SAND2019-7233C

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Odd artifacts induced by Ga and Xe ion exposures

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U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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SAND2018-7819 C

Microstructural alteration due to ion irradiation

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Effects of Irradiation:

Grain growth

Crystallographic orientation changes

Phase formation due to chemical effects

Ferrite formation from unstable austenite

Many others

Previous work

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Preferred orientation development during ion assisted deposition of thin films
(previous work considered Ar ion bombardment during deposition of metal films)

Films oriented in channeling directions
< 110 >FCC or <111> BCC

Some work studied ion bombardment with low energy Ar after deposition

Noted preferred orientation development

Ga+ bombardment of Cu caused Cu_3Ga to form

Ga+ bombardment of Cu, Ni and Au reported to cause recrystallization of fine grained films.

Recrystallization was reported to be reversible.

The Problem – dark regions appear with Ga+ exposure

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Similar behavior noted in Cu, Ni, Au (and other FCC metals)

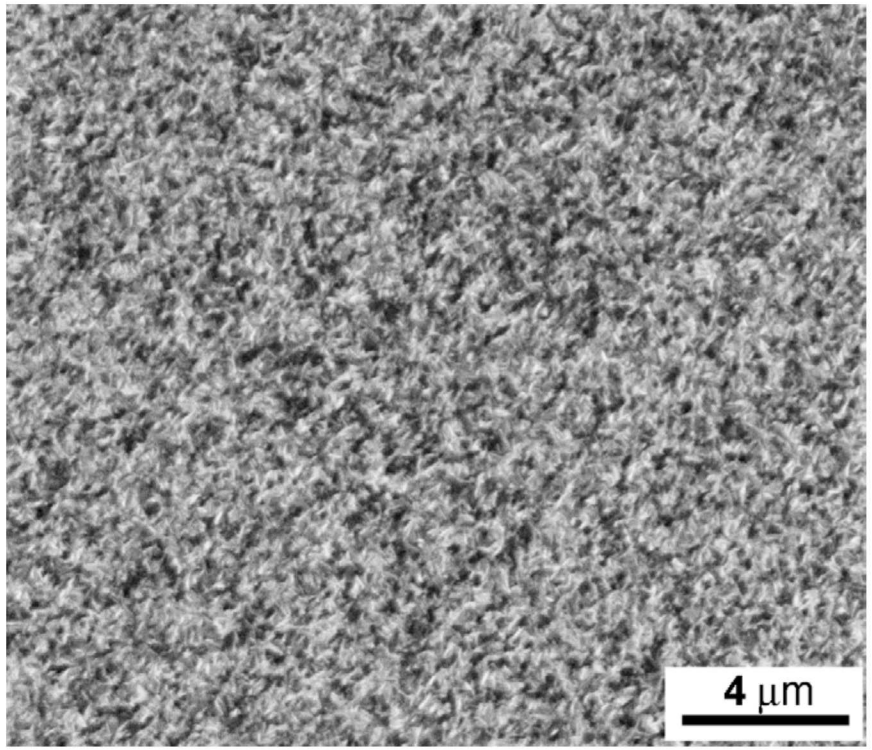
Similar behavior noted in W and Ta (and other BCC metals)

All show the development of dark imaging regions

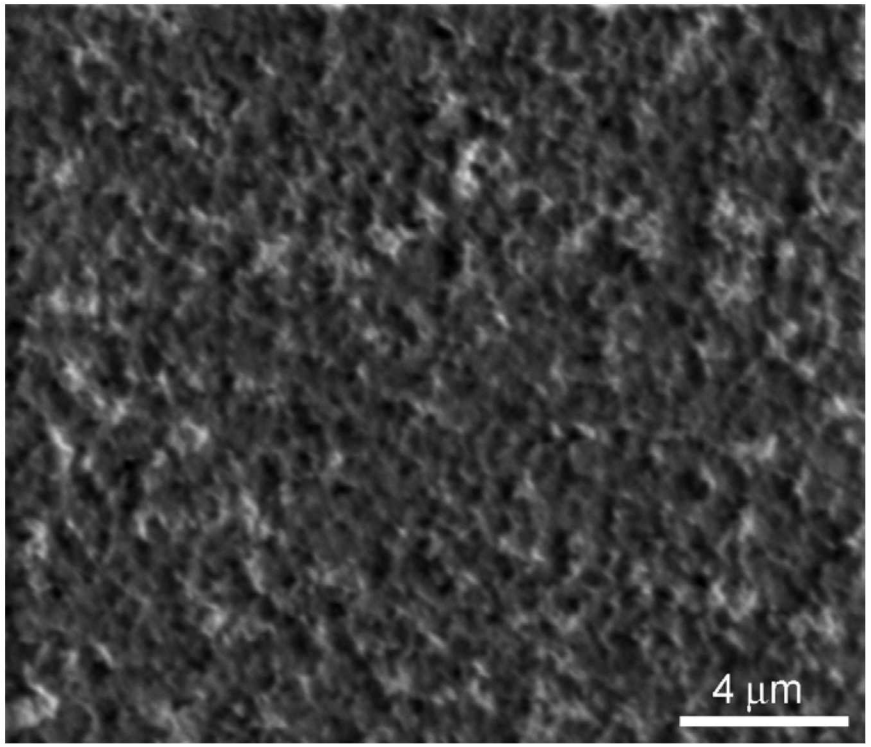
Growth of dark imaging regions occurs more slowly in coarse grained materials

Is this recrystallization, texture development or Ga intermetallic formation in the ion beam exposed regions?

The Problem – dark imaging areas appear with Ga+ exposure



1 frame at 1 nA



20 frames at 1 nA

Evaporated W sample irradiated with 30 kV Ga+

The Problem – dark imaging areas appear with Ga+ exposure

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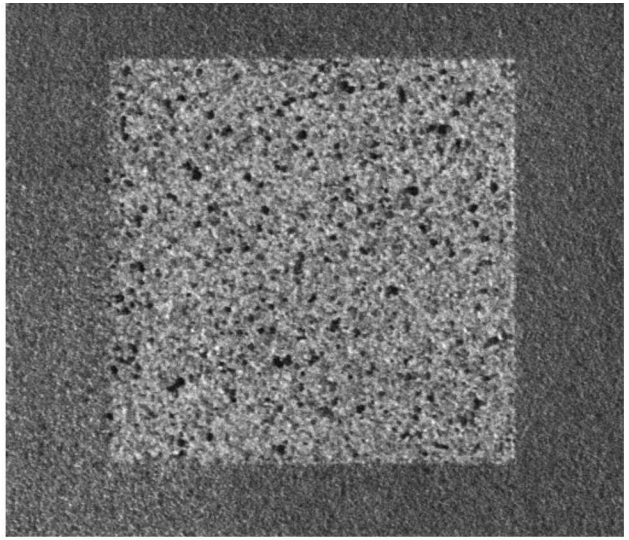
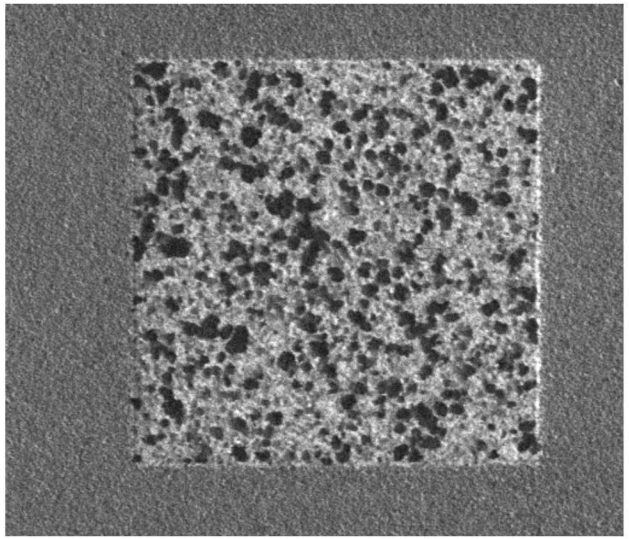
1 min

1.1 x 10^{16} $Ga^{+}/\mu m^2$



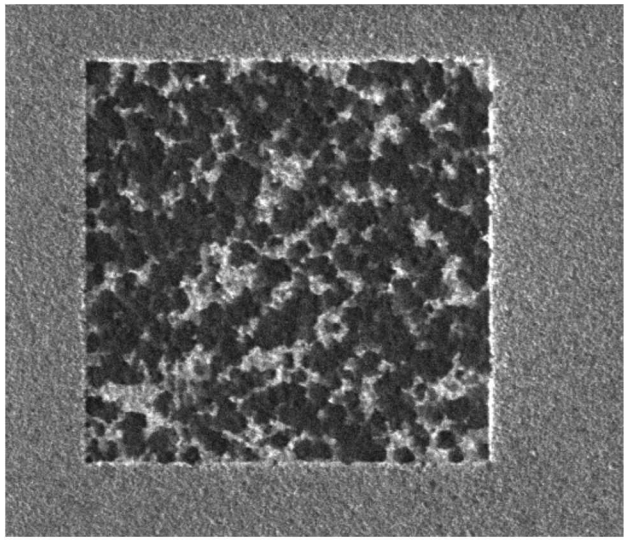


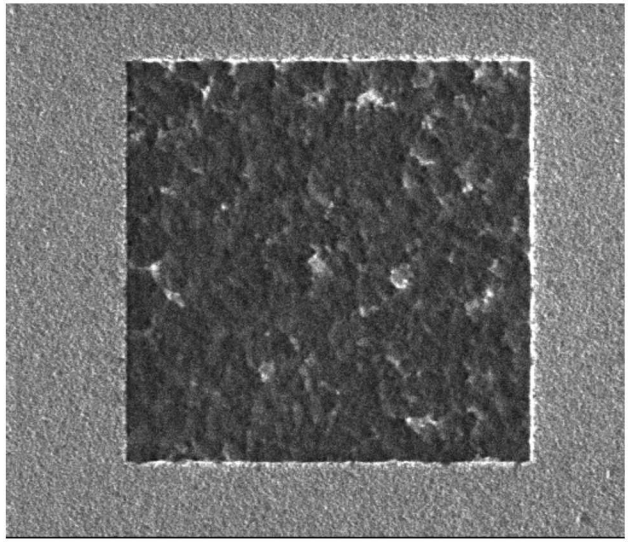
3 min

3.4 x 10^{16} Ga+/ μm^2

6 min

6.8 x 10^{16} $Ga^{+}/\mu m^2$





10 min

11 x 10^{16} $Ga/\mu m^2$

Evaporated Cu sample irradiated at 30 pA in 100 μm^2 area

Orientation changes in ion milled regions of fine-grained Cu

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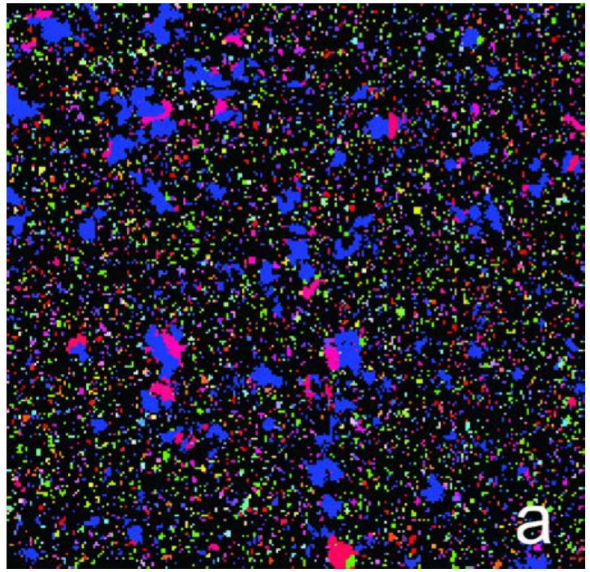
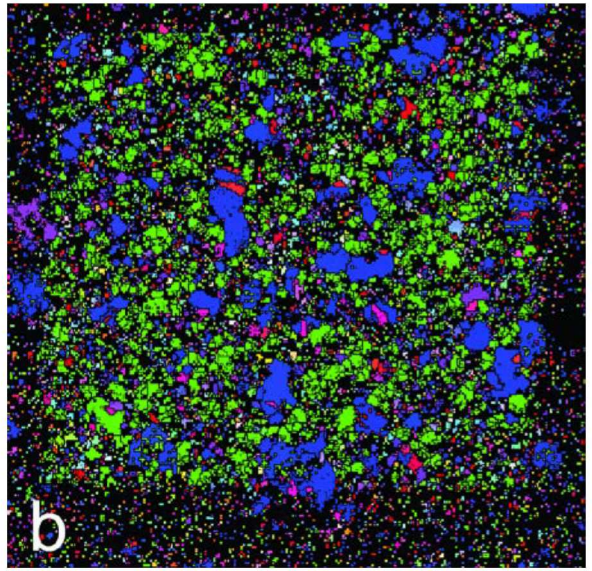
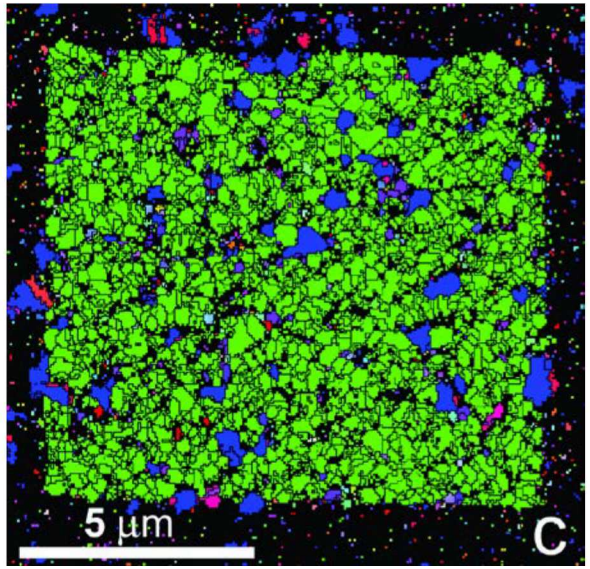
As deposited

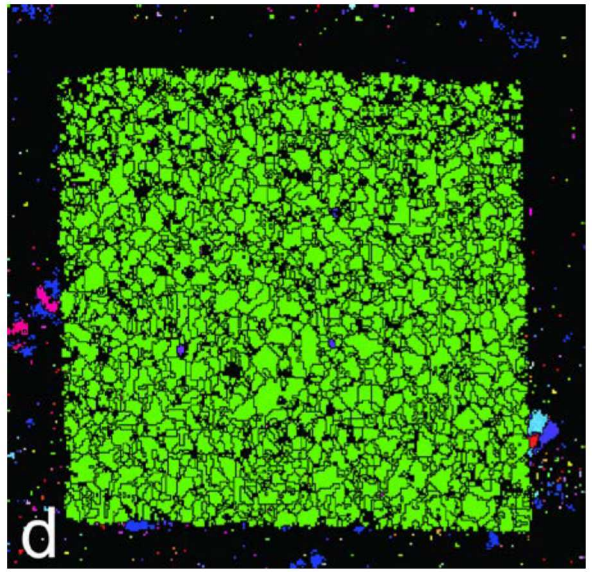




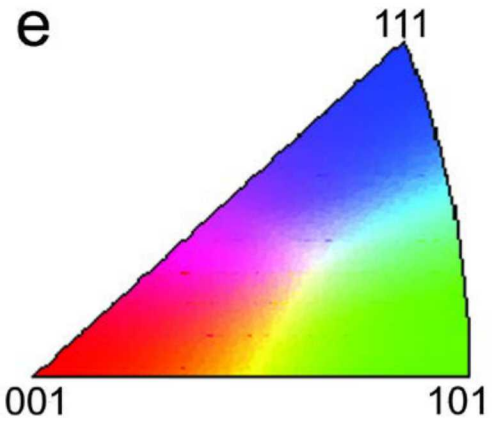
3.6×10^{16} Ga+/ μm^2

5.2×10^{16} $Ga^+/\mu m^2$





1.1×10^{17} $Ga/\mu m^2$



IPF Z of evaporated Cu sample irradiated at 30 pA in 100 μm^2 area

Phase Distributions in ion milled regions of fine-grained Cu

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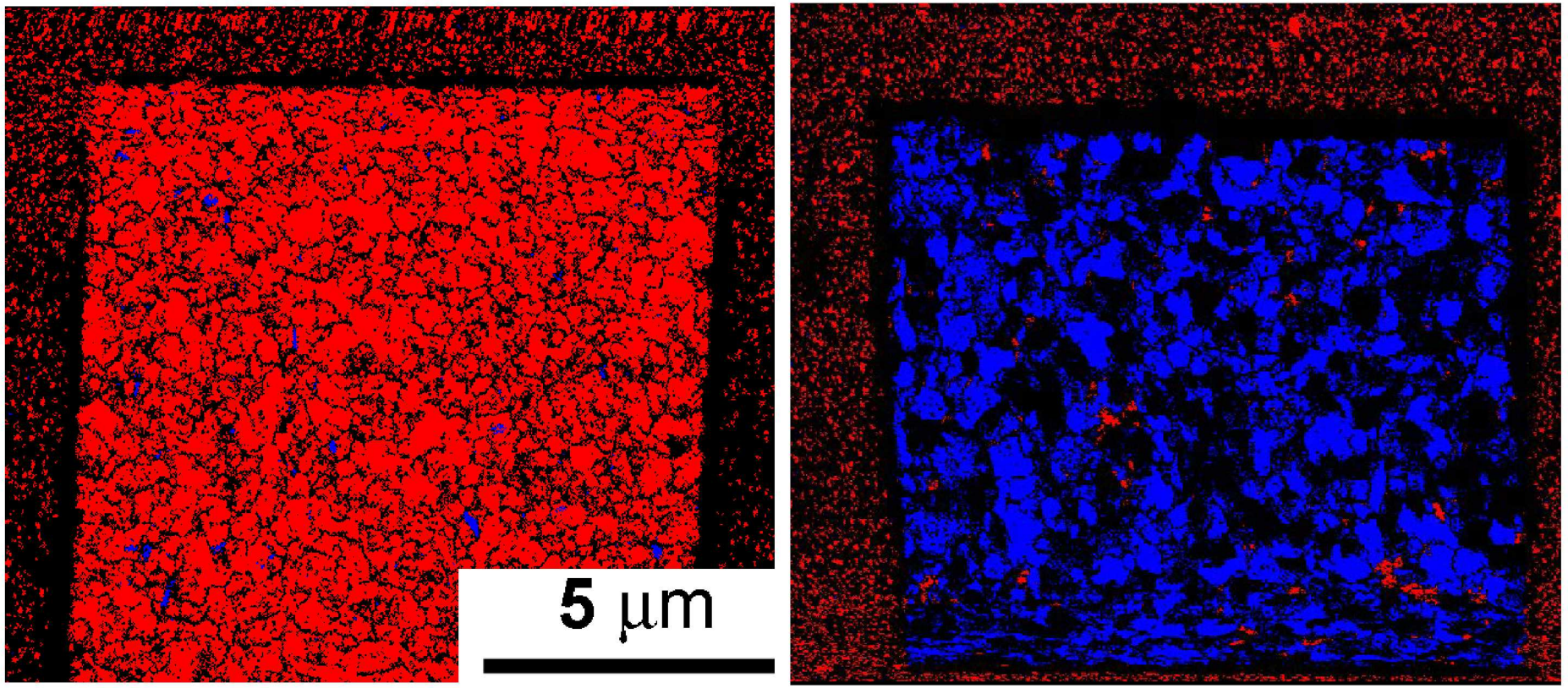


2 min 330 pA - 2.5 x 10^{16} $Ga^{+}/\mu m^2$

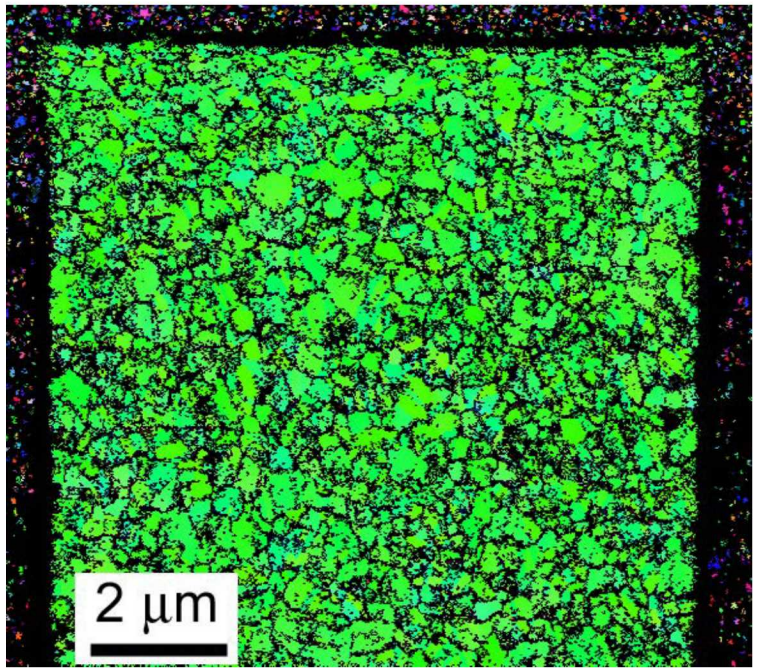
3 min 330 pA - 3.7 x 10^{16} $Ga^{+}/\mu m^2$

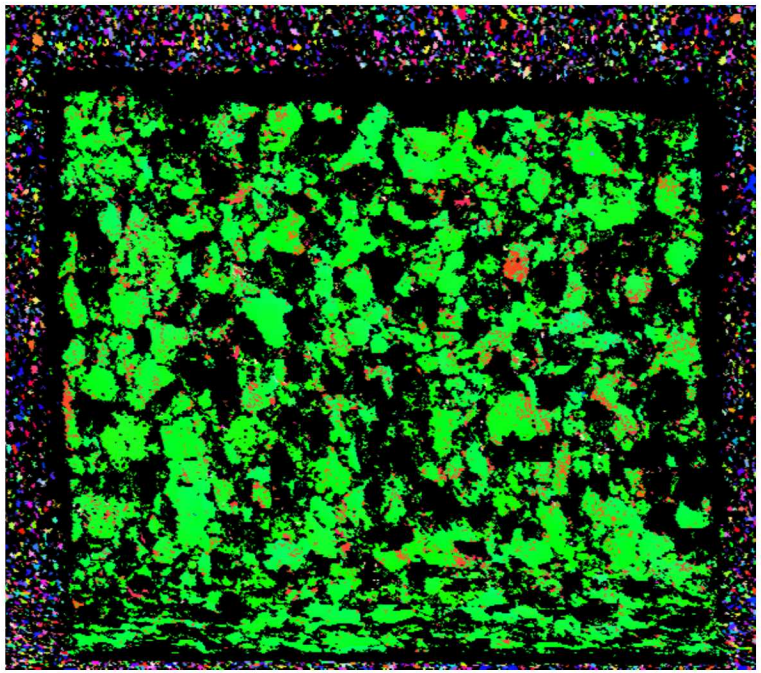
Red = Cubic phase (Cu)

Blue = Cu_3Ga (hexagonal)

Orientation changes in ion milled regions of fine-grained Cu

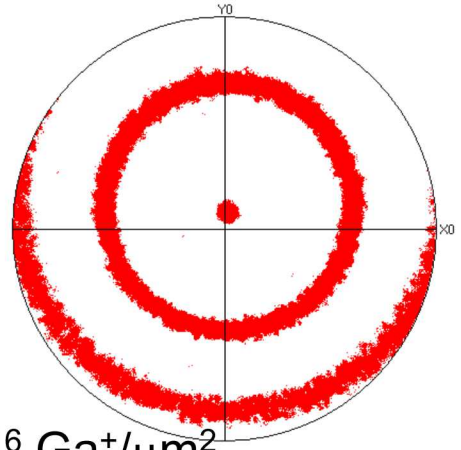
Cu IPF Z





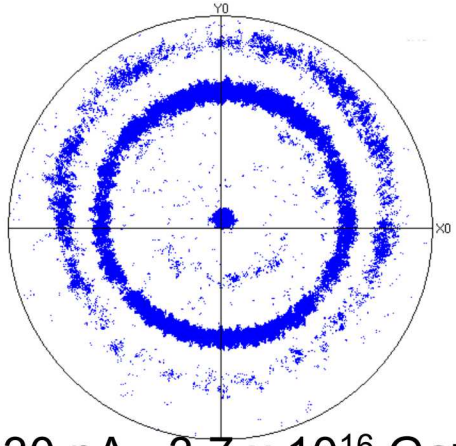
Cu_3Ga IPF Z

(110)



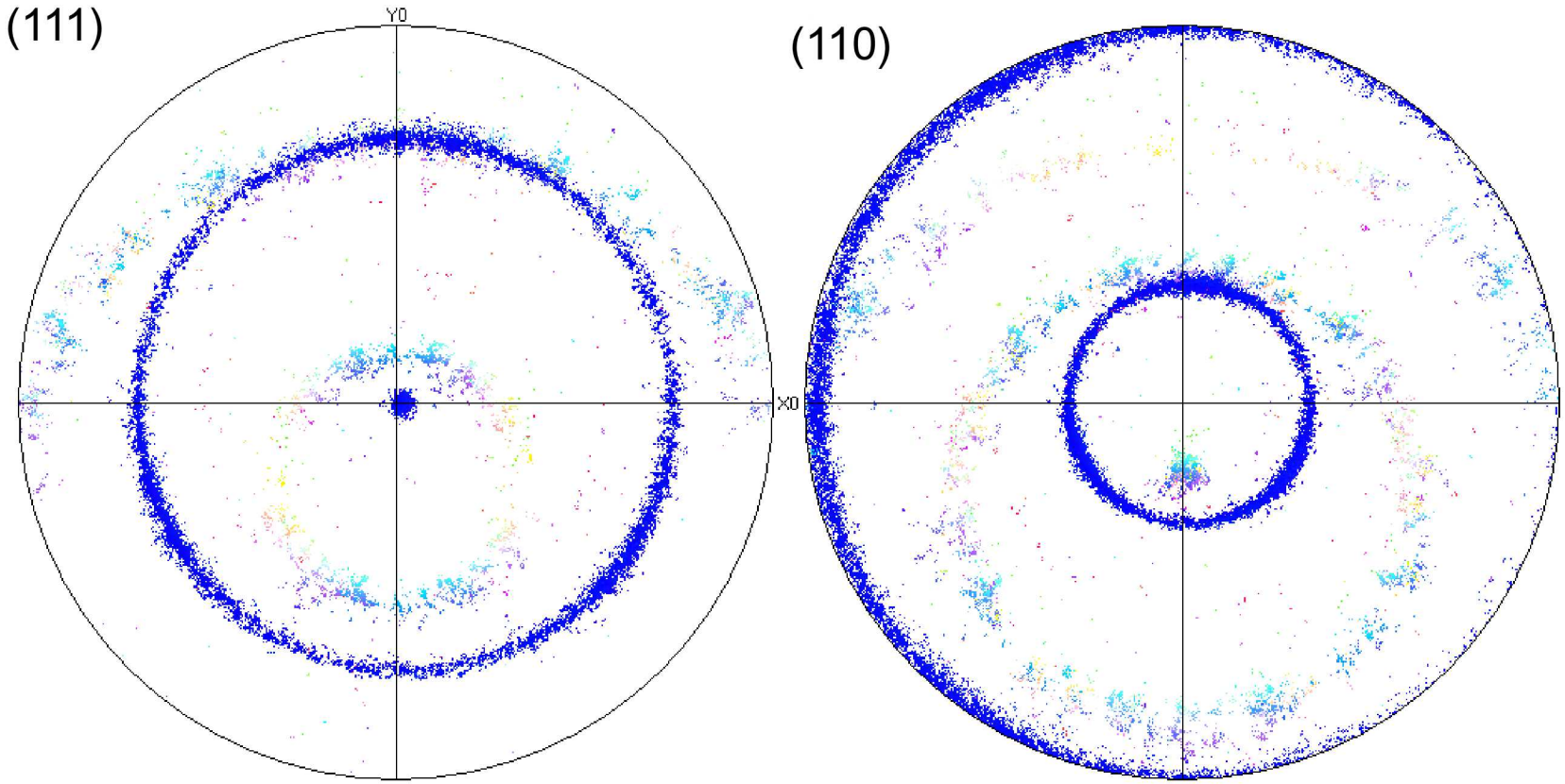
2 min 330 pA - 2.5 x 10^{16} $Ga^+/\mu m^2$

(1120)



3 min 330 pA - 3.7 x 10^{16} $Ga^+/\mu m^2$

New grains form with respect to the ion beam direction

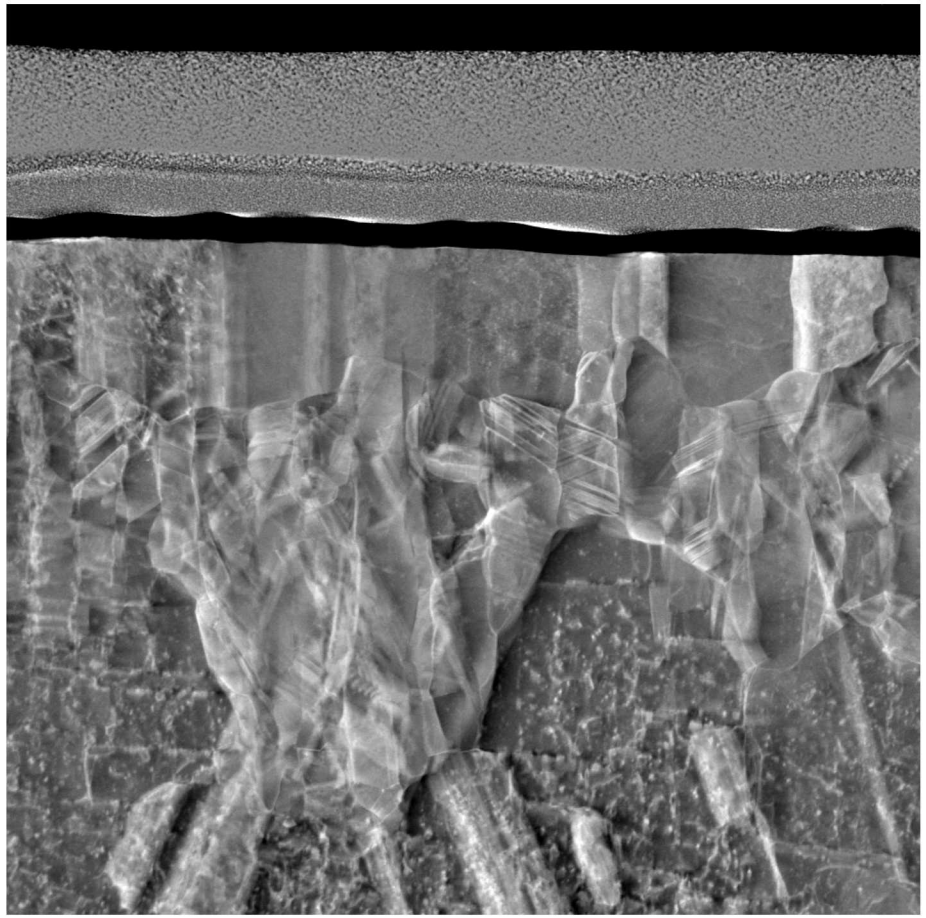


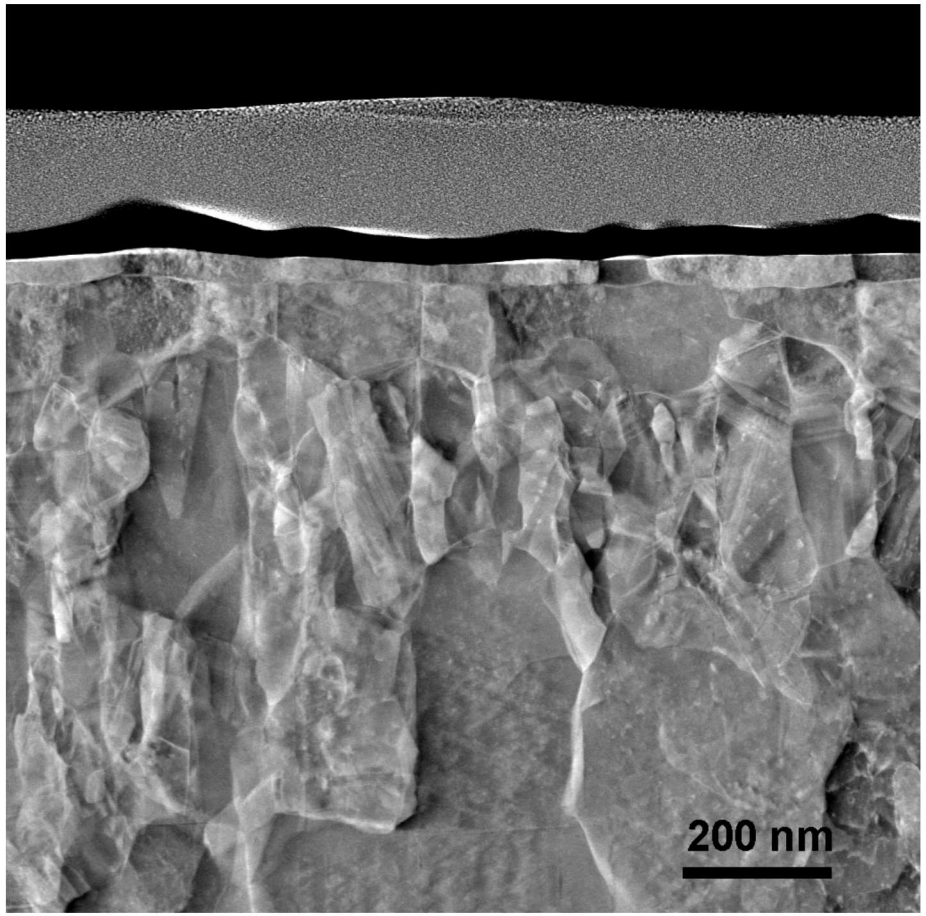
Ga+ ion beam tilted 23˚ with respect to normal

New (110) texture develops along beam direction

Au sample

STEM imaging and microanalysis of Ga+ into Cu





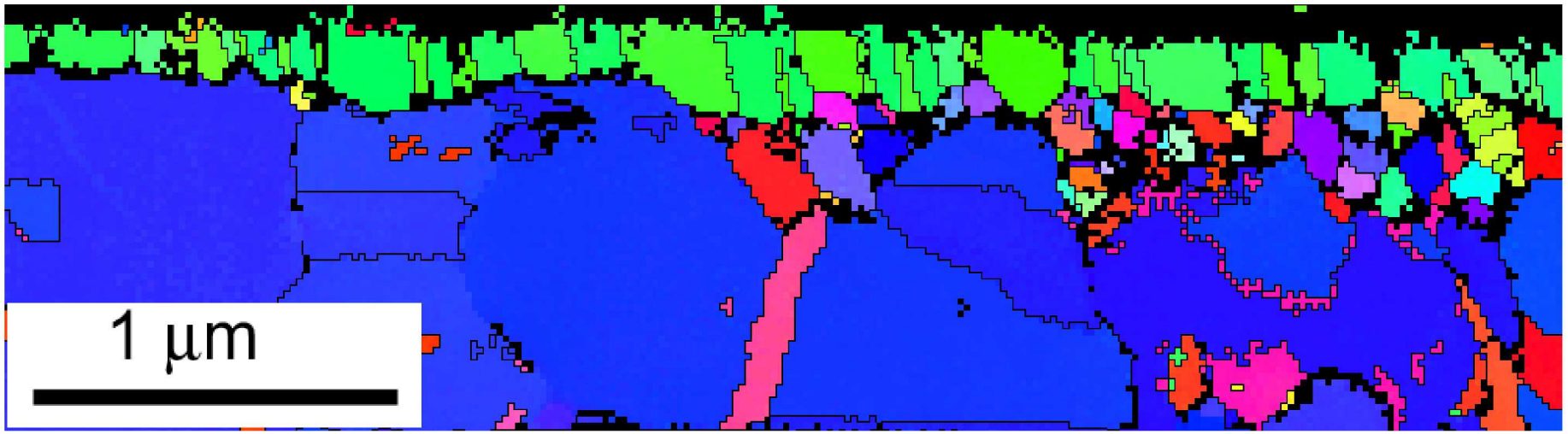
SRIM estimates the range of 30 Ga+ in Cu to be 10 nm

2 min 330 pA - 2.5 x 10^{16} $Ga^{+}/\mu m^{2}$

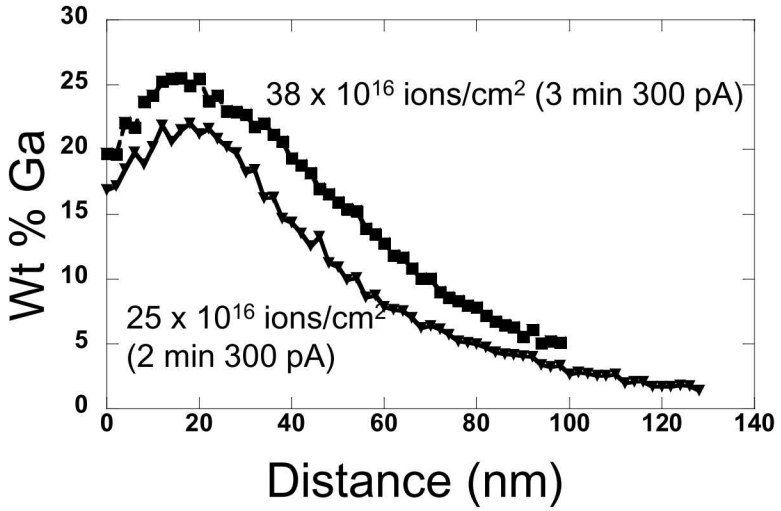
3 min 330 pA - 3.7 x 10^{16} $Ga^{+}/\mu m^{2}$

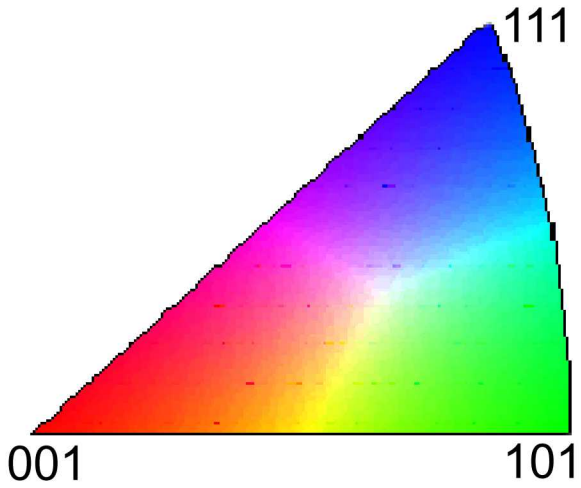
FIB prepared TEM samples of irradiated Cu

EBSD orientation mapping of Ga+ milled Cu



2 min 330 pA - 2.5 x 10^{16} $Ga^{+}/\mu m^{2}$





Orientation changes in ion milled regions of fine-grained W

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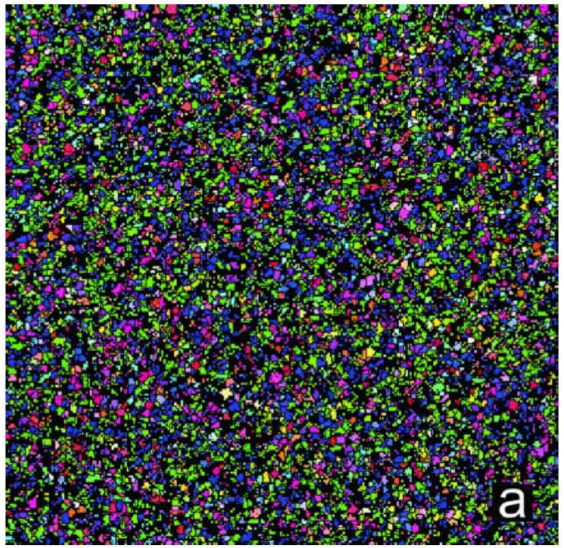
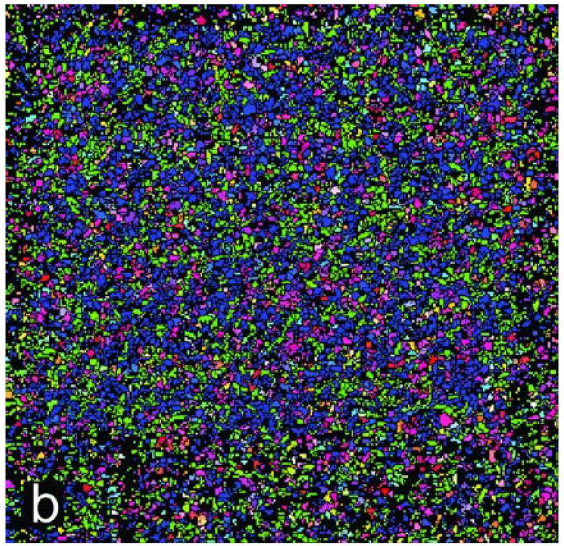
IPF Z

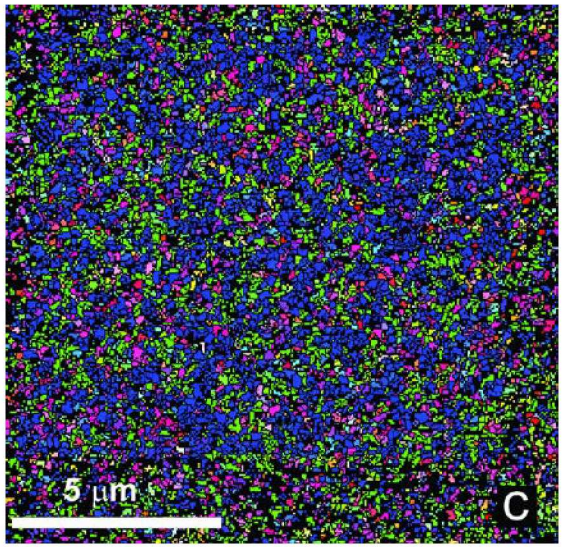
As deposited

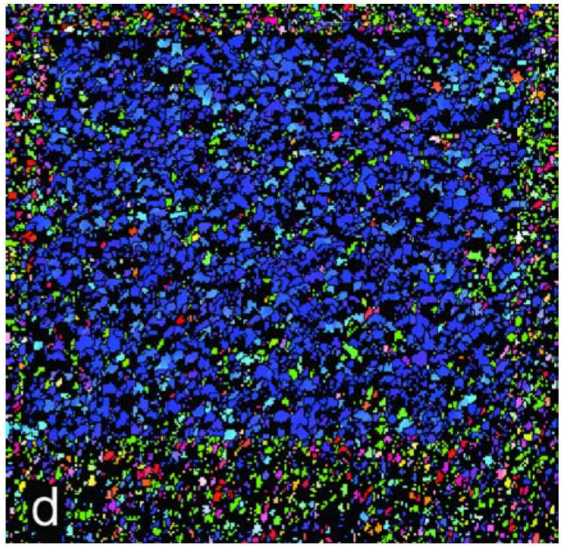




3.6×10^{16} $Ga^+/\mu m^2$

5.4×10^{16} $Ga^+/\mu m^2$



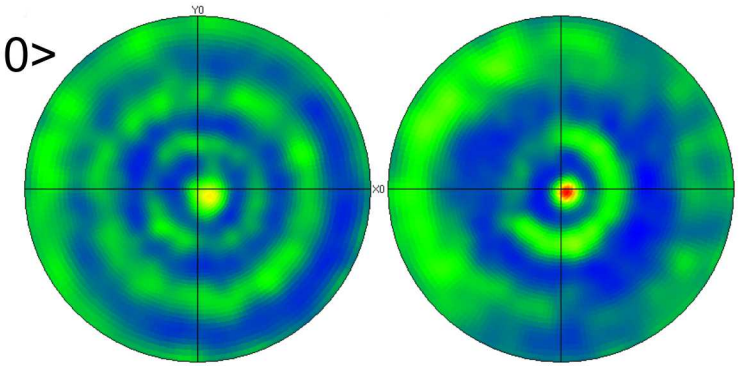


2.1×10^{17} $Ga^+/\mu m^2$

Orientation changes in ion milled regions of **fine-grained** W

<110>

<111>

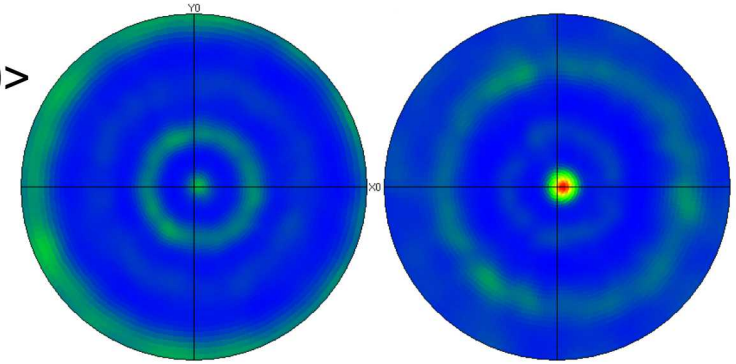


As-deposited

3 times random

<110>

<111>

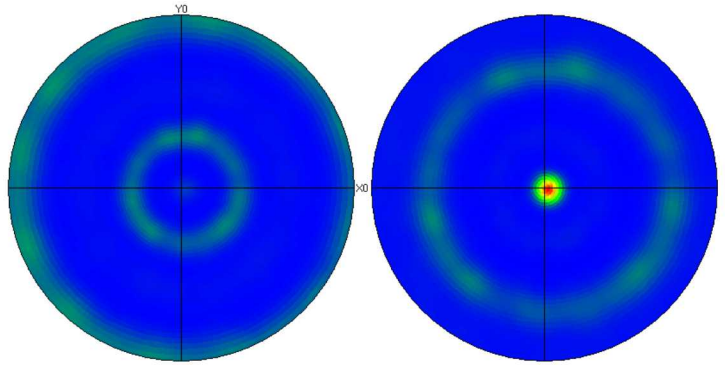


7.5 x 10^{16} $Ga^{+}/\mu m^2$
4 min at 50 pA in 100 μm^2

12 times random

<110>

<111>



1.9 x 10^{17} $Ga^{+}/\mu m^2$
10 min at 50 pA in 100 μm^2

21 times random

Summary of ion irradiation of FCC and BCC metals

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Non-Channeling fraction in Cu and Au

Direction	Au C_0	Cu C_0
[110]	0.150	0.132
[100]	0.252	0.222
[112]	0.342	0.300
[130]	0.502	0.441
[111]	0.575	0.510

Non-channeling fraction in W

Direction	W C_0
[111]	0.146
[100]	0.181
[110]	0.303
[112]	0.695

Consistently, the metals form orientations that are along the highest probability channeling direction.

Kempshaw, B. W., Schwarz, S. M., Prenitzer, B. I. and Giannuzzi, L. A.,(2001) Ion channeling effects on the focused ion beam milling of Cu. *J, Vac. Sci. Technol. B*. **19**,
749-754.

Crystallographic orientation changes due to ion irradiation

Ga^+ irradiation results in new surface grains with orientations consistent with the highest probability channeling direction aligned with the ion beam direction. FCC - <110> , BCC - <111>

Higher total ion doses can result in Ga intermetallic phase formation as shown with Cu where Cu_3Ga (hexagonal) forms with Ga^+ irradiation. But alteration is not dose rate dependent.

The rate of orientation alteration is higher for fine grained materials, but is observed in coarse grained samples.

Although the end states can be described by the differential damage models described in the literature, the intermediate stages cannot be and must result from ion beam-assisted nucleation of new grains with the easy channeling direction aligned with the ion beam.

Xe^+ does not appear to cause similar reorientation issues when compared to Ga^+ - reason for this is unclear and may possibly be due to a limited range of operating parameters, smaller ion range for Xe^+ compared to Ga^+, other possibilities also include sputter rate and damage associated with different ions.

Transformation of austenite to ferrite due to Ga^+ ion irradiation of stainless steel

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Recent work has cited that Ga^+ ion milling of some austenitic stainless steels causes **transformation to ferrite** in the milled region. Ferrite forms with specific orientation relationships with prior austenite.

Published papers conclude that **Ga is a ferrite stabilizer** and thus the change in the composition results in ferrite formation in an austenitic alloy. (Other paper mentions that Ga is a weak ferrite stabilizer)

Published papers also mention the possibility that the transformation is related to strain due to implantation.

Babu, R. Prasath, S. Irukuvarghula, A. Harte, and M. Preuss. "Nature of gallium focused ion beam induced phase transformation in 316L austenitic stainless steel." *Acta Materialia* 120 (2016): 391-402.

Basa, Adina, Christian Thaulow, and Afrooz Barnoush. "Chemically induced phase transformation in austenite by focused ion beam." *Metallurgical and Materials Transactions A* 45, no. 3 (2014): 1189-1198.

Knipling, K. E., D. J. Rowenhorst, R. W. Fonda, and G. Spanos. "Effects of focused ion beam milling on austenite stability in ferrous alloys." *Materials Characterization* 61, no. 1 (2010): 1-6.

Kolman, David G., John F. Bingert, and Robert D. Field. "The microstructural, mechanical, and fracture properties of austenitic stainless steel alloyed with gallium." *Metallurgical and Materials Transactions A* 35, no. 11 (2004): 3445-3454.

Transformation of austenite to ferrite due to Xe^+ ion irradiation

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What happens with Xe irradiation to austenite?

Some data in the literature about high energy 100kV to 400kV Xe implantation

Transformation to ferrite observed with NW or KS orientation relationships between the ferrite and the austenite.

Need to compare Xe^+ and Ga^+ ion irradiation.

Sakamoto, I., N. Hayashi, B. Furubayashi, and H. Tanoue. "Ion-induced phase transformation in type 304 austenitic stainless steel by rare-gas ion irradiation." *Journal of applied physics* 68, no. 9 (1990): 4508-4512.

Xie, Guoqiang, Minghui Song, Kazutaka Mitsuishi, and Kazuo Furuya. "Orientation of γ to α transformation in Xe-implanted austenitic 304 stainless steel." *Journal of nuclear materials* 281, no. 1 (2000): 80-83.

Xie, Guoqiang, Minghui Song, Kazutaka Mitsuishi, and Kazuo Furuya. "Orientation of γ to α transformation in Xe-implanted austenitic 304 stainless steel." *Journal of nuclear materials* 281, no. 1 (2000): 80-83.

Stainless steel – Austenitic phases are not stable in many stainless steels.

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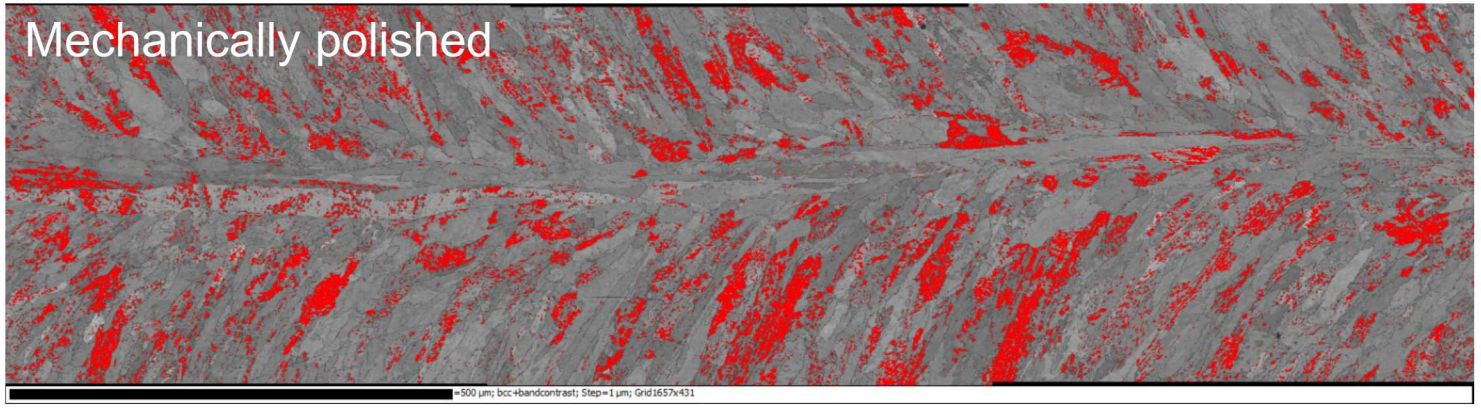
Bead on plate welds for 304 SS –Comparison of electropolished and metallographic polishing

Band contrast image with ferrite in red (0.1 area % ferrite).



Band contrast image with ferrite in red (12 area % ferrite).

Careful sample preparation required to avoid inducing ferrite in lean stainless steel alloys.

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Transformation of austenite to ferrite due to ion irradiation

Material: Cast CF-8 (very similar to the composition of 304 – 18 wt. % Cr, 8.5 wt% Ni, 1 Wt% Mn)

Ion irradiated with both Ga^+ and Xe^+ ions

Ga^+ ion irradiation accomplished with FEI Helios G3 dual beam FIB

Xe^+ ion irradiation accomplished with a Applied Beams PFIB column on an FEI DB235 dual beam FIB.

Transformation of austenite to ferrite due to Ga^+ ion irradiation

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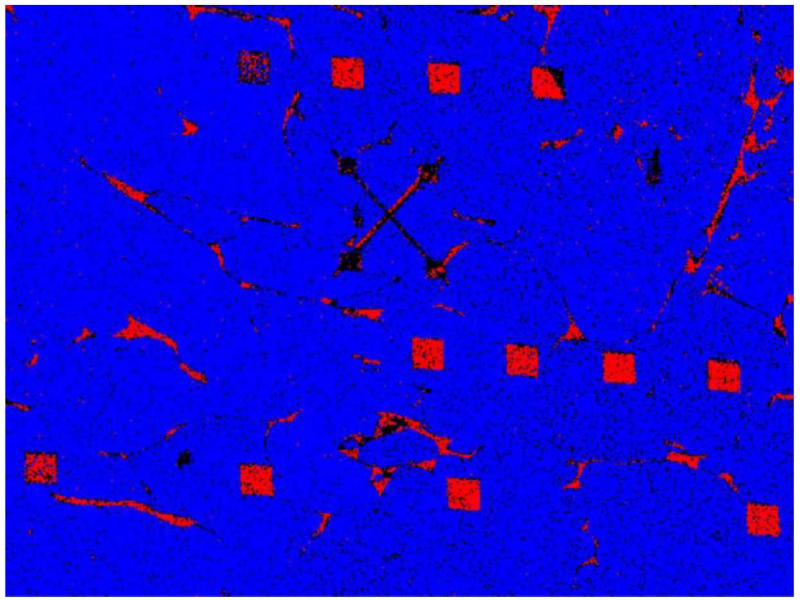
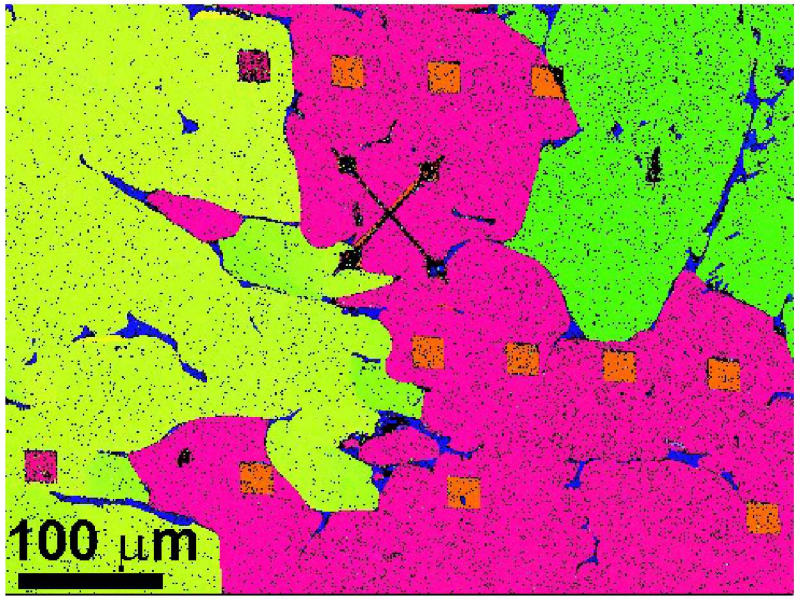
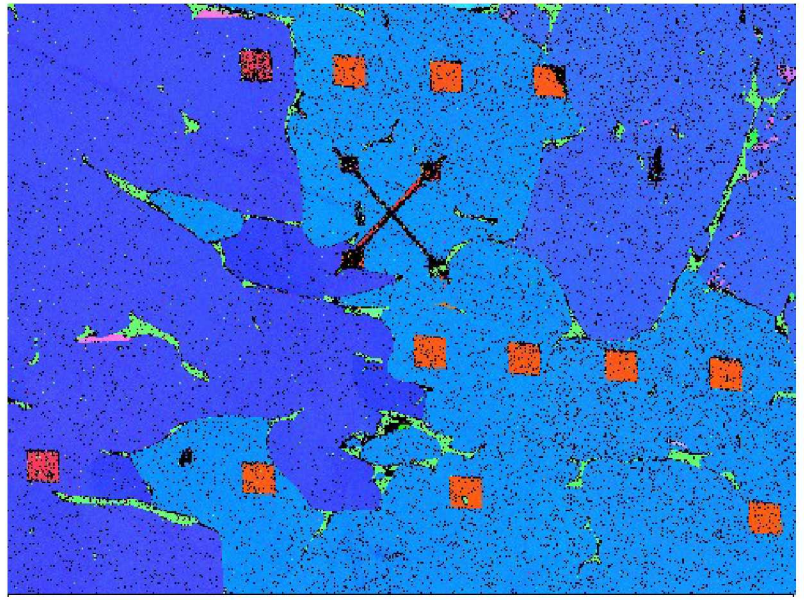
Phase (red=ferrite blue=austenite)



IPF X in plane



IPF Z Ga beam direction



30 kV Ga^+ at 0.93 nA beam current for varying total doses
Top row doses $9X10^{16}$, $5X10^{17}$, $9X10^{17}$, $1X10^{18}$ ions/cm^2
Middle row below X all are $5X10^{17}$ ions/cm^2
Bottom row are all $9X10^{16}$ ions/cm^2

In all cases the ferrite formed during irradiation has the KS or NW OR with respect to austenite

Transformation of austenite to ferrite due to Ga^+ ion irradiation

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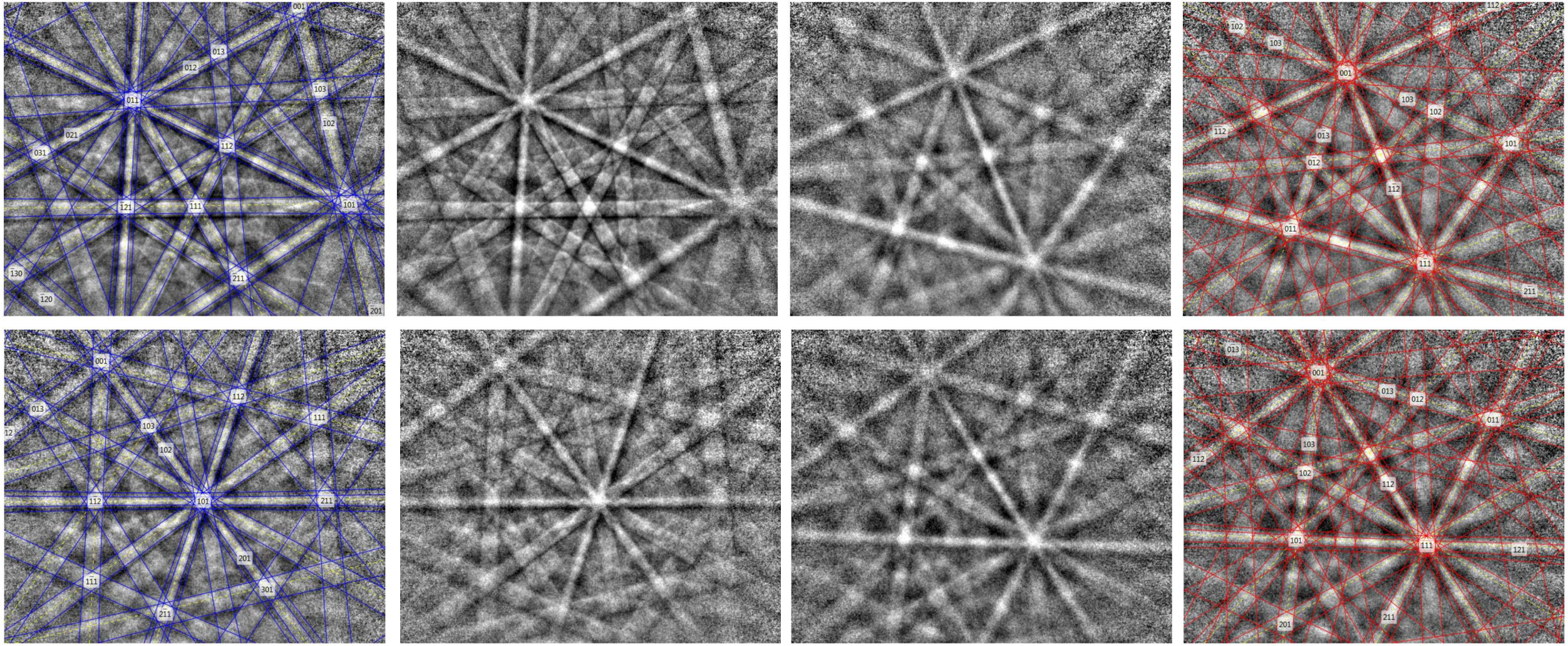
austenite

ferrite



Identification of ferrite is not due to incorrect indexing of the EBSD patterns

Transformation of austenite to ferrite due to Ga^+ ion irradiation

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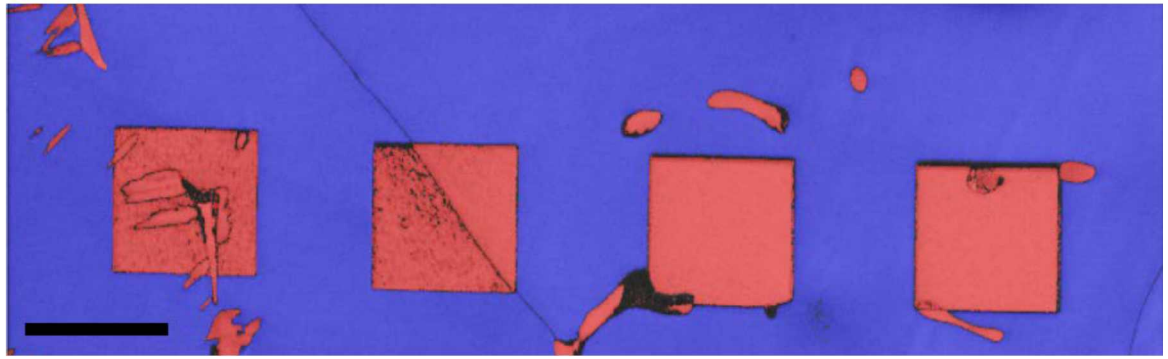
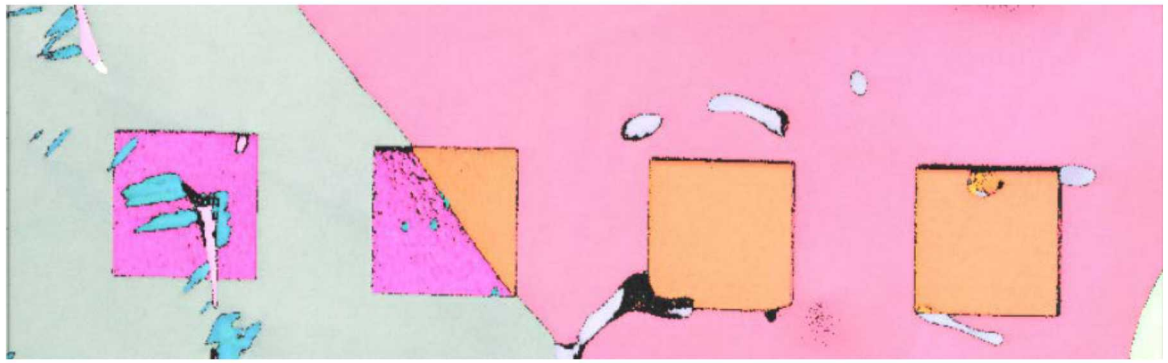


Phase (red=ferrite blue=austenite)
Scale bar = 20 μm

IPF X in plane



IPF Z Ga beam direction

Note that all ion milled areas are the same orientation within grains (not including pre-existing ferrite)

Transformation of austenite to ferrite due to Xe^+ ion irradiation

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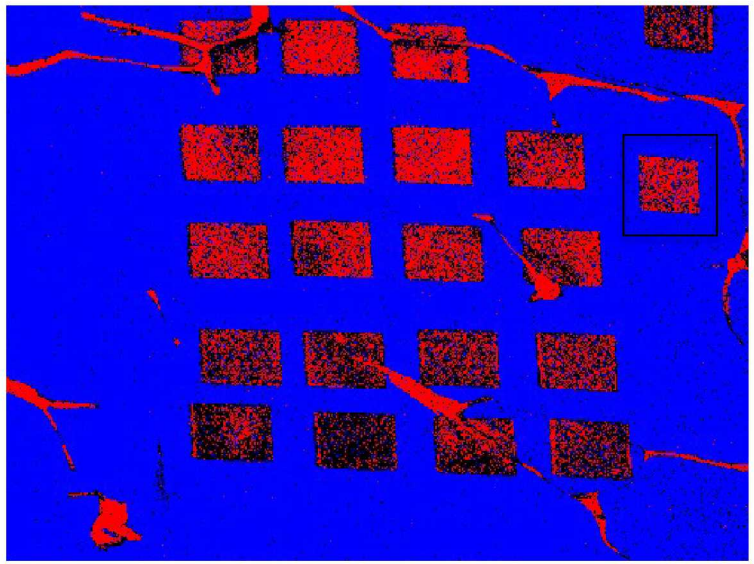
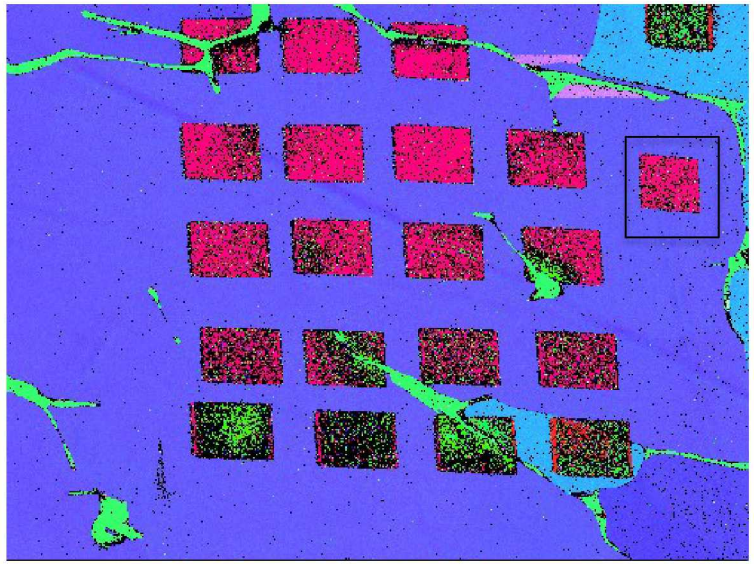
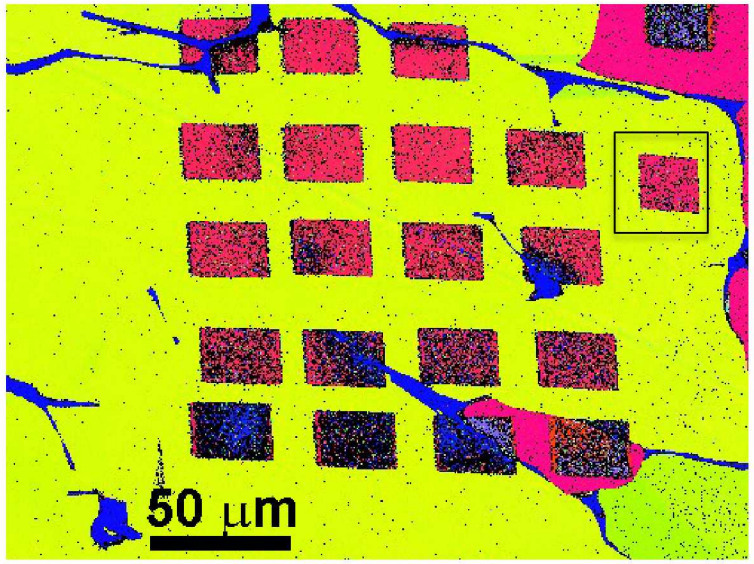
Phase (red=ferrite blue=austenite)



IPF X in plane



IPF Z Xe beam direction



First row– 10 seconds at 1 nA - $7X10^{15}$ ions/cm^2
Second row– 20 seconds at 1 nA - $1.4X10^{16}$ ions/cm^2
Third row– 20 seconds at 1 nA - $1.4X10^{16}$ ions/cm^2
Fourth row– 30 seconds at 1 nA - $2.1X10^{16}$ ions/cm^2
Fifth row– 45 seconds at 1 nA - $3.1X10^{16}$ ions/cm^2

Boxed region is Ga^+ exposed at $9X10^{16}$ ions/cm^2

In all cases the ferrite formed during irradiation has the KS or NW OR with respect to austenite

Transformation of austenite to ferrite due to Xe^+ or Ga^+ ion irradiation

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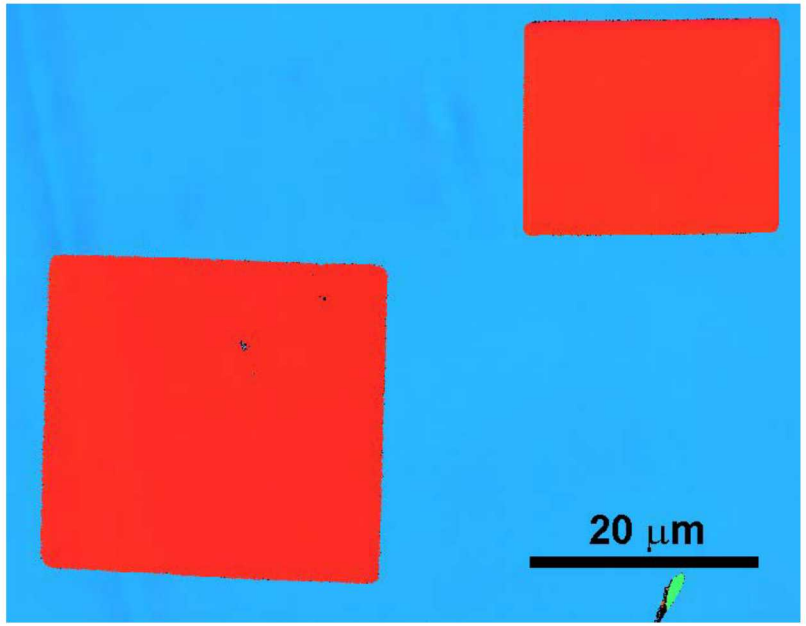
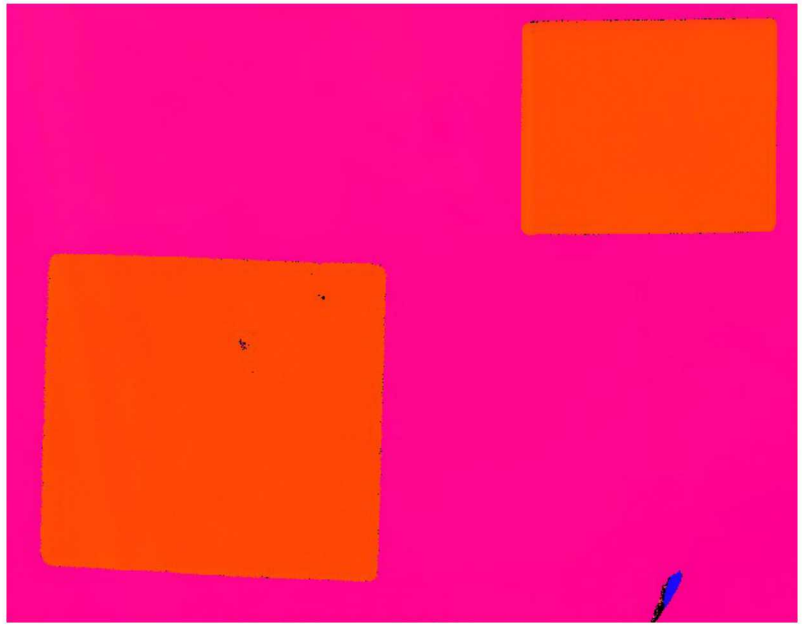
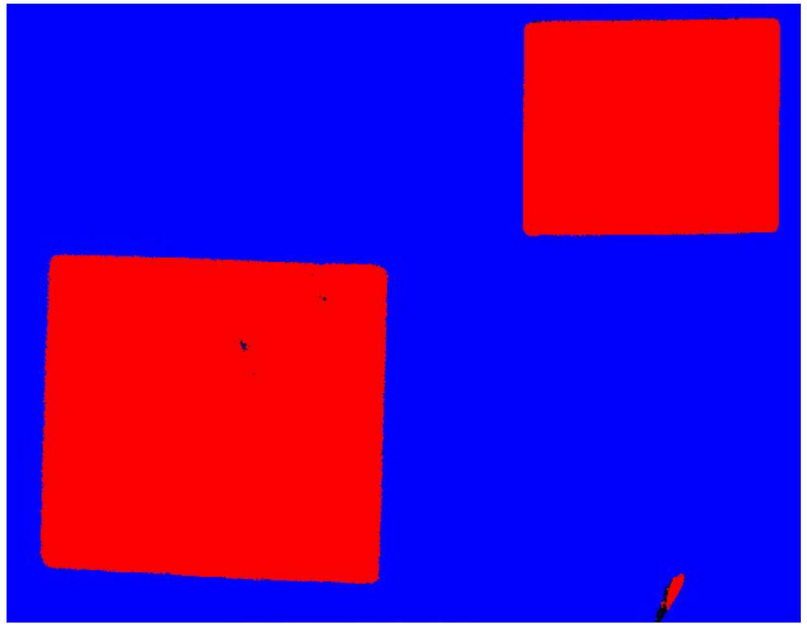


IPF X in plane



IPF Z Ga beam direction

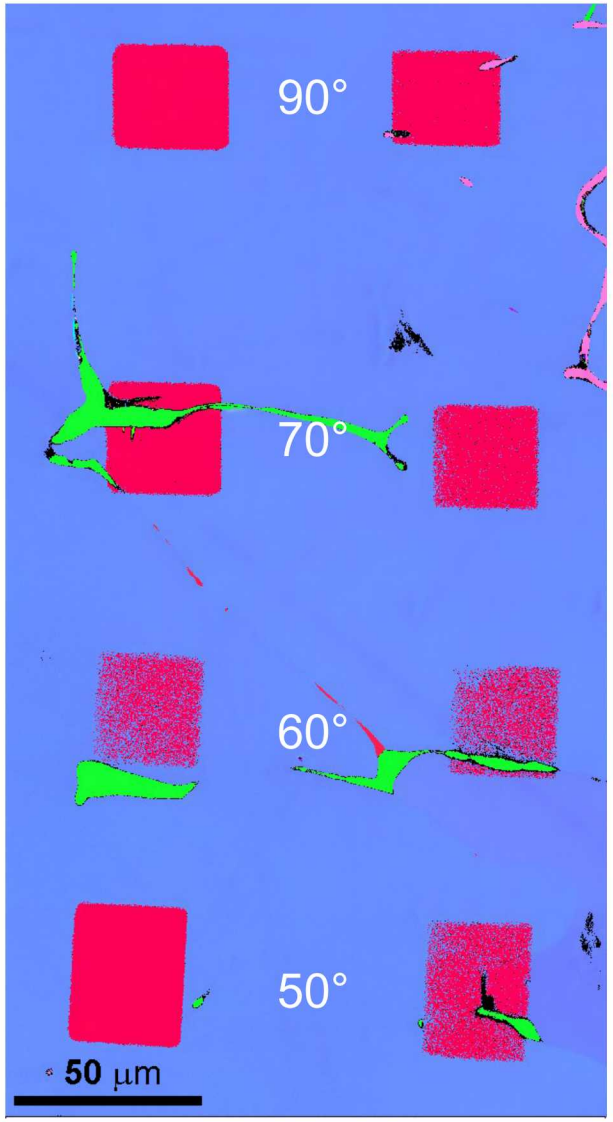


Phase (red=ferrite blue=austenite)

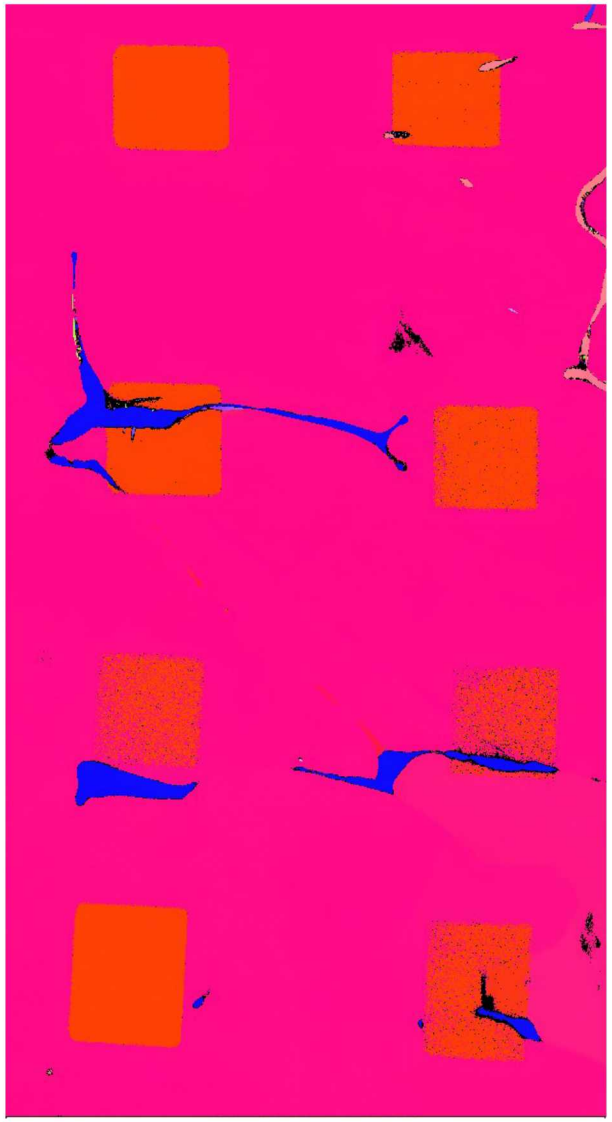
The orientation of the ferrite formed during ion irradiation is independent of ion species

Xe^+ dose = $6.9X10^{15}$ ions/cm^2 Ga^+ dose = $1.5X10^{16}$ ions/cm^2

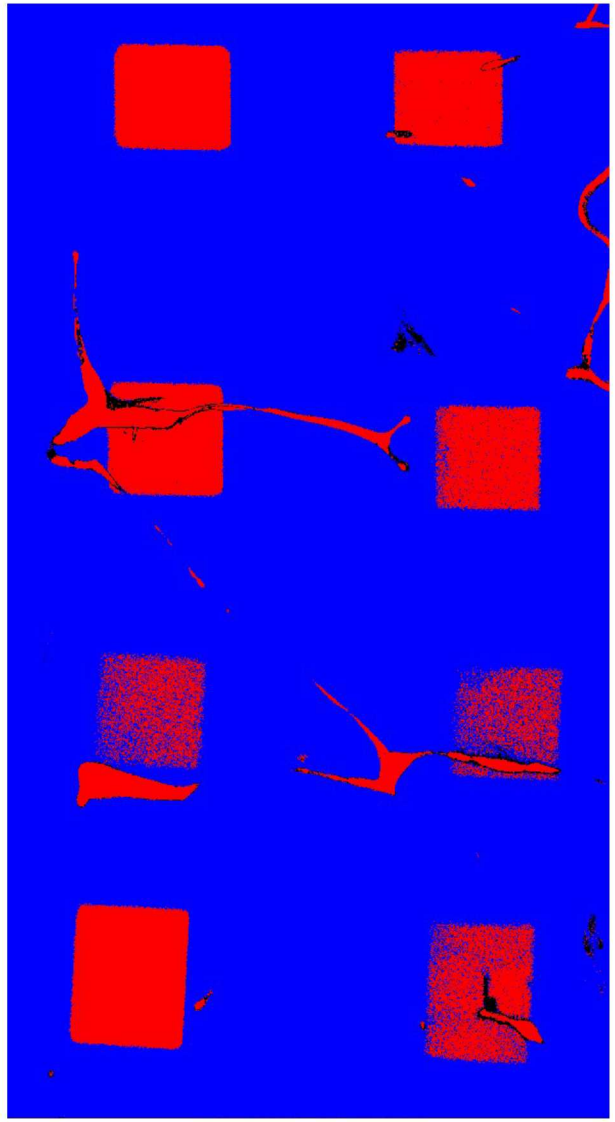
Transformation of austenite to ferrite due to Xe^+ ion irradiation – incident angle



IPF X in plane



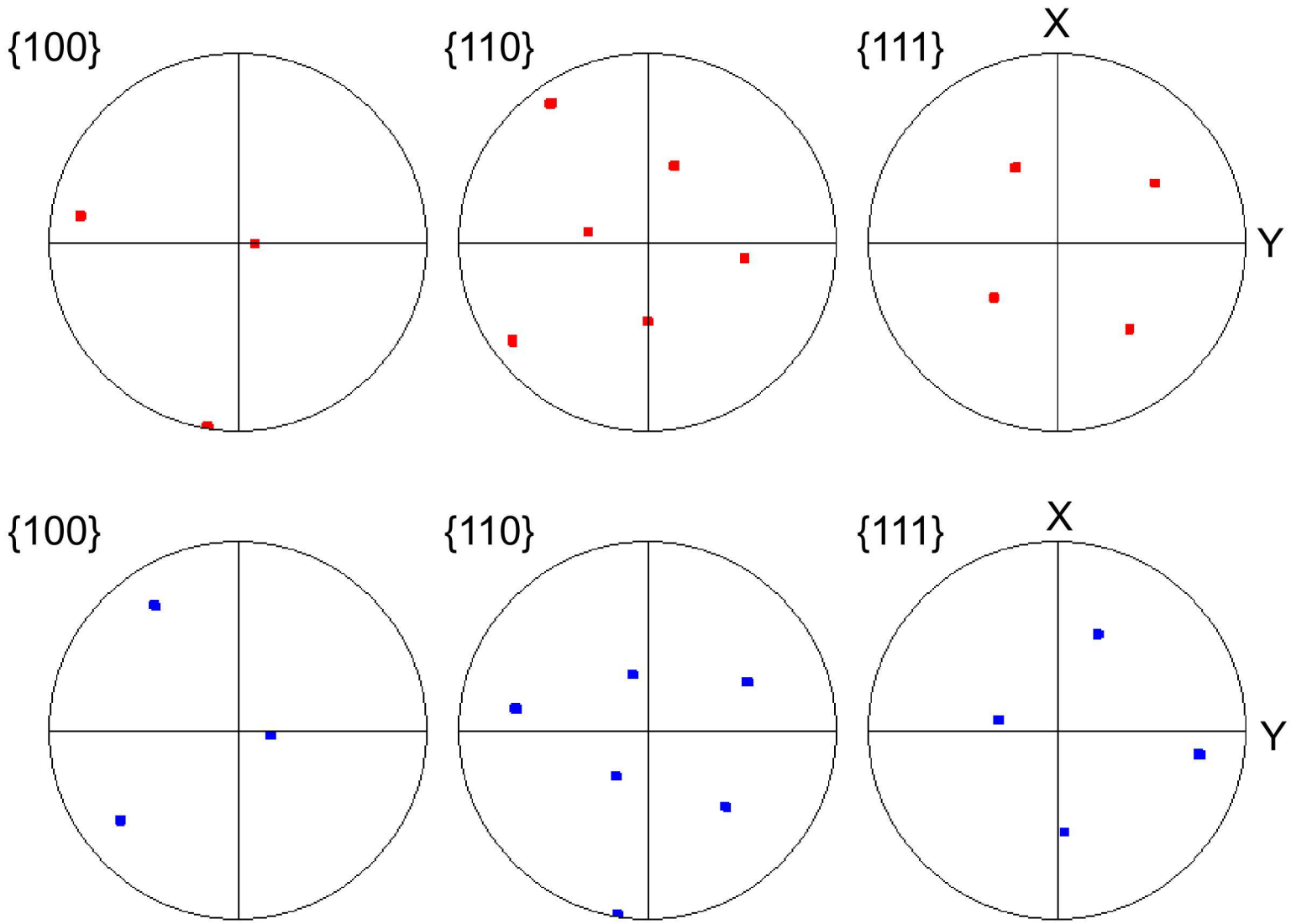
IPF Z Ga beam direction



Phase (red=ferrite blue=austenite)

Ion beam incident angle does not change the orientation of the ferrite formed during ion irradiation

Transformation of austenite to ferrite due to Xe^+ ion irradiation – incident angle



All Xe ion beam induced ferrite

Surrounding austenite

Ferrite orientation is independent of ion beam incident angle

Comparison of Ga^+ and Xe^+ ion irradiation of stainless steel

Observations from this work:

- Both Ga^+ and Xe^+ can cause ferrite to form from an austenitic stainless steel.
- The total ion doses are similar with the transformation happening at lower total doses for Xe^+.
- For both Xe^+ and Ga^+ the resulting ferrite is always single crystal with respect to the underlying austenite and has a typical orientation relationship with the surrounding grain (KS or NW).
- For both Xe^+ and Ga^+ the ferrite forms with the one orientation from the same starting orientation of austenite. Normally, would expect multiple variants of ferrite to form from a single orientation of austenite.
- Ion incidence angle does not change the orientation of the ferrite that is formed.

Above results are not consistent with simple chemical stabilization of ferrite by Ga^+ irradiation. This cannot describe all these observations from both Xe^+ and Ga^+ irradiation.

The only way to explain the observations is that the formation of ferrite is due to the strain and atomic disorder caused by the ion irradiation. The ferrite is formed with a preferred variant with respect to the austenite.

Summary

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Irradiation of specific types of samples with an ion beam may result in microstructural alterations that are not representative of the bulk material.

Fine grained materials form new grains with an easy channeling orientation parallel to the ion beam direction.

High dose ion irradiation with a reactive species like Ga can result in the formation of second phases that are not present in the bulk material.

Phase transformations in stainless steel

In specific stainless steel alloys, austenite will transform to ferrite due to ion beam irradiation and this is most likely a result of the strain and lattice damage introduced by the energetic ion beam. This transformation is **not** a result of ferrite chemical stabilization.

The only way to explain the observations is that the formation of ferrite is due to the strain and atomic disorder due to the recoils caused by the ion irradiation. The ferrite is formed with a preferred variant with respect to the austenite.