The Formation of Amorphous and Crystalline Damage in Metallic and Semiconducting Materials under Gallium Ion Irradiation

DISSERTATION

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Abstract

Gallium ion irradiation in dual-beam FIB microscopes is well known to cause some degree of damage during the milling process. Although it has been established that cleaning passes with low energy ions can mitigate the extent of this damage, the mechanisms, extent, and type of damage caused have not been well studied due to geometrical limitations inherent to thin foils. By adapting the needle geometry used for atom probe and tomographic work, we can directly measure the extent of damage layers created during milling. Needles were made of multiple semiconductor, intermetallic, and metal systems, confirming previous estimates of damage thickness in Si and GaAs. Materials tested fell into two distinct classes, amorphous dominated and crystalline defect dominated. Amorphous dominated materials consisted of semiconductors and narrow phase field intermetallics, fitting previous radiation work. Crystalline defect dominated materials had semi-crystalline damage layers under 5 nm at all accelerating voltages, and residual defects were shown to have significant effects on lattice clarity in HAADF-STEM. Contrast between amorphous layers in HAADF-STEM was found to be minimal even under ideal conditions, and HRTEM was necessary to accurately confirm and measure damage layer thickness. The causes and extent of damage layer minimization during low keV milling steps were shown to be consistent across all materials.
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Chapter 1: Introduction

The newest generation of electron and ion beam microscopes is redefining the way researchers approach materials characterization problems. New microscopes are easier to use than ever, cutting-edge aberration correction is beginning to make atomic resolution TEM and STEM routine, and advances in both computer control and detector hardware allow data collection on an unprecedented scale and resolution. As with any large leap in capability this has led to a host of new techniques, theories, and the inevitable stumbling blocks that accompany any stride forward. While increased microscope capabilities are the backbone of recent advances, the utility of the resulting data often relies on our ability to accurately model and validate the subsequent information. In the case of atomic resolution XEDS, PACBED, and even well-established techniques such as EELS modeling has become key in order to get quantifiable results. An essential requirement for every model is a basic understanding of the samples geometry and structure. Almost equally vital is determining the degree of sample damage resulting from sample preparation. In recent years the method of choice for (S)TEM sample prep has rapidly become focused ion beam extraction (FIB) due to its speed of preparation, site specific nature, and in situ imaging capabilities. While the advantages of FIB processing are overwhelming, like all specimen preparation techniques some degree of damage develops
during the process. As the need for modelling goes up and sample size and damage requirements go down it becomes vital that the mechanisms and extent of FIB damage be well understood.

Figure 1: Schematic diagram of Dual Beam FIB components

Although the FIB allows a number of options for specimen preparation, TEM foils are often produced using some variation on the “lift out” model, variations of which are summarized by Giannuzzi et al [1]. For in situ lift out as depicted in Figure 2 a strip of platinum or tungsten is laid down using an organometallic precursor and the ion beam. This layer protects the area of interest during the high energy trenching step using gallium ions; this step removes two channels of material leaving a narrow slab with a protective cap. After trenching, the sample is tilted in order to undercut the slab which is
then attached to a nano manipulator, as seen in Figure 2. The wedge is then attached to a TEM grid and tilted in order to orient the foil parallel to the ion beam. Once oriented, it is then tilted in a range of ± 1-10° and thinned to an electron transparent wedge.

Figure 2: Example of in-situ FIB lift out and attachment to TEM grid

The lift out model allows the user to create thin TEM samples from specific sites using its inbuilt imaging abilities, or using orientation and chemical data. It also allows the creation of thin foils from areas and materials difficult to sample using normal TEM sample prep techniques [2]. Site specific foils may be pulled from fracture surfaces, semiconductor devices, biological materials, and corrosion areas with little large scale disruption of the sample. The resulting sample can be made extremely thin even when composed of dissimilar materials [3]. However, like all sample preparation tools the FIB damages the material to some extent. The question this dissertation tries to address is what qualifies as damage, what techniques can we use or develop to view this damage,
how damage varies with material or energy, and ultimately to what degree this damage truly matters when imaging.

The question of importance is not one to discard hastily, several authors [3,4] have shown that a series of milling steps of decreasing accelerating voltage are sufficient to qualitatively increase lattice clarity and remove black dot contrast associated with FIB damage. Hundreds of authors have successfully used this method to create FIB foils used to measure features such as precipitate size, grain orientation, and composition. It is no surprise then that upon seeing this research presented, one scientist asked the natural question. “If we can get rid of FIB damage why do we care?” The trivial “because we are scientists” ignores the larger realities of research. Producing a FIB foil requires expensive equipment, dedicated infrastructure, and trained operators. Traditional methods of quantitatively measuring FIB damage are slow and difficult, yielding only a single data point. If several foils yielding useful reliable results can be produced in the same time what reasonable researcher wouldn’t choose to maximize their output at the expense of some uncertainty? Put in such light the scope of the problem becomes obvious, we must gather enough information to generate quantitative estimates of damage, and figure out ways to do so that can be realistically used within the real world constraints.

1.1 Ion Damage Cascades

To understand the physical processes that result in FIB damage requires a closer look at the sputtering process used to remove material. The accelerated Ga ions impact the surface of the material, depositing their energy into the sample and ejecting a portion of
the bulk. The initial stages of ion solid interactions are well described by collision
cascade theory as laid out by P. Sigmund in 1969 [5]. However while the basic processes
of ion solid interactions are well known, it is not yet been described fully from first
principles. The reasons for this are succinctly laid out by Ziegler et al in their book on
SRIM [6] a widely used ion interaction model.” The development of the theory of an ion
slowing in a solid has been difficult because the problem of describing both the ion and
the target is complex. Once the ion penetrates a solid, it is quickly stripped of some of its
electrons, and its charge state becomes a function of the target. The target feels the ion
coming, and its electrons polarize around the moving ion. The charge state of the ion is
modified by the polarized target, which then further affects the target. The merging of the
incident ion’s electrons with the electrons of target atoms causes quantum exclusions of
some available states – a complicated matter which is very important in evaluating
energy transfer from the ion to the target. Finally, all of these effects depend on the
constantly changing ion velocity.” However while a fully first principle explanation of
ion solid interactions is currently out of reach, a wide body of literature has driven
development of empirical Monte Carlo models such as SRIM which often match
experimental data within ten percent.

The collision cascade begins when an energetic ion impinges upon the sample. It
begins to shed energy primarily by inelastic electron cloud interactions and elastic core
interactions, as mentioned above some other effects to contribute, but generally assumed
to be minor [7][6]. The electron cloud interactions lead to the production of secondary
electrons and x-rays. If the energy of the incident ion is above the threshold for
displacement of the target atom (~25 eV) during an elastic core collision the target atom will be knocked free from its lattice position. If the energy of the incident ion is well above the threshold for displacement, i.e. 30 kV for FIB processes, then the target atom knocked free may have enough energy to knock yet more target atoms free, which in turn may continue to knock yet other atoms free. If the energy of the incoming ion is high enough, this set of reactions will cause a cascade of ions creating a wave of outwardly traveling interstitials surrounding a core of vacancies [5]. Some of these ejected interstitials may backscatter out of the material, either coming back to rest on the surface or leaving the sample entirely. The incident ion may also back scatter out of the material, but may often come to rest in the material, creating an implanted atom.
The atom interactions during this phase may be considered primarily ballistic, taking place over the course of picoseconds. This makes MD modeling well suited to deal with the timescales and energies of initial cascade formation, with studies like swift ion track simulations seen in Figure 3 providing good evidence for cascade formation as theorized [8]. Almost all MD simulations such as H. Zhu’s et al [9] work on 10 kV cascades in NiAl support the theory that the majority of defects created during a cascade event recombine to restore the initial lattice within a certain range. Interstitials beyond the recombination range will remain after the majority of the cascade affected area has
reverted back to the original lattice, leaving vacancies behind. The accumulation of these defects during sustained ion bombardment then creates a layer of interstitials and vacancies clustered within the material at a depth dependent on the incident ion energy. However after the initial ballistic stage the displaced atoms rapidly equilibrate to bulk energy levels and the interactions taking place between the resulting damaged lattice, interstitials, and vacancies are limited by diffusion. As diffusion occurs on timescales in measured in seconds or longer atomistic simulations must give way to longer empirically based models such as kinetic Monte Carlo defect simulations [10]. Due to this restraint defect behavior after cascade formation and its contribution to broader consequences of ion damage such as amorphization is limited.

One of the most commonly used models of ion solid interactions is the SRIM/TRIM software, a Monte Carlo program which uses empirically corrected approximations to simulate the stopping of ions in amorphous targets [6]. B.I. Prenitzer et al [11] show that TRIM calculations predict milling differences between most materials to be highest at 80 deg, matching empirical results showing the same dependence [7]. They show that in Si, Cu, Zn, and Al material removal rates match TRIM models to within ~ 10%. They also show that the nuclear stopping power simulations used seem to correlate well to periodic trends in density and melting temp. Calculated sputtering yield appears to be the complete converse of melting temp. However, experimentally Cu sputters ~3.5 times Si, yet the melting point only indicates ~20% weaker bonding, an example of the limitations of the TRIM model.
Figure 4: Calculated plots of atomic stopping power and melting point vs atomic number (Z) by Prenitzer et al [11]
1.2 Silicon Damage

Due to the overwhelming dominance of silicon as a semiconductor material and the prevalence of ion implantation techniques used to create many IC devices silicon ion reactions are among the most studied ion solid interactions. The FIB was initially developed as tool for IC repair and testing, only later being widely adopted by the material science community. As such the vast majority of research on FIB damage focuses on the effect of gallium ions on silicon, research built on a large body of work concerning general silicon ion interactions. To summarize the entirety of the literature in this area would be beyond the scope of this dissertation, so I will be limiting myself to an overview of the damage mechanisms found in silicon and their extension to understanding other systems. However should the reader desire a more in depth review, I recommend L. Pelaz’s [12] review of ion-beam-induced amorphization and recrystallization in silicon.

During FIB milling silicon samples always form an amorphous layer. This amorphous layer acts to screen features of interest, changes conductivity and properties, and reduces the usable cross section in TEM foils. A number of authors have found that the amorphous depth in silicon shows a linear relationship with beam energy over FIB accelerating voltages, the majority of which are displayed in Figure 5. It should be noted however that while a trend is visible the spread in reported values at 30 keV is 15 nm across eight measurements. It seems premature to state that the extent of amorphous damage in silicon has been qualitatively determined based on these numbers. This is
concerning as FIB damage has been most extensively studied in silicon, and most estimates of amorphous layer thickness derive from this data set.

![Diagram](https://via.placeholder.com/150)

Figure 5: Reported amorphous layer thickness in FIB-prepared silicon samples. Data taken from various authors [3,13–26].

While the depth of amorphous formation during FIB prep has been found to be moderately consistent across multiple studies, the mechanism of amorphous formation is still debated. The onset of amorphization is sudden for light ions, occurring over a narrow range of fluence before saturating. Increasing the fluence beyond this level results only in growth of the amorphous region into nearby crystal. The critical dose goes down with increasing ion mass. The critical dose goes up with temp and ion mass, this is considered
a result of competition between damage recovery and defect accumulation. Low mass ions have a limited range, while heavy ions do not, and may directly form pockets of amorphous damage. Due to these factors small shifts in temperature, dose, and ion species may have a large effect on the degree of amorphization.

When considering the mechanisms of FIB damage it is important to remember that while the amorphous damage in silicon is the most obvious and deleterious result in regards to imaging, it is not the only result of ion bombardment. Amorphous material only comprises a portion of the damage produced during ion irradiation. As R. Schreutelkamp et al [13] demonstrated ion cascades cause a large amount of crystalline defects, which may lead to dislocations. G. Spoldi et al explored the extent of those crystalline defects using scanning spreading resistance microscopy (SSRM) and scanning capacitance microscopy (SCM) to measure changes in conductivity in Si exposed to normal 30 kV gallium ions at different doses [14]. As conductivity in silicon is heavily dependent on defect concentration this allows for precise measurements of damage. They found that SSRM and SCM results agreed to show that defects extend well beyond the amorphous sidewall layer detected by AFM. The degree and extent of these crystalline defects has not been studied in cross sectional TEM studies of FIB damage.
1.3 Ion Sample Interactions in the FIB

1.3.1 Ion Damage during Platinum Deposition

Depositing platinum is accomplished by flooding the needed area with an organometallic platinum precursor Methylcyclopentadienyl trimethyl platinum, (MeCp)PtMe₃. The ion beam is then rastered over the area of interest, breaking down the precursor and depositing a layer of platinum, gallium and carbon. T.Tao et al [15] reported that the highest content of platinum is obtained at high beam currents, peaking at Pt 46%, Ga 28%, C 24%, and O 2% at a beam current of 78 pA. The high levels of carbon in the deposited platinum may possibly migrate during high energy electron bombardment in the TEM and should be considered as a possible source of contamination. During deposition the ion beam is rastered normal to the surface, and not all incoming ions are adsorbed by the precursor, allowing some to interact with the material, resulting in damage cascades. The result is a layer of ion damage and implantation under the platinum layer laid down in order to protect the sample. S. Rubanov [16] investigated the effect of gold coating to protect the surface of AlAs-InAs thin films sensitive to surface damage. Although SRIM calculations predict that the penetration depth of Ga in Au should be 15 nm areas at and above this thickness showed disorder and loss of super lattice spots indicating ion induced mixing. They report 60 nm of gold was required to stop any damage from forming during Pt deposition. They theorize that the vacuum sputtered gold may be more porous than bulk gold, allowing deeper penetration of incident ions.
1.3.2 Ion Damage Effect on Properties

The potential for FIB processing to affect mechanical properties is addressed by S. Shim et al during their investigation of Mo alloy micropillars. They found as grown Mo alloy single crystal micropillars tested in compression approach the theoretical yield stress. However the failure stress of FIB produced Mo alloy single crystal micropillars was an order of magnitude lower, as well as exhibiting strain hardening behavior and localized failure at the tip vs. the catastrophic collapse observed in as grown micropillars [Figure 6]. They also compared the FIB pillars to 4% and 8% pre-strained as grown pillars, which showed similar behavior but higher average yield strength than the FIB produced pillars.

Figure 6: Stress strain curves of as grown Mo single crystal micro pillars vs FIB processed micropillars by Shim et al [48]
S. Shim et al also used microhardness tests on a single crystal Mo sample exposed to 30 kV Gallium ions at a normal and glancing angle and compared the results to results from electropolishing. They found that while the electro polished surface exhibited elastic behavior up till a “pop in” effect consistent with onset of dislocation nucleation; the FIB affected surfaces showed no pop in and rapidly deviated from elastic behavior. Hardness in the FIB surface normal to the ion beam almost doubled the electropolished hardness, while areas exposed at a glancing angle only showed a hardness increase of ~28%. S. Shim et al clearly demonstrate that FIB processing has a dramatic effect on the mechanical properties, “either introduces dislocations or creates other defects that dramatically reduce the stresses need for dislocation nucleation” [17]. This result is echoed by Kiener et al [18] who found that models of FIB Cu micro pillars with 50 nm of amorphous damage predict large effects on properties, and question the applicability of FIB processed micro-compression tests. It should be noted that they did not find the degradation of micro compression tests solely due to decreases in strength, their models project that SSS, Taylor, or precipitation strengthening could theoretically yield local MPa level stress increases.

1.3.3 Atom Probe

The effect of FIB processing also comes into play when considering atom probe sample production. When K. Thompson et al [19] examined atom probe tips produced using FIB, they found gallium implantation levels of ~12% in silicon needles produced at 30 kV. Analysis shows a penetration depth of ~30-40 nm into the sidewalls [Figure 7].
This result agrees with predictions from TRIM calculations. They did find that a 5 kV cleaning step was sufficient to reduce the apparent levels of gallium implantation to less than 2%. However this result is for the portion of the atom probe remaining after the field stabilized enough for imaging, and the authors estimate the loss during this step to be 20-25 nm based on SEM imaging before and after. While this result definitely shows that gallium implantation takes place in side walls at 30 kV, due to the indeterminate amount of loss it would be premature to specify the amount of reduction due to 5 kV cleaning, as TRIM calculations show the penetration depth for 5 kV to be near or below the amount of material removed during the startup process. It should also be noted that sample preparation techniques play a large part in the degree of gallium implantation. G. Thompson [20] showed that application of a Pt cap during rough milling and allowing the tails of the beam to eat away the Pt cap before testing reduced measured levels of gallium implantation in atom probe needles to less than 2% for 30 kV. However they do not discuss how much material was removed from the sample before imaging.
1.3.4 Damage, Channeling, and Grain Growth in Copper

One limitation of the SRIM model is its assumption of amorphous material, which neglects channeling. J.R. Phillips et al [21] found that channeling in copper materials results in preferential milling. The highest amount of sputtering was found for areas when channeling was lowest i.e. along the <111> direction. In randomly oriented alloys (no 111 texture) the milling followed normal milling parameters with tilt. Similarly J. Casey et al found that single crystal Cu milled preferentially for different orientations [22] [Figure 8] and was worst along a 110 orientation and had a tendency towards formation of Cu$_3$Ga layers under incident irradiation.
R. Spolenak \textit{et al} [23] showed that the effect of channeling goes beyond penetration depth and sputtering yield, noting growth of channeling grains in fine grained Cu under 30 kV Ga bombardment. Channeling grains grew depending on incident ion direction, by tilting back and forth the experimenters where able to grow and shrink grains by putting them into and out of channeling conditions. They found the same phenomenon in gold specimens. Cross sections showed that growth was limited to \(~100\) nm, the calculated range of effect of ions in Cu and Au under certain assumptions. However TRIM simulations put the penetration depth much shallower, leading the authors to theorize that the interaction distance is extended by growth of channeling regions allowing deeper penetration and thus growth into underlying non channeling grains. The author posits that grain growth occurs because ion interactions with channeling grains results in fewer defects than nearby non channeling grains. This results in channeling grains with lower free energy than the non-channeling orientations with higher concentrations of defects. The authors make no assumptions about alloying effects caused by gallium implantation. Although B. Kempshall \textit{et al} [24] have shown that evening out channeling contrast
between grains by tilting reduced differential sputtering in many cases no such option is available.

In addition to channeling and grain growth issues Kiener et al [18] found that Cu films thinned with Ga ions reveal a damage structure consistent with a dislocation network in two-beam imaging conditions. The networks totally obscured or removed evidence of preexisting defect structures. The authors report 5 kV broad ion milling was insufficient to remove damage caused during 30 kV thinning. They report that their samples did form an amorphous layer, but the layer did not interfere with EBSD patterns, disputing other reports that Cu forms no amorphous layer [25].

Figure 9: Cu grains along border between ion damaged and undamaged regions. (a) Dark field (b-c) Bright field by Kiener et al [49]

1.3.5 General Damage Studies

J. Cairney et al [26] compared electro polished and FIB produced FeAl-WC TEM foils and showed that dislocations seen in FIB samples are not present in electropolished foils. EDX signals from WC areas indicated 4-7% FeAl while areas of FeAl showed
3-8% WC. As tungsten carbide is insoluble in FeAl, the authors attribute this to redeposition noting that such signals varied across the specimen. Separate samples were coated with gold post trenching, retrenched and thinned perpendicular to the original trench, allowing the researchers to get a cross section of the FIB affected surface. In this experiment tungsten was found to make up a large part of an amorphous layer preserved by the gold over FeAl grains. The authors opine this indicates the amorphous layer is not entirely directly damaged material, containing some contribution of redeposited material. They did find that FeAl formed an amorphous layer consistent in thickness with TRIM simulated Ga cascade depths, and postulate that the layer is a combination of ion beam mixing of directly damaged and redeposited material. They also found that low keV cleaning did not reduce the redeposition layer, and postulate that the damage reduction seen in semiconductors is due to a reduction in direct damage. Although they also report that broad beam 5 keV cleaning did not remove dislocations formed during 30 keV steps they do note that cleaning cross sections are known to reduce redeposition and amorphous layer thickness and strongly encourage their use. In addition to a failure to remove dislocations they also found low energy mills had no effect on the thickness of redeposited material.

H. Idrissi et al [27] also address dislocation nucleation during FIB processing of aluminum specimens. His assumption is FIB processing may generate defects and loops which act to pin preexisting dislocations. They did 3D reconstructions of the partial loops and dislocations using a STEM tomographic tilt series. In Figure 10 it can be seen that all
long dislocations are only found in the top orthoslice near the surface which the authors attribute to pinning by FIB induced defects and loops.

Figure 10: Top - STEM tomographic reconstruction of dislocations in Al Bottom - Orthoslices from positions A, B, and C in Top by Idrissi et al [58]

Bals et al [28] examined both SrTiO₃/SrRuO₃ multilayers and NiTi. EDX of the strontium titanate films found Ga content of less than 1% (the detection limit of the system) after 5 keV and 2 keV cleaning steps. They did not show any direct evidence of
amorphization, but claim that any existing amorphous material did not have a noticeable effect on HAADF imaging. In a similar multilayer LaAlO$_3$/SrTiO$_3$ E. Montoya et al [29] reported an amorphous layer thickness of ~5 nm and also reported 5 keV cleaning resulted in clear atomic STEM images. Y. Yabuuchi used a slit milling method to observe sidewall damage in three materials GaAs, Al$_{0.3}$Ga$_{0.7}$As, and Al$_{0.6}$Ga$_{0.4}$As [30]. He reports that amorphous layer thickness has an inverse relationship to aluminum content [Figure 12]. The differences in layer thickness between phases indicates damage layers may not be as uniform as previously assumed.

![Figure 11: Amorphous layer variation in GaAs-Al multilayers by Yabuuchi et al [30]](image)

Selected area diffraction of the NiTi sample revealed amorphous rings in patterns taken near the edge of the sample. Post 5kV and 2 kV cleaning NiTi samples also contained Ga under the 1% detection limit. However before the low keV cleaning steps the authors
detected Ga concentrations as high as 25% along the edge, in areas which also showed strong diffuse rings in SAD.

T Kamino et al [31] examined FIB sample damage using using 40 keV and 10 keV steps on a Mg 9 wt.% Al alloy with tungsten cap rather than platinum protective cap. Using Monte Carlo simulations the author’s estimated Ga implantation at 40 keV and 10 keV should be approximately 2 and 4 percent respectively, which they claim matched their EDS results. They conclude that 10 keV is sufficient to totally remove FIB generated point defects, which they claim are responsible for black dot damage and extra diffraction features/spots. However their HRTEM images show a fair amount of mottling in contrast after 10 kV indicating residual defects, and the authors do not address the possibility of amorphous damage.

J. Yu et al [32] examined ex-situ lift out foils of Ti-added IF steel cut and thinned using 30 keV Ga ions. They found a distinct increase in Ga in areas which had been undercut at the bottom after thinning, with Ga EDS spectra showing almost 20 mol% Ga, while areas away from the edge/bottom showed only ~2 mol%. The bottom of the foil also showed a distinct damage region characterized by dark dot contrast. SAD of the area revealed extra diffraction spots consistent with the intermetallic FeGa₃, a result which seems consistent with previous work showing formation of Cu₃Ga [22] in copper. However it should again be noted that FIB technique may have a large effect on the final sample. With the ex-situ technique used by the authors a good deal of material at the bottom of the sample is left in place, were as the in-situ technique removes much of the material exposed to the incident undercutting beam during thinning.
C. Hutchinson et al [33] compared electropolished Cu-Ti TEM foils with FIB foils produced at 30 keV. They found that the gallium beam caused no compositional variation or mixing between Cu-rich FCC and Cu₄Ti areas. They report a significant increase in dislocation density in the FIB processed foils relative to the electropolished samples. Z. Tong et al [34] used cross sectional techniques to examine normal incidence damage in FIB sharpened single crystal diamond used for nanomachining. They reported amorphous layer depths of 11.5, 19.4, and 27.6 nm for accelerating voltages of 8, 16, and 30 keV respectively. As the damage was measured at normal incidence angles it is expected to be significantly thicker than damage layers produced at glancing angles. S. Rubanov et al [35] confirm the tendency of diamond to amorphize under gallium ion irradiation, and further note a significant degree of expansion during amorphization.
Figure 12: Reported FIB damage layer thicknesses for various materials [3,30,34,36–47]

1.3.6 Effect of Argon Milling on FIB samples

Genc et al [48] showed argon milling increases clarity and resolution of Ti-64 and nickel based super alloys. R.R. Cerchiara et al [49] also reported the same result for Bi$_4$Ti$_3$O$_{12}$, BaTiO$_3$ and SrTiO$_3$. Z. Huang [50] found that low keV argon milling of Cu increased imaging sharpness and contrast, but noted that it also resulted in the formation of dark areas on the sample, which he attributed to Pt and Cu redeposition during argon milling. Unocic et al [51] used STEM and EDX to show that gallium implanted during
FIB processing in aluminum alloys preferentially diffuses to grain boundaries and voids. However they report that sufficient argon milling removed the gallium from those areas. They put forward the hypothesis that the argon milling acts to “wicks” away Ga, however they do not address the possibility of thinning playing a role in decreasing Ga x-ray counts. To date it remains an open issue.

E. Zelaya et al. [52] found that 30 keV gallium milling resulted in the formation of additional FCC diffraction spots around the base BCC patterns in β phase Cu-22.7at.% Zn-12.7at.% Al shape memory alloy. Comparison of EDS spectra showed significant platinum in the cap but no detectable levels in the material, ruling out platinum redeposition. Analysis of the moiré contrast was characteristic of FCC material surrounding a core of BCC material. Samples produced by electropolishing and post low argon milling had no FCC spots in diffraction. The authors put forward the claim that the argon beam does not form FCC due to its lower dosage rate, rather than due to the difference in ion species. They base this on their supposition that the transformation is driven by preferential sputtering of the Zn driving disordering in order to create a free energy change. They do not address the possibility of gallium implantation resulting in structural or chemical changes affecting the free energy, which would not occur for argon milling. They also report that the degree of FCC precipitation varied with crystal orientation, but do not address the possibility of channeling.
1.3.7 Gallium Ion Milling effects on EBSD

R. Williams et al [53] showed that 5 kV gallium cleaning could significantly improve EBSD patterns over samples prepped with 30 keV gallium ions. J Michael et al [11] also reported this effect in silicon. T.L. Matteson et al [25] also reproduced this effect in silicon and copper. They reported that copper does not form an amorphous layer since the redeposited Cu nucleated nearly epitaxially, a result Kiener et al dispute [18]. They found that copper cleaned with 30 kV ions was clean enough to neglect background subtraction, while Si was significantly diffuse at 30 keV, but generated much cleaner patterns post 5 keV cleaning.

1.4 Implications and Plan of Attack

Taken as a whole the literature on FIB damage identifies three major types of artifacts generated during milling, crystalline defects, amorphous material, and redeposition products. All artifacts are generated in a thin surface layer corresponding to the cascade size created by incoming gallium ions. In a standard thin foil configuration these layers are oriented perpendicular to the electron transparent dimension [Figure 13]. Stage tilt restrictions and a relative width of several microns preclude directly measuring layer thickness in the TEM. Standard two-beam diffraction techniques may be used to identify the presence of crystalline damage in the form of dislocations, and their location in the foil partially identified using stereo pairs or tomographic reconstructions. However point defects or small clusters below 10 nm are not readily identified using standard TEM imaging techniques. Some scientists hypothesize that such point defects result in an effect
called “black dot” damage, a mottling in contrast found in TEM foils produced by FIB. Redeposition and amorphous layers scatter incoming electrons, reducing lattice clarity, and are only visible when viewed in cross section. This limits direct observation of amorphous layers in TEM foils to the tip of a wedged specimens.

Figure 13: Two possible damage layer configurations at the tip of wedged foils

Figure 14 provides an example of amorphous layers at the tip of wedged Ti-64 foils produced using ions at varying accelerating voltages. The reduction in amorphous layer width at the tip corresponds to decreasing accelerating voltage (Unpublished research courtesy Dr. Robert Williams). A reduction in the “black dot” damage can be seen in the 2 keV and 500 V foils, the 2 keV foil has noticeable contrast mottling across the lattice, in some places obscuring the lattice fringes. The 500 V foil has no significant mottling, indicating reduced accelerating voltage is sufficient to decrease both crystalline and amorphous damage layers. Although the decrease in thickness and increase in lattice clarity is obvious the visible amorphous width does not directly correspond to the layer
thickness. There is no evidence to show that the visible edge damage is a perfect continuation of the damage layer. Figure 13 illustrates two equally likely potential damage layer configurations which could be said to reflect ideal conditions, i.e. no bending due to residual strain or imperfect milling. Should such conditions exist any potential geometrical ideals simply go out the window. Measurements of edge damage simply cannot be qualitatively linked to actual layer thickness without exact knowledge of the tip geometry.
Cross sectioning is a technique developed to allow direct measurement of the damage layer thickness. To start a trench is made in the material to a depth of several microns.
The goal of cross trenching is to preserve the amorphous layer created on the walls of this trench by use of an ex-situ sputtered coating, platinum deposition, or redeposition from a secondary milling operation. Ex-situ coating is the dominant method and requires the sample be removed from the FIB and transferred to an external sputtering machine in order to deposit a protective layer into the trench. The specimen is then put back into the FIB and the now coated trench is backfilled with ion or e-beam deposited platinum. Platinum deposition systems can be used to directly fill in the trench; however this approach does not see much use. The ion beam is not completely adsorbed by the platinum precursor gas, resulting in additional ion damage which skews later measurements. S. Rubanov et al [16] showed that a gold layer of 60 nm is necessary to stop this ion damage, defeating the point of directly using platinum. If e-beam deposition is used the precursor gas breaks down slowly and the platinum layer retains a significant degree of carbon, the resulting layer tends to cause carbon contamination of the TEM. Nearby milling operations may be used to redeposit significant material onto trench wall. The problem with this approach is twofold, as the amorphous layer, base material, and redeposited material are the same it may be difficult to identify the interfaces. Secondly some materials may redeposit epitaxially, as was reported by T.L. Matteson et al [25] who found that copper redeposited in grains oriented a few degrees off the base orientation. My initial experiments with this technique in nickel resulted in similar epitaxial redeposition.

Once the trench wall has been suitably encapsulated the sample is rotated 90° and a platinum strip is deposited across the filled trench. Two trenches are milled to either side
of this strip to create a wedge containing a cross section of the damaged sidewall [Figure 15]. The resulting wedge is then undercut, extracted, and thinned as per normal in-situ lift out techniques. Although effective for materials with thick distinctive amorphous layers, such as silicon, the cross trenching method has several drawbacks. The first is the time needed to make an ex-situ coated cross trenched foil. The coating process adds an entire venting and pumping cycle during which the microscope is not being utilized, as well as the time needed to transport, load, operate, and vent the sputtering machine of choice. The method requires extended trenching and platinum operations, by nature time intensive. In addition the coating layer modifies the damage layer surface and extends across the whole surface, limiting further imaging of the bulk sample. As the damage layer is formed in a confined trench, redeposition artifacts are more likely to form than during on grid thinning. The resulting foil takes 6-8 hours and provides only a single data point. For comparison a skilled FIB user can generate a typical TEM foil in 2-3 hours.
Figure 15: Cross trenching - an initial trench is made and filled with redeposited material, a foil is then removed perpendicular to the initial trench.

The downsides inherent to the cross trenching method result from the steps necessary to capture a damage cross section in foil form. However, the difficulty viewing damage cross sections arises directly from the geometry of a thin foil. The geometrical challenge may be sidestepped through the use of a previously established technique. The FIB is routinely used to produce atom probe needles on the order of 100 nm thick. The resulting needles are symmetric, electron transparent, and may be produced by a variety of different methods [54,55]. Figure 16 shows two published TEM images of atom probe needles with apparent amorphous damage. The damage layers on the sides of the needle are symmetric, with cross sections perpendicular to the beam direction allowing direct measurement. Needles can be produced quickly and require significantly less material than a standard TEM foil.
In order to establish the needle geometry as a potential means of measuring FIB damage layer thickness we need to establish the viability of the method. Although the ion beam orientation is identical during needle and foil preparation the needles radius of curvature raises the possibility of unforeseen effects. The wide body of work on silicon makes it the ideal candidate for a benchmark material. If silicon needles reliably reflect the same degree of damage reported by cross sectional experiments we can assume that the addition of curvature does not severely affect the damage layer generation. Previous radiation work in intermetallics also offers a potential material for testing the proposed mechanisms for damage growth. NiAl has been reported to not amorphize above 90° K using Xe, Ar, or Ni ions up to the MeV range [58]. Evidence of amorphous layer formation in a NiAl needle would provide evidence that gallium induced strain plays a
part in amorphous layer formation. In addition NiAl has a wide range of stable composition, forming Ni$_{Al}$ antisites when nickel rich and V$_{Ni}$ vacancies when aluminum rich. The diffusivity of NiAl is lowest at or near stoichiometry, with a diffusion coefficient of $\sim 10^{-15}$ m$^2$/s at 1000° C and rising to almost $\sim 10^{-13}$ m$^2$/s with four percent deviation in either direction [59]. These variations allow precise control of vacancy and antisite concentration up to several atomic percent, with a corresponding variation in defect mobility. Increasing vacancy concentration supplies more possible sites for recombination, offering a possible mechanism for reducing damage generated during a cascade. Defect mobility has been proposed as a possible factor in determining the extent of damage. Faster diffusion coupled with a vacancy concentration far in excess of normal should have a recognizable effect on the damage formation.
Chapter 2: Experimental

2.1 Arc Melting

Three NiAl samples with compositions of 47/53, 50/50, and 53/47 at% were produced by arc melting in a water cooled copper hearth in an argon atmosphere. The nickel was placed above the aluminum in the hearth to avoid loss of aluminum through arc induced sublimation. The nickel was heated at low arc current until the reaction began, at which point the heat generated melted all remaining material. Once the reaction had completed the arc current was raised significantly to melt the resulting NiAl. A note of caution, the NiAl reaction is among the most exothermic of known intermetallics, if the nickel was heated too quickly the vigorousness of the reaction caused material to splatter out of the hearth. Attempts to create NiAl gradients using an Optomec LENS powdered metal additive system failed due to similar splattering during the build, which resulted in porosity and uneven melting. Once fully melted the NiAl samples were flipped and re-melted five times to ensure full homogeneity. The samples were then encapsulated in quartz tubes in an argon atmosphere. In order to fully equilibrate concentration they were heat treated in a tube furnace at 1205° C for 120 hours then furnace cooled. The stoichiometric composition was later supplied by a single crystal of NiAl with a wet chemistry determined composition of 50.3 at% Ni 49.7 at% Al.
Pure metals were arc melted from pure stock or directly sectioned in the case when large chunks of material where available. Samples were cut using EDM and mounted in conductive Bakelite. Each specimen was polished using 180, 240, 320, 400, 600, and 800 grit silicon carbide paper. With the exception of aluminum, magnesium, and iron each sample was then given a final polish for several hours on a vibratory polisher filled with 0.05 µm colloidal silica. The exceptions were final polished using diamond paste in 8, 5, 3, and 1 µm sizes. Semiconductor samples were FIB milled in as received condition after gold coating. In the case of orientation specific foils each sample was imaged in SEM using backscattered or secondary electron imaging as appropriate, with grain orientation measured via EBSD.

2.2 Needle Preparation

Needle prep begins as a normal insitu lift out method [1]. The sample is tilted to 52° in order to bring the surface perpendicular to the ion beam. The Pt gas needle is inserted and a layer of platinum is deposited using the ion beam to protect and define the sample area during trenching. The Pt gas needle is retracted to avoid secondary deposition from residual gas during trenching. Multiple cleaning cross sections with scan direction moving towards the platinum are placed on either side of the strip, leaving room to account for the large tails of the high current beam. The trenching step is repeated until the trench has reached a desired depth, which varies with both desired sample size and material. Charging of poorly conductive materials is most pronounced during this step, and care must be taken that the pattern does not drift over the platinum cap. Once
trenching is complete the sample is tilted to 7° and three box patterns are placed to cut all but a single tab of material free. Traditional in-situ techniques often leave two tabs, but for the needle work the second tab is obscured by the Omniprobe nanomanipulator needle during attachment, as the needle must be placed in the far corner to maximize the number of needle posts created, and a single tab easily maintains the sample position even in soft materials. Care must be taken during undercutting to fully penetrate the sample wall and to avoid redepositing material in the corners, effectively re-welding the material in place. This redeposition primarily occurs if the initial trench is not deep enough for the sample size attempted. Once fully undercut the Omniprobe needle and Pt gas needle are brought in and the Omniprobe needle attached to the corner opposite the anchoring tab using a small tab of platinum. The Omniprobe needle is not brought fully into contact with the specimen at this point, as the deposited platinum can easily bridge a 1-2 µm gap, this offset is necessary to avoid being forced to cut into the Omniprobe needle when removing it, a step that may lead to excessive milling and possible tungsten contamination. Once the Omniprobe needle is attached the anchoring tab is cut using the ion beam and the resulting slab of material removed from the trench. The Omniprobe needle and Pt gas needle are retracted and the chamber vented in order to prepare for the Omniprobe grid.

The blanks which will become the needles may be put on separate grid posts or even grids if multigrid holders are available. For many experiments, I used a two grid holder to increase the number of potential attachment sites. Two Omniprobe grids were loaded into the holder making sure to maintain the suitable orientation for later attachment.
Cleanliness of the grids is vital to avoid microscope contamination and ensure positive attachment; unfortunately grids may not arrive totally spotless, often having a thick layer of contamination. To avoid this all grids were cleaned using methanol in a 10 minute ultrasonic bath, then air dried. Once loaded in the FIB the posts to be used for attachment are further cleaned using a gallium ion beam current of 21 nA until any visible contamination is removed. The Pt needle and Omniprobe needle are then reinserted and the slab of material brought down to within 1.5-2.5 µm of the tip of the post, with the top aligned with or slightly over the top edge. This positioning is vital to avoiding later loss of the needle during shaping. If the bottom of the slab is brought fully into contact with the grid the deposited Pt may “arch” over the gap leaving a void under what becomes the center of the needle. During shaping the material is milled from both the grid and post, meaning there must be continuous material attaching the needle to the grid. Platinum is deposited into this gap in a 1.5 µm wide tab, once done the Pt should extend slightly above and below the attached slab. The current is then raised and a box pattern used to cut the remaining slab material free, leaving a roughly 1.5 µm × 1.5 µm post suitable for further shaping. Multiple posts may be made from a normal size slab, and for much of the work done here I attached four posts to one grid, and had enough material to place two posts and a ~ 15 µm slab suitable for thinning into a foil on the second grid. This allowed for three needles and a foil, while also allowing one mistake on each grid during shaping. When shaping multiple needles within a hundred microns of each other it is necessary to leave a post between them to avoid redeposition (see Section 3.5). On the grid with four
posts, I would shape one needle at 30 keV and one at 5 keV, then shape one 5 keV needle and a 5 keV foil on the second grid.

Needle milling parameters were determined by placing 11 needle blanks onto one grid and systematically varying current, pattern size, and number of shaping steps. The experimental process window was centered on parameters provided by Dan Huber for milling 30 keV tomography needles. Initial shaping steps smaller than 1.5 µm resulted in over milling during final shaping. Dropping the final shaping diameter below 100 nm resulted in beam tail overlap, resulting in overly conical needles. To produce 5 keV needles required a second milling step to reduce the initial post size to 400 nm. The increased beam spread at 5 keV required increasing the final shaping diameter to 200 nm. Those final parameters used for subsequent experiments are listed in Table 1. Alignment of the column played a large part in needle quality. For the 5 keV needles to turn out correctly it is vital that the column be perfectly aligned with correct stigmation and focus. Failure to properly align both the beam and pattern result in lopsided or ovular needles.
Table 1: Milling Parameters for needles

<table>
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<tr>
<th>Step</th>
<th>Pattern</th>
<th>Dimensions (µm)</th>
<th>Diameter (µm)</th>
<th>Sample Tilt</th>
<th>Current (pA)</th>
<th>Voltage (keV)</th>
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<td></td>
<td>X</td>
<td>Y</td>
<td>Z</td>
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<td>Outer</td>
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<td>0.8</td>
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<td>-</td>
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<tr>
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<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Attaching micromanipulator</td>
<td>Platinum Box</td>
<td>0.4</td>
<td>0.4</td>
<td>2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Attaching post base</td>
<td>Platinum Box</td>
<td>1.5</td>
<td>3</td>
<td>1.25</td>
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<td>-</td>
</tr>
<tr>
<td>Cutting post free of slab</td>
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<td>6</td>
<td>1.25</td>
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<td>-</td>
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<tr>
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<td>-</td>
<td>-</td>
<td>2</td>
<td>1.5</td>
<td>4</td>
</tr>
<tr>
<td>Final 30 keV needle shaping</td>
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<td>-</td>
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</table>

2.3 Measurement

When measuring amorphous layers in needles 10-20 images were taken along both the top and bottom of the needles at a magnification sufficient to reveal necessary detail. Of those four images were selected, two from the top and bottom respectively. The amorphous layer in each of the images was measured four times using a line tool in Digital Micrograph or ImageJ, resulting in a total of 16 measurements per needle. The uncertainty in each measurement was taken to both reflect user error and the degree of interface waviness.
Chapter 3: Imaging – Methods to Measure Amorphous, Crystalline, and Redeposition Damage

Transmission electron microscopy is divided into two main configurations, Conventional TEM (CTEM) utilizing a single static source of illumination and scanning transmission electron microscopy (STEM) which raster’s a focused probe over the sample. Each system configuration can be used to achieve atomic resolution and has unique benefits and drawbacks. TEM is well suited to identifying dislocations and crystal orientations, by condensing the beam and viewing the back focal plane in diffraction mode the user can readily identify orientation using Kikuchi bands formed by inelastic scattering. The sample can then be tilted into either two beam or weak beam diffraction conditions and the beam expanded to a parallel condition. In combination with an objective aperture this configuration results in diffraction contrast from strongly bent planes near the dislocations, allowing identification of the dislocation orientation and burgers vector. When the beam is oriented down or near a zone axis the atomic columns may be imaged by means of lattice fringes formed by phase contrast. However, the positions of the lattice fringes may or may not indicate the actual location of atomic columns in the material. The lattice fringing is strongly affected by aberrations and contrast reversals induced by the magnetic lenses used to form the beam. These
aberrations may be controlled through use of an image corrector, allowing uniform imaging. However, even with an image corrected system, image simulations are needed in order to quantify atomic position.

STEM imaging allows for quantifiable atomic resolution imaging. In high resolution systems the electron beam is focused down to sub angstrom sizes and rastered over the sample. As the probe size is less than most atomic spacing, signal peaks when the beam is placed over an atomic column and drops over the gap between atoms. Signal can be collected using a variety of detectors, including a high angle annular detector (HAADF) which is sensitive to atomic weight. The X-rays generated during imaging may be measured using an EDS detector, allowing mapping of chemical composition at each point on the sample. Although the sample can still be oriented into diffraction condition’s the converged nature of the beam complicates analysis. STEM imaging is also quite sensitive to amorphous layer formation. Amorphous layers scatter the focused probe, decreasing clarity and reducing the effective resolution. Both TEM and STEM imaging systems are commonly used in material science and engineering, and many systems have the ability to switch back and forth between each imaging mode. In order to properly evaluate the effects damage layers have on characterization efforts it is vital we examine their effects in both imaging modes.

3.1 Imaging with HAADF-STEM

Initial imaging of silicon needles using HAADF-STEM showed no amorphous damage. However when the needle was oriented on the zone axis the amorphous layer
contrast drastically increased [Figure 17]. Tilting only half a degree off zone resulted in a significant drop in contrast. When oriented off zone the beam is scattered by both the amorphous layer and the atomic columns. When oriented on zone the intensity is increased on the columns, while the amorphous layer continues to scatter the beam. This behavior indicates that the difficulty of doing a tomographic reconstruction of the amorphous layer in STEM would be extremely high.

![Figure 17: 30 kV silicon needle viewed off and on zone axis orientation in HAADF-STEM](image)

Figure 17 shows a high magnification view of the amorphous layer when viewed down zone. The interface between the amorphous layer and crystalline layer is diffuse and the contrast in the amorphous layer drops off rapidly with the needle curvature. Signal intensity drops with thickness as less material scatters electrons to the HAADF detector. This makes determination of the amorphous layer thickness in HAADF-STEM
questionable at best. Figure 19 shows the same contrast drop in a NiAl 47/53 needle.

What appears to be an amorphous layer is almost invisible in the as imaged condition, however if the contrast and brightness are adjusted it becomes apparent that the layer is thicker than it appears in the first image.

Figure 18: 30 kV silicon damage layer in HAADF-STEM viewed on zone axis
Figure 19: 30 keV NiAl 47-53 damage layers viewed on zone axis in HAADF-STEM. Left: Unadjusted image. Right: Brightness +20%, contrast -40%, note increased visibility of damage layer.

Despite the contrast issues it is readily apparent in Figure 20 that there is no difference in the damage layer thickness between NiAl alloys with 3 at% deviation from stoichiometry. However, upon closer examination it becomes clear that while the damage layers are the same thickness, the lattice clarity decreases in the 47/53 alloy. Figure 21 shows FFT’s taken from the crystalline region of each alloy. Spots corresponding to the lattice are clearly visible in the 53/47 FFT, indicating a strong degree of periodicity. The same spots in the 47/53 alloy FFT are barely visible, and close examination of the image reveals hard to distinguish lattice.
Figure 20: HAADF-STEM images of NiAl alloys milled at 30 keV, no visible difference in damage layer width

Figure 21: Clarity differences in NiAl alloys viewed using HAADF-STEM. FFT patterns indicate less distinct lattice points in aluminum rich NiAl 47-53
The Titan 60-300kV system used to images for this study is equipped with a Chemistem™ EDS system equipped with four silicon drift detectors. This system allowed rapid collection of x-ray signals at high count rates. When used in STEM mode the x-ray signal from each point in the scan pattern can be collected to form composition maps. Although many reports on silicon damage indicate gallium levels below the detection range of 1-2% some reports have indicated levels as high as 5-10% in the side wall layers [20]. Figure 22 shows raw gallium EDS signals from a 20 minute map of the silicon needle, after quantification the relative level of gallium signal is barely detectable. Signal across the entire needle indicated an atomic concentration of 0.46%, signal solely from the amorphous layer indicated a level of 0.94 at%. The silicon oxide level identified as 69% oxygen and 30.5% silicon, reasonably close to the expected 2:1 ratio. Gallium levels are elevated several percent in the platinum layer, along with significant silicon and oxygen peaks indicating that a large degree of mixing takes place during the deposition process. The level of gallium in NiAl needles conversely did not show detectable gallium peaks. From this we can conclude that gallium implantation in the sidewalls appears to be limited, and can safely be assumed to be less than 1%.
Figure 22: Raw gallium counts collected during EDS mapping of a silicon needle produced at 30 keV

3.2 Imaging with HRTEM

The issues with determining interface position in HAADF-STEM disappeared when using HRTEM. In Figure 23 the damage layer in silicon milled at 30 keV is plainly visible. The layer is clearly amorphous and both the surface and interface can be readily distinguished. The wavy nature of the interface hinted at in HAADF-STEM is obvious and the lattice can clearly tracked up to the interface rather than fading to invisibility. Although the lattice fringing visible in the crystalline region may not directly map to lattice positions the clear transition to the amorphous damage layer allows accurate measurement. The lack of contrast reversals and Fresnel fringing at the edge of the sample at high resolution is due to the use of the image corrector. Figure 24 shows an example of NiAl imaged using an uncorrected Titan microscope, increased fringing and ghost images are visible both in and beyond the specimen. Although the damage layer is still apparent the uncertainty introduced by these effects make the image corrected system the more suitable choice for quantitative measurements.
Figure 23: Edge of silicon needle milled at 30 keV, amorphous layer boundaries are clearly visible
When the NiAl was imaged in HRTEM the damage layer thickness in all three compositions once again appeared the same thickness [Figure 25]. However unlike silicon the damage layers did not appear to be fully amorphous. Figure 26 contains FFT’s taken from the crystalline regions of the needle and the damage layer. Unlike the HAADF-STEM images no strong difference exists between the crystalline patterns from the off stoichiometric samples. The FFT’s from the damage layer do have some diffuse haloing suggestive of a loss of order, but contain multiple spots indicating the presence of a significant degree of periodicity. This result is in agreement with previous literature indicating NiAl does not readily amorphize at room temperature. However a disrupted region of 3.3 nm is apparent, and does not show any apparent differences which could potentially explain the clarity issue in HAADF-STEM. As the difference observed in
HAADF-STEM does not appear to be a result of this layer it seems likely that another factor is causing the difference in clarity.

Figure 25: 30 kV NiAl needles viewed in HRTEM, damage layer thickness is equal over composition range.
3.3 Using advanced techniques to image crystalline defects

TEM imaging methods for characterizing crystalline defects such as dislocations, loops, and clusters of vacancies or interstitials rely on the presence of localized strain fields surrounding discontinuities in the lattice. The crystal is oriented such that the beam is in a strong diffraction condition in which a single plane is in Bragg condition (ideally). When an objective aperture is inserted regions of high local strain deflect the beam in such a way as to create contrast changes in the area of the defect. There are three general
ways such diffraction conditions are set up, dynamical two-beam, kinematical two-beam, and weak-beam conditions. In the dynamical two-beam condition the foil is tilted to bring one set of planes into a Bragg condition [Figure 27]. The objective aperture is placed around the transmitted disk to create a bright field image. If a dark field image is required the diffracted spot is tilted into the optical axis using the beam tilt coils and the objective aperture centered on the diffracted spot. In dynamical two beam conditions there is a strong interaction between the two primary Bloch waves. If small centers of strain such as precipitates or small loops exist near the surface of the foil anomalous adsorption between the two waves may lead to black white contrast lobes which vary with orientation, depth, and size [60].
Kinametical two-beam conditions are initially set up in the same way as dynamical two-beam conditions. Once the crystal is oriented into a Bragg condition the specimen is slightly tilted, generally introducing a slightly positive deviation $s_g$ [Figure 28]. Tilting away from a perfect Bragg condition reduces dynamical effects between the two beams and minimizes anamalous adsorption [60,61]. This has the effect of shrinking the region of contrast, creating finer contrast features closer to the defects. The localized nature, increased contrast, and lack of complex dynamical effects makes this configuration popular for imaging dislocations and large loops.
Figure 28: Kinematical two-beam in NiAl, note superlattice spots and orientation of diffraction spots with s+ deviation

Weak beam imaging is done by putting the objective aperture around a weakly excited reflection. The bulk of the crystal planes are oriented well away from a strong Bragg condition, leading to low overall intensity. If high strain exists close to defects in the material crystal planes may be bent into a diffracting condition. The result is a strong rise in intensity very close to the defects. The extremely localized intensity and strong contrast makes weak beam imaging particularly well suited for imaging small defects. The technique has been successfully used to characterize loops with diameters as small as 8 nm [60]. Some authors have estimated that this limit may be lowered to 5 nm with the use of image corrected microscopes.

Initial defect imaging in NiAl was done using an uncorrected CM-200 microscope. The needles where tilted to a (002) zone axis and kinematical two-beam conditions set up at various g vectors around the zone. When viewed in this manner several differences
between the various compositions become visible [Figure 29]. The NiAl 47-53 composition features thickness fringes and nanoscale streaking in the \(<110>\) directions. The 50-50 composition appears to have a large proportion of loops clustered at the edge of the needle and a lack of readily apparent thickness fringes. The NiAl 53-47 composition has fairly uniform black dot contrast and also lacks readily apparent thickness fringes. Although these images indicate a variation in the type of crystalline defects with composition, it does not prove that the defects are a result of FIB milling. To determine if the defects are intrinsic or developed during milling requires a way to confirm defect position. The simulated penetration depth of 30 kV gallium ions in NiAl is roughly 30 nm using SRIM models. If the visible defects were limited to the surface of a 100 nm dia. needle we can safely assume they are generated during milling rather than intrinsic. Unlike amorphous layers crystalline damage is dispersed throughout the material, and does not form a continuous layer with different phase contrast. Instead defects should form a cloud throughout the ion interaction volume symmetrically surrounding the needle. As the image is a projection these defects will be uniformly projected down, resulting in an apparently uniform distribution across the needle surface.
Figure 29: Kinematical two-beam conditions. Top: <110> streaking and visible thickness fringes. Middle: Loops clustered along sides of needles. Bottom: Uniform black dot contrast (contrast adjusted for clarity)
This projection effect may be avoided by using a stereo pair technique. The crystal is tilted into kinematical diffraction condition and imaged. The sample is then tilted several degrees, usually 8-10°, while maintaining the same diffraction vector. The sample is then reimagined. This introduces a parallax shift between the two images. Using a stereo pair viewer to project each image into a different eye creates a 3D projection. This allows the determination of the depth of defects in the needle. Figure 30 shows an example of a stereo pair taken of a 5 keV NiAl 53-47 needle. Examination of several stereo pairs of both needles and foils determined that the bulk of features do in fact exist in a shell surrounding the needle.
Figure 30: Stereo pair of NiAl 53-47 milled at 5 keV at 8° tilt
Once the defects were determined to be milling artifacts the question became what type of artifacts are they? With the exception on NiAl 47-53 the alloys all appear to have numerous loops. As both interstitial and vacancies are generated during the cascade process these loops have the potential to form both intrinsic and extrinsic loops. The resulting loops should only form on favorable slip planes. Dislocations in NiAl prefer edge dislocations with a slip direction of $a <100>$ rather than the expected $\frac{1}{2} <111>$ due to the heavy energy penalty for displacements which result in APB’s. However determining the burgers vector of the loops proved impossible with kinematical two beam techniques. Although the extent of crystalline damage was reduced heavily by using 5 keV ions the density of defects remained high. The small size of the loops and high density combined to make isolation of a single defect difficult. When a defect could be successfully followed the small sizes of the loops resulted in hard to interpret contrast conditions. In addition the highly sloped needles resulted in thickness fringes when viewed in two beam diffraction conditions [Figure 31]. To avoid possible issues raised by these contrast reversals thin foils were prepared of NiAl 50-50.
Figure 31: 30 keV NiAl 50-50 needle showing thickness fringing

Figure 32 shows one such foil prepared at 30 keV in several different imaging conditions including dynamical two-beam and weak-beam. Initially dynamical two-beam appeared particularly well suited for identifying FIB induced loops, as the defects were close to the surface and had large strain fields. However the defect density again caused issues. Few defects generated firmly identifiable black white lobe contrast, and others could not be reliably tracked when tilting to new g vectors. Defects appeared either as small loops or simple black dots as small as 3-5 nm. Weak-beam imaging conditions did result in a tightening of features and increased contrast; however the density of defects once again prevented accurate tracking of individual features. 5 keV cleaning steps did decrease the
size of the features, but did not decrease density to a tractable level [Figure 33]. This result makes sense when considering the high ion fluence in FIB vs previous radiation studies. Sputtering efficiency in the FIB is in the range of 5-12%, it follows that every atom within average cascade depth of the surface will have been disrupted several times. Even in the case of a strongly reconstructing material, this is likely to induce a large number of interstitials and vacancies. It follows that the density of crystalline defects should be much higher than neutron studies, which often have DPA’s of well below one.
Figure 32: Small loops/defect clusters in 30 keV NiAl 50-50 foil viewed in various imaging conditions.
Although the exact nature of defects was not established the experiments provide valuable insight into the mechanisms of FIB damage. The sheer density of defects indicates significant disruption within the cascade penetration depth. Should the layer damaged in such a manner not amorphize, as in the case of silicon, the remaining material is likely to have a significant number of crystalline defects which will take a form dependent on the material in question. Aluminum has high defect mobility, self-annealing at room temperature at high purities. It seems likely that the dislocation nucleation reported by Idrissi et al [27] was a result of similar amounts of defects being free to agglomerate and form dislocations, lowering the free energy of the crystal.
comparison defect mobility and diffusion is much lower in NiAl, making it more likely that defects generated during milling are “frozen” in place, forming the cloud of small features seen above. This is supported by experiments done using the focused 300 keV beam in the TEM to expose the NiAl to 2 nA of current over a region 100 nm in diameter. The material exposed to this level of current showed a slight contrast changes, but no migration or agglomeration of defects over exposures of several minutes.

### 3.4 Electron Beam Effects on Damage Layers

When attempting to characterize small defects using high voltage (S)TEM care must be taken to account for electron beam induced defects. The Titan microscopes used to do the majority of the imaging in these studies run at 300 keV. At this voltage additional point defects may be generated in metals due to electron knock on damage. In STEM in particular the high current density can easily begin to mill away material if the focused probe is left in place for more than a few moments, in some cases fully penetrating a foil creating holes. In more sensitive or weakly bonded materials the energy deposited by the beam may induce state changes, fundamentally altering the material being viewed. The energy deposited has also been shown to enhance defect mobility, providing enough energy to allow conglomeration of point defects into dislocations.

The tendency of electron beams to recrystallize amorphous regions in silicon was reported by Jencic et al [62], who reported the process activated at 50 keV and occurred along the crystalline to amorphous interface. This phenomenon was observed during STEM-EDS mapping of the amorphous layer in a 30 keV cross trenched foil. In Figure
recrystallization moving outward from the original interface is clearly visible. The effect happened quickly enough that the boundary noticeably moved after viewing for several minutes. Although prominent in STEM the recrystallization behavior was not apparent when viewing needles in TEM, and could be largely avoided in STEM by using lower current densities.

Figure 34: Recrystallization in silicon cross trenched foil after EDS scan in STEM

Recrystallization of the damage layer in NiAl was also observed during TEM imaging. Areas imaged for longer periods of time appeared to be more crystalline than unviewed sections of the needles. In order to test this ~2 nA beam was condensed to roughly 20 nm across to maximize beam damage and a series of images taken at 5 second intervals. Figure 35 shows one area tested before and after ~40 seconds of exposure. The layer in the beam has noticeably recrystallized into several large grains and a degree of reordering
is obvious in the crystalline region. After 2 minutes the damage layer in the illuminated area had disappeared entirely and the previously crystalline region was noticeably altered.

Figure 35: Recrystallization along needle edge in 30 keV NiAl 53-47 when viewed at 2 nA and 300 keV

Counter intuitively the beam damage in NiAl also led to growth of the damage layer. Figure 36 shows a NiAl 53-47 needle before and after imaging in TEM mode for roughly 20 minutes with a beam current of ~2 nA (uncorrected images). The damage layer has visibly grown several nm. This casts a certain degree of doubt on the accuracy of damage layer measurements and the true degree of ordering in the layers post FIB. In order to avoid these effects all imaging was done in TEM first and as quickly as possible to minimize the possibility of growth or recrystallization. However even with these precautions some degree of layer modification seems likely, and could account for some discrepancies in the data.
In an attempt to identify crystalline defects during weak-beam imaging, I deliberately damaged the surface of the foil using a condensed beam. The idea was to deliberately induce conglomeration and growth of the defects into features large enough to image properly. Figure 37 shows the effect focusing a ~2 nA beam down to ~75 nm for 20 minutes had on defects formed during 5 keV milling of NiAl 50-50. Intensity of the defects in the affected region does rise relative to the background, however careful comparison before and after indicates little to no change in the size or position of the features. Contrast appeared to peak relatively quickly (~5 min) then settle down with little further change.
3.5 Redeposition Experiment

Early experiments with multiple needles were often hampered by redeposition buildup on adjacent needles. In one initial experiment two silicon needles milled 11 µm apart resulted in 45 nm of redeposition on first needle. If you assume that material is sputtered equally radially then the amount of redeposition deposited on a needle some distance R away should be proportional to the degree of the sputtered needle subtended by the degree of arc the diameter of the second needle makes in a circle of radius R. Thus yield should be proportional to some constant times a power law. In order to test this assumption four needle post blanks where placed on a grid 4, 8, and 16 µm apart [Figure 38]. Each needle was shaped down to 1.5 µm in diameter before final shaping, which accounts for the discrepancy in redeposition thickness between this experiment and the noted example. Each needle was then shaped to final dimensions using a 2 µm ·
100 nm annular pattern as described in Section 2.2. The needles were shaped from the left to right. The actual measured distance tip to tip in the TEM ended up 4.2, 8.5, and 16.1 µm. The degree of redeposition is visible in Figure 39, and noticeably drops as the distance between needles increases. When a curve was fitted to the data the best fit was a power law as expected. EDS line scans across the needles indicated the redeposition layer had large amounts of gallium, platinum, and oxygen. This indicates a significant portion of redeposited material originates from the protective platinum cap and oxide layer. The high levels of gallium could account for reports of elevated gallium levels by previous authors.

Figure 38: Redeposition experimental needles in FIB post shaping
Figure 39: Redeposition layers on silicon needles, distances indicate spacing of needles.

Figure 40: Line scan across the redeposition layer
Historically the rule of thumb applied to FIB damage was to expect roughly one nm of amorphous damage per keV based on silicon experimental results. SRIM simulations of gallium penetration depth in metal alloys like Ti-64 largely matched this result, and studies of amorphous edge damage [Figure 14] appeared to fit the data moderately well. Yet the large differences in visible damage layer thickness between silicon and NiAl raises questions about this assumption. Either the results are anomalous or FIB damage is more variable than previously thought. Without further measurements in other materials no long term trends can be identified. In order to lay the question to rest needles were made in a variety of materials, including semiconductors, pure metals, intermetallics, and alloys of various complexity. A wide variety of physical parameters was collected including diffusivities, defect energies, enthalpies, crystal structure, cohesive energy, and oxidation states in order to find any correlations with damage layer thickness.

4.1 Semiconductors

Initial measurements started with silicon, a covalently bonded material with a diamond cubic structure known for forming a fairly stable amorphous layer. The damage layers at 30 keV averaged 23.94 nm and 5 keV at 6.6 nm [Figure 41], results which matched previously reported values. The damage layers under both conditions were fully
amorphous, as indicated by FFT images taken from both the crystalline regions and damage layer [Figure 42].

Figure 41: Si amorphous layers in needles milled at 30 and 5 keV

Figure 42: FFT patterns taken from a silicon needle milled at 30 keV. Right: Crystalline region. Left: Amorphous layer.
The damage layers in germanium had amorphous layer thicknesses just under those found in silicon, a semiconductor with similar bonding and properties. 30 keV needles averaged 22.9 nm of damage and 5 keV needles 5.9 nm [Figure 43]. Germanium has an FCC crystal structure, indicating that the shift from diamond cubic to FCC does not strongly affect damage layer width. In addition, the wavy appearance of the crystalline interface and smooth surface matched silicon results.

![Figure 43: Ge amorphous layers in needles milled at 30 keV and 5 keV](image)

Amorphous layers in gallium arsenide however appeared noticeably smaller, with a thickness of 16.7 nm at 30 keV and 2.8 nm at 5 keV [Figure 44]. These results are essentially identical to the amorphous layer thicknesses reported by Y. Yabuuchi [30]. Although the layer itself appeared thinner the interface and surface appearance matched well to silicon.
In contrast to the covalently bonded semiconductors Si, Ge, and GaAs, SrTiO$_3$ has mixed covalent and ionic bonding properties, forming a perovskite structure. The mix of bonding types did not appear to affect the structure of the damage layer, which again appeared fully amorphous with a wavy crystalline interface. Damage layer thickness was noticeably smaller than Si or Ge, with values of 14 nm at 30 keV and 1.8 nm at 5 keV [Figure 45].
Diamond posed several issues while milling, default needle pattern and currents were essentially ineffective. In order to successfully create a needle the current needed to be tripled and the inner annulus increased to 300 nm to account for beam tails at 30 keV. Milling at 5 keV faced similar issues, but was more strongly affected by diamonds tendency to terrace while milling. Due to these difficulties the damage layers displayed in Figure 46 should be taken independently from the rest of the needles displayed, as they were generated under drastically different beam conditions. The results however do indicate similar trends to the rest of the semiconductors. At 30 keV the damage layer appears fully amorphous with a thickness of 14.17 nm, while the thickness at 5 keV appeared minimal or nonexistent. This result is in stark contrast to the amorphous layer thicknesses reported in diamond by Z. Tong et al [34] who reported amorphous layers of
27.6 nm at 30 keV. The discrepancy is likely due to incidence angle, the layers reported by Z. Tong were produced at normal incidence, rather than glancing.

Figure 46: Diamond amorphous layers in needles milled at 30 and 5 keV

Figure 47 shows the variation in amorphous layer thickness with accelerating voltage for the five semiconductors imaged. Although the width of the damage layers varies between materials the slope of the change between 30 and 5 keV is remarkably similar. Also notable is the similarity between damage layers in each material. Each contains a wavy crystalline to amorphous interface and fairly smooth surface. This has two major implications for modelers simulating (S)TEM electron interactions in these materials. The first is a validation of the assumption that FIB milling generates planar surfaces in thin foils. The second is the assumption of a uniformly thick crystalline region is wrong, although the variation is limited to roughly +/- 1 nm and may not have a large effect. The
large variation between Si and diamond, both diamond cubic materials, and the similarity between Si and Ge, indicate that crystal structure is unlikely to play a significant role in determining damage layer thickness. The results also indicate that in semiconductors Si and Ge appear to be worst case scenarios from the perspective of amorphous damage.

Figure 47: Semiconductor damage layer thickness versus accelerating voltage

4.2 Pure Metals

Amorphization in metals is well known to be difficult, with recrystallization occurring at both low temperatures and high cooling rates. Pure metals are not known to form amorphous layers under irradiation conditions [63]. The addition of alloying elements is
required to achieve amorphization. Although previous EDS results in NiAl and Si indicate that gallium implantation levels remain low in FIB sidewall damage the potential does exist that small degrees of implantation might make amorphous layer formation more favorable. Should gallium implantation have an effect it seems most likely it would be significant in aluminum. Gallium is particularly soluble in aluminum, diffusing rapidly along grain boundaries at room temperature leading to embrittlement. K. Unocic et al [51] reported significant gallium enrichment in several aluminum alloy TEM foils milled using a FIB. The gallium concentration peaked in micro voids and along grain boundaries, although they report that an argon ion milling step at low voltage appeared to “wick” material away from these regions. The damage layers in needles of pure aluminum appear fully amorphous, with an average thickness of 2.1 nm [Figure 48]. Interestingly EDS scans of the edge resulted in less gallium signal than NiAl, a result confirmed by EDS scans of Al 7075 needles. It appears that despite aluminum’s affinity for gallium no excess mixing appears to occur in the sidewalls during milling. Each needle was extracted from a single grain, so there were no grain boundaries or voids to act as sinks for excess gallium. This may provide support for Unicoc et al.’s argument that the observed gallium enrichment was a surface dominated phenomenon. However the aluminum layer appeared extremely beam sensitive, after a few minutes in TEM the damage layer had almost entirely disappeared. As beam density is much higher in STEM the layer may have been removed before sufficient x-ray signal was collected, and an excess amount of gallium simply missed.
The damage layers in iron needles milled at 30 keV were roughly double the thickness found in aluminum needles, measuring on average 3.7 nm. In contrast to aluminum the damage layer in iron had a large degree of order. FFT patterns taken from the layer indicate significant periodicity. This order may have been the cause of intermittent moiré patterns visible over the crystalline region of the needle.
Figure 49: Fe damage layers in needle milled at 30 keV. FFT patterns from crystalline and damage regions

Figure 50 depicts damage layers in cobalt with average thicknesses of 1.3 nm at 30 keV and 3 nm at 5 keV. FFT’s taken from the damage layer indicate a high degree of periodicity which does not match the pattern pulled from the crystalline region [Figure 51]. In addition a strong moiré effect can be seen throughout the 30 keV needle, indicating a strongly diffracting crystalline layer.
Figure 50: Co damage layers in needles milled at 30 and 5 keV

Figure 51: FFT patterns taken from a cobalt needle milled at 30 keV. Right: Crystalline region. Left: Damage layer

Damage layers in chromium needles were minimal, on average 1.3 nm for 30 keV and 1.8 nm for 5 keV conditions [Figure 52]. FFT patterns taken from the damage layer again indicates a strong degree of periodicity which does not match patterns taken from the crystalline region [Figure 53]. However the strong moiré effects seen in cobalt are absent.
Copper needles milled at 30 keV have a number of what appears to be randomly oriented moiré patterns. The damage layers averaged 1.92 nm at 30 keV and 2.8 nm at 5 keV [Figure 54] and created FFT patterns indicating a partially amorphous layer with
some spots indicating a degree of periodicity. The presence of a damage layer is interesting, as Matteson et al [25] reported that copper redeposited epitaxially on a FIB milled surface, using it as evidence that copper did not form amorphous layers which would affect EBSD imaging. As the redeposition in question was done without removing the sample from the FIB this raises a question. If the in FIB copper surface was clean enough for epitaxial redeposition, yet needles contain a measurable layer, what accounts for the difference? The most likely possibility is that an oxide surface formed during storage and transportation to the TEM.

Figure 54: Cu damage layers in needles milled at 30 and 5 keV
Magnesium needles had a significant degree of damage in comparison to other metals. The average damage thickness at 30 kV was 4.77 nm and 4.61 nm at 5 keV [Figure 56], the highest of all the pure metals examined in this study. The damage layer in magnesium appeared to very crystalline, FFT patterns [Figure 57] of the layer indicate a large degree of periodicity not matching the base material.
Figure 56: Mg damage layers in needles milled at 30 and 5 keV

Figure 57: FFT patterns taken from a magnesium needle milled at 30 keV. Right: Crystalline region. Left: Damage layer

Molybdenum damage layers were practically nonexistent after 5 keV cleaning [Figure 58]. This raises some questions about the possibility these damage layers are oxide layers, if so a clear reduction in damage layer width from 30 to 5 keV should not be apparent. Yet the average thickness at 30 keV was 1.86 nm and arguably nonexistent at 5
keV. FFT patterns taken from the 30 keV damage layer indicate that it has a strong
degree of order [Figure 59].

Figure 58: Mo damage layers in needles milled at 30 and 5 keV

Figure 59: FFT patterns taken from a molybdenum needle milled at 30 keV. Right: Crystalline region. Left: Damage layer
Redeposition cross trenching experiments in nickel resulted in epitaxial regrowth similar to that reported in copper. However Figure 60 reveals a clearly visible damage layer in both 30 and 5 keV needles, both showing a significant degree of periodicity and strong moiré patterns in both 30 and 5 keV needle [Figure 61]. The 30 keV layer averaged 1.43 nm and the 5 keV was 1.5 nm.

Figure 60: Ni damage layers in needles milled at 30 and 5 keV
Figure 61: FFT patterns taken from a nickel needle milled at 30 keV. Right: Crystalline region. Left: Damage layer

Titanium had the second thickest damage layers of the pure metals, second only to magnesium. Damage layers averaged 4.08 nm for 30 keV and 3.21 nm at 5 keV [Figure 62]. Unlike magnesium however the damage layer appeared amorphous, with diffuse rings clearly present in the FFT patterns [Figure 63]. As both cobalt and magnesium have an HCP crystal structure the difference in amorphous layer formation seems independent of crystal structure.
Figure 62: Ti damage layers in needles milled at 30 and 5 keV

Figure 63: FFT patterns taken from a titanium needle milled at 30 keV. Right: Crystalline region. Left: Damage layer

Tungsten had the least damage of any of the pure metals, with arguably only 0.5 nm of damage on average at 30 keV and no discernable damage layer at 5 keV. However in Figure 64 moiré patterns similar to cobalt are present in the image, implying that a small layer of some sort is causing interference.
Figure 64: W damage layers in needles milled at 30 and 5 keV
Examining the trends in Figure 65 reveal two facts, the first being damage layer thickness in pure metals appears to be relatively constant between 30 and 5 keV. What little deviation that exists can be explained by small sample sizes, measurement accuracy at the nm scale, and layer growth during imaging. The second is the lack of any damage above 5 nm. EDS scans of the needles did not pick of appreciable amounts of oxygen in the damage layers, however due to the small dimensions of the layers and high radius of curvature count rates at needle edges were too low to draw quantitative conclusions from.
4.3 Alloys

The addition of alloying elements has several effects which could play a role in modifying the damage layers created during FIB milling. The addition of alloying elements can in some cases extend the stability region of amorphous phases, play a large role in defect diffusion, and result in various phases with wildly different properties, bond strengths, and structures. The effect of phase field width in intermetallics has been correlated with the tendency to amorphize under irradiation conditions [64]. In the case of NiAl previous experiments have reported no amorphization during irradiation. However as previously stated, and illustrated in Figures 65-66, needles formed using FIB milling appear to have a semi crystalline damage layer which may both grow, shrink, or recrystallize in response to electron beam irradiation. The damage layer thickness does not significantly vary with compositions shifts up to +/- 3 at% on either side of stoichiometry. However, the presence of up to 3% NiAl antisites or V$_{Ni}$ vacancies does appear to alter the appearance of FIB induced crystalline defects (Chapter 3). Damage layers in NiAl 47-53 averaged 4.8 nm for 30 keV and 3.2 nm for 5 keV [Figure 66]. Damage layers in NiAl 50-50 averaged for 30 keV and for 5 keV [Figure 67]. Damage layers in NiAl 53-47 averaged 4.5 nm for 30 keV and 3.7 nm for 5 keV [Figure 68]. FFT patterns taken from 30 keV damage layers indicate the presence of a significant degree of order [Figure 26].
Figure 66: NiAl 47-53 damage layers in needles milled at 30 and 5 keV

Figure 67: NiAl 50-50 damage layers in needles milled at 30 and 5 keV
Of the pure metals measured only titanium and aluminum appeared to have an actual amorphous layer. The addition of alloying elements in aluminum appeared to double the amorphous layer of Al-7075 (Al-0.2Cr-1.5Cu-2.5Mg-5.5Zn) over pure aluminum. The average 30 keV layer thickness increased from 2.1 nm in pure aluminum to 4.3 nm in Al-7075. The addition of alloying elements did not appear to affect the crystallinity of the damage layer; FFT patterns reveal a lack of strong periodicity in the layer.
Figure 69: Al-7075 damage layers in needle milled at 30 keV. FFT patterns from crystalline and damage regions

Damage layers in alpha Ti-64 milled at 30 keV averaged only 4.4 nm thick [Figure 70], showing no significant increase over pure titanium layer thickness of 4.1 nm. FFT patterns indicate a fairly amorphous damage layer, although a degree of periodicity above and beyond pure titanium is visible. Most importantly this allows us to directly compare the degree of amorphous damage visible at the edge of a Ti-64 foil milled at 30 keV [Figure 14] to the actual layer thickness. In the figure the width of the amorphous zone is 27 nm, over 6 times wider than the actual layer thickness. This confirms that edge damage in wedged foils cannot be taken as an indication of true thickness.
Figure 70: Ti-64 damage layers in needle milled at 30 keV. FFT patterns from crystalline and damage regions

Needles milled from alpha globs in Ti-62222 (Ti-6Al-2Sn-2Zr-2Mo-2Cr) also exhibited an amorphous damage layer. The average thickness at 30 keV was noticeably higher than pure Ti and Ti-64 at 5.34 nm and 3.01 nm at 5 keV [Figure 71]. Molybdenum is known to diffuse slowly in titanium, creating strain in the lattice that works to block defect movement. It is possible the addition of molybdenum acted as a barrier to defect recombination, leading to an increase in amorphous layer thickness.
If molybdenum does have a noticeable effect on amorphous layer formation then we should notice a trend as content increases. To investigate this three needle sets were removed from a LENS Ti-Mo gradient running from 0-20 wt% Mo. Composition of each needle set was 6.5, 9.8, and 12.3 at% Mo. Needles with a composition of 6.5% had damage layers 5 nm thick at 30 keV and 4.5 nm at 5 keV [Figure 72]. Layer thickness dropped slightly when moly content rose to 9.8%, with thicknesses of 3.6 nm at 30 keV and 3.5 nm at 5 keV [Figure 73]. Thickness rose slightly at 12.3%, 4.1 nm at 30 keV and 3.9 nm at 5 keV [Figure 74]. Damage layers at all compositions appeared amorphous, and no significant variations in structure were observed. Molybdenum content does not appear to have a significant effect on amorphous layer formation in titanium [Figure 75].
Figure 72: Ti-6.5Mo damage layers in needles milled at 30 and 5 keV

Figure 73: Ti-9.8Mo damage layers in needles milled at 30 and 5 keV
Figure 74: Ti-12.3Mo damage layers in needles milled at 30 and 5 keV

Figure 75: Damage layer variation in Ti-Mo gradient
A second titanium gradient between titanium and iron was provided by Dan Huber. The gradient was made by arc melting iron into a CP titanium plate, creating a gradient running between pure Ti to 50 at% Fe over the space of roughly 30-35 microns. This allowed extraction of a slightly overlarge FIB slab which spanned 0-50% Fe. The slab was then cut into 11 individual pillars, mounted on two Omniprobe grids, and shaped at 30 keV. Unfortunately during loading one grid slipped and brushed against the spacer ring, resulting in the fifth needle being bent. Despite this setback the remaining ten needles were successfully imaged using HRTEM to get damage layer thicknesses. The microscope was then switched to STEM mode and the needles mapped for 30 min each using a quad sensor ChemiSTEM™ XEDS detector to get composition. Three phases where identified, a mix of α and β titanium below 8 at% Fe, fully β between 8-10 at% Fe, then what appeared to be intermetallic TiFe at 44 at% Fe. The measured damage layer thicknesses can be seen in Figure 76. While variation between phases is high the in-phase variation is insignificant. In particular the lack of variation over ~30 at% Fe in the β phase is striking.
Damage in the alpha phase averaged 4.3 nm, matching the damage layer thickness found in commercially pure titanium alpha. However unlike pure titanium the FFT pattern for the Ti-Fe gradient layer indicated a significant degree of periodicity.

Figure 76: Damage layer variation in Ti-Fe gradient
The β phase however was both thicker, averaging 5.9 nm, and clearly amorphous. The transition in thickness between the two phases can clearly be seen in Figure 78, depicting a small region of β embedded in α. FFT patterns taken from the β damage layer indicate it to be largely amorphous, with significantly less periodicity than the α layer [Figure 79]. At a composition of ~44 at% iron the damage layer thickness increased to 16 nm [Figure 80]. The layer appeared fully amorphous in both TEM and FFT patterns. As TiFe was reported by Brimhall et al [64] to amorphize it seems likely that the final heavily amorphized phase is in fact a TiFe intermetallic. The EDS quantification used to arrive at the value of 44 at% was done using standard calculated k-
factors, which along with the ~2% phase width of TiFe could account for the deviation reported. If so this would provide support for the notion that the energy penalty associated with defects in narrow phase field intermetallics can stabilize the amorphous phase.

Figure 78: Ti-Fe gradient α to β damage layer transition in damage layer thickness
Figure 79: Ti-Fe gradient β damage layers in needle milled at 30 keV.

Figure 80: Ti-Fe gradient TiFe intermetallic damage layers in needle milled at 30 keV. FFT patterns from crystalline and damage regions
High Entropy Alloys (HEA), sometimes referred to as compositionally complex alloys, are a new alloy class composed of five or more roughly equiatomic metallic elements. A number of these alloys form a two phase mixture characterized by one BCC phase and one B2 phase. One such alloy is AlMo$_{0.5}$NbTa$_{0.5}$TiZr, which forms a B2 phase rich in Al and Zr and a BCC solid solution rich in Ta, Nb, and Mo. The alloy became of interest after group members reported difficulty obtaining clear lattice images despite multiple cleaning passes with argon at low voltage. When a set of needles was made of the material it quickly became obvious that the two phases damage very differently. The BCC phase had an amorphous layer averaging 2 nm thick at 30 keV [Figure 81]. The B2 phase however sported an amorphous layer 19.8 nm thick at 30 keV, extending well into needle [Figure 82].
Figure 81: HEA-BCC damage layer in needle milled at 30 keV.

Figure 82: HEA-B2 damage layer in needle milled at 30 keV. FFT patterns from crystalline and damage regions
Damage layers in needles shaped at 5 keV were again amorphous, with damage layers in the BCC phase remaining relatively steady at 3.1 nm thick. Amorphous layer penetration in the B2 phase dropped to an average of 8.4 nm, still more than doubling the thickness of the BCC phase [Figure 83]. The extent of the variation is clear in Figure 84, which depicts a 5 keV needle in both HRTEM and HAADF-STEM. It should be noted that at first blush the HAADF-STEM image gives the appearance of no damage. Only careful comparison between the HRTEM and STEM image allows one to correlate the faint contrast change in the B2 phase to the amorphous regions. This explains how despite previous needles of this alloy being extensively imaged for tomographic reconstructions no one noticed the significant variation in damage layer thickness. HAADF-STEM images of the previous needles were viewed by myself, others in the group, and presented at major conferences without a single person noticing the presence of edge damage. This strongly illustrates the danger in assuming a needle or foil is free from FIB damage based solely on contrast in HAADF-STEM. The effect of uneven amorphous layer formation on traditional FIB foils can be seen in Figure 86. The regions of B2 material are clearly amorphous, while the BCC phase is still crystalline. Similar differences in amorphous layer formation between phases was noted by Y. Yabuuchi [30] in multilayers of Al$_{0.6}$Ga$_{0.4}$As and Al$_{0.3}$Ga$_{0.7}$As. Figure 11 and Figure 82 show how significantly the amorphous layer width can vary between phases within a single material.
Figure 83: Damage layers in HEA needles milled at 5 keV. Left: BCC phase. Right: B2 phase within BCC phase.

Figure 84: HRTEM and HAADF-STEM images of 5 keV HEA needle along same orientation.
Figure 85: Raw x-ray counts from 5 keV HEA needle used to identify phases
Figure 86: Extent of B2 amorphization in 5 keV HEA foil, A = amorphous B2, C = crystalline BCC

As the nickel super alloy LSHR is also a two phase material comprised of an ordered phase and a solid solution it seemed likely that a similar variation in damage layers might be present. Dr. Samuel Kuhr had noticed in his own research that the $\gamma$ FCC matrix appeared to damage more readily than the ordered L12 $\gamma'$ particles. In his experience the FCC gamma phase seemed to form dislocations during high voltage milling, while the $\gamma'$ particles appeared relatively unaffected. This apparent difference could be minimized by the careful use of decreasing accelerating voltage and argon milling steps at 500 eV. To investigate a set of needles was pulled from a LSHR sample. Figure 87 shows the resulting damage layers, averaging 2.95 nm at 30 keV and 1.82 nm at 5 keV. FFT
patterns from the 30 keV damage layer indicate a fairly amorphous layer [Figure 88]. Conspicuously missing was any variation in damage layer thickness, initially leading me to believe I’d extracted a needle from a single phase region. However EDS scans of a needle shaped at 5 keV laid that concern to rest. In Figure 89 two chromium depleted regions typical of $\gamma'$ reveal the presence of two precipitates. Clearly damage layer thickness in LSHR is independent of the phases.

Figure 87: LSHR damage layers in needles milled at 30 and 5 keV
Figure 88: FFT patterns taken from a LSHR needle milled at 30 keV. Right: Crystalline region. Left: Damage layer
Figure 89: Raw x-ray counts from 5 keV LSHR needle used to identify presence of γ’, indicated by Cr depletion and Ti enrichment
Re-imaging the LSHR in HRTEM after a 30 minute EDS run in STEM revealed an unusual phenomenon. The damage layer had apparently grown to 6.9 nm thick, appearing fully amorphous [Figure 90]. My initial theory was that carbon had migrated from the platinum cap during imaging, growing out outward from the needle. As the layer thickness dropped to 4.1 nm after 5 minutes of plasma cleaning, a method meant to remove carbon deposition, this seemed a reasonable assumption. However similar EDS scans of HEA and nickel needles did not result in similar growth. Three possibilities seem most likely. The first is that chamber cleanliness was low due to the recent cracking of the column for repairs; this seems most plausible due to the inability to replicate the results. The second option is that the layer grew during transportation between the two sessions. The final option is that some property of LSHR led to the growth; however time limitations prevented further experimentation which could have proved or disproved this theory.
Figure 90: 5 keV LSHR needle before and after 30 min STEM-EDS scan

The lack of variation in damage between the $\gamma$ and $\gamma'$ phases stands in contrast to the significant disparity in layer thicknesses between Ti $\alpha/\beta$ and HEA B2/BCC phases. Of the four ordered phases viewed two, NiAl and $\gamma'$, did not form amorphous layers. TiFe and the HEA B2 did form significant amorphous layers with thicknesses well above the 5 nm limit typical of the pure metals and solid solutions [Figure 91]. Alloying appeared to have significantly less impact on amorphous layer formation. This result seems to support the supposition that amorphization in metallic compounds requires the presence of high energy defects.
Figure 91: Metal alloy damage layer thickness vs accelerating voltage

Figure 92 is the complete chart of measured damage layer thickness vs accelerating voltage for every material viewed. From this chart FIB damage can be divided into two distinct classes of damage, materials which strongly amorphize and those which do not. Strongly amorphized materials consist of semiconductors and select intermetallics, and form layers well in excess of 5 nm when milled at 30 keV. Damage layers in these materials appear to decrease by the same amount when milled at 5 keV, regardless of
initial layer thickness. Materials which do not strongly amorphize do not form visible damage layers over 5 nm thick, and the layers are independent of accelerating voltage.

Figure 92: Damage layer thickness in various materials versus accelerating voltage
Chapter 5: Modeling

A number of theories for the crystal to amorphous transition have been put forward, but to date none of them properly predict all experimental results across all materials systems. Several models are common, namely, the critical defect density model, cascade overlap damage model, nucleation limited model, and a number of defect based models. The critical defect density model is a free energy approach, as defects accumulate they increase the energy of the lattice above a critical value which exceeds the free energy of the amorphous state, prompting a phase change. This model was put forward by M. Swanson et al [65] to explain amorphization in neutron and ion bombarded Ge and Si based on, among other concerns, their observation using infrared absorption that initial knock on produced a number of divacancies but no amorphization using neutrons. J. Brimhall et al [64] applied this model to intermetallics, pointing to the trend towards amorphization by intermetallics with narrow compositional ranges. J.L. Brimhall et al [64] bombarded a number of intermetallic systems with 2.5 MeV Ni+ ions to study their susceptibility to amorphization. A diffuse ring in the SADP was used as evidence for amorphization. A summary of their findings can be seen in Tables 2-3, including atom size ratio, irradiation vs. transition temp, avg. group number, and enthalpy of formation. Each parameter has been at some point put forward as a candidate for various
amorphization predictions. However as is reflected in the table, while such methods may seem to apply for limited systems, over the range of intermetallics shown, no obvious trends exist. In materials that became amorphous the only strong correlation found by Brimhall et al was with the intermetallics range of composition, with all line compounds other than Ni$_3$Ti showing amorphization. While Ni$_3$Ti did not appear to develop any amorphous rings, post irradiation the superlattice spots are weaker indicating moderate disorder. The authors theorized the second exception ReTa may not have amorphized due to the low temperatures during irradiation relative to its transition point, which may have not allowed sufficient diffusion. This observation is perhaps reasonable given that in a second paper by P. Moine et al [58] it was found that NiAl irradiation by 360 keV Xe ions also results in amorphous material at cryogenic temperatures (<120º K). However it is interesting to note that they report no amorphization resulted from bombardment of nano crystalline NiAl at any temp, indicating the presence of sinks strongly influences the amorphization kinetics.

In the materials which did not amorphize, strong networks of dislocations could be observed to form, although in some cases such as Ni$_3$Al chemical disordering appeared to increase, others including NiAl remained strongly ordered. The presence of dislocations post irradiation is troubling; one of the primary uses of TEM is to identify dislocation nature and density. If the FIB process induces dislocations, the veracity of such measurements is thrown in doubt. They also found that the spacing of all amorphous rings corresponded closely to ring spacing reported for liquid quenched metal amorphous alloys, rather than molten metals. All amorphous phases formed by 1 dpa or not at all up
to 40 dpa. They attributed this to the addition of a chemical disordering penalty which increases the defect energy in highly ordered materials. In another paper J. Brimhall and E. Simonen summarize even more papers showing this trend [Table 3] [66]. They point out that the estimated energy for nucleation of loops in irradiated metals is two orders of magnitude lower than that predicted for critical defect density for amorphization. This is supported by the fact that dislocations and loops do not appear in materials which amorphize before amorphous rings appear, but do appear in materials which do not. This could be because materials which amorphize may have lower defect mobilities or the cluster energy needed to nucleate a dislocation is high.
Table 2: Amorphization in intermetallics vs composition range, size ratio, irradiation temp, enthalpy, and structure by Brimhall et al [64].

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<th>Phases that become amorphous</th>
<th>Range of composition</th>
<th>Atom size ratio</th>
<th>Irrad. temp</th>
<th>Average group number</th>
<th>ΔH form. (kJ/mol)</th>
<th>Structure</th>
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Table 3: Summary of amorphization in intermetallics vs. composition range and irradiation temp by Brimhall et al [31]

Table 1:
Classification of compounds into amorphous and non-amorphous transformation

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<td>PdAl</td>
<td>~10?</td>
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<td>[10]</td>
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The critical defect model as applied by J. Brimhall and E. Simonen appears to directly predict the tendency to observe a thick amorphous layer in intermetallic experimental needles. The narrow phase field TiFe intermetallic had a significant amorphous layer at 30 keV, while the wide phase field NiAl showed no significant amorphization. This behavior fits predictions based on results reported by J. Brimhall’s [66]. The critical defect density theory for ordered or intermetallic materials is also given credence by the reaction of \( \gamma' \) in LSHR and the HEA B2 phase. The \( \gamma' \) phase is well known to have a wide composition range, accommodating a large number of substitutional atoms used to tune mismatch between the matrix and gamma precipitate. Damage layers in LSHR showed no variation between \( \gamma' \) and the matrix, as expected from a critical defect density viewpoint. The HEA B2 phase however did heavily amorphize. Unfortunately the HEA in question is a new material, and the phase field width of the chemically complex B2 phase is unknown. Should the phase field be narrow, it may provide excellent support for the critical defect density model in ordered materials, however the tendency to amorphize may be a result of the excess of constituents.

While the solubility range seems to show a reasonable correlation with susceptibility to amorphization, it doesn’t extend to solid solutions. W Grant [67] compares known bulk metallic glass formers and points out that a majority of the known formers seems to consist of a transition metal and a metalloid, a transition metal and rare earth, or a noble metal and metalloid. While Johnson et al [68] note that amorphous materials seem to fit metalloid/metal combinations known to be good glass formers. In a parallel effort to predict bulk metallic glasses, X Yang et al [69] divide up materials based on two terms,
an enthalpy, $T_m$, and entropy term vs an atomic size misfit term to identify where regions of solid solutions, intermetallics, mixtures of both, and BMGs may form [Figure 93]. The tendency of the HEA B2 phase to amorphize may in fact be independent of the compound’s phase field width, and governed more by the presence of a significant number of constituents positioning the composition into the poorly understood BMG region.

![Figure 93: Formation term vs atomic size misfit, an attempt to predict BMG's by Yang et al [69]](image)

J. Dennis et al [70] apply both the critical defect density and the cascade overlap model, finding that the doses necessary for amorphization correspond to predicted critical densities. One should note that application of critical density and the overlap model together is common, as there is some similarity between the two theories. Cascade
overlap is in fact central to M. Swanson’s treatment, which assumes overlap is necessary to reach critical density. The model assumes homogeneous amorphization triggered as soon as the local defect density reaches a critical point. However, while this model applies well to low mass ions creating a scattering of defects or ordered intermetallic systems with high defect energies, it does not account for heavy ion behavior, which do not tend to amorphize in an homogenous fashion, nor the presence of bond defects in covalently bonded materials. E.C. Baranova et al [71] point to discrepancies in the critical dose and temperature for amorphous creation in silicon between high and low z ions as evidence that a critical size for amorphous regions exists in addition to a critical defect density.
F. Morehead and B. Crowder [72] put forward the overlap damage model in 1970. Their theory assumes that the cascade directly creates an amorphous region surrounded by a core of vacancies and that full amorphization requires sufficient overlap at a rate fast enough to render the entire specimen amorphous before defect annealing restores the crystal structure. The theory has been modified for light ions, assuming multiple cascades creating defects must overlap in a small region to cause amorphization by ballistic mixing or due to critical defect density. While heavy ions do directly create amorphous cascade regions, the theory breaks down for light ions. R. Schreutelkamp et al [13] examined the amount of pre-amorphization defects created during ion bombardment of Si using
Rutherford backscattering. They found that not only is a large number of crystalline defects created before amorphization, but also that a critical level of defects was necessary for dislocations to form after a post-process anneal. They found that as ion mass increased, this critical dose also increased, and theorized this was due to heavy ion cascades creating more local damage resulting in fewer free interstitials. Both J. Dennis et al [70] and E.C. Baranova et al [71] point to these factors as reason to believe a necessary critical defect density is necessary for light ions, while the direct amorphization of the overlap model holds for heavy ions.

The nucleation limited model is based on observations that amorphization in silicon occurs preferentially at preexisting amorphous defects or interfaces [73][74]. They posit that amorphous nuclei are created either by direct amorphization by heavy ions, a local critical accumulation of defects to act as nucleation sites, or preexisting amorphous material. Once the initial nucleus has formed they grow via accumulation of crystalline defects, which is mediated by the rate of annealing and defect production. This theory differs from critical defect density theory in that it proposes a nucleation driven model rather than homogenous transformation. However the theory assumes that defect type and behavior are similar across all material ion combinations, which is not in agreement with calculated and experimental activation energies.

The defect model assumes that the transition to amorphous material is the result of specific defect interactions, and could more properly be classified as a refinement or specific extension of the three theories listed above. Defects that have been put forward include vacancies [75], divacancies [76], bond defects [77], and complex interactions.
between vacancies, divacancies, and interstitials [78]. Some have put forward self-interstitial clusters as necessary nuclei due to their formation of five and seven member rings characteristic of amorphous damage in silicon [79]. A recent model by M. Tang et al [80] shows some potential, where they have used MD simulations to predict an “IV pair” formed when a vacancy and <110> interstitial combine to form a metastable defect. The model predicts an activation energy of 1.23 eV for symmetric annihilation of a single interstitial and vacancy, but only 0.43 eV for a non-symmetric recombination producing the 5 and 7 member rings characteristic of amorphous silicon [77]. Further MD simulations by L. Pelaz et al [12,77] show that the IV pairs are metastable alone, but stabilize when they join up with other IV pairs. The activation energy for recrystallization at the crystalline amorphous boundary is 2.4 eV, while recrystallization within fully amorphous regions requires an activation energy of 5 eV. Taken together this implies that growth or shrinkage of amorphous regions in silicon would then be interface dominated, similar to the heterogeneous nucleation model. Smaller pockets with high curvature would be more susceptible to recrystallization. This behavior would explain the trends seen in silicon recrystallization and growth, and the metastable nature of the IV bond explains dose dependence when using light ion irradiation. However amorphous layer formation in silicon has also been well modelled by K. Mok et al [81] without strong dependence on the stability of the isolated IV pair, instead the activation energy of recrystallization varies as a function of amorphous pocket size.

Molecular dynamics simulations of collision cascades in semiconductors and fcc metals do reveal differences which may partially account for the differences in defect
generation between semiconductors and metals during the initial temperature spike. Nordlund et al [82,83] report that the initial temperature spike in silicon and germanium results in branching pockets of liquid like atoms with kinetic energies exceeding the melting temperature. Their simulations of FCC metals Au, Cu, Al, Pt, and Ni resulted in contained globular pockets. They attribute the branching nature of the thermal spike region in semiconductors to the lack of close packed planes. The isolated liquid like regions form amorphous pockets upon cooling. The single globular liquid like region found in metals was found to almost entirely reorder, sucking remaining vacancies into a cluster in the center of the region while leaving a shell of interstitials around the edge. The authors attribute this difference mainly to the difference in crystal structure and bonding.

Regardless of the model used, the dosage levels seen during gallium FIB milling far exceed the critical dosage necessary for amorphization in silicon. Dosage levels in the FIB may be calculated by dividing the current per point [Figure 95] by the effective milling spot size of the beam. For currents of 150-1,500 pA at 30 keV S. Rubanov and P. Munroe calculated gallium ion doses ranging from $9.8\cdot10^{13} - 0.36\cdot10^{14}$ Ga$^+$ ions/cm$^2$ for an FEI xP200 workstation [38]. The gallium ion columns used in current generation have effective ion beam resolutions an order of magnitude better, with FEI reported ion beam resolutions of 4 nm at 30 keV ions using a Helios NanoLab. The narrower beams in modern FIB’s increases the dosage per point by 1-2 orders of magnitude, with doses for commonly used thinning currents at 5 keV being as high as $5.06\cdot10^{14}$, and $8.2\cdot10^{16}$ at 30 keV. S. Rubanov calculated milling depths of 0.03 nm per pass for mills done with a
beam current of 1000 pA at 30 keV with 1 µs dwell times and a radius of 40 nm [38]. Even assuming this number is slightly increased at high incident angles as sputtering is maximized this effectively means the material is exposed to the beam roughly 30 times per each nm of material removed, with a corresponding increase in dosage.

![Ion Dose per Point](image-url)

**Figure 95:** Ion dose per point in raster pattern, delivered over 1 µs. Width of beam varies with current

The critical amorphizing dose at room temperature in silicon using 80 keV antimony ions required a critical dose of $1.2 \times 10^{13}$ ions/cm$^2$, while with Ar$^{40}$ ions the dose required $1.05 \times 10^{14}$ ions/cm$^2$ [71]. As the critical amorphizing dose in silicon decreases with ion weight the critical amorphizing dose for gallium ions is expected to be somewhere between the two providing a reasonable estimation. These values are of the same order of
magnitude as the dosage per point calculated by S. Rubanov, and an order of magnitude lower than dosages calculated for modern columns. Even a single pass with the gallium ion beam at normal thinning currents should be sufficient to fully amorphize the affected region. As thinning of the foil, by its nature, requires material removal, the expected dosage in the cascade affected area will be roughly 30 times higher. Although interstitial and vacancies in silicon are expected to diffuse at temperatures lower than room temperature [84], the sheer number of defects being generated is likely to be the dominating factor. Simply put, the dosage levels in the FIB are so far in excess of the critical dosage for amorphization in silicon that a uniform amorphous layer is the only logical outcome. Once the damaged materials have been fully amorphized, recrystallization kinetics are then fully governed by the movement of the crystalline amorphous interface, rather than the movement of individual defects.

5.1 SRIM

SRIM is a commonly used Monte Carlo simulation package used to predict ion interactions using a binary collision approximation. Outputs from the model include cascade size, vacancy concentration, sputtering rate, gallium implantation depths, and ion energy loss. Error estimates of simulations in pure elements are less than 5%, and a large body of empirical potentials used by the model is updated to match current experimental data each software upgrade [6]. Users may modify model outputs by varying input parameters such as average displacement, lattice, and surface energies as well as ion energy, incidence angle, and target thickness. Although well suited for first order
approximation of cascade size and vacancy generation, SRIM makes several assumptions which limits its applicability. The binary collision model does not include the influence of neighboring atoms assuming a fully amorphous material in which channeling does not occur. The recombination of interstitial and vacancy pairs is excluded in the model, as well as the tendency of defects to cluster, a feature which has strong implications for damage formation in metals. Finally, sputtering is treated as a simple cut off function in which atoms reaching the surface with energy above a semi-empirical value are ejected.

SRIM calculations of gallium and argon ion cascades formed at commonly used FIB and broad beam argon milling voltages adequately explain the increased clarity seen in TEM foils cleaned with decreasing accelerating voltages. Figure 96 shows the estimated sizes of damage cascades in titanium at 87° incidence angle. Penetration into the substrate drops from ~30 nm to ~10 nm when gallium ion energy is dropped from 30 to 5 keV. Beam penetration of 500 V argon atoms at 80° incidence angle, drops to 4-5 nm. Assuming each cleaning step fully removes the previous damage layer, the method of decreasing voltage in steps can be used to reduce the total damage layer thickness to a few nm.
Figure 96: SRIM simulations of cascade sizes in titanium at various accelerating voltages

Although SRIM does not provide insight into the behavior of defects post cascade, the degree of initial damage during FIB milling can be approximated by looking at the number of vacancies, displaced atoms, and implanted gallium ions predicted by TRIM for a certain depth. Figure 97 illustrates the how the predicted number of implanted gallium ions in silicon and molybdenum varies with incident angle over 80-89.9º, which covers the full range of tilt angles commonly used when milling in the FIB. Silicon and tungsten were chosen as they represent the materials with the highest and the lowest damage thickness layers. Respectively, the predicted depth of implantation in W is only approximately 10 nm less than that in Si, which does not correlate with the 25 nm difference in thickness between the two materials visible damage layers.
Figure 97: SRIM predictions of 30 keV gallium implantation at incident angles between 80-89.9° in Si and W
The predicted vacancy formation for silicon and tungsten shows even less of a variation in penetration depth [Figure 98]. Vacancy formation can generally be thought of being proportional to interstitial formation during damage cascades, and should thus reflect the degree of induced damage. If the thickness of the damage layer was simply a function of cascade penetration depth in various materials one would expect to see a large variation in these numbers. The similarity in gallium implantation and vacancy formation depth is not limited solely to Si and W. Figure 99 illustrates the damage profiles for multiple materials at an incidence angle of 87º (on the high side of normal thinning angles). Not only is there no significant variance with material, what variations exist do not correlate to damage layer thickness in any way.
Figure 98: SRIM predictions of 30 keV vacancy formation at incident angles between 80-89.9° in W and Si
Figure 99: SRIM predictions of gallium implantation and vacancy formation at 30 keV gallium ions in multiple materials at 87° incidence angle.
In addition to vacancy and gallium implantation SRIM also allows one to examine possible damage influences such as vacancy generation, atomic displacements, sputtered atoms per ion, and percentage of displaced atoms sputtered. As beam current is a constant, increases in vacancy generation per ion could indicate higher damage rates, which could in turn lead to more rapid accumulation of a critical density of defects. However vacancy generation per ion did not vary significantly with material type and whatever variation that existed did not correspond to measured thickness values [Figure 100].

Figure 100: Predicted vacancy formation in multiple materials per ion at incident angles 80-89.9°
Target displacements per ion are another measure of total damage, indicating the number of atoms affected by the ion. However, no significant variation or correlation was observed [Figure 101].

![Figure 101: Predicted total target displacements in multiple materials per ion at incident angles 80-89.9°](image)

Sputtering rate could theoretically have a significant effect on the damage layer formation. If higher percentages of cascade affected atoms are sputtered, the number of remaining defects will be lower, thus decreasing the local concentration of defects. However, the two measurements of sputtering rate, namely the sputtered atoms per ion [Figure 102] and the percentage of displaced atoms sputtered [Figure 103] show no significant variation or correlation with measured damage layers.
Figure 102: Predicted sputtered atoms in multiple materials per ion at incident angles 80-89.9°

Figure 103: Predicted ratio of sputtered atoms to displaced atoms per ion in multiple materials at incident angles 80 - 89.9°
Three significant observations can be made when reviewing SRIM modeling results. First the gallium ion cascade size is effectively the same in most materials, neglecting possible factors like channeling assisted penetration. Likewise, secondly the number of defects generated during damage cascades is effectively the same in most materials. On the other hand, considering observed variance in visible damage layer thickness between materials leads to the third major implication that is the type of damage present after FIB milling is a result of the defect interactions post cascade. Materials which do not form amorphous layers can still have a beam affected region roughly the same size as amorphous damage layers in silicon. Damage layer thickness may only truly be decreased by successive milling steps at low voltage, and only if each step fully removes the damage layer generated in previous steps.

With this in mind, the question of why some materials amorphize and some do not, becomes one of defect behavior, rather than cascade behavior. MD simulations of collision cascades have shown that a large majority of disrupted atoms move back into place restoring much of the original lattice structure. The resulting interstitials and vacancies remaining are those separated far enough to inhibit recombination. Defect movement post irradiation, to either cluster around dislocations or recombine with other defects, will be limited by the individual defect diffusivity. This leads straight to a hypothesis in which the presence and thickness of amorphous layers might be directly tied to the speed or the rate of self-diffusion. The behavior however is not so straightforward, as illustrated by Figure 104 and Figure 105, in which no correlation of damage
thickness with self-diffusivities can be seen (diffusion data taken from the NIMS diffusion database).
Figure 104: Calculated diffusivities at room temperature vs damage layer thickness

Figure 105: Calculated diffusivities at 500º C vs damage layer thickness
5.2 Defect Diffusion Model

The buildup of defects can be modelled by considering the balance between defect accumulation, migration, recombination, and annihilation at sinks. If direct amorphization during ion cascades is neglected, the onset of an amorphous transition is assumed to occur when local defects exceed a critical generation rate or concentration. H. Cerva et al found this critical point defect density in silicon to be $1.15 \times 10^{22}$ cm$^{-3}$ [85]. Swanson et al determined the critical concentration in Si and Ge necessary for amorphization to be 0.02 - 0.04 [65]. D. Pedraza also arrived at a critical concentration of 0.02 for intermetallic compounds [86] based on crystallization enthalpies of formation in ZrCu, ZrNi, and CuTi systems [87–89]. E. Simonen back calculated a similar value (0.02) in intermetallics using rate equations to match the predicted trends with known amorphization kinetics [90]. If the critical dose is assumed to be 0.02 in all materials, then the depth, extent, and required dose for amorphization may be directly deduced from rate equations modeling the defect build up. However as pure metals and wide phase field intermetallics have been shown to remain crystalline well up into the MeV range this assumption may not be appropriate for metals.

The simplest model assumes radiation defects are generated relatively homogenously throughout the material during irradiation and consist solely of Frenkel interstitial and vacancy pairs. In this model, the defect concentration is solely a function of the recombination and irradiation rate, with concentration rising linearly until the critical tipping point. While this model has some use for simulating high energy irradiation of thin films, the assumption of homogeneous defect generation does not apply to the FIB
milling process. SRIM simulations of vacancies generated by ion induced cascades in foil sidewalls illustrate the highly nonlinear nature of defect generation during FIB milling [Figure 98]. A complete treatment of defect buildup requires the addition of a diffusion term to account for drift from high to low concentration areas. As the defect generation is expected to be uniform in the plane of the cut, and varies only with depth the model may be safely reduced to one dimension. The change in defect concentration at each node can then be assumed to vary according to two rate equations, one for each defect type being considered. Concentration at each node is a function of the flux from nearby nodes, the local recombination rate, the local sink strength, and the irradiation strength [Equation 1].

\[
\frac{\partial C_I(x)}{\partial t} = D_I \frac{\partial^2 C_I(x)}{\partial x^2} - k_{IV}(C_I(x)C_V(x) - C_I^*C_V^*) - k_{sink}(x)C_I(x) + \frac{\partial C_I^{irr}(x)}{\partial t}
\]

\[
\frac{\partial C_V(x)}{\partial t} = D_V \frac{\partial^2 C_V(x)}{\partial x^2} - k_{IV}(C_I(x)C_V(x) - C_I^*C_V^*) - k_{sink}(x)C_V(x) + \frac{\partial C_V^{irr}(x)}{\partial t}
\]

Equation 1: Diffusion reaction equations for interstitials and vacancies (Where \(Dv\) is the defect diffusivity, \(C\) is the defect concentration, \(k_{IV}\) is the recombination rate, \(C^*\) is the equilibrium defect concentration, \(k_{sink}\) is the sink rate, and \(C^{irr}\) is the concentration of defects added during irradiation.)

Aluminum was chosen as a model system for several reasons. Damage layers in pure aluminum appeared fully amorphous with straight crystalline to amorphous interfaces indicating a uniform distribution of defects in the plane of the surface. Aluminum has also been extensively modeled, and defect activation energy, migration energy, and
diffusivity prefactors are readily available in the literature [91]. The calculated diffusivity of interstitials at room temperature $5.21 \cdot 10^{-8}$ m$^2$/s was several orders of magnitude higher than the vacancy diffusivity of $1.33 \cdot 10^{-17}$ m$^2$/s due to the low interstitial migration energy of 0.115 eV. Conversely the equilibrium interstitial concentration in aluminum at room temperature is negligible due to the high activation energy (3 eV). By comparison the vacancy activation energy in aluminum is only 0.7 eV, resulting in an equilibrium concentration of $2.8 \cdot 10^{-13}$ 1/m$^3$.

The diffusion term may be solved numerically by applying a central difference approximation [Equation 2] to approximate the local gradient. This approximation is only stable when the diffusivity term is less than $1/2$. The practical implication of this constraint is that each doubling in resolution requires the time step be dropped by a factor of four. For example, when gallium ion cascades affect a region of ~30 nm, the model is effectively limited to a resolution of 1 nm. At this scale the model is only stable for time steps measuring in tenths of picoseconds. This limits practical application of the model at timescales necessary to explore the effects of long range diffusion effects. However, this resolution is sufficient to gain insight into the mechanisms by which defects equilibrate post irradiation, and offers a potential explanation for the presence of damage layers in pure metals. Boundary conditions were set to equilibrium concentration values.
\[
C_{x+1}^t = C_x^t + \frac{D_{def} \Delta t}{\Delta x^2} (C_{x+1}^t - 2C_x^t + C_{x-1}^t)
\]

Equation 2: Central difference approximation used to numerically solve Fick’s 2\textsuperscript{nd} law, unstable if diffusivity term goes above \( \frac{1}{2} \).

Authors have come up with multiple ways to estimate defect recombination rate \( k_{IV} \), taking into account factors like nearest neighbor sites \( Z_{IV} \), atomic volume \( \Omega \), diffusivity coefficients \( D_i \), and unit cell atom concentration \( N_{conc} \) [Equation 3]. Common to all these methods are the terms that estimate the geometrical range of recombination and the diffusivity of the defects in question. As interstitial and vacancy pairs interact and annihilate beyond nearest the neighbor, the spacing \( Z_{IV} \) is often estimated as \( \sim 500 \) to account for 2\textsuperscript{nd} and 3\textsuperscript{rd} neighbor sites [92]. In the case of aluminum the first equation was used, as the predicted diffusivity rate of vacancies at room temperature in aluminum should render interstitials the only mobile defect.

\[
k_{IV} = \frac{Z_{IV} \Omega D_i}{a^2}
\]

\[
k_{IV} = \frac{4\pi}{\sqrt{N_{conc}}} (D_i + D_V)
\]

Equation 3: Interstitial-vacancy recombination rate equations

The interstitial–vacancy generation rate was approximated by fitting an exponential function to the vacancy profile generated by SRIM simulations of 30 keV gallium ions with an incidence angle of 87\textdegree in aluminum [Figure 106]. This led to defect concentrations well in excess of 0.02, however even when capping the maximum
concentration at this level the central difference approximation became unstable. Stabilization required dropping the initial defect profile maximum until the simulation no longer indicated the volatility, roughly around $\sim 2.6 \cdot 10^{19}$ cm$^{-3}$.

Figure 106: Aluminum damage function fitted to SRIM vacancy concentration results

As the model does not include a sputtering term and experiences instability at high defect concentrations levels the irradiation term was only applied during the first time step. The initial defect concentrations after the first time step can be seen in Figure 107, in which the vacancy profile is slightly higher due to the presence of equilibrium defects.
If the recombination term is set to zero, the diffusion behavior of each defect species can be examined in isolation. The assumption of essentially static vacancies over simulation timescales is confirmed by plotting the variation in vacancy profile with respect to increasing number of steps [Figure 108]. After 90 ns, the vacancies have not diffused any noticeable distance. Interstitials however show significant diffusion after $9 \cdot 10^{-12}$ seconds, and by 90 ns the concentration profile is essentially flat [Figure 109].
Figure 108: Simulated vacancy diffusion in aluminum. Legend indicates number of simulation steps, each step represents $9 \cdot 10^{-13}$ seconds (10,000 steps = 9 ns).

Figure 109: Simulated interstitial diffusion in aluminum. Legend indicates number of simulation steps, each step represents $9 \cdot 10^{-13}$ seconds (10,000 steps = 9 ns).
If recombination is turned on, the defect concentration drops close to zero across the initial damage range. This result is in hindsight to be expected, as rapid recombination rates due to high interstitial diffusivity and the overlap in initial damage curves does not leave the potential for defects to escape. A potential solution to this problem may be identified by going back to SRIM cascade simulations [Figure 96]. Damage cascades create a core of vacancies surrounded by a shell of interstitials. The distribution of interstitials will be forward biased relative to the incidence angle, resulting in a relative increase in interstitial concentration deeper into the material. MD simulations of silicon cascades have resulted in interstitial offsets from vacancies averaging 1.4 nm, and 1.6 nm in aluminum [83]. This can be simulated in 1D by offsetting the initial concentration of interstitials slightly deeper into the material. Figure 110 shows the result of a 3 nm offset in profiles.
The recombination radius is still large enough to allow total annihilation of defects. However when the offset is increased to 4 nm the residual vacancy concentrations spike, and continue to grow as offset increases. The discrepancy between the offsets needed for the vacancy concentration spike and simulated values are likely due to two factors. The first is the possibility that the recombination term used is over estimating the recombination radius. The $Z_{IV}$ factor of 500 does not take into account material specific factors such as true nearest neighbor spacing. The second is the reported tendency of point defects to migrate deeper into the material during prolonged heavy irradiation [93]. The simulated residual vacancy concentrations remain steady up to 90 ns, as the interstitial concentrations spread out evenly in both directions from the initial spike, leaving a stable region of vacancy rich material at the surface [Figure 111]. This result
raises a possible explanation for the observation of damage layers in pure materials considered to be impossible to amorphize.

![Variance in Residual Vacancies with Offset](image)

**Figure 111**: Residual vacancies remaining after recombination as defect profile offset increases. Legend indicates nm of offset between interstitial and vacancy profiles.

If vacancy rich regions in real materials do have a slight offset from interstitial rich regions deeper in the material recombination in materials may not proceed to completion. Interstitials outside the recombination radius have an equal chance of diffusing into the material or towards the surface, meaning roughly half may be expected to move irretrievably beyond recombination range in a matter of nanoseconds. This would result in a vacancy rich region, a few nm thick adjacent to a free surface. As predicted vacancy concentration in real materials is several orders of magnitude higher than 0.02 near the surface and the presence of a free surface drastically changes the local constraint and
therefore it seems likely normal recrystallization behavior would be altered. The variance in defect layers in the pure metals would then be explained by variance in the degree of offset between initial vacancies and interstitial concentrations, rather than bulk material properties such as diffusivity or melting temperature.

5.3 Amorphous Layer Stress

During the FIB thinning process bending of the foil is often a concern. Much of this bending is likely due to preexisting strain in the material being relieved as the sample moves from a bulk condition to a thin film condition. However in relatively stress free materials our past experience shows bending to be moderately predictable. If a foil is overly thinned at 30 keV the initial cleaning pass with 5 keV will result in the foil bending into the beam. Yet this behavior is not as common in foils which are left relatively thick before 5 keV cleaning. This behavior may be explained by a simple stress state model. Amorphous silicon has been measured as 1.8 ± 0.1% less dense than crystalline silicon under both relaxed and unrelaxed conditions [94]. Amorphous layer thicknesses at 30 keV have been measured in silicon at ~25 nm thick. If one imagines a stress free silicon foil thinned to 75 nm before 5 keV cleaning, the resulting foil would consist of 50 nm (2/3\textsuperscript{rd}) amorphous material. The expansion of the amorphous layers would be constrained in the plane of the foil by the remaining 25 nm of crystalline material. If the amorphous layer thickness is even on both side of the foil the forces are balanced. If the amorphous layer on one side is then removed at 5 keV the compressive forces in the other amorphous side are no longer balanced, and the foil will bend towards
the ion beam to relieve the stress. When the foil is then tilted and the remaining side cleaned the stress is relieved and the foil will once again bend towards the beam.

However, since the foil was bent during the second milling step the removal of amorphous material will not be planar, creating uneven amorphous layers on the second side. This could induce more uneven constraint, resulting in increasingly unpredictable bending behavior as the foil is thinned.

Figure 112: Bending in thin foils: a. Foil with two 25 nm amorphous layers after 30 keV milling. b. Foil after single 5 keV pass bending to relieve strain. c. Foil after second 5 keV pass, uneven milling results in erratic bending.

As foil thickness at 30 keV increases the proportion of amorphous to crystalline material drops. At a certain point the remaining crystalline material will be thick enough to resist the strain induced by the initial reduction of amorphous thickness during the first 5 keV cleaning step. Once the second side has been thinned at 5 keV the strains are once
again balanced, so thinning may proceed without bending. It should be noted that while this simple model does explain a significant degree of bending behavior in the FIB it is by no means complete. Even after neglecting to include residual strains this model does not account for implantation effects or uneven sputtering rates of species. Experienced FIB users consistently report bending behaviors that defy logical explanation even in thick foils.
Chapter 6: Conclusion

The needle technique is fast, cost effective, and may be used in parallel with classical TEM foils. Needles can be made from small slices of a normal FIB slab, allowing collection of data from both foil and needle on the same grid. Amorphous layer thicknesses in silicon and GaAs needles matched previously reported values, making them an effective means of measuring FIB damage. In addition needles are well suited for additional calibrations, three of which have been explored during the course of this research. The symmetry of needles allows accurate measurement of sample-thicknesses, a parameter needed for simulation and quantification of signal in the TEM. Measuring foil thickness is difficult, for the same geometrical reasons that make measuring amorphous thickness on foils problematic. One technique for measuring foil thickness is to compare EELS zero loss peak height to total spectrum intensity, with an estimated accuracy of ±20%. Due to the large uncertainty involved this measurement is not often used, however if the intensity ratio can be calibrated against a specimen of known thickness (i.e. needles) the accuracy can be satisfactorily increased. Zeta factors used for EDS quantification also require knowledge of specimen thickness, and can be directly calculated by collecting signal from needle specimens. Needles may also be used to resolve projection artifacts, as their rotational symmetry is well suited to tomographic
reconstruction. In each case the measurement value is enhanced because the needles used are milled from the same material as the foil and viewed under the exact same microscope conditions. Factors calculated this way will not suffer from changing conditions between microscope sessions, composition differences between samples, or orientation effects, and the overhead added by attaching a needle is minimal (~15-20 min).

The shorter time period and minimal materials needed to create needles allows large quantities to be produced in a small timespan. For example, 11-12 needles were produced in a ~6 hour period from several samples, as compared to one cross sectional foil in the same time. This allowed rapid experimentation with milling parameters and multiple measurements over small compositional gradients. For measurements of damage layer thickness in single materials four needles could be prepared at multiple accelerating voltages in 2-3 hours, allowing double measurements of both 5 and 30 keV damage in a single microscope session. This boost in both speed and number of measurements allowed characterization of multiple material systems. Previously published thru thickness measurements of FIB damage had covered seven materials, six of which were semiconductors, three of which were in the same alloy family, and of those only two materials had been measured by multiple authors [Figure 12]. By comparison, the needles in this study have been made from over 30 compositions, with multiple needles made for the majority of compositions at both 30 and 5 keV. The materials investigated include semiconductors, metals, and intermetallics, the four major crystal systems, and atomic numbers ranging from 12 to 74.
Of those materials SRIM simulations of gallium ion cascade depth varied no more than a few nanometers from sample to sample. Cascade depth did shrink across the board with accelerating voltage, but variation between materials at low voltages remained similar. In silicon and germanium, the cascade penetration depth mapped closely to the measured amorphous layer thickness after both 30 and 5 keV milling. However in other semiconductors and metals, the amorphous layer thickness was several to tens of nm’s lower than predicted cascade sizes. Examination of the results as a whole [Figure 92] indicates that the damage layer formation falls into two categories, namely strong amorphization and linear damage. Materials with a strong amorphous response had amorphous layers well above 5 nm thick when milled at 30 keV, and the thickness of the layer decreased at an average rate of 0.57 nm per keV, with a standard deviation in slope of 0.1 nm. Materials with a linear damage response had little to no variation in damage layer thickness between 30 and 5 keV, and damage layer thickness did not rise above 5 nm thick.

Of the heavily amorphized materials silicon had the thickest amorphous layer. This indicates that despite being considered a standard for FIB damage, silicon actually represents the worst case scenario for amorphous damage. In comparison diamond, SrTiO$_3$, and GaAs amorphous layers were 8-10 nm thinner than silicon, demonstrating that amorphous damage varies fairly widely even within semiconductors. In addition to semiconductors, several ordered materials also showed a strong amorphous response, including TiFe and an HEA B2 phase. While the composition range of the HEA B2 phase is unknown, TiFe has been identified by previous authors as susceptible to
amorphization, which they attributed to its narrow phase field. NiAl on the other hand was identified as resistant to amorphization, and both NiAl and nickel based $\gamma'$ ($Ni_3Al$) both are well known to have wide composition ranges. Both phases showed a linear damage response, and the visible damage layer had significant degrees of order, unlike the strongly amorphized materials. Of the linear damage response materials, only titanium and aluminum had damage layers which could be positively identified as amorphous. All other materials had significant degrees of order evident in their damage layers, with strong moiré patterns indicating the presence of surface crystallinity in several phases.

The presence of observable damage layers is contrary to the established reports of zero amorphization in pure metals. Although oxidation is to be expected in the majority of these materials, the variation in damage layer thickness did not align with susceptibility to corrosion. Damage layers did also not appear to grow over time, aluminum needles examined over a year after being made and stored in atmosphere showed not significant growth or variation in the amorphous layer thickness. Modeling of defect movement and recombination post cascade offers a potential explanation for the layers. If interstitial and vacancies concentration is offset, to be expected due to forward scattering of interstitials during cascades, vacancy concentration at the surface can spike. This heavy increase in disorder, with vacancy concentrations potentially in the tens of percent, could lead to the formation of small damage layers. These layers would likely be incredibly susceptible to oxidation due to the increased mobility of excess vacancies, but no experimental evidence confirms this. It seems likely that if this phenomenon does exist then damage
layers in materials with linear response are likely a mixture of both excess vacancies and oxides.

Damage layers in both damage classes were shown to be susceptible to beam damage in the TEM. At high beam current densities the amorphous layer in silicon recrystallized from the crystalline interface. In NiAl, the damage layers also recrystallized under high beam current densities. Recrystallization occurred throughout the layer, and beam damage was shown to affect the structure of the underlying crystal as well. Damage layer shrinkage and growth was also shown to be an issue. Damage layers in NiAl thickened after imaging at lower beam current densities, while aluminum damage layers shrank under similar beam current densities. The ability of high voltage electron beams to both induce and move defects coupled with the wide variety of damage layer responses to beam damage means imaging can strongly affect the defects seen in both TEM and STEM. If quantifiable imaging is a goal, a great care must be taken to minimize beam damage and account for the effect of changing damage layer structure.

Although recrystallization and oxidation of the damage layers can explain the presence of moiré patterns in TEM, they do not properly account for the differences in clarity seen between off stoichiometric samples of NiAl in HAADF-STEM. Damage layers in off stoichiometric compositions showed the same degree of order when oriented along the same zone axis. The difference in clarity must then be in response to another factor. Investigation of crystalline defects in both materials showed that a significant degree of crystalline damage existed which was not visible in HAADF-STEM. The type of crystalline damage in the two samples was significantly different, consisting of small
loops in one case and streaking in the other. From this we can conclude that the
difference in lattice clarity was not caused by surface damage layers, but rather caused by
the presence of numerous small centers of strain. The strain generated by the defects
could potentially act as scattering centers, reducing channeling and misaligning atomic
columns. In addition the scattering is likely to be non-uniform, as defect clusters in
metals are often constrained to specific orientations making the distortion anisotropic.
This is in contrast to amorphous layers which scatter incoming electrons isotopically,
lowering signal to noise ratio rather than affecting channeling in the crystal.

As the penetration depth and defect generation rate of gallium ion cascades are
expected to be similar in most materials, the crystalline defects should be expected to
form in phases which do not strongly amorphize. The two classes of damage seen in the
experimental work can then be divided into two new classifications, namely the
amorphous dominated and the defect dominated. Materials with intermediate levels of
amorphous layer thickness are likely mixed mode to some extent, with both a thick
amorphous layer surrounding a shell of crystalline defects. These defects may not be
limited to the shell delineated by the cascade depth. In metals with high defect mobility
such as aluminum and copper, the defects generated during FIB milling have been shown
to agglomerate into dislocations, and those dislocations could potentially migrate deeper
into the needle. The presence of both dislocations and loops post milling poses a great
hazard for microscopists examining defect structures in FIB produced foils. Care should
be taken to ensure that the characterized defects are actually native to the material.
The danger can be mitigated to some extent by low accelerating voltage cleaning steps. Penetration depth drops significantly as accelerating voltage drops, corresponding to the drop in amorphous layer thickness in amorphous dominated materials. As long as each successive cleaning step fully removes the previous layer, the damage thickness can be dropped to 6-8 nm at 5 keV, and can be even significantly lowered through use of low voltage argon cleaning at sub keV voltages. This drop in both crystalline and amorphous layer thickness accounts for the increased clarity noted by previous authors. It also provides support for the notion that clarity issues in metals are a result of crystalline damage rather than surface layers, as surface layer thickness has been shown to be consistent between 5 and 30 keV. The need to fully remove previous damage layers, in particular the ~30 nm layer formed at 30 keV should be addressed by ensuring 5 keV cleaning steps occur before the sample has been thinned to full electron transparency. A metal sample thinned down to 75 nm would consist of only 15 nm of unaffected material, 5 keV thinning down to 50 nm would increase clarity slightly, but leave a full 35 nm of crystalline damage not easily viewable in most conditions. Potential expansion of damaged layers also poses a probable issue if samples are over thinned at 30 keV, leading to bending issues which can lead to lost foils or increased damage due to higher incidence angles.

Characterization of damage layers requires HRTEM; amorphous layer contrast in HAADF-STEM is minimal even in optimal conditions and easily mistaken for phase of thickness contrast. Variation of over 15 nm between amorphous layers in HEA phases was missed in HAADF-STEM images by previous authors, and clarity issues were
mistakenly attributed to the material as a whole rather than to specific phases. Likewise surface position and modulation of the crystalline-amorphous interface in materials with thick amorphous layers was barely visible in HAADF-STEM. The potential for both uneven interfaces in and between phases poses a significant issue for modelers, who have previously assumed both straight interfaces and uniform damage. In multiphase materials containing semiconductors or intermetallics, it is vital that the actual edge damage be measured to ensure that variations in damage are not misleading the user.

Taken as a whole the experimental evidence appears to best support the critical density defect theory, as the materials with strong amorphous responses solely consisted of semiconductors and narrow phase field intermetallics. In semiconductor materials, in particular Ge and Si, the stability of the amorphous layers is raised by the ability of the atoms to form stable bonds despite deviation from the preferred orientation. Amorphous silicon forms 5 and 7 member rings which allow the majority of atoms to form four nearest neighbor bonds. This lowers the energy penalty for forming an amorphous layer as the local atomic bonding is still fairly stable. Although experimental and theoretical data indicates that these bond defects are likely unstable in isolation, the base activation energy for recrystallization in silicon is 5 eV. Once the material is fully amorphized, which the dose rate in the FIB practically assures, this means a significant barrier to recrystallization exists, resulting in a stable amorphous layer. In narrow phase field intermetallics the energy penalty associated with deviating from equilibrium composition is high enough to make the amorphous transition favorable. This would probably look something like Figure 113, in which the free energy curve for the amorphous state is
fairly close to the equilibrium crystal energy curve. If a sufficient number of defects are introduced they will raise the crystalline free energy curve above the amorphous curve, providing a driving force for amorphous layer formation.

Figure 113: Possible schematic free energy curves for semiconductor materials

In metals however the crystalline energy minima is extremely low relative to the amorphous free energy curve. This is likely affected by several factors, chief of which are the higher mobility of defects and the ability of point defects to conglomerate into lower energy structures such as clusters and dislocations [86]. Unless formation of defects has an extremely high energy penalty, such as in line compound intermetallics, the energy increase due to defects is unlikely to raise the crystalline energy curve higher than the
amorphous curve, so there is no driving force for an amorphous transformation [Figure 114].

![Metallic Free Energy Curves](image)

Figure 114: Possible schematic free energy curves for metallic materials

Fully proving the theories lay out within this dissertation will require further characterization of FIB damage in various other materials. Further testing of intermetallics across a wide range of systems will be needed to confirm the previous radiation work holds true for gallium ion damage. The presence, type, and number of crystalline defects in metallic systems needs to be further explored, and the significant work remains in uncovering the mechanisms governing defect annihilation and
conglomeration. The use of needles as a tool for calibration can be further refined and milling parameters additionally optimized.
References


