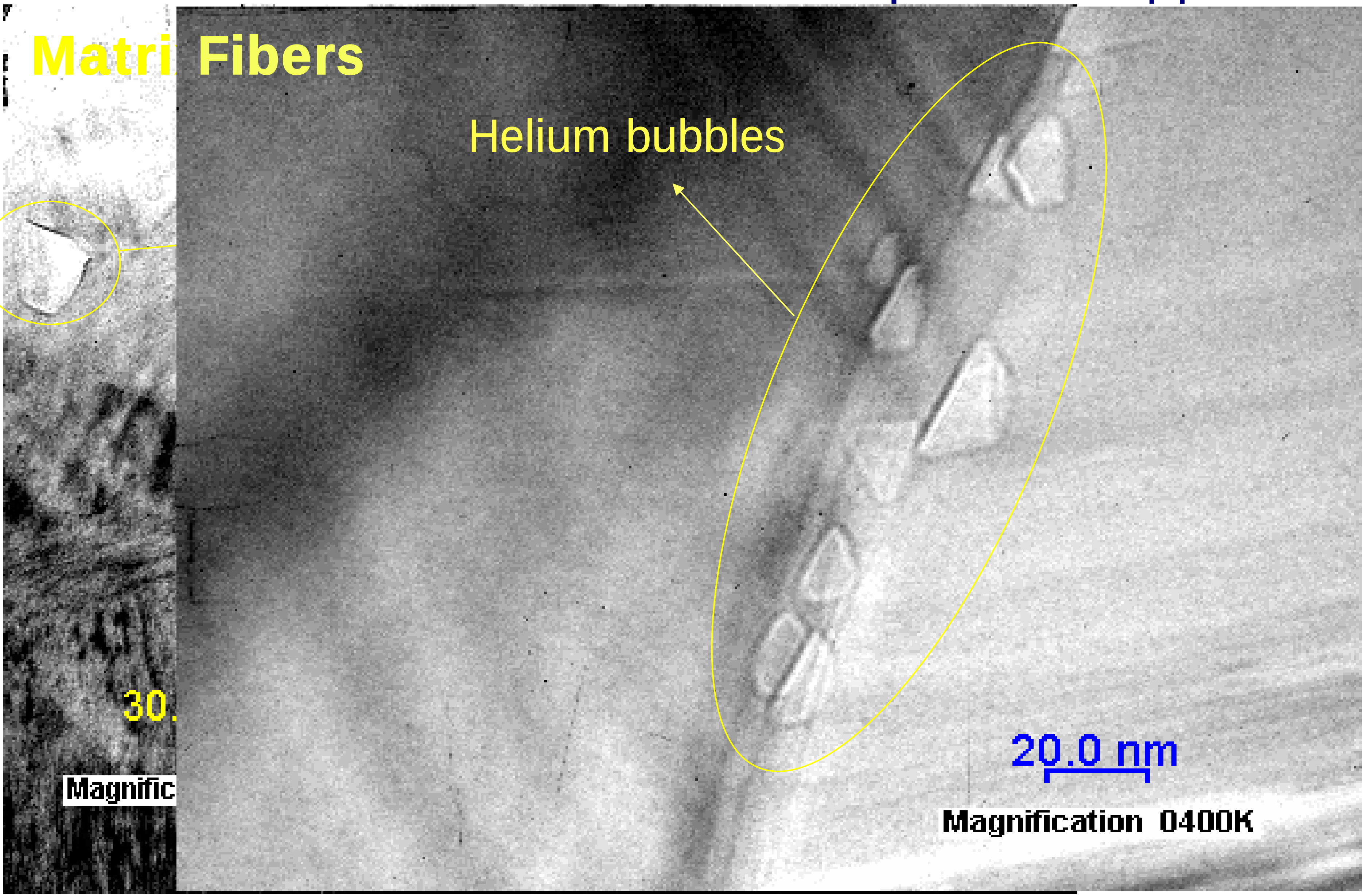
Dual beams implant (Si^{3+} and He^{+}) @800°C, 10dpa/1500appm



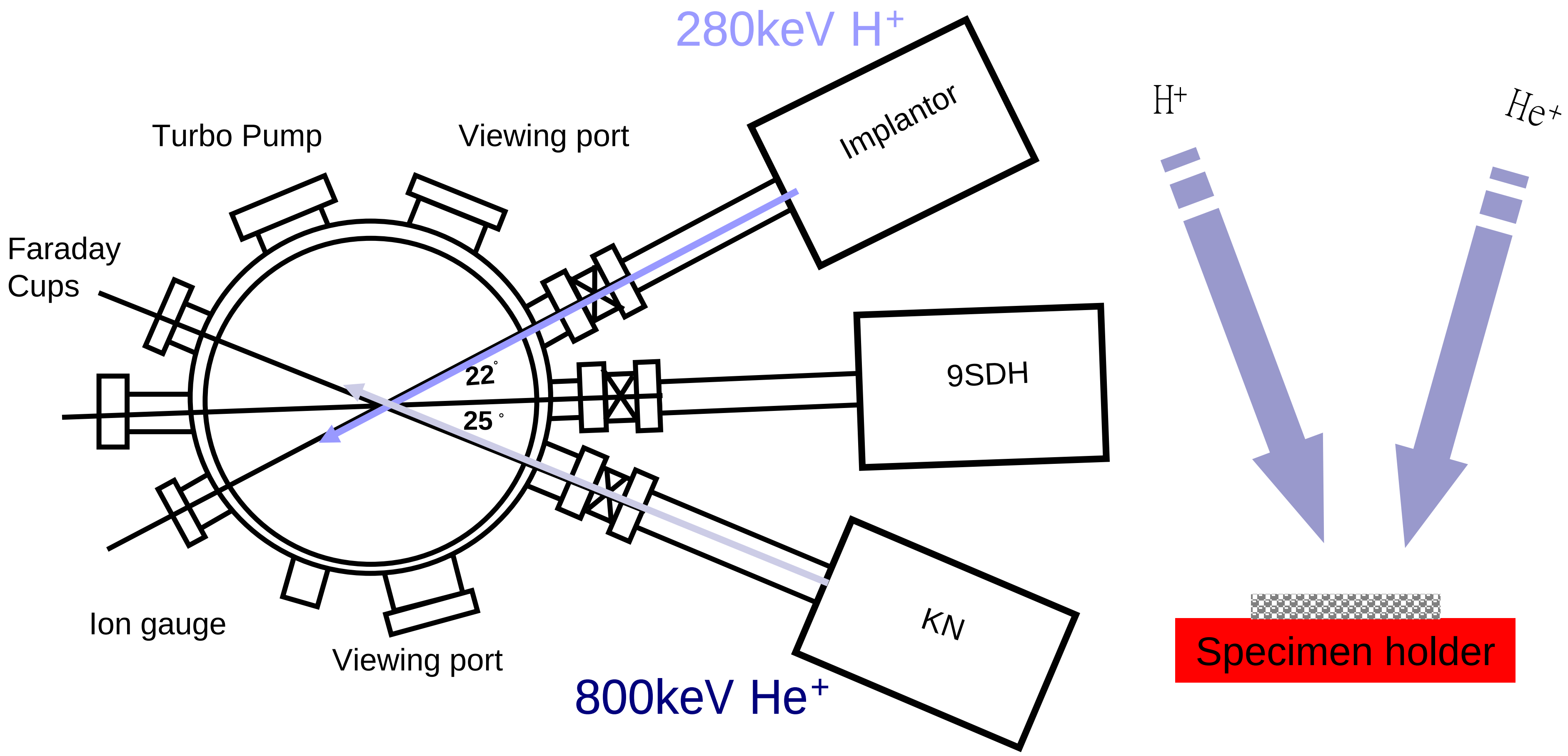
Dual beams implant (Si^{3+} and He^{+}) @800°C, 100dpa/15000appm



Dual beams implant (Si^{3+} and He^{+}) @1000°C, 100dpa/15000appm

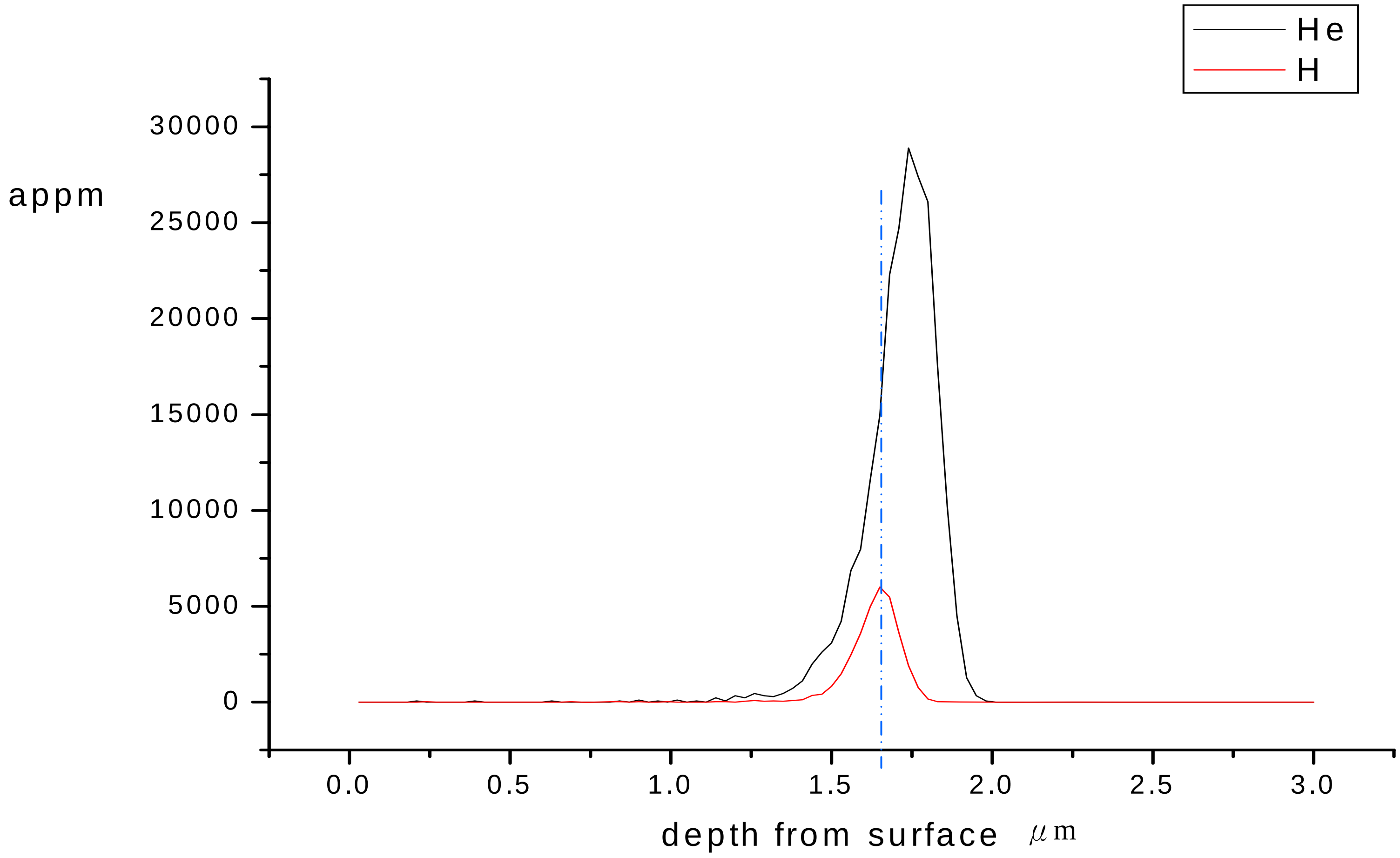


H/He Dual-beam Irradiation

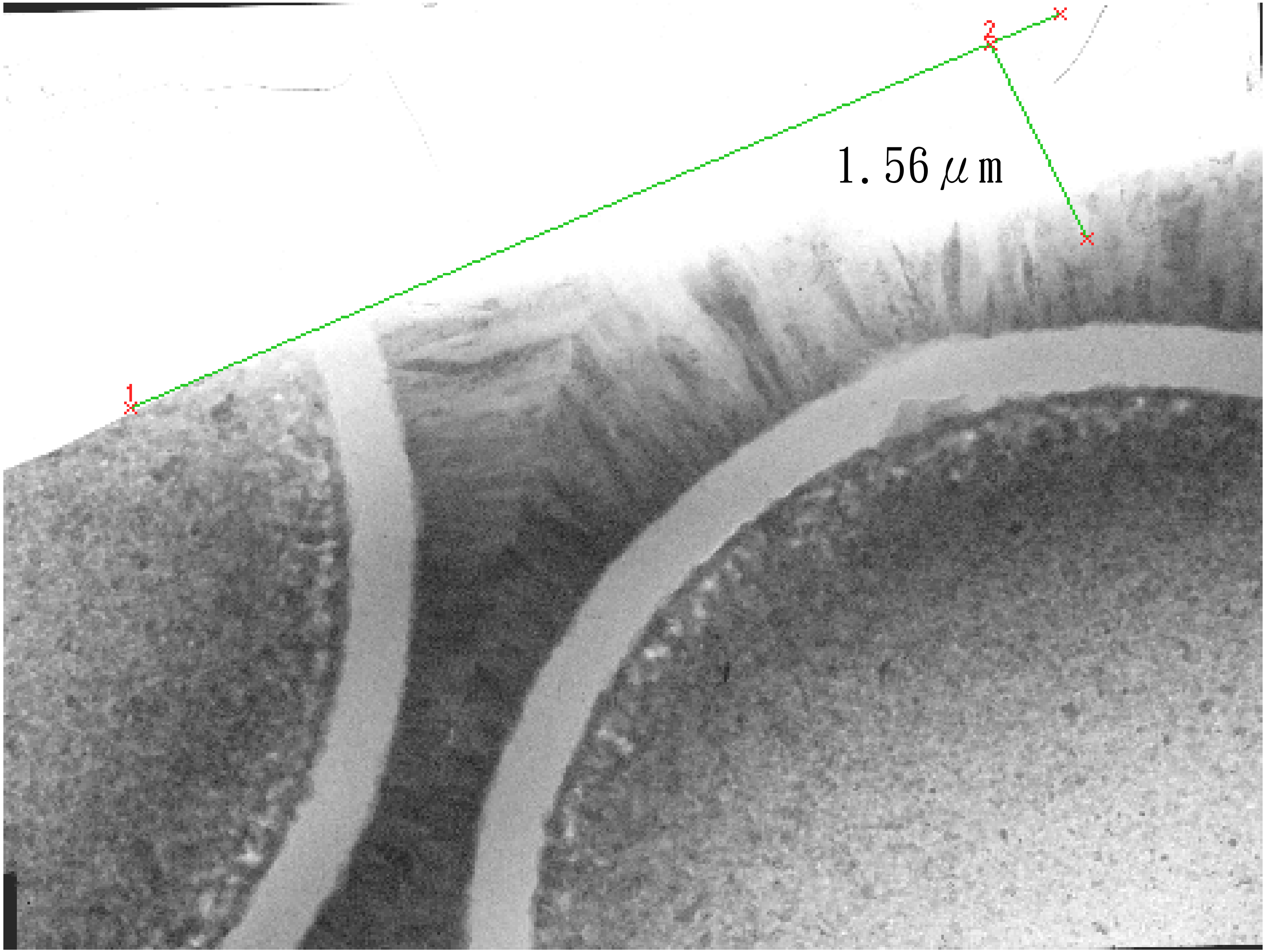


Schematics of the Triple-beam Irradiation Facility

He/H Dual-beam Irradiation calculated by SRIM



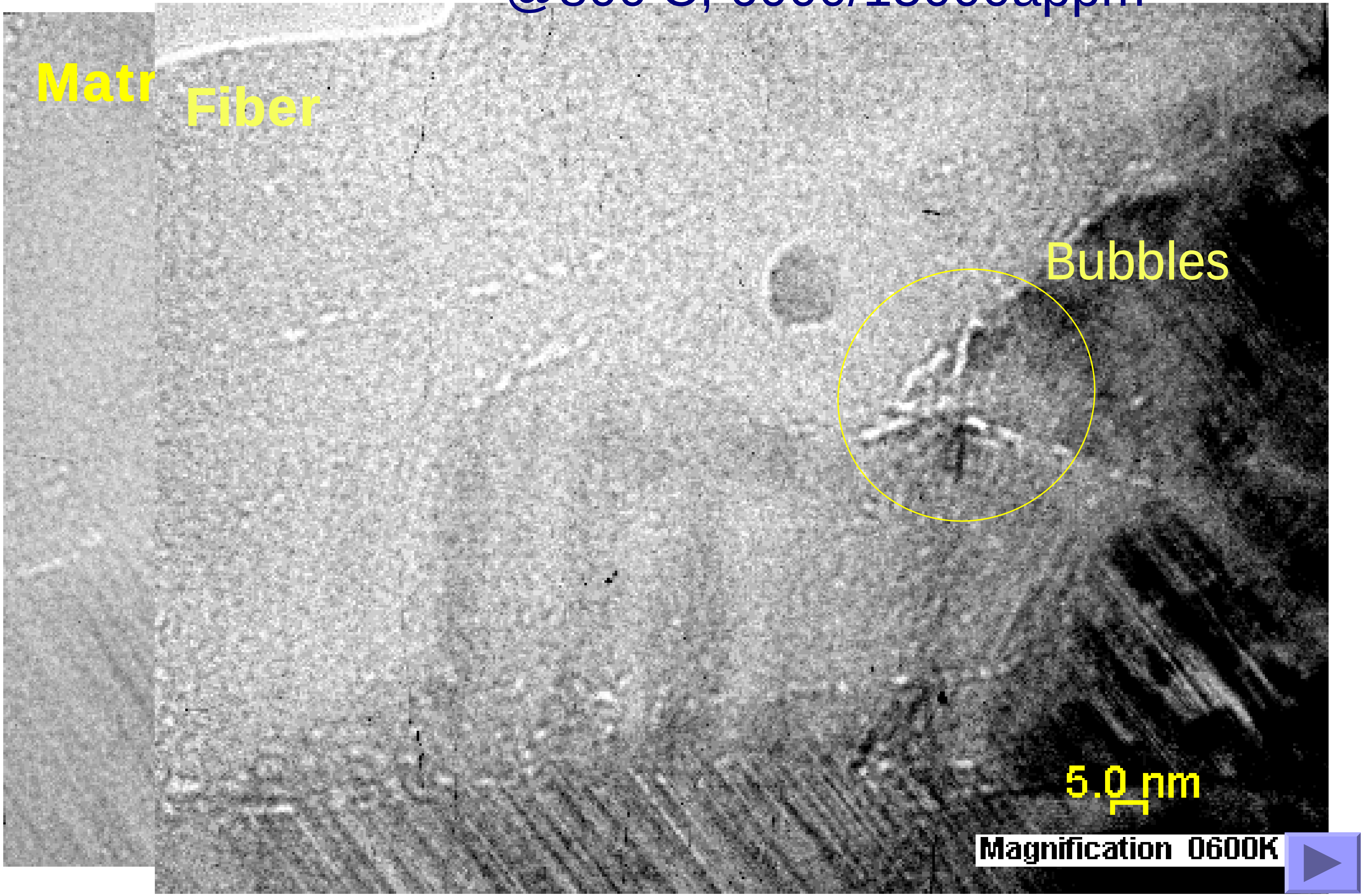
At 1.56 μm depth the He/H ration is15000/6000 appm



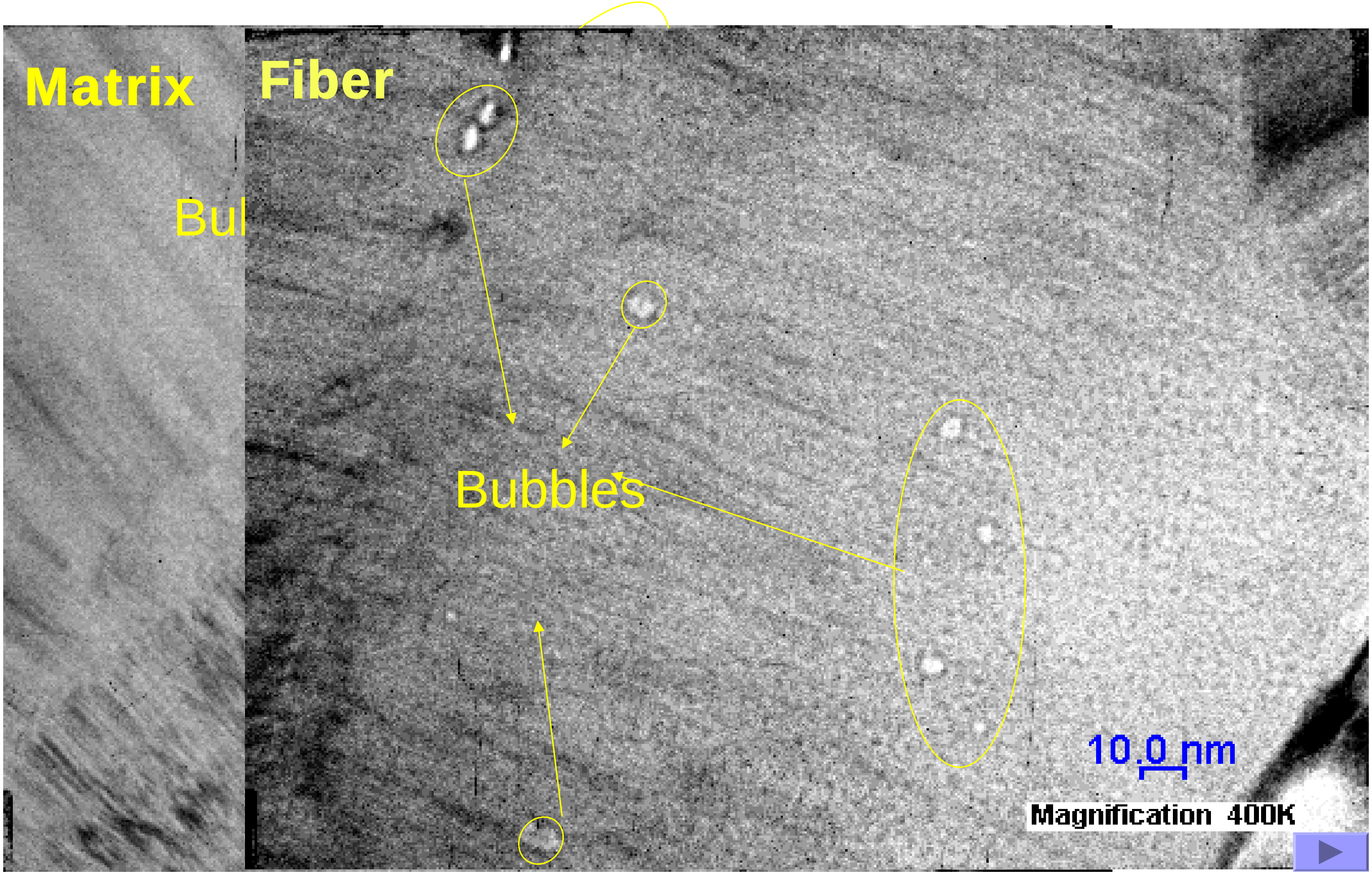
app

depth from surface μm

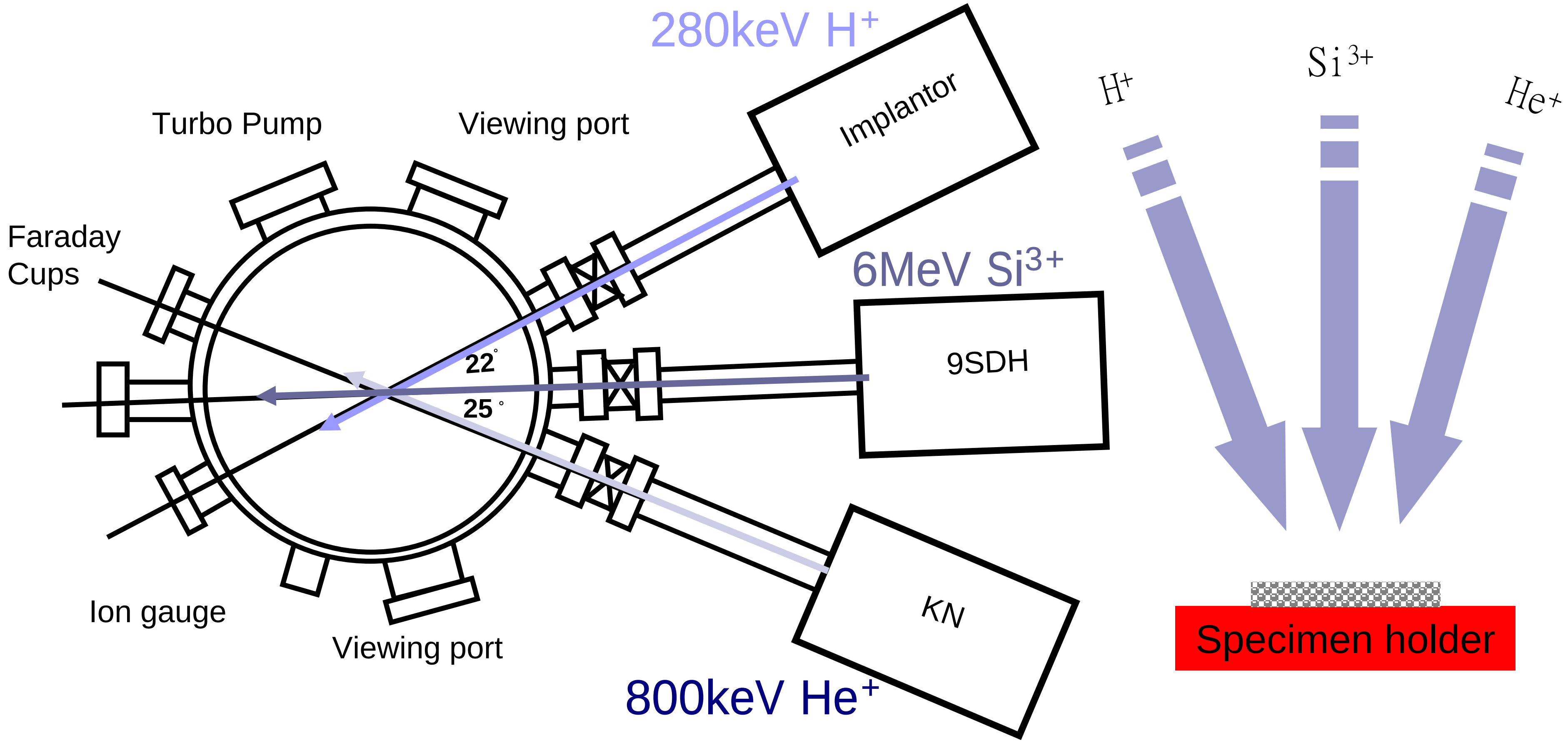
Dual beams implant (H^+ and He^+) @800°C, 6000/15000appm



Dual beams implant (H^+ and He^+) @1000°C, 6000/15000appm

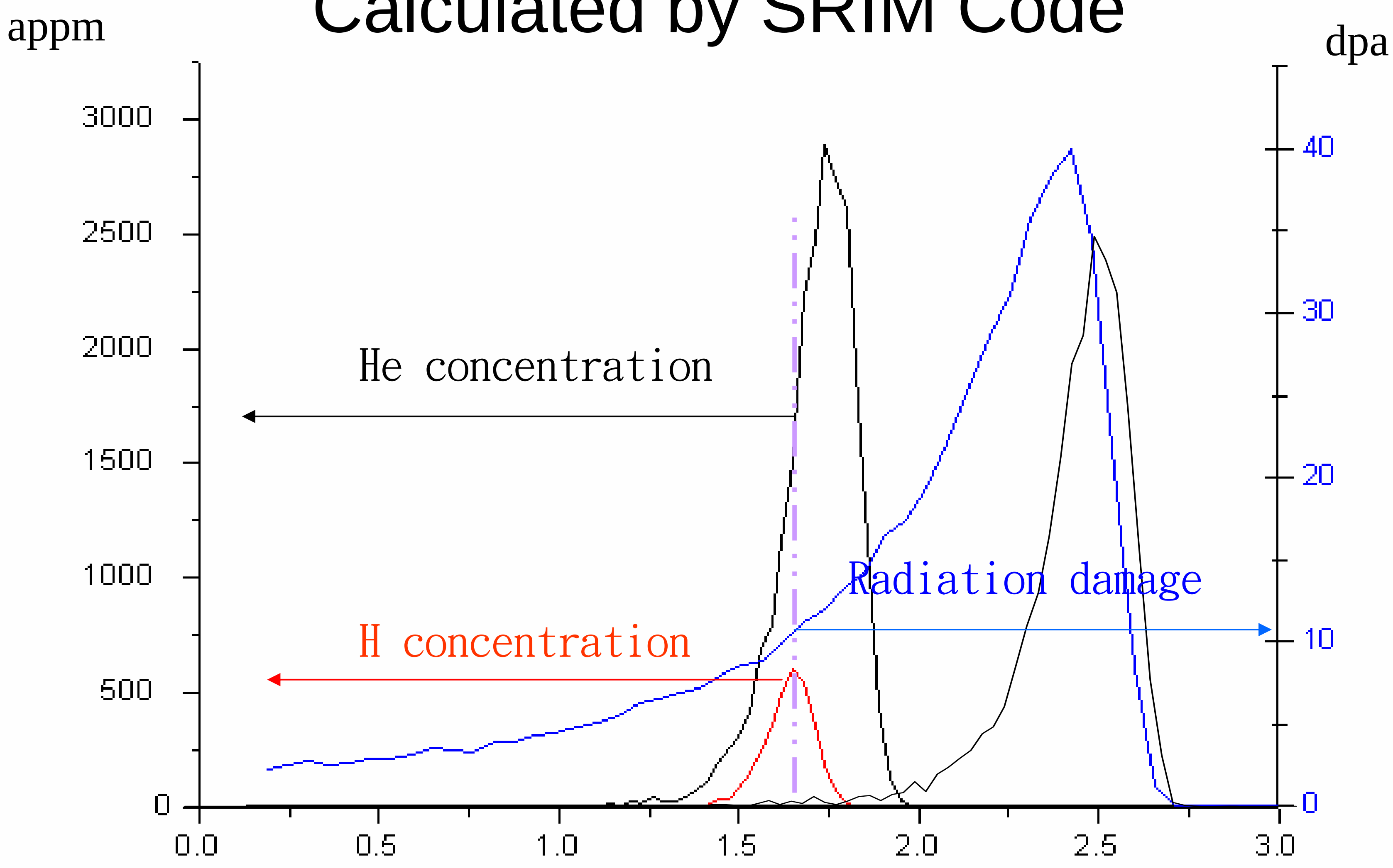


Si/He/H Triple-beam Irradiation



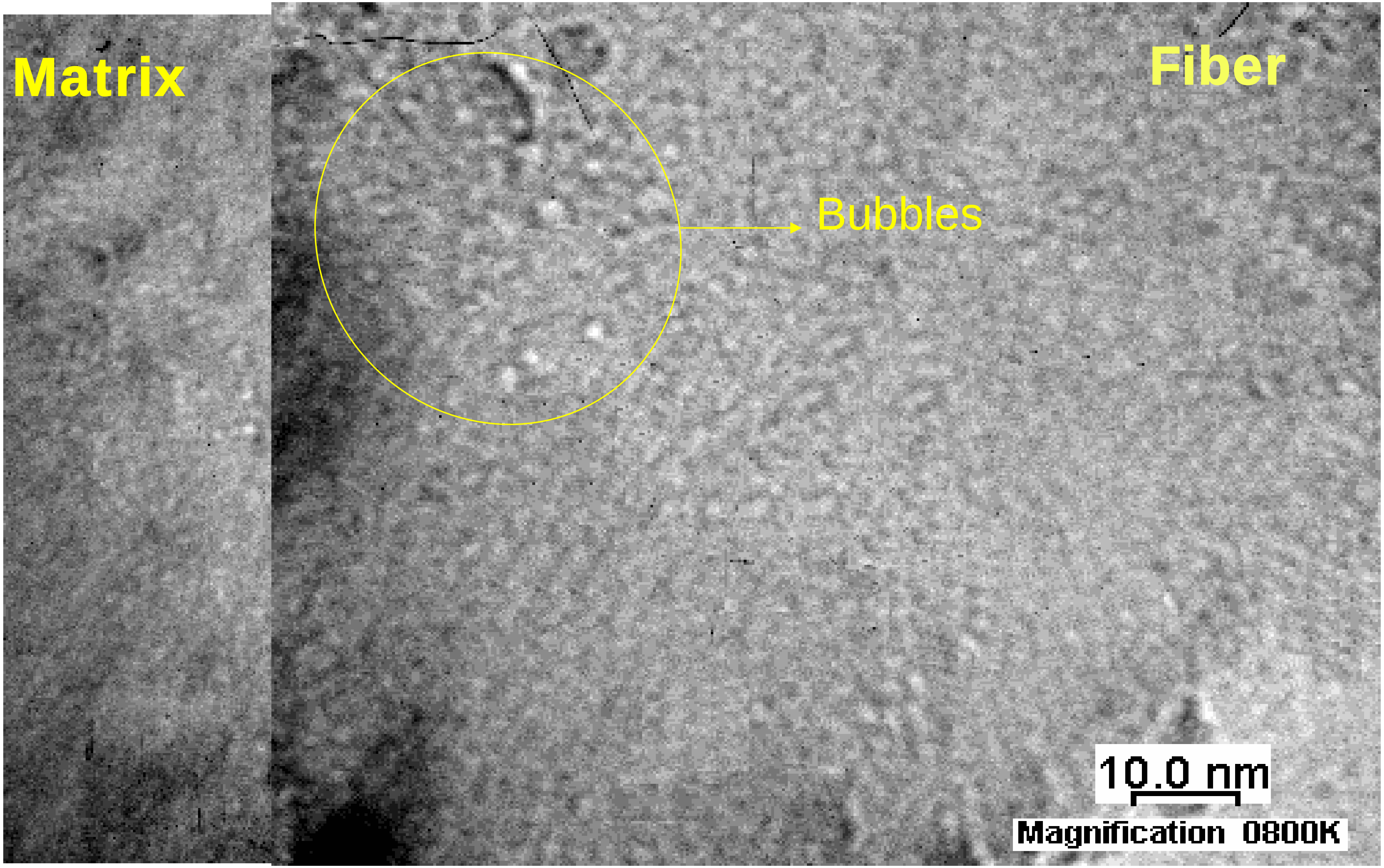
Schematics of the Triple-beam Irradiation Facility

Si/He/H Triple-beam Irradiation Calculated by SRIM Code

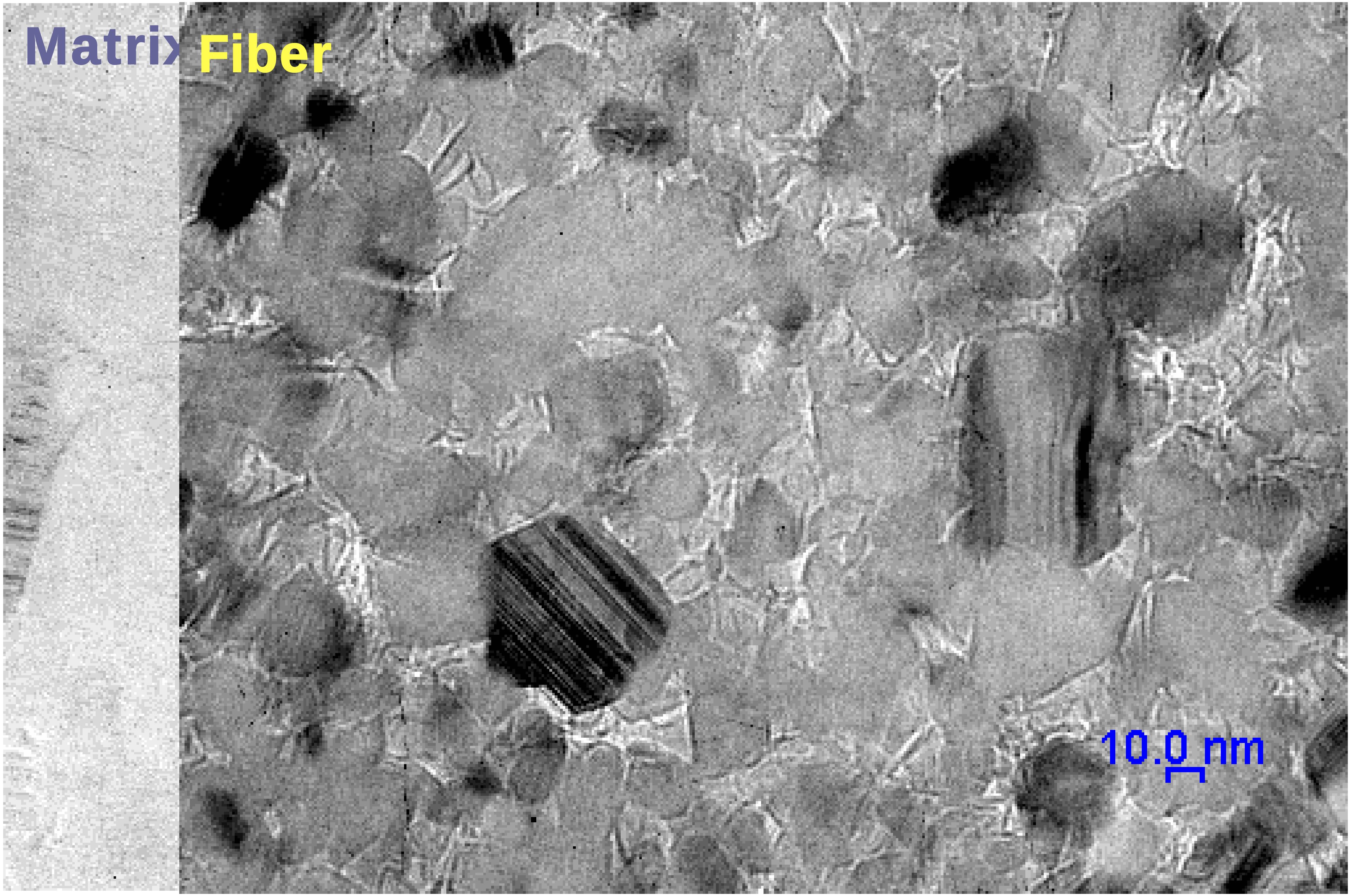


At 1.56 μm depth we get 10dpa/1500appm/600appm

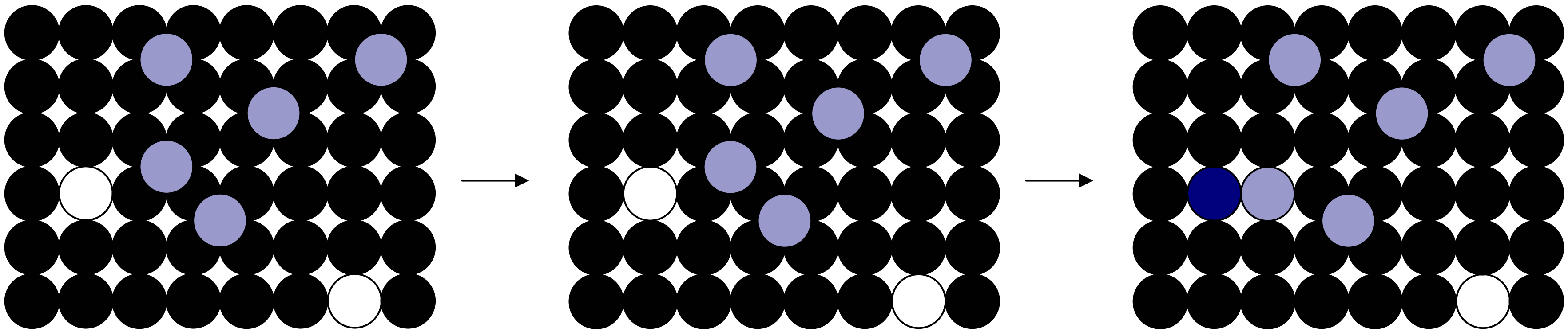
Triple beams implant (Si^{3+}, H^{+} and He^{+}) @800°C, 10dpa/6000appm/15000appm



After 67 hours annealing @1000°C

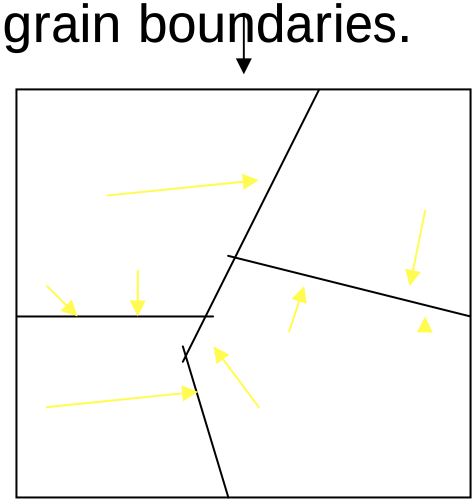


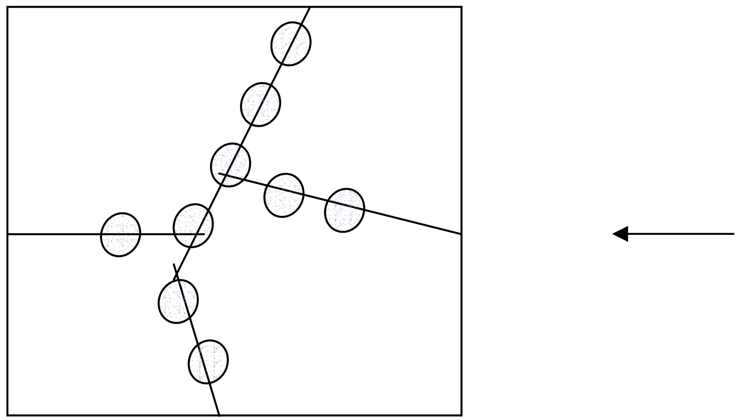
Bubble formation mechanism in dual-beam irradiation conditions



He atoms in the lattice

At high temperatures vacancies can move which assist He atoms migrate to grain boundaries.





He bubbles form at grain boundaries.

■ Temperature Effects

Comparison between temperatures

- 600°C and 800°C (Si^{3+}/He^{+}= 10dpa/1500appm)
- 800°C and 1000°C (Si^{3+}/He^{+}= 100dpa/15000appm)
- 800°C and 1000°C (H^{+}/He^{+}= 6000appm/15000appm)

Comparison between 600°C and 800°C Dual-beam (Si^{3+}/He^{+}= 10dpa/1500appm)

- There is no bubbles found in the SiC matrix or fibers in 600° C dual-beam irradiated specimens.

- We found bubbles in the SiC matrix but not in the Tyranno-SA fibers in 800° C irradiated specimens.

Comparison between 800°and 1000°C Dual-beam (Si^{3+}/He^{+}= 100dpa/15000appm)

800°C	Si/He = 100dpa/15000 appm		1000°C	Si/He= 100dpa/15000 appm	
	Matrix	Fiber		Matrix	Fiber
Bubble size	10nm	5nm	Bubble size	40nm	15nm
Density($\#/m^3$)	2.6 $\times10^{21}$	4.5 $\times10^{21}$	Density($\#/m^3$)	1.4 $\times10^{21}$	2.7 $\times10^{21}$

- Higher temperature gives larger in bubble size but fewer in number density.
- Smaller bubbles and higher density found in Tyranno-SA SiC fibers than in the SiC matrix.

Comparison between 800°C and 1000°C Dual-beam (H^+/He^+= 6000appm/15000appm)

800°C	H/He= 6000/15000appm		1000°C	H/He= 6000/15000appm	
▶	Matrix	Fiber	▶	Matrix	Fiber
Bubble size	2~3 nm	1nm	Bubble size	10nm	2nm
Density(#/m^3)	3.4 x10^{22}	5.6 x10^{22}	Density(#/m^3)	0.9 x10^{22}	2.7 x10^{22}

➡ Higher temperature gives larger in bubble size and fewer in number density.

➡ Fibers contain higher density but smaller diameter of bubbles than in the matrix.

Higher dose effects

800˚C dual-beam irradiation
- (Si^{3+}/He^{+}=100dpa/15000appm)
- (Si^{3+}/He^{+}=10dpa/1500appm)

800˚C	Si/He= 10dpa/1500 appm		Si/He= 100dpa/15000 appm	
	matrix	fiber	matrix	fiber
bubble size	1.2nm	X	10nm	5nm
density (#/m^3)	$0.85x10^{22}$	X	$2.6x10^{21}$	$4.5x10^{21}$

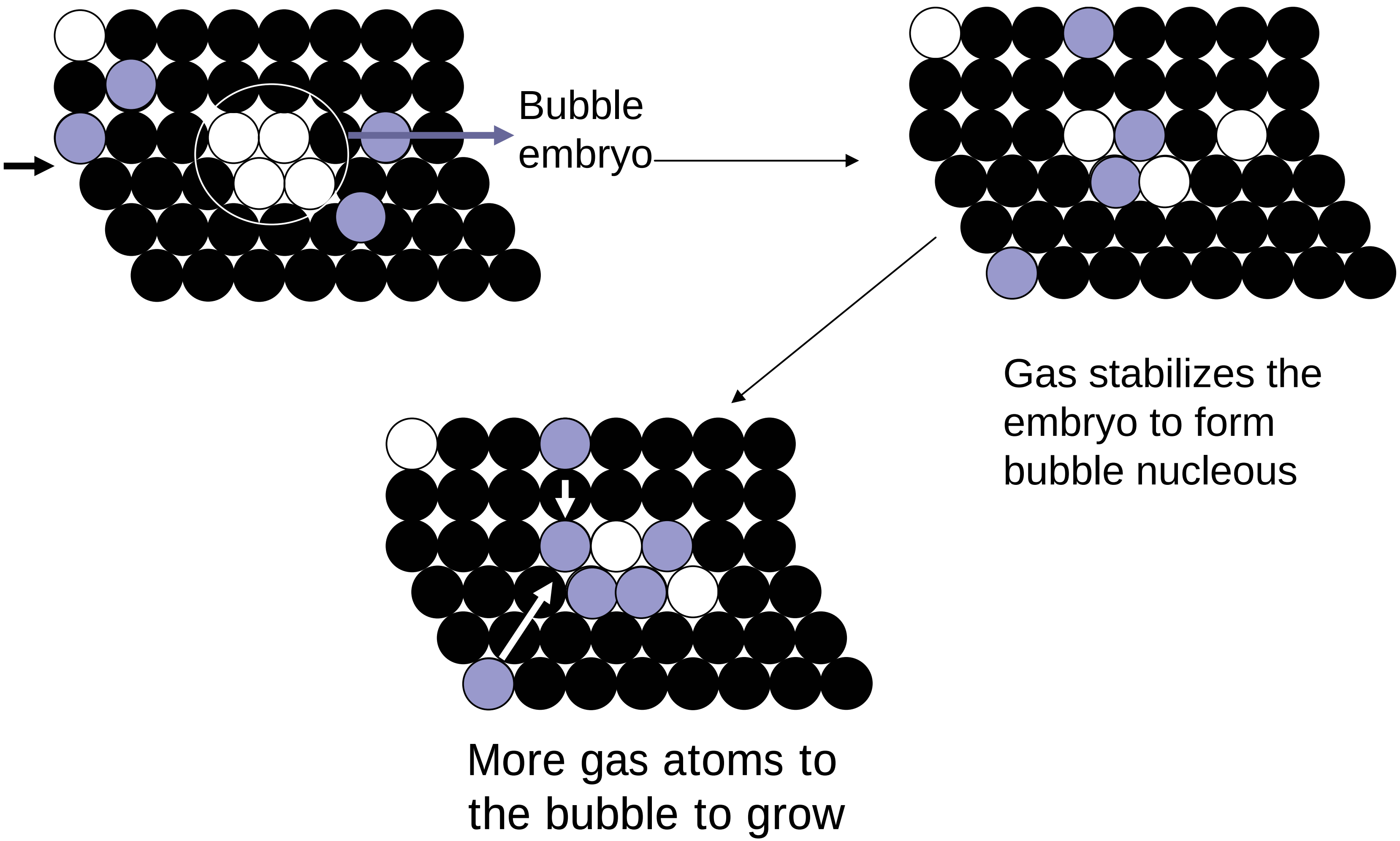
Hydrogen Effects

800°C $\left\{\begin{array}{l}(Si^{3+}/He^{+}=10dpa/1500appm) \\ (Si^{3+}/He^{+}/H^{+}=10dpa/1500/600appm)\end{array}\right.$

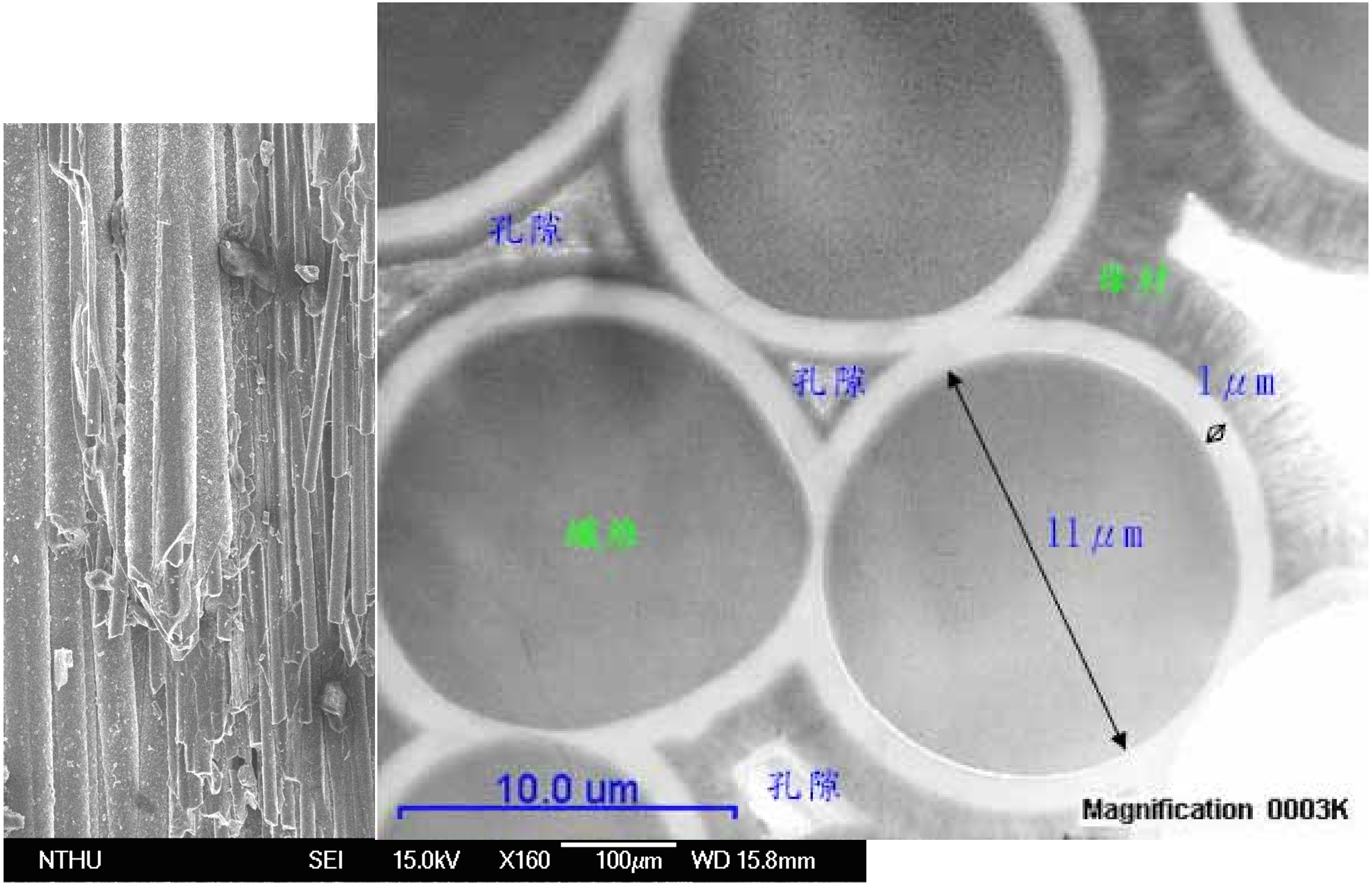
800°C	Si/He= 10dpa/1500 appm		Si/He/H =10dpa/1500 /600appm	
	matrix	fiber	matrix	fiber
bubble size	1.2nm	X	1nm	<1nm
Density (#/m^3)	0.85 x10^{22}	X	1.2 x10^{22}	3 x10^{22}

⇨ Hydrogen plays a role to enhance the bubble nucleation in the Tyranno-SA fiber and also increase the number density in the matrix.

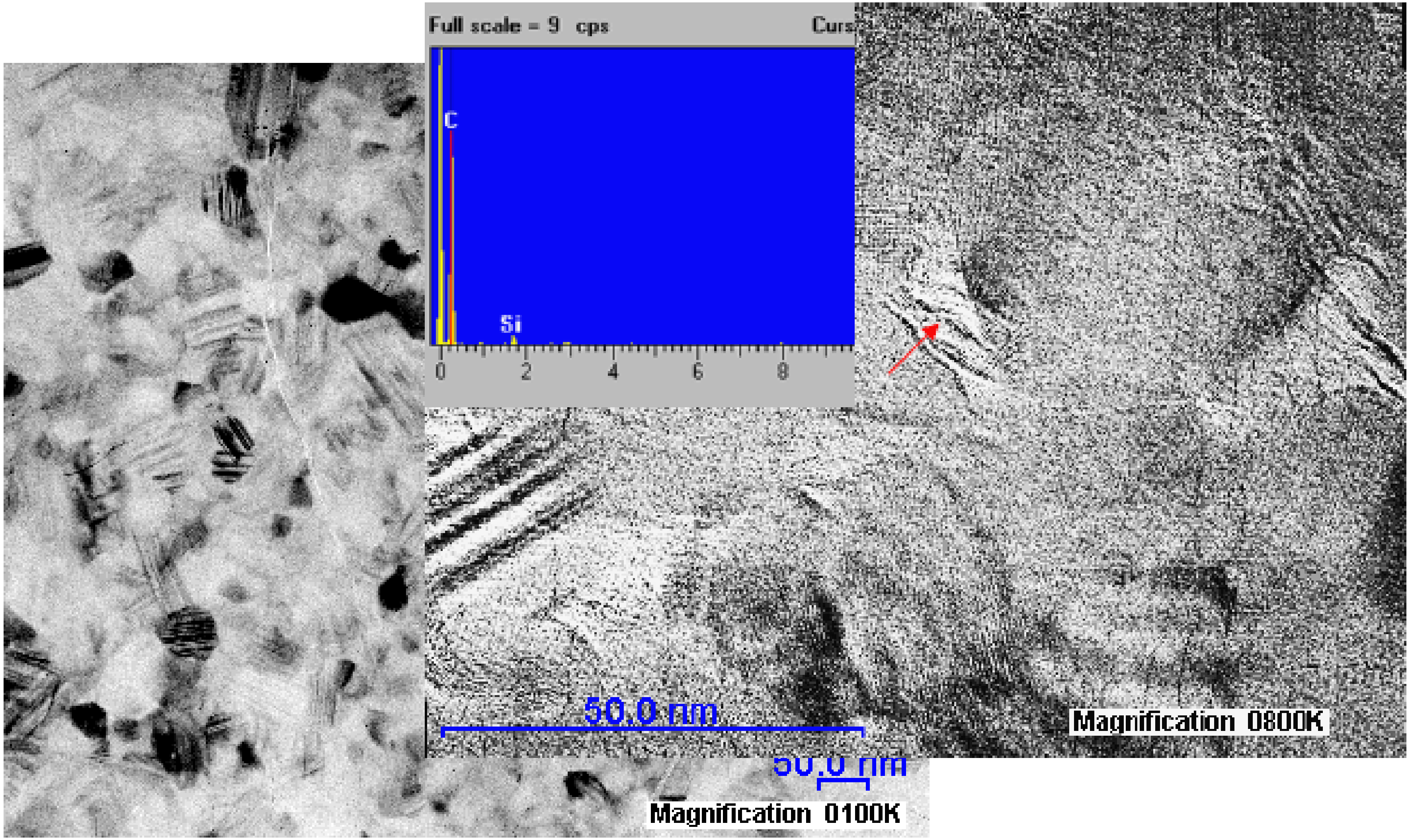
The role of He and H atoms in the bubble nucleation



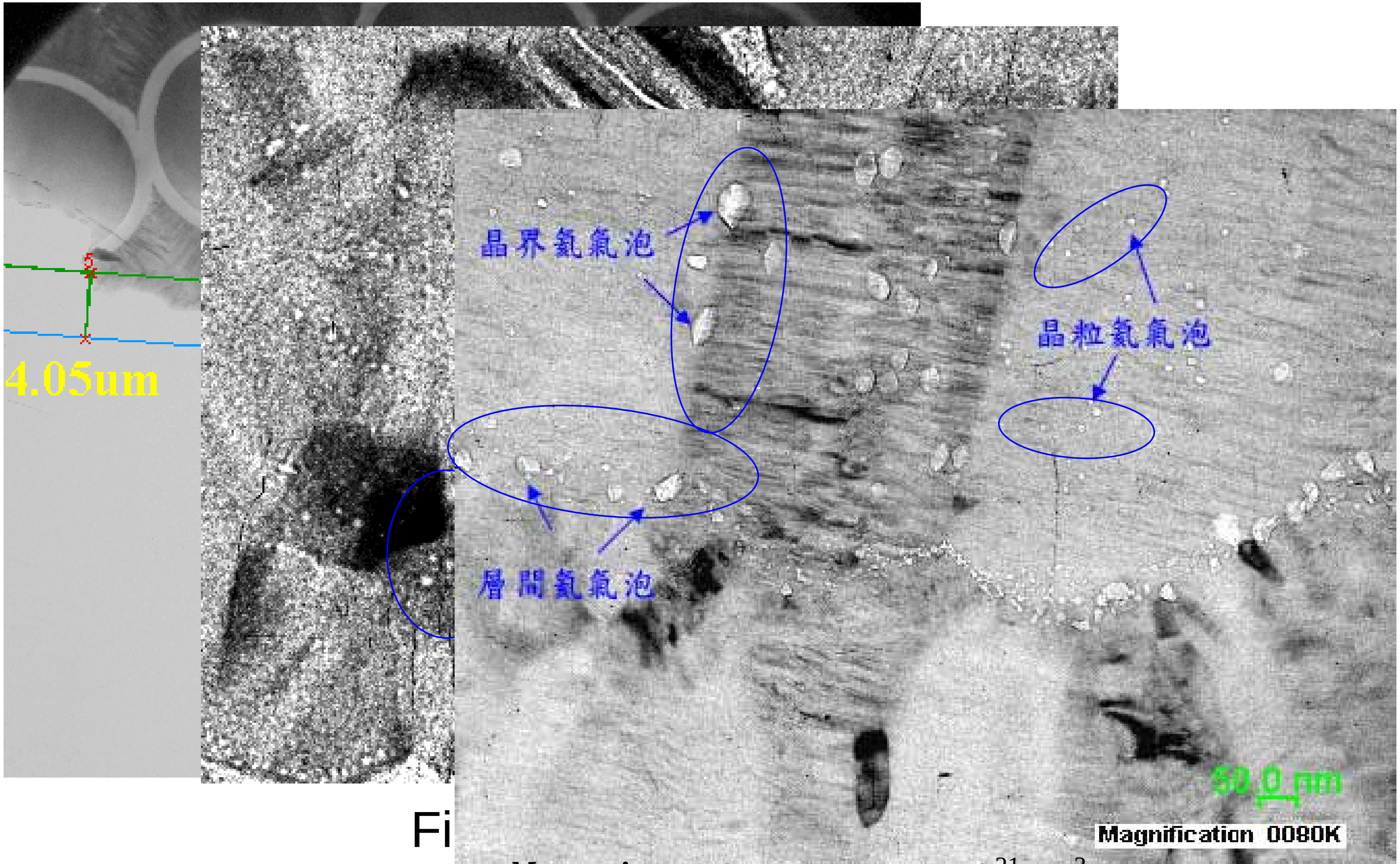
Unirradiated Microstructures of CVI SiC Matrix with Hi-Nicalon Type-S Fibers



Hi-Nicalon Type-S fibers (grain size 10-50 nm)



1000°C He/Si dual-beam irradiation (15000appm/100dpa)



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Matrix:30nm, $5.7\times10^{21}/m^3$

Irradiation Conditions	600˚C He/Si 1500appm/ 10dpa	800˚C He/Si 1500appm/ 10dpa	800˚C He/Si 15000appm /100dpa	1000˚C He/Si 15000appm /100dpa
Hi-Nicalon Type-S SiC Fiber	none	none	none	1.5nm $9.9\times10^{21}/m^3$
CVI SiC Matrix	none	2.5nm $7.6\times10^{21}/m^3$	8.5nm $6.2\times10^{21}/m^3$	30nm $5.7\times10^{21}/m^3$

Comparison among single-, dual- and triple-beam irradiations at 800°C to 10 dpa

Irradiation Conditions	800°C Si,10dpa Hasegawa et al. J.Nucl.Master 329-333(2004)582-586	800°C He/Si 1500appm/ 10dpa	800°C He/H/Si 1500appm/ 600appm/10dpa
Hi-Nicalon Type-S Sic Fiber	none	none	none
CVI SiC Matrix	none	2.5nm $7.6 \times 10^{21}/m^3$	1.8nm $3.1 \times 10^{22}/m^3$

Comparison between Hi-Nicalon Type-S and Tyranno-SA Fibers

800 °C	Si/He 10dpa/1500 appm		Si/He/H 10dpa/1500/600 appm		Si/He 100dpa/15000 appm		H/He 6000/15000 appm	
	HNS	**TSA**	**HNS**	**TSA**	**HNS**	**TSA**	**HNS**	**TSA**
Bubble size	Non	Non	Non	<1nm	Non	5nm	1nm	1nm
Density (number/m^3)	Non	Non	Non	$3*10^{22}$	Non	$4.5*10^{21}$	$9.6*10^{22}$	$5.6*10^{22}$
1000 °C					Si/He 100dpa/15000 appm		H/He 6000/15000 appm	
					HNS	**TSA**	**HNS**	**TSA**
Bubble size					1.5nm	15nm	1.6nm	2nm
Density (number/m^3)					$9.9*10^{21}$	$2.7*10^{21}$	$4.2*10^{22}$	$2.7*10^{22}$

Comparison between two types of fiber

- Hi-Nicalon Type-S fiber has better resistance to bubble formation is probably due to its smaller grain size (10-50 nm) than that of Tyranno-SA fiber (50-100 nm) which in turn diverse the segregation of He atoms to delay the formation of He bubbles.

- However, when it does form He bubbles, due to its higher grain boundary area which induces more nucleation sites that let the Hi-Nicalon Type-S fiber shows higher number density and smaller bubble size.

- Hi-Nicalon Type-S fiber does have a better irradiation stability in terms of bubble formation than that of Tyranno-SA fiber.

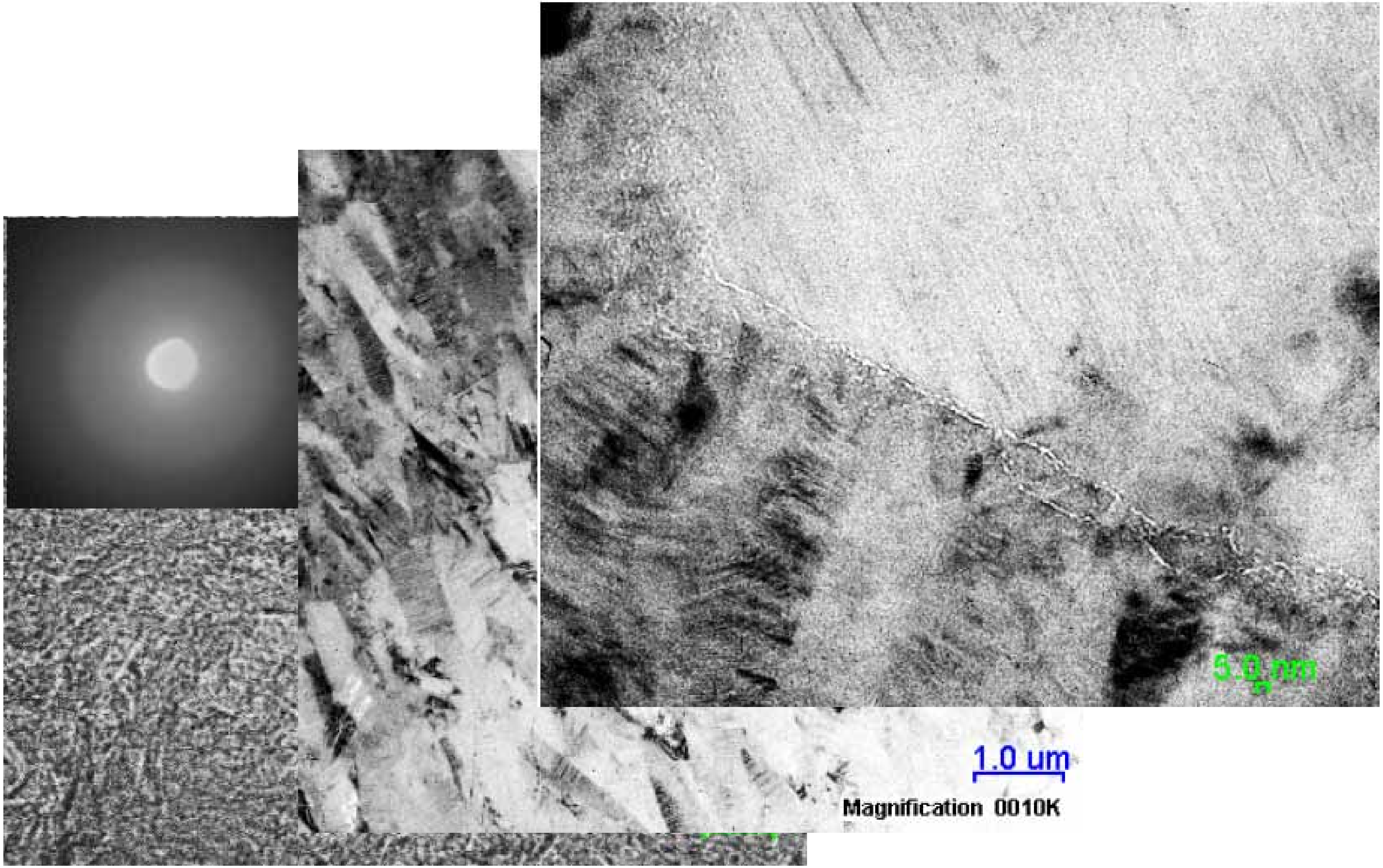
SUMMARY

- Hi-Nicalon Type-S fiber shows a better irradiation stability in terms of bubble formation than that of Tyranno-SA fiber. The main reason for this is due to the smaller grain size.
- Hydrogen plays some role in bubble nucleation which increases the number density of bubble formed both in the matrix and in the fibers.
- We will perform more triple-beam irradiation experiments to higher temperature and higher dose levels to further study the mechanism of bubble formation.
- We will also focus on the other microstructural evolution during irradiation (such as: dislocation loops, stacking fault tetrahedron, ..etc) in **Hi-Nicalon Type-S fiber SiC/SiC composites**.

Acknowledgement

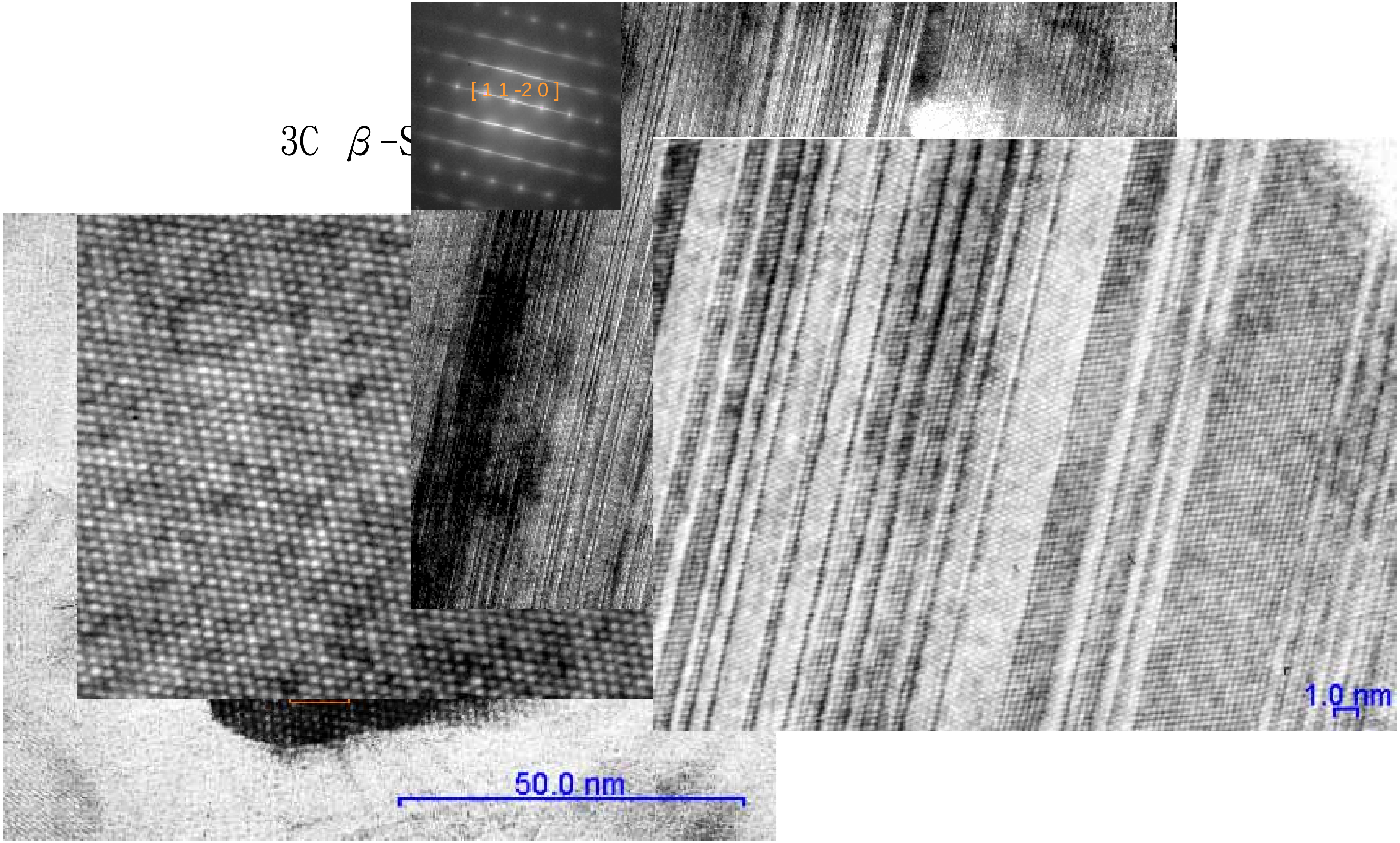
- This work is financially supported by the National Science Council of TAIWAN, R.O.C.
- The SiC/SiC composite material is offered by Dr. Y. Katoh (ORNL, USA) and Prof. Kohyama (Kyoto Univ., JAPAN).
- Ion-irradiation was performed in the Accelerator Group of the Nuclear Science and Technology Development Center in the National Tsing Hua University.

Amorphous carbon interlayer and SiC matrix

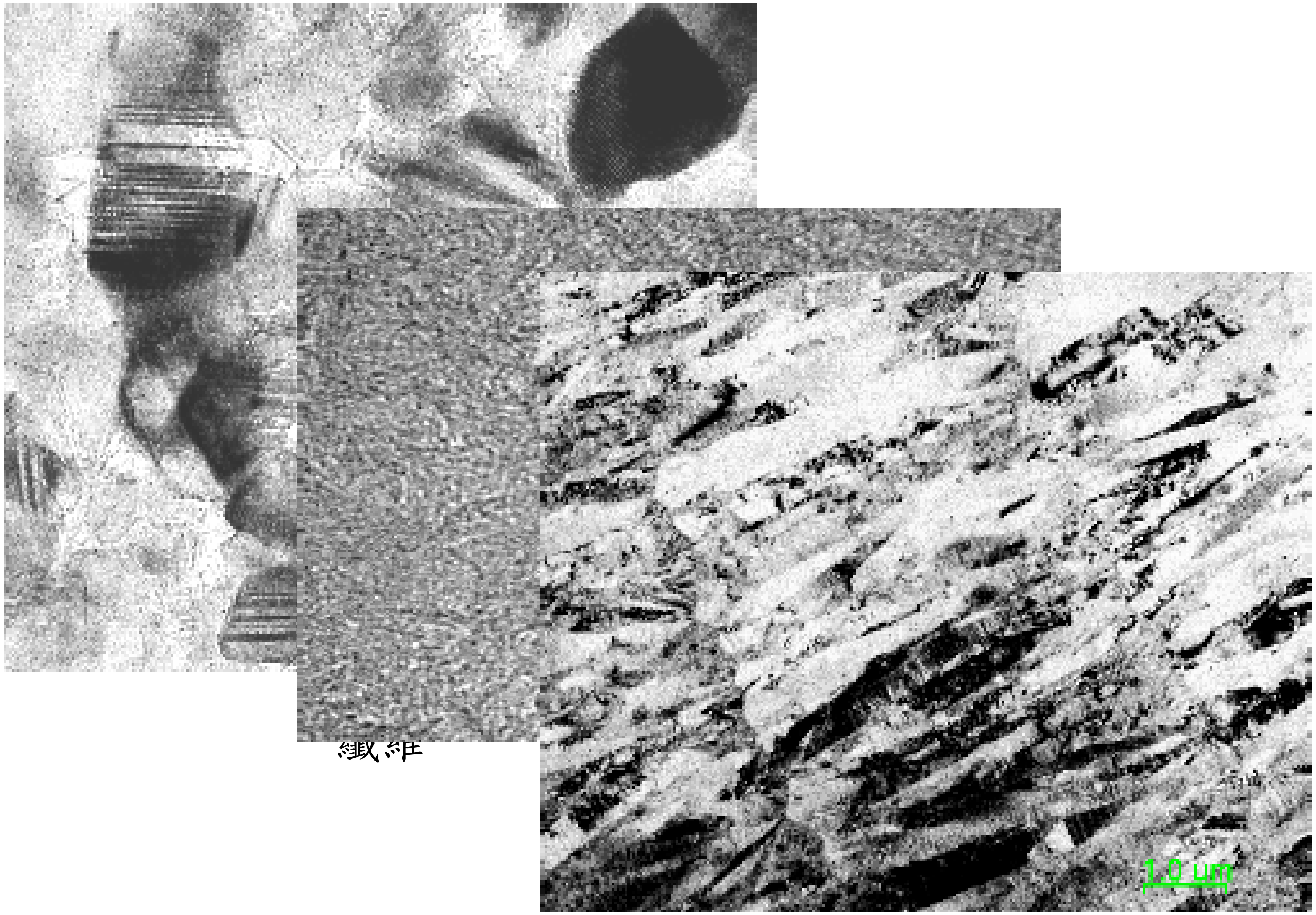


3C、2H、4H、6Hintermixing microstructures

3C β-S



Annealed at 1000°C for 67 hours



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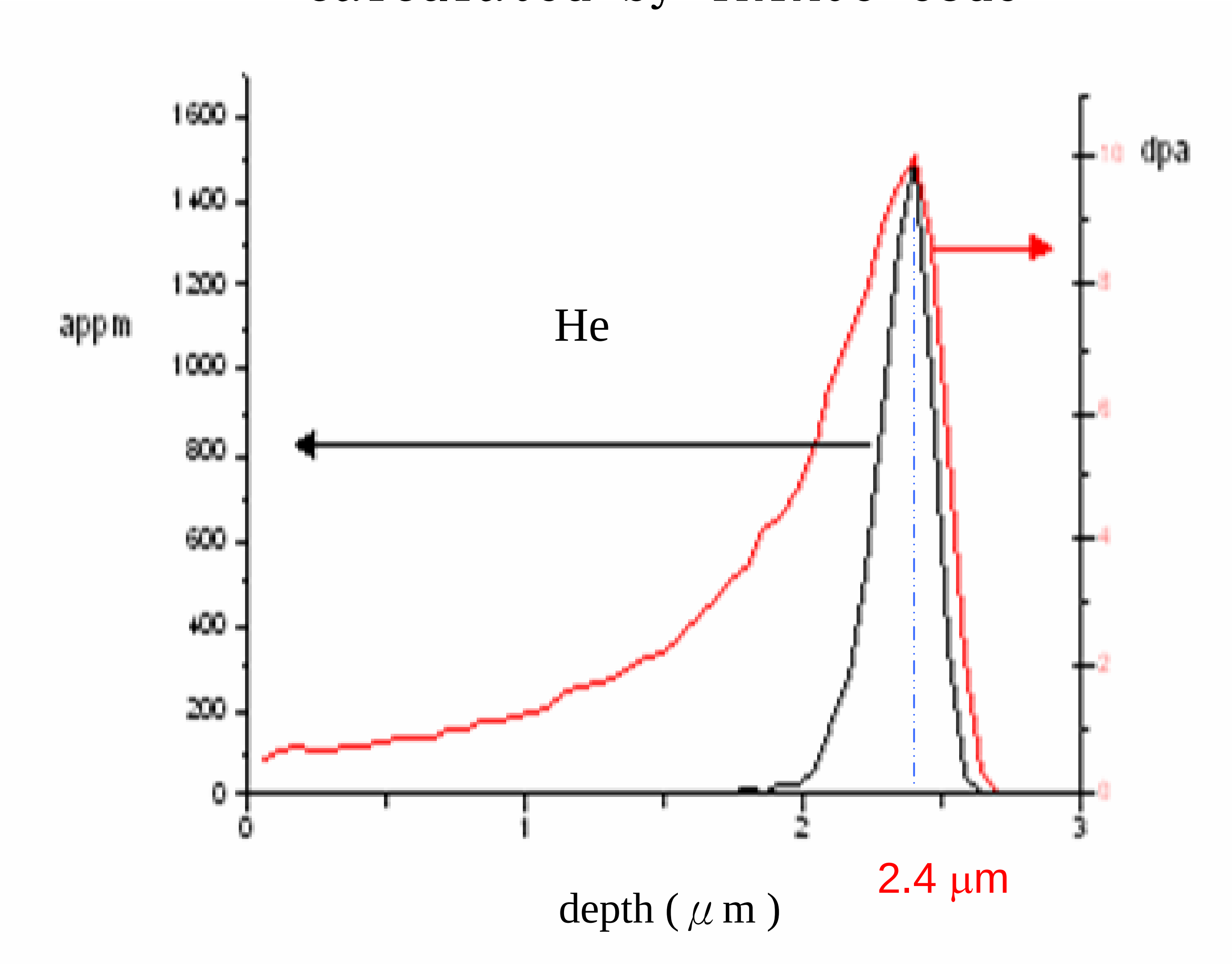
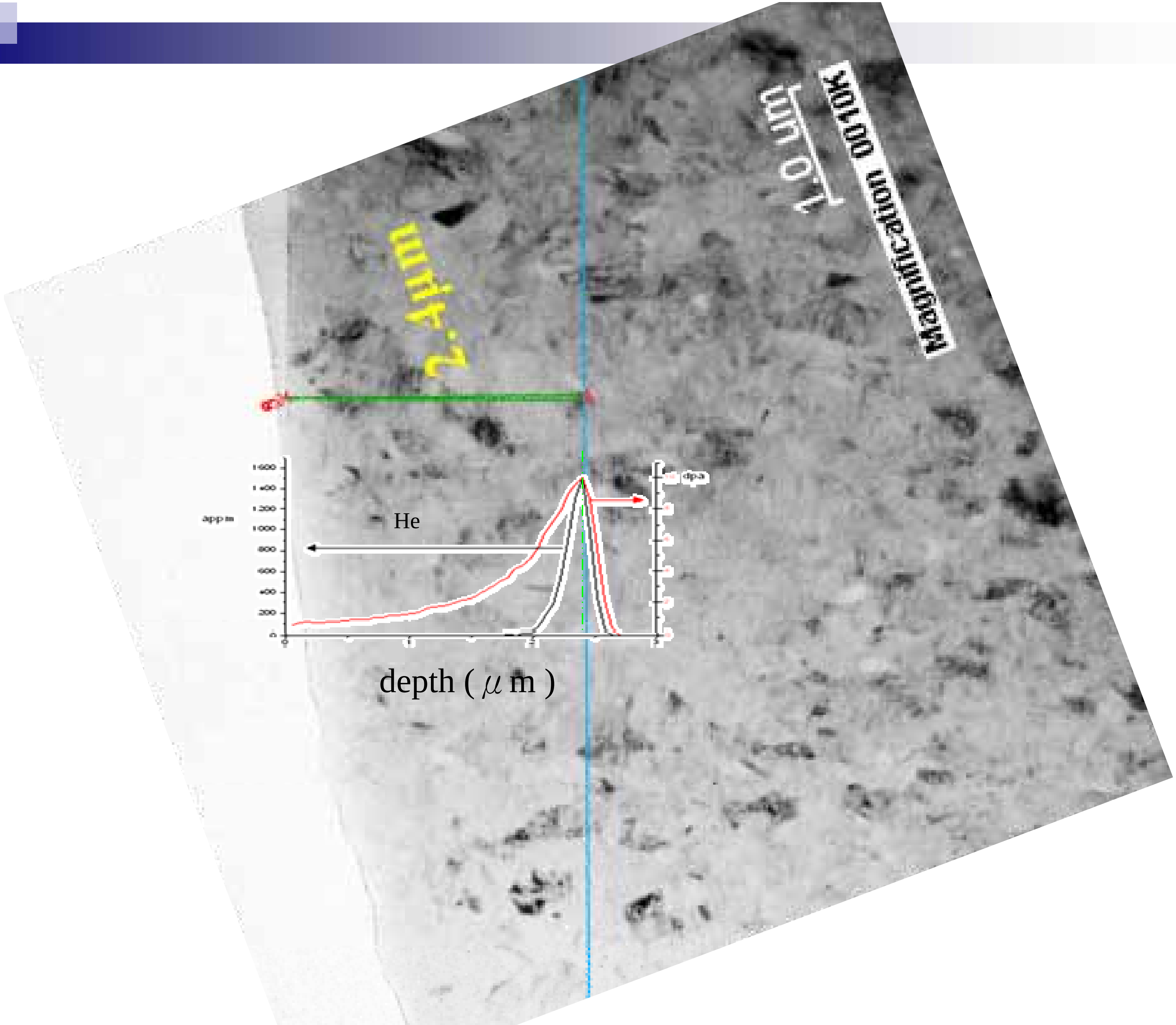
母材

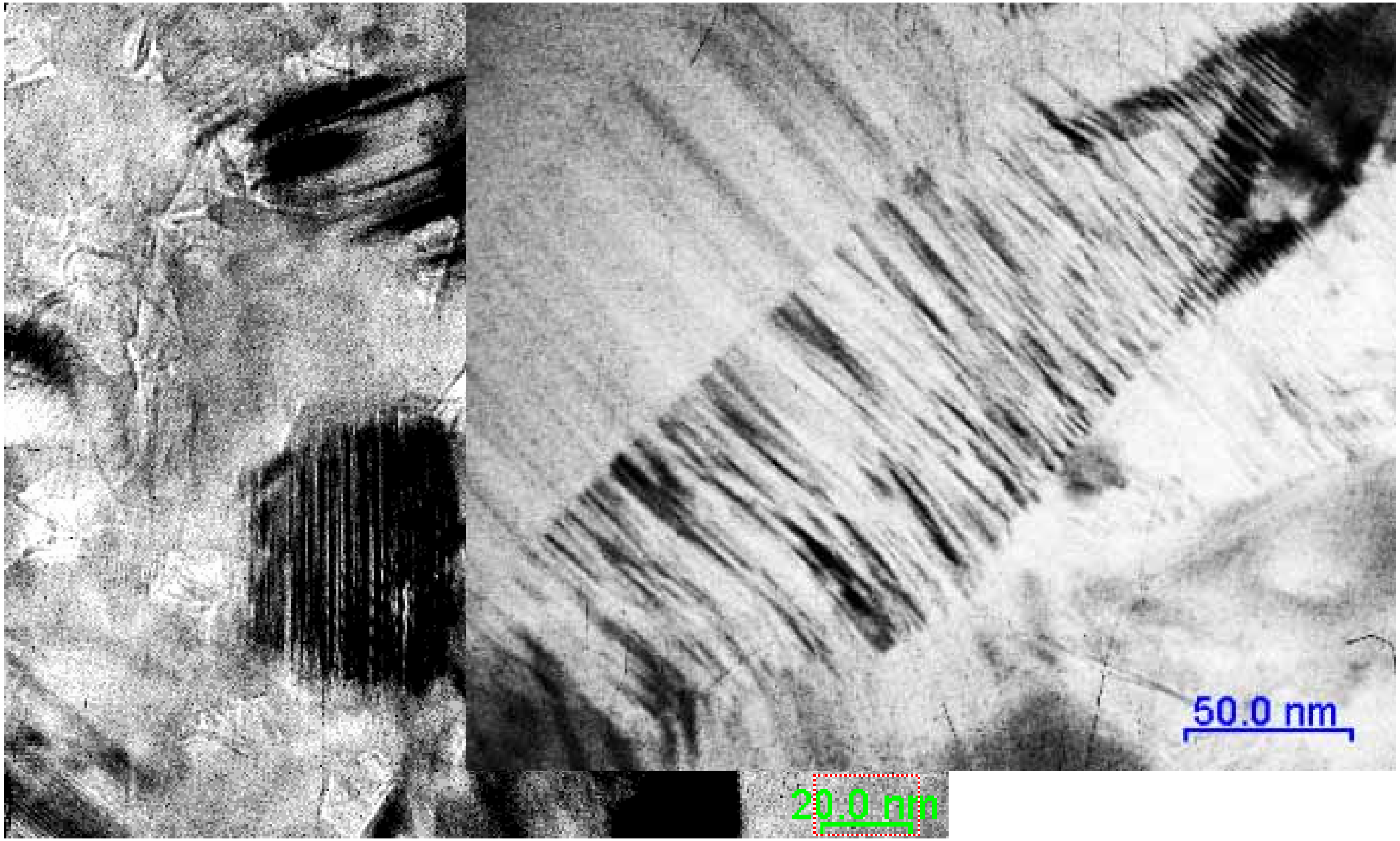
Si-He Dual-beam irradiation calculated by TRIM98 Code



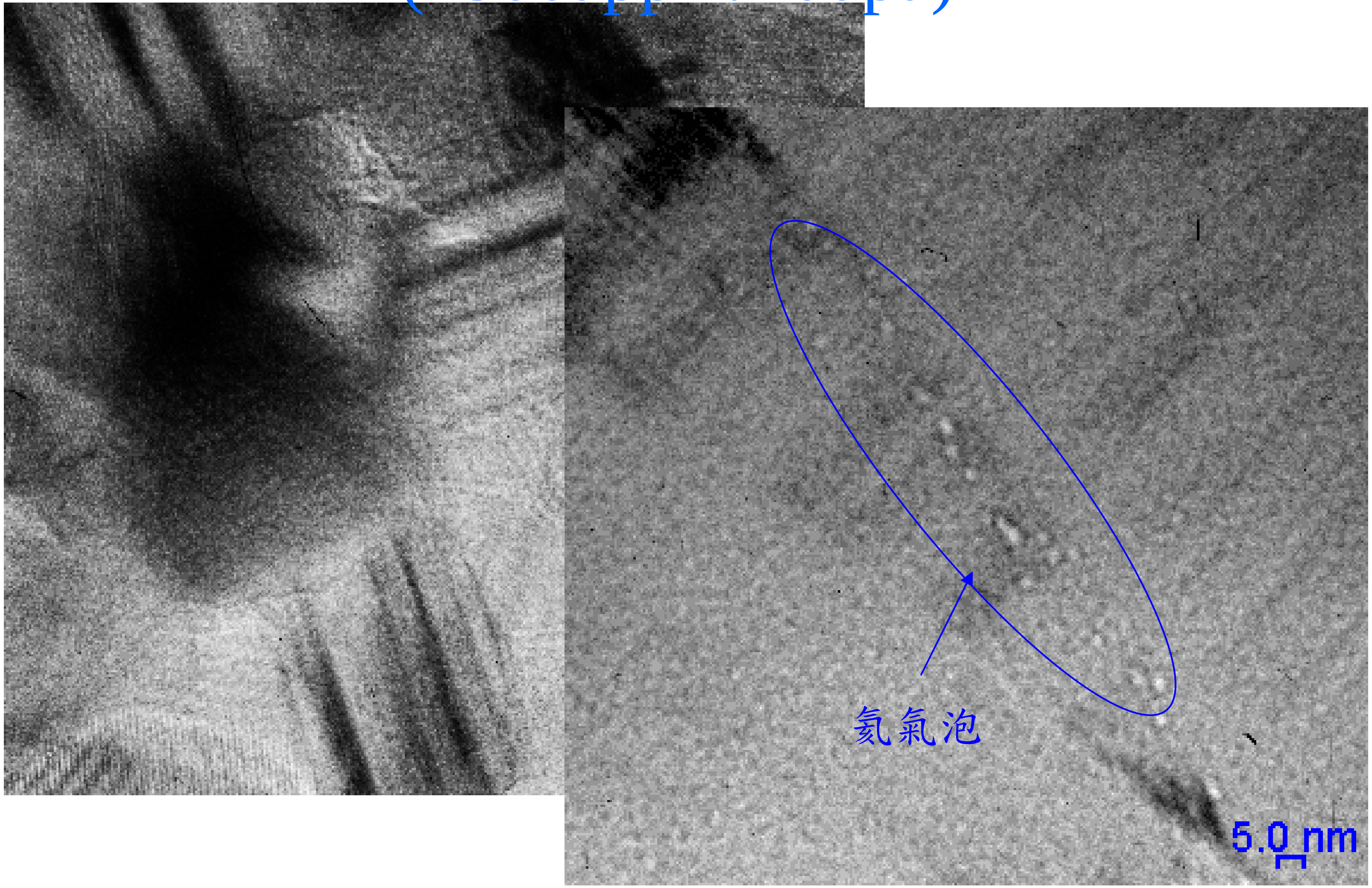

appm
1600
1400
1200
1000
800
600
400
200
0
He
dpa
depth (μm)

600°C He/Si dual-beam irradiation

(1500appm/10dpa)

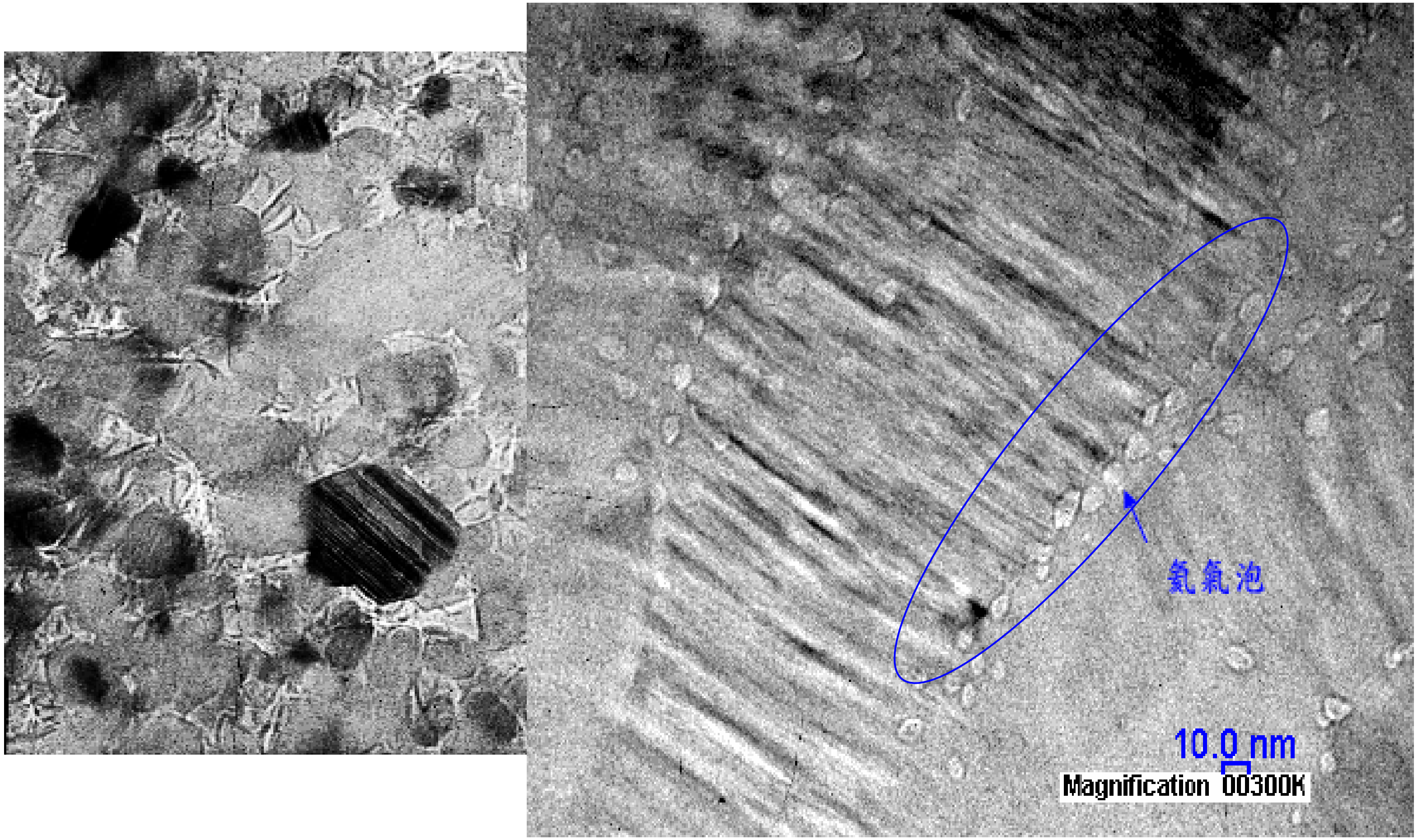


800°C He/Si dual-beam irradiation (1500appm/10dpa)



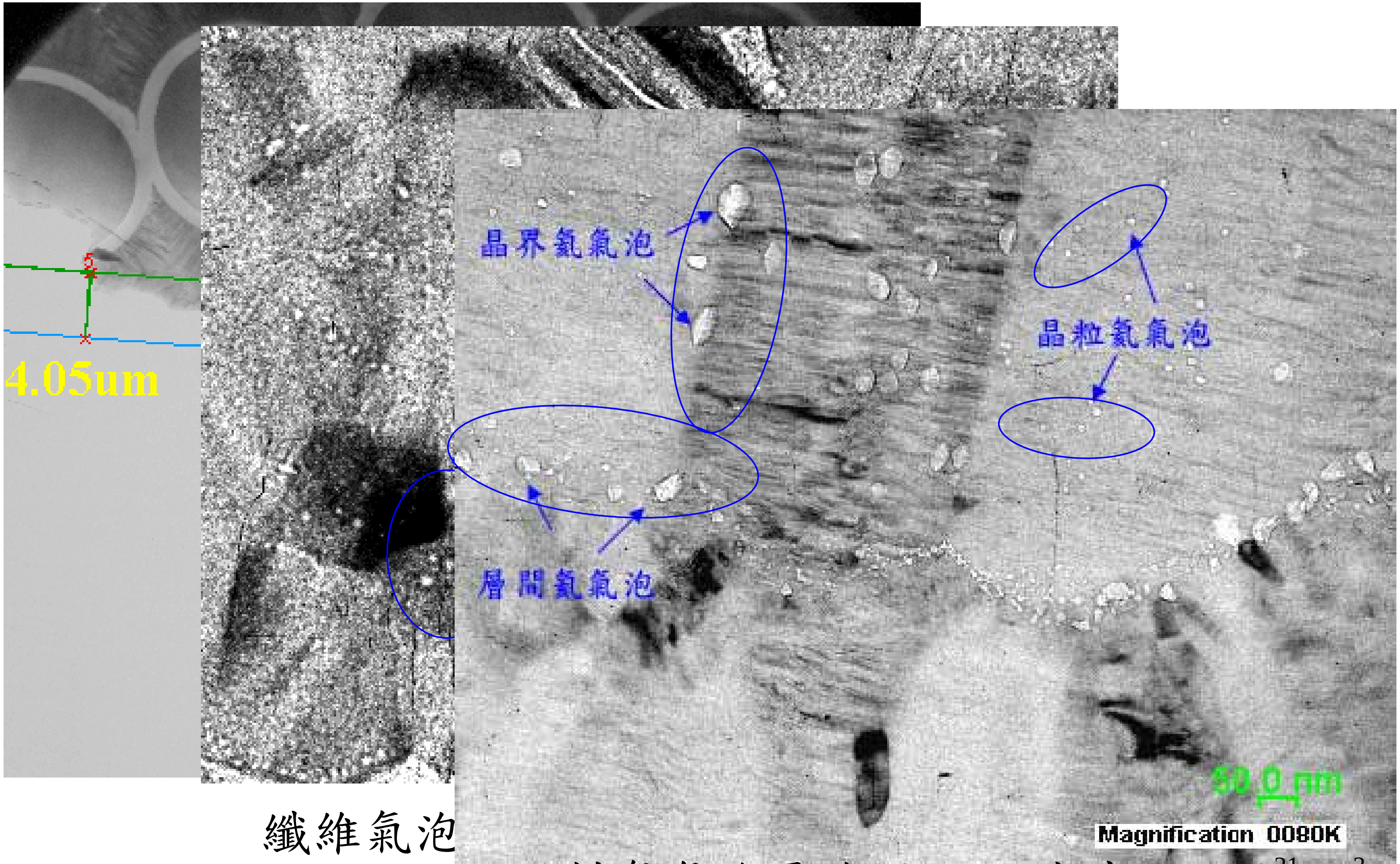
母材氦氣泡平均2.5nm；密度$7.6\times10^{21}/m^3$

800°C He/Si dual-beam irradiation (15000appm/100dpa)



母材氦氣泡平均8.5nm；密度$6.2.\times10^{21}/m^3$

1000°C He/Si dual-beam irradiation (15000appm/100dpa)



纖維氣泡

母材氦氣泡平均30nm；密度$5.7\times10^{21}/m^3$

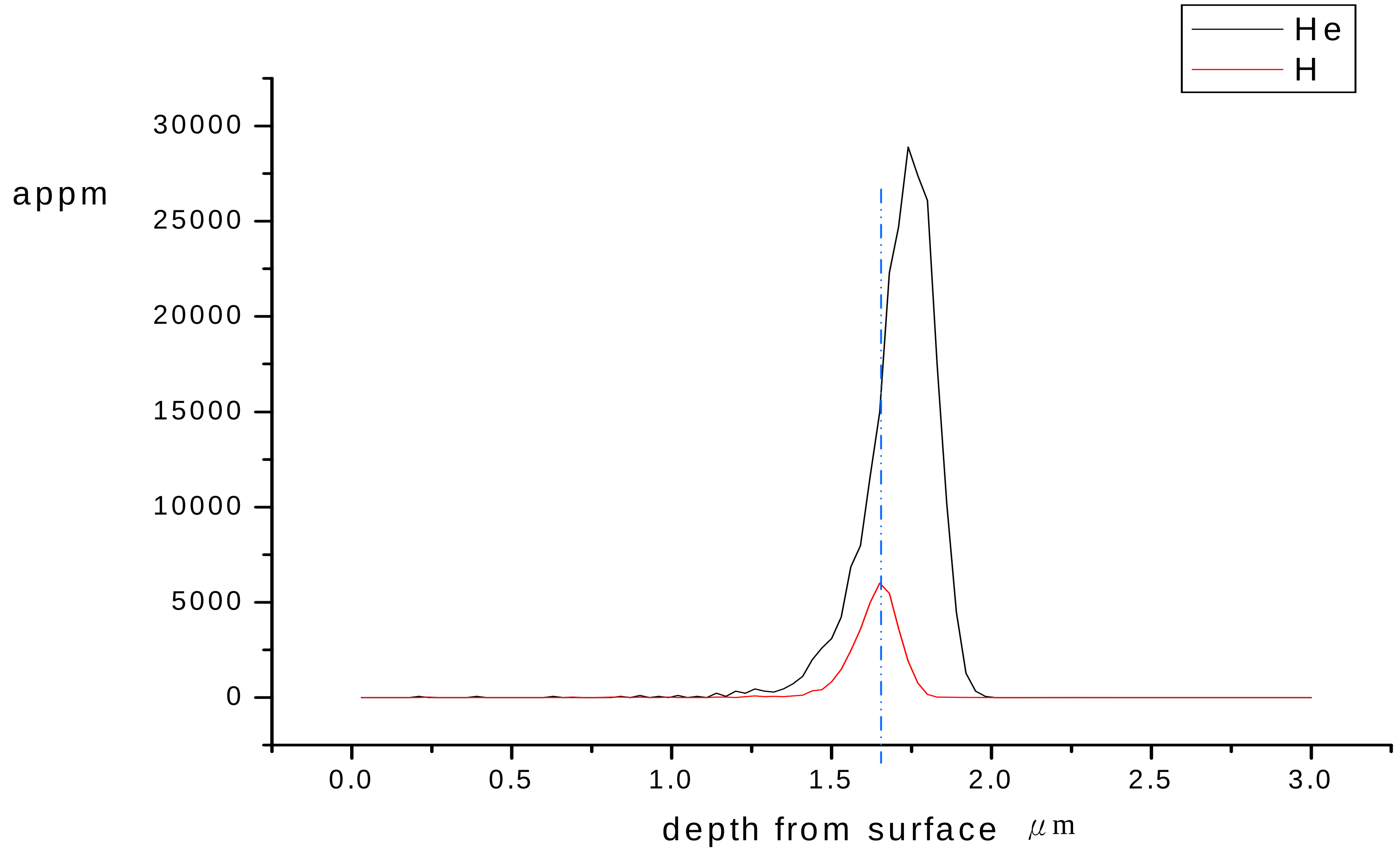
Irradiation Conditions	600°C He/Si 1500appm/ 10dpa	800°C He/Si 1500appm/ 10dpa	800°C He/Si 15000appm /100dpa	1000°C He/Si 15000appm /100dpa
Hi-Nicalon Type-S SiC Fiber	none	none	none	1.5nm $9.9 \times 10^{21}/m^3$
CVI SiC Matrix	none	2.5nm $7.6 \times 10^{21}/m^3$	8.5nm $6.2 \times 10^{21}/m^3$	30nm $5.7 \times 10^{21}/m^3$

- P. Jung has proved that the diffusivity of He atoms in amorphous carbon is 30 times faster than in SiC so that the thicker carbon interlayer offers a fast diffusion channel for He atoms to diffuse out.
  P. Jung, J. Nucl. Mater. 191–194 (1992) 377.

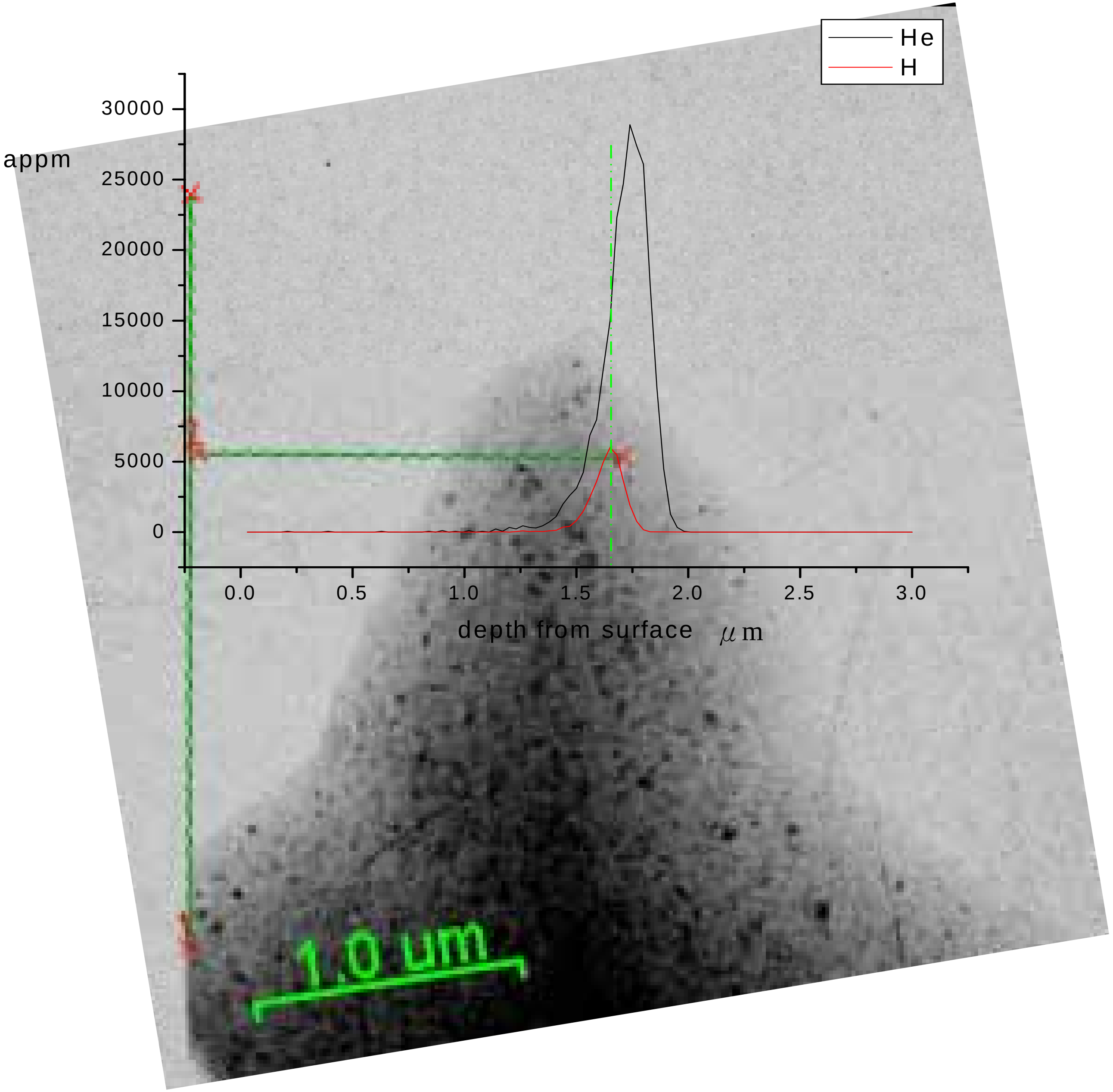
- Smaller grain size gives much higher grain boundary area which in turn diverse the segregation of He atoms to delay the formation of He bubbles.

- Higher dose and higher temperature irradiation enhances bubble coarsening which increases the bubble size but reduces the number density.

He/H Dual-beam Irradiation calculated by SRIM

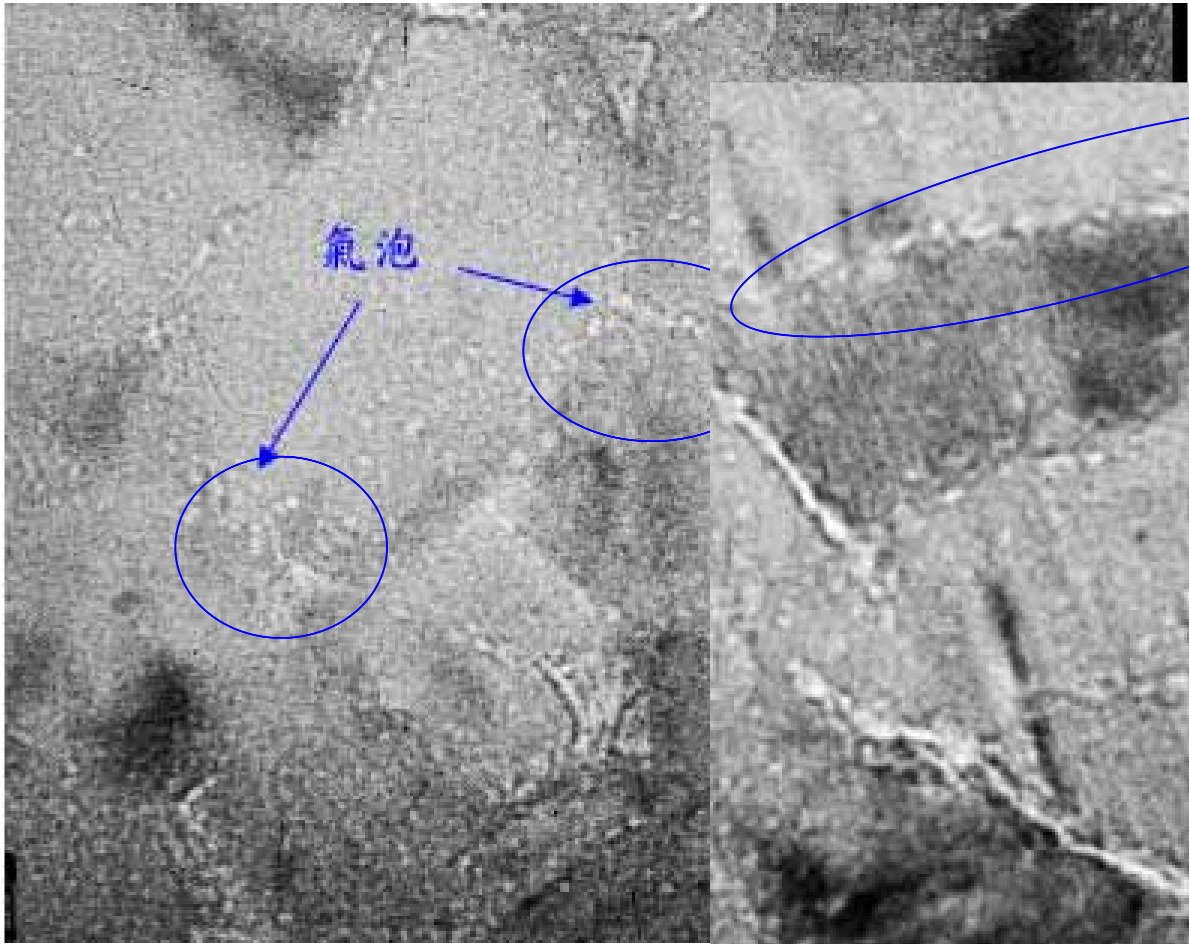


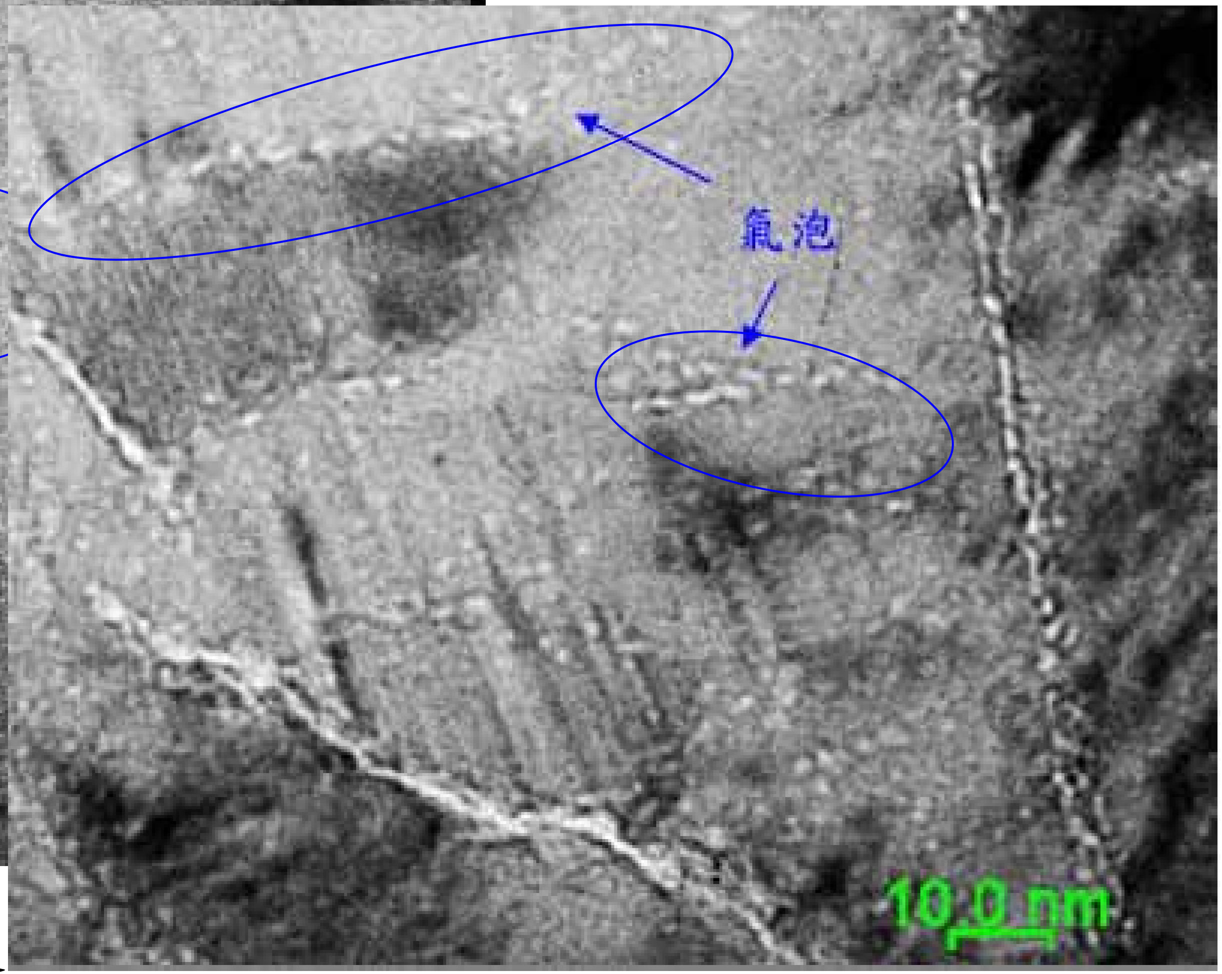
At 1.56 μm depth the He/H ration is15000/6000 appm



He
H
30000
25000
20000
15000
10000
5000
0
appm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
depth from surface μm
1.0 um

800°C He/H dual-beam irradiation 15000/6000appm

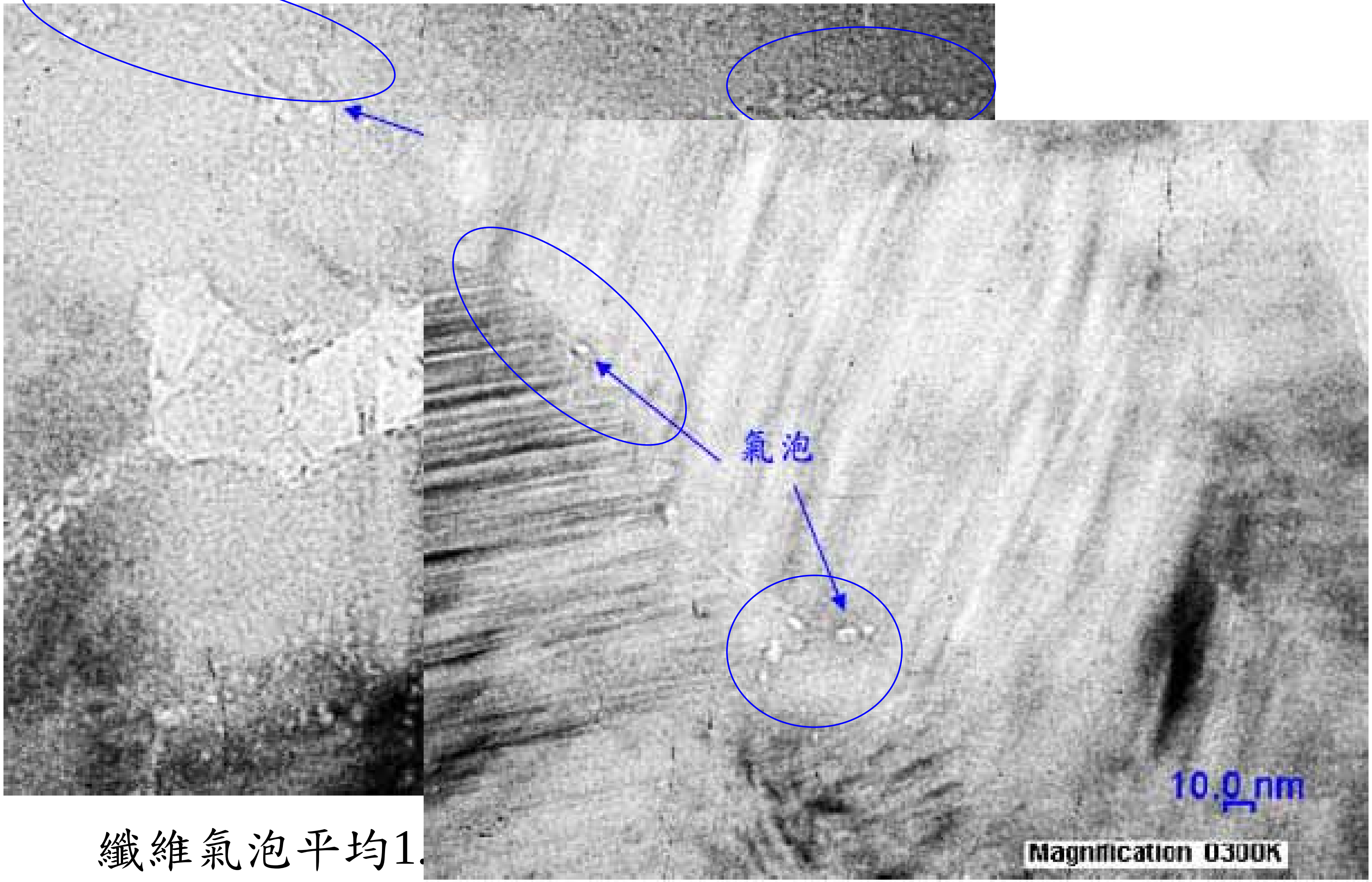




纖維氣泡平均1nm；密度

母材氣泡平均2nm；密度$6.8 \times 10^{22}/m^3$

1000°C He/H dual-beam irradiation15000/6000appm



纖維氣泡平均1.

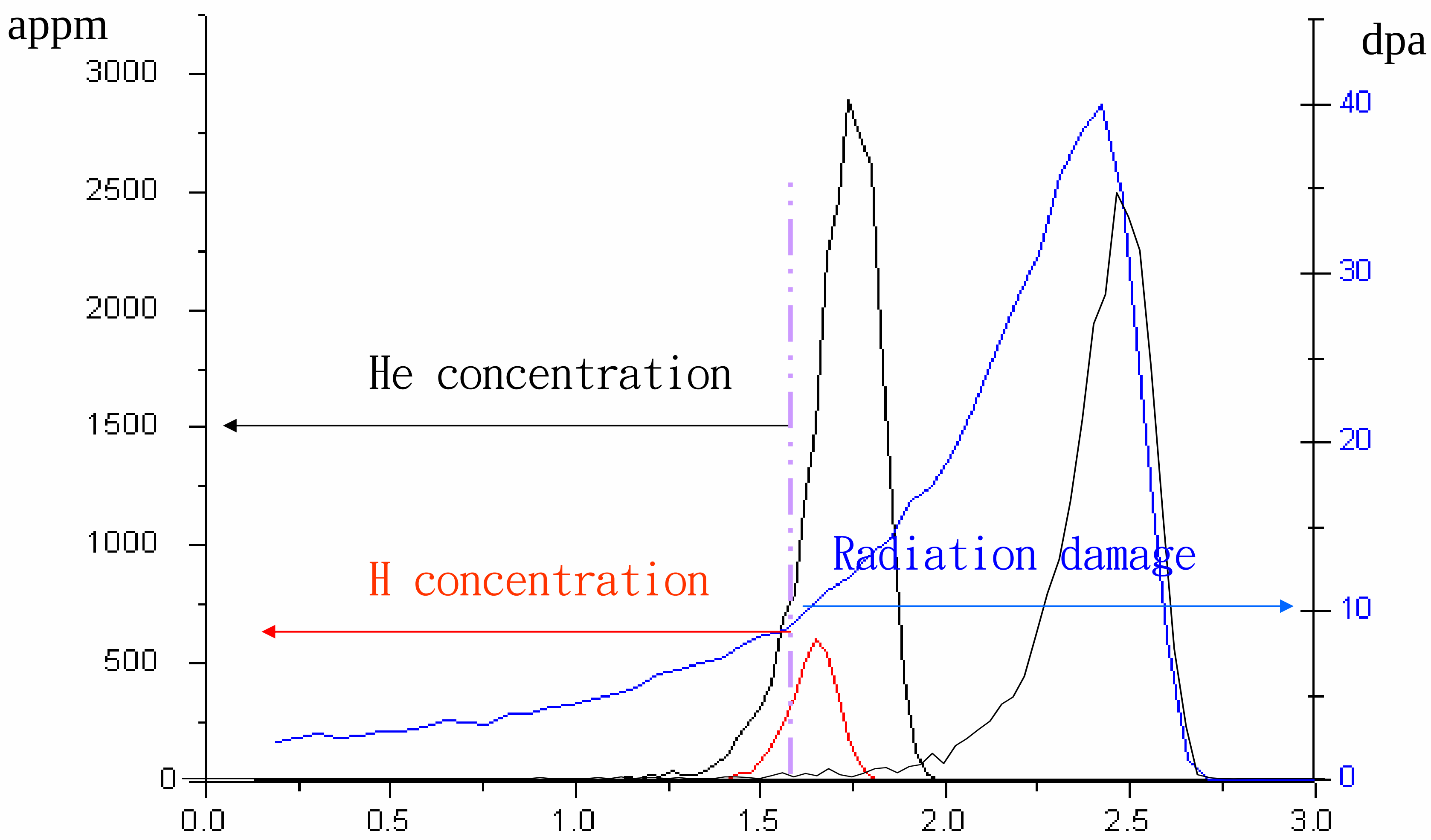
母材氣泡平均7nm；密度$1.8\times10^{21}/m^3$

Irradiation Conditions	800°C He/H 15000appm/ 6000appm	1000°C He/H 15000appm/ 6000appm
Hi-Nicalon Type-S Sic Fiber	1nm $9.6\times10^{22}/m^3$	1.6nm $2.4\times10^{22}/m^3$
CVI SiC Matrix	2nm $6.8\times10^{22}/m^3$	7nm $1.8\times10^{21}/m^3$

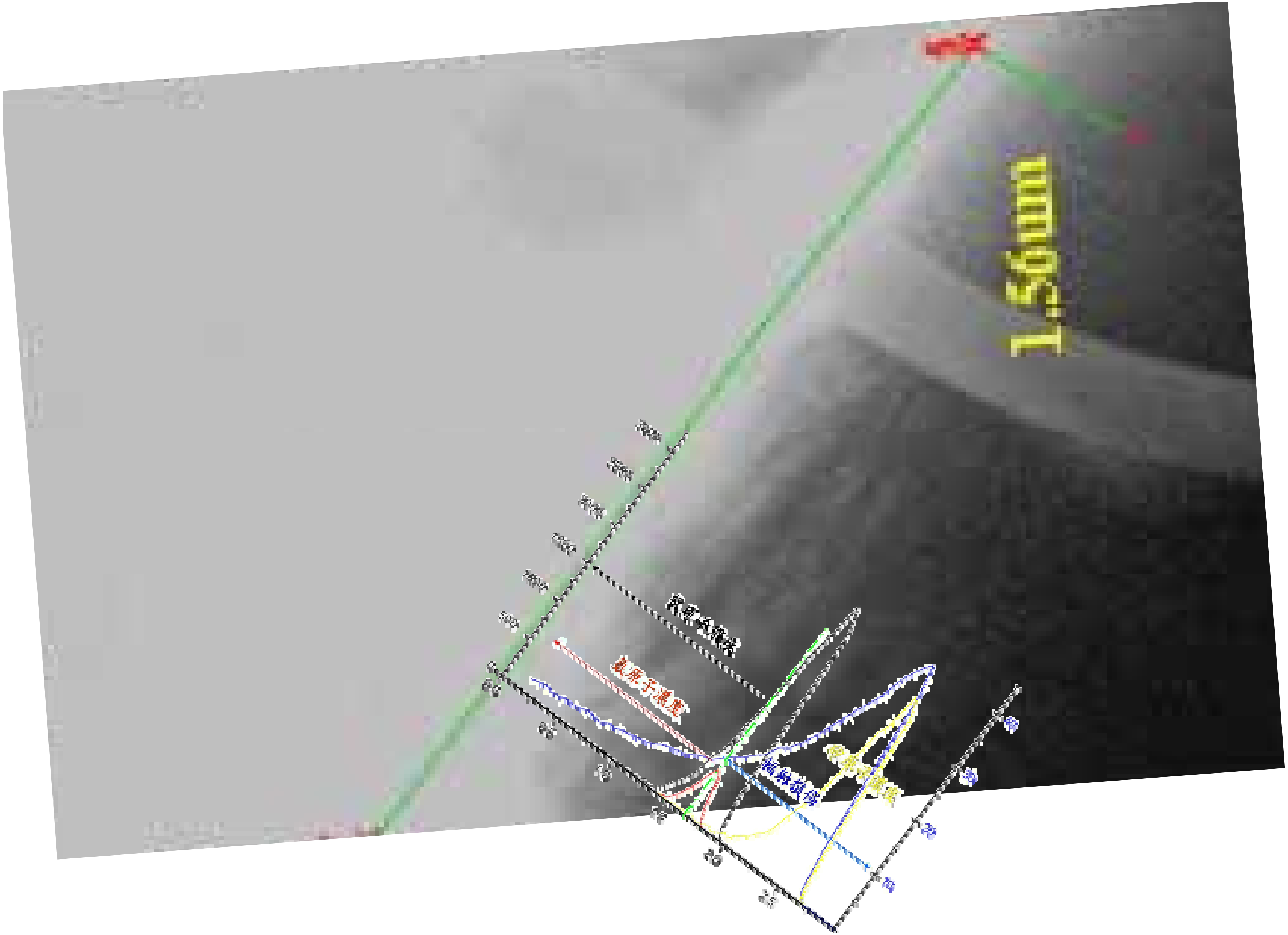
- 在800^{0}C以上氦氫原子、過飽和空孔、氦−空孔、氫−空孔，皆能擴散移動到晶界聚集成氣泡，但因為氫氦會個自穩定化空孔的關係，使氣泡成核點變多，所以800°C實驗的中，氣泡小又多可由此解釋

- 1000°C氦氫原子與過飽和空孔在晶界聚集更多，加上更高溫的擴散，因此非常容易被群聚成大氣泡而造成氣泡體積變大數目變少

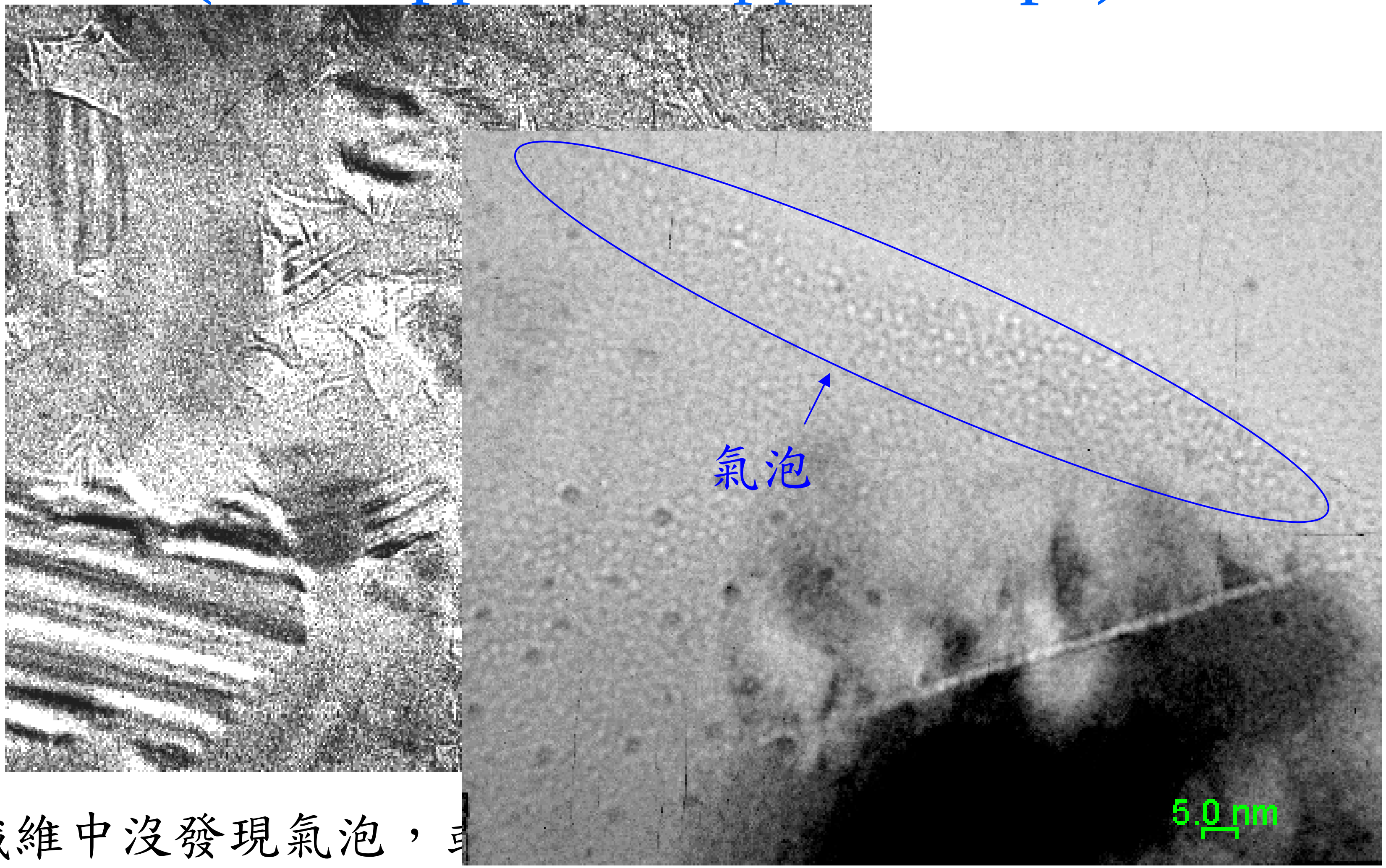
Si/He/H Triple beam irradiation
Calculated by SRIM Code



At 1.56 μm depth we get 10dpa/1500appm/600appm


1.56um

800°C He/H/Si triple-beam irradiation (1500appm/600appm/10dpa)



纖維中沒發現氣泡，

母材氣泡平均1.8nm；密度$3.1\times10^{22}/m^3$

Comparison among single-, dual- and triple-beam irradiations at 800°C to 10 dpa

Irradiation Conditions	800°C Si,10dpa Hasegawa et al. J.Nucl.Master 329-333(2004)582-586	800°C He/Si 1500appm/ 10dpa	800°C He/H/Si 1500appm/ 600appm/10dpa
Hi-Nicalon Type-S Sic Fiber	none	none	none
CVI SiC Matrix	none	2.5nm $7.6 \times 10^{21}/m^3$	1.8nm $3.1 \times 10^{22}/m^3$

氦氫矽三射束比較

- 比較本實驗中三射束和雙射束，發現三射束的氣泡密度多，但體積稍微變小，應該是氫氦分散掉過飽和空孔以至於氣泡成核數目多體積變小之緣故

- 比較Hasegawa等人同樣條件的雙射束以及三射束比較(J.Nucl.Master329-333(2004)582-586)，卻發現氣泡密度差不多，但三射束氣泡較大，其推測是氫貢獻進氣泡裡面增加體積，並不是分散成核點

→ 但是本實驗結果和T.Taguchi 等人(Journal of Nuclear Materials 335 (2004)508－514)，大致符合