



Marshall Plan Scholarship Report

Investigating Similarities in Mechanical Behavior of
Nanocrystalline Metals and Metallic Glasses

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1 Introduction

1.1 Nanocrystalline metals

Since the seminal works of E.O. Hall [1] and N.J. Petch [2], demonstrating that the yield strength of metals increases with decreasing grain size, fervent academic and industrial efforts have been made to study microstructural refinement. Vast progress has been made in this regard. Summarized by Gleiter [3, 4] in his seminal works, production of metals with grain sizes in the nanometer regime became feasible in the late 1990s due to advancements in processing capabilities. Processing routes ranging from bulk refinement techniques utilizing severe plastic deformation, such as high pressure torsion (HPT) [5], to electrochemical [6] and sputter deposition processes [7] that can easily produce microscale samples of nanocrystalline material have been studied extensively. While bulk samples with dimensions larger than a few cm are difficult to produce, nanocrystalline metals are currently used in several industrial applications [8, 9], and have great promise as coating materials for structural applications in the future. Although nanocrystalline metals exhibit desirable properties, such as high strength and hardness, wear resistance, and other mechanical and electrical properties [10], the scientific understanding of the mechanical deformation, particularly plastic instabilities, of these materials is still nascent. As grain sizes approach the nanoscale, the typical Hall-Petch scaling of $\frac{1}{\sqrt{d}}$ no longer holds, as the deformation physics at the nanoscale is fundamentally different than in coarse grained ($> 1 \text{ }\mu\text{m}$) materials [11]. The typical mechanistic understanding of Hall-Petch behavior in coarse grained materials is that dislocation pileup at grain boundaries hinders subsequent dislocation motion due to the repulsive force between neighboring dislocation of the same sense [12]. However, in materials with grain sizes in the nanometer regime ($< 100 \text{ nm}$), intragranular dislocation content is seldom observed in TEM experiments [13]. This has been explained energetically by showing that a Frank-Read source cannot be operative in grains this small, so intragranular dislocations are inherently unstable, and are not expected to remain after deformation. Indeed, post-mortem and in-situ deformation experiments have shown that dislocations mediate the deformation in materials with grain sizes in the 50-100 nm regime, but are not stored by the material [13]. Since there are few dislocations present initially, the deformation in these materials is primarily governed by the nucleation, propagation, and absorption of dislocations from grain boundaries [13–16]. While the hardening behavior changes in this size regime from pile-up-based hardening to grain boundary-dislocation pinning/bowing, increases in strength are still observed as the grain size is reduced. However, as grain sizes are refined even further ($< 20 \text{ nm}$), additional deformation mechanisms such as grain rotation, grain boundary sliding, partial dislocation-mediated deformation, civilian or military shuffling of grain boundary atoms [6, 17–19], become operative. With the activation of such deformation mechanisms, it is typically observed that further reductions in grain size reduce the flow stress of these materials, although the mechanistic understanding for this behavior is hotly debated [20, 21].

One fascinating feature of the mechanisms operative in these very fine grain (< 20 nm) nanocrystalline microstructure is that they are all grain boundary mediated. Attempts to modify the grain boundaries themselves to elicit enhanced mechanical or thermal behavior have been quite successful. Prominent examples of these attempts include heat treatments or deposition techniques to produce a large concentration of special boundaries [22, 23], and controlled alloying or doping to alter the chemistry of grain boundaries [24–26]. The central aim in all of these processing routes is to increase the activation barrier for plasticity in grain boundary regions. These investigations have vastly improved both the scientific understanding of the mechanical deformation of these materials, as well as suggesting processing strategies to mitigate several of the known mechanical instabilities in these materials such as stress-assisted coarsening [27–29] and any “inverse Hall-Petch” behavior (i.e. where the strength decreases as grain size decreases) [11, 17, 30].

Nevertheless, there are several instabilities that have not been well explained, particularly the propensity for strong shear localization during plastic deformation [31–33]. Recently, several experimental reports on the effect of “grain boundary state” have been shown to correlate well with strong shear localization (or shear banding) in nanocrystalline metals. Early experimental and simulation-based work from Rupert [34, 35] showed that either low temperature annealing or mechanical cycling can reduce the overall energy of the system and promote increases in hardness. This behavior has been termed grain boundary relaxation. Work from Khalajhedayati and Rupert [33] indicates that while such grain boundary relaxation provides an increase in strength, it also increases the propensity for shear banding instabilities. There have been some suppositions in the literature to explain this behavior, although no consensus has been reached. Molecular dynamics (MD) simulations from Han, et al. [36] studying bicrystal geometries indicate that there is a multiplicity of grain boundary energies for a given misorientation. The presence of these metastable grain boundaries has also been shown to promote deformation behavior similar to that of extremely fine grain (< 20 nm) nanocrystalline metals, where grain boundary sliding and atomic shuffling are dominant mechanisms [37]. Recent work by Balbus, et al. suggests that femtosecond laser processing is capable of producing these metastable grain boundary structures in nanocrystalline metals, dramatically decreasing their hardness, and may decrease the propensity for shear localization [38]. The term “rejuvenation” is used to describe such a process, noting the marked similarities between this behavior and similar processing techniques utilized in the metallic glass community.

1.2 **Metallic glasses**

Metallic glasses are a fascinating class of materials due to their unique properties afforded by the combination of an amorphous atomic structure and metallic bonding [39]. The ability to produce a “bulk” (i.e. non thin-film) samples of amorphous metal was first reported in the 1960s for rapidly quenched Au-Si alloys [40], and research into understanding this class of materials has been fervent since. Technologically, metallic glasses are interesting due to their desirable properties such as corrosion and wear resistance, and interesting soft magnetic properties [41, 42].

Applications of metallic glasses cover a broad range including everyday goods such as sporting equipment and kitchen supplies to precisely formed components for high-performance robotics [43]. While there are several aforementioned niche applications for metallic glasses, they are not often used for structural applications due to severe mechanical instabilities originating from their amorphous structure.

Mechanical deformation in amorphous solids is quite different from their crystalline counterparts. Unlike in crystalline materials where dislocations mediate plastic deformation, defining such a defect in amorphous solids is impossible. Nevertheless, it has been observed in simulations [44] and experimentally in amorphous colloidal solids [45] that there is a fundamental unit of plastic deformation, termed a shear transformation zone (STZ) [46]. STZs are small regions of collective atomic (or particulate) rearrangement caused by an applied shear stress [44, 47]. STZ-mediated deformation occurs in virtually all amorphous solids from organic glasses [48] to colloidal suspensions [49], although the mechanistic origins in various material classes are diverse [46].

Unlike plastic deformation in metals which can exhibit work hardening, metallic glasses and other amorphous solids tend to shear soften. During plastic deformation of metallic glasses, STZs tend to coalesce into soft regions known as shear bands. Shear bands are regions within the material, typically tens of nanometers thick, where deformation is extremely localized. The formation of shear bands in metallic glasses often results in the early, catastrophic failure of the material. Shear band formation and propagation is one of the primary reasons metallic glasses are not widely used as structural materials.

Recent attempts to suppress shear band formation through various processing routes, have shown promise in expanding the potential uses for metallic glasses. By altering the thermal history of a metallic glass (i.e. aging) [50, 51], changing substrate conditions during sputtering of thin film metallic glasses [52, 53], subjecting the material to controlled mechanical deformation [54, 55], the properties of a metallic glass can be tailored isochemically from quite hard and brittle to soft and ductile. These changes can be understood through the concept of fictive temperature – the temperature at which the liquid is frozen to form a glass [56]. Glasses with higher fictive temperatures exhibit structures that are more “liquid like”, and glasses with lower fictive temperatures are more “solid like”. Fictive temperature has been shown to correlate well with mechanical properties [52], where more “liquid like” glasses exhibit lower hardness and modulus than more “solid like” glasses. By combining this description with the oft invoked potential energy landscape (PEL) of materials, it can be understood that glasses with a higher fictive temperature occupy higher energy metastable states than lower fictive temperature glasses. In the metallic glass literature, processes that reduce the potential energy of the glass, decreasing the fictive temperature, are known as “relaxation” processes. The inverse – i.e. increasing the energy of the glass – are referred to as “rejuvenation” processes. These behaviors correlate well with other unique thermal and dynamic properties, such as increases in glass transition – often called ultrastability [57], and suppression of beta relaxations [58]. This fundamental understanding, in combination with various processing routes to practically produce materials with a variety of properties, may enable the more ubiquitous use of metallic glasses.

1.3 Similarities between nanocrystalline metals and metallic glasses

In recent decades, researchers have noted stark similarities between metallic glasses and nanocrystalline metals, owing to the high degree of structural disorder in both material systems. Trelewicz and Schuh [17] noted a transition to “glassy” deformation behavior in electrodeposited nanocrystalline Ni-W alloys in the 10-20 nm regime. At large grain sizes, they observed traditional dislocation-mediated or dislocation-grain boundary-mediated deformation, but as they decreased the grain size below 20 nm, inhomogeneous plastic deformation via shear band formation became the dominant mechanism. Concomitant increases in activation volume were observed at the finest grain sizes as well, a further indication of glass-like behavior. Simulations from Lund and Schuh [20] indicate STZ-like motion of atoms at grain boundaries in nanocrystalline materials with ultrafine grain sizes 2-4 nm may be responsible for shear band formation in these systems. Additionally, parallels between the PEL for glasses and “grain boundary state” in nanocrystalline metals are numerous. Recent large-scale computational efforts have shown that the initiation of plasticity in both metallic glasses and nanocrystalline metals with extremely fine grain sizes can be predicted using extremely similar machine learning parameters originally developed for amorphous materials [59]. Khalajhedayati and Rupert [33] have shown experimentally using pillar compression experiments that annealing (grain boundary relaxation) increases propensity for shear band formation, akin to that of glasses. Work from Balbus, et al. [38] has shown that rejuvenation-like processes are also possible in these alloys, although the effects on shear localization in nanocrystalline metals have not been studied.

2 Research Goals

The aim of the work presented in this document is to better understand structure-processing-property relationships in metallic glasses and nanocrystalline metals. There are still many outstanding questions, particularly in correlating dramatic changes in macroscopic properties with changes in atomic structure both at grain boundaries and in an amorphous medium. To address these outstanding questions, we have conducted two somewhat separate investigations: (1) the effects of cryogenic cycling on nanocrystalline metals and (2) investigations of ultrastable thin film metallic glasses.

Cryogenic cycling is a rejuvenation processing route that has been extensively studied for metallic glasses [51]. It has been shown that thermally cycling a metallic glass, particularly those with high pressure sensitivity, between cryogenic (liquid nitrogen) and room temperatures can dramatically enhance the plastic strain to failure of a glass. Mechanistically, this is due to non-affine strains induced by a variety of local atomic structures and neighborhoods, which all respond differently under thermal excitation. The accumulation of these strains causes structural modifications and a concomitant change in mechanical behavior, typically manifest as a decrease in hardness, modulus and

yield strength and increase in ductility. Additional studies have elucidated other interesting dynamics of this behavior, such as a lower temperature “gamma” relaxation [60].

In this work we have studied the effects of cryogenic cycling on nanocrystalline metals. Our hypothesis is that, analogous to the behavior in metallic glasses, local responses to the applied thermal strain will cause structural rearrangements and affect subsequent mechanical behavior. During cryogenic cycling in a nanocrystalline solid, we expect that the local incompatibilities between neighboring grains may lead to locally high strains (and stress), which may induce atomic shuffling or other deformation accommodation mechanisms during cryogenic cycling, thus locally altering the structure of grain boundaries. We expect that this will elicit changes in mechanical properties similar to simulations of metastable grain boundaries [37], as well as our previous work regarding rejuvenation in nanocrystalline metals [38]. By combining nanoindentation measurements, which enable us to measure changes in mechanical behavior, with high resolution electron microscopy experiments, we will be able to correlate changes in the mechanical behavior of these materials with changes to the structure of grain boundaries.

The second study discussed in this work investigates the structural differences between ultrastable and liquid-like metallic glasses. Our group has performed a great deal of work on thin film metallic glasses, particularly regarding how various processing parameters affect properties [52, 61, 62]. Magagnosc, et al. [52] recently demonstrated that by controlling temperature during deposition, one can dramatically tune the mechanical properties of a metallic glass. They propose a model correlating the mechanical properties with changes in fictive temperature(T_f), and suggest that cooling rates necessary to achieve such low T_f would be impossible for bulk samples. Other work has also shown that glasses deposited within a specific temperature range exhibit enhanced thermal stability [57].

In this work we have conducted similar measurements as those in Ref [52] on Cu-Zr binary metallic glasses, but also attempt to explain the structural origins of the enhanced thermal and mechanical behavior of the ultrastable glasses. By coupling nanoindentation measurements with detailed electron microscopy and calorimetry experiments on the same material, we are able to correlate changes in short and medium range order with enhanced thermal and mechanical stability of these structures.

3 Nanocrystalline Metals

3.1 Experimental Details

3.1.1 Sample Preparation

Samples of nanocrystalline 316L stainless steel were prepared using HPT. Disks with 35mm diameter and height of 7.5mm were deformed at room temperature for 15 revolutions at a constant rotation speed of 0.07 rpm. Using the

geometric relation

$$\epsilon = \frac{2\pi r N}{\sqrt{3}h} \quad (1)$$

where where ϵ is the total equivalent strain, r is the radius, N is the number of turns and h is the height, this deformation results in a total equivalent strain of $\epsilon = 116$. Additional details regarding the preparation of this particular sample have been reported in Ref [63]. The effects of relaxation annealing have been well studied for this particular material [63]. To fully relax the samples after HPT while preventing the precipitation of secondary phases at grain boundaries, the samples were then annealed at 823K for 90 minutes. Slices were then extracted as shown in Figure 1 from the HPT disk and polished electrochemically. Slices investigated were sectioned from regions >10mm from the torsion axis to eliminate any inhomogeneities in the microstructure. To ensure homogeneity across the sample, microhardness measurements were conducted using a Vickers indenter and a load of 500g. The results of this experiment are shown in Figure 1, indicating a consistent microstructure throughout the sample. The region in which all subsequent indentation measurements were conducted is outlined in red. These samples were then cryogenically cycled by submerging them in a bath of liquid nitrogen (LN2). The cycling procedure was performed as follows: all samples were submerged for 1 minute in LN2 and then removed. at which point they were brought to room temperature by flowing compressed room temperature air over them for 1-2 minutes. This procedure was performed between 0 and 50 times and interrupted for various indentation and electron microscopy investigations.

3.1.2 Indentation

To note any changes in mechanical behavior of the cryogenically cycled nanocrystalline 316L austenitic steel, nanoindentation measurements were performed using a Keysight Technology G200 nanoindenter equipped with a berkovich tip and dynamic indentation unit to perform continuous stiffness measurement (CSM) tests. Traditional indentation tests at an indentation strain rate of 0.05 s⁻¹ were performed after 0, 25 and 50 cryogenic cycles, and strain rate jump tests were performed at 0 and 50 cycles to note any apparent change in hardness, modulus, strain rate sensitivity, and activation volume. To minimize the effects of thermal gradients, samples less than 1mm in thickness were used during cryogenic cycling. This thickness constraint can be calculated using the Biot number, which was done as follows:

$$Bi = \frac{h * L}{\kappa} \quad (2)$$

where h is the heat transfer coefficient, κ is the thermal conductivity and L is the characteristic length scale of the sample, in this case chosen to be the thickness. For samples with a Biot number less than 0.1 we can safely ignore the

effects of any thermal gradients during cycling. For 316L stainless steel with a thickness of 1 mm, the Biot number is:

$$Bi = \frac{1355 \frac{W}{m^2s} * 10^{-3}m}{16.3 \frac{W}{mK}} = 0.083 < 0.1. \quad (3)$$

We can thus safely ignore any effects of thermal gradients for the samples investigated in this study. Samples were mounted on a brass support using a silver-based epoxy for the indentation measurements.

3.1.3 Transmission Electron Microscopy

We investigated the microstructural effects of cryogenic cycling by TEM and STEM. Samples were prepared from a different slice of the HPT disk which was further from the HPT axis to ensure uniformity. Two 3 mm diameter disks were prepared from this sample, one of which was subjected to 50 cryogenic cycles by submerging in liquid nitrogen for 1 minute and removing and allowing to come to ambient temperature for 1 minute. These samples were then jet polished to create an electron transparent region and further thinned with a broad beam ion mill. We hypothesize that any effects manifested mechanically are primarily due to differences in grain boundary structure, but investigations of the average grain size and dislocation content were performed to eliminate these effects. We have also attempted high resolution TEM imaging of grain boundaries, in order to note and significant differences in the predominant structures in these regions. These experiments are tedious, and broadly speaking inconclusive – there is such a wide array of grain boundary structures in a nanocrystalline material that drawing broad conclusions with limited statistics is futile. Nevertheless, we can attempt to discuss the degree of equilibrium in each of the samples by investigating the presence of defects pre[sent in STEM images, as well as contrast variations near grain boundaries to give some insight into local strain in these regions. By conducting these measurements at several representative grain boundaries in both the annealed and cryogenically cycled configuration, we may be able to detect changes microstructure that are responsible for the global change in mechanical behavior.

3.2 Results and Analysis

3.2.1 Grain Size and Defect Content

Figures 4 and 2 show bright field conventional TEM and STEM images of the HPT deformed and annealed 316L stainless steel after zero and fifty cryogenic cycles. Average grain sizes were measured from the STEM images. Using image processing software, we measured the grain size of at least 50 grains from each sample and have plotted these results in Figure 5. The mean grain size, indicated by the vertical lines in Figure 5, was 45 nm for the annealed sample and 43 nm for the cryogenically cycled sample. The grain sizes of both the annealed and cryogenically cycled samples had standard deviations of 14 nm, which suggests that there is not a significant difference in the average grain size

between these two samples.

Figure 3 shows high resolution TEM images of grain boundaries in the annealed and after being subjected to 50 cryogenic cycles.

3.2.2 Softening Observed in Indentation

Figure 6 shows the hardness and Figure 7 shows the modulus data collected for the 316L stainless steel. While the decrease in hardness observed here is significantly smaller than our previous measurements on similar material (316L stainless steel refined by HPT using a 6 mm diameter anvil as opposed to a 30 mm diameter anvil, hardness measurements shown in Appendix Figure 29), there is still a notable decrease between the as annealed material and the material subjected to 50 cryogenic cycles. The negligible decrease between the as-annealed sample and the sample subjected to 25 cryogenic cycles is due to slight differences in how the material was cycled during the first 25 cycles. During the first 25 cycles, the samples were contained within a mesh container and lowered into liquid N₂, which may have limited their ability to reach 77K and 296K during each cycle. Subsequent cycles were performed by manually inserting and retracting samples from a liquid N₂ bath with tweezers during cycles 25-50. Nevertheless, we do see a decrease in the average hardness measured in these conditions. Figure 8 shows the load-depth profile and Figure 9 shows indentation strain rate-depth data for a typical strain rate jump test to elucidate strain rate sensitivity and activation volumes. Figure 10 shows the strain rate sensitivity and corresponding activation volumes measured for the as-annealed sample and for the sample subjected to 50 cryogenic cycles. As described in great detail in a recent work published by Maier-Kiener, et al. [64], nanoindentation measurements are extremely powerful for elucidating thermally activated and time dependent deformation mechanisms. Strain rate sensitivity in this work was calculated as presented in [64], first derived by [65].

3.3 Discussion

3.3.1 TEM/STEM: Role of Grain Boundaries

To reiterate, nanocrystalline metals, due to their highly nonequilibrium nature, are extremely sensitive to their thermal and mechanical history. There are numerous reports in the literature [33–35] of low temperature annealing being utilized to relax nanocrystalline metals, simultaneously increasing their strength and propensity for catastrophic failure via shear band formation. Similar effects have been observed as a result of mechanical cycling in simulations [35]. However, there have been few indications that the inverse processing route is feasible. Work from Balbus, et al. [38] first suggested that there are processing routes that may elicit rejuvenation – i.e. a process which raises the overall energy of the system, the converse of relaxation – in nanocrystalline metals. These rejuvenation processing routes have potential as a means by which to reduce the propensity for shear band formation and catastrophic failure

in nanocrystalline metals.

It is evident that the grain interiors play a minor role during deformation in nanocrystalline metals, whereas the grain boundaries are critical. Simulations have shown that metastable grain boundaries are mechanically weaker – resulting in significantly lower yield stresses [37]. These simulations also suggest that grain-boundary mediated deformation mechanisms such as grain boundary sliding and atomic shuffling at grain boundaries are favored over dislocation-mediated plasticity when metastable grain boundaries are present.

Rejuvenation processing routes attempt to modify grain boundaries, allowing them to occupy higher-energy metastable configurations. Previous work from Balbus, et al. [38] showed that a very near surface layer of grain boundaries can be affected by low-energy femtosecond laser irradiation. Unlike more conventional thermal processing routes, the femtosecond laser may preferentially localize energy at grain boundaries due to local phonon modes that are not present in the interior of the grains. There has been some discussion about if this is a local heating or stress-related phenomena. Nevertheless, while the precise mechanism is not yet elucidated, the effects on mechanical properties are quite extreme. For nanocrystalline Al-O films, Balbus et al. [38] report over an 80% decrease in the hardness as a result of the laser processing. However, this route is limited due to the volume of material that can be affected – the optical penetration depth is several nanometers, and the induced stress wave only propagates several hundreds of nanometers. More traditional “bulk” processing routes may eliminate this problem. Cryogenic cycling is a “bulk” processing route that has been used as a rejuvenation processing route for several metallic glasses [51] but has not been applied to nanocrystalline metals. In metallic glasses, local non-affine strains are induced due to local variations in bonding, and thus thermal expansion behavior. Similarly, nanocrystalline metals may be susceptible to similar effects due to the local misorientation between grains and the incompatibility that arises during thermal cycling. Given the limited thermal stability in nanocrystalline metals due to the abundance of interfaces, cryogenic cycling presents a unique opportunity to induce large amounts of strain without the risk of temperature-induced grain growth. Local incompatibilities due to misorientation differences across a grain boundary can be calculated analytically [66], but are mathematically quite complex and do not explicitly account for the atomistic behavior at the grain boundary – and thus the effect of grain boundary metastability. The magnitude of the global strains induced during cryogenic cycling may enable us to better understand the effects of cryogenic cycling on nanocrystalline metals. For 316L stainless steel, the coefficient of thermal expansion (CTE) is $17 \times 10^{-6}/^{\circ}\text{C}$ according to [67]. When cycling between liquid nitrogen and ambient temperature, the magnitude of the global thermal strain is:

$$\epsilon = 17 \frac{10^{-6}}{^{\circ}\text{C}} * (296 - 77) = 0.0037. \quad (4)$$

This level of global strain is greater than the typical 0.2% offset used to measure the onset of yielding during a typical tension test, thus large enough to induce plastic deformation. Given the grain size of the HPT refined steel, we expect

both dislocation and grain boundary mediated deformation mechanisms to be triggered as a result of this global strain. It is clear from our electron microscopy investigations of the cryogenically cycled 316L stainless steel in Figures 4 and 2 and corresponding grain size distribution in Figure 5 that the grain size does not change as a result of the cryogenic cycling. This eliminates the potential role of grain coarsening in the observed softening. Nanocrystalline metals have been shown to exhibit stress assisted coarsening and grain growth during mechanical deformation [27], although these are typically observed in pure or dilute binary alloys. While the chemical complexity and impurity content of the 316L stainless steel may prevent stress assisted coarsening, it is noteworthy that such a high level of global strain does not trigger coarsening in this material. Additionally, we note no obvious difference in the defect content present as a result of cryogenic cycling. This is not an unexpected result, as it is unlikely to store intragranular dislocation content in materials with grain sizes below 50 nm. Figure 6 suggests that cryogenic cycling induces small, recoverable changes in hardness. This data, combined with the TEM investigations which eliminate the roles of grain size and intragranular dislocation content, suggests that cryogenic cycling affects the grain boundaries of the material, and thus the subsequent mechanical behavior of the steel. With a relatively large average grain size, we expect that nucleation, propagation and absorption of dislocations at grain boundaries is the predominant deformation mechanism. Atomistic simulations have shown that the absorption of dislocations at grain boundaries creates a large increase in the average energy of atoms involved in the absorption event, as well as an increase in the deviatoric stress in these regions [19, 68]. Given that the global strain imposed by the cryogenic cycling is greater than that necessary to initiate plasticity, we expect that during each cycle dislocations are nucleated and move to accommodate the imposed strain. If the dislocation is nucleated at a grain boundary, propagates through the interior of the grain and is absorbed by the boundary on the opposite side of the grain, it will induce atomic rearrangements at that boundary to accommodate the dislocation. By repeating this process numerous times through repeated cryogenic cycling, the energy of the grain boundary may increase due to repeated dislocation absorption events, occupying a higher energy metastable configuration as a result. This highly stressed grain boundary is expected – and has been shown in simulations – to respond differently under subsequent mechanical loads, and may then accommodate deformation at lower loads through mechanisms such as grain boundary sliding or atomistic shuffling at a grain boundary, which manifests as a reduction in hardness. This hypothesis is supported by the strain rate sensitivity and activation volume data in Figure 10. Typically, a decrease in activation volume is observed with decreasing grain sizes for conventional materials. An inflection point in this behavior was observed by Trelewicz [17], at which the activation volume increases as the grain size decreases, generally below 20 nm. Our data suggest that while the grain size remains fixed, there may be a small increase in the activation volume. This change, while not statistically significant by any means, is another suggestion that the deformation mechanisms of nanocrystalline materials may evolve with the incorporation of more metastable grain boundaries. A less plausible explanation of the observed softening is that the cryogenic cycling induced deformation directly activates grain boundary mediated mechanisms such as grain boundary sliding. Many

researchers have noted the activation of grain boundary sliding in nanocrystalline materials [18, 19, 69], however these are primarily in pure materials tested at a high homologous temperature (i.e. Al alloys tested at room temperature) or in materials with grain sizes below 20 nm. Given that the materials involved in this study have a larger grain size, and are both deformed and indented at low homologous temperatures, we do not expect these mechanisms to be responsible for the behavior observed. Additionally, there are several studies that investigate the role of grain boundary sliding in HPT refined metals [70], all of which seem to indicate that grain boundary mediated deformation mechanisms are relatively inactive compared with dislocation-boundary mediated ones. Future work will be undertaken to investigate the mechanism by which these materials study the effects of post-cryogenic cycle-annealing to relax the structure, any saturation phenomena observed after many cycles, as well as the effects on different alloy compositions, particularly Ni-based alloys. DSC measurements may also enable quantification of excess energy stored in grain boundaries as a result of cryogenic cycling. Finally, the effect of cryogenic cycling on propensity for shear band formation has not been elucidated, but is expected to enhance the ductility by preventing the formation of a single catastrophic shear band.

4 Metallic Glasses

4.1 Experimental Details

4.1.1 Sample Preparation Via Sputter Deposition

Amorphous binary Cu-Zr thin films were produced by sputter deposition in an AJA International ATC 1800 system with 2-inch diameter sputter sources. The system was run in a confocal arrangement with one Cu target (99.999% purity) and one pre-alloyed 90 at.% Zr -10 at.% Cu target (99.95% purity). For the substrate temperature studies, powers of 50 and 200 W were selected for the Cu and Zr/Cu sources, respectively, in order to sputter near equiatomic Cu-Zr metallic glasses. Base pressures prior to deposition were all below 10^{-7} Torr in order to minimize oxygen and other impurity incorporation into the film during deposition. Substrate heating was performed using a custom quartz lamp heater being controlled by a SHC-10 PID heater controller. All reported deposition temperatures were extracted from a calibration curve measured at the substrate prior to all deposition. Soak times of at least 5 minutes at temperature were performed after a ramp of $0.5^{\circ} \frac{C}{sec}$ to ensure adequate thermal uniformity and stability during the deposition runs. Deposition rates were measured in-situ by using a quartz crystal monitor (Inficon SQM-160). For the alloy target, pure Zr was used as an atomic mass calibration for rate measurements. For substrate temperature studies, all films were deposited using 3mTorr Ar as the process gas. To investigate the effects of deposition rate, samples were deposited at room temperature and at 150°C at 18 nm min^{-1} and 2 nm min^{-1} . To ensure similar chemical composition of the 2 nm min^{-1} samples to the others investigated in this study, individual rate measurements of the Cu and Zr/Cu

targets were performed at different sputtering powers, and the ratio of Cu to Zr/Cu deposition rate was kept constant. For instance, for the 18 nm min⁻¹ deposition experiments, individual rates of 1.8 Å s⁻¹ and 0.75 Å s⁻¹ were measured for the Zr/Cu and Cu targets respectively, resulting in a ratio of 7:3 for the deposition rate of Zr/Cu and Cu. For the 2 nm min⁻¹ samples, powers of 5W and 30W were selected for the Cu and Zr/Cu targets. These settings resulted in a 0.1 Å s⁻¹ rate for Cu and 0.25 Å s⁻¹ for Zr/Cu, yielding a similar deposition ratio and chemistry.

4.1.2 Sputtering of Flash DSC Chips

Differential scanning calorimetry (DSC) was performed using a Flash 1 DSC (Mettler Toledo). UFS chips with a maximum operating temperature of 500°C were used. To directly sputter these chips with the Cu-Zr metallic glass of interest, the chips were inverted and suspended over a washer made of 316L stainless steel to prevent damage to the chip during deposition. The reference side (see image) was masked using 316L stainless steel foil held in place on the substrate holder with a clip. One Cu TEM grids with ultrathin carbon support (Ted Pella, Inc.) were held on the PC board of the DSC chip to ensure that both the DSC chip and the TEM grid experienced similar conditions during deposition. Another TEM grid was fixed directly to the substrate holder itself to note any difference due to slightly different thermal boundary conditions.

All temperature studies were conducted at a fixed deposition rate of 2.77 Å s⁻¹ (18 nm min⁻¹). DSC chips and TEM grids were sputtered with 30 nm of material at temperatures of 27°C, 150°C, 360°C and 451°C.

Rate effects were studied for room temperature and 150°C by depositing films at a high rate (18 nm min⁻¹) and a low rate (2 nm min⁻¹). Glasses deposited at low rates have been shown to exhibit similar behavior to those deposited at high rates and elevated substrate temperatures [52, 57] but direct comparison of these effects or the combined effect of low rate and elevated deposition temperature has not been shown.

4.1.3 Indentation

To test mechanical behavior of these materials, 500 nm thick films were deposited on Si (100) wafers at a variety of substrate temperatures. Indentation experiments on these thicker sputtered films were conducted using a Nanomechanics® iMicro nanoindenter equipped with a 50mN load cell with a Berkovich tip. The instrument was operated in a continuous stiffness measurement (CSM) mode, in which a dynamic oscillation is superposed over the loading curve [71]. CSM enables extraction of depth dependent hardness and modulus of the material. All reported values of hardness and modulus were extracted from depths of 175 nm. This depth was chosen by investigating the $\frac{P}{S^2}$ curves for each indentation experiment and selecting a value for which the curve was constant as a function of depth, according to the Saha-Nix methodology [72]. Hardness and modulus values reported are the result of at least 20 indentation experiments per data point, with error bars representing one standard deviation.

4.1.4 Transmission Electron Microscopy

To investigate the effects of substrate temperature on the atomic structure of the metallic glasses in this work, 10 nm thick electron transparent samples were characterized in the TEM using nanobeam diffraction (ND) experiments and traditional high resolution TEM (HRTEM) using a JEOL 2200FS. Samples were sputter deposited to the desired thickness using a quartz crystal monitor, eliminating any concerns regarding TEM sample preparation (electropolishing, FIB, etc.), which have been shown to affect the atomic structure of these glasses. Energy filtered selected area diffraction patterns were collected for each sample to characterize clear changes in short range order as a result of various deposition conditions. ND experiments were performed with a probe size of 1.8 nm and a camera length of 50-60 cm.

4.1.5 DSC

Chip DSC measurements were conducted with a Mettler Toledo Flash® 1 DSC device. All experiments were tested in an Ar atmosphere with a heating rate of $1000 \frac{K}{s}$. To eliminate the thermal behavior of the chip itself from affecting the heat flow curves, two heating and cooling segments were performed, and the second heating segment was subtracted from the first.

Traditional DSC measurements were conducted using the 500 nm thick films sputtered on (100) Si with a Mettler Toledo DSC 3+. This instrument is connected to a liquid N₂ reservoir to ensure precise heating and cooling control. All samples were placed in Alumina (Al₂O₃) crucibles and had samples masses ranging from 10.52 to 15.62 mg (including the Si). Experiments were performed in an Ar environment to minimize oxidation and with a constant heating rate of $20 \frac{K}{min}$. Similarly to the chip DSC measurements, two heating and cooling runs were performed on these samples and the second run was subtracted from the first to minimize any effects of the crucible and oxidation of the sample.

4.2 Results and Analysis

4.2.1 Hardness Measurements

Figures 11 and 12 show hardness and modulus values extracted from indentation experiments on the sputtered Cu-Zr glasses. The effect of controlling substrate temperature during deposition is dramatic, affording tuneability of the hardness by over 1GPa and modulus by 50GPa. The data shown here is strikingly similar to that reported by Ref [52], where they showed an increase in hardness and modulus as substrate temperatures approached $0.7 - 0.8T_g$ in a Pd-based ternary metallic glass.

Interestingly, the samples deposited at room temperature and at 451°C have both higher hardness and moduli than expected. Samples deposited between 30°C-360°C follow trends similar to that reported by Ref [52], which may

suggest that both the room temperature and 451°C samples are partially crystalline. This will be discussed in more detail in the context of the results of the TEM investigations.

4.2.2 DSC Measurements

Figure 13 shows heat flow curves of the Cu-Zr glasses sputtered on UFS chips at three/four substrate temperatures. The scale bar in this plot has a height of 0.1 mW and the data was plotted with the anti-ICTA convention, where endothermic phenomena result in positive changes and exothermic phenomena cause decreases. This convention is quite common in the metallic glass community. While use of the Flash® DSC, which enables heating and cooling rates up to several thousand Kelvin per second, has greatly enhanced the communities understanding of metallic glasses, the chips did not behave as expected during our measurements. As can be seen in Figure 13, it is difficult to identify a clear glass transition or crystallization peak in any of the samples. This is due to the extremely small sample volume deposited in this study. While having a fixed sample thickness for both TEM and DSC investigations would enable more direct comparison, the 30 nm thick films had such a small mass that the DSC was unable to resolve any clear trends. In addition to the small sample mass, as evident for the sample deposited at 360°C, there were very large jumps in the calorimetry data, which we believe to be a result of stress relaxation during heating or other artifacts for the particular chip used to make these measurements. Unfortunately, due to these issues, it is difficult to analyze this data or draw conclusions. Additionally, the data for the rate studies is not shown, as it is even more difficult to interpret

Figure 14 shows heat flow curves of the Cu-Zr glasses sputtered on (100) Si wafers and measured using conventional DSC. These data are plotted using the same convention as Figure 14 where endothermic phenomena are positive and exothermic phenomena are negative. Despite the small signal, we attempted to identify glass transitions in these curves by using the common tangent method. The midpoint between the onset and endset of these curves is identified in each plot. While this method is quite sensitive to small irregularities in the curve, as well as any potential stress relaxation during annealing, we see a slight increase in T_g for the glasses deposited in the “ultrastable” regime near $0.75T_g$. This behavior has been seen for other sputtered deposited glasses by controlling substrate temperature [52, 57] and deposition rate [53]. The smaller magnitude seen in this work compared to [53, 57] may be due to the small DSC signal and our ability to accurately resolve T_g for such small sample volumes.

4.2.3 ND-STEM/Fluctuation Microscopy

For crystalline materials, interpretation of electron microscopy measurements is relatively straightforward – given a set of experimental conditions (probe size, sample thickness, etc.) one can achieve conditions where sub-Å resolution is possible, and measurements of atomic structure directly from images are possible [73]. In amorphous materials, due to the lack of long range periodicity, diffraction experiments like traditional high resolution TEM (HRTEM) or STEM

imaging do not provide meaningful insight into atomic structure. Nevertheless, to ensure no obvious crystallization, Figure 15 shows HRTEM images of 10 nm thick Cu-Zr glasses sputtered at various substrate temperatures. Figure 16 shows zero loss energy filtered diffraction patterns from the same 10 nm thick samples. Streaking present in this image is due to the short exposure time utilized to record the image. To quantify these images, we plotted the mean intensity of the azimuthal projection of these diffraction patterns. The intensity as a function of scattering vector magnitude for the samples deposited at 150°C, 360°C and 451°C is shown in Figure 17, indicating that there are clear differences in atomic structure between these materials, as evident by changes in both the shape and location of the peak, particularly between the glasses deposited at 150°C and 451°C. There is no clear peak shift between the samples deposited at 360°C and 150°C.

While it is difficult to draw meaningful conclusions about the atomic structure of amorphous materials from traditional TEM measurements, a recent technique called Fluctuation Electron Microscopy (FEM) has been used to study the effects of microalloying [74, 75], annealing [76], and other processing effects on the structure of metallic glasses and other amorphous materials [77]. FEM is a technique that analyzes the variance of an image as a function of both probe size and scattering vector, which is sensitive to the structure of amorphous materials. While originally proposed utilizing hollow cone dark field illumination, nanobeam diffraction or STEM FEM have been used recently for structural characterization of metallic glasses [77]. Despite being a relatively new technique, many of the possible artifacts of the measurement have been studied, such as the effect of sample thickness, spherical aberrations, probe coherence, etc. [78]. Additionally, simulation packages to ease interpretability of FEM maps have also been developed, allowing scientists to simulate FEM patterns with various microscope conditions including aberrations and defocus [79]. Other packages enable the construction of atomic positions from FEM measurements through hybrid reverse Monte Carlo simulations [80]. In this work we utilize ND-FEM, which utilizes diffraction patterns generated using a small, convergent probe in the TEM. To extract structural information from these patterns, the variance in intensity of the diffraction patterns can be plotted as a function of scattering vector (and probe size, although this has not been performed in this work). By looking at various peaks in this variance data, one can make conclusions about the medium range order in amorphous materials [81]. The variance is calculated as follows:

$$V(k, Q) = \frac{\langle I^2(k, Q) \rangle}{\langle I(k, Q) \rangle^2} - 1 \quad (5)$$

Despite this mathematical formulation, the order and manner in which the variance computation is performed for large datasets is non-trivial. Four different methods for calculating fluctuation maps are shown schematically in Figure 18 (reproduced from Ref [75]). These all yield similar information, although some are utilized more frequently than others [75]. To study the effects of substrate temperature on atomic structure and medium range order, we calculated the normalized variance for each diffraction pattern as a function of scattering vector, and then take the mean of each

of these. This calculation was chosen, despite its computational expense, because it may enable us to conduct spatial mapping of medium range order of these materials in future works.

Figures 19 and 20 shows the result of the fluctuation analyses described above on a large 25X25 diffraction pattern dataset. While Figure 20 is interesting, let us focus on Figure 19. This data is quite noisy for several reasons, but primarily because it includes material sputtered across interfaces between the 3 nm ultrathin C support film and the thicker 20 nm thick C film, that itself supports the 3 nm regions. At these interfaces, crystallization is promoted at lower temperatures, and it is expected that the amorphous structure in these regions is different as well. To minimize these effects, we extracted smaller 5X5 datasets from only regions supported by the ultrathin 3 nm C film. These smaller datasets are shown in Figures 21 and 22. It can be seen that the peak changes in height, shape, and scattering vector of highest variance (position) as a function of deposition conditions. The first prominent peak appears to increase in height and scattering vector as a function of increasing substrate temperature. The sample deposited at 451°C appears to have two clear peaks at 3.4 nm^{-1} and 4.5 nm^{-1} as well as several peaks at larger scattering vectors, which is indicative of a partially crystallized material. The samples deposited at 150°C and 360°C have a clear first peak at 4.1 nm^{-1} and 4.3 nm^{-1} respectively. They also appear to have secondary peaks at 6.6 nm^{-1} for the sample deposited at 150°C sample and 7.2 nm^{-1} for the sample deposited at 360°C.

Despite these smaller 5X5 datasets being slightly more representative of the atomic structure, the small number of diffraction patterns makes interpretability more difficult and diminishes the statistical significance. To mitigate this, we constructed datasets of 200-300 diffraction patterns for each of the 4 deposition temperatures in which no obvious crystallites were present. To clarify, four schematic ND patterns are shown in Figure 23. Samples were only selected for this dataset if they had no evidence of crystallinity, or only like Figure 23D, A-C were all eliminated. In this case, we are potentially ignoring small crystallites within the amorphous matrix on the ultrathin carbon membrane, however we are not interested in the ND patterns of the crystallites anyway. The results of the FEM analysis on these datasets is shown in Figures 24 and 25. These data are the most representative of the atomic structure out of the FEM plots shown. We have also performed the 2D FEM analysis on these datasets, which is shown in Figures 26 and 27 and is qualitatively similar to Figures 24 and 25, but with slightly different peak heights.

4.3 Discussion

4.3.1 Mechanistic Understanding of Enhanced Mechanical Behavior

Several researchers have proposed mechanisms that may cause the apparent increase in mechanical properties of glasses sputtered in the ultrastable regime [52, 57, 82]. Singh, et al. [82] argue that during the deposition process, increased substrate temperatures enable adatoms to explore a broader spectrum of the PEL by enhancing their mobility. Thus, glasses deposited at high temperature can access equilibrium states inaccessible via conventional quenching.

However, in glasses deposited at temperatures greater than $0.7 - 0.8T_g$ this observation no longer holds. Adatoms in this regime have such high mobility that they can become trapped in energetically unfavorable configurations, and thus the mechanical behavior of these glasses is expected to be more liquid like than the ultrastable glasses. Magagnosc, et al. [52] have extended this explanation to link the mechanical behavior with changes in fictive temperature.

While no direct connection between prominent structural motifs present in ultrastable metallic glasses and mechanical properties has been explored in the literature, this is an excellent area for future work.

4.3.2 Mechanistic Understanding of Thermal Behavior

The connection between the enhanced thermal behavior of ultrastable glasses and local atomic structure have not been well explored in the literature. This is due to experimental difficulties observing medium range order of glasses. From the seminal work of Yu, et al. [57], to more recent work expanding on available processing routes for ultrastable metallic glasses [53], there is little mechanistic understanding as to what structural motifs are most thermally stable and responsible for the enhanced glass transition and crystallization temperature.

Singh, et al. [82] using Lennard-Jones models show that packing arrangements of ultrastable glasses are significantly more homogeneous than traditional liquid-quenched glasses with fewer ordered clusters. These authors suggest that for vapor deposited metallic glasses, the shape of the most prominent structural motif becomes more regular compared to metallic glasses prepared through quenching. For simulated $\text{Ni}_{80}\text{P}_{20}$ alloy, glasses prepared through vapor deposition exhibited four certain preferred polyhedra, whereas glasses prepared through conventional quenching exhibited a broad range of (often irregular) polyhedra.

From a thermodynamic perspective, the explanation for the enhanced glass transition of ultrastable glasses hinges on the depth of the local metabasin on the potential energy landscape of the glass. Ultrastable glasses are suggested to occupy lower energy basins than traditional glasses, so more thermal energy is required to overcome these barriers and cause the glass to flow. No particular mechanisms have been proposed for understanding the kinetics of these behavior or diffusive pathways in metallic glasses to cause these rearrangements.

4.3.3 FEM Indications of Local Ordering

Zhang, et al. [76] have conducted similar FEM studies on Cu-Zr-Al metallic glasses prepared by melt spinning. Utilizing a hybrid reverse monte carlo (HRMC) algorithm developed by Maldonis, et al. [80], they utilize FEM data to generate atomistic models of these glasses. From the atomistic model, they investigate the effects of sub- T_g annealing, as well as the effects of Al incorporation on the medium range order of the Cu-Zr glasses. The result of these simulations indicate that Al incorporation, and hence glass formability, can be understood by looking at the presence of two prominent structural motifs – icosahedral ordering and crystal-like ordering – which manifest as two

distinct peaks in the variance for fluctuation microscopy experiments. Five-fold icosahedral solute-centered packing has been widely accepted as the primary structural motif in metallic glasses [83, 84], but other structural motifs such as distorted fcc-crystal-like packings can be observed in these systems [76]. Figure 28 is reproduced from Ref [76] to illustrate the effects of these distinct motifs on FEM peaks. Zhang, et al. [76] show that glasses with enhanced glass formability have a higher concentration of crystal-like packing.

Given that the composition of glasses investigated in this study is quite similar to that of Ref [76], we suggest that the interpretation presented in [76] can be extended to this study. In the FEM data for both the small and large datasets, the peaks indicative of both icosahedral and fcc-like packing are present. Samples deposited at high temperature (360°C and 451°C) exhibit peaks indicative of fcc/crystal-like packing located around 4.7 nm^{-1} with a clear shoulder around 5.3 nm^{-1} . This is unsurprising for the sample deposited at 451°C, as this is clearly above the crystallization temperature observed in the DSC data, and evident as small crystallites in the nanodiffraction patterns. The ultrastable sample deposited at 360°C is quite interesting, as it also exhibits a high fraction of crystal-like structural motifs, but has a larger peak at a smaller reciprocal vector around 3.8 nm^{-1} than the 451°C sample and fewer crystallites. The peak around 3.8 nm^{-1} , as suggested by Ref [76], is indicative of icosahedral packing. Extending this interpretation to the 27°C and 150°C samples, it is clear that icosahedral packing is the predominant structural motif in these samples, indicated by the peaks around 4.2 nm^{-1} .

Sarac, et al. [85] performed FEM studies on thermoplastically formed Cu-Zr based glasses to investigate the effects of annealing and thermoplastic forming on the atomic structure and embrittlement of these materials. In this work, they conclude that elastostatic loading can reduce the local ordering induced during thermoplastic forming. This reduction in local order is indicated by a reduced peak height in the variance data collected using FEM. While caution in interpreting FEM signals is paramount, we suggest that given the compositional and experimental similarities between these measurements and the data presented here, extension of the interpretation of Sarac, et al. [85] is appropriate.

Comparing the peak heights of the 150°C, 360°C, and 451°C allows us to discuss the degree of ordering between these samples. Looking at the result of the FEM analysis on the smaller dataset, the sample deposited at 360°C exhibits a higher, more prominent peak than the sample deposited at 150°C, suggesting that the sample deposited at 360°C (the ultrastable sample) has a higher degree of structural order than the sample deposited at 150°C. However, the larger dataset FEM analysis suggests a different interpretation. Due to the presence of peaks at larger reciprocal space vectors indicative of crystal-like packing, we suggest that the ultrastable glass has a high degree of ordered crystal-like packing compared to the 150°C deposited glass, and relatively disordered icosahedral packing. This is further supported by the FEM data for the glass deposited at 451°C, which has a majority of crystal-like packing as confirmed by both the presence of crystallites in the diffraction patterns and the increased height of the variance peak around 4.7 nm^{-1} . The slight shift in this peak location relative to the (110) planes for an ordered B2 CuZr intermetallic phase which is expected at 4.4 nm^{-1} is likely due to the camera length calibration of the TEM being slightly off as well as the binning

process used on each diffraction pattern.

The atomic origin of ultrastability in metallic glasses is a hotly debated topic. For organic glasses, simulations and experiments [82] have shown that enhanced surface mobility during vapor depositions allows adatoms to explore extremely low energy configurations, resulting in preferred molecular orientations in the deposited glass. These preferred orientations can be modeled well for molecular glasses, but the structure of ultrastable metallic glasses has not been characterized. Our work indicates that the molecular structure of ultrastable metallic glasses exhibit predominantly crystal-like packing motifs, with a moderate competition between icosahedral packing. The presence of these crystal-like structures is thus responsible for the enhanced mechanical and thermal properties of the ultrastable glasses.

5 Conclusions

The results of two investigations of the effects of metastability on mechanical deformation and atomic structure have been reported in this work. The first investigation elucidated the effect of cryogenic cycling on a nanocrystalline 316L stainless steel prepared by high pressure torsion. Our conclusions from this study can be summarized as follows:

- Cryogenic cycling of nanocrystalline metals results in moderate softening that is grain size dependent – smaller grain sizes exhibit larger softening than larger grain nanocrystalline metals.
- The modulus of nanocrystalline materials subjected to cryogenic cycling appears to decrease with increasing cycles, although this effect must also be investigated further.
- Cryogenic cycling does not affect the average grain size or intragranular dislocation content, despite a macroscopic strain of 0.37%.
- The effects on mechanical behavior post cryogenic cycling can be ascribed exclusively to grain boundaries.
- There is a slight change in activation volume and strain rate sensitivity, but further investigations are necessary to elucidate the significance of these measurements.

These results suggest that cryogenic cycling may be potential processing route that enables suppression of shear localization through the creation of metastable grain boundaries. Unlike other processes investigated in the literature, cryogenic cycling affects the entirety of the sample and is not confined to near surface regions. The second investigation elucidated the atomistic origin of ultrastability in binary Cu-Zr thin film metallic glasses and corresponding mechanical properties. Our conclusions can be summarized as follows:

- Ultrastable glasses deposited at substrate temperatures of $0.87T_g$ exhibit enhanced hardness, modulus, and glass transition compared to more conventional glasses deposited at the same rate but at lower substrate temperatures.

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- Fluctuation electron microscopy experiments suggest that ultrastable glasses exhibit a significantly higher fraction of crystal-like packing than conventional glasses which exhibit more icosahedral ordering.

Future work to quantitatively determine the relative fraction of icosahedral and crystal-like volume as a function of deposition temperature and rate is underway, in addition to higher-resolution DSC experiments. Additionally, the effects of fragility of the liquid and glass forming ability on ultrastability and atomic packing would be quite informative, and may inform future alloying strategies to enable the more ubiquitous application of metallic glasses as structural materials. Molecular dynamics simulations to determine the effects of predominantly crystal-like and icosahedral packing on mechanical and thermal properties may also be informative.

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7 Appendix

Indentation experiments were performed on a 6 mm 316L stainless steel sample that was deformed via HPT and cryogenically cycled at UCSB using a iNano indenter from Nanomechanics with a berkovich tip at an indentation strain rate of 0.05 s^{-1} . The results of these indentation experiments are shown in Figures 29 and 30

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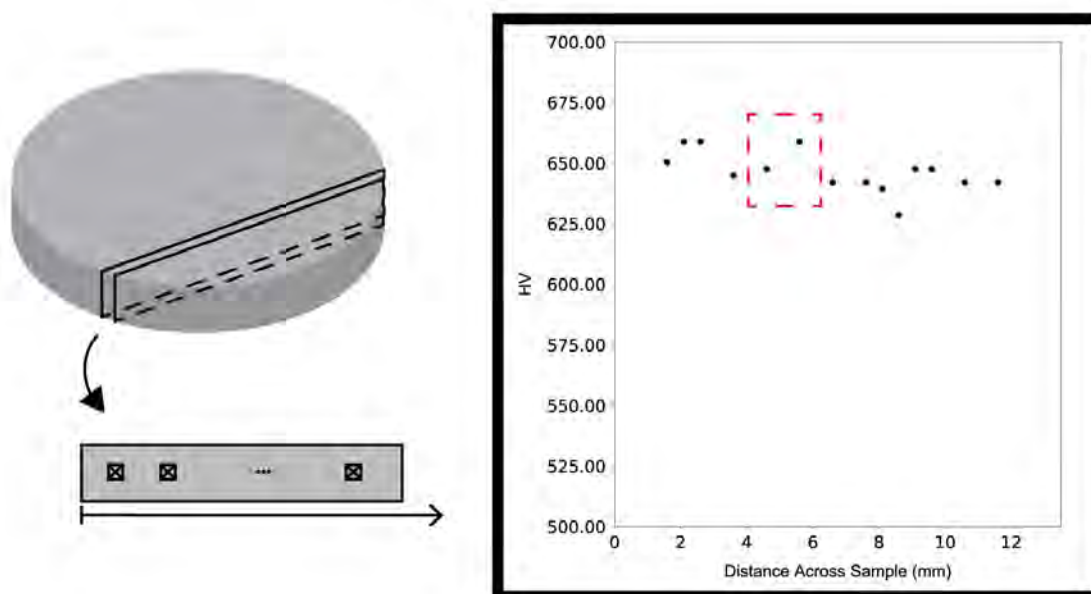


Figure 1: HPT sample schematic and preliminary Vickers microhardness screening.

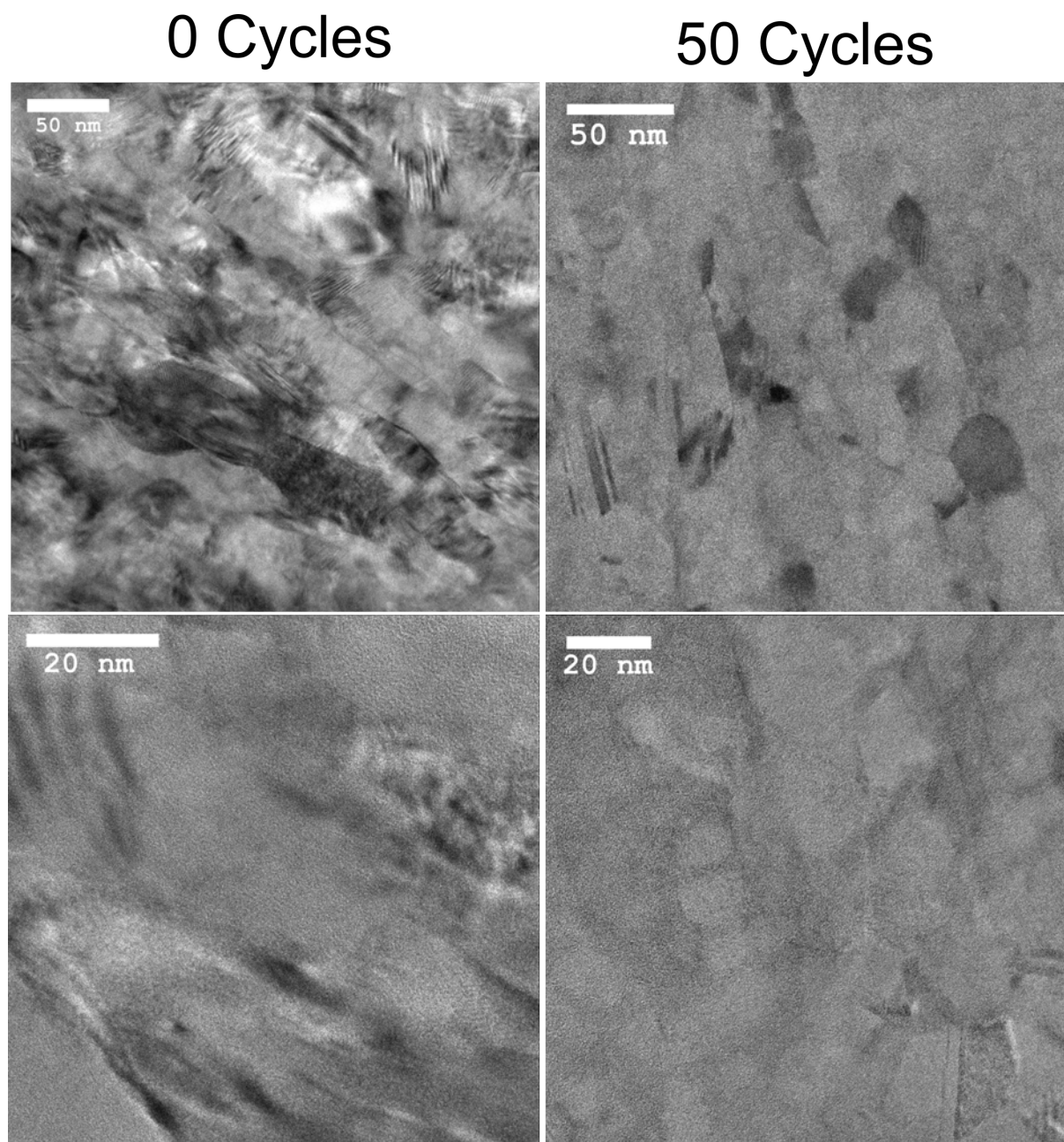


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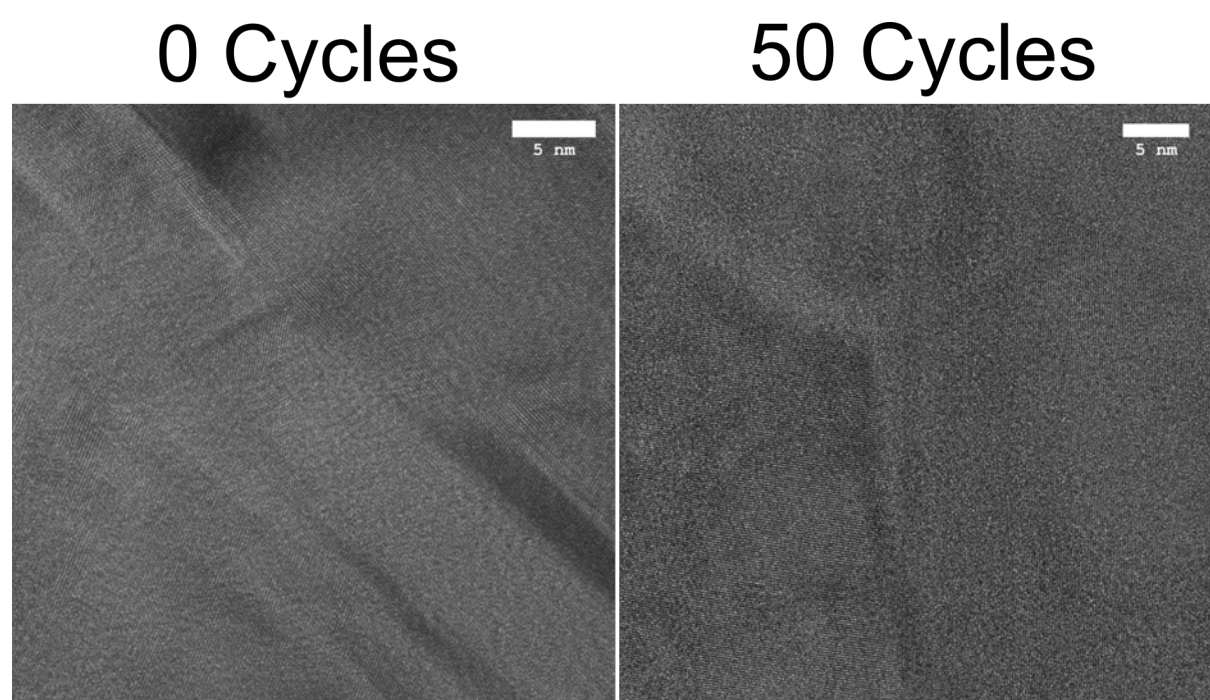
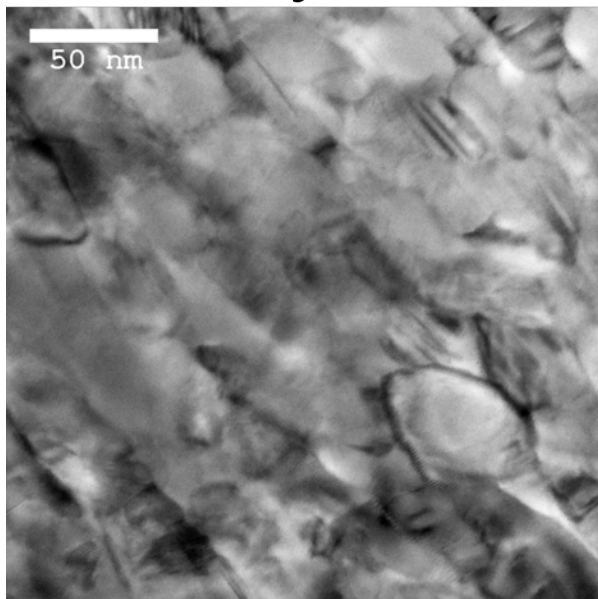


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0 Cycles



50 Cycles

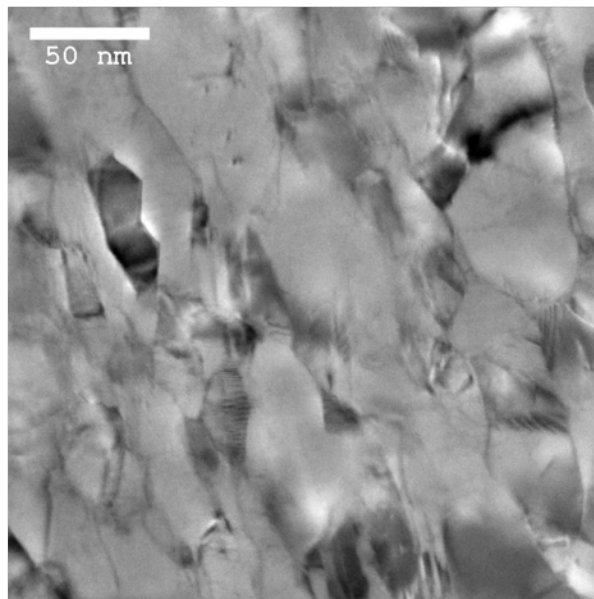


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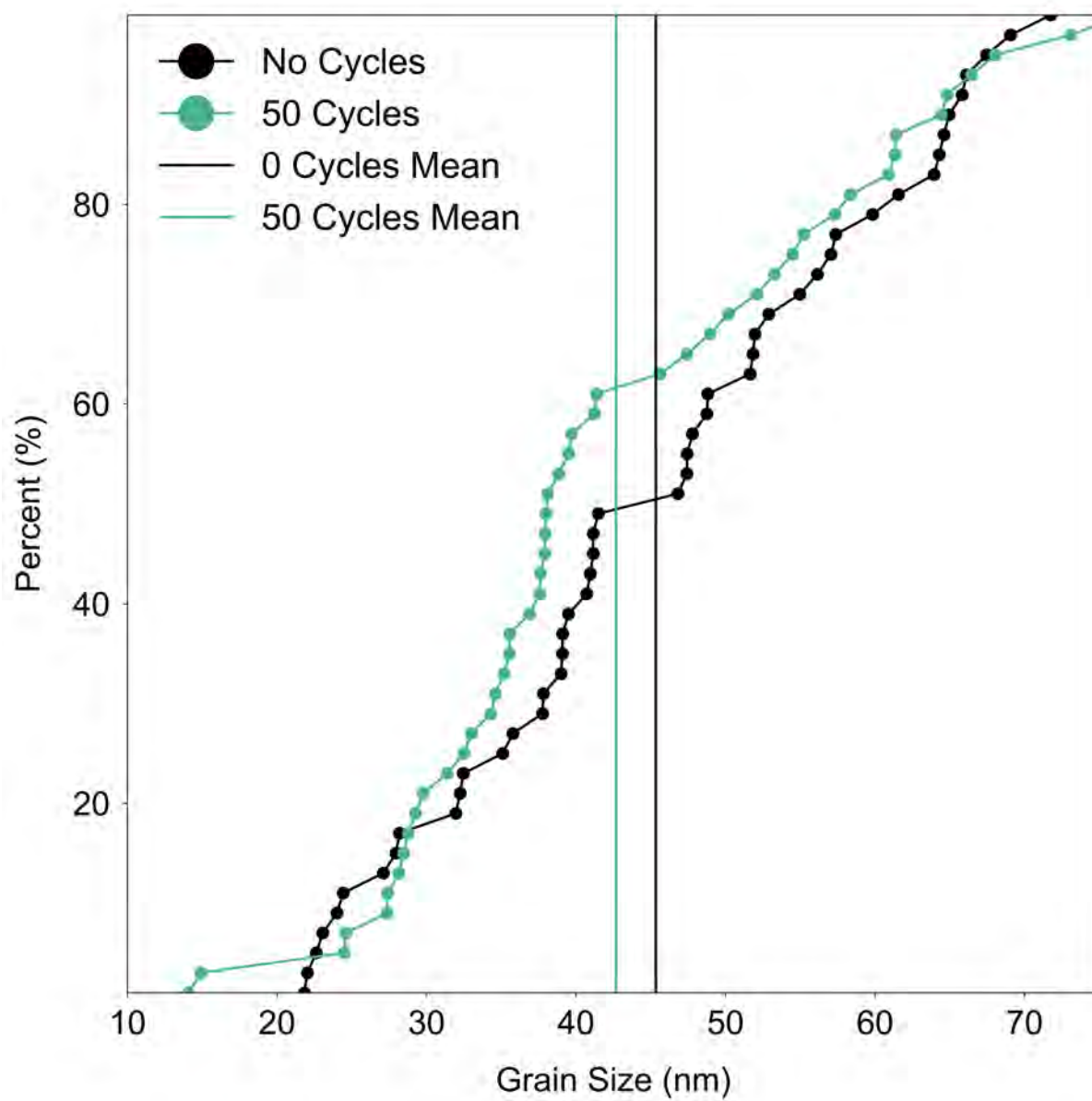


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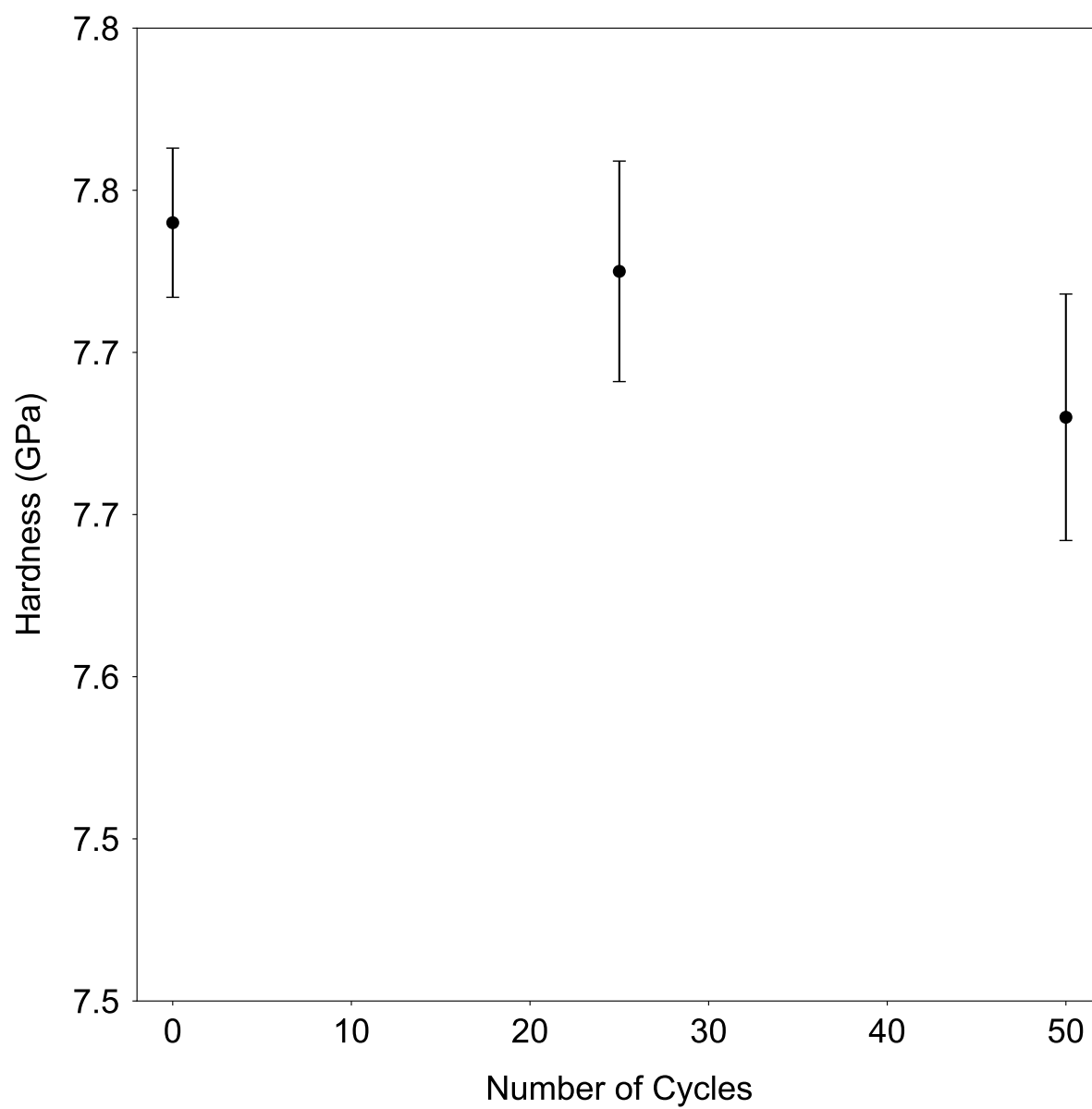


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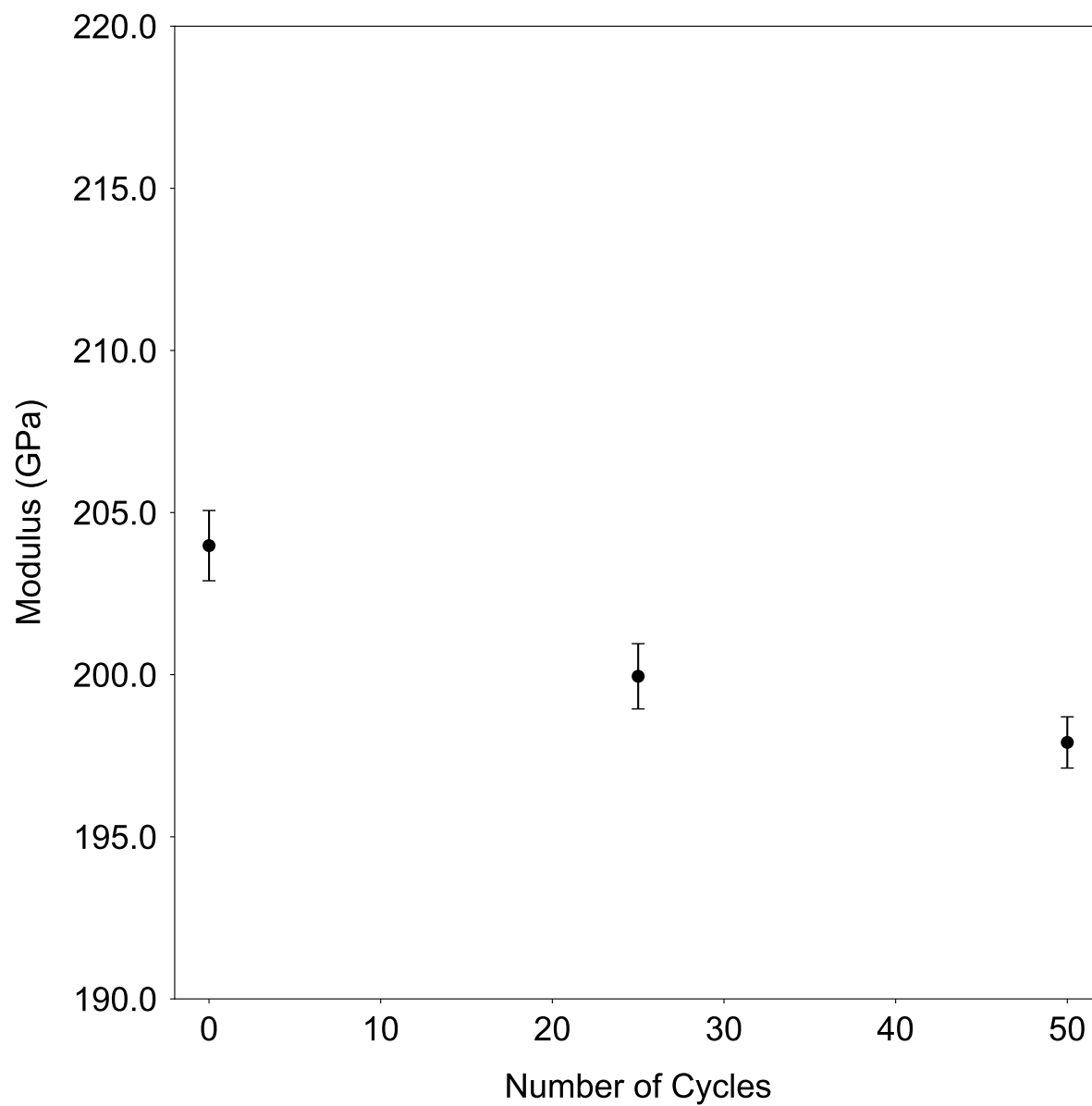


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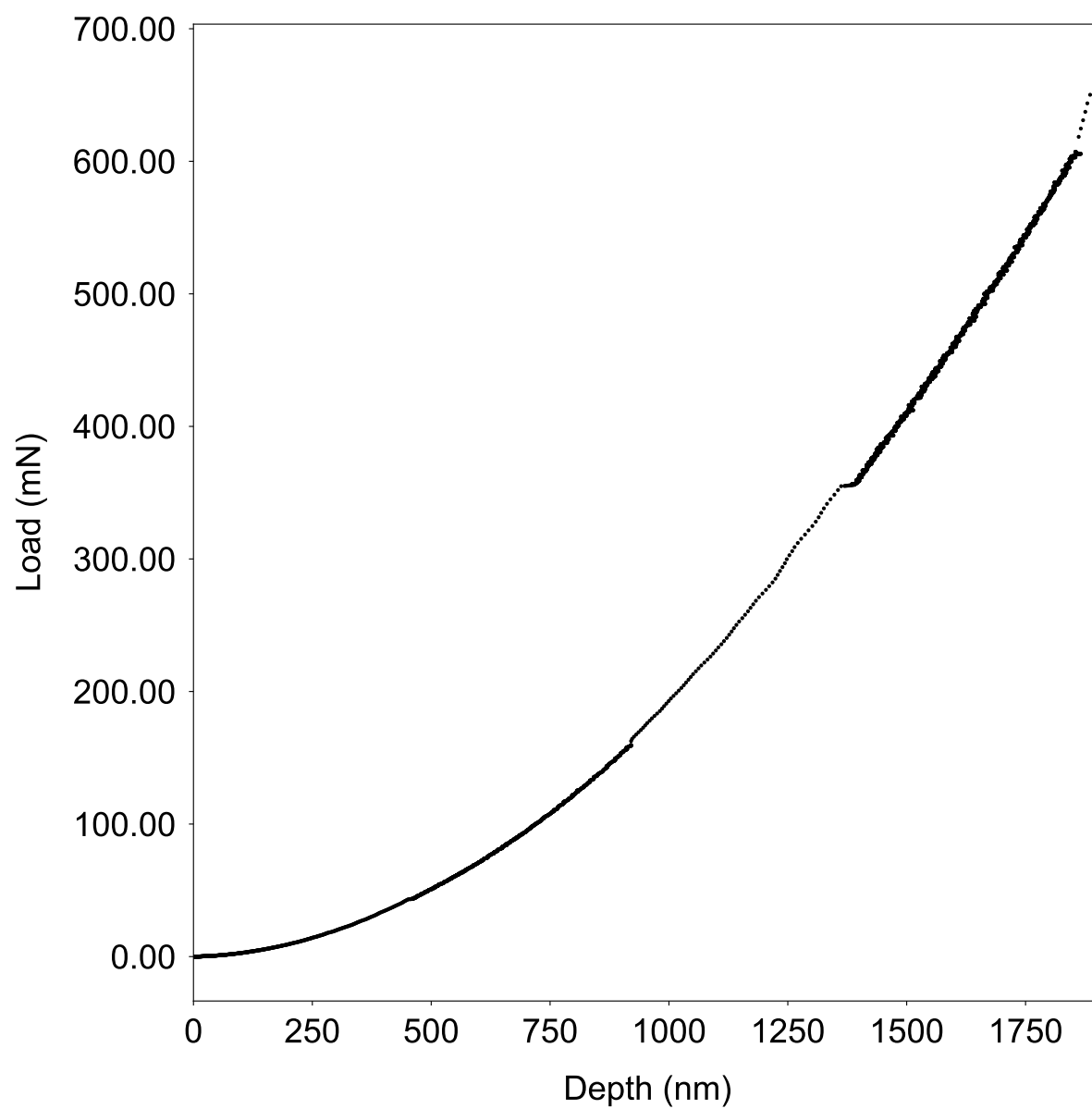


Figure 8: Load-depth profile for a representative strain rate jump test performed on the 316L steel

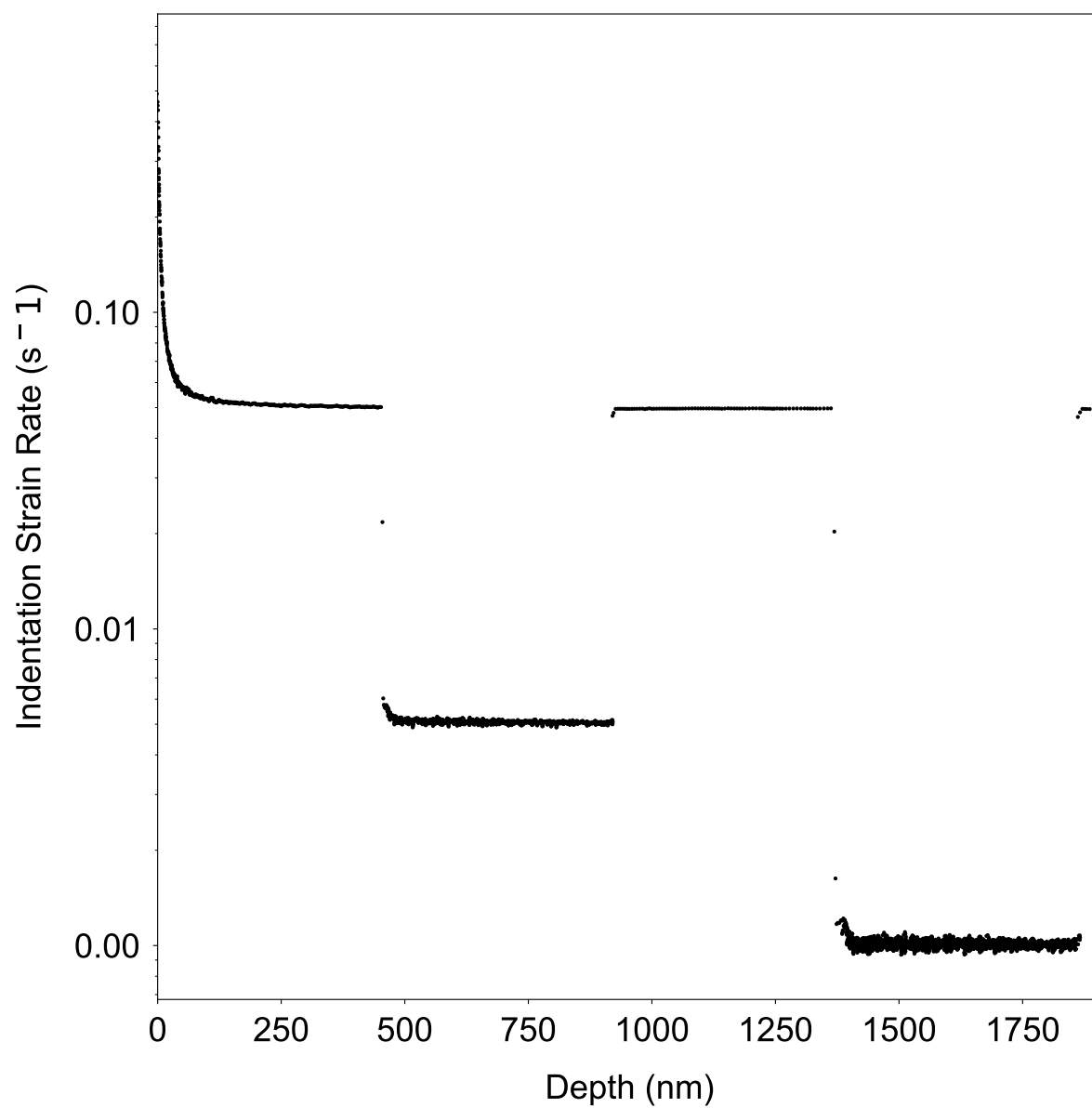


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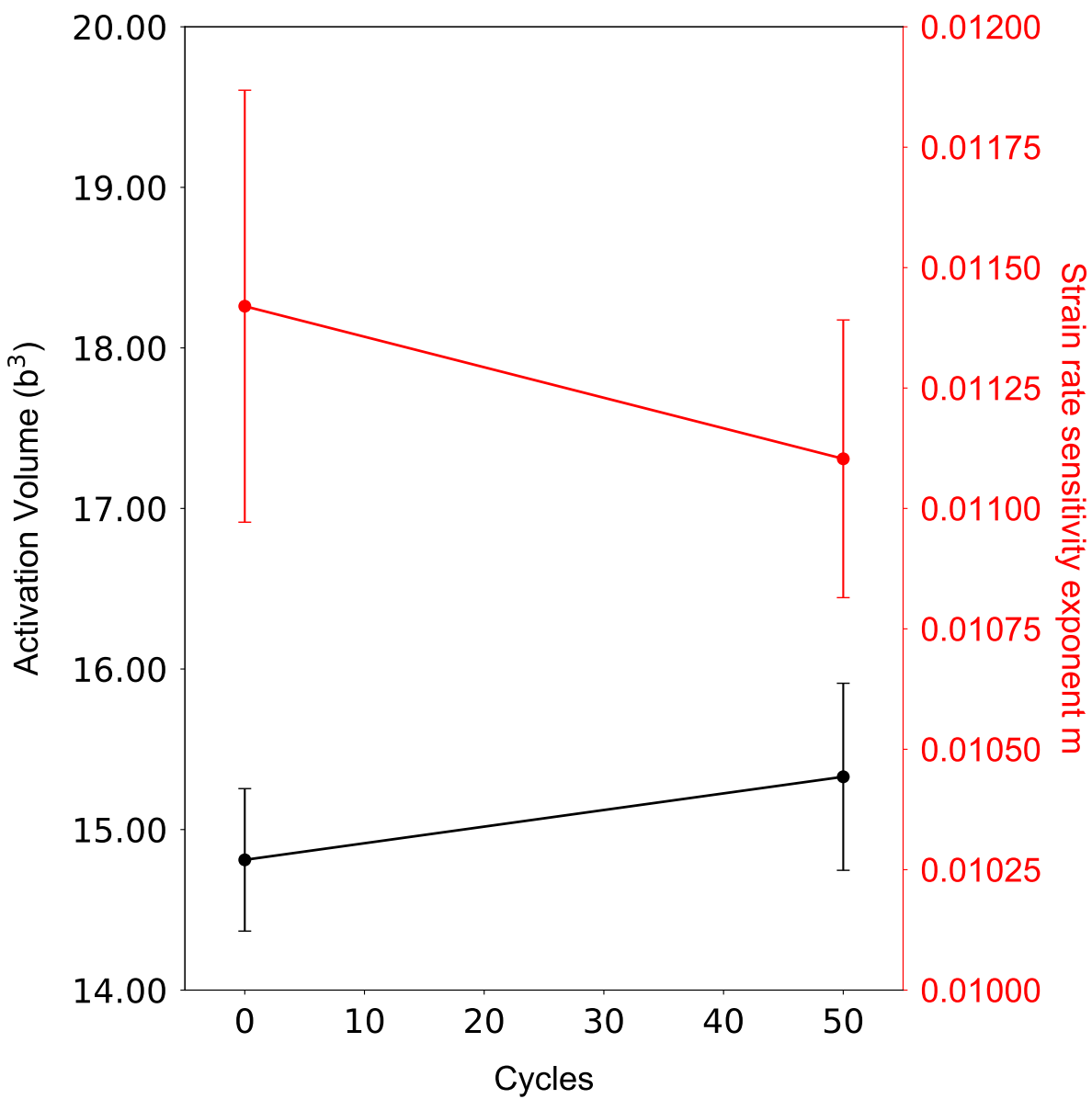


Figure 10: Strain rate sensitivity exponent and corresponding activation volume measured for the as-annealed and cryogenically cycled 316L steel

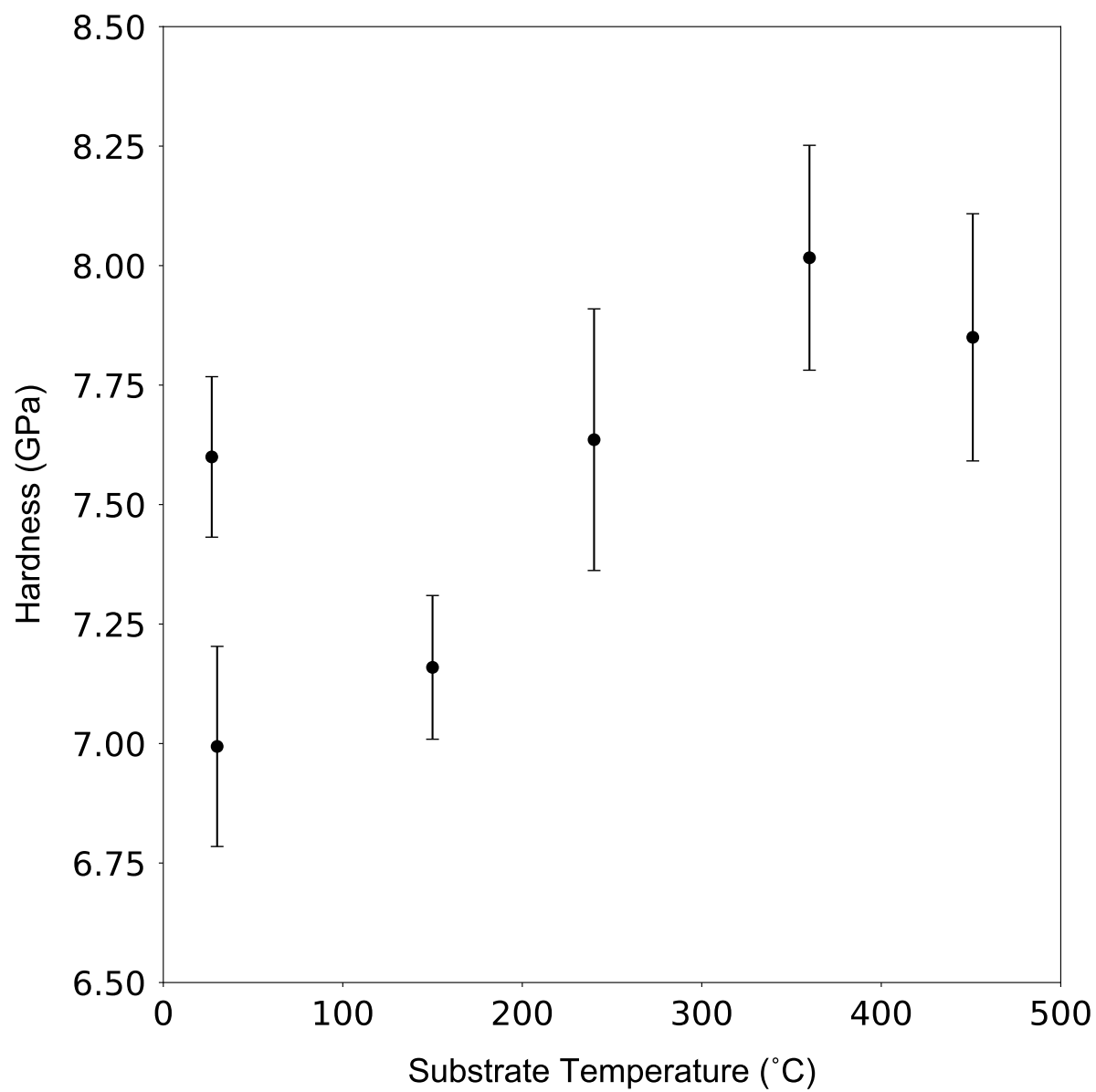


Figure 11: Hardness of binary Cu-Zr metallic glass thin films measured by nanoindentation as a function of substrate temperature during deposition

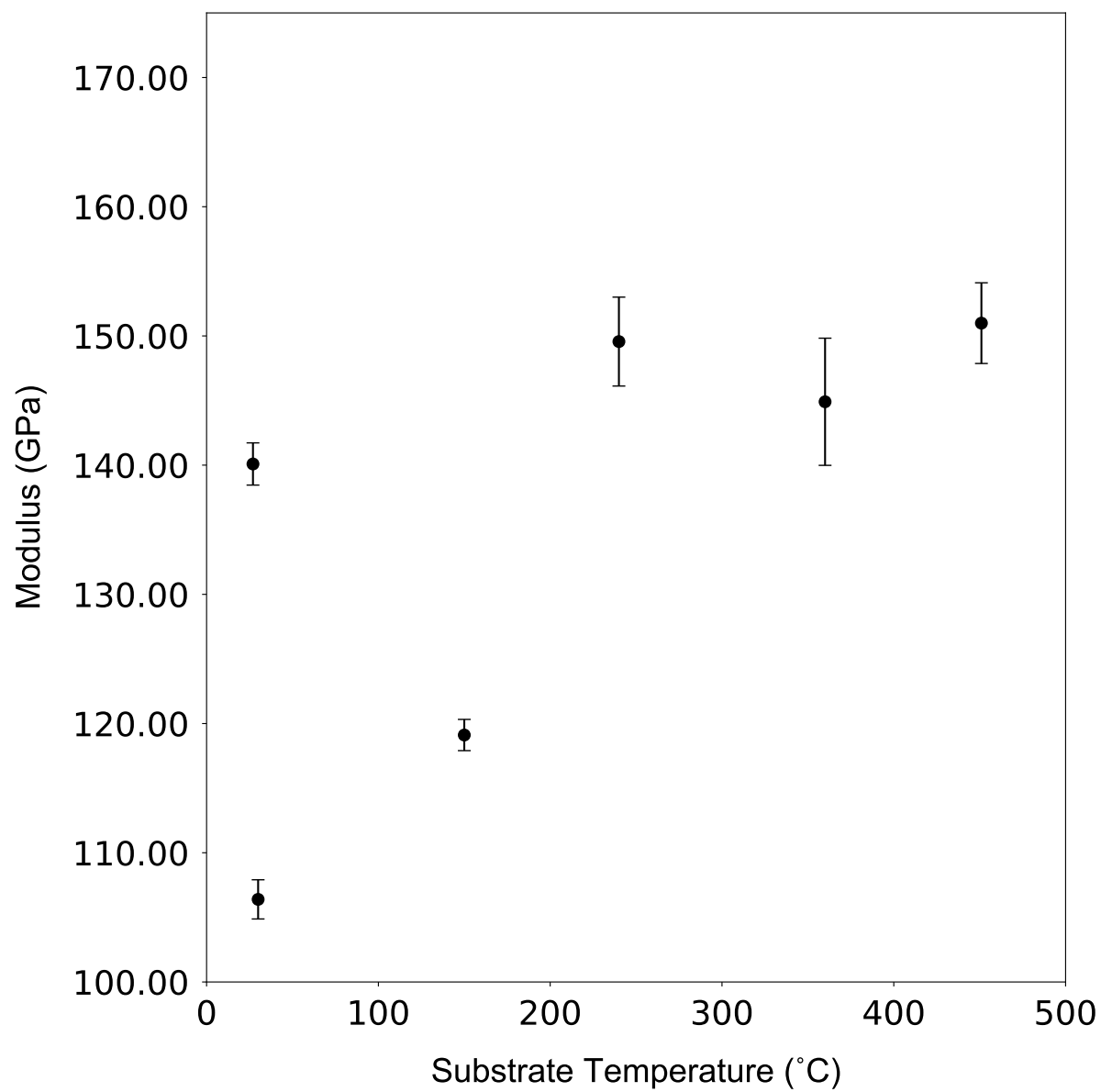


Figure 12: Modulus of binary Cu-Zr metallic glass thin films measured by nanoindentation as a function of substrate temperature during deposition

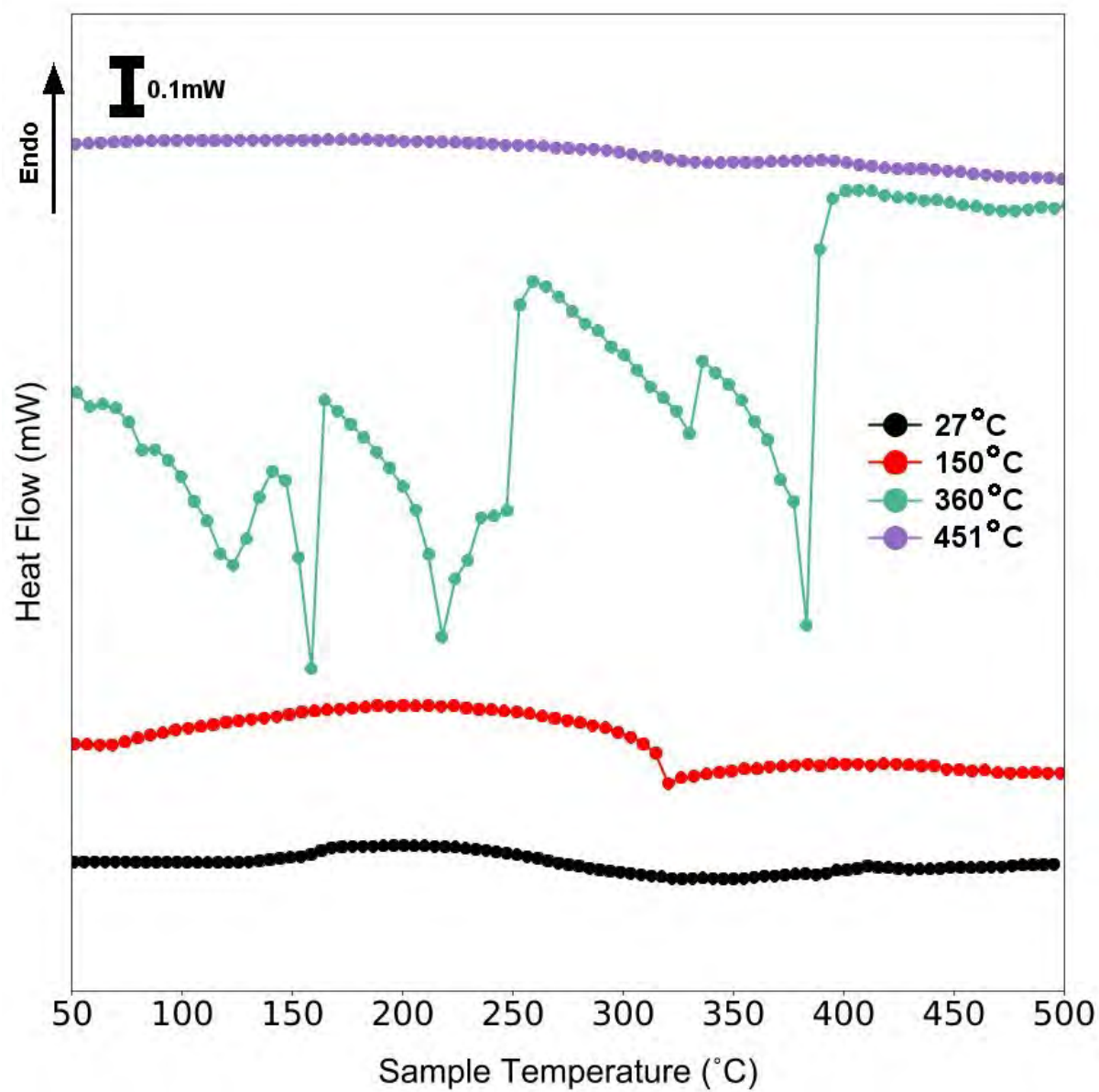


Figure 13: Flash DSC curves for 30 nm thick sputtered Cu-Zr glasses on chip calorimeters. Heating rates of $1000 \frac{K}{s}$ were utilized

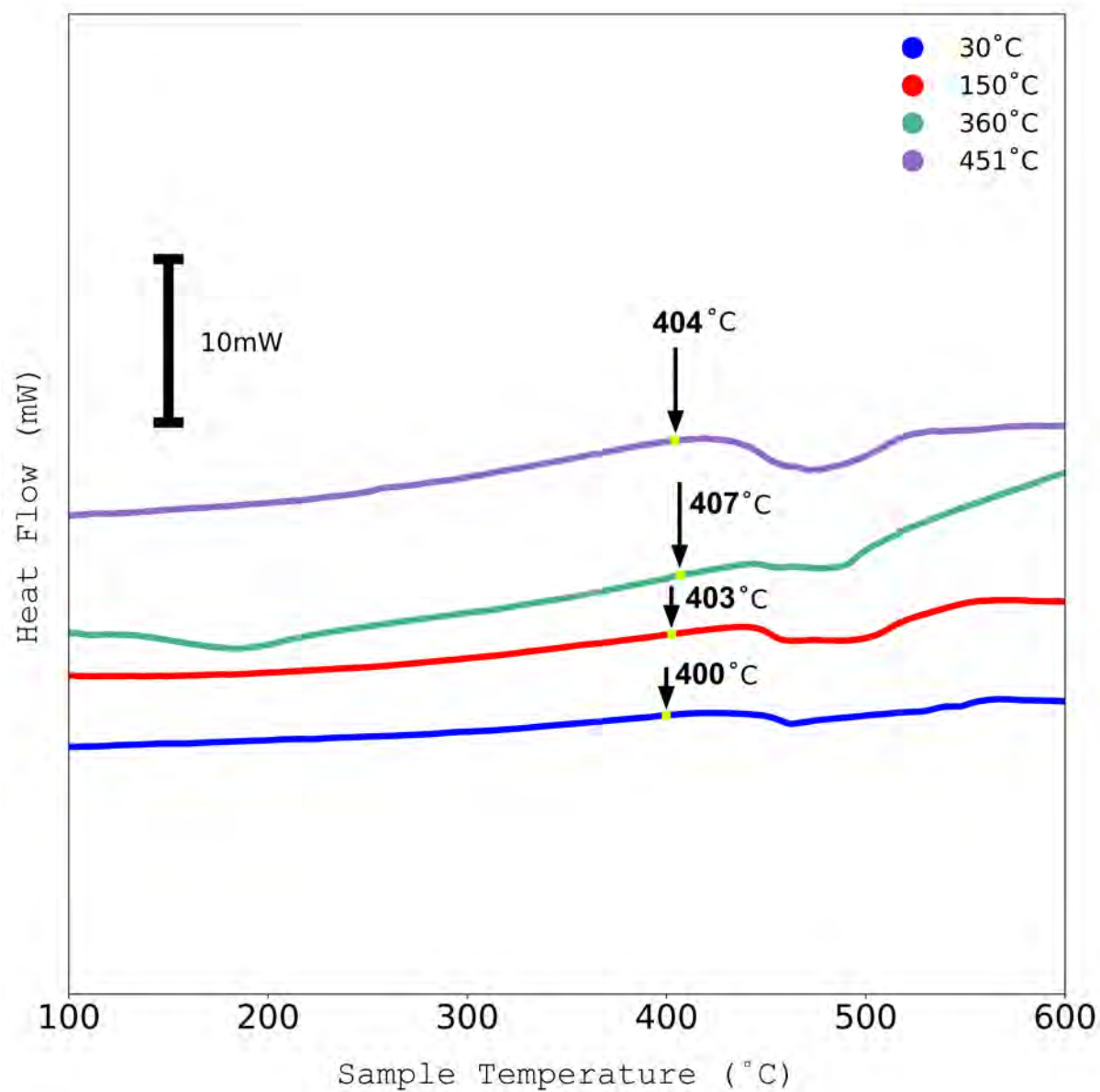


Figure 14: Traditional DSC curves for 500 nm thick sputtered Cu-Zr glasses on Si wafers. Heating rates of $20 \frac{K}{min}$ were utilized. Approximate glass transitions are noted.

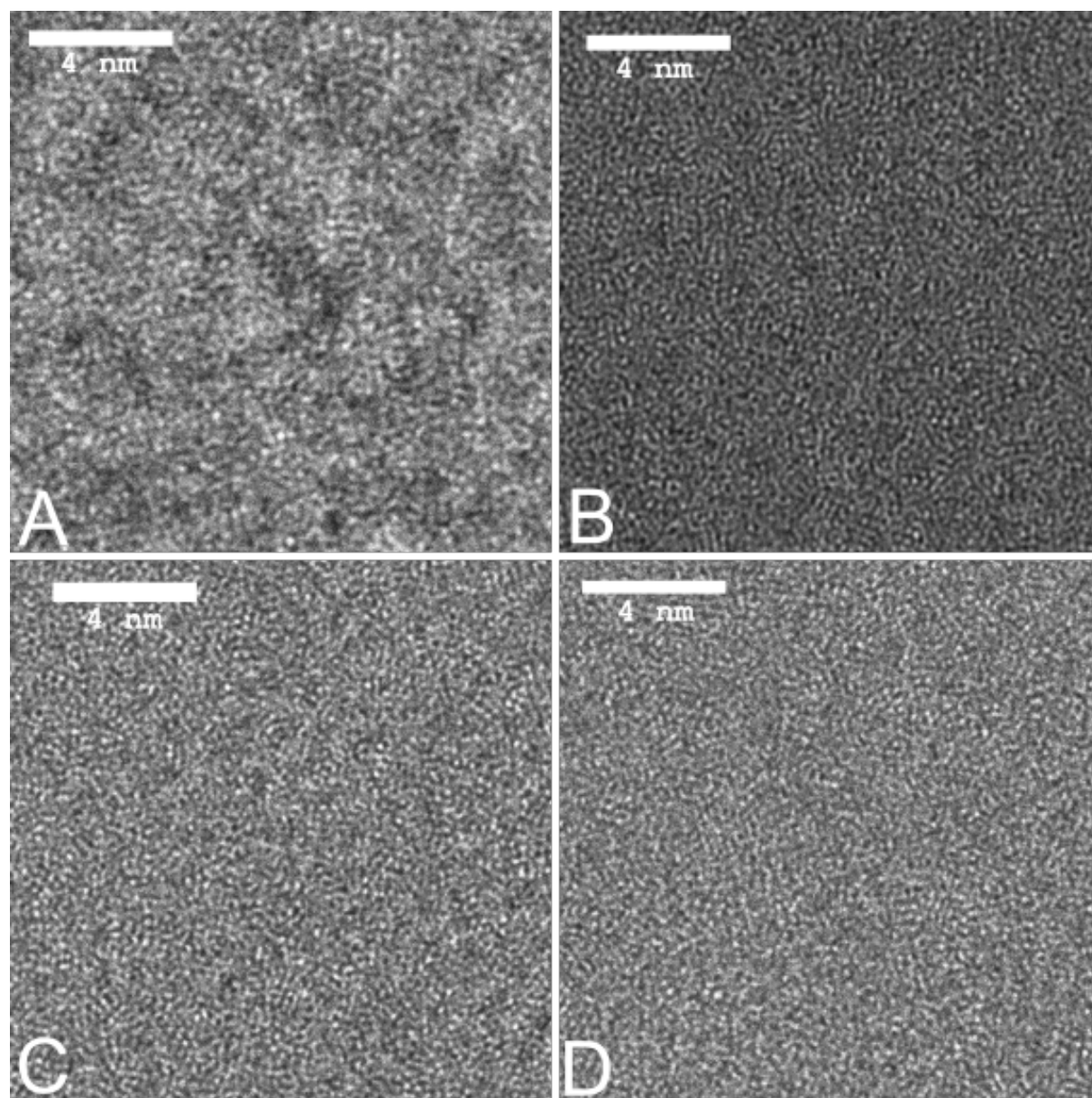


Figure 15: HRTEM images of 10 nm thick Cu-Zr binary metallic glasses sputtered on ultrathin C grids. A: 27°C deposition recorded at not-Scherzer defocus. B: 150°C deposition at Scherzer defocus. C: 360°C deposition at Scherzer defocus. D: 451°C deposition at Scherzer defocus.

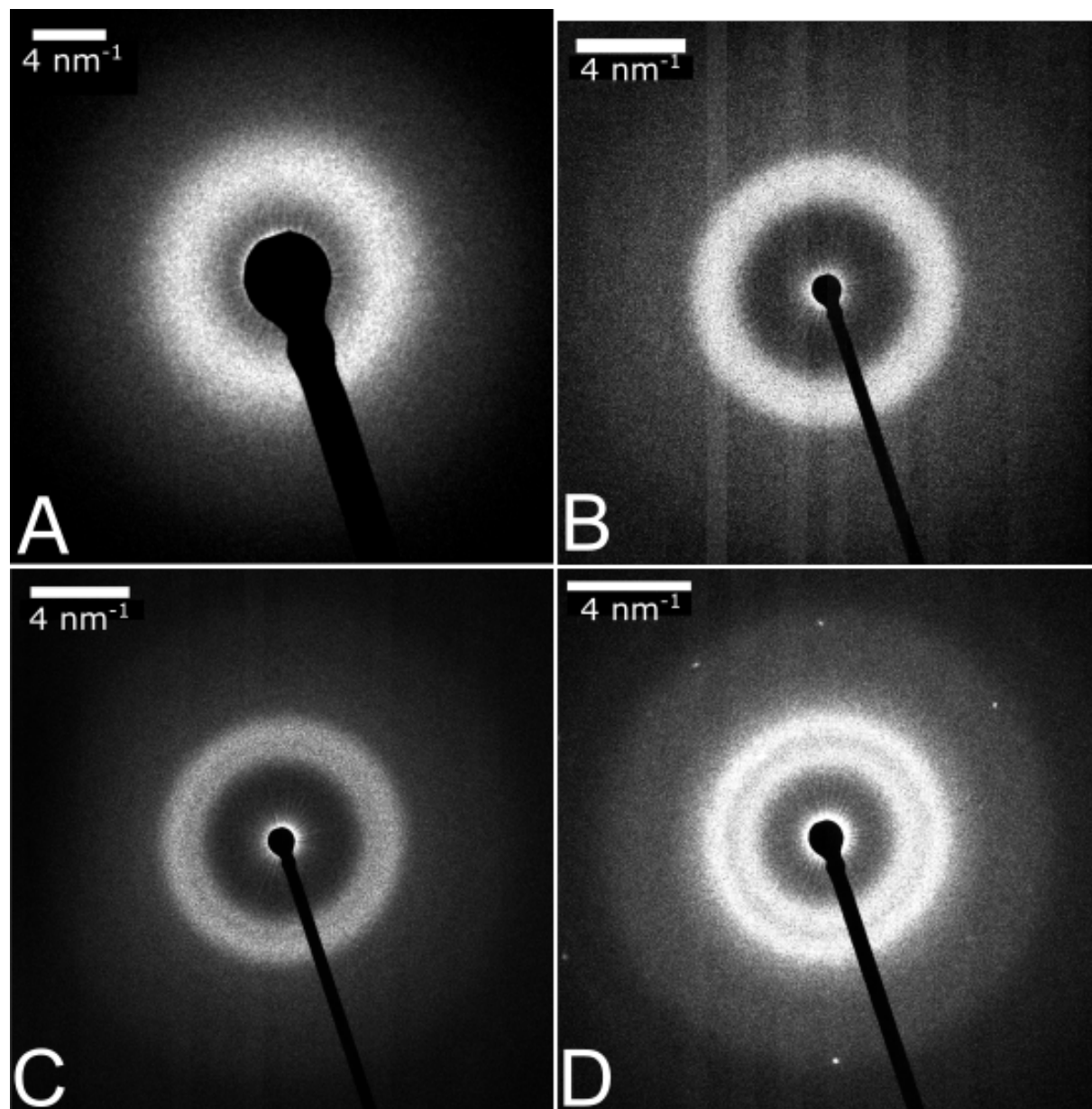


Figure 16: Zero loss filtered selected area diffraction patterns of 10 nm thick Cu-Zr binary metallic glasses sputtered on ultrathin C grids. A: 27°C deposition. B: 150°C deposition. C: 360°C deposition. D: 451°C deposition.

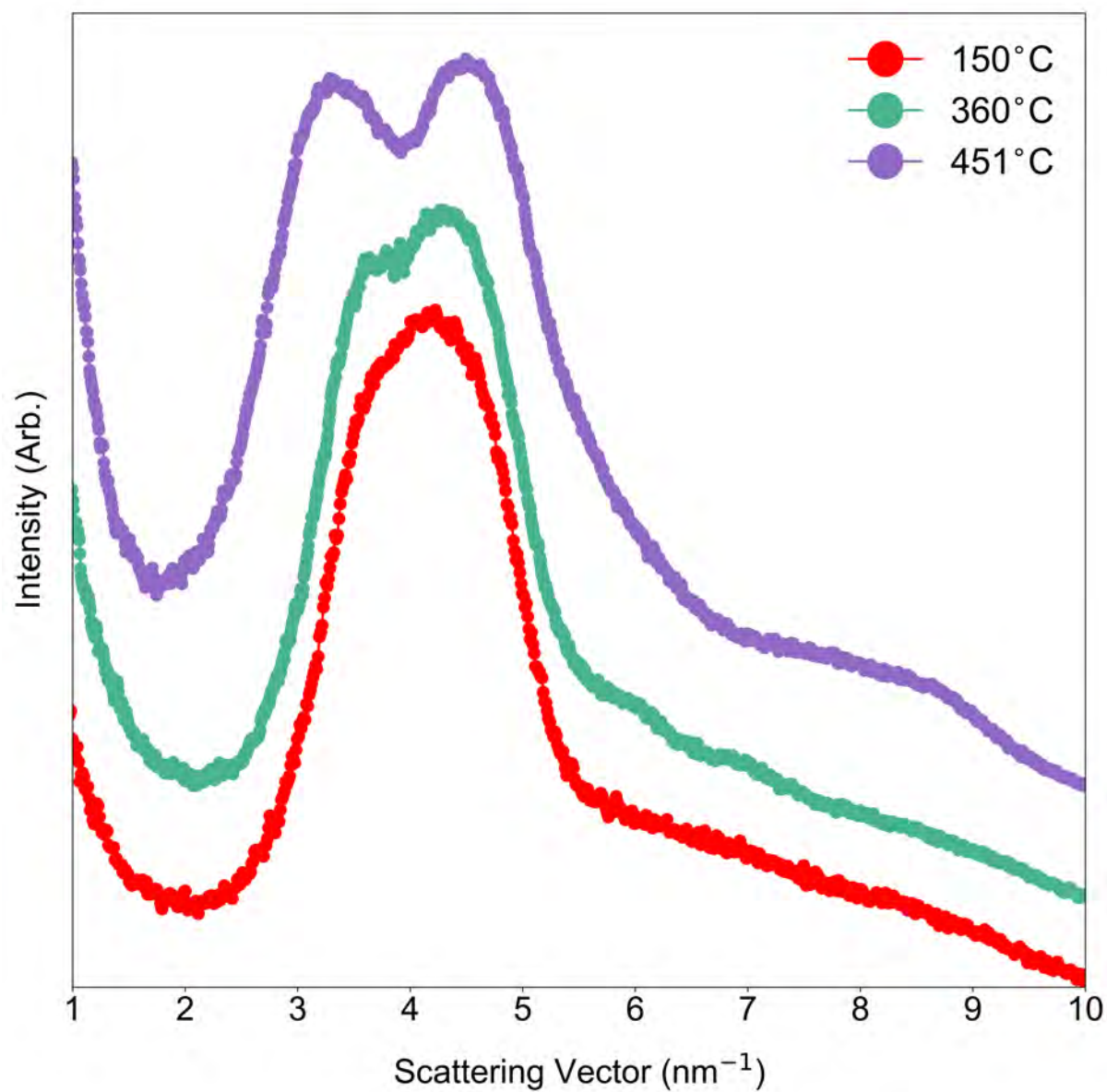


Figure 17: Averaged azimuthal intensity of energy filtered diffraction patterns for the three elevated temperature depositions plotted as a function of scattering vector

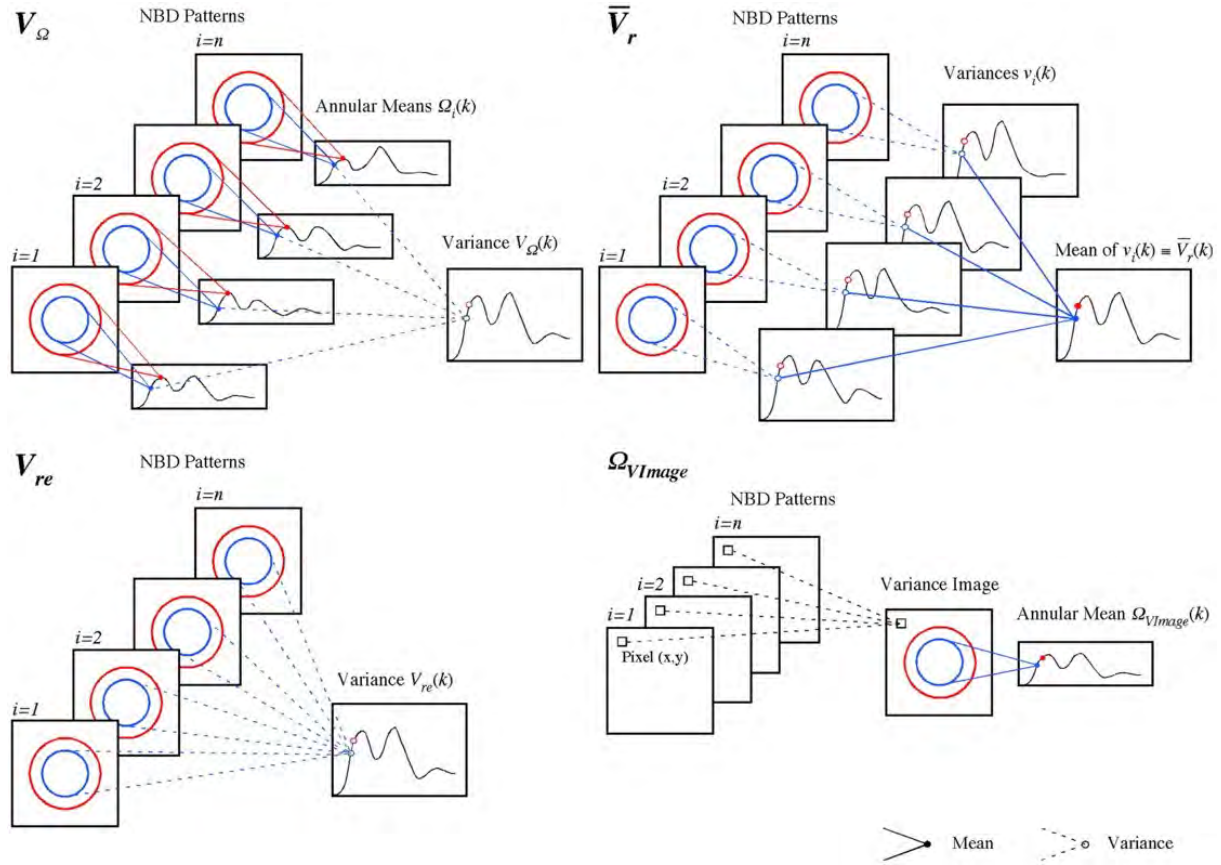


Figure 18: Four unique ways of computing variance information from nanodiffraction patterns of amorphous materials. In this work, we performed the right two calculations. Reproduced from [75] without explicit permission

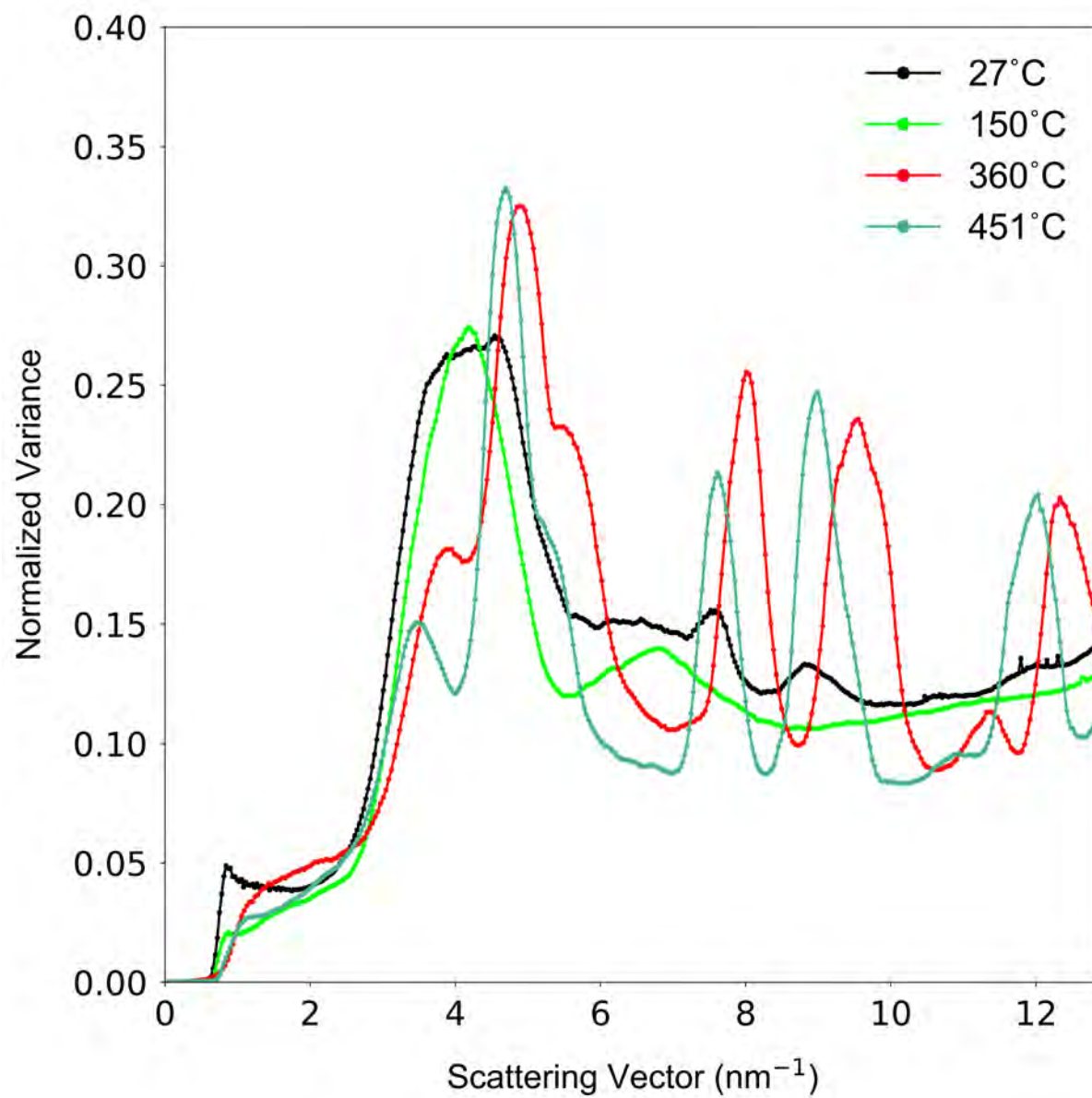


Figure 19: FEM analysis of the variance of the 25X25 nanobeam diffraction pattern datasets collected for each deposition temperature

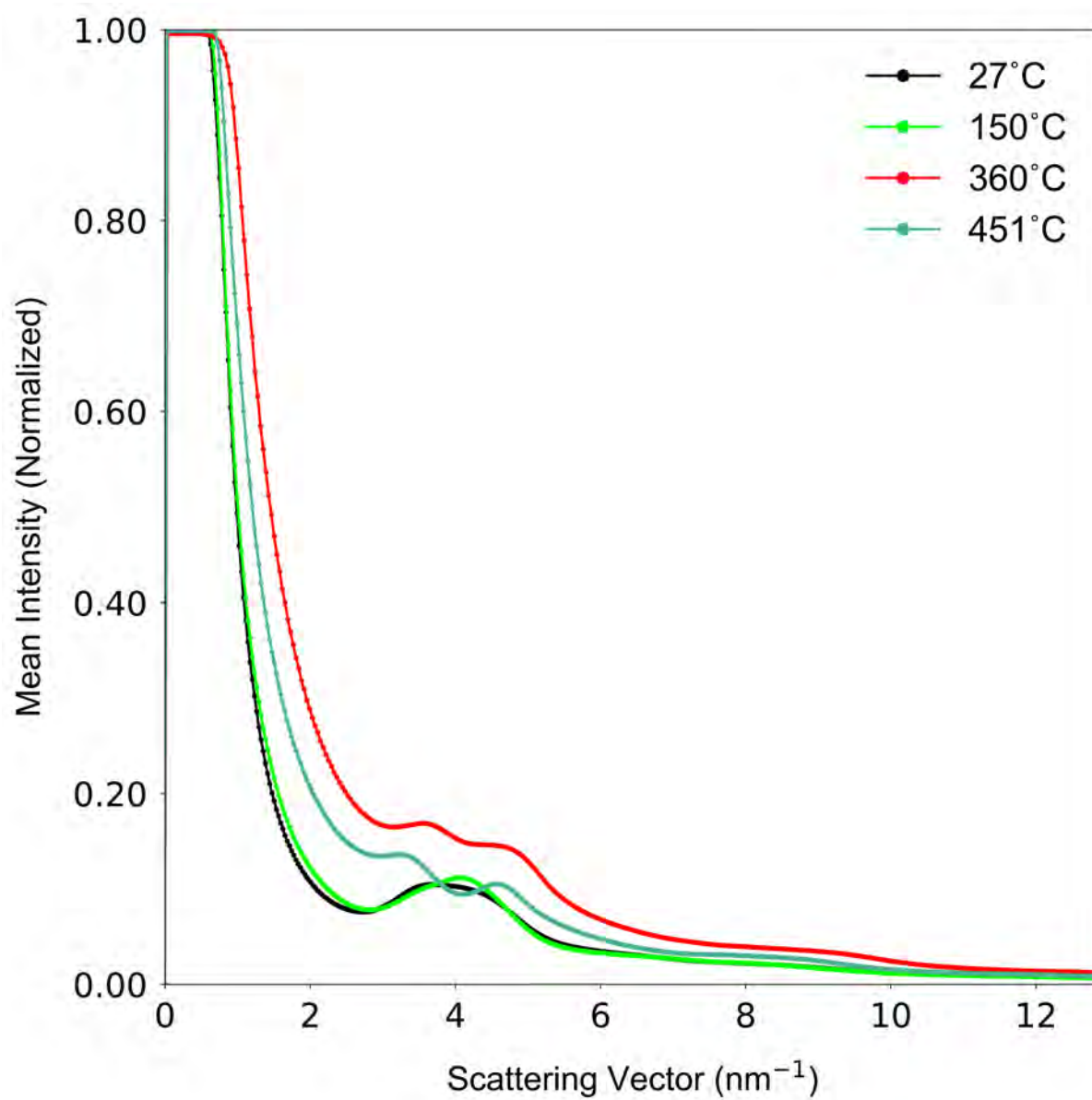


Figure 20: FEM analysis of the variance of the 25X25 nanobeam diffraction pattern datasets collected for each deposition temperature

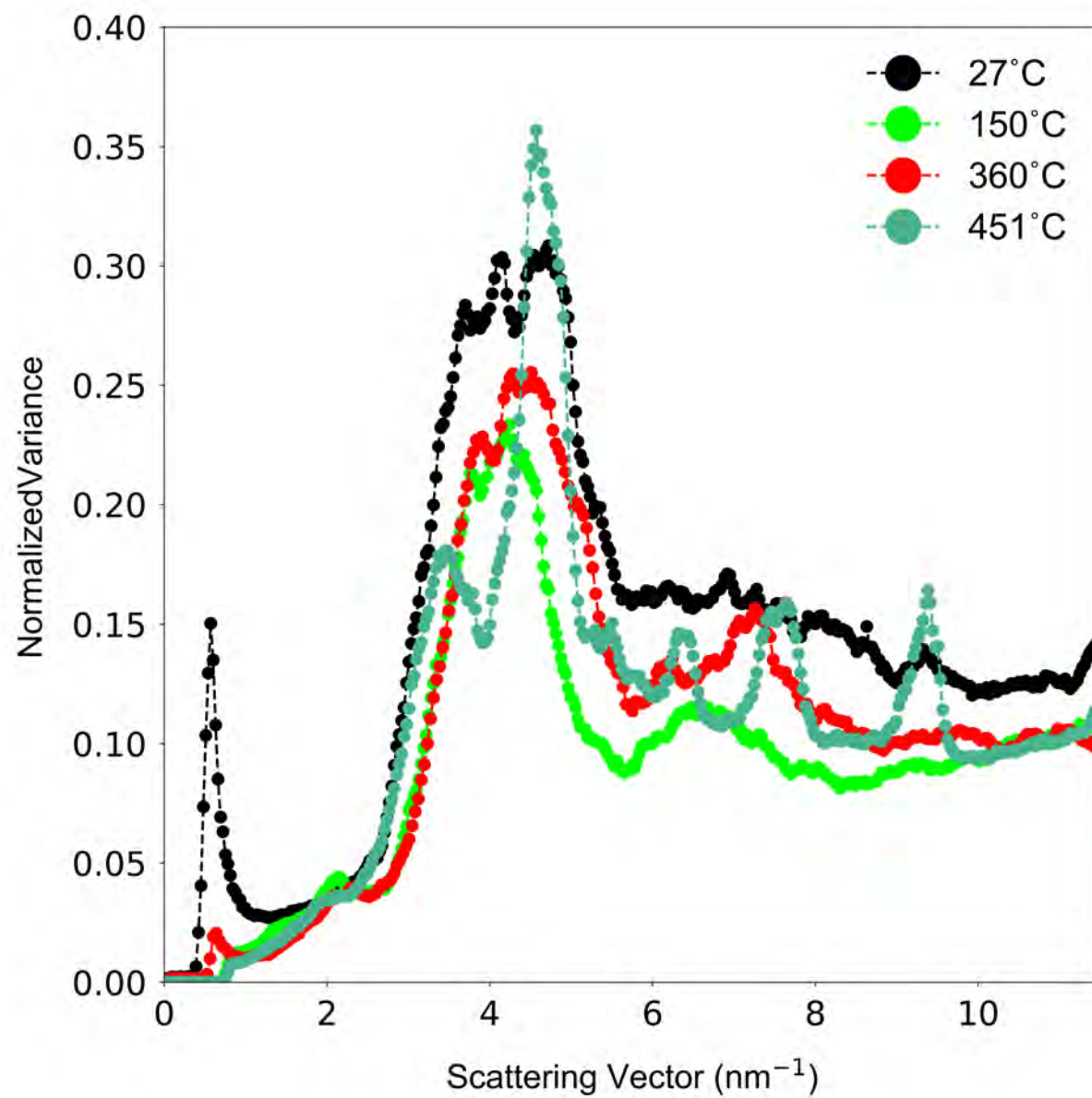


Figure 21: FEM analysis of the selected 5X5 nanobeam diffraction pattern datasets collected for each deposition temperature

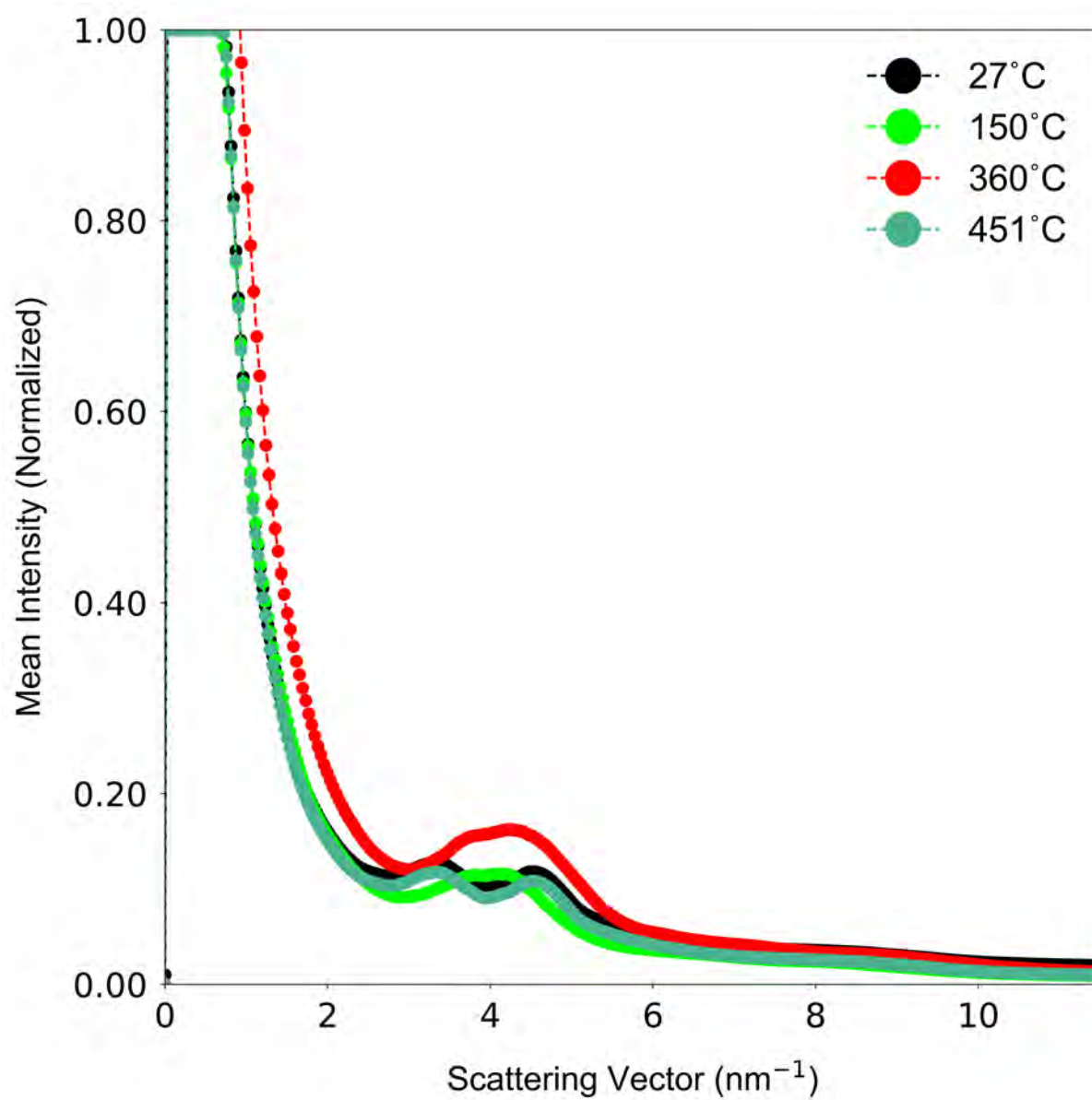


Figure 22: FEM analysis of the selected 5X5 nanobeam diffraction pattern datasets collected for each deposition temperature

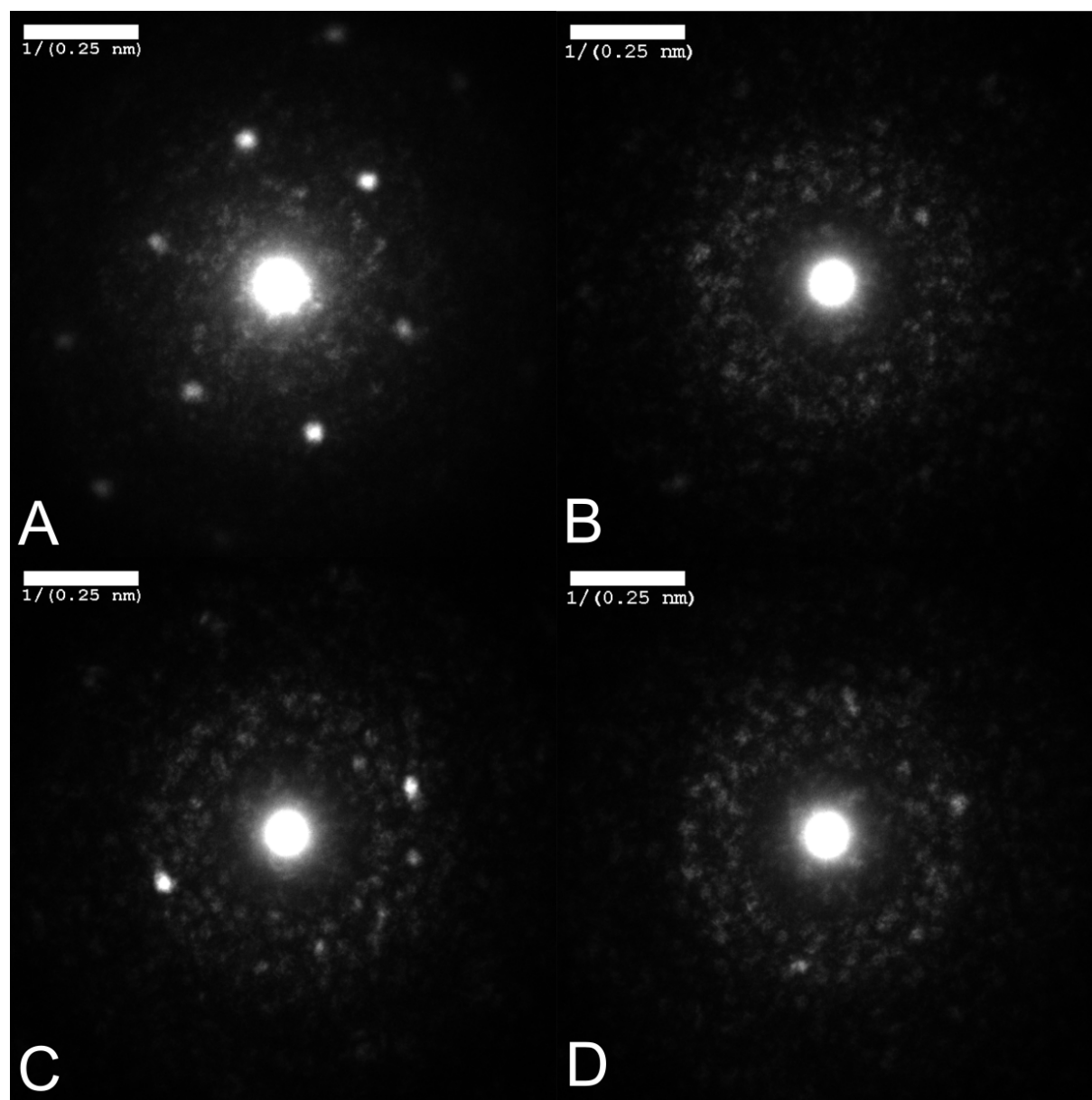


Figure 23: Four representative nanobeam diffraction patterns from the Cu-Zr sample deposited at 451°C. A exhibits clear crystalline ordering. B exhibits slight crystallinity, and perhaps the beginning of a systematic row. C, while difficult to see, has clear three-fold symmetry in the edges of the pattern. D is a representative pattern for this dataset

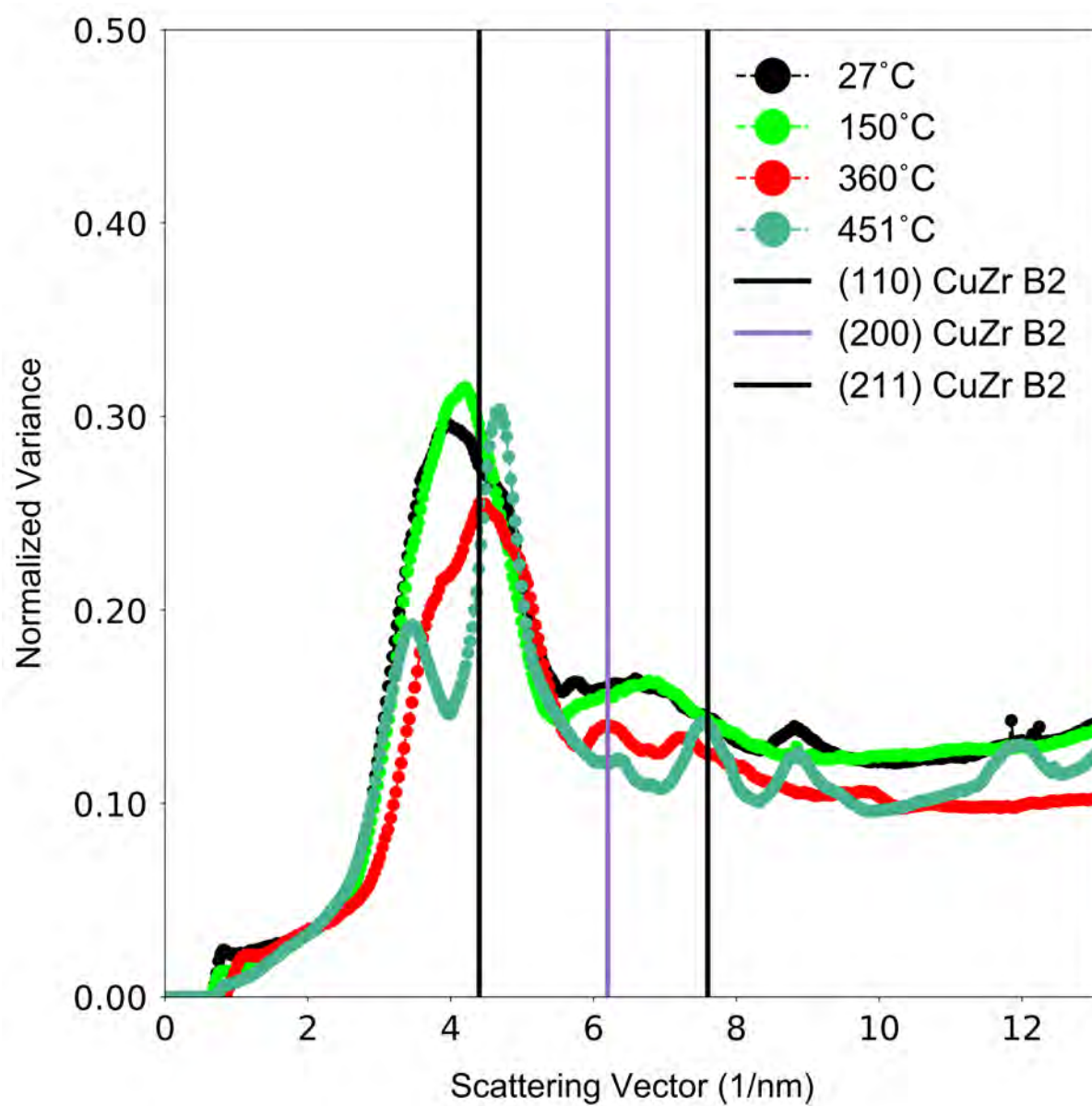


Figure 24: FEM analysis of the variance of the selected 200-300 amorphous nanobeam diffraction pattern for each deposition temperature. Crystalline peak locations are indicated as reference

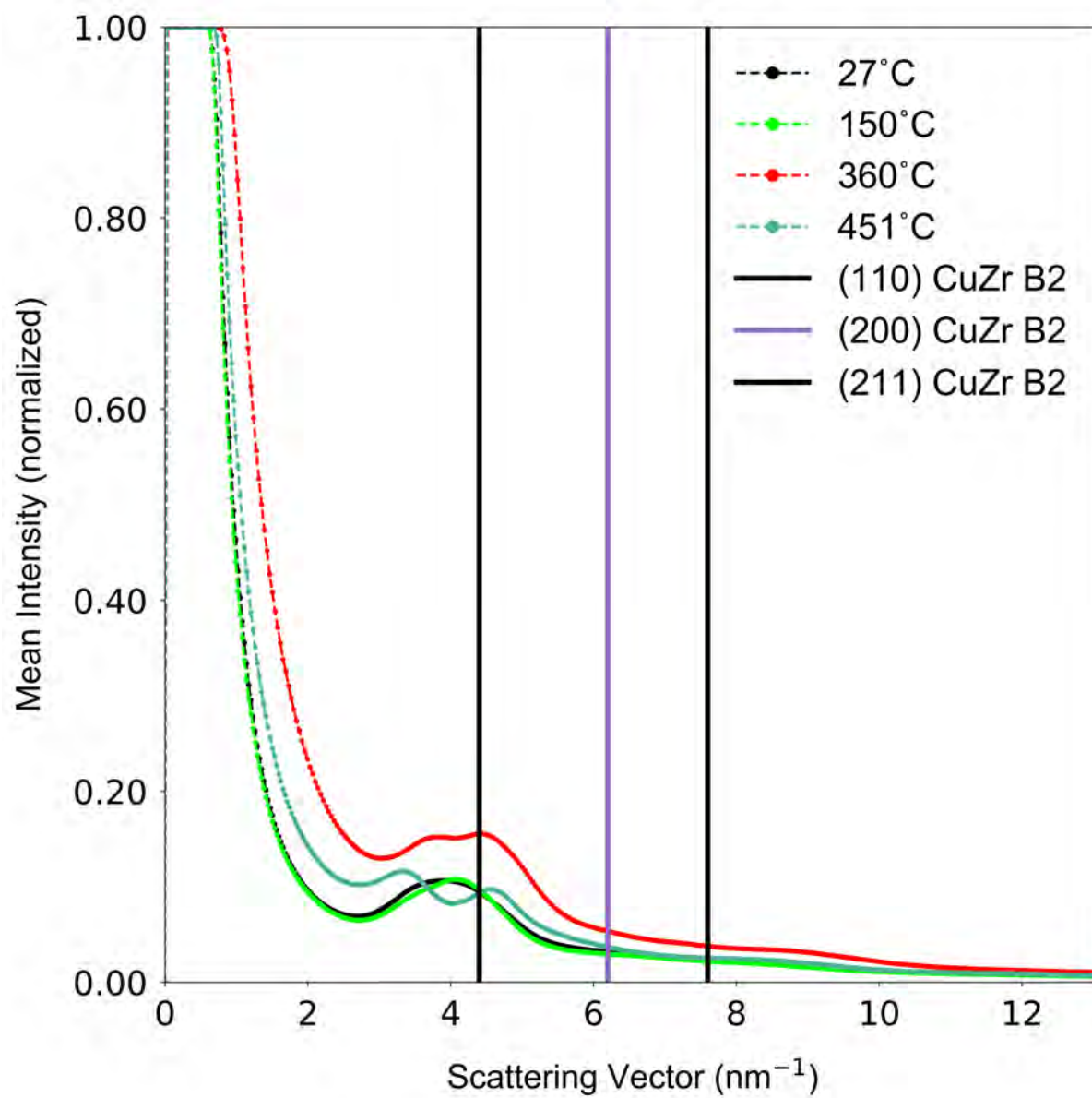


Figure 25: FEM analysis of the mean of the selected 200-300 amorphous nanobeam diffraction pattern for each deposition temperature. Crystalline peak locations are indicated as reference

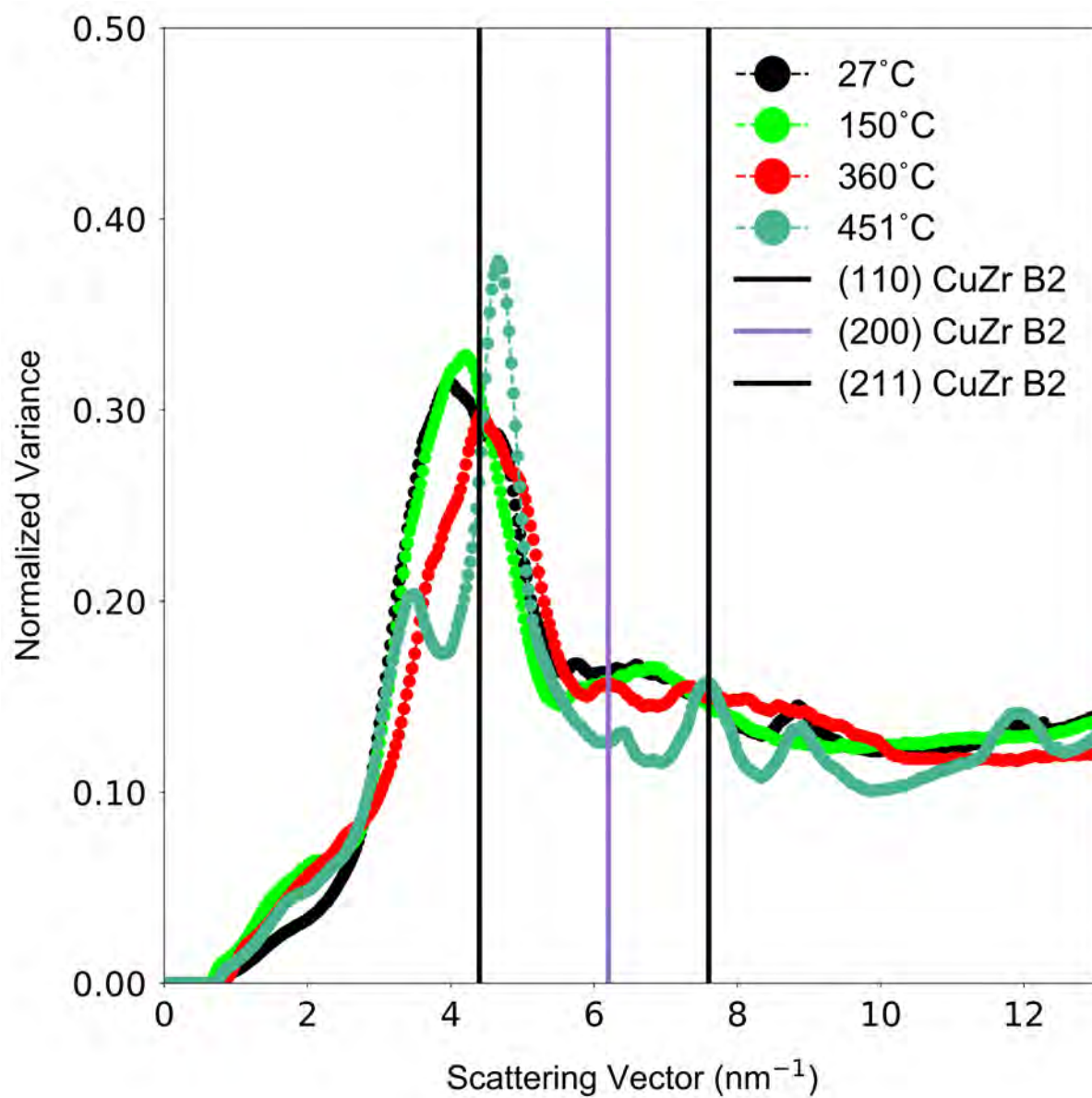


Figure 26: FEM analysis of the variance of the selected 200-300 amorphous nanobeam diffraction pattern for each deposition temperature calculated using a 2D pixel-by-pixel method. Crystalline peak locations are indicated as reference

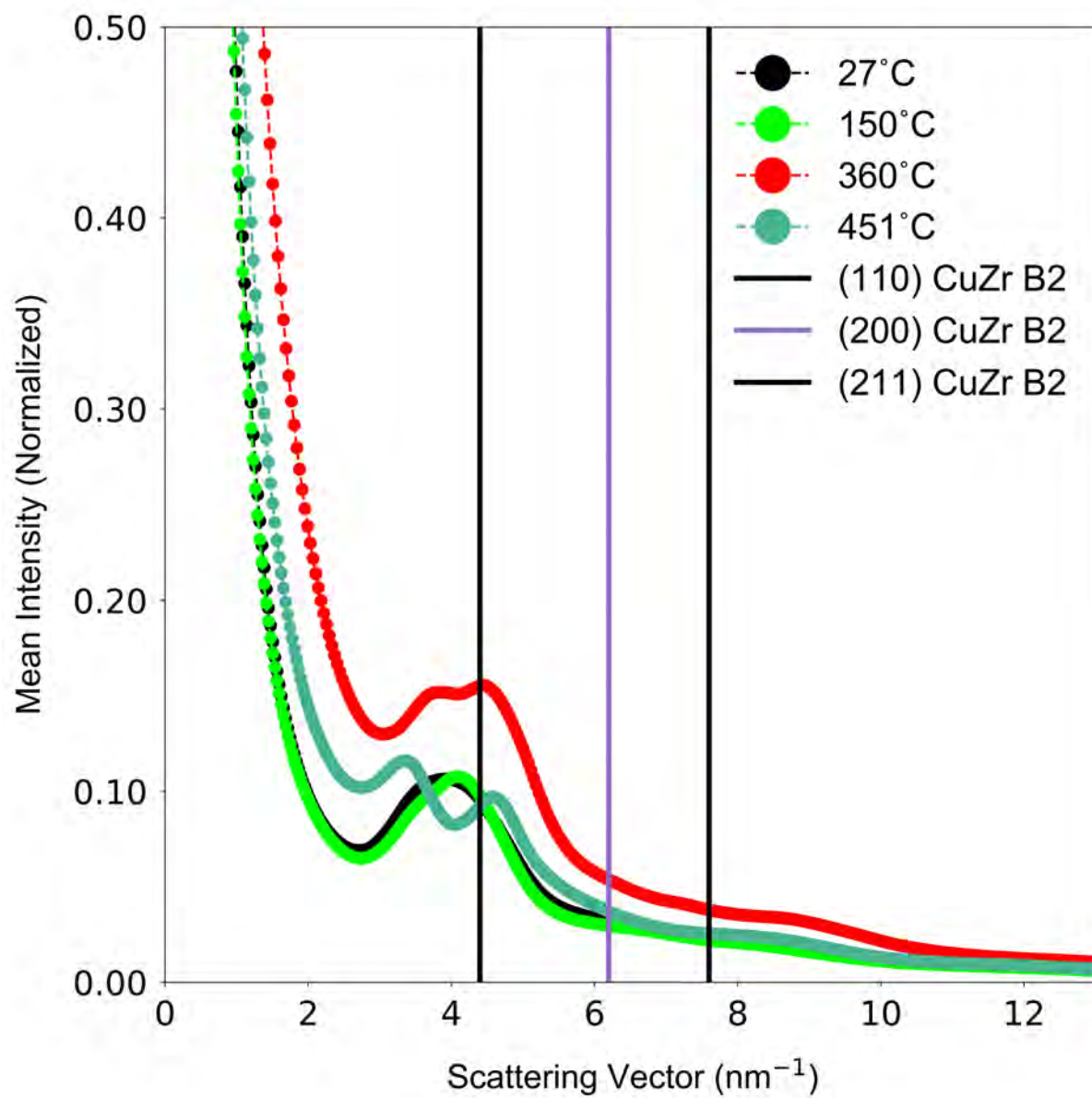


Figure 27: FEM analysis of the mean of the selected 200-300 amorphous nanobeam diffraction pattern for each deposition temperature calculated using a 2D pixel-by-pixel method. Crystalline peak locations are indicated as reference

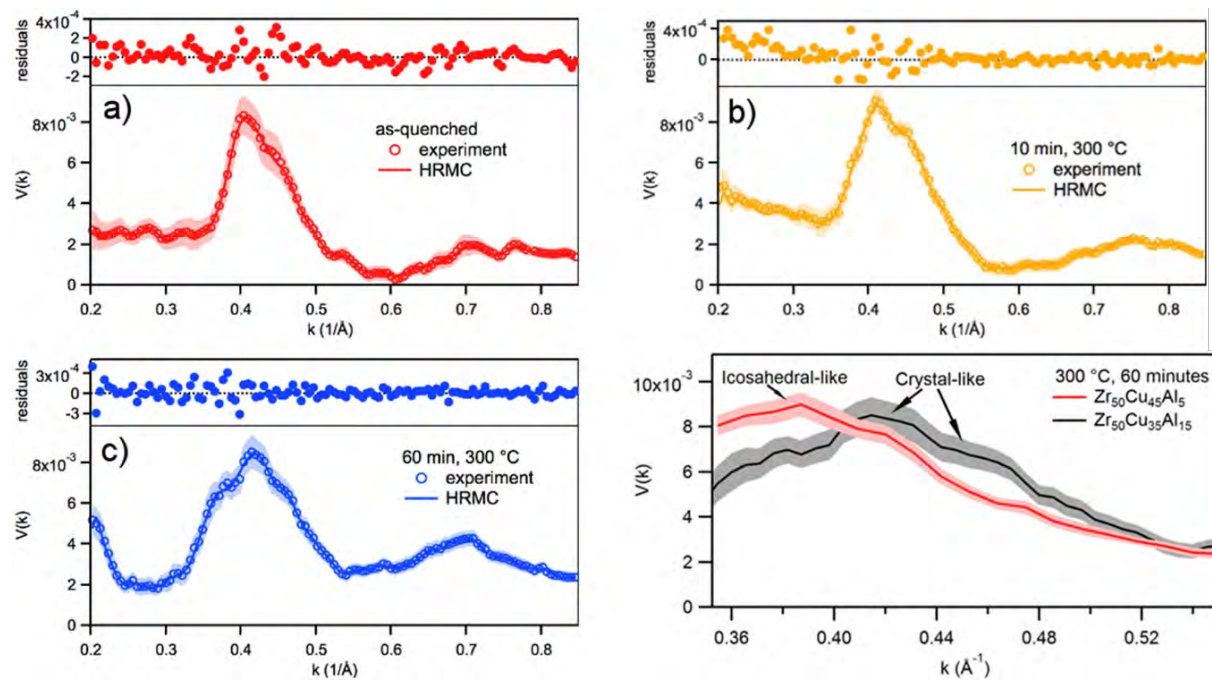


Figure 28: FEM data for Cu-Zr-Al glasses after various annealing times investigated using HRMC methods from Ref[76]

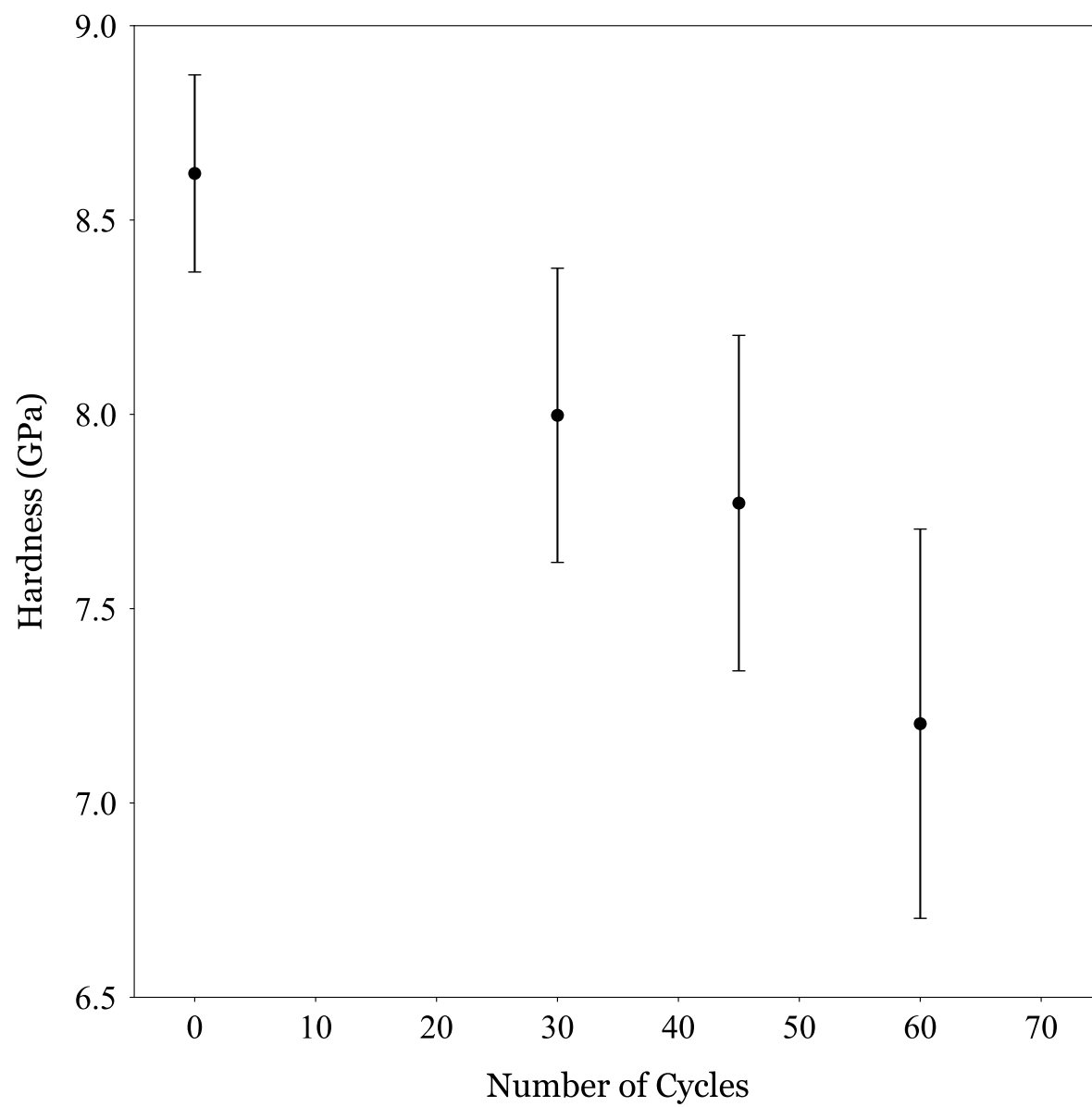


Figure 29: Hardness values of the 6 mm 316L steel at different stages of cryogenic cycling measured by nanoindentation

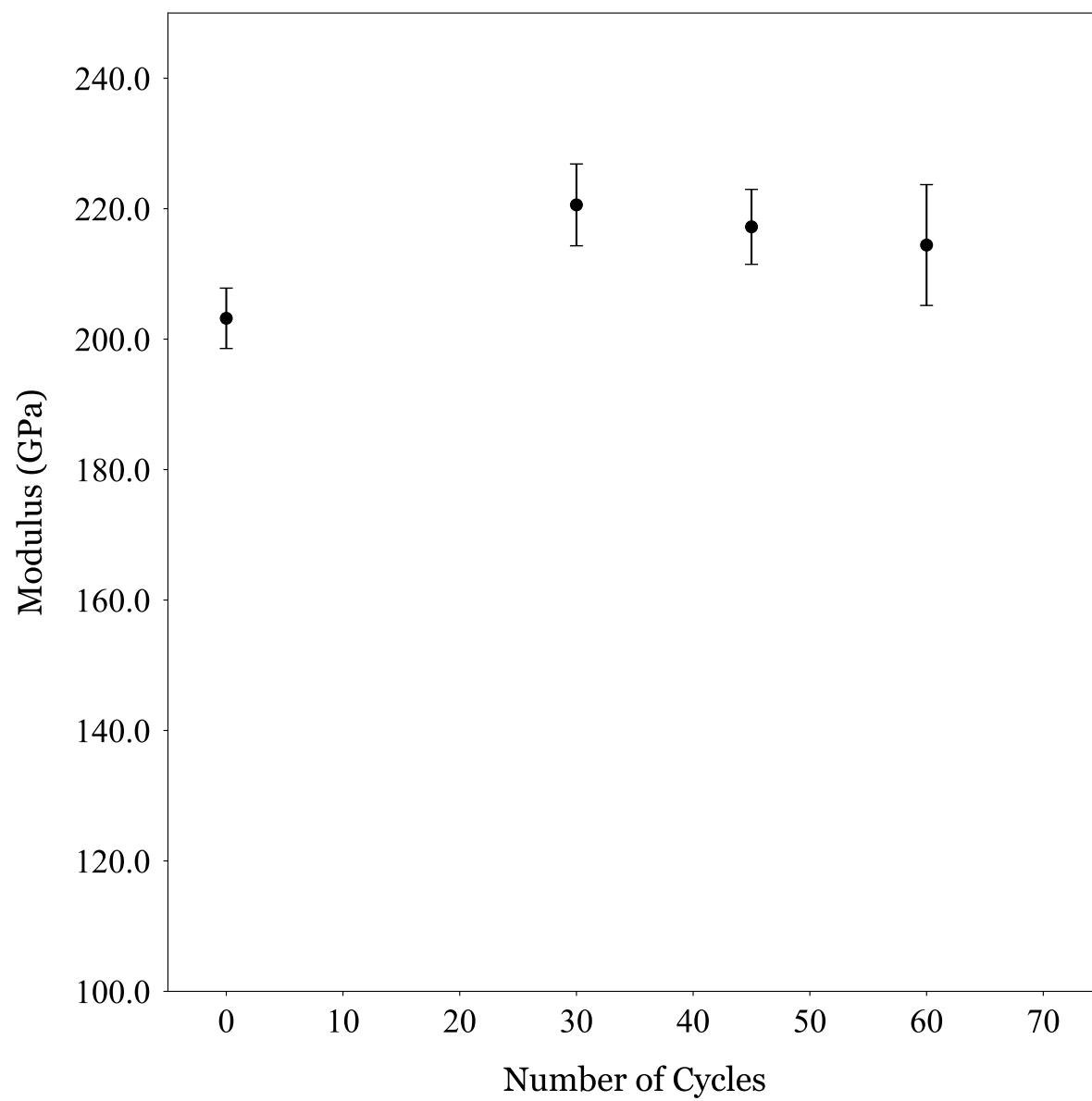


Figure 30: Modulus values of the 6 mm 316L steel at different stages of cryogenic cycling measured by nanoindentation